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Historical trends of heavy metal contamination and their sources in lacustrine sediment from Xijiu Lake, Taihu Lake Catchment, China

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Abstract

Concentrations of Cd, Cr, Cu, Pb, Zn and Hg in Xijiu Lake sediment from the Taihu Lake catchment, China, were analyzed. Their contamination state was investigated based on the geoaccumulation index and enrichment factors. Statistical analysis was used to differentiate the anthropogenic versus natural sources of heavy metals (HMs), and the anthropogenic accumulation fluxes were calculated to quantify anthropogenic contribution to HMs. The results indicated that the lake sediment had been heavily contaminated by Cd, enrichment of Zn and Hg was at a relatively high level, while that of Cu and Pb was in the lower-to-moderate level and Cr was in the low enrichment level. Sources of Cr in the sediment were mainly from natural inputs, while other metals, especially Cd, were predominantly derived from anthropogenic sources. In the past century, anthropogenic accumulation fluxes of Pb, Zn and Hg increased by 0.1–47.3 mg/(cm^2·yr), 2.4–398.1 mg/(cm^2·yr), and 3.7–110.3 ng/(m^2·yr), respectively, accounting for most inputs of HMs entering the sediment. The contamination state of HMs varied with industrial development of the catchment, which demonstrated that contamination started in the early 20th century, reached the maximal level between the mid-1970s and mid-1990s, and decreased a little after the implementation of constraints on high contamination industries, although the contamination of some HMs, such as Cd, Zn and Hg, is still at high levels.

Key words: accumulation fluxes; contamination; heavy metals; human activity; sediment; Xijiu Lake

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Introduction

Compared with other contaminants, heavy metals (HMs) are widespread persistent contaminants, which are potentially harmful, non-biodegradable, and accumulate in living organisms through the food chain (Fan et al., 2002; Buccolieri et al., 2006). After reaching certain concentrations, they cause toxic effects in many organisms (Bryan and Langston, 1992) and seriously threaten ecological safety and human health.

With rapid economic development within the Taihu Lake catchment in recent years, Taihu Lake and its surroundings have suffered from serious environmental issues such as eutrophication and heavy metal contamination. Previous research has explored the relationship of heavy metal concentrations on surrounding soil and surface lake sediment (Yuan et al., 2002), investigated the bio-availability of HMs in the surface sediment of Taihu Lake (Wang et al., 2002), described the temporal distribution of HMs over the last hundred years based on the sediment cores (Liu et al., 2004; Zhu et al., 2005), and demonstrated sedimentary evidence for atmospheric contaminant deposition (Rose et al., 2004). These studies have shown that the state of heavy metal contamination varies significantly in different lakes.

Seventy percent of contaminants in Taihu Lake originate from the surrounding tributaries (Wu et al., 2007). The Yili River, which discharges into the Taihu Lake after passing Xijiu Lake, is one of the largest tributaries and a major pathway of contaminants from the catchment to the lake. Heavy metal contamination has become a serious problem along Yili River, especially Cd which has been found at high contamination level in some sections of the river (Fan et al., 2002). To rehabilitate the aquatic environment and improve water quality, it is vital to determine the sources, state and history of heavy metal contamination.

Geoaccumulation index (I_{geo}) and enrichment factors (EFs) have been widely used in evaluating the state of heavy metal contamination (Loska et al., 1997; Soto-Jiménez and Páez-Osuna, 2001; Loska and Wiechuła, 2003; Acevedo-Figueroa et al., 2006; Jara-Martin et al.,

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2008; Amin et al., 2009; Mil-Homens et al., 2009), and can visibly and effectively demonstrate the HM contamination levels by comparing concentrations in the sediment and their baselines (Loska et al., 1997; Groengroeft et al., 1998). They can also reflect anthropogenic impact on heavy metal enrichment in the sediment (Aloupi and Angelidis, 2001a; Conrad and Chisholm-Brause, 2004). In addition, combined with the geochronology, I_{geo} and EFs can identify the enrichment process and sources of HMs (Ruiz-Fernández et al., 2001; Soto-Jiménez et al., 2003).

