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

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

[a] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, PR China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China
[c] Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, PR China
[d] College of Resources and Environment, Guizhou University, Guiyang 550025, PR China
[e] College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310032, PR China

Abstract

Historical zinc smelting in Hezhang, southwestern China, has resulted in significant heavy metal contamination of the surrounding ecosystems. The Caohai wetland system, which is 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 concentrations in the surface sediments being up to 71, 160 and 1200 $\mu g\ g^{-1}$, respectively. The heavy metals in the sediments were strongly associated with the organic/sulphide and residual fractions. A more oxidized condition induced by aquatic plants tended to cause the Cd, Pb and Zn bound to the Fe–Mn oxide fraction to become more dominant. Pb isotopic compositions in the sediments indicated that the inventories of Pb in the Caohai wetland sediments were mainly derived from the historical zinc smelting in the Hezhang area, although other anthropogenic sources, such as the gasoline Pb, also made a substantial contribution to the 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, including humans.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Heavy metals; Sediments; Pb isotopes; Aquatic plant; Zinc smelting; Caohai wetland; China

1. Introduction

Sediment is 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 aquatic organisms. It is well accepted that the total concentrations of heavy metals in sediments cannot provide sufficient information about their impact on the ecosystem because the mobility, bioavailability and toxicity of metals depend 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 commonly used methods, although the disadvantages of this extraction scheme have been well recognized (e.g., non-specificity of extraction and re-sorption of metals) (Rapin et al., 1986; Nirel and Morel, 1990; Gomez-Ariza et al., 1999).

Metal fractionations in sediment are strongly dependent on the substrata geochemical conditions, such as the pH and redox potential. Typically, the Fe–Mn oxide bound fraction is 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/sulphide bound fraction. In contrast, the residual fraction, which is generally involved within the crystal structure of primary and secondary minerals, is not easily released under normal conditions encountered in nature (Tessier et al., 1979). However, many studies (e.g., Almeida et al., 2004; Jacob and Otte, 2004a,b) 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, and even the residual fraction. 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 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 (Hozhina et al., 2001; Cymerman-Samecka and Kempers, 2004; Deng et al., 2004). Therefore, the investigation of metal accumulations in plants can provide vital information on the extent to which the contamination has impacted 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 pollutions and have been widely used in a wide range of environmental studies (e.g., Mukai et al., 1993, 2001; Gélinas and Schmit, 1997; Zhu et al., 2001; Bacon and Hewitt, 2004; Wong and Li, 2004; Gallon et al., 2006; Lee 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 because not only China is the largest zinc producer in the world, but also most zinc industries in China have used old techniques of 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 has 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 depositions from the Hezhang zinc smelting emissions on a natural freshwater wetland (Caohai) is investigated. The objectives of the present research are (1) to evaluate the metal (Cd, Pb, Zn and Cu) enrichment characteristics in the wetland sediments; (2) to determine the geochemical fractionations of heavy metals in the sediments using the 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), is an important national nature reserve for migratory birds in China and 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 2170 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. Due to the effect of bedrock, the water is alkaline with pH around 8.8. The major sources of water in the Caohai wetland are precipitation and groundwater. 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,
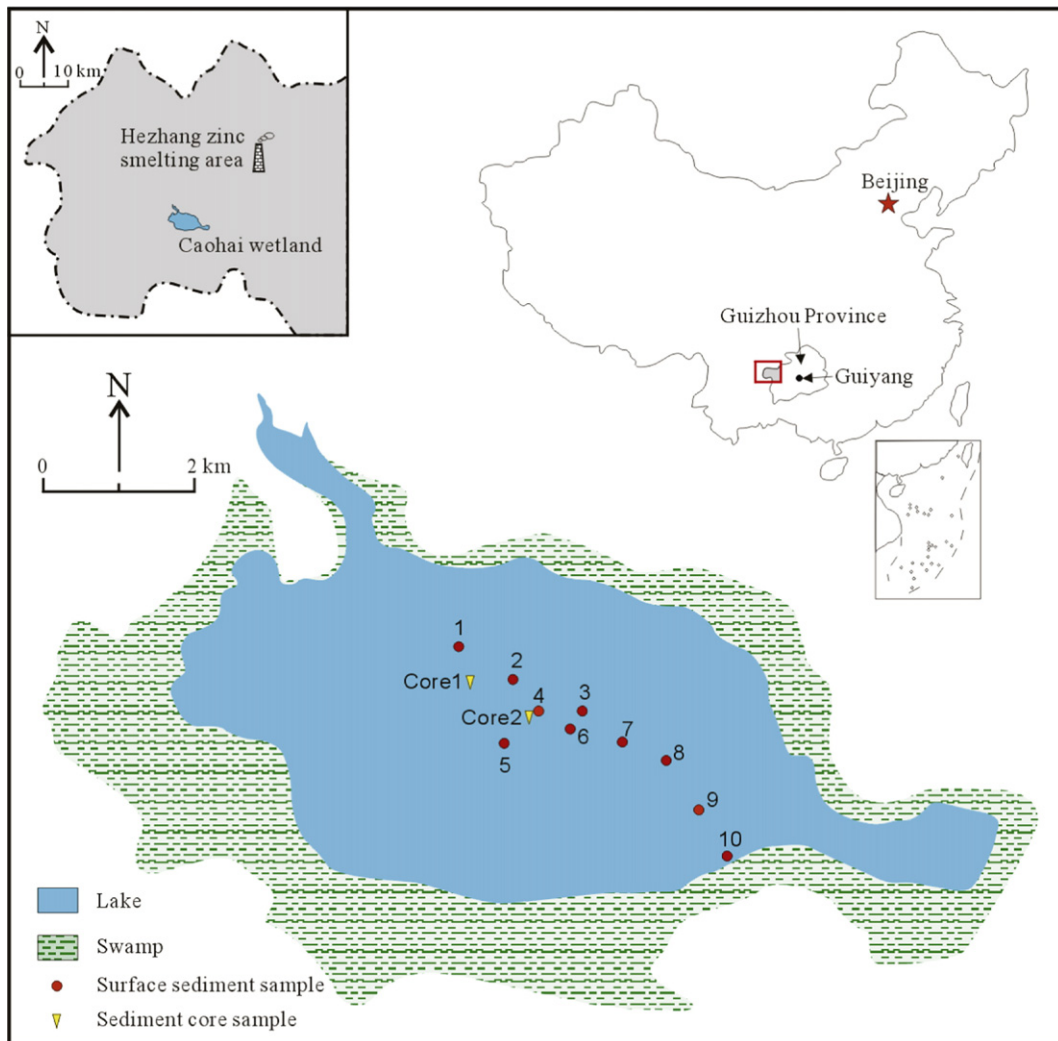
Fig. 1. Study area (the Caohai wetland) and sampling locations.

