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ORIGINAL ARTICLE

Sediment records of the metal pollution at Chihu Lake near a copper mine at the middle Yangtze River in China

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ABSTRACT

Two short sedimentary cores were collected in 2012 from Chihu Lake in the middle Yangtze River Basin using a gravity corer. Heavy metals, including Pb, Cu, Zn, Cd, Cr, Co, Ni and Mn, and major elements, including Al, Fe, K, Mg and Ti, were measured. Radionuclides, including ^{210}Pb and ^{137}Cs, were analyzed to date the sediments. The Mn enrichment in the sediments of the two cores did not significantly influence the distribution of the heavy metals. The Pb, Cu, Zn, Cd, Co and Ni contents have increased over the past 30 to 40 years. The decrease in the ^{206}Pb/^{207}Pb ratios toward the surface also indicated increasing mining sources of Pb loading to the lake sediments. The maximum concentration of Cu, Zn and Cd recorded in the 1990s was 2047, 1343 and 60.9 mg kg^{-1} dry mass, respectively, and the maximum enrichment factors of Cu, Zn and Cd were 62, 16 and 206, respectively. The heavy metal enrichment at Chihu sediment was high overall because of the mining waste discharge.

Key words: Yangtze River; Chihu Lake; sediment; copper mining.

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INTRODUCTION

Heavy metals in the environment are not only from natural sources, such as erosion and weathering process, but also from anthropogenic emissions, of which the most important have been the human activities of mining and smelting (Nriagu, 1998; Boyle *et al.,* 1999; Pacyna and Pacyna, 2001; Audry *et al.,* 2004; Couillard *et al.,* 2008; Balogh *et al.,* 2009; Wu *et al.,* 2010). Heavy metals can be released into the water environment from mining tailings or transported with metal-rich dust during mining activities (Ek and Renberg, 2001; Salonen *et al.,* 2006; Laperriere *et al.,* 2008; Grayson and Plater, 2009; Ostrofsky and Schworm, 2011). For example, heavy metals can be released into the atmosphere during the refining process due to high temperature smelting (Boyle *et al.,* 1999; Ek and Renberg, 2001). Acid mining drainage (AMD) is formed in mining exploitation and the associated production activities. The AMD effect on the environment, often the aquatic environment, can be easily shown at locations in which heavy metals pose a serious threat to organisms in the receiving water (Michelutti *et al.,* 2001; Ostrofsky and Schworm, 2011). Many heavy metals are toxic to the biota when the concentration exceeds a specific level (Arnason and Fletcher, 2003; Salonen *et al.*, 2006). The toxicity of heavy metals is due to their ability to form stable complexes, which may be with the active site of the denatured protein conformation or the substitution for the activity of a metal cofactor.

The construction of the Wushan Copper Mine began in the 1960s (Wu, 1987b), and the goal was to develop the largest copper mine in Jiangxi, China. The copper remains active today. During the same period of mine construction and exploitation, the population of the mine company grew from 175 in 1966 to 4,077 in 1992 (Li, 1999). Chihu Lake is located to the northeast of the Wushan Copper Mine, and the lake shoreline is partly connected to the mine tailing. Prior to 1989, there was no sewage process system. The waste water from the spoil and the mine waste was discharged into Chihu Lake through surface or underground runoff without treatment (Zhao, 1994). The Chihu Lake water quality has been severely affected by the mine drainage (Li, 1999). The waste water loading to Chihu Lake was up to 3.8 million tons, and the Cu loading was 30 tons in 1989, resulting in a Cu concentration up to 200 mg L^{-1} in the lake water (Compilation Committee of Chorography of Science and Technology of Wushan Copper, 1994). In 1989, two sewage treatment plants were installed (Compilation Committee of Chorography of Science and Technology of Wushan Copper, 1994). Improved rock processing and the implementation of waste water treatment can lead to a reduction in the heavy metal loading to Chihu Lake, but the risk of the mining activities on Chihu Lake remains. According to a simple surface sediment survey conducted by the Nanjing Institute of Geography and Limnology of the Chinese Academy of Sciences in 2007, the Cu content ranged from 36.3-382.3 mg kg^{-1}, and the Cd content ranged from 0.292-10.35 mg kg^{-1} dry mass.

Paleolimnology offers a unique historical perspective for the study of the effects of the Wushan Copper Mine activities on Chihu Lake and the pre-disturbance environmental conditions of the lake. An analysis of the trace metals in the lake sediment cores with the chronology can provide valuable insights into the historical metal inputs (Boyle *et al.,* 1999; Rose *et al.,* 2004; Yang and Rose, 2005; Couillard *et al.,* 2008). Heavy metals in the Chihu Lake sediments include not only the anthropogenic source but also the metal from the natural input of the catchment. Geochemical methodologies use highly conserved elements, such as aluminum, iron, lithium and rubidium, to detect and quantify the anthropogenic metals input (Franco-Uria *et al.,* 2009; Yao *et al.,* 2009), assuming that these elements are not influenced by human activity and can reflect catchment input. In addition, the use of stable Pb isotopes can enhance our understanding about the sources of the Pb in the input, and this analytical tool has been widely used in different ecosystems, including lake sediments(Farmer *et al.,* 1997; Marcantonio *et al.,* 2002; Cheng and Hu, 2010).

Mining activity is as a point source pollution, and its effect may primarily be limited to the surrounding environment. In this study, we analyzed two sediment cores from Chihu Lake, examining the changes in the heavy metals over time and evaluating the anthropogenic and natural heavy metal inputs on the whole Lake Chihu ecosystem.

METHODS

Study site

Chihu Lake

Chihu Lake, lying on the southern bank of the Yangtze River (Fig. 1), is situated in the administrative region of Ruichang County and Jiujiang County. Chihu Lake had an area of 100.4 km^2, but the reclamation during the 1950s-1970s (Compilation Committee of Chorography of Ruichang County, 1990) and the project from 2011-2013 reduced the lake to 30.4 km^2 (Fig. 1). The lake is shallow with a mean depth of 2.8 m and max depth of 3.5 m. The catchment area is 360.0 km^2 (Wang and Dou, 1998). Chihu Lake is controlled by a subtropical monsoon climate with an average annual temperature of 16.5°C, 1394 mm of annual precipitation and 260 frost-free days in each year (Wang and Dou, 1998).

Nanyang River, originating from the northwestern hillocks, is the most important inlet river, with a length of 30 km. In the 1970s, the river turned into two adjacent rivers for flood control during the summer. In 1954, a dam was installed at Pengjiawan (PJW) (Compilation Committee of Chorography of Ruichang County, 1990) (Fig. 1). Since then, Chihu Lake has become a reservoir-type lake under artificial control. A significant amount of materials from the Yangtze River entered the lake during the summer when flooding occurred and was deposited in the lake before the establishment of the dam. The water level averaged 14.60 m asl, with a maximum of 17.00 m in July 1983 and a minimum of 12.49 m in July 1968 (Wang and Dou, 1998).

The pH of the Chihu Lake water is 8.0-8.7. The Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} contents are 37.9 (27.2-48.7) mg L^{-1}, 7.63 (6.08-9.73) mg L^{-1}, 4.53 (0.97-3.57) mg L^{-1} and 2.25 (3.21-6.40) mg L^{-1}, respectively. The TN and TP values are 0.72 (0.23-3.6) and 0.040 (0.025-0.070) mg L^{-1}, respectively. Macrophytes are abundant in Chihu Lake. According to an investigation in 1964, the biomass of the macrophytes in the entire lake averaged 2180 kg per acre (Wu, 1987a). A survey conducted in 1985 revealed that the lake was dominated by *Potamogeton malaianus Miq., Vallisneria spiralis L.* and *Hydrilla verticillata Royle* (Wu, 1987a).

Copper mine

The Wushan Copper Mine contains two ore belts, the Wushan south ore belt and the Wushan north ore belt. The south ore belt contains skarn and porphyry Cu orebodies, which occur at the contact zone of the granodiorite porphyry. The north ore belt contains stratiform Cu ore bodies at the lithological boundary between the basal siliciclastic rocks and the overlying carbonates of the Middle Carboniferous Huanglong Formation or in fracture zones within the Huanglong Formation carbonates. The mine contains 1.04-1.17% Cu and a smaller amount of Au and Ag (Huang *et al.,* 1990).

Mine exploration in Wushan began in 1959 and continued until 1965. The Wushan Copper Mine construction was between 1966 and 1985(Compilation Committee of Chorography of Science and Technology of Wushan Copper, 1994). In 1970, a contemporary extraction plant was constructed, and 649.4 tons of copper was extracted until 1971(Compilation Committee of Chorography of Science and Technology of Wushan Copper, 1994). From 1977-1983, 300,855 tons of rock was processed in the new extraction plant, averaging approximately 220 tons per day. From 1986-1990, the extraction plant was reconstructed, and approximately 800 tons of rock could be processed per day (Compilation Committee of Chorography of Science and Technology of Wushan Copper, 1994). During the *9th Five-Year* (1996-2000), the rock processing capacity at the extraction plant elevated from approximately 1100 tons to 2500 tons per day (Wu *et al.,* 2001). The ore process in 2009 was as high as 5000 tons per day.

