Heavy metals in an impacted wetland system: a typical case from southwestern China

Xiangyang Bi[a, b], Xinbin Feng[a, *], Yuangen Yang[a], Guangle Qiu[a], Xiaoli Qian[a, c], Feili Li[a, d], Taoze Liu[a, b], Tianrong He[a, b], Ping Li[a, b], Zhiyou Fu[a, b], Xiangdong Li [e] and Grace Shin [e]

[a] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, P. R. China;

[b] Graduate School of the Chinese Academy of Sciences, Beijing 100039, P. R. China;

[c] Guizhou University, Guiyang 550025, P. R. China;

[d] College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310032, P. R. China

[e] Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

[*] Corresponding author. Tel.: +86-851-5891356; fax: +86-851-5891609.

E-mail address: fengxinbin@vip.skleg.cn

Abstract

Historic zinc smelting in Hezhang, southwestern China, has resulted in significant heavy metal contamination to the surrounding ecosystems. The Caohai wetland system, an important national nature reserve close to the Hezhang zinc smelting area, was investigated in the present study. Results showed that sediments from the Caohai wetland system have been seriously contaminated by Cd, Pb and Zn with the highest enrichment factors (*EF*) up to 91, 16 and 41, respectively. The heavy metals in the sediments were mainly presented in the organic and residual fractions, both of which can be changed into Fe-Mn oxide fraction in a more oxidized condition induced by the aquatic plants. Pb isotopic compositions in the sediments indicated a ternary mixing model with ore Pb, gasoline Pb and geogenic Pb as the three end members/sources which accounted for about 60, 26, and 14%, respectively, of the inventory of Pb in the sediments. Heavy metal contamination in aquatic plants was also studied and the results indicated that heavy metals accumulated by plants may pose a potential threat to the higher trophic-level organisms, even humans.

Keywords: Heavy metals; Pb isotopes; Sequential chemical fraction; Aquatic plant; Zinc smelting; Caohai wetland; China

1 Introduction

Sediments are recognized as an important sink for heavy metals emitted from anthropogenic sources, as well as a potential non-point pollution source which may directly affect overlying waters and the aquatic organisms. It is well accepted that the total concentrations of heavy metals in sediments can not provide sufficient information about their impacts to the ecosystem because the mobility, bioavailability and toxicity of metals depends not only on their total concentrations but also on the geochemical fractions in which they occur. Thus, various extraction procedures have been developed to assess the partitioning of sediment/soil-associated metals among various geochemical fractions and to evaluate the metal mobility and bioavailability (Tessier et al., 1979; Kersten and Förstner, 1986; Ure et al., 1993). The Tessier sequential extraction procedure is among the most common used methods, although the disadvantages of this extraction scheme have been well recognized (e.g., non-specificity of extraction and re-sorption of metals) (Nirel and Morel, 1990; Gomez-Ariza et al., 1999; Rapin et al., 1986).

Metal fractionations in sediment are strongly depended on the substrata geochemical conditions, such as the pH and redox potential (Tessier et al., 1979). Many studies (e.g., Jacob and Otte, 2004a, b; Almeida et al., 2004) found that aquatic plants can alter the chemistry of the sediment (for instance, causing changes in pH and redox potential), modifying the metal fractionations in the sediment. For example, Almeida et al. (2004) reported that metals associated with the residual fraction were significantly lower in the rhizosediment than in the sediment. On the other hand, metals settled in the sediment can be accumulated by aquatic plants. Many studies reported that high metal concentrations in sediments often result in high levels of metals in the onsite vegetations (Deng et al., 2004; Hozhina et al., 2001; Cymerman-Samecka and Kempers, 2004). Therefore, the investigations of metal accumulations in plants can provide vital information on what extents the contamination has impacted on an aquatic ecosystem.

In addition to the quantitative measurement of heavy metals, Pb isotopic compositions can be very useful for identifying sources and contributions of anthropogenic Pb and have been widely used in a wide range of environmental studies (Mukai et al., 1993, 2001; Gélinas and Schmit, 1997; Zhu et al., 2001; Wong and Li, 2004; Lee et al., 2006; Gallon et al., 2006). As a general rule, anthropogenic Pb derived from an ore is less radiogenic than the geogenic Pb. For example, the $^{206}Pb/^{207}Pb$ ratios of Pb used to manufacture gasoline additives in south China are generally lower than 1.17 (Zhu et al., 2001). In comparison, the $^{206}Pb/^{207}Pb$ ratios of naturally derived Pb are often higher than 1.20 (Wong and Li, 2004; Lee et al., 2006).

Zinc smelting activities have caused many serious environmental problems in China in terms of heavy metal pollution due to the fact that not only China is the largest zinc producer in the world, but also to the fact that most zinc industry in China has used the old technique in smelting without the necessary pollution control measures. However, this kind of pollution has not been well studied so far. Hezhang, located in southwest China, is a typical region which had been seriously impacted by historical zinc smelting activities (Feng et al., 2004, 2006; Bi et al., 2006a, b; Yang et al., 2006). In this study, the impact of the deposits from the Hezhang zinc smelting emissions on a natural freshwater wetland (Caohai) was investigated. The objectives of the present research are (1) to evaluate the metal enrichment characteristics in the wetland sediments; (2) to determine the geochemical fractionations of heavy metals in the sediments using Tessier sequential extraction method for their mobility and bioavailability; (3) to identify the potential origins of the sediment Pb by lead isotopes; and (4) to delineate the extent to which these metals accumulate in the onsite vegetations.

