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Acid Volatile Sulfides and Simultaneously Extracted Metals in a Metal-Polluted Area of Taihu Lake, China

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Abstract There were similar distribution characteristics for acid volatile sulfides (AVS) and simultaneously extracted metals (SEM) in surface sediments, and the concentrations of AVS and SEM decreased from the deposition area to the center of the bay (lake). The ratio of AVS to SEM was <1 in the surface sediments, indicating that heavy metals in surface sediments may be bioavailable. The concentration of AVS increased with sediment depth, followed by a decrease with large variation, while the concentration of SEM remained constant. By comparing the concentration of SEM with total metals, it was shown that extracted Cu and Ni decreased with sediment depth, indicating increasing association of Cu and Ni with sulfides in deeper sediment layers. The lower extracted ratios for Pb and Zn compared with sulfidic sediment illustrated that AVS should not have strong control on sediment Pb and Zn. The molar ratio of AVS and reactive iron showed that heavy metals were dynamic and active in sediments in this lake.

Keywords Acid volatile sulfide (AVS) · Simultaneously extracted metals (SEM) · Sulfide-bound phase · Taihu Lake

Taihu Lake is situated in the middle and lower reaches of the Yangtze River. It is the third largest freshwater lake in China and has a surface area of 2,338 km^2. Its mean depth is 2 m and is a large, shallow, freshwater lake. The lake suffers severe eutrophication due to high input of domestic sewage and industrial wastewater since the 1980s. Taihu Lake sediments are characterized by no heavy metal pollution in the southern area to moderate pollution in the northern area (Qu et al. 2001). Meiliang Bay and Wuli Lake have suffered the most serious heavy metal pollution, including Hg, Pb, Cd, Cr, As, Ni, and Cu. The main purposes of this study are (1) to characterize the spatial and vertical distribution patterns of acid volatile sulfides (AVS) and simultaneously extracted metals (SEM) in Meiliang Bay and Wuli Lake, and (2) to evaluate the relationships among AVS, SEM, and total heavy metals along sediment profiles in the shallow, eutrophic areas of Meiliang Bay and Wuli Lake.

Materials and Methods

Surface sediments and sediment cores were collected in April 2007 (Fig. 1 and Table 1). The surface sediments (8 cm) were collected using a grab sampler, and sediment cores were sampled using a core sampler (10 cm internal diameter, 50 cm long). Triplicate sediment cores were collected at sites 0, 1, and 15. The cores were kept upright and transported to laboratory on ice within 5 h of collection. These sediments were sliced into 1 cm intervals for 0–2 cm, 2 cm intervals for 2–10 cm, and 4 cm intervals for 10–22 cm depth. Each slice was performed with 2 min, and the sliced sediments were immediately preserved under nitrogen below 4°C until analysis.

Sediment water content was measured by weight loss after drying at 105°C for 24 h, and organic matter content was determined by weight loss on ignition of dried sediment after heating for 4 h at 550°C. Acid volatile sulfide

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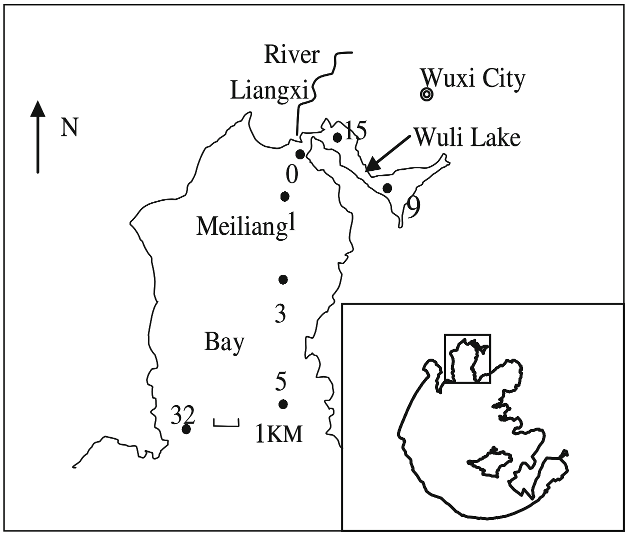

