Comparison of lead, zinc and cadmium accumulation in sediments as affected by smelting activities

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INTRODUCTION

- Sediments are recognized as an important sink/source for heavy metals from anthropogenic sources, which affects overlying water quality and aquatic organisms. The fractionations and bioavailability of the metals are strongly dependent on sediment geochemical conditions, such as pH and redox potential (Tessier et al., 1979).
- In addition to quantitative measurement, lead (Pb) or S isotopic composition can be useful for identifying sources and contributions of anthropogenic metals and has been widely used in a wide range of environmental studies (Zhu et al., 2001; Wong and Li, 2004; Gallon et al., 2006). As a general rule, anthropogenic Pb is less radiogenic than the geogenic Pb, therefore, $^{206}Pb/^{207}Pb$ ratios in gasoline additives in south China are generally lower than 1.17 (Zhu et al., 2001). In comparison, $^{206}Pb/^{207}Pb$ ratios in Pb ores are often higher than 1.20 (Wong and Li, 2004; Lee et al., 2006).
- Zinc (Zn) smelting activities using traditional techniques have caused serious environmental problems in Guizhou province, southwest China (Yang et al., 2006; Bi et al., 2006). Heavy metal emission during smelting activities sprayed far away around smelting furnaces. In this study, we investigated and compared the differential accumulation of heavy metals in sediments of a natural freshwater wetland (Caohai), 10 km northeast of the smelting location, and a natural river system in the smelting area.

OBJECTIVES

The objectives of this study were: (1) to compare heavy metal enrichment in sediment of the two watersheds; (2) to compare fractionation of heavy metals in the sediments; and (3) to trace heavy metal sources using isotopes.

MATERIALS AND METHODS

- River sediments were collected in a river in the smelting region, while lake sediments were collected in a lake ca. 10 km downwind from Zn smelters.
- For total metal concentration, sediment samples (0.5g) were digested by 10 mL concentrated HNO_3-HCl-HF acid mixture in a sealed Teflon vessel. Metal fractionations were discriminated using the method of Tessier et al. (1979). Metal (Cd, Pb, and Zn) concentrations in all the extracts were determined using ICP-OES (Vista MPX, Varian Inc
- Lead isotopic composition analysis was performed on selected sediment samples by ICP-MS (Perkin-Elmer Elan 6100 DRCplus). The details of the procedure were reported by Lee et al. (2006).
- For microscope observation, samples with high heavy metal contents were washed in distilled water to remove very fine particles; the coarse parts were then air-dried, fixed on a copper supporting net, coated with graphite and then ready for observation and identification on a TEM instrument (JEM-2000FXⅡ, Japan) equipped with EM-ASID20 imaging system and Oxford Link ISIS energy spectrum in IGCAS.

Table 1. Lead, Zn, and Cd concentrations (mg kg^{-1}) and the Pb/Cd and Zn/Cd ratios in the river and lake sediment,.

		Pb	Zn	Cd	Pb/Cd	Zn/Cd
River sediment (11)	Mean	11450	20768	67.0	160	279
	STDEV	7097	11404	26.0	84	120
Lake sediment (32)	Mean	88.4	543	25.2	10.3	37.8
	STDEV	51.4	472	27.2	9.1	23.8