2. Materials and methods

2.1. Study site

The Caohai natural wetland (104°12′-104°18′ E，26°49′-26°53′ N), an important national natural reserve for migratory birds in China, is situated in northwestern Guizhou, approximately 350 km west of Guiyang, the capital of Guizhou Province. It lies on the Yunnan-Guizhou Plateau with an altitude of about 2100 m above sea level. Its climate represents a typical subtropical humid monsoon type with an average temperature of 10.6°C and an average annual rainfall of 951 mm. The Caohai wetland is underlain mainly by Carboniferous limestone and dolomite with water surface area about 25 km^2 and depth of 1-5 m. The major source of water in the Caohai wetland is precipitation. The Hezhang zinc smelting area is located approximately 15 km northeast of the Caohai wetland (Fig. 1)

2.2. Sample collection and analysis

Field sampling at the Caohai wetland was carried out in September 2005 and June 2006. Ten surface sediment samples (from the top 5 cm) were collected by grab sampler for heavy metal screening. In order to develop profiles of heavy metals with respect to sediment depths, two cores were also collected by gravity sampler. Both core and grab samples were air dried and ground < 100 mesh prior to the chemical analysis. For the total metal concentration analysis, sediment samples (0.5g) were digested by a 10 mL HNO_3 (65%, v/v), HCl (30%, v/v) and HF (40%, v/v) mixture in a sealed Teflon vessel. Metal fractionations were performed using a modified version of the method described by Tessier et al. (1979). The sequential extraction procedure consisted of extractions in the following order with associated chemical reagents and conditions: exchangeable fraction (1 M $MgCl_2$, pH 7.0, for 1h), carbonate fraction (1 M NaOAc, pH 5.0, for 5h), Fe-Mn oxide bound fraction (0.04 M $NH_2OH{\cdot}HCl$ in

25% (v/v) HOAc at 96°C for 6h), organic fraction (30% H_2O_2 and 0.02 M HNO_3 for 2h, second 30% H_2O_2 at 85°C for 3h), and residual fraction (total digestion with concentrated HNO_3-HCl-HF acid mixture). After each extraction step was completed, the samples were centrifuged at 3000 *g* for 15 minutes at room temperature, and the resulting supernatant was filtered through a 0.45 μm filter and saved for analysis. Between each reaction step, samples were rinsed with 8 mL of deionized water, and the wash solution was discarded after centrifuging for 15 minutes.

Plant samples, including emergent, submerged and floating aquatic vegetations, were taken from a range of species present at the Caohai wetland. The submerged species, primarily *C. demersum*, *M. spicatum.* and *P. malainus*, were the most common type of aquatic macrophyte. They grow in most parts of the wetland, especially in the deep water region. Whereas the emergent and floating species are generally found in the shallow water near the edge of the wetland. The above and under water stem and leaves (aboveground tissues) of plants were collected by hand with gloves. Each sample consisted of 5-10 subsamples collected from about 20 m^2 area. Plant samples were thoroughly washed with tap water and de-ionized water to remove soil particles before being oven-dried at about 60 °C. The dried plant samples were then cut into pieces and ground to powder. The prepared plant samples (0.5g) were digested by a 10 mL HNO_3 (65%) and H_2O_2 (30%) solution in a sealed Teflon vessel for total metal analysis.

Metal (Cd, Cu, Pb and Zn) concentrations in all prepared solutions were determined using ICP-OES (Vista MPX, Varian Inc.). Quality assurance and quality control of metal analysis were assessed using duplicates, method blanks and standard reference materials (SRM2710, SMR8704 and GBW07603). Reliability of the sequential extraction procedure was determining by comparison of the sum of fractions with independent total metal digestion concentrations. In most cases, agreement was within

20% indicating the extraction results were reliable and accurate.

The Pb isotopic composition analysis was performed on selected sediment samples by ICP-MS (Perkin-Elmer Elan 6100 DRC^{plus}). The details of the procedure were reported by Lee et al. (2006). The analytical parameters were set as 190 sweeps/reading, one reading/replicate, and 10 replicates per sample solution. Dwell times of 40, 25, 25, and 25 ms were used for ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb, respectively. The Pb counts of the procedural blank were below 0.5% of the samples. The relative standard deviations (RSD) of the 10 replicates were generally below 0.5%. A standard reference material (NIST SRM981 Common Pb Isotopic Standard) was used for quality control. The measured Pb ratios of ^{204}Pb/^{207}Pb, ^{206}Pb/^{207}Pb, and ^{208}Pb/^{207}Pb were 0.0645±0.0001, 1.0938±0.0011, and 2.3710±0.0030, which were in good agreement with the standard reference values of 0.0645, 1.0933, and 2.3704, respectively.

Analysis of organic matter in the sediments was performed using the potassium dichromate-volumetric method (Liu, 1999).

3. Results

3.1. Total metals in sediments

The total concentrations of Cd, Pb, Zn and Cu in the surface and core sediment samples collected from the Caihao wetland are shown in Table 1. Metal concentrations in the surface sediments exhibited relatively wide ranges of 2.6-71 μg g^{-1} for Cd, 66-160 μg g^{-1} for Pb and 140-1100 μg g^{-1} for Zn. The relatively high levels of metals in the surface sediments were generally found in the north sampling sites (e.g., site 1, 3 and 4), and metal concentrations decreased gradually along the transect from north to south, except for Cu, probably reflecting the dispersion of the emissions from the zinc smelting area located at the northeast part of Caohai. The metal profiles in the two sediment cores showed the similar trends with significant elevated Cd (10-81 μg g^{-1}), Pb (68-200 μg g^{-1}) and Zn (320-1500 μg g^{-1}) concentrations in the upper layers (<20 cm), which was consistent with the intensified zinc smelting activities in the Hezhang area since the last few decades. It was therefore reasonable to assume from the metal concentrations and the spatial-temporal distribution patterns of heavy metals in the sediments that the metal contamination was derived principally from past smelting operations in this area.