A tailing reservoir near the Chihu Lake was established in 1970. The storage capacity of the tailing reservoir is 460,000 m^3. Up to 1990, 845,500 tons of waste rock was deposited in the tailing reservoir. Waste rock deposited before 1992 in the tailing reservoir contains 0.538% Cu, whereas waste rock deposited after 1992 contained 0.3% Cu (Wang, 1997). Large amounts of spoil were deposited in the land area of the mine region. An analysis in 1977 revealed that the Cu concentration in the leaching water from these spoils was as high as 4750 mg L^{-1} during raining days (Anomournas, 1977). The mine is located on the western shore of Chihu Lake (Fig. 1) and is one of the primary environmental factors affecting the lake water quality in addition to non-point-source loading from land uses in the lake catchment area.

Sampling and laboratory analysis

Two short sedimentary cores, CH1 and CH2, were obtained in 2012 from the eastern and western parts of Chihu

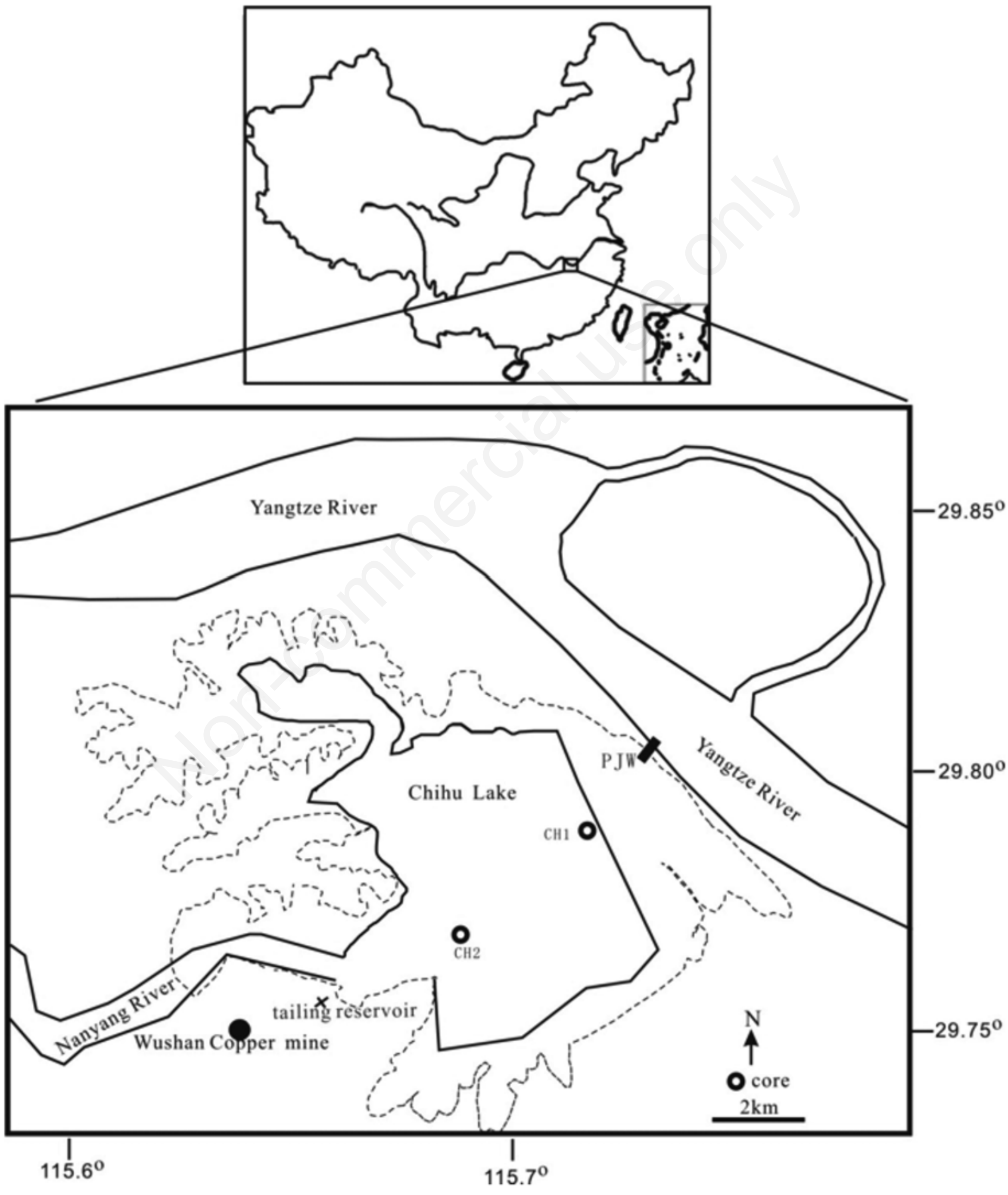

Fig. 1. Location of the study area showing Chihu Lake and the coring sites. The dotted line representing the lake area is modified from Wang and Dou (1998).

Lake, respectively, using a gravity corer with a diameter of 5.9 cm (Fig. 1). The lengths of the two cores were 89 and 95 cm, respectively. The core sediments were sectioned at 1.0 cm intervals. The slices were oven dried at 60°C for approximately 72 h. The two cores were selected for radiometric dating using ^{210}Pb and ^{137}Cs.

^{210}Pb and ^{137}Cs were determined using EG and G Ortec Gamma Spectrometry at the Nanjing Institute of Limnology and Geography of the Chinese Academy of Sciences. ^{137}Cs was measured at 662 keV, whereas ^{210}Pb was determined via gamma emission at 46.5 keV. ^{226}Ra was detected in 295 and 352 keV γ-rays emitted by its daughter isotope ^{214}Pb (Wan *et al.,* 1987). The magnetic susceptibility was measured using a dual frequency Bartington Instruments MS2 sensor. The loss-on-ignition (LOI_{550}) procedure followed the protocol by Heiri *et al.* (2001). The dried and ground samples (approximately 0.125 g each) were digested with HCl-HNO_3-$HClO_4$ in a Teflon beaker. Elements, including Pb, Cu, Zn, Cd, Cr, Co, Ni and Mn, were measured using inductively coupled plasma mass spectroscopy (ICP-MS) (Agilent Technologies, Santa Clara, CA, USA, 7700x). Elements, including Al, Fe, K, Mg, Ti, Ca and total phosphorus (TP), were measured using ICP-AES (Leeman Labs, Hudson, NH, USA; Profile DV). The data quality was ensured using duplicates, blanks, and standard reference materials, such as GSD-18, which was supplied by the Chinese Academy of Geological Sciences. The recoveries of the metals varied, but all of the values were over the range of 92-105%, and the relative standard deviation (RSD) was less than 8%. Replicates were measured on each sediment sample. The isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb were measured using ICP-MS. An international standard reference material (SRM981-NIST) was selected for calibration. The average measured ratio of $^{206}Pb/^{207}Pb$ of the external standard (GBW04426) was 1.1518±0.0008 (for seven replicates). A good agreement was obtained between the measured lead isotope ratios and the certified values for GBW04426 (1.1525).

RESULTS

Sediment chronology

In the CH1 core, the first appearance of ^{137}Cs was recorded at 28.5 cm (Fig. 2), which can be dated to the early 1950s, assuming that there was no vertical immigration of ^{137}Cs in the core. ^{137}Cs peaked at 20.5 cm, which may be dated to 1963 and corresponds to a nuclear test in the early 1960s, although there was another peak at a depth of 8.5 cm. The later peak was not selected as the 1963 time marker because erosion could have subsequently brought deposited ^{137}Cs in the catchment into Chihu Lake. ^{137}Cs peaked at 20.5 cm in the CH1 core, suggesting an average sediment rate of 0.42 cm a^{-1}.