Lake sediment serves as the ultimate sink for contaminants. Heavy metals enter the lake from the weathering of rocks, soil erosion, as well as anthropogenic sources in the catchment area, and are finally deposited in the sediment. Apart from I_{geo} and EFs, a series of geochemical and statistical methods have been developed in recent years to identify the sources of HMs. Different methods validate each other and achieve ideal results, especially in differentiating anthropogenic versus natural sources (Ruiz-Fernández et al., 2001; Soto-Jiménez et al., 2003; Wu et al., 2007).

Heavy metals in fine-grained sediment are often bound to organic matter. A number of factors must be considered when identifying sources of HMs, including grain size, mineral composition and sedimentary environment. However, geochemical methods, such as correction of heavy metal concentrations (Horowitz et al., 1990; Szefer et al., 1996) and using Al or other reference elements to normalize heavy metal concentrations (Covelli and Fontolan, 1997; Aloupi and Angelidis, 2001b; Liu et al., 2004), can eliminate influences of grain size, mineral composition, and sedimentary environment. Statistical methods such as the cluster analysis (CA) and principal component analysis (PCA) enable a reduction in data and description of a given complex and multidimensional system by means of a small number of new variables, which can also identify sources of HMs in the sediment (Ruiz-Fernández et al., 2001; Tuncer et al., 2001; Loska and Wiechula, 2003; Soto-Jiménez et al., 2003; Wu et al., 2007; Nguyen et al., 2009; Zaharescu et al., 2009).

The aim of the present study on the sediment of Xijiu Lake within Taihu Lake catchment was to (1) investigate the state of heavy metal contamination by using the indices of I_{geo} and EFs, (2) differentiate anthropogenic versus natural sources of HMs, (3) reconstruct the contamination history of HMs, and (4) quantify anthropogenic contribution to heavy metal enrichment.

1 Material and methods

1.1 Sample collection

Xijiu Lake is located in Yixing City, Jiangsu Province, China. Along with Tuanjiu and Dongjiu Lakes, Xijiu Lake is the last water area before Yili River discharges into Taihu Lake. Xijiu Lake is 12.4 km^2, with a maximum depth of 5.8 m and mean depth of 1.9 m. Since 1970s, rapid urbanization and boosting of industry, especially the development of non-ferrous metal work, galvanization industry, and the printing and dyeing enterprise, has increased contamination load and accelerated contamination of the water and soil environment in the Yili River drainage area (Wu et al., 2008).

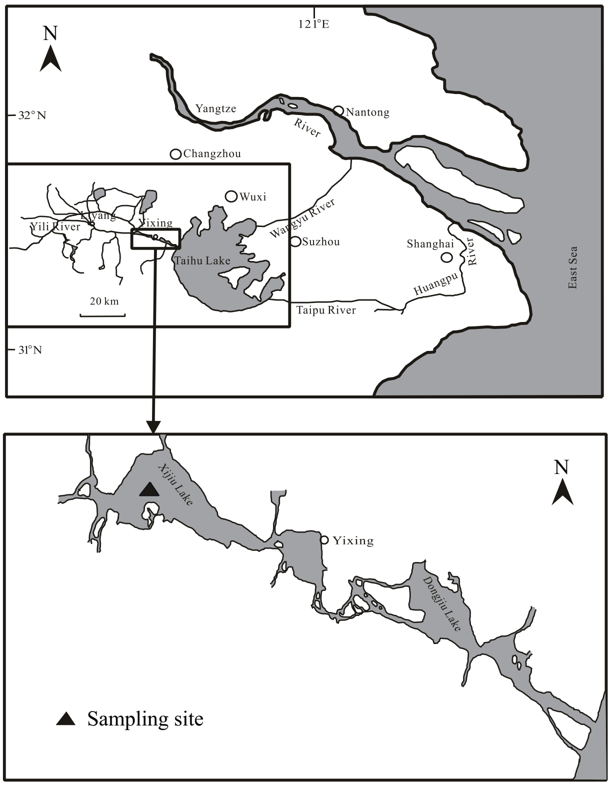

Fig. 1 Location of sampling site in Xijiu Lake.

A 56-cm core (XJ) was taken from Xijiu Lake (31°23′48.8″N, 119°43′33.8″E) using a gravity corer in September 2004. The sampling site was selected in an open area of the lake with little human disturbance (Fig. 1). The long sediment core was used to record temporal information about the lake environment, the impact of human activities and/or climatic changes in the lake catchment.