3.2. Metal fractionation in sediments

The sequential chemical fraction of Cd, Pb, Zn and Cu in the selected sediment (surface sediments and Core 2 sediments) samples is depicted in Fig. 2. In the surface sediments, Cd and Pb were mainly present in the organic fraction (Cd, 31-84%; Pb, 34-82%), while the residual fraction was second dominant (Cd, 4.0-55%; Pb, 14-39%). As for Zn and Cu, the residual fraction became more important (Zn, 17-69%; Cu, 50-75%) than the organic fraction (Zn, 3.8-46%; Cu, 6.6-49%). In general, heavy metals in the exchangeable, carbonate and Fe-Mn oxide fractions were less important for most samples (generally less than 10%), except for two, i.e., Sample 1 and 3, which exhibited abnormally high percentage of Fe-Mn oxide fraction for Cd (63-76%), Pb (42-47%) and Zn (62-63%).

The distribution of metal fractions in the sediment core (especially the upper layers) was similar to those of the surface sediments with organic and residual fractions being dominant phases. But their distribution trends varied with depth (Fig. 2b). In general, the percentage of Cd, Pb and Zn in the organic fraction decreased and the residual fraction increased with depth. The metals in the sediment core were also slightly associated with the Fe-Mn oxide fraction with a rapid increase in the lowermost profile. This was probably due to a Fe-Mn oxide boundary existing in these layers. A slightly increase of the exchangeable and carbonate fractions for Cd and Pb were also observed in the deeper sediments.

In contrast, the chemical fractions for Cu were evenly distributed in the profile.

3.3. Pb isotope ratios

Pb isotopic analysis results of the selected sediment (the upper layers (≤ 20 cm) of the Core 2), local background soil and the feeding ore samples are given in Table 2. Generally, the local background soils have relatively high $^{206}Pb/^{207}Pb$ (1.2441-1.2489) ratios. In contrast, the $^{206}Pb/^{207}Pb$ ratios of the upper core sediments fell within a relatively low range of 1.1778-1.2016, which increased with depth, suggesting a mixing of anthropogenic sources and geogenic Pb. The zinc smelting in Hezhang mainly used the native ores. The $^{206}Pb/^{207}Pb$ ratios of the feeding ores were 1.1756-1.1877, which corresponded to the previous study (1.1736-1.1870) (Zheng, 1994). These values for ores were comparable to those measured in the sediments, thus indicating their predominant contribution to the Pb burden in the sediments.

However, the sediment samples also showed slightly lower $^{208}Pb/^{207}Pb$ (2.4611-2.4732) ratios than either the background soils (2.4771-2.4782) or the ores (2.4837-2.4987). This result suggested that other unknown anthropogenic sources with low $^{208}Pb/^{207}Pb$ ratios (at least should be lower than those of the sediments) must be involved. It is reasonable to assume that the coal combustion and gasoline Pb might be the possible important sources of Pb due to the lack of other large anthropogenic emissions in the study area.

3.4. Metals in plants

Cd, Pb, Zn and Cu concentrations in the aquatic plants (aboveground tissues) collected from the Caohai wetland are shown in Table 3. The data show that the metal concentrations in the plants varied among species, indicating their different capacities for metal uptake. Generally, the submerged species

C. demersum. accumulated the highest concentrations of Cd (8.2 μg g^{-1}), Pb (22 μg g^{-1}) and Zn (200 μg g^{-1}), and the floating species (*Azolla imbricata* and *Spirogyra communis*) contained the second highest values of Cd (4.4 μg g^{-1}) and Pb (20 μg g^{-1}). While the lowest metal concentrations (Cd, 0.4 μg g^{-1}; Pb, 1.4 μg g^{-1}; Zn, 34 μg g^{-1}; and Cu, 12 μg g^{-1}) were found in the emergent species *S. triqueter*. In summary, all the metals (especially Cd, Pb and Zn) found in the plants had much lower concentrations than those measured in the sediments.

4. Discussion

4.1. Enrichment factors in sediments

In this study, enrichment factor (*EF*) was used to assess the anthropogenic contribution of metals in the sediments. For a given sediment, the metal concentration was normalized to that of Al, a conservative element relative to silicate crustal materials, to calculate the enrichment factors according to the following equation:

$$EF = \frac{[M/Al]_{sample}}{[M/Al]_{background}} \quad (1)$$

where *EF* is the enrichment factor, $[M/Al]_{sample}$ is the ratio of given metal and Al concentration of the sample, and $[M/Al]_{background}$ is the ratio of given metal and Al concentration of a background. In this study, the relatively low metal concentrations from the deeper sediment layers (35-50cm) of Core 2 was used as the less impacted background values (μg g^{-1}): Cd, 2.1±0.53; Pb, 29±2.5; Zn, 82±23; and Cu, 21±1.6 (Fig. 2). These results are comparable to the background values in the local soil, except for Cd, which is some what elevated (China Environmental Monitoring Station, 1990).