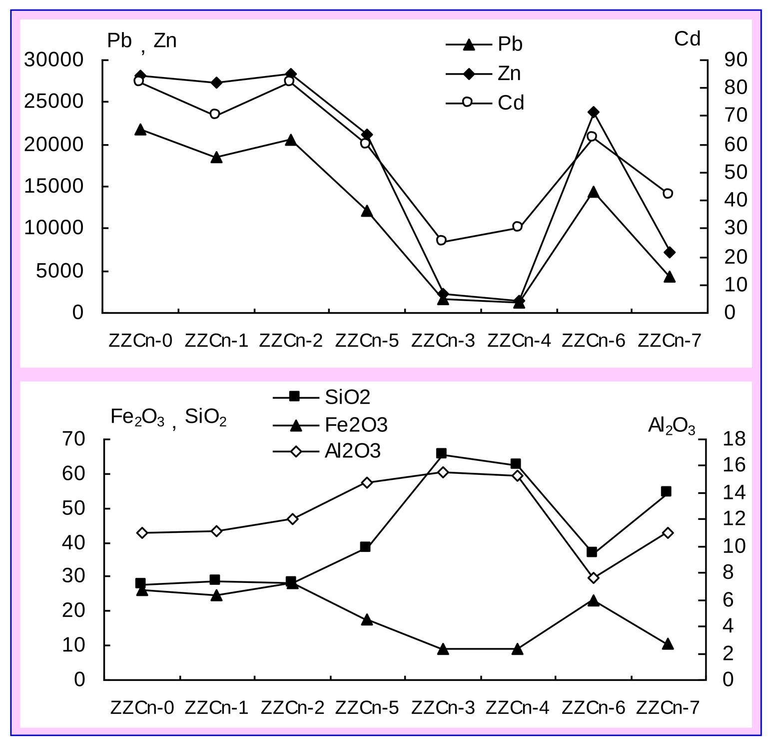

Fig. 1. Variation of Pb, Zn, and Cd concentrations in river sediments along downstream direction and their relations to sediment Fe, Al, and Si contents.

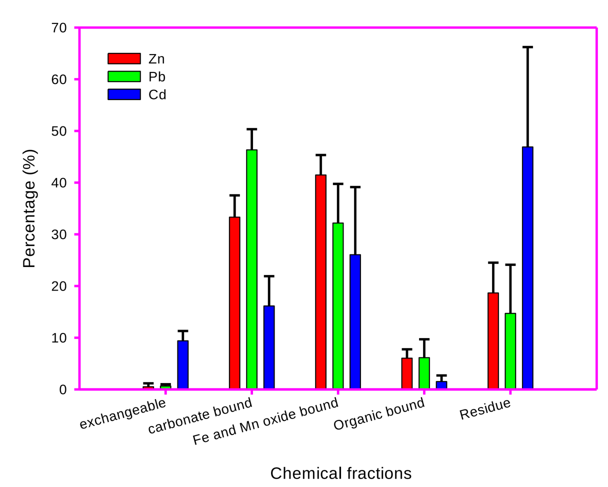

Fig. 2. Chemical fractionation of Zn, Pb, and Cd in river sediments.

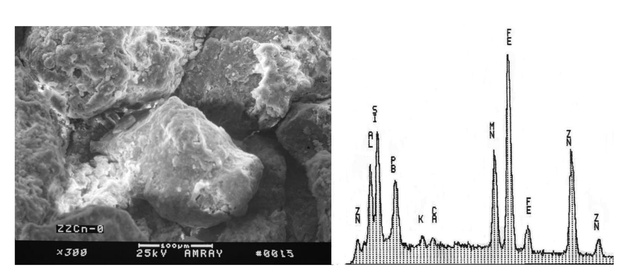

Fig. 3. Metal Pb and Zn were attached to Fe and Mn oxides in river sediments as observed under microscopy.