Fig. 1 Location of sampling sites in Meiliang Bay and Wuli Lake of Taihu Lake

Table 1 Sampling sites in Meiliang Bay and Wuli Lake

Sampling site	Longitude	Latitude	Water depth (m)	Water temperature (°C)
0	120°13′9.9″N	31°32′22.8″E	1.55	22.8
1	120°11′26.4″N	31°30′47.4″E	1.75	22.9
3	120°11′39.5″N	31°28′34.8″E	2.20	22.8
5	120°11′14.4″N	31°24′40.2″E	2.40	22.9
32	120°8′45.4″N	31°24′24.5″E	1.90	24.1
9	120°15′11.4″N	31°30′46.8″E	2.60	22.6
15	120°14′10.1″N	31°31′23.2″E	2.20	22.8

was extracted in duplicate from sediment samples that had been stored under nitrogen below 4°C for no longer than 48 h. Acid volatile sulfide was measured using the Hsieh's cold diffusion method, with the use of ascorbic acid to prevent interferences from Fe(III) (Hsieh and Yang 1989; Hsieh et al. 2002). Approximately 5 g of wet sediment was added to an oxygen-free flask with a test tube containing 5 ml of 3% alkaline zinc solution. Then, 20 ml of 6 M HCl was poured onto the sediment, and the cap of the flask was tightened. After reacting for 18 h, the flask was opened, and the sulfide traps were removed from the bottles. A homogeneous ZnS suspension was ensured by vigorously vortexing the traps followed by treatment with a sonicating water bath for about 30 s (Glenn et al. 1997). Sulfide was quantified in aliquots of this suspension by using the methylene blue method (Cline et al. 1969). An average recovery of AVS from ZnS in the control could reach 97.8% using this method (Hsieh and Yang 1989; Hsieh et al. 2002). The sediment suspension remaining in the flask was filtered though a 0.45-μm membrane, and the concentration of heavy metals were determined by ICP-AES. The precision of duplicate analyses was within 5% for Fe, 10% for Cd, Zn, and Cu, and 8% for Ni and Pb. Total heavy metals was determined using a microwave-assisted acid digestion procedure (US EPA, Method 3052 1996). Three replicates of 0.5 g certificated samples (GBW07309, from National Quality and Technology Supervise Agency of China) have a precision for all elements within 7%. The recovery from analysis of GBW-9 was 104%, 82%, 97%, 102%, 93%, 95%, and 115% for Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, respectively. Duplicate analyses of the sediment samples have a precision within 10% for all elements. The total concentrations of metals in digests were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Perkin-Elmer DV4300).

Comparison of mean AVS concentrations between sites were determined using a one-tailed analysis of variance (ANOVA) test, where $p < 0.05$ indicated a significant difference in analyte concentrations between sites.

Results and Discussion

The concentrations of AVS and SEM in surface sediments are presented in Table 2. The concentration of ΣSEM

Table 2 The concentrations of AVS, SEM (μmol/g), and the ratio of $\sum$SEM and AVS in surface sediments of Meiliang Bay and Wuli Lake

Sampling site	$\mathrm{SEM_{Cd}}$	$\mathrm{SEM_{Cu}}$	$\mathrm{SEM_{Pb}}$	$\mathrm{SEM_{Ni}}$	$\mathrm{SEM_{Zn}}$	$\sum$SEM	AVS ± SD	$\sum$SEM/AVS
0	0.0072	0.69	0.128	0.48	2.55	3.85	1.22 ± 0.22	3.16
1	0.0045	0.47	0.109	0.62	1.59	2.80	1.17 ± 0.08	2.39
3	0.0039	0.27	0.097	0.43	1.03	1.83	1.08 ± 0.01	1.69
5	0.0029	0.15	0.074	0.23	0.52	0.97	0.82 ± 0.22	1.18
32	0.0038	0.47	0.090	0.49	1.34	2.40	0.66 ± 0.12	3.64
9	0.0027	0.22	0.105	0.21	0.66	1.19	0.76 ± 0.08	1.57
15	0.0044	0.30	0.072	0.33	0.74	1.44	0.32 ± 0.07	4.50
COV (%)	36.0	50.9	20.5	38.0	58.7	49.3	37.2	47.1