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 (0.5 g) 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 1 h), carbonate/specifically adsorbed fraction (1 M NaOAc, pH 5.0, for 5 h), Fe–Mn oxide fraction (0.04 M $NH_2OH\cdot HCl$ in 25% (v/v) HOAc at 96 °C for 6 h), organic/sulphide fraction (30% H_2O_2 and 0.02 M HNO_3 for 2 h, second 30% H_2O_2 at 85 °C for 3 h), 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 min 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 min.

Plant samples, including emergent, submerged and floating aquatic vegetations, were taken from a range of species presented at the Caohai wetland. The submerged species, primarily *Ceratophyllum demersum*, *Myriophyllum spicatum* and *Potamogeton malainus*, are the most common type of aquatic macrophytes. They grow in most parts of the wetland, especially in the deep water region. The emergent and floating species are generally found in

Table 1
Metal concentrations in surface sediments from the Caohai wetland ($\mu g \ g^{-1}$, dry weight)

Element	Caohai wetland	Canada [a]		Netherlands [b]	
		ISQG	PEL	Target	Intervention
Cd	26 (2.6–71)	0.60	3.50	0.8	12
Pb	99 (66–160)	35.0	91.3	85	530
Zn	540 (130–1200)	123	315	140	720
Cu	27 (17–33)	35.7	197	36	190

Metal concentrations are presented in mean and range values (in parenthesis); ISQG: interim sediment quality guideline; PEL: probable effect level; Target values: levels of metals should be achieved; Intervention values: above which remedial actions should be taken.

[a] Canadian Environmental Quality Guidelines.
[b] Netherlands Environmental Quality Guidelines.

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 an approximate 20 m^2 area. Plant samples were thoroughly washed with tap water and deionized water to remove soil/sediment 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 (0.5 g) 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, Pb, Zn and Cu) concentrations in all of the 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). The reliability of the sequential extraction procedure was determined 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. Procedural blanks, duplicates and reference material (NIST SRM981 Common Pb Isotopic Standard) were used for quality control. The analysis was repeated when the differences between the measured and certified values of the standard reference material exceed 0.5%. The Pb counts of the procedural blank were <0.5% of the samples, and the precision (% RSD)

of the Pb isotope ratios of ten replicates were typically <0.5%. The average 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 sediment samples collected from the Caohai wetland are shown in Table 1 and Fig. 2. Metal concentrations in the surface sediments exhibited wide ranges of 2.6–71 $\mu g \ g^{-1}$ for Cd, 66–160 $\mu g \ g^{-1}$ for Pb, 130–1200 $\mu g \ g^{-1}$ for Zn, and 17–33 $\mu g \ g^{-1}$ for Cu. 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.

The metal profiles in the two sediment cores are shown in Fig. 3. Metal concentrations in the lower part of the cores (>20 cm) were relatively low. However, Cd, Pb, and Zn concentrations in the upper part of the cores (<10 cm) were significantly elevated, reflecting the intensified metal inputs. The highest metal concentrations were generally higher in core 1 (81, 200, and 1500 $\mu g \ g^{-1}$ for Cd, Pb and Zn, respectively) than in core 2 (53, 140, and 1200 $\mu g \ g^{-1}$ for Cd, Pb and Zn, respectively), and the highest Cd, Pb and Zn in core 1 were found in the subsurface (∼7 cm), while in core 2 they were constantly distributed within the upper layers (∼10 cm). In
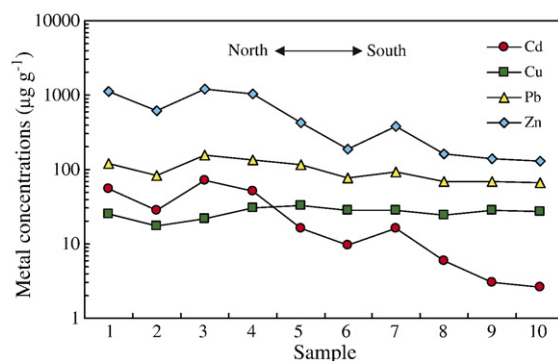