On extrusion, the sediment in contact with the walls of the core barrel was discarded. The sediment profiles were sectioned on a plastic sheet, and the upper 20 cm of the core was sampled at intervals of 0.5 cm, while the sampling interval of the rest was enlarged to 1 cm. Samples for geochemical analysis of HMs were air-dried at normal temperature in the laboratory before analysis.

1.2 Element analysis

The elements (Al, Cd, Cr, Cu, Pb and Zn) were determined using American Leeman Labs Profile Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) after digestion with nitric acid-hydrofluoric acid-perchloric acid. Standard solution SPEX^{TM} from the US was used as the standard. Quality control was assured by the analysis of duplicate samples, blanks and reference materials (GSD-9 and GSD-11, Chinese geological reference materials). Measurement errors were less than 10%.

A Direct Mercury Analyzer (Hydra-C type) (Teledyne Leeman Labs, US) was used to determine Hg concentration as per US EPA (1998) (Wu et al., 2008). Standard material ESS-3 was used to control measurement quality, and the measurement errors were less than 2.7%.

1.3 Geochronology analysis

The core was dated using ^{210}Pb, ^{137}Cs and sediment characteristics. The activities of ^{137}Cs, ^{210}Pb and ^{226}Ra were detected using an Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detector after samples were dried at low temperature (< 40°C) and weighed. The excessive ^{210}Pb (^{210}Pb$_{exc}$) in each sample was obtained by subtracting the activity of ^{226}Ra from the total activity of ^{210}Pb (^{210}Pb$_{tot}$). Then ^{210}Pb$_{exc}$ was used to develop a chronology using the constant rate of supply (CRS) dating model (Appleby and Oldfield, 1978). Geochronology in Xijiu Lake sediment has been discussed by Wu et al. (2008) in detail and the results were cited in this study.

1.4 Normalization of heavy metal concentrations

To discuss heavy metal enrichment in the lake sediment, concentrations should be normalized to eliminate the influence of grain size and mineral composition. Several reference elements, such as Al, Li, Fe and Sc, have been used for normalization (Loring, 1990; Herut et al., 1993; Grousset et al., 1995; Aloupi and Angelidis, 2001b; Wu et al., 2007; Amin et al., 2009; Mil-Homens et al., 2009), with Al most commonly used (Windom et al., 1984; Zhang et al., 1988) due to its geochemical properties. The solubility of Al is relatively low in natural water column, so that its content in the sediment has better comparability with that in the rock. In addition, Al is an inert element in the course of weathering and its concentration decreases linearly with increasing grain size in the sediment.

1.5 Statistical analysis

Analysis of multidimensional data sets without spatial or temporal information is the advantage of multivariate statistics. Factor analysis is a multivariate statistical method that allows data reduction by extracting eigenvalues and eigenvectors from a covariance or a correlation matrix (Davis, 2002). Cluster analysis can reveal the specific linkage between sampling sites or several elements, and is therefore a good method for indicating the similarities or dissimilarities between them (Simeonov et al., 2000). All statistical analysis in this study is performed using SPSS16.0 analysis software.

1.6 I_{geo} and EFs calculation

The I_{geo} of HMs in the Xijiu Lake sediment was calculated according to the following Eq. (1) (Loska and Wiechula, 2003):

$$I_{geo} = \log_2(C_n/(1.5 \times B_n)) \quad (1)$$

where, C_n is the concentration of HMs measured in the sediment and B_n is their baseline.

The EFs of HMs in the Xijiu Lake sediment was calculated according to the following Eq. (2) (Soto-Jiménez and Páez-Osuna, 2001):

$$\mathrm{EF} = (\mathrm{M/Al})_\mathrm{S}/(\mathrm{M/Al})_\mathrm{B} \quad (2)$$

where, $(\mathrm{M/Al})_\mathrm{S}$ is the ratio of HMs and Al concentrations in the samples and $(\mathrm{M/Al})_\mathrm{B}$ is that in the baseline.