COV = Cofficient of variation (SD/average.100%); $\sum\mathrm{SEM} = \mathrm{SEM_{Cd}} + \mathrm{SEM_{Cu}} + \mathrm{SEM_{Pb}} + \mathrm{SEM_{Ni}} + \mathrm{SEM_{Zn}}$

SD = Standard deviation

decreased from site 0 to the center of Meiliang Bay. Suspended particles being transported to the lake from the river were deposited in the area of the estuary first due to the slow water current velocity. With increasing distance from the estuary, the concentration of heavy metals decreased sharply. The distribution characteristics of SEM was the same to Meiliang Bay as in Wuli Lake; site 9 had higher concentration of SEM than site 15, since the former site received wastewater from Wuxi city. The distribution pattern of AVS resembled SEM; the higher concentration was in the deposition area (site 0 and 9) in Meiliang Bay and Wuli Lake, and its concentration decreased further away from the area of estuary. Gagnon et al. (1995) and Lyons (1997) have demonstrated that high AVS concentrations occur in sediments with high deposition rates. The distribution characteristics of AVS and SEM in Meiliang Bay and Wuli Lake indicated that the deposition area favors the formation of AVS and SEM. The mean concentration of AVS in Meiliang Bay was higher than Wuli Lake ($p < 0.05$). Sampling was performed in spring when the concentration of AVS had not reached its maximum, which provided a realistic, worst-case scenario for characterizing AVS distribution in lake sediments in the context of assessing metal bioavailability. The $\sum$SEM/AVS were all >1 in surface sediments of Meiliang Bay and Wuli Lake (Table 2), indicating potential bioavailability to biota (Di Toro et al. 1990).

The vertical distribution of AVS in sediment cores is shown in Fig. 2. The concentration of AVS varied greatly among the sediment cores, which was low in the top several centimeters (8 cm), then increased abruptly, and decreased gradually with depth.

The observed AVS distribution pattern varied greatly by location, which is relative to sediment physical and chemical properties, redox potential, deposition environment and availability of SO_4^{2-} (Oehm et al. 1997; Griethuysen et al. 2003; Morse et al. 2004). In surface sediments, O_2, NO_3^-, Mn(IV), and Fe(III) all can function as electron acceptors during minerlization of organic carbon, thereby making the reduction of SO_4^{2-} an inferior pathway (Roden et al. 2002). In addition, AVS in surface sediments could be oxidated by O_2 due to resuspension, which occurs frequently in this shallow eutrophic lake (Fang et al. 2005). With increasing sediment depth, conditions become more reducing, which favors the reduction of SO_4^{2-}, and the concentration of AVS then accumulated in deeper sediment. But, if SO_4^{2-} is scarce, AVS may not accumulate in quantity due to low diffusive flux of SO_4^{2-} from the overlying water column to deeper sediment (Berg et al. 1998).

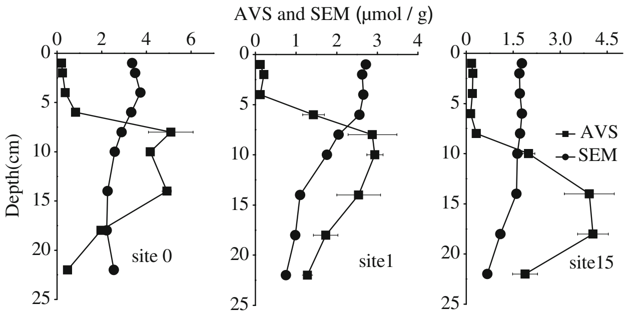

Fig. 2 The vertical distribution of AVS and SEM in sediment cores

According to Berg et al. (2001) definition, AVS peaks below the sediment water interface could be explained by unsteady deposition due to sudden changes in depositional environment, particle size, etc. This may be relative to observed sediments color change, which was brown in upper sediment and then became black down the sediment profile.

Leonard et al. (1993) reported that AVS concentration ranged from 4 to 13 μmol/g in unpolluted lake sediments. The AVS content at sites 0, 1 and 15 were in the ranges of 0.21–5.09 μmol/g, 0.12–2.94 μmol/g and 0.14–4.05 μmol/g, respectively. The studied sites are all hypereutrophic (visible algae was seen when sampling), but the AVS content are in the range of unpolluted lakes. There might be two reasons for this: First, the AVS content in sediments correlate positively with the temperature of overlying water (Leonard et al. 1993), and the sampling was performed in spring, when AVS has not reached its maximum; Second, AVS formation might be limited by SO_4^{2-}, which usually occurs in freshwater lakes.