EF values were interpreted as suggested by Birch (2003) where $EF<1$ indicates no enrichment; <3 is minor; 3~5 is moderate; 5~10 is moderately severe; 10~25 is severe; 25~50 is very severe; and >50 is extremely severe. In this case, only the surface and upper core (<20 cm) sediment samples would reflect the anthropogenic impacts. In most samples, Cd has the highest *EF* values varying from moderately severe (5.5) to extremely severe (91) enrichment, followed by Zn (2.7-41) and Pb (2.8-16), while Cu only shown minor anthropogenic enrichment (generally *EF*<3) (Table 1). These results were comparable to the previous study which reported that moss samples collected close to the same smelting area were seriously contaminated by Cd, Pb and Zn, but less impacted by Cu (Bi et al., 2006b). However, the much lower *EF* value for Pb relative to Cd and Zn in the sediments suggested that the sediments received less Pb pollutant, which is quite different from that in the moss samples. Pb in the moss samples exhibited equal or even higher contamination level compared to Cd and Zn (Bi et al., 2006b). Considering metal pollutants in the Caohai wetland are derived mainly from the emissions of the zinc smelting, and the wetland is much farther away from the smelting area (~15 km) than the sites (~2 km) where the moss samples were collected, this result thus indicates that smelting emitted Pb might prefer to deposit in the close vicinity of the smelter. Telmer et al. (2004) also found a higher enrichment of Pb compared to Cd and Zn in the near surrounding area (< 5 km) of a smelter.

4.2. Metal motility in sediments

Sequential extraction procedure despite known limitations does provide some insight information on the potential mobility and redox sensitively of metals in sediments. In a given environment, different chemical fractions of metals may reveal various degrees of potential mobility and bioavailability depending on the substrata geochemical conditions and the nature of the metals. Exchangeable and carbonate fractions are considered to be weakly bonded metals which may equilibrate with the aqueous phase and thus become more rapidly bioavailabile (Pardo et al., 1990). The low percentages of these fractions of metals in the Caohai sediments thus indicated the low mobility and bioavailability of metals in the sediments. Typically, the Fe-Mn oxide bound fraction are thermodynamically unstable under anoxic conditions (i.e., low redox potential), while under oxidized conditions, organic matter can be degraded, leading to a release of trace metals from the organic bound metal fraction (Tessier et al., 1979).

Heavy metals in the sediments were strongly associated with the organic fraction. This could be related to the high OM levels (14-45%) of the sediments. Previous studies also reported high percentages of metals bound to the organic fraction with the high OM concentrations in sediments (Dollae et al., 2001; Olivares-Rieumont et al., 2005). Stoeppler (1992) demonstrated that major factors, such as metal uptake by plants and subsequent decomposition, metal complex formation with soluble OM, and metal absorption onto settable minerals, were all possible vehicles that might contribute to metal accumulation in the organic fraction.

However, in some cases, i.e., the surface sample 1 and 3, the Fe-Mn oxide fraction of Cd, Pb and Zn was dominant instead of the organic fraction (Fig. 2a). This was not due to the relatively low OM concentration of these two samples (Table 1), but a reflection of the influences of the aquatic plants. The fact is that the sites from which the samples were collected have much more biomass of the macrophytes than other sites. Many studies reported that living plants can induce sediment oxidation (higher redox potential) through increased root radial oxygen loss (Madureira et al., 1997; Jacob and Otte, 2004a, b; Almeida et al., 2004), by which may lead to an increase of metals bound to the Fe-Mn oxide. Indeed, Carroll et al. (2002) also demonstrated that the sulfides of Cd and Zn in sediments can dissolve under oxidized conditions and the majorities of these dissolved concentrations will eventually undergo sorption to or co-precipitation with an iron (oxy)hydroxide.

The oxidized conditions induced by plants can simultaneously lead to a decay of the organic matter

(Tessier et al., 1979), therefore, the lower OM level of the Sample 1 and 3 was not a cause, but a result/reflection of the influences of the plants.

It is clear that the increased metals in the Fe-Mn oxide fraction must be derived from the transformation from other fractions, such as the organic and residual fractions. By comparing the difference of metal fractionations between sample1, 3 and others (especially sample 2 and 4) (Fig. 2a), it was reasonable to assume that the increase of the Fe-Mn oxide fraction for Cd and Zn in the sediments was attributed to both the organic and residual fraction conversion, while for Pb the increase was principally derived from the organic fraction change.

In comparison with other metals, the Cu, representing a less impacted element in the sediments, had the chemical fractions seemed to be independent to the substrata conditions such as the redox potential.

The sediments from the deeper layers of the core seemed to be less impacted by human activities and their metals derived mainly from the geogenic sources. The increasing trend of the residual fraction of Cd, Pb and Zn with depth in the sediment core thus indicated that the geogenic originated metals tend to be associated with the residual fraction, i.e., were retained in the crystal lattice of minerals. In contrast, anthropogenic inputted metals prefer to bind to the non-residual fractions, especially the organic fraction, in the Caohai sediments, posing a potential hazard on the ecosystem.

4.3. Source attribution of Pb in sediments

The Pb isotopic compositions indicated that the Pb burden in the sediments were a mixing of geogenic Pb and a variety of anthropogenic sources, including the ore Pb and other sources with low ^{208}Pb/^{207}Pb ratios. It is well known that gasoline Pb has been an important source of Pb to the atmosphere in the last few decades, in addition, coal combustion has also contributed significantly to the atmospheric Pb in southwestern China (Mukai et al., 1993, 2001). Besides, no other large anthropogenic emissions were present in the study region. Although no isotopic data are available for coal in southwestern China, the values from the aerosol can be used because aerosol Pb in southwestern China was derived principally from the coal combustion (Mukai et al., 1993, 2001). The Pb isotope ratios in the aerosol from Guiyang were 1.170-1.205 and 2.444-2.476 for ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb, respectively (calculated from Mukai et al. (2001)). The tetraethyl Pb additives in China gasoline were mainly from the Octel Inc. (UN). According to Zhu et al. (2001), the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios in south China gasoline were 1.1562-1.1632 and 2.4182-2.4260, respectively.