2 Results

2.1 Variations of heavy metal concentrations in the sediment

All concentrations of the studied elements varied obviously around 33 cm (1965 AD) in the XJ core (Fig. 2, Table 1). The concentrations of Cd, Cr, Cu, Pb, Zn and Hg increased markedly from 33 cm upwards, while that of Al decreased generally. Although Cd concentration was under the detection limit of the instrument below 33 cm, it increased notably afterwards with a maximum value of 21.6 mg/kg and a mean value of 12.1 mg/kg. The Cr concentration varied from 51.0 to 90.9 mg/kg, with a mean value of 72 mg/kg. Other HM concentrations in the XJ core varied between 27.7 and 118.6 mg/kg for Cu, 35.2 and 90.1 mg/kg for Pb, 74.7 and 644.8 mg/kg for Zn, 25.0 and 173.1 ng/g for Hg.

2.2 Baselines of HMs

As shown in Fig. 2, the concentrations of HMs were relatively low and varied with little fluctuation at the bottom of the core. Geochronology results (Wu et al., 2008) revealed that the bottom samples corresponded to the age from the end of 19th century to the early 20th century before industrialization within the lake catchment had developed and anthropogenic contribution to HMs might be neglected. Therefore, the mean concentrations of Al, Cr, Cu, Pb, Zn and Hg in the bottom 6 cm in the XJ core were regarded as their baselines. The global mean

Table 1 Characteristics of trace metal concentrations in the sediment of Xijiu Lake

Elements	Global mean values in soil	Estimated baselines	Mean values below 33 cm	Mean values upper 33 cm	Total mean values
Al (mg/kg)	69,300	72,072	71,925	56,250	61,612
Cd (mg/kg)	0.2	ND	2.6	12.8	12.1
Cr (mg/kg)	71	68	71	73	72
Cu (mg/kg)	32	30	43	74	64
Pb (mg/kg)	16	39	53	65	61
Zn (mg/kg)	127	106	255	385	340
Hg (ng/g)	ND	25.5	80.3	118.2	105.3

ND: no data.