Using the CIC (constant initial concentration) model of ^{210}Pb, the average sediment rate of 0.84 cm a^{-1} can be calculated in the section in the CH1 core, which was quite different from ^{137}Cs result. ^{210}Pb CRS (constant rate of supply of ^{210}Pb) model and composite model from CRS are commonly used to date sediment ages of shallow lakes at Yangtze River Basin (Rose *et al.,* 2004; Wu *et al.,* 2008; Liu *et al.,* 2012; Yao and Xue, 2015). The CRS model

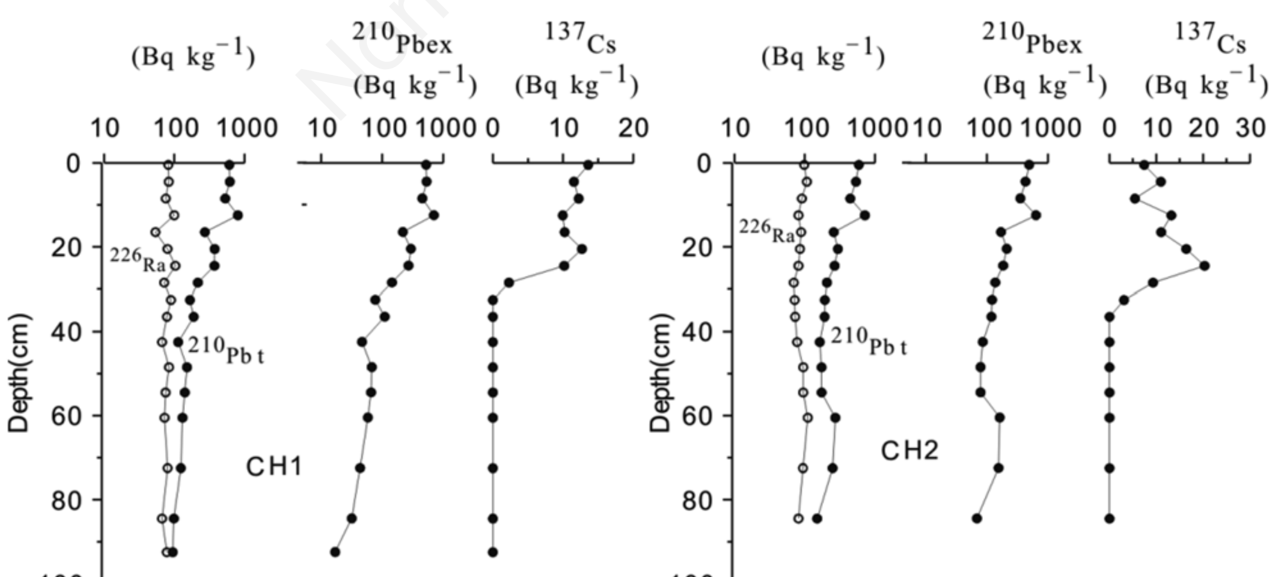

Fig. 2. Vertical profiles of ^{226}Ra, ^{210}Pbt (total ^{210}Pb), $^{210}Pbex$ and ^{137}Cs at Chihu Lake.

gave an age of around 2000 at 20.5 cm depth where ^{137}Cs peaked revealing the discrepancy between the two methods. It can be found that at the bottom of the CH1 core, the ^{210}Pb reached equilibrium with ^{226}Ra, implying that the bottom of the core was approximately 130-150 years old. In this study we selected composite model of ^{210}Pb to date CH1 core using the ^{137}Cs date as a reference point.

In the CH2 core, the first appearance of ^{137}Cs was recorded at 32.5 cm, and ^{137}Cs then peaked at 24.5 cm (Fig. 2), corresponding to the early 1960s. The ^{137}Cs marker gave an average sediment rate of 0.51-0.56 cm a^{-1}. An average sediment rate of 0.71 cm a^{-1} in the layers of 0-42.5 cm also can be obtained using the CIC model based on the relationship between the excess ^{210}Pb and the sediment depth in the CH2 core. The inconsistency between the two independent methods suggested that the ^{210}Pb CIC dating method was unsuitable for sediment layers of 0-42.5 cm at the CH2 site. For sediments below 54.5 cm, the dates also cannot be obtained due to the very high activities of the excess ^{210}Pb (Fig. 2). In this study, we established the sediment chronology of the upper 32.5 cm layers of the CH2 core from the ^{137}Cs distribution. For the lower parts of the core, the sediment age was used based on the comparison of the magnetic susceptibility, showing an excellent correlation between CH1 and CH2 with small differences in the depth of the two significant peaks (Fig. 3).

LOI_{550}, Ca and TP

Generally, the two cores showed an increase in the LOI_{550} with decreasing depth, except for the top 10 cm layers of the CH1 core (Fig. 4). Very low values of the LOI occurred in certain layers between 40 and 65 cm of the CH2 core. The continuous increase in the LOI_{550} represents the increasing organic matter in the lake sediment, which is comparable to the pattern in the organic matter previously reported for recent lacustrine sediments from the Yangtze River Basin (Xue *et al.,* 2010; Zhang *et al.,* 2010). The TP concentrations were relatively low at depths less than 60 cm in the two Chihu cores (Fig. 4). In the upper 60 cm sediments, the TP value remained relatively stable, although a small increase can be observed in the uppermost layers. The Ca concentrations were higher in the upper 25 sediments compared with those in the lower part in the CH1 core (Fig. 4). In the CH2 core, the Ca contents generally decreased from the bottom to approximately 30 cm then increased upward to 8.5 cm and, finally, showed a decrease to the surface sediment (Fig. 4).

Changes in the metals and the $^{206/207}Pb$ in the cores

In the CH1 and CH2 cores, the Fe, Al, K, Mg and Ti contents decreased from 30 cm to approximately 15 cm

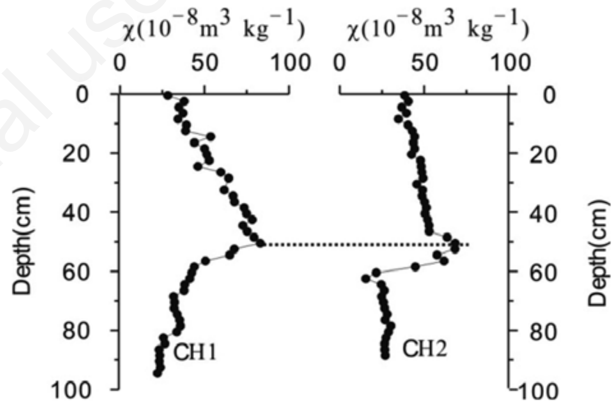

Fig. 3. Sediment magnetic susceptibility (χmass) of the CH1 core and the CH2 core.

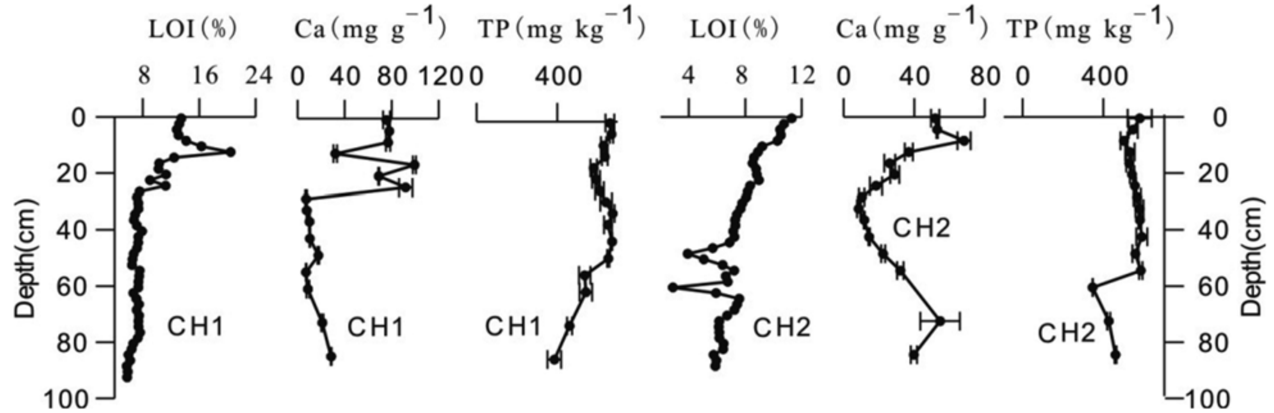

Fig. 4. Depth profiles of the LOI, Ca and TP in the cores from Chihu Lake.

and then remained relatively stable (Fig. 5). Significant changes in the Fe, Al, K, Mg and Ti contents can be observed between 40 and 65 cm in the CH2 core. Fe is diagenetic and mobile in many aquatic systems, depending on the redox conditions (Boyle *et al.,* 1999). The small increase in the Fe content in the upper sediments and the synchronous changes with Al, K and Mg indicated that this metal was not significantly influenced by the diagenetic remobilization process (Fe:Mn) within the Chihu sedimentary cores (Fig. 5).

Fig. 6 presents the heavy metal profiles for the Chihu Lake cores. Generally, Pb, Cu, Zn, and Cd increased sharply from approximately 25 cm to 12.5 cm and then a slight decrease until 4.5 cm. The maximum concentrations for Pb, Cu, Zn and Cd were 77.6, 337, 325 and 9.31mg kg^{-1} dry mass, respectively in the CH1 core. Cr, Co and Ni profiles paralleled those of Fe, Al, and K in the CH1 core (Figs. 5 and 6). The Mn concentration demonstrated a very high value in the 13-14 cm sediment in the CH1 core. The maximum concentrations for Pb, Cu, Zn and Cd were 174, 2047, 1343 and 60.9 mg kg^{-1} dry mass, respectively, in the CH2 core. The Mn concentration increased sharply in the uppermost sediments in the CH2 core.

The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios showed a significant decrease or increase (P<0.01) after the 1960s (at approximately 25 cm) in the CH2 core (Fig. 7). At depths less than 15 cm, the $^{206}Pb/^{207}Pb$ or $^{208}Pb/^{206}Pb$ ratios were relatively stable, and these ratios showed a linear relationship.

PCA analysis

After testing the suitability of the dataset for factor analysis, the multivariate technique of principal components analysis (PCA) varimax rotation was applied to the analyzed matrix of the metals, the LOI, TP and magnetic susceptibility of the Chihu sediments. Rotation of the factor solution is required for an improved interpretation. Two significant components were distinguished from the analyzed data. To interpret a group of variables to be associated with a particular factor, loadings greater than 0.6 were considered.