Fig. 2. Cd, Pb, Zn and Cu distributions in surface sediments from the Caohai wetland.
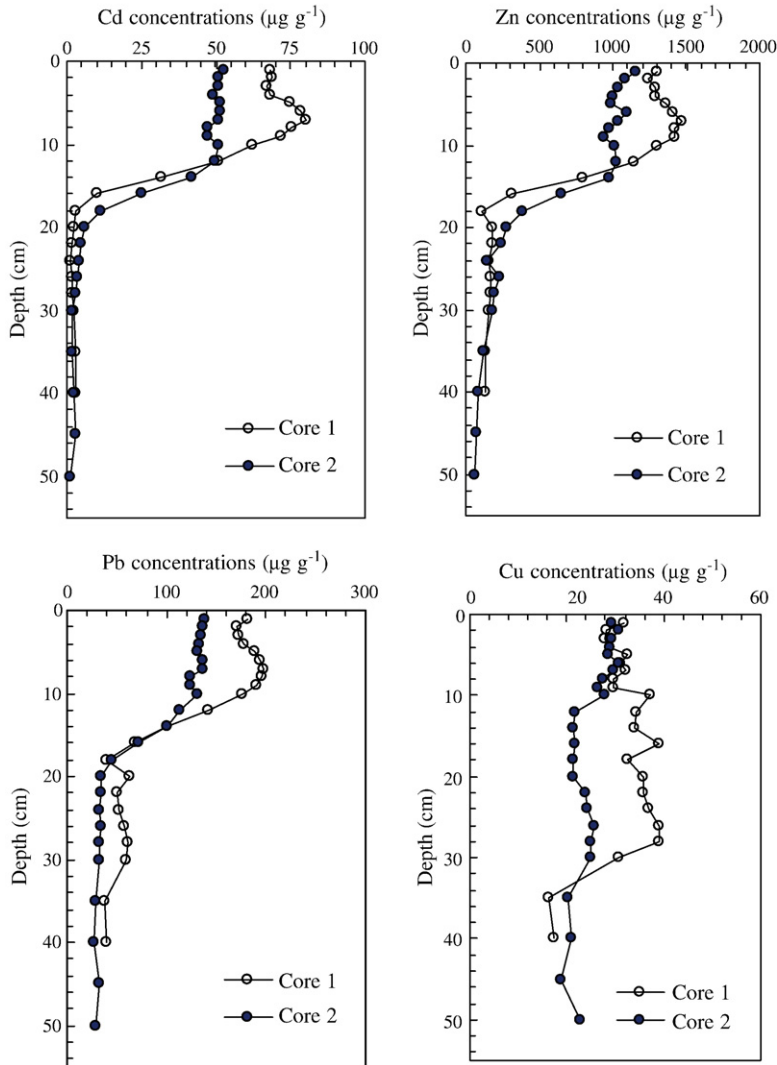
Fig. 3. Cd, Pb, Zn and Cu distributions in the sediment cores from the Caohai wetland.

comparison, the distributions of Cu seemed to have been more independent on atmospheric deposition, and the overall variations in Cu concentrations were small.

3.2. Metal fractionation in sediments

The sequential chemical fractions of Cd, Pb, Zn and Cu in the selected sediment samples (surface sediments and the core 2 sediments) are depicted in Fig. 4. In the surface sediments, Cd and Pb were mainly present in the organic/ sulphide 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 (Zn, 17– 69%; Cu, 50–75%) became more important than the organic/sulphide fraction (Zn, 3.8–46%; Cu, 6.6–49%).

In general, heavy metals in the exchangeable, carbonate/ specifically adsorbed 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 levels 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 the organic/sulphide and residual fractions being dominant phases. In general, Cd, Pb and Zn concentrations in the organic/sulphide and residual fractions decreased with depth, but the proportion of the residual fraction tended to increase with depth. For ex- ample, the proportion of residual fraction for Cd increased from about 10% in the upper part of the cores to more than

50% in the deeper part of the cores. In contrast, the chemical fractions for Cu were evenly distributed in the profile.

3.3. Pb isotope ratios

In this study, Pb isotopes were measured for the selected sediment samples (the upper layers (≤ 20 cm) of core 2), local background soil and the ore samples to identify the potential pollution sources. The results are presented in a three isotope graph ($^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{206}Pb$) (Fig. 5). Generally, the local background soils have more radiogenic Pb characterized by relatively high $^{206}Pb/^{207}Pb$ (1.244–1.249) and low $^{208}Pb/^{206}Pb$ (1.198–1.199) ratios. In contrast, zinc ores used in the smelting exhibit a less radiogenic signature with $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios of 1.176–1.188 and 2.103–2.112, respectively, which corresponded to the previous study (1.174–1.187 and 2.103–2.127 for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$, respectively) (Zheng, 1994). Sediments from the Caohai wetland have intermediate $^{206}Pb/^{207}Pb$ (1.178–1.202) and $^{208}Pb/^{206}Pb$ (2.058–2.096) ratios, which varied with depth ($^{206}Pb/^{207}Pb$ ratios increased, while $^{208}Pb/^{206}Pb$ ratios decreased with depth) (Fig. 6), suggesting a mixing of anthropogenic sources and geogenic Pb.