The vertical distribution of total heavy metals and SEM are shown in Fig. 3. In Core 0 and Core 1, the total heavy metals concentration decreased with sediment depth, which indicated increased pollution in recent years. The peaks of total metals content were not in the surface sediment (0–1 cm) but below the sediment-water interface (2–6 cm). This enrichment pattern probably was caused by resuspension, sediment transport, bioturbation, etc. Zhu et al. (2005) found that metal contents in suspended particle matter contribute to metal enrichment in surface sediments in Meiliang Bay. In Core 15, no distinct enrichment pattern was found for total heavy metals, which may have resulted from dredging activity performed in 2003 (the upper 60 cm sediment was removed).

In Core 1, the vertical distribution pattern of total heavy metals resembled SEM, indicating a possible close relationship between the total metals and the SEM concentration. This was confirmed by the Pearson correlation coefficients in Table 3. In core 0, SEM_{Cu}, EM_{Zn}, and SEM_{Ni} also show a close relationship with total metals.

By calculating the percentage of SEM to total metal concentration, we could generally get metal association phase in sediments. The percentage of SEM_{Cu} to total Cu

Fig. 3 The total metals and SEM concentration in sediment profiles sites 0, 1, and 15 (a-site 0, b-site 1, c-site 15)

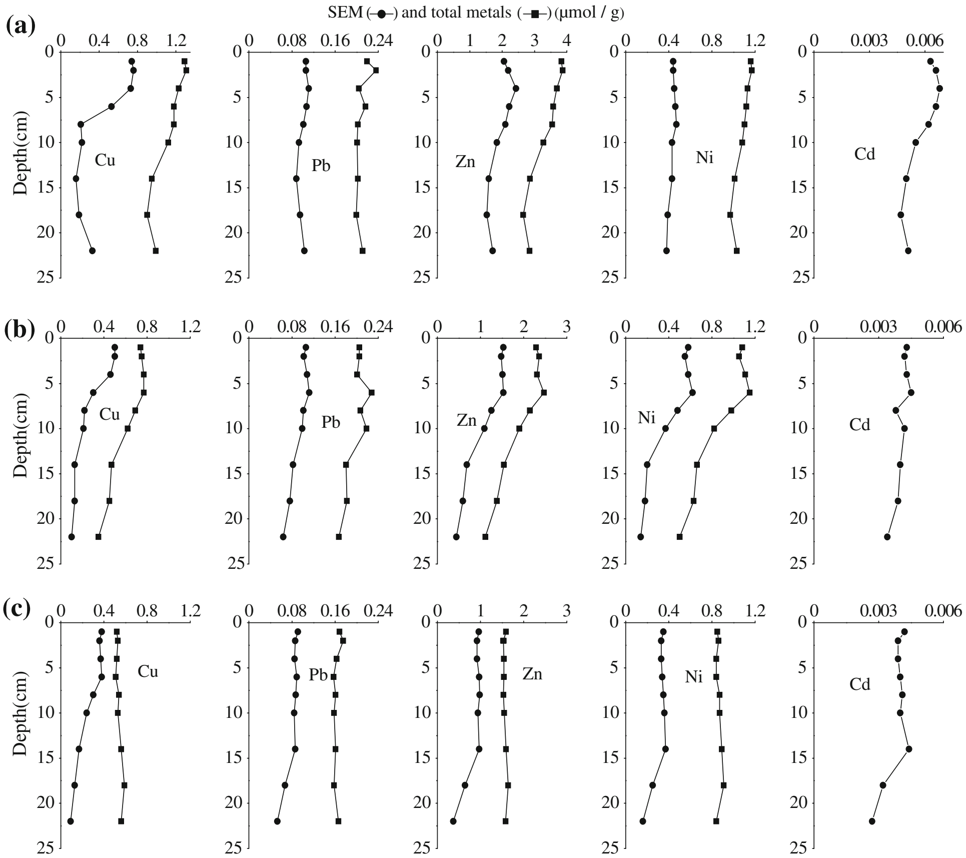

Table 3 Pearson correlation coefficients of SEM to total metal concentrations in the sediment cores