The first axis explains 58% of the total variance contribution in the CH1 core sediment, correlate positively with Al, Fe, K, Mg, Ti, Cr, Co, Ni and the magnetic susceptibility and negatively with Ca (Tab. 1). The first axis primarily reflected the detrital input from the catchment. The second axis, explains 33% of the common variance of the data set, is highly loaded with Cu, Cd, Pb, Zn, Mn, LOI and TP (Tab. 1), which primarily represented the materials of anthropogenic influence. The results of the PCA analysis of CH2 were different from those of CH1 (Tab. 1). The first axis explains 46% of the total variance contribution in the CH2 core sediment, correlate positively with Cu, Cd, Pb, Zn, Mn, Co, Ni and LOI, whereas the second axis is positively loaded with Al, Fe, K, Mg, Ti, Cr, TP and the magnetic susceptibility, and negatively with Ca (Tab. 1).

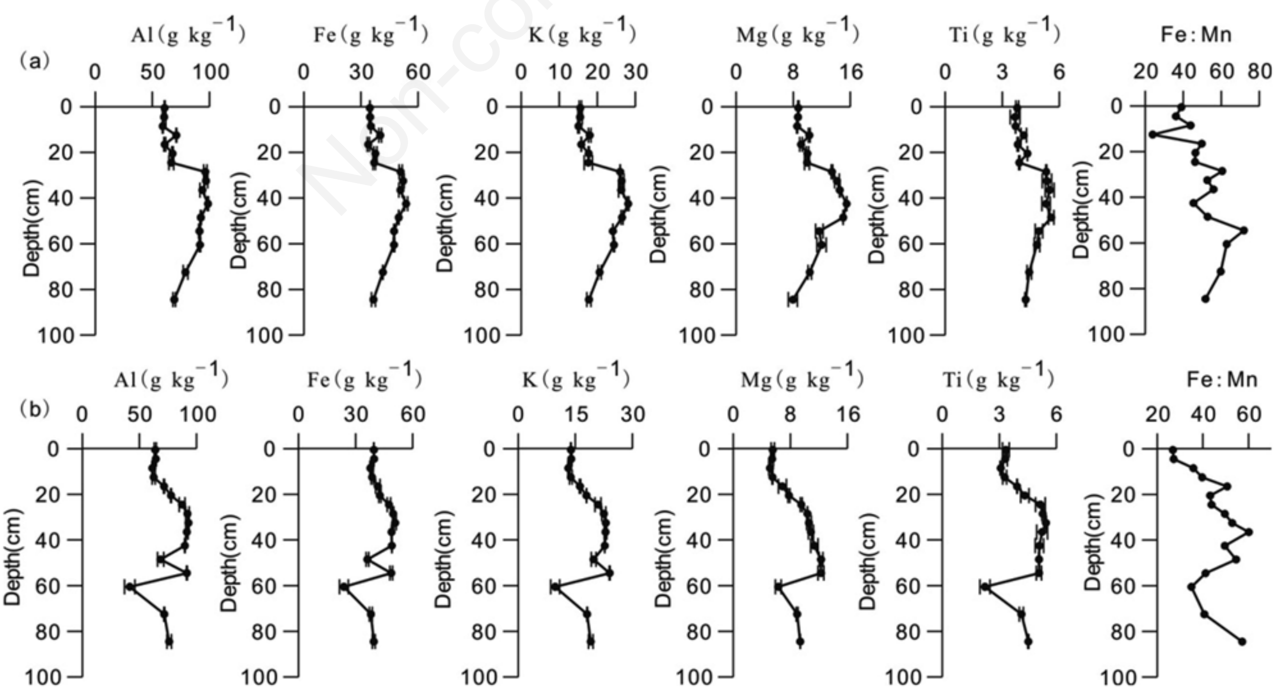

Fig. 5. Depth profiles of the major elements and Fe:Mn ratio in the cores from Chihu Lake. a) CH1 core. b) CH2 core.

Enrichment factors

Enrichment factors (EF) are commonly used to point out the degree of heavy metal pollution in sediments by normalizing the elemental distributions to a conservative element, such as Al, Fe or Ti (Covelli and Fontolan, 1997).

These elements including Al, Fe and Ti are derived from the weathering of the parent materials in the local bedrock and reflect the natural variability in the sediments. Al, Fe and Ti have been widely used as tracer elements in heavy metal pollution studies. In this study, Al was used to generate the enrichment factors. If the lake sediments completely originated from the initial soil or bed-rock without an anthropogenic influence, then the EF value should be 1. When the EF value is larger than 1, there should be another source in addition to a natural input, which can be attributed to an anthropogenic input. The contents of the metals in the lower section of the two Chihu Lake cores (deposited before 1950s) were generally low and constant, indicating limited pollution due to a lower population, few industrial activities (such as mining and refining) in the catchment. Thus, the sediments prior to 1950s were used as the background for the assessment of trace metals pollution in the present work.

The EF values of Cr showed nearly no fluctuation from the bottom to the surface, which indicated that the element in the lake sediments had little or no anthropogenic influence. The EF values of Cd, Cu, Pb, and Zn retained the synchronous trends with their concentrations, which started to increase approximately during the 1960s (Fig. 8). This fact implies that these elements received more anthropogenic inputs after the 1960s in Chihu Lake than prior to that decade. The anthropogenic input of Cd, Cu, Zn, and Pb increased rapidly to 13 cm and, afterwards, showed a small increase or remained stable.

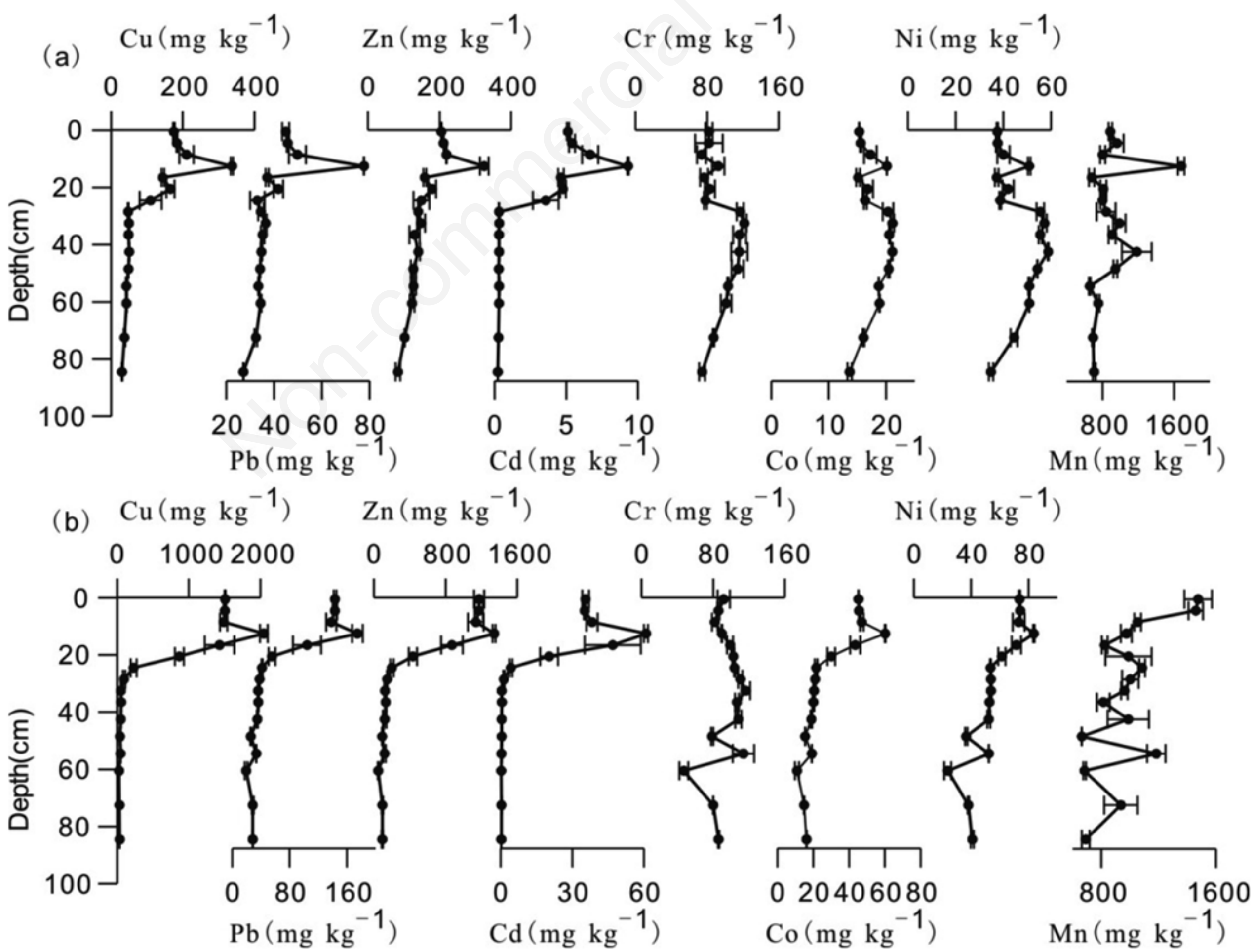

Fig. 6. Depth profiles of the heavy metals in the cores from Chihu Lake. a) CH1 core. b) CH2 core.