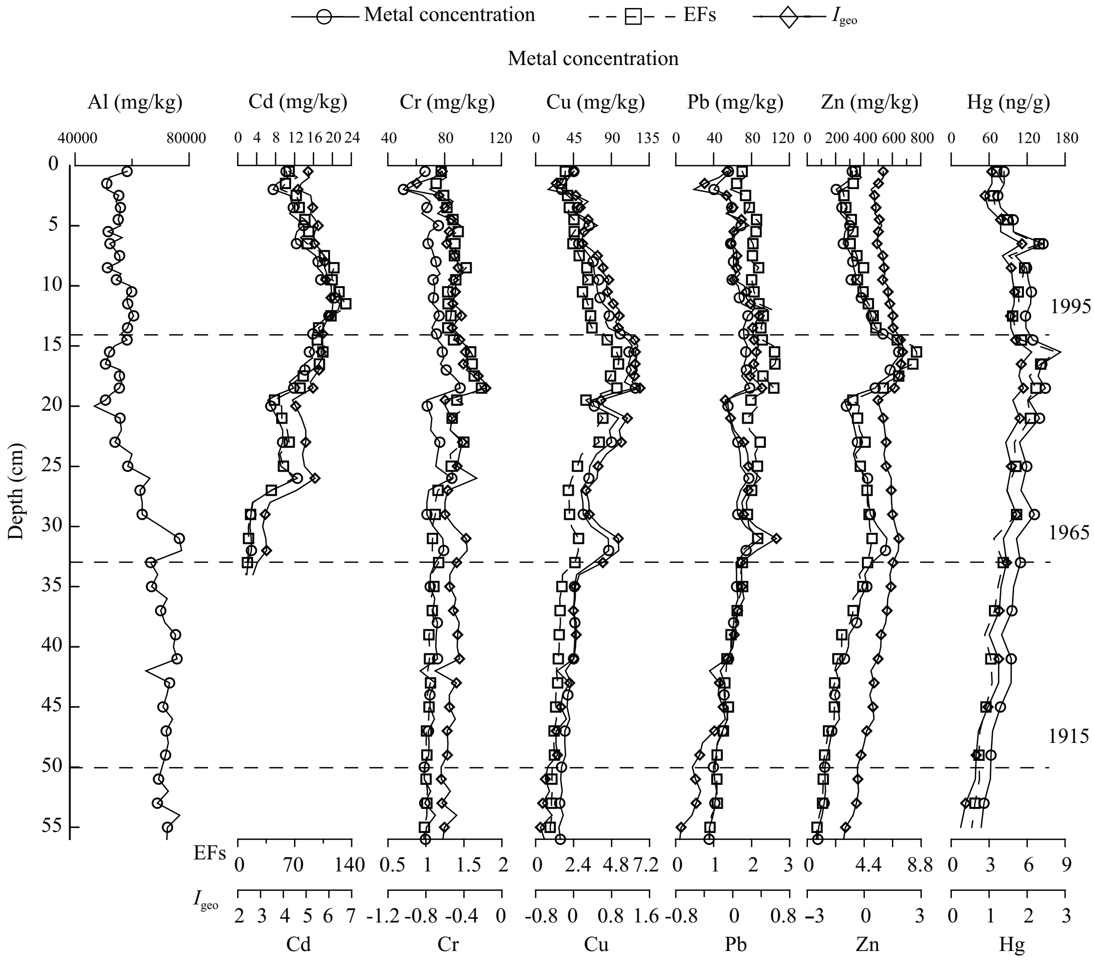

Fig. 2 Profiles of heavy metal concentrations, the geoaccumulation index (I_{geo}) and enrichment factors (EFs) in the sediment of Xijiu Lake.

concentration of Cd in soil (Mason, 1966) was used as its baseline, for its concentration in the lower part of the core was under the detection limit of the instrument (Table 1).

2.3 EFs and I_{geo}

The variation trends of EFs and I_{geo} of HMs in the XJ core were similar to that of their concentrations (Fig. 2). The EF (Cd) varied between 10.0 and 132.8, and I_{geo} between 2.7 and 6.2 (Table 2). The values of EF and I_{geo} of Cd culminated in the 1970s, higher than 50.0 and 5.0, respectively. The EF (Cr) ranged between 1.0 and 1.7, I_{geo} lower than zero. The higher value for EF (Cr), appeared in the 1970s and 1980s. The EF (Cu) varied between 0.9 and 5.3 with mean I_{geo} lower than 1.0. The EFs values varied from 0.9 to 2.7 for Pb, 0.7 to 8.5 for Zn, and 1.6 to 8.3 for Hg; I_{geo} of Pb was lower than 1.0, while I_{geo} of Zn and Hg was lower than 2.0. The EFs values of Cu, Pb, Zn and Hg were about 1.0, I_{geo} lower than zero (except Hg) before 1915; thereafter the EFs and I_{geo} values of all HMs began to increase gradually, and peaked with a little variation in the mid-1990s. In the late 1990s, however, values decreased slightly and reached the same values as the 1960s.

3 Discussion

3.1 Contamination state of HMs in the sediment

Based on the values of EFs (HMs) in the XJ core, the mean value of EF (Cd) was 77.3 (Table 2), higher than 50.0, suggesting that serious Cd contamination was present in Xijiu Lake sediment. Nevertheless, the mean value of EF (Cr) was 1.3, a low enrichment level indicating that Cr contamination was not a major concern in the sediment at present. The mean EFs values of Cu and Pb (2.6 and 1.9, respectively) confirmed moderate enrichment in Xijiu Lake sediment; however, the mean values of Zn and Hg (3.9 and 4.5, respectively) reflected higher enrichment

Table 2 Enrichment factors (EFs) and geoaccumulation index (I_{geo}) of HMs in the XJ core

Parameters	Cd	Cr	Cu	Pb	Zn	Hg
EFs	10.0~132.8 (77.3)	1.0~1.7 (1.3)	0.9~5.3 (2.6)	0.9~2.7 (1.9)	0.7~8.5 (3.9)	1.6~8.3 (4.5)
I_{geo}	2.7~6.2 (5.1)	–1.0~–0.2 (–0.5)	–0.7~1.4 (0.4)	–0.7~0.6 (0.0)	–1.1~2.0 (1.0)	0.3~2.1 (1.3)

Data in the bracket are the mean values.

levels.

According to I_{geo}, Cd was still at a serious contamination level, with a mean value of 5.1 (Table 2), while Cr enrichment was low ($I_{geo} < 0$), which was in agreement with the EFs results (HMs). However, the enrichment state of Cu and Pb (lower enrichment level) and Zn and Hg (moderate enrichment level) was a little lower by the I_{geo} method than that of EFs, indicating that using I_{geo} to evaluate contamination or enrichment level of HMs might lead to under-estimation.