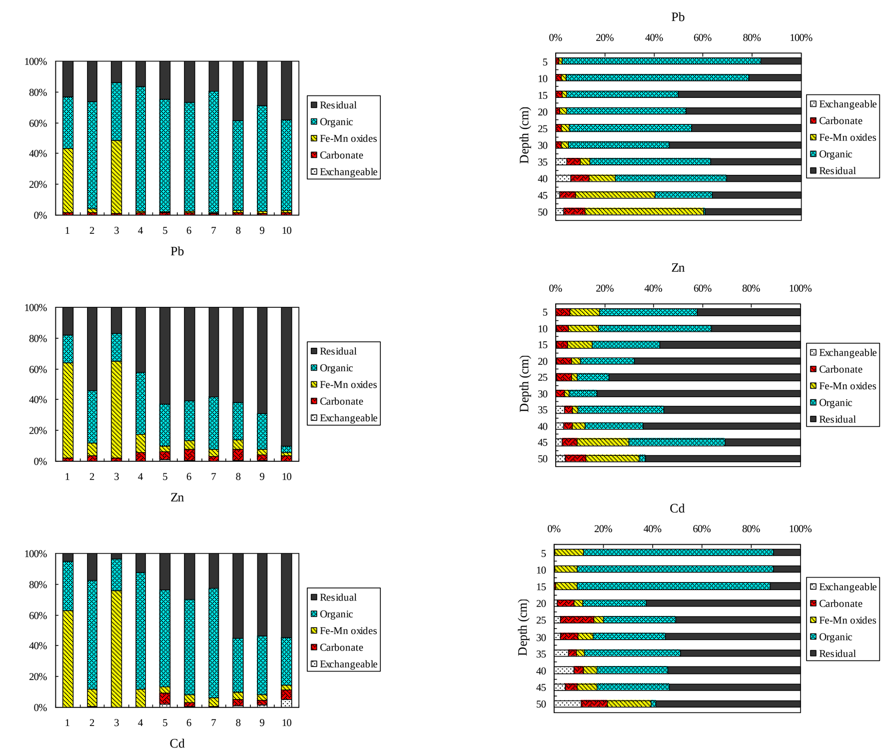

Fig. 4. Fractionation of heavy metals varied in different sampling locations in lake sediments (left) and varied with profile depth of lake sediments (right).

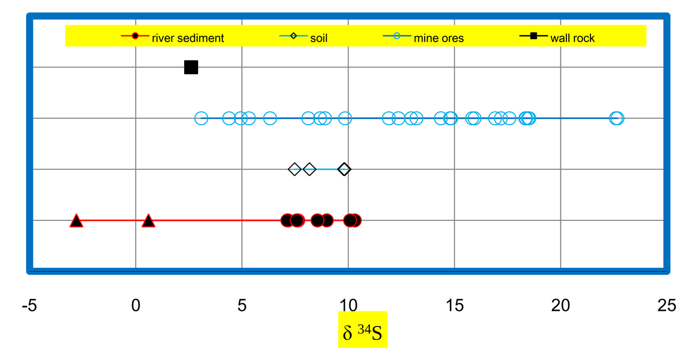

Fig. 5. S isotope composition in river sediment and comparison with soils, mine ores and wall rocks.

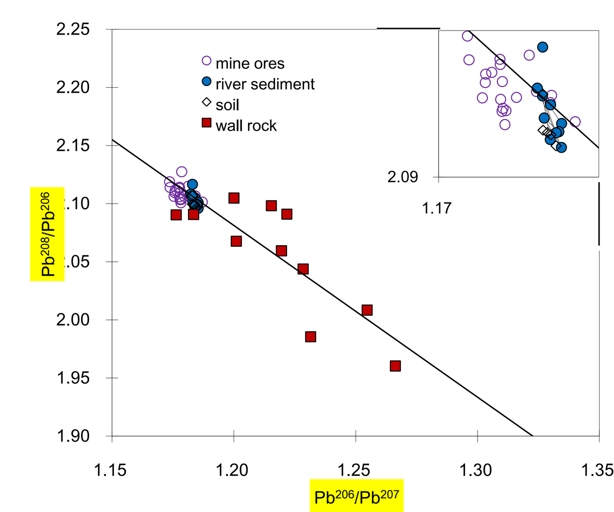

Fig. 6. Lead isotope composition in river sediment and comparison with soils, mine ores, and wall rocks.