DISCUSSION

Metal mobility

For heavy metals released from mining waste, the studied lake is a suitable sink because heavy metal records have demonstrated a succession, which most likely relates to different solubility and adsorption properties of the metal cations. These metals were released via the oxidation process and were transported with acid waters leaking from the mine area until they were buried in the Chihu Lake sediment by adsorbing to the organic matter or by precipitation process. The solubility of lead is less than that of copper and zinc (Adriano, 1986), which most likely explains the anthropogenic lead increase approximately 10 years later (Fig. 8).

Manganese enrichment in the surface sediments of the lakes around the world is common, which may cause metal redistribution (Boyle, 2001). In our study, the Mn contents in the surface sediments (the top 5 cm) were significantly elevated in the CH2 core, and a very high Mn value occurred at 13 cm of the CH1 core (Fig. 6). The PCA revealed that the Mn changes are not controlled by debris input in the lake (Tab. 1). The source of Mn from mining activities can also be excluded because the Mn profiles were not parallel to Cu and Cd, which were primarily from mining waste. Therefore, these extreme changes in Mn imply a reactive Mn redox chemistry. The Mn in the sediments is dissolved under reducing conditions, migrates upward and accumulates in the oxidized surface sediments. However, in this study, the Mn redox cycling did not appear to significantly influence the redistribution of the trace elements because these elements did not show very high concentrations in most of the layers in which Mn was enriched.

The changes in the heavy metal contents related to mining are reproduced among the two cores, suggesting that they exhibit a relatively conservative behavior in the Chihu Lake sediments. The rapid upcore increase in the Cu, Pb, Zn and Cd concentrations in the two cores indicates little reworking of these metals within the sediments. Therefore, once incorporated into the sediments, it is unlikely that these mining-related metals were significantly altered by post depositional processes in the Chihu Lake sediments.

Evidence for anthropogenic heavy metal contamination

The pre-mining heavy metal concentrations (*e.g.*, Cu, Zn, and Cd) were relatively stable and were similar to the historic concentrations reported from Poyang Lake in Jiangxi (Liu, 1990; Yuan *et al.*, 2011). The recent sediment Cu, Cd, Zn and Pb concentrations in the Chihu Lake were more variable due to the effect of human activities, such as mining. The maximum sedimentary contents of the heavy metals related to copper mining were exceptionally high and above the standards for marine sediment and soils (GB18668-2002, GB15618-2008). The maximum concentration for Zn exceeds 1000 mg kg^{-1} dry mass (DM), 2000 mg kg^{-1} DM for Cu and 60 mg kg^{-1} DM for Cd (Fig. 6). These values are more than one or two orders of magnitude higher than the mean background levels for unpolluted lake sediments in the middle Yangtze River

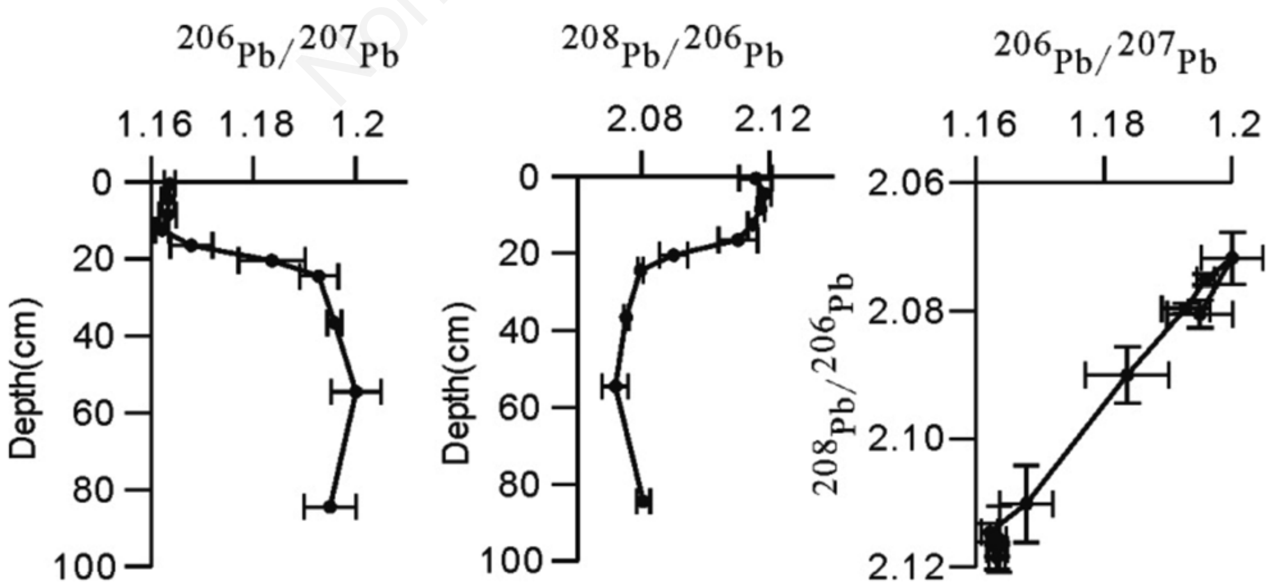

Fig. 7. Depth profiles of the Pb isotope ratios, ^{206}Pb/^{207}Pb *vs* ^{208}Pb/^{206}Pb, at the CH2 core from Chihu Lake.

drainage (Liu, 1990; Liu *et al.,* 2007; Yuan *et al.,* 2011; Wu *et al.,* 2012; Bing *et al.*, 2013). However, comparable high heavy metal contents have been found elsewhere, *e.g*., from Moshui Lake, receiving a high metal load due to the rapid urbanization and industrialization in Wuhan City (Liu *et al.*, 2008). Chen *et al.* (2008) have also reported that the lead, zinc and copper concentrations in stream sediments exceeded 1% DM, extending kilometers away from the mining activities.

Hilton *et al*.'s (1985) procedure can be used to detect the contribution of the anthropogenic heavy metal pollution. This procedure is performed by identifying a depth at which the heavy metal concentrations vary independently. At the Chihu Lake, such a depth can be simply identified for Pb, Cu, Cd, Zn, Co or Ni, thus making it possible to determine the anthropogenic heavy metal contribution (Fig. 9). For Cr, the depth cannot be identified, thus making it difficult to determine the anthropogenic Cr contribution (Fig. 9). A lower anthropogenic contribution of Cr to the Chihu Lake sediments relative to the natural sources may explain the difficulty. In addition, high sediment rates further caused the low enrichment of Cr in the lake. Therefore, mining activities did not appear to significantly influence the Cr concentration.

Lead (Pb) is a particularly well-known pollutant associated with mining and other human activities, such as vehicle transportation, coal combustion, lead ore exploitation and use, among others. Lead can be easily transported to aquatic systems by river or atmosphere. The $^{206}Pb/^{207}Pb$ ratios for the pre-mining Chihu sediments were approximately 1.20. And the value of 1.20 for $^{206}Pb/^{207}Pb$ can be regarded as background value at Chihu Lake. The copper mining source of lead showed a $^{206}Pb/^{207}Pb$ value of 1.151-1.152 (Huang *et al.*, 1990). Regional sources of lead also have a relatively low value of $^{206}Pb/^{207}Pb$ (Fig. 10). In the CH2 core of Chihu Lake, the $^{206}Pb/^{207}Pb$ ratios remained low or continued to decrease in recent sediments, indicating the increasing anthropogenic source of lead to the CH2 site over the past decades (Fig. 7).

Sources of anthropogenic heavy metal

The legacy of this Cu mining manifests itself within the local soils and the sediments of Chihu Lake. Cu, Pb, Zn and Cd anomalies in the local soils have been identified in the mining area (Liu *et al.*, 1986) and have been linked to mining activities at the Wushan Copper Mine. The concentrations of Cu, Pb, Zn and Cd in the Chihu Lake sediments were significantly enriched, also reflecting the influence of the mining waste at the Wushan Copper Mine.

The mining effect may be limited in areas adjacent to the mine, or they can be transported off-site. There is a heavy metal (Cu, Pb, Zn, and Cd) decline with the distance from the source in the Chihu Lake sediment record. The distance-decline effect is related to the mechanism by which the pollution metal is transferred to the sediment record. The sediments of the CH2 core, located near the Wushan Copper Mine, received large amounts of heavy metals from the drainage of the mine waste and a lesser amount of atmospheric deposition of heavy metals. The lead isotopic ratios and the metal contents revealed anthropogenic loading of the heavy metals into the lake after the 1960s, which corresponds to a period of Wushan Copper Mine exploitation and development.

In contrast to Cu or Cd, which showed very high EF values, the enrichment factors of Pb in the topmost sedi-

Tab. 1. Factor loadings after the Varimax rotation (PC extracted 2 factors).