Therefore, all the measured and literature isotopic data for various samples in the ^{206}Pb/^{207}Pb vs ^{208}Pb/^{207}Pb diagram is plotted in Fig. 3. It is clear to note that all the data from the Caohai sediments fall within a triangle region with ore, gasoline and background soil as the three end members. This suggests that Pb in the Caohai sediments derived mainly from these three sources: the geogenic Pb, the gasoline Pb, and of course, the ore Pb from the smelting operations. In contrast, as shown in this Figure, the coal Pb may not be regarded as a possible end member due to its similar or even higher isotope ratios compared to those of the sediments.

If the Pb in the Caohai sediments was from just these three sources, it is possible to calculate the relative amounts of the three sources according to a ternary mixing model:

$$X = \frac{R_{sample} - (R_{gasoline} - R_{gengenic})Y - R_{gengenic}}{R_{ore} - R_{gengenic}} \qquad (2)$$

where X and Y are the proportion of ore Pb and gasoline Pb in the sediments and R_{sample}, R_{ore}, R_{gasoline} and R_{geogenic} are the isotope ratios (^{206}Pb/^{207}Pb or ^{208}Pb/^{207}Pb) in the sediment samples, ore, gasoline and local background soils, respectively. The values of ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios for background soils, ore and gasoline are the average of the measured or reported ratios for these groups of samples. Using the above equation, it was estimated that on the average 60% (47-68%) and 26% (15-37%) of the inventory of Pb in the Caohai sediments originated from the ores used in the smelting and from the gasoline, respectively. The remaining 14% (5-38%) derived from the geogenic Pb.

4.4 Metal accumulations in plants

Plant species differ widely in their ability to accumulate heavy metals. Our study showed that the emergent plants accumulated lower amounts of metals than submerged and floating aquatic vegetation. This is consistent with previous observations (Albers and Camardese, 1993; Yurukova and Kochev, 1994; Rai et al., 1995). In order to determine whether significant bioaccumulation occurred in the Caohai vegetations, it is necessary to compare our data with those of previous studies. Outridge and Noller (1991) reported that Cd, Pb, Zn and Cu concentrations in normal plants were 1.9, 6.3-9.9, 66 and 37 μg g^{-1}, respectively. Baldantoni et al. (2005) observed that Cd, Pb, Zn and Cu concentrations in plants *Najas marina* shoots and *P. Pectinatus* leaves from a less impacted site on Lake Averno, Naples, were generally lower than 0.4, 4.0, 60 and 5.0 μg g^{-1}, respectively. Hozhina et al. (2001) investigated aquatic plants *Equisetum fluviatile*, *Typha latifolia* and *Scirpus sylvaticus* in the Kemerovo region, Russia, and found that the aboveground tissues of these plants from the control area contained 0.023-1.8 μg g^{-1} of Cd, 0.89-23 μg g^{-1} of Pb, 26-84 μg g^{-1} of Zn and 4.7-39 μg g^{-1} of Cu. Our data indicated that Cd, Zn and Pb in most plants had higher concentrations than these thresholds, but were still within the range found in contaminated plants (Deng et al., 2004; Hozhina et al., 2001; Cymerman-Samecka and Kempers, 2004). In contrast, Cu values in our study were similar to the literature values mentioned above. The extents of metal accumulations in plants agreed well with the metal contamination conditions of the Caohai sediments and thus confirming that contamination on plants did occur.

However, the much lower metal concentrations found in the plants compared to those in the sediments suggested the limited bioavailability of the metals in the sediments, which corresponds to the metal chemical fractionation results in sediments. Nevertheless, the elevated metals accumulated in the aquatic plants, especially Cd and Pb in *C. demersum*, *Azolla imbricate* and *Spirogyra communis*, would be a potential threat to a number of higher trophic-level organisms, especially the migratory birds, once they enter their food chain. In addition, the local people often take some of the aquatic plants, such as *C. demersum*, *P. malainus.* and *Azolla imbricata*, as the food for poultry and livestock, by which the metals accumulated in these plants could probably enter human body through food chain.

5. Conclusions

The present field investigation shows that Chaohai wetland has been seriously contaminated by Cd, Pb and Zn due to the historic zinc smelting activities in the Hezhang area. Contaminated metals in the wetland sediments were mainly presented in the organic and residual fractions. However, these fractions of metals were quite unstable and might be changed into other chemical forms, such as the Fe-Mn oxide fraction, if the substrata conditions change, such as the increase of the redox potential. The aquatic plants may act as an important trigger to alter the metal fractionations in the Caihao wetland. The elevated metal accumulations in the plants should deserve to be particularly concerned since these metals can enter into higher trophic-level organisms, even humans, through food chain.

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Fig. 1

Study area (Caohai wetland) and sampling locations.

Fig. 2

Percentages of different chemical fractions of Cd, Pb, Zn and Cu for the surface (a) and core (b) sediments collected from Caohai.

Fig. 3

A plot of ^{206}Pb/^{207}Pb vs ^{208}Pb/^{207}Pb for different samples.