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 2. 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}). 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 *Schoenoplectus triqueter*. In summary, the concentrations of the metals (especially Cd, Pb and Zn) in the plants were much lower than those in the sediments.

4. Discussion

4.1. Metal distribution characteristics and the extent of sediment contamination

The Caohai wetland is located in a basin with its three sides (east, south and west) facing high mountains and

atmospheric particles can only easily reach the wetland from the north side. It is, therefore, not surprising that metal concentrations in the Caohai wetland sediments
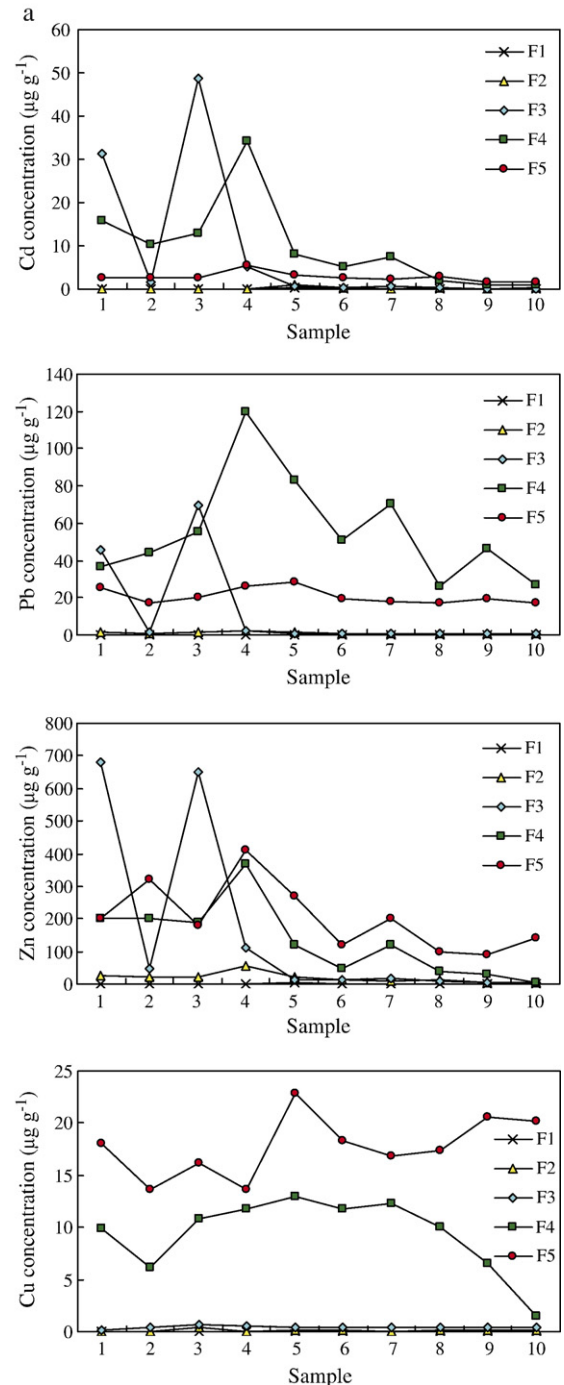

Fig. 4. Chemical fractionation of Cd, Pb, Zn and Cu in surface (a) and core (b) sediments from the Caohai wetland. F1, exchangeable fraction; F2, carbonate/specifically adsorbed fraction; F3, Fe–Mn oxide fraction; F4, organic/sulphide fraction; F5, residual fraction.
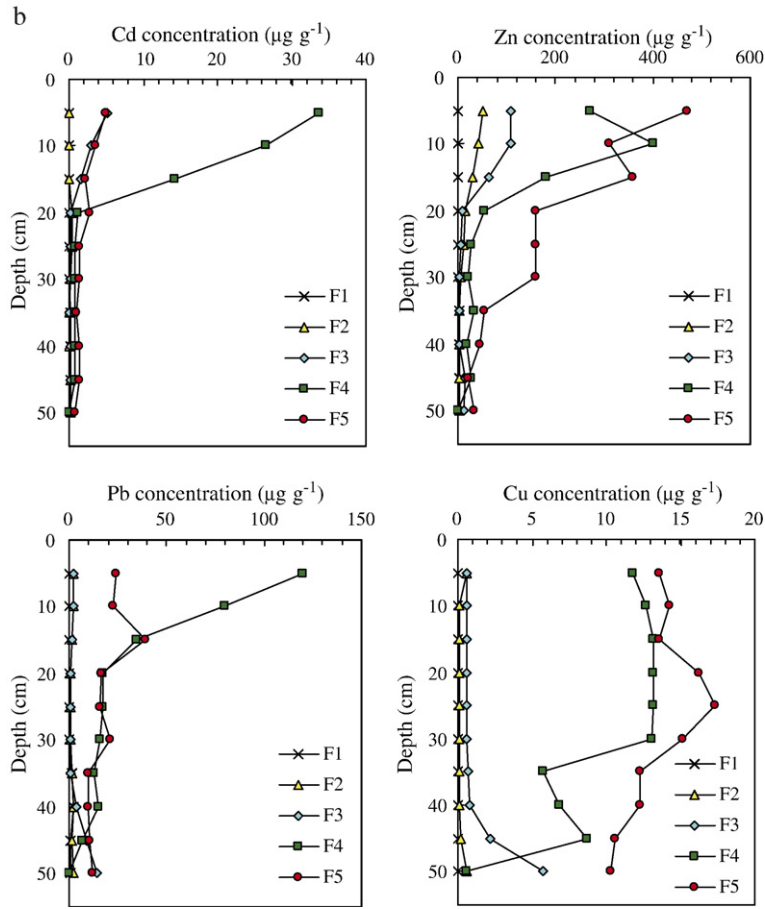
b