	CH1 core		CH2 core	
	Axis 1	Axis 2	Axis 1	Axis 2
Al	0.94			0.94
Fe	0.98			0.97
K	0.95			0.89
Mg	0.97		-0.72	0.65
Ti	0.94			0.88
Mn		0.83	0.66	
Ca	-0.81			-0.93
TP		0.62		0.89
χ	0.87			0.79
Zn		0.97	0.97	
Cr	0.98			0.96
Co	0.95		0.98	
Ni	0.99		0.97	
Cu		0.89	0.96	
Cd		0.83	0.93	
Pb		0.95	0.97	
LOI		0.89	0.89	

LOI, loss on ignition.

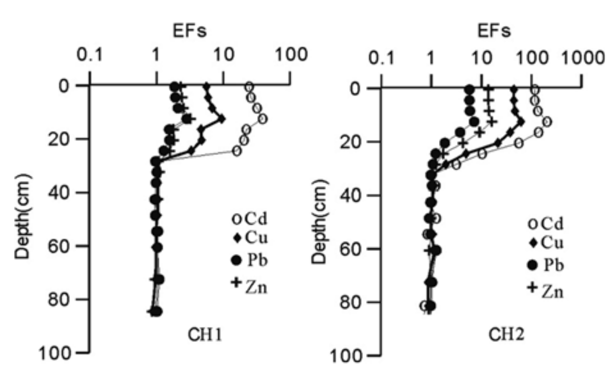

Fig. 8. Enrichment factors of the heavy metals at the Chihu Lake sediment cores.

ments were approximately 7 and 2 in CH2 and CH1, respectively (Fig. 8). The extent of the Pb enrichment at the CH1 site was comparable to many lakes located in the middle and Yangtze River Basin in which there is no point pollution of Pb (Rose *et al.,* 2004; Liu *et al.,* 2007; Yao *et al.,* 2009; Yuan *et al.,* 2011). The low enrichment of Pb at CH1 implies that the atmospheric source of Pb loading to the lake cannot be ignored or may even be a major source to the lake sediment at the CH1 site.

To further investigate the possible sources of Pb in the sediments, the Pb isotopic compositions of the sediments were compared with the mining ores and other environmental samples (Fig. 10). The plot of the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios of the CH2 core sediments represents the Pb isotopic compositions during different historical periods. Prior to the 1960s, the $^{206}Pb/^{207}Pb$ ratios were at their highest, representing the background values during the pre-mining era (Fig. 10). Since the 1960s, the $^{206}Pb/^{207}Pb$ ratios have decreased, and have more closely resembled those of the mining materials (the Wushan copper) (Huang *et al.,* 1990) and the regional sources of lead (Mukai *et al.,* 2001; Zhang *et al.,* 2006). The similar signature of the isotopic composition makes it difficult to quantitatively identify the local or regional sources of lead pollution of the Chihu Lake sediment. If the CH1 site primarily receives an atmospheric input of lead, then the mining waste source of Pb at CH2 was 0.001 g cm^{-2} estimated from the comparison of the anthropogenic flux of Pb in the two cores.

Historical change in the anthropogenic heavy metals

The similar heavy metal pollution signals identified within the two sediment cores of Chihu Lake allows them to be compared with the mining activities and the Cu production at the Wushan Copper Mine. Detailed records exist for the Wushan Copper Mine, including dates for the start of Cu mining, the population of the mine and for ore production (Compilation Committee of Chorography of Science and Technology of Wushan Copper, 1994; Li, 1999; Wu *et al.,* 2001).

Mining began in 1970 in the Wushan Copper Mine area; however, the onset of changes in the sedimentary heavy metal profile was approximately during the early 1960s in the two cores, which appears to predate the opening of the copper mining era. Although there is a level of uncertainty in the ^{210}Pb dating and the bioturbation, resuspension, and diffusion that can distort the onset of changes in the sedimentary record, another explanation must be considered. The Wushan Copper Mine construction that started in 1966 can also enhance the metal (such as Cu) loading into the Chihu Lake sediment. Population changes at the Wushan mine demonstrated a strong relationship with the Cu concentration after 1965 (Fig. 11), further confirming the above explanation. From 1978-1985, new techniques were introduced, leading to a rapid increase in the production and processing (Compilation Committee of Chorography of Science and Technology of Wushan Copper, 1994). In addition, the population in-

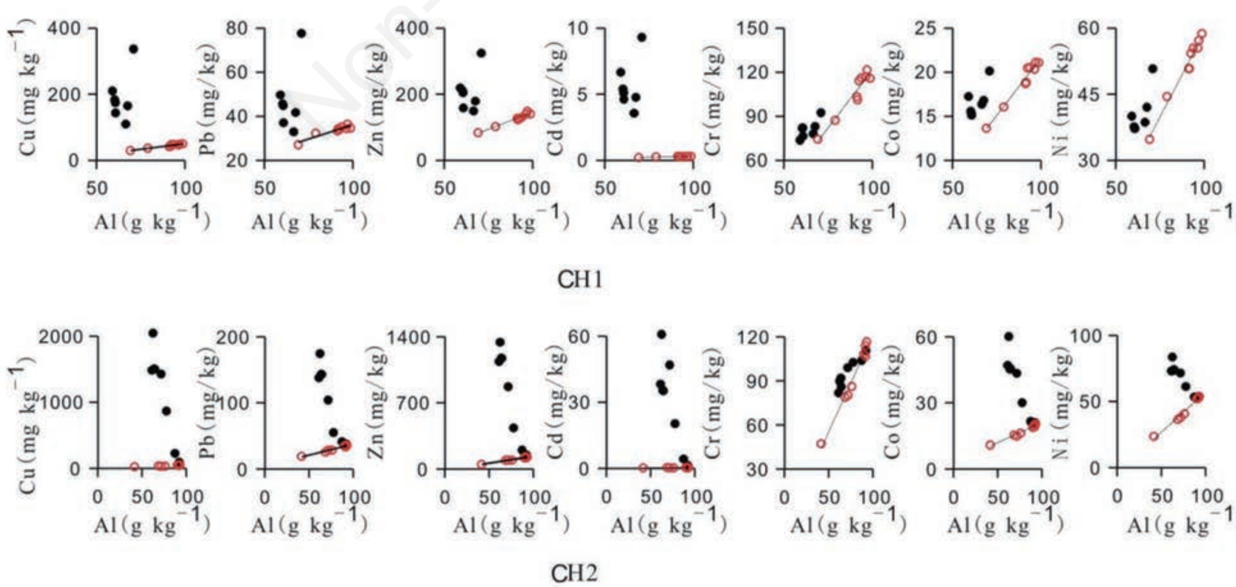

Fig. 9. Baseline estimates based on the procedure of Hilton *et al.* (1985). The filled squares represent samples that have a metal contribution from pollution. The open circles are those samples in the pre-mining period.

creased rapidly during this time. Therefore, copper and other metals in the Wushan Lake sediments increased sharply during this period. However, after the mid-1980s, the Cu concentration did not parallel the ore production (Fig. 11). An analysis of the waste rock from the tailing reservoir revealed that after 1992, the Cu content decreased from 0.538% to 0.3% (Wang, 1997), which indicated the effect of the introduction of mining waste treatment in 1989.Additionally, most likely after 1989, the environmental protection, such as waste treatment, resulted in the reduced loading of the heavy metals from the mining waste to Chihu Lake.

Influence of mining pollution on the lake plants

The LOI began to increase after the 1950s in both of the cores. However, the magnitude of the increase of the LOI in CH1 was larger than that in CH2 (Fig. 12). There are two explanations for the difference in the two cores. First, more phosphorus inputs in the CH1 site caused more aquatic plants to grow; therefore, more organic matter was deposited compared with the CH2 site. Second, the abundance of aquatic plants was affected by the mining waste. The CH2 site was close to the Wushan copper mining area, whereas the CH1 site was relatively distant from the copper mine. The heavy metal analysis also revealed that the CH2 site was heavily polluted with a Cu concentration above 1000 mg kg^{-1} dry mass. The macrophyte surveys conducted in 1985 indicated the decrease of the aquatic plants in the lake area near the mine (Wu and Wu, 1996). In addition, human actives in the lake, such as crab farming, may be the reason for the LOI decline after the 1980s in the CH1 core.