Table 1

Metal concentrations (μg g^{-1}, dry weight), EF and organic matter (%) of sediments

Sample ID	Depth (cm)	OM	Cd	Pb	Zn	Cu	EFCd	EFPb	EFZn	EFCu
Surface sediment										
1	0-5	23	56	120	1100	25	61	9.4	31	2.7
2	0-5	29	29	84	630	17	14	2.8	7.5	0.8
3	0-5	20	71	160	1200	22	38	5.8	16	1.2
4	0-5	32	51	140	1000	30	41	7.6	21	2.4
5	0-5	44	16	120	430	33	7.6	3.8	5.0	1.5
6	0-5	38	9.6	76	190	28	5.5	3.1	2.7	1.6
7	0-5	33	16	92	380	28	9.8	4.0	5.9	1.7
8	0-5	24	6.0	69	160	25	6.9	5.6	4.7	2.8
9	0-5	32	3.0	70	140	29	1.7	2.7	1.9	1.6
10	0-5	14	2.6	66	130	28	1.2	2.2	1.6	1.3
Core 1										
	2	44	69	170	1200	28	91	16	41	3.6
	5	42	76	190	1400	32	89	16	40	3.8
	7	43	81	200	1500	32	91	16	42	3.6
	10	46	51	140	1100	34	48	9.5	27	3.2
	15	47	10	68	320	39	6.4	3.1	5.1	2.5
	20	32	2.1	62	190	36				
	25	28	1.7	57	170	39				
	30	29	2.2	58	160	31				
	35	14	2.8	38	130	16				
	40	14	3.1	40	130	17				
Core 2										
	2	30	51	140	1100	31	39	7.4	21	2.3
	5	31	52	130	1000	28	43	7.8	21	2.4
	7	31	51	140	1000	30	42	8.0	21	2.4
	10	33	50	110	1000	22	51	8.2	26	2.2
	15	25	25	71	660	22	21	4.1	13	1.8
	20	17	4.9	35	240	24				
	25	15	3.3	34	230	26				
	30	23	2.0	32	180	25				
	35	26	1.9	28	110	20				
	40	16	2.2	27	88	21				
	45	13	2.8	33	70	19				
	50	1.2	1.5	29	58	23				

Table 2

Pb isotope ratios measured in the selected sediments and the local background soils

Sample type	Depth (cm)	^{204}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb
Sediment				
	2	0.0636	1.1796	2.4611
	5	0.0637	1.1791	2.4664
	7	0.0637	1.1778	2.4682
	10	0.0637	1.1788	2.4664
	15	0.0636	1.1855	2.4715
	20	0.0638	1.2016	2.4732
Local background soil				
		0.0635	1.2442	2.4776
		0.0635	1.2451	2.4771
		0.0635	1.2489	2.4781
Zinc ore				
smithsonite		0.0635	1.1760	2.4837
smithsonite		0.0635	1.1756	2.4987
sphalerite		0.0636	1.1877	2.4975

Table 3

Metal concentrations in different aquatic plant species collected from Caihai (μg g^{-1}, dry weight)

Species	N	Cd	Pb	Zn	Cu
Submerged					
Ceratophyllum demersum	2	8.2 (6.8-9.6)	22 (20-25)	200 (170-220)	18 (17-18)
Myriophyllum spicatum	4	2.8 (1.9-4.6)	14 (2.3-30)	120 (85-180)	17 (7.4-21)
Potamogeton malainus	3	1.6 (1.2-2.1)	2.4 (1.2-4.6)	62 (52-69)	14 (9.0-22)
Potamogeton pectinatus	3	3.0 (2.0-4.8)	8.2 (7.8-8.7)	90 (80-107)	16 (12-23)
Potamogeton lucens	1	3.2	13	120	20
Potamogeton maackianus	1	2.6	4.6	84	26
Floating					
Azolla imbricata	3	4.4 (4.2-4.7)	12 (9.4-17)	100 (95-110)	11 (7.2-15)
Spirogyra communis	3	4.2 (2.3-7.5)	20 (13-31)	99 (69-150)	16 (7.2-26)
Emergent					
Alternanthera philoxeroides	3	1.5 (1.1-1.7)	10 (2.7-22)	82 (78-88)	15 (13-16)
Scirpus triqueter	3	0.41 (0.35-0.46)	1.4 (0.44-3.3)	34 (19-43)	12 (11-13)
Nymphoides peltata	3	2.6 (2.1-2.9)	9.5 (5.0-14)	81 (71-92)	18 (14-25)

Metal concentrations are presented in mean and range values (in parenthesis); N, number of analyzed samples.