Based on EFs and I_{geo}, the contamination state of HMs in Xijiu Lake sediment was: Cd, serious contamination; Zn and Hg, moderate to higher level enrichment; Cu and Pb, lower to moderate enrichment level; and Cr enrichment was low.

3.2 Source analysis of HMs in the sediment

Heavy metals in the sediment came from numerous natural and anthropogenic sources (Wu et al., 2007, 2008). To elucidate the potential sources of HMs in Xijiu Lake sediment, associations between HMs in the sediment were investigated using factor analysis.

Through factor analysis, two major components, whose eigenvalues were higher than one accounting for 85.5% of the cumulative variance, were extracted for the analyzed data (Table 3). Factor one, which included Cr, Cu, Pb, Zn and partly Hg, accounted for 52.5% of the total variance contribution. Significant positive correlations were found between them (Table 4), which might represent similar sources of these metals from both natural and anthropogenic origins. Factor two accounted for 33.0% of the total variance, and was mainly characterized by Al, Cd, Hg and partly Cr. Based on correlation analysis (Table 4), significant negative correlations were found between Al and Cd in the core, indicating that they might be from different sources. As a conservative element, Al was the main product of aluminosilicate weathering, which represented natural material. The Cd source was mostly from anthropogenic input. In addition, no strong correlation was found between Cd and Cr, which confirmed that the Cr source was different from Cd. According to the distribution of principle components (Fig. 3), three different metal source models existed in the sediment. Compared with preliminary studies (Wu et al., 2007, 2008), we deduced that the presence of Cr in Xijiu Lake sediment was mainly from natural factors, while Cd, Pb, Cu, Zn and Hg were primarily attributed to anthropogenic origins, especially Cd.

Table 3 Factor loadings (Varimax normalized) for two principle components*

Elements	Component	
	1	2
Al	0.203	**0.545**
Cd	–0.097	**0.438**
Cr	**0.341**	**–0.246**
Cu	**0.204**	**0.063**
Pb	**0.271**	–0.072
Zn	**0.261**	–0.051
Hg	**0.134**	**0.154**

* Extraction method: principal component analysis.

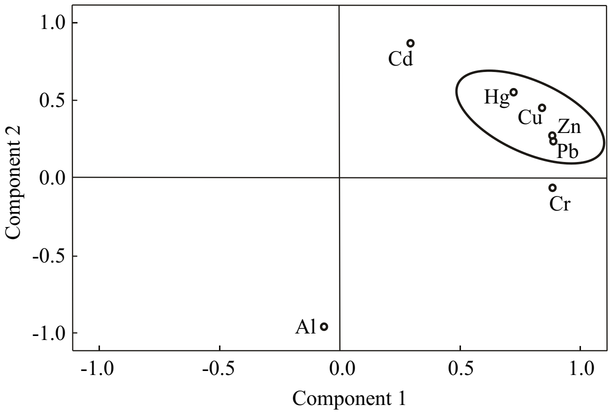

Fig. 3 Factor analysis scores plot (Component 1 vs. Component 2) for the metals in the sediment of Xijiu Lake.

To further confirm the sources of HMs, cluster analysis was carried out to reveal the specific linkage among these metals. The results (Hierarchical clustering, Ward's method) showed that three subgroups could be incorporated into two major groups (Fig. 4): the first included the heavily contaminated metal Cd, while the other indicated the lower to moderate contaminated metals. There were two crystal-clear subgroups in the second major group where the first subgroup included metal Cr which substantially came from the natural source, and the other, however, reflected the contaminated metals deriving from both natural and anthropogenic sources. Generally, the cluster analysis results were in agreement with that of factor analysis. Sun et al. (2009) discussed the fractions of Cd, Cr, Zn, Cu and Pb in the sediment of Xijiu Lake by using sequential extraction procedure. Their results also denoted that the contamination of Cd, Zn, Cu and Pb was mainly from anthropogenic origins.

3.3 Reconstructing the contamination history of HMs in the sediment of Xijiu Lake

To identify the unusual increase of heavy metal concentrations in different sections of the XJ core as a result of contamination events, it was necessary to reconstruct the contamination history of HMs through the exact geochronology (Wu et al., 2008) in the sediment.