Fig. 4 (*continued*).

decreased from north to south, and the metal inputs were likely related to the emissions from the Hezhang zinc smelting area located at the northeast part of the Caohai wetland (Fig. 1). Although the sediment cores had not been age dated, the increasing trend of metal concentrations in the sediment cores from ∼20 cm was
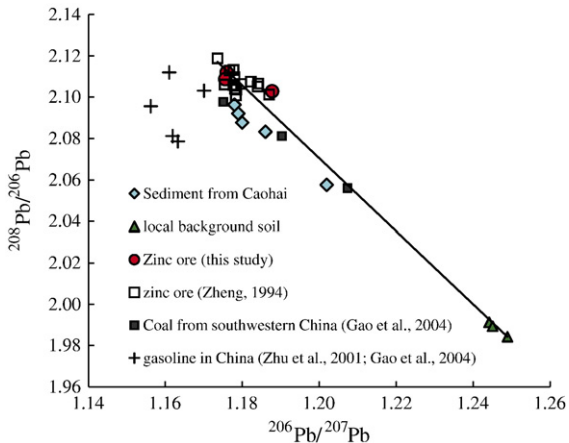

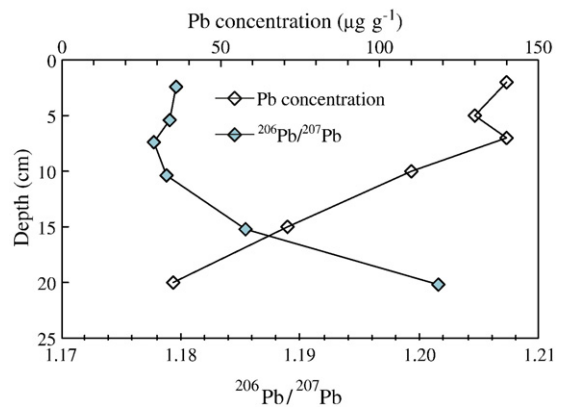Fig. 5. A plot of $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{206}Pb$ for different samples.

Fig. 6. Pb concentrations and $^{206}Pb/^{207}Pb$ ratios down the sediment core 2 from the Caohai wetland.

Table 2
Metal concentrations in different aquatic plant species from the Caohai wetland ($\mu g\ g^{-1}$, 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.

comparable to the local zinc smelting history, which began thriving after 1985, as shown in Fig. 7, confirming the impact of the zinc smelting. However, the different distribution patterns of Cd, Pb and Zn within the upmost layers (0 – 10 cm) between cores were not well consistent with the zinc smelting activities (Fig. 3), suggesting that metals in these sediments would undergo dissolution and redistribution, although the mechanism was not clear.

When compared with probable effect levels (PELs) of the Canadian Environmental Quality Guidelines recommended by Canadian Council of Ministers of the Environment (CCME, 1997), the mean Cd, Pb and Zn concentrations of the surface sediments from the Caohai wetland would be considered contaminated with a potential to cause toxic ecological effects (Table 1). In contrast, Cu concentrations in the sediments were far below its PELs. These results were comparable to the previous study which reported that moss samples collected close to the same smelting impacted area were seriously contaminated by Cd, Pb and Zn, but less impacted by Cu (Bi et al., 2006b). The intervention values recommended by the Netherlands Sediment Quality Guidelines (Department of Soil Protection, Netherlands, 1994) represent the maximum threshold values of trace metals in sediments, above which remedial actions should be considered. The comparison with the intervention values showed that more than half (six out of ten) surface sediment samples had Cd concentrations and three samples had Zn concentrations exceeding the corresponding intervention concentrations (12 μg Cd g^{-1} and 720 μg Zn g^{-1}; see Table 1). These results thus indicated that further investigation for ecological impacts and remediation actions should be taken.

4.2. Metal mobility in sediments

The sequential extraction procedure despite known limitations can provide useful information on the potential mobility and redox sensitivity 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/specifically adsorbed fractions are considered to be weakly bonded metals which may equilibrate with the aqueous phase and thus become more rapidly bioavailable (Pardo et al., 1990). The low concentrations of these fractions of metals in the Caohai wetland sediments thus indicated the low mobility and bioavailability of metals in the sediments.

Heavy metals in the sediments were strongly associated with the organic/sulphide 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/sulphide fraction with the high OM concentrations in sediments (Dollar et al.,
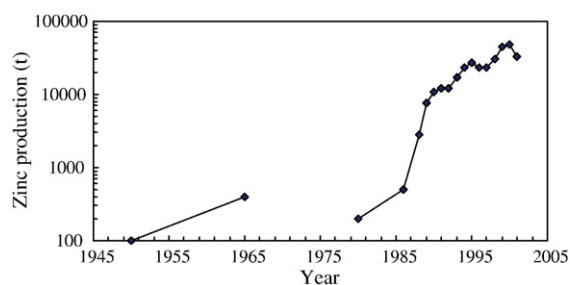

Fig. 7. Historical zinc production in Hezhang.