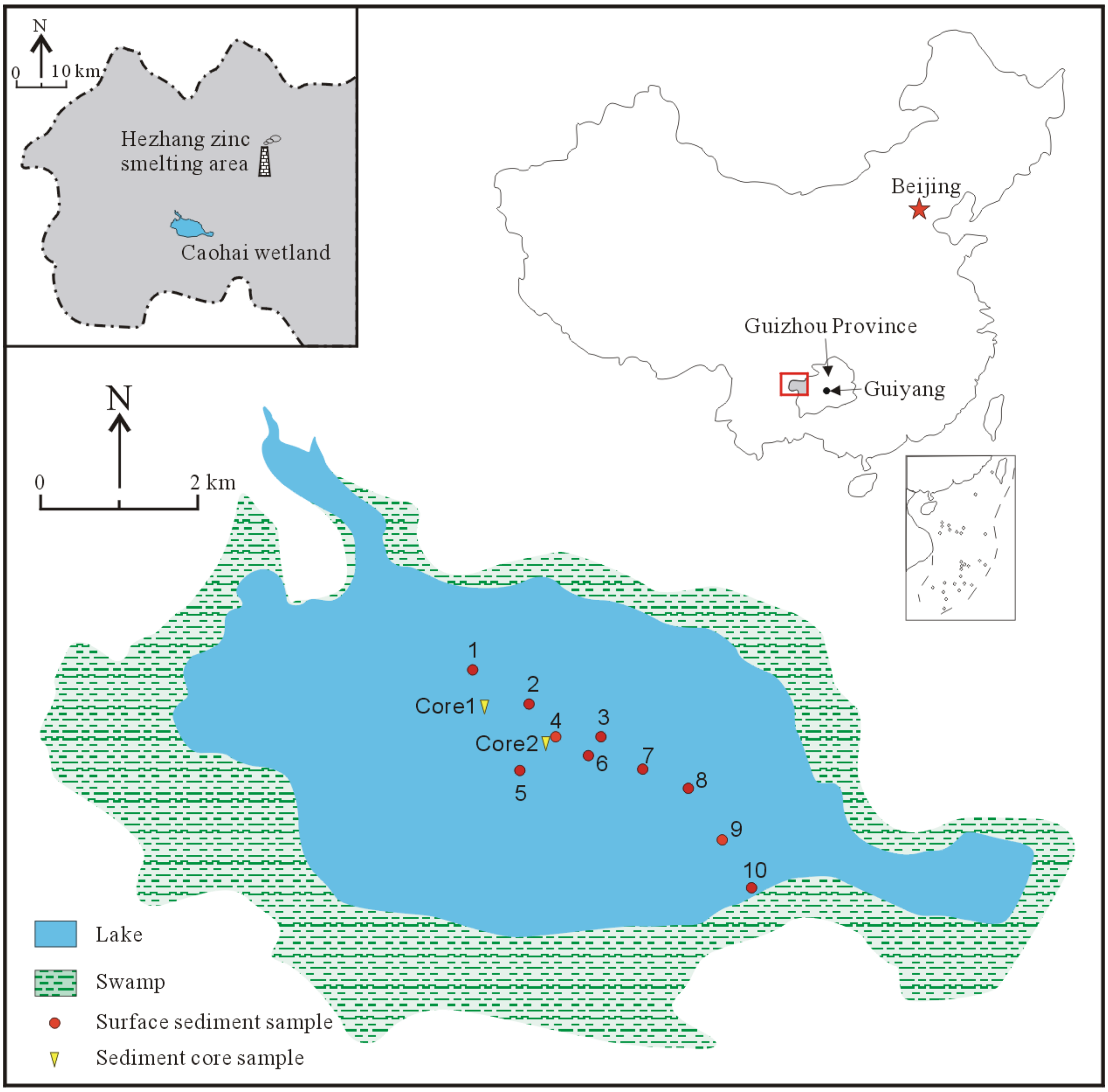

N
0
10 km
Hezhang zinc smelting area
Caohai wetland
Beijing
Guizhou Province
Guiyang
N
0
2 km
1
2
Core1
4
3
Core2
7
6
5
8
9
10
Lake
Swamp
Surface sediment sample
Sediment core sample