The anthropogenic phosphorus was estimated from the TP normalized by Al for Chihu Lake sediments (Fig. 12) (Wu *et al.,* 2008; Liu *et al.,* 2012). The increasing anthropogenic phosphorus inputs to Chihu Lake seems not to be related to the mining waste input because the phosphorus profiles did not parallel those of Cu, Zn, Pb and Cd. In addition, anthropogenic phosphorus contents were lower in CH2 than those in CH1 (Fig. 12); the latter being the site closer to the mine pollution source. Re-

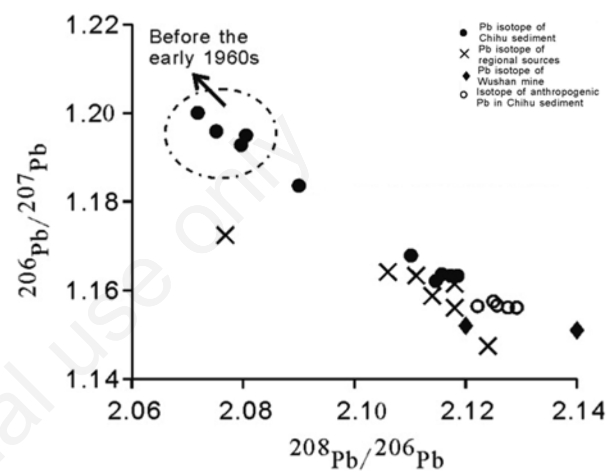

Fig. 10. The relationship between the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of the sediments from Chihu Lake with other sources (ores, aerosols, coal dust, gasoline) from the middle and lower Yangtze region as reported in the literature (Mukai *et al.*, 2001; Zhang *et al.*, 2006). The anthropogenic Pb that accumulated in the CH2 core sediments of Chihu Lake was estimated from the enrichment factors (Shotyk *et al.*, 2003; Yao *et al.*, 2013).The isotopic compositions of the anthropogenic Pb were estimated using the mixing model following Bindler *et al.* (2001).

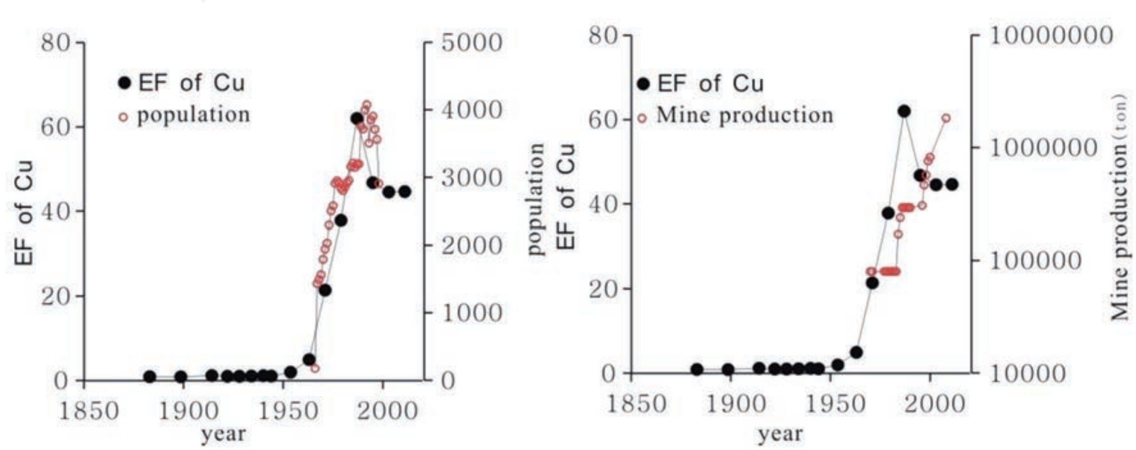

Fig. 11. Comparison of the enrichment factors of Cu in the CH2 core with the population at the Wushan Copper Mine (left) and with the mine production (right) (Wu *et al.*, 2001).

gional development, including farming activities and sewage input, can be the primary contribution to the rising phosphorus in the sediments over the past decades in Chihu Lake. Increases in the organic matter over the past decades should be primarily due to the increased growth of the aquatic plants rather than catchment input at CH1 site. Preservation was an important factor for the increasing organic matter deposition in CH2 site.

A survey conducted in 2007 showed that Chl*a* was 3.6 μg L^{-1}, and TP was 40 μg L^{-1}. The water TP concentration was in the range of the background value of the Yangtze lakes (Yang *et al.,* 2008; Chen *et al.,* 2011). The increased nutrient input to Chihu Lake, caused macrophyte communities to flourish, and contribute the low TP concentration in the water. Brenner et al (1999) and Zhang *et al*. (2012) have found this phenomenon in macrophytes-dominated shallow lakes. The gradual loss of the macrophytes near the mining area, including the CH1 site, risked the transformation of macrophytes domination to algae domination.

CONCLUSIONS

The heavy metal content, the reference elements and the lead isotope ratios were used to detect the heavy metal pollution in the sediments from two cores extracted from Chihu Lake in the middle Yangtze River Basin in China. The Pb, Cu, Zn, Cd, Co and Ni contents have increased over the past 30 to 40 years. The maximum concentration of Cu, Zn and Cd recorded in the 1990s was 2047, 1343 and 60.9 mg kg^{-1}, respectively. The heavy metal enrichment was high overall because of the mining waste discharge from the Wushan Copper Mine. The Cu concentrations in the sediment cores were not completely parallel to the copper ore production because the environmental protection measures, such as waste treatment, have resulted in the reduced loading of heavy metals from mining waste to Chihu Lake after the late 1980s.

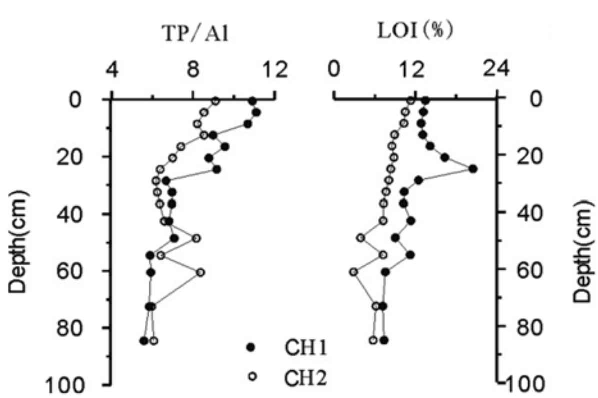

Fig. 12. Comparison of the Al-normalized TP and LOI in the CH1 and CH2 cores.

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REFERENCES

Adriano DC, 1986. Trace elements in the terrestrial environment. Springer: 867 pp.

Anomournas, 1977. [Test of Wushan Copper sewage treatment].[Article in Chinese]. Nonferrous Metals (Extractive Metallurgy): 27-32.

Arnason JG, Fletcher BA, 2003. A 40+ year record of Cd, Hg, Pb, and U deposition in sediments of Patroon Reservoir, Albany County, NY, USA. Environ. Pollut. 123:383-391.

Audry S, Schafer J, Blanc G, Jouanneau JM, 2004. Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). Environ. Pollut. 132:413-426.

Balogh SJ, Engstrom DR, Almendinger JE, Mcdermott C, Hu J, Nollet YH, Meyer ML, Johnson DK, 2009. A sediment record of trace metal loadings in the Upper Mississippi River. J. Paleolimnol. 41:623-639.

Bindler R, Renberg I, Anderson NJ, Appleby PG, Emteryd O, Boyle J, 2001. Pb isotope ratios of lake sediments in West Greenland: inferences on pollution sources. Atmos. Environ. 35:4675-4685.

Bing HJ, Wu YH, Nahm WH, Liu EF, 2013. Accumulation of heavy metals in the lacustrine sediment of Longgan Lake, middle reaches of Yangtze River, China. Environ. Earth Sci. 69:2679-2689.

Boyle JF. 2001. Inorganic geochemical methods in palaeolimnology, p. 83-141. In: W.M. Last and J.P. Smol (eds.), Tracking environmental change using lake sediments. 2. Physical and geochemical methods. Kluwer, Dordrecht.

Boyle JF, Rose NL, Bennion H, Yang H, Appleby PG, 1999. Environmental impacts in the Jianghan plain: Evidence from lake sediments. Water Air Soil. Poll. 112:21-40.

Brenner M, Whitmore TJ, Lasi MA, Cable JE, Cable PH, 1999. A multi-proxy trophic state reconstruction for shallow Orange Lake, Florida, USA: possible influence of macrophytes on limnetic nutrient concentrations. J. Paleolimnol. 21:215-233.

Chen CH, Ni SJ, He BB, Zhang CJ, 2008. [Spatial-temporal variation of heavy metals contamination in sediments of the dexing mine, Jiangxi province].[Article in Chinese]. Acta Geoscientica Sinica 29:639-646.

Chen X, Yang XD, Dong XH, Liu QA, 2011. Nutrient dynamics linked to hydrological condition and anthropogenic nutrient loading in Chaohu Lake (southeast China). Hydrobiologia 661:223-234.

Cheng HF, Hu YA, 2010. Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: a review. Environ. Pollut. 158:1134-1146.

Compilation Committee of Chorography of Ruichang County, 1990. [Chorography of Ruichang County].[Report in Chinese].

Compilation Committee of Chorography of Science and Technology of Wushan Copper, 1994. [Chorography of science and technology of Wushan copper]. Article in Chinese

Couillard Y, Cattaneo A, Gallon C, Courcelles M, 2008. Sources and chronology of fifteen elements in the sediments of lakes affected by metal deposition in a mining area. J. Paleolimnol. 40:97-114.

Covelli S, Fontolan G, 1997. Application of a normalization procedure in determining regional geochemical baselines. Environ. Geol. 30:34-45.

Ek AS, Renberg I, 2001. Heavy metal pollution and lake acidity changes caused by one thousand years of copper mining at Falun, central Sweden. J. Paleolimnol. 26:89-107.