2001; Olivares-Rieumont et al., 2005). Stoeppler (1992) demonstrated that major factors, such as metal uptake by plants and subsequent decomposition, metal complexes formation with soluble OM, and metal absorption onto minerals, were all possible vehicles that might contribute to metal accumulation in the organic fraction, particularly for metals originating from atmospheric deposition (Jones, 1987; Stewart and Fergusson, 1994).

However, in some cases, i.e., the surface sediment sample 1 and 3, the Fe–Mn oxide fraction of Cd, Pb and Zn was dominant instead of the organic/sulphide fraction (Fig. 4a). This was not due to the relatively low OM concentrations of these two samples compared to the other samples (20–23% versus others generally >30%), but was a reflection of the influence of the aquatic plants. The fact was that the sites from which the samples were collected had much more biomass of the macrophytes than other sites. Many studies have reported that living plants can induce sediment oxidation (higher redox potential) through increased root radial oxygen loss (Madureira et al., 1997; Almeida et al., 2004; Jacob and Otte, 2004a,b), which might 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 could dissolve under oxidized conditions and the majorities of these dissolved concentrations would eventually undergo absorption 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), and so the relatively lower OM level of the sample 1 and 3 was not a cause, but a result/reflection of the influence of the plants.

Compared to the significantly elevated concentrations of Cd, Pb and Zn bound to the Fe–Mn oxide fraction in the surface sediment sample 1 and 3, the Cu in these samples was strongly bound to the organic/sulphide and residual fractions like other samples, while the Fe–Mn oxide fraction did not show elevated concentrations, indicating the lower vulnerability of Cu to redox potential or/and stronger affinity for complexation by organic matter than other metals (i.e. Cd, Pb and Zn). This result was comparable to the results of previous studies, which reported that Cu in stream sediments, with theoretically a more oxidized condition relative to lake environment, was strongly associated with the organic/sulphide fraction, while Cd, Pb and Zn in this situation showed a strong preference for the Fe–Mn oxide fraction (Ettler et al., 2006; Wong et al., 2007). In addition, Cu in organic/sulphide fraction in sediments is dependent on the pH. Rausch et al. (2005) reported that low pH would hinder the complexation of Cu by organic matter. However, the pH of the Caohai wetland water is so

high (8.8) that it can protect the organic/sulphide bound Cu from being degraded.

Human activities have less impact on the sediments in the deeper layers of the core, since the metals in the core were derived mainly from the geogenic sources. The increasing proportions of the residual fraction of Cd, Pb and Zn varied with depth in the sediment core thus indicating that the geogenic metals tended to be associated with the residual fraction. In contrast, metals derived from anthropogenic sources preferred to bind to the non-residual fractions, especially the organic/sulphide fraction, in the Caohai wetland sediments, posing a potential hazard to the ecosystem.

4.3. Source attribution of Pb in sediments

The $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{206}Pb$ three isotope graphs of the ore, local background soil and sediment samples revealed a linear relationship (Fig. 5). The ores and local background soils tended to lie at the ends of the line, and the sediments scattered between the two groups of samples, indicating the mixing of ore Pb and geogenic Pb. However, all the sediment data points were slightly shifted downward from the mixing line, as seen in Fig. 5. This probably doesn't arise from the variation of Pb isotopic compositions in the ores over the operating years since the zinc smelting in Hezhang mainly used the native ores, which have a narrow range of Pb isotope ratios (Fig. 5). It is therefore reasonable to conclude that other anthropogenic sources must be involved.

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 emission sources present in the study region. It can be seen from Fig. 5 that the Pb isotopic data points of coal from southwestern China (Gao et al., 2004) are more consistent with the sediment samples than the ores so that it appears as if the coal combustion is the main pollution sources instead of the ores. This is not the case, as emissions from coal combustion cannot introduce such high levels of metal concentrations in the sediments (see Table 1, Figs. 2 and 3). In fact, Bi (2007) reported that the lake sediments impacted by coal burning power plant from the same province (Guizhou) contained only 1.6 µg g^{-1} Cd, 37 µg g^{-1} Pb and 130 µg g^{-1} Zn, respectively. In addition, given the Pb isotopic ratios here (1.175–1.274 and 2.056–2.098 for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$, respectively), the coal alone could not shift the sediment data points out from the mixing line mentioned above if it was not the dominant source of Pb in the sediments.

Therefore, we assume that the shift of sediment data points arise from the influence of other anthropogenic sources with lower $^{206}Pb/^{207}Pb$ ratios, such as the gasoline Pb, rather than the coal Pb, as seen from the Fig. 5.