Based on the concentrations, EFs and I_{geo} of HMs and the geochronology in Xijiu Lake sediment (Fig. 2), the heavy metal contamination was very low before the early 20th century when the inputs of HMs were from natural

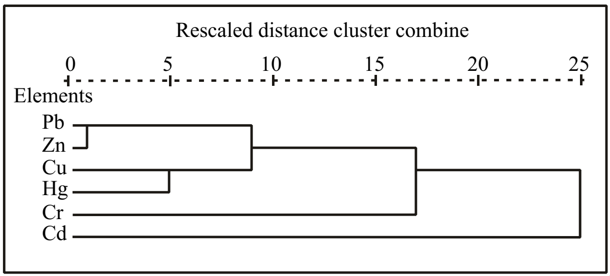

Fig. 4 Hierarchical clustering analysis shows the relevant association among the metals. Distance metrics are based on the Euclidean distance single linkage method (nearest neighbor).

Table 4 Correlation matrix of HMs in the sediment of Xijiu Lake

Correlation matrix	Al	Cd	Cr	Cu	Pb	Zn	Hg
Al	1.000						
Cd	–0.770**	1.000					
Cr	–0.038	0.248	1.000				
Cu	–0.497*	0.618**	0.750**	1.000			
Pb	–0.256	0.506*	0.678**	0.784**	1.000		
Zn	–0.0309*	0.452*	0.626**	0.839**	0.884**	1.000	
Hg	–0.582**	0.603**	0.569**	0.835**	0.720**	0.781**	1.000

* $P < 0.05$; ** $P < 0.01$.

and atmospheric sources. Industrial development during the early 20th century in the catchment area led to HMs entering into the lake, and thus all indicators of HMs in the sediment increased slowly between the early 20th century and the mid-1960s. Thereafter, the contamination of HMs increased markedly due to the rapid development of industry, agriculture, and transportation within the catchment area. During the 1970s and 1980s many small scale enterprises with high consumption and heavy contamination were built around Yixing City, which correspondingly brought large amounts of sewage discharge into the Yili River (Han and Xie, 1990; Xie and Chen, 2002) and caused the rapid increase of heavy metal concentrations and contamination indices in the sediment. There was an evident valley of all indices in this period, since the mass accumulation rates (MARs) of the sediment were high and the significant amounts of detrital materials entered the lake from the catchment diluted the concentrations of HMs in the sediment (Wu et al., 2008). Therefore, it couldn't conclude that the anthropogenic contribution to HMs has largely reduced, although some small enterprises were indeed closed or merged into a larger company by the government from 1970s to 1990s. The government reinforced many protection measures in the 1990s to improve the aquatic quality; the contamination of HMs, however, still reached the maximal level in the mid-1990s. It was not until the late 1990s that HM contamination began to decline, while the contamination indices suggested that some HMs were still at high contamination level, which revealed the strong anthropogenic contribution to HMs in the last several decades.

3.4 Contribution of human activities to HMs in the sediment

Mass accumulation fluxes (MFs) could quantify the contribution of human activities to HMs in the sediment more exactly than heavy mental concentrations (Liu et al., 2007; Wu et al., 2008). To quantify the anthropogenic contribution to HMs, the MFs of Pb, Zn and Hg were calculated based on the concentrations of Pb, Zn and Hg and their mass accumulation rates (MARs) in this research. In the last hundred years, the MFs of Pb, Zn and Hg varied from 5.9 to 89.9 mg/(cm^2·yr), 12.5 to 478.2 mg/(cm^2·yr), and 7.9 to 136.9 ng/(cm^2·yr), respectively.

Combining anthropogenic concentrations with MARs, the anthropogenic accumulation fluxes (AFs) of Pb, Zn and Hg were calculated by subtracting their baselines from the measured data (Fig. 5). In the past century, the concentrations of anthropogenic contribution to Pb, Zn and Hg ranged between 0.6 and 51.1 mg/kg, 13.2 and 538.8