Fig. 1

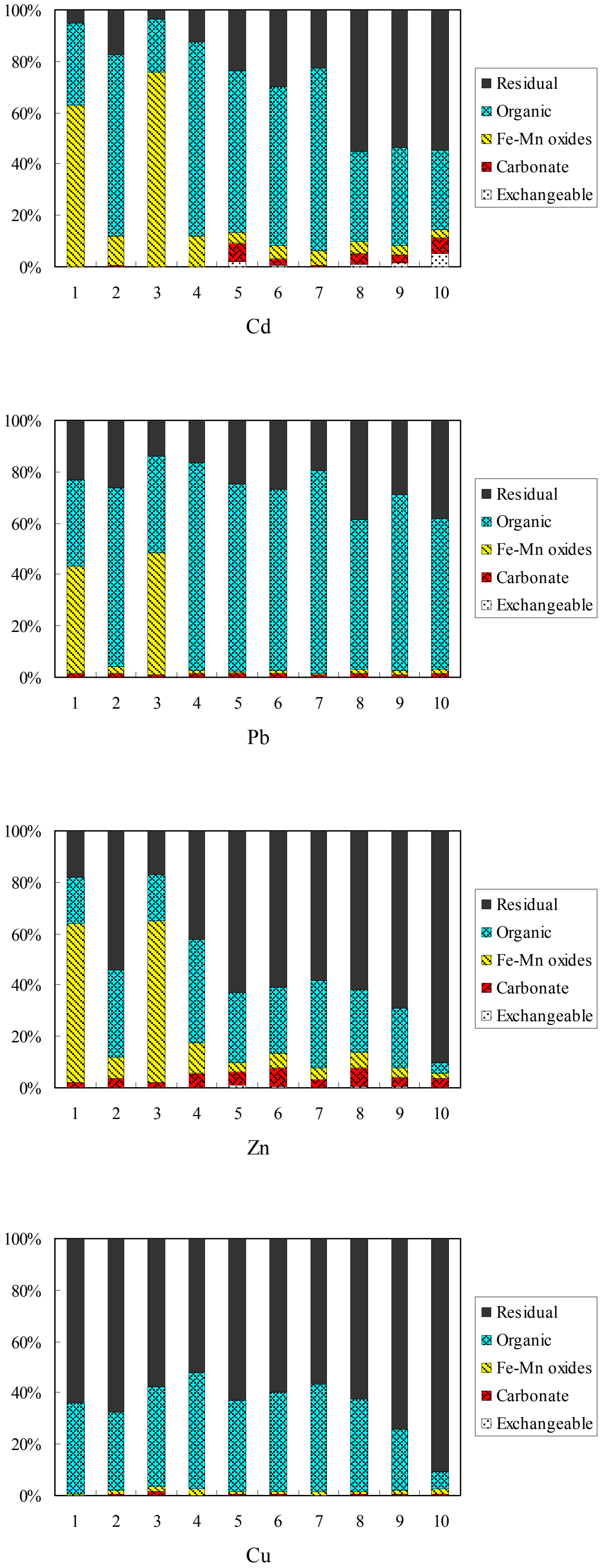
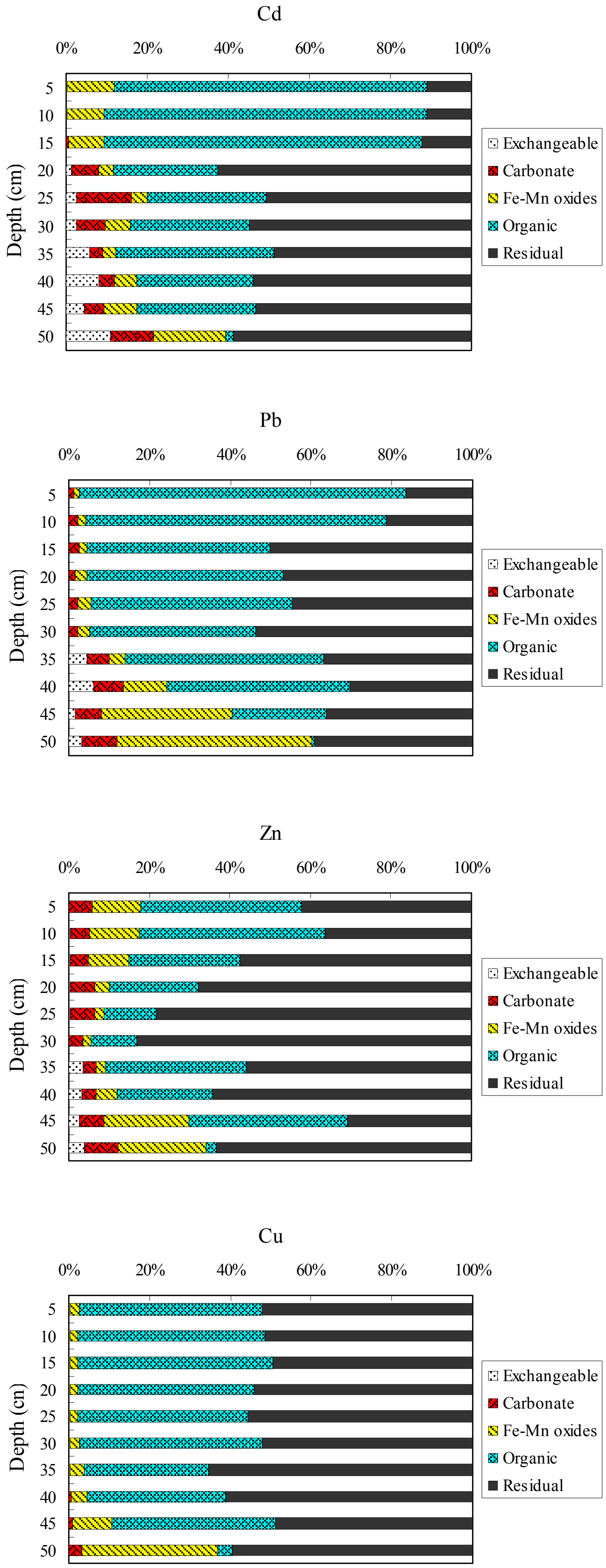

100%
80%
60%
40%
20%
0%
1
2
3
4
5
6
7
8
9
10
Cd
Pb
Zn
Cu
Residual
Organic
Fe-Mn oxides
Carbonate
Exchangeable

Fig. 2a


Cd
Pb
Zn
Cu
0%
20%
40%
60%
80%
100%
Depth (cm)
Depth (cn)
5
10
15
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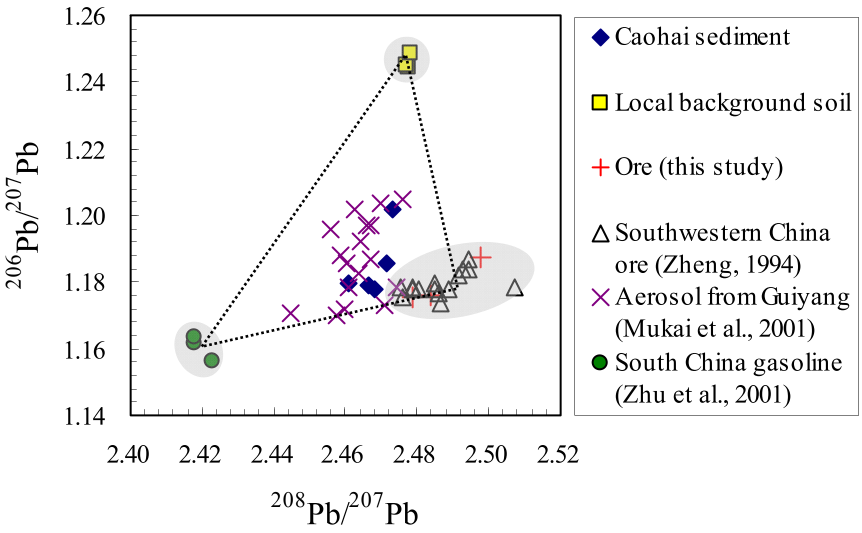
25
30
35
40
45
50
Exchangeable
Carbonate
Fe-Mn oxides
Organic
Residual

Fig.2b


1.26
1.24
1.22
1.20
1.18
1.16
1.14
2.40
2.42
2.44
2.46
2.48
2.50
2.52
$^{206}Pb/^{207}Pb$
$^{208}Pb/^{207}Pb$
Caohai sediment
Local background soil
Ore (this study)
Southwestern China ore (Zheng, 1994)
Aerosol from Guiyang (Mukai et al., 2001)
South China gasoline (Zhu et al., 2001)

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478 Fig. 3