In summary, we can conclude from the Pb isotopic data that the inventories of Pb in the Caohai wetland sediments were mainly derived from the historical zinc smelting in Hezhang area, and the Pb emitted from the gasoline combustion made a substantial additional contribution to the Pb in the sediments. In contrast, the influence of coal Pb was not important, at least compared with that of gasoline 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 the previous observations (Albers and Camardese, 1993; Yurukova and Kochev, 1994; Rai et al., 1995). In order to determine whether a 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 $\mu g\ g^{-1}$, respectively. Baldantoni et al. (2005) observed that Cd, Pb, Zn and Cu concentrations in plant shoots (Najas marina) and leaves (Potamogeton pectinatus) from a less impacted site on Lake Averno, Naples, were generally lower than 0.4, 4.0, 60 and 5.0 $\mu g\ g^{-1}$, respectively. Hozhina et al. (2001) investigated aquatic plant Equisetum fluviatile, Typha latifolia and Scirpus sylvaticus in the Kemerovo region of Russia, and found that the aboveground tissues of these plants from the control area contained 0.023–1.8 $\mu g\ g^{-1}$ of Cd, 0.89–23 $\mu g\ g^{-1}$ of Pb, 26–84 $\mu g\ g^{-1}$ of Zn and 4.7–39 $\mu g\ g^{-1}$ of Cu, respectively. 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 (Hozhina et al., 2001; Cymerman-Samecka and Kempers, 2004; Deng et al., 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 wetland sediments thus confirming that metal contamination of 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, A. imbricate and S. communis, would be a potential threat to a number of higher trophic-level organisms, especially the migratory birds. In addition, the local people often take some of the aquatic plants, such as C. demersum, P. malainus and A. imbricata, as the food for poultry and livestock, by which the metals accumulated in these plants could probably enter the human body through the food chain.

5. Conclusions

The present field investigation shows that Chaohai wetland, from southwestern China, has been seriously contaminated by heavy metals. The metal distribution patterns and Pb isotopic data from the sediments revealed that the contaminations were strongly related to the historical zinc smelting of the Hezhang area, but other anthropogenic sources, such as gasoline Pb, also made substantial contribution to the Pb in the sediments. Heavy metals in the wetland sediments were strongly associated with the organic/sulphide and residual fractions, exhibiting relatively low mobility. However, Cd, Pb and Zn bound to the Fe–Mn oxide fraction tended to become dominant when the sediments were oxidized by the aquatic plant activities. This process would probably release some proportions of metal contaminations, which were previously held by the organic matter, into the water. The elevated metal accumulations in the plants should be of particular concern since these metals can enter into higher trophic-level organisms, even humans, through the food chain.

Acknowledgements

References

Albers PH, Camardese MB. Effects of acidification on metal accumulation by aquatic plants and invertebrates. 1. Constructed wetlands. Environ Toxicol Chem 1993;12:959–67.
Almeida CMR, Mucha AP, Vasconcelos MTSD. Influence of the sea rush Juncus maritimus on metal concentration and speciation in

estuarine sediment colonized by the plant. Environ Sci Technol 2004;38:3112–8.

Bacon JR, Hewitt I. Heavy metals deposited from the atmosphere on upland Scottish soil: chemical and lead isotope studies of the association of metals with soil components. Geochim Cosmochim Acta 2004;69:19–33.

Baldantoni D, Maisto G, Bartoli G, Alfani A. Analyses of the three native aquatic plant species to assess spatial gradients of lake trace element contamination. Aquat Bot 2005;83:48–60.

Bi X. Environmental contaminations of heavy metals induced by historical zinc smelting in southwestern China. PhD thesis, Institute of Geochemistry, Chinese Academy of Sciences, China. 2007.

Bi X, Feng X, Yang Y, Qiu G, Li G. Quantitative assessment of cadmium emission from zinc smelting and its influences on the surface soils and mosses in Hezhang County, southwestern China. Atmos Environ 2006a;40:4228–33.

Bi X, Feng X, Yang Y, Qiu G, Li G, Li F, et al. Environmental contamination of heavy metals from zinc smelting areas in Hezhang County, western Guizhou, China. Environ Int 2006b;32:883–90.

Carroll S, O'Day PA, Esser B, Randall S. Speciation and fate of trace metals in estuarine sediments under reduced and oxidized conditions, Seaplane Lagoon, Alameda Naval Air Station (USA). Geochem Trans 2002;3:81–101.

CCME. Recommended Canadian Soil Quality Guidelines. CCME1-895-925-92-4; 2002.

Cymerman-Samecka A, Kempers AJ. Toxic metals in aquatic plants surviving in surface water polluted by copper mining industry. Ecotoxicol Environ Saf 2004;59:64–9.

Deng H, Ye Z, Wong M. Accumulation of lead, zinc, copper and cadmium by 12 wetland plant species thriving in metal-contaminated sites in China. Environ Pollut 2004;132:29–40.

Department of Soil Protection, Netherlands. The Netherlands Soil Contamination Guidelines. Netherlands Intervention Values for Soil Remediation; 1994.

Dollar NL, Souch CJ, Filippelli GM, Mastalerz M. Chemical fractionation of metals in wetland sediments: Indiana dunes national lakeshore. Environ Sci Technol 2001;35:3608–15.

Ettler V, Mihaljevič M, Šebek O, Molek M, Grygar T, Zeman J. Geochemical and Pb isotope evidence for sources and dispersal of metal contamination in stream sediments from the mining and smelting district of Příbram, Czech Republic. Environ Pollut 2006;142:409–17.

Feng X, Li G, Qiu G. A preliminary study on mercury contamination to the environment from artisanal zinc smelting using indigenous method in Hezhang County, Guizhou, China: Part 1. Mercury emission from zinc smelting and its influences on the surface waters. Atmos Environ 2004;38:6223–30.

Feng X, Li G, Qiu G. A preliminary study on mercury contamination to the environment from artisanal zinc smelting using indigenous method in Hezhang County, Guizhou, China: Part 2. Mercury contaminations to soil and crop. Sci Total Environ 2006;368:47–55.

Gallon C, Tessier A, Gobeil C. History perspective of industrial lead emissions to the atmosphere from a Canadian smelter. Environ Sci Technol 2006;40:741–7.