Farmer JG, Mackenzie AB, Sugden CL, Edgar PJ, Eades LJ, 1997. A comparison of the historical lead pollution records in peat and freshwater lake sediments from central Scotland. Water Air Soil. Poll. 100:253-270.

Franco-Uria A, Lopez-Mateo C, Roca E, Fernandez-Marcos ML, 2009. Source identification of heavy metals in pastureland by multivariate analysis in NW Spain. J. Hazard. Mater. 165:1008-1015.

Grayson RP, Plater AJ, 2009. A lake sediment record of Pb mining from Ullswater, English Lake District, UK. J. Paleolimnol. 42:183-197.

Heiri O, Lotter AF, Lemcke G, 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. J. Paleolimnol. 25:101-110.

Hilton J, Davison W, Ochsenbein U, 1985. A Mathematical-Model for Analysis of Sediment Core Data - Implications for Enrichment Factor Calculations and Trace-Metal Transport Mechanisms. Chem. Geol. 48:281-291.

Huang EB, Zhang NT, Luo ZS, 1990. [The genesis of the Chengmenshan and Wushan copper deposits].[Article in Chinese]. Mineral deposits 9:291-300.

Laperriere L, Fallu M-A, Hausmann S, Pienitz R, Muir D, 2008. Paleolimnological evidence of mining and demographic impacts on Lac Dauriat, Schefferville (subarctic Québec, Canada). J. Paleolimnol. 40:309-324.

Li H, 1999. [Statistical analysis and risk evaluation of annual casualties at Wushan Copper Mine].[Article in Chinese]. Jiangxi Nonferrous Metal 13:15-18.

Liu EF, Shen J, Birch GF, Yang XD, Wu YH, Xue B, 2012. Human-induced change in sedimentary trace metals and phosphorus in Chaohu Lake, China, over the past half-millennium. J. Paleolimnol. 47:1-15.

Liu EF, Yang XD, Shen J, Dong XH, Zhang EL, Wang SM, 2007. Environmental response to climate and human impact during the last 400 years in Taibai Lake catchment, middle reach of Yangtze River, China. Sci. Total Environ. 385:196-207.

Liu HL, Li LQ, Yin CQ, Shan BQ, 2008. Fraction distribution and risk assessment of heavy metals in sediments of Moshui Lake. J. Environ. Sci (China) 20:390-397.

Liu M, 1990. Heavy metal pollution at Poyang Lake. Enviromental Science and Technology 48:1-5 (in Chinese).

Liu YH, Zhao ZJ, Zeng YY, Zhang NZ, 1986. [An appraisal about the effects of the opening of Wushan Copper mine to the local soils and crops].[Article in Chinese]. Acta Agricultural Universities Jiangxiensis 8:75-82.

Marcantonio F, Zimmerman A, Xu YF, Canuel E, 2002. A Pb isotope record of mid-Atlantic US atmospheric Pb emissions in Chesapeake Bay sediments. Mar. Chem. 77:123-132.

Michelutti N, Laing TE, Smol JP, 2001. Diatom assessment of past environmental changes in lakes located near the Noril'sk (Siberia) smelters. Water Air Soil. Poll. 125:231-241.

Mukai H, Tanaka A, Fujii T, Zeng YQ, Hong YT, Tang J, Guo S, Xue HS, Sun ZL, Zhou JT, Xue DM, Zhao J, Zhai GH, Gu JL, Zhai PY, 2001. Regional characteristics of sulfur and lead isotope ratios in the atmosphere at several Chinese urban sites. Environ. Sci. Technol. 35:1064-1071.

Nriagu JO, 1998. Tales told in lead. Science 281:1622-1623.

Ostrofsky ML, Schworm AE, 2011. A history of acid mine contamination, recovery, and eutrophication in Sandy Lake, Pennsylvania. J. Paleolimnol. 46:229-242.

Pacyna JM, Pacyna EG, 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ. Rev. 9:269-298.

Rose NL, Boyle JF, Du Y, Yi C, Dai X, Appleby PG, Bennion H, Cai S, Yu L, 2004. Sedimentary evidence for changes in the pollution status of Taihu in the Jiangsu region of eastern China. J. Paleolimnol. 32:41-51.

Salonen VP, Tuovinen N, Valpola S, 2006. History of mine drainage impact on Lake Orijarvi algal communities, SW Finland. J. Paleolimnol. 35:289-303.

Shotyk W, Goodsite ME, Roos-Barraclough F, Frei R, Heinemeier J, Asmund G, Lohse C, Hansen TS, 2003. [Anthropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the 14C "bomb pulse curve"].[Article in Chinese]. Geochim. Cosmochim. Ac. 67:3991-4011.

Wan GJ, Santschi PH, Sturm M, Farrenkothen K, Lueck A, Werth E, Schuler C, 1987. Natural (Pb-210, Be-7) and Fallout (Cs-137, Pu-239-240, Sr-90) Radionuclides as Geochemical Tracers of Sedimentation in Greifensee, Switzerland. Chem. Geol. 63:181-196.

Wang LM, 1997. [Analysis of tailings recovery from Wushan Copper plant].[Article in Chinese]. Nonferrous Metallurgy Design and Research 18:38-52.

Wang SM, Dou HS, 1998. [Chinese Lake Annals].[Book in Chinese]. Science Press: 265 pp.

Wu HY, Zhang JC, Yu J, 2001. [Potential from the analysis of the production and operation during 9th Five-Year at Wushan Copper Mine].[Article in Chinese]. China Metal Bulletin 18-21.

Wu JL, Zeng HA, Yu H, Ma L, Xu LS, Qin BQ, 2012. Water and sediment quality in lakes along the middle and lower reaches of the Yangtze River, China. Water Resour. Manag. 26:3601-3618.

Wu WP, 1987a. [Preliminary investigation on the Chihu Lake aquatic vascular plants in Jiangxi Province].[Article in Chinese]. Journal of Jiangxi University (Natural Science) 11:64-71.

Wu WP, 1987b. [The vegetation of Wushan Copper Mine field in Jiangxi and environmental protection].[Article in Chinese]. Journal of Jiangxi University (Natural Science) 11:54-61.

Wu WP, Wu ZZ, 1996. [The aquatic vascular plants of Chihu Lake of Jiangxi Province and their environmental impact].[Article in Chinese]. Journal of Nanchang University (Natural Science) 20:188-192.

Wu YH, Liu EF, Yao SC, Zhu YX, Xia WL, 2010. Recent heavy metal accumulation in Dongjiu and Xijiu lakes, East China. J. Paleolimnol. 43:385-392.

Wu YH, Lucke A, Wang SM, 2008. Assessment of nutrient sources and paleoproductivity during the past century in Longgan Lake, middle reaches of the Yangtze River, China. J. Paleolimnol. 39:451-462.

Xue B, Yao SC, Xia WL, Zhu YX, 2010. Some sediment-geochemical evidence for the recent environmental changes of the lakes from the middle and lower Yangtze River basin, China. Quatern. Int. 226:29-37.

Yang XD, Anderson NJ, Dong XH, Shen J, 2008. Surface sediment diatom assemblages and epilimnetic total phosphorus in large, shallow lakes of the Yangtze floodplain: their relationships and implications for assessing long-term eutrophication. Freshwater Biol. 53:1273-1290.

Yang HD, Rose N, 2005. Trace element pollution records in some UK lake sediments, their history, influence factors and regional differences. Environ. Int. 31:63-75.

Yao SC Xue B, 2015. Sedimentary geochemical record of human-induced environmental changes in Huanggaihu Lake in the middle reach of the Yangtze River, China. J. Limnol. 74:31-39.

Yao SC, Xue B, Tao YQ, 2013. Sedimentary lead pollution history: lead isotope ratios and conservative elements at East Taihu Lake, Yangtze Delta, China. Quatern. Int. 304:5-12.

Yao SC, Xue B, Xia WL, Zhu YX, Li SJ, 2009. Lead pollution recorded in sediments of three lakes located at the middle and lower Yangtze River basin, China. Quatern. Int. 208:145-150.

Yuan GL, Liu C, Chen L, Yang ZF, 2011. Inputting history of heavy metals into the inland lake recorded in sediment profiles: Poyang Lake in China. J. Hazard. Mater. 185:336-345.

Zhang EL, Cao YM, Langdon P, Jones R, Yang XD, Shen J, 2012. Alternate trajectories in historic trophic change from two lakes in the same catchment, Huayang Basin, middle reach of Yangtze River, China. J. Paleolimnol. 48:367-381.

Zhang EL, Liu EF, Jones R, Langdon P, Yang XD, Shen J, 2010. A 150-year record of recent changes in human activity and eutrophication of Lake Wushan from the middle reach of the Yangze River, China. J. Limnol. 69:235-241.

Zhang GL, Tan MG, Li XL, Zhang YX, Yue WS, Chen JM, Wang YS, Li AG, Li Y, Zhang YM, Shan ZC, 2006. [Comprehensive study of lead pollution in atmospheric aerosol of Shanghai].[Article in Chinese]. Environ. Sci. 27:831-836.

Zhao JX, 1994. [Wushan copper mine waste water treatment and comprehensive utilization].[Article in Chinese]. Journal of Kuming Institute of Technology 19:125-130.