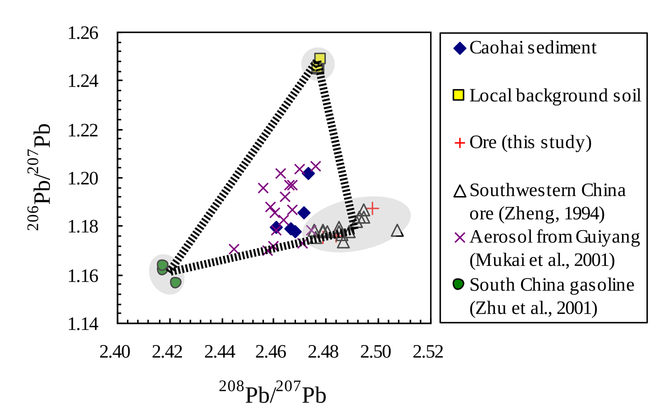

Fig. 7. Pb isotope composition in Caohai lake sediment and comparison with soils, mine ores, and gasoline.

RESULTS AND DISCUSSION

- The concentrations of Pb, Zn, and Cd in the river sediments varied in the range of 4375-21850, 7275-30425, and 42.0-95.0 mg kg^{-1}, with Pb/Cd and Zn/Cd ratios of 104-266 and 173-390, respectively. However, the concentrations of Pb, Zn, and Cd in the lake sediments were in the range of 66.0-160, 130-1200, and 2.60-71.0 mg kg^{-1}, with Pb/Cd and Zn/Cd ratios of 2.14-25.4 and 16.9-50.0, respectively (Table 1). The differences in Pb/Cd and Zn/Cd ratios may suggest the differences in their sources.
- The concentrations of Pb, Zn, and Cd decreased from upstream near the smelting furnaces to downstream locations, and were positively correlated with Fe_2O_3 contents in the river sediments (Fig. 1).
- In the river sediments, Pb and Zn were mainly bound to carbonate (35-51%, 32-39%) and Fe/Mn oxides (26-47%, 38-48%); whereas Cd was mainly associated with residue (16-59%) and carbonate bound fraction (15-45%) (Fig. 2). Under microscopy, metal Pb and Zn coexisted with Fe-Mn oxides in river sediments (Fig. 3).
- In surface sediment of Caohai lake, organic bound fraction was the dominant chemical form of Pb (34-82%), Zn (3.8-46%), and Cd (31-84%) (Fig. 4). Distribution of Pb, Zn, and Cd fractions in lake sediment cores varied with depth. Percentages of Pb, Zn, and Cd in the organic fraction decreased but their residual fraction increased down sediment core profiles. Lead, Zn, and Cd in sediment cores were increasingly associated with Fe-Mn oxides with core depth. Exchangeable and carbonate bound fractions of Cd and Pb were also observed to increase with core depth (Fig. 4).
- In river sediments, their $\delta^{34}S$ values were in the range of mine ores , which is significantly different from those of wall rock, suggesting that their sources were different (Fig. 5) .
- In river sediments, $^{206}Pb/^{207}Pb$, $^{206}Pb/^{208}Pb$ ratios were 1.182-1.185 and 0.399-0.403, respectively, as compared with 1.178-1.2202, 0.477-0.486 in lake sediments (Figs. 6 and 7). In river sediments, Pb isotope composition was similar to those of mine ores, but different to wall rocks, suggesting a Zn smelting –related source of the metals in river sediment (Fig. 6). In lake sediments, different sources including Zn smelting attributed to their Pb isotope compositions, suggesting a mixing of anthropogenic sources and geogenic Pb, and coal combustion and gasoline Pb may attribute to the low $^{208}Pb/^{207}Pb$ ratios in the lake sediments (Fig. 7).

CONCLUSIONS

1. Zinc smelting activities in southwestern China caused Pb, Zn, Cd enrichment in river and lake sediments, but the metals were fixed into the sediments in different mechanism. In river sediments, metals were mainly associated with Fe-Mn oxides, whereas lake sediments, they were dominantly bound to organic matter.
2. Lead, Zn, and Cd in river sediments were mainly originated from release of Zn smelting slags, whereas in the lake sediments, they came in a large part from the deposition of metal-enriched dust from the smelting activities.

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