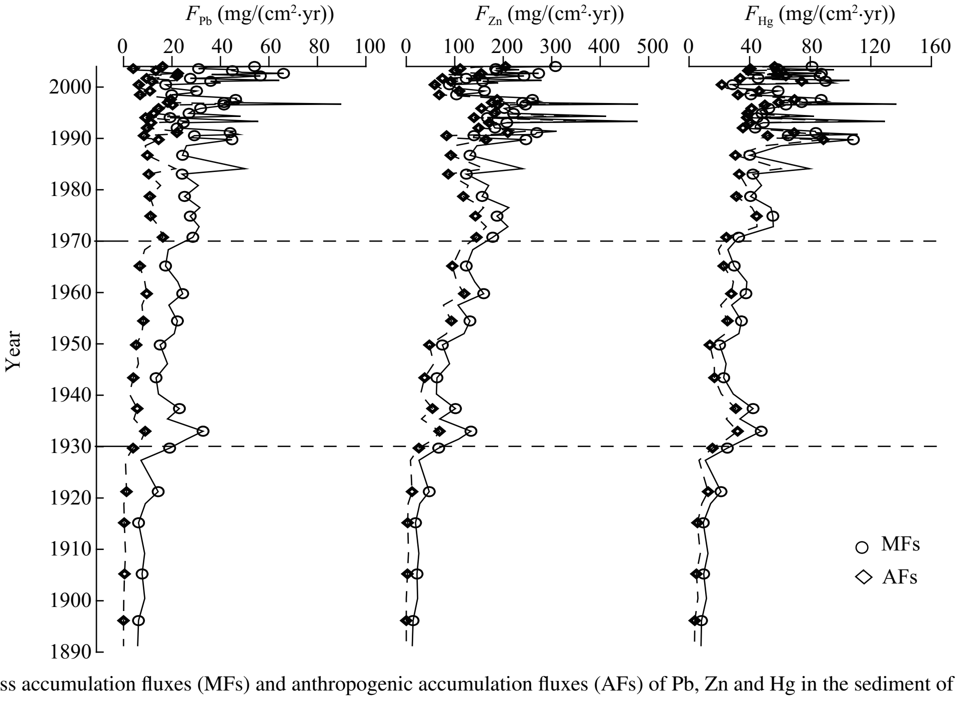

Fig. 5 Mass accumulation fluxes (MFs) and anthropogenic accumulation fluxes (AFs) of Pb, Zn and Hg in the sediment of Xijiu Lake.

mg/kg, 21.9 and 147.6 ng/g, respectively, while the AFs varied between 0.1 and 47.3 mg/(cm^2·yr) for Pb, 2.4 and 398.1 mg/(cm^2·yr) for Zn, 3.7 and 110.3 ng/(cm^2·yr) for Hg.

The MFs and AFs of Pb, Zn and Hg increased stably since the early 20th century. Since the 1950s, however, the anthropogenic accumulation fluxes have contributed 39% (mean value) for Pb, 70% for Zn and 77% for Hg to the total mass accumulation fluxes of HMs. The maximal contribution ratio were 50% for Pb, 84% for Zn and 85% for Hg in the 1990s when heavy metal contamination was at its highest level, confirming that Pb, Zn and Hg contamination in Xijiu Lake sediment was chiefly attributed to human activities within the catchment.

4 Conclusions

The study of the sediment collected from Xijiu Lake indicated that, based on concentrations, EFs and I_{geo} of HMs, Cd was at a serious level; Zn and Hg were at a relatively high enrichment level; Cu and Pb were at a lower-to-moderate enrichment level; and Cr enrichment level was low. The presence of Cr in the sediment was mainly influenced from natural factors, while Cd, Pb, Cu, Zn and Hg were predominantly of anthropogenic origins. The anthropogenic contamination of HMs in Xijiu Lake sediment was quantified by the calculation of anthropogenic accumulation fluxes. The mass accumulation fluxes of Pb, Zn and Hg by human activities increased by 0.1–47.3 mg/(cm^2·yr), 2.4–398.1 mg/(cm^2·yr), 3.7–110.3 ng/(cm^2·yr), respectively, reflecting the anthropogenic contribution to the heavy metal enrichment in Xijiu Lake sediment.

In the early 20th century, heavy metal input was attributed to urbanization and fossil fuel consumption surrounding the Taihu Lake, as well as the worldwide atmospheric deposition since the industrial revolution. The contamination of HMs increased with industrial development in the catchment, reached a maximum between the mid-1970s and mid-1990s, and decreased a little after the mid-1990s with constraints on high contamination industries. Therefore, heavy metal contamination revealed the way and intensity of human activities in the region.

Acknowledgments

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