Sites	n	Cu	Pb	Zn	Ni
0	9	0.861**	0.495	0.901**	0.709**
1	9	0.835**	0.904**	0.990**	0.994**
15	9	−0.895**	0.000	−0.517	0.053

** $p < 0.01$

showed large variations along the sediment depth profile, indicating a changeable binding phase at greater depth. Copper and More (1998a) found that only 12% CuS and 23% NiS could be recovered by HCl. The decreasing percentage of $\mathrm{SEM_{Cu}}$ to total Cu indicated increasing association of Cu with sulfides in sediment profiles (Fig. 4). The extraction efficiency of Ni suggested that it had the same binding phase characteristic as Cu. The HCl-extractability for Pb and Zn was in the range of 23–67% and 32–57%, respectively, and their extractability decreased while the concentration of AVS increased in sediment profiles. Burton (2006) found that near-total recovery of Pb and generally >70% of total Zn were extracted by HCl in sulfidic sediments. The recovery of Pb and Zn by extraction with 1 M HCl indicated that AVS was not the major binding phases, and Pb and Zn might mainly be associated with Fe/Mn-oxide or organic matter.

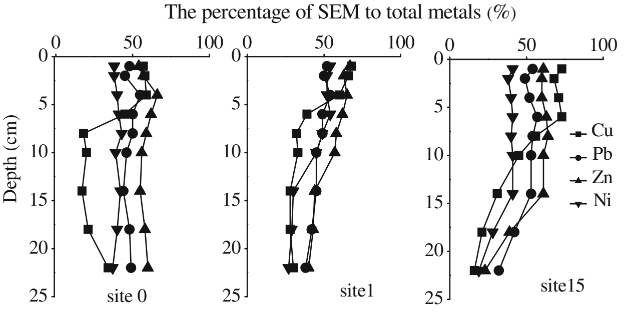

Fig. 4 The percentage of SEM to total metals in sediment profiles of sites 0, 1, and 15

Compared with the concentration of AVS, the $\sum$SEM contents were consistent along the sediment cores (Fig. 2). In all three sediment cores, $\sum$SEM contents were larger than AVS in surface sediments, and $\sum$SEM contents were smaller than AVS at greater depths in cores 1 and 15, while it was larger than AVS again in deeper sediments of core 0. The results indicated that metals are bioavailable to benthic biota, and AVS was not the major binding phase in surface sediments. With increasing sediment depth, metals were incorporated into the sulfide phase. But with limitation of SO_4^{2-}, metals could not be bound by AVS entirely in Core 0.

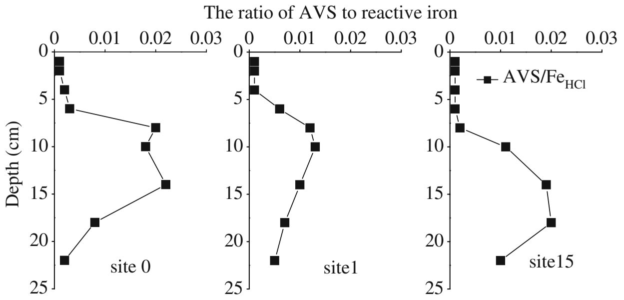

Fig. 5 The ratio of AVS to reactive iron in sediment profiles of sites 0, 1, and 15

For the temporal variation of AVS contents, AVS therefore exerts only a temporary control on the availability and mobility of trace metals. Cooper and Morse (1998b) found that when AVS was larger than 20% of 1 M HCl extracted Fe on a molar basis (%AVS/Fe > 20), there is enough sulfide to efficiently trap trace metals, and temporal variations in AVS do not necessarily result in temporal variations of metals bioavailability to biota. In the present study (Fig. 5), the ratio of AVS to 1 M HCl extracted Fe was less than 0.03 in the entire sediments, indicating that trace metals in studied sediments of Taihu Lake were dynamic.

This study found that the concentration of AVS and SEM decreased from the deposition area to the center of the bay (lake). The concentration of AVS increased with sediment depth, followed by a decrease with large variation, while the concentration of SEM remained constant. From the molar ratio of AVS and reactive iron, it is known that the heavy metals were dynamic and active in sediments of studied sites.

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