Gao Z, Yin G, Ni S, Zhang C. Geochemical feature of the urban environmental lead isotope in Chendu city. Carsol Sin 2004;4:267–72 [in Chinese with English abstract].

Gélinas Y, Schmit JP. Extending the use of the stable lead isotope ratios as a tracer in bioavailability studies. Environ Sci Technol 1997;31:1968–72.

Gomez-Ariza JL, Giraldez I, Sanchez-Rodas D, Morales E. Metal readsorption and redistribution during the analytical fractionation

of trace elements in oxic estuarine sediments. Anal Chim Acta 1999;399:295–307.

Hozhina EI, Khramov AA, Gerasimov PA, Kumarkov AA. Uptake of heavy metals, arsenic, and antimony by aquatic plants in the vicinity of ore mining and processing industries. J Geochem Explor 2001;74:153–62.

Jacob DL, Otte ML. Long-term effects of submergence and wetland vegetation on metals in a 90-year old abandoned Pb–Zn mine tailings pond. Environ Pollut 2004a;130:337–45.

Jacob DL, Otte ML. Influence of Typha latifolia and fertilization on metal mobility in two different Pb–Zn mine tailing types. Sci Total Environ 2004b;333:9–24.

Jones JM. Chemical fractionation of copper, lead and zinc in ombrotrophic peat. Environ Pollut 1987;48:131–44.

Kersten M, Förstner U. Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments. Water Sci Technol 1986;18:121–30.

Lee CS, Li X, Shi W, Cheung SC, Thornton I. Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. Sci Total Environ 2006;356:45–61.

Liu R. Analytical methods for soil and agricultural chemistry. Beijing: China Agricultural Science and Technology Press; 1999.

Madureira MJ, Vale C, Goncalves ML. Effect of plants on sulphur geochemistry in the Tagus salt-marshes sediments. Mar Chem 1997;58:27–37.

Mukai H, Furuta N, Fujii T, Ambe Y, Sakamoto K, Hashimoto Y. Characterization of sources of lead in the urban air of Asia using ratios of stable lead isotopes. Environ Sci Technol 1993;27:1347–56.

Mukai H, Tanaka A, Fujii T, Zeng Y, Hong Y, Tang J, et al. Regional characteristics of sulfur and lead isotope ratios in the atmosphere at several Chinese urban sites. Environ Sci Technol 2001;35: 1064–71.

Nirel PMV, Morel FMM. Pitfalls of sequential extractions. Water Res 1990;24:1055–6.

Olivares-Rieumont S, Rosa D, Lima L, Graham DW, Alessandro KD, Borroto J, et al. Assessment of heavy metal levels in Almendares River sediments⎯Havana City, Cuba. Water Res 2005;39:3945–53.

Outridge PM, Noller BN. Accumulation of toxic trace elements by freshwater vascular plants. Rev Environ Contam Toxicol 1991;121: 1–63.

Pardo R, Barrado E, Perez L, Vega M. Determining and association of heavy metals in sediments of the Pisucrga River. Water Res 1990;24:373–9.

Rai UN, Sinha S, Tripathi RD, Chandra P. Wastewater treatability potential of some aquatic macrophytes: removal of heavy metals. Ecol Eng 1995;5:5–12.

Rapin F, Tessier A, Campbell PGC, Carignan R. Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure. Environ Sci Technol 1986;20:836–40.

Rausch N, Ukonmaanaho L, Nieminen TM, Shotyk W. Porewater evidence of metal (Cu, Ni, Co, Zn, Cd) mobilization in an acidic, ombrotrophic bog impacted by a smelter, Harjavalta, Finland and comparison with reference sites. Environ Sci Technol 2005;39: 8207–13.

Stewart C, Fergusson JE. The use of peat in the historical monitoring of trace metals in the atmosphere. Environ Pollut 1994;86:243–9.

Stoeppler M. Hazardous metals in environment. Amsterdam: Elsevier Press; 1992.

Tessier A, Campbell PGC, Blsson M. Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 1979;51: 844–51.

Ure AM, Quevauviller Muntau H, Griepink B. Speciation of heavy metals in solids and harmonization of extraction techniques undertaken

under the auspices of the BCR of the Commission of the European Communities. Int J Environ Anal Chem 1993;51:135–51.

Wong C, Li X. Pb contamination and isotopic composition of urban soils in Hong Kong. Sci Total Environ 2004;319:185–95.

Wong C, Wu S, Duzgoren-Aydin N, Aydin A, Wong M. Trace metal contamination of sediments in an e-waste processing village in China. Environ Pollut 2007;145:434–42.

Yang Y, Liu C, Wu P, Zhang G, Zhu W. Heavy metal accumulation from zinc smelters in a carbonate rock region in Hezhang County, Guizhou Province, China. Water Air Soil Pollut 2006;174: 321–39.

Yurukova L, Kochev K. Heavy metal concentrations in freshwater macrophytes from the Aldomirovsko swamp in the Sofia District, Bulgaria. Bull Environ Contam Toxicol 1994;52:627–32.

Zheng C. An approach on the source of ore-forming metals of lead–zinc deposits in northwestern part, Guizhou. J Guilin Coll Geol 1994;14:113–24 [in Chinese with English abstract].

Zhu B, Chen Y, Peng J. Lead isotope geochemistry of the urban environment in the Pearl River Delta. Appl Geochem 2001;16: 409–17.