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Seasonal and Vertical Distributions of Acid Volatile Sulfide and Metal Bioavailability in a Shallow, Subtropical Lake in China

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Lake Donghu, a subtropical shallow lake near the Yangze River, was divided by artificial dikes into several parts in early 1960s, and the trophic levels diverged greatly during the past decades due to different sewage input. Lake Donghu suffers heavy metal pollution due to massive input of domestic sewage and industrial waste water. Based on total phosphorus (TP) and chlorophyll-a, Station I is defined as hypertrophic, Station II as eutrophic, and Station III as mesotrophic (Figure 1) (Shei, 1993). The main purposes of this paper are (1) to describe the seasonal and vertical variation of acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) (defined as the sum of Ag, Cd, Co, Cr, Cu, Ni, Pb and Zn) levels in the sediments of three stations with different trophic levels in Lake Donghu, and (2) to discuss the possible mechanisms underlining these patterns with emphasis on the possible effects of organic matter.

MATERIALS AND METHODS

Sediment cores were taken at three stations in Lake Donghu (Figure 1). Average water depths were 3.0 m at Station I, 3.3 m at Station II and 2.5 m at Station III. The cores were collected by a stainless steel tube (diameter 3.5 cm, length 50cm). The cores were tightly sealed in homemade tubes and were stored in the dark at a temperature of 4℃ until further analysis, which is usually carried out within three days after sampling. The sediment cores were sampled monthly from December 2000 to December 2001 at the three stations. To study the seasonal distribution of AVS and SEM, the monthly samples were subsampled at three depths below the sediment surface: 5-6cm, 15-16cm, and 30-31cm. To study the vertical distribution of AVS and SEM, the sediment cores (0-40cm) sampled in January and July were separated into 20 segments at an interval of 2 cm. The moisture content of the sediment samples was determined by measuring the weight loss after drying at 105 ℃ for 8 h. The sediment sample was naturally dried at room temperature and screened with a 20 mesh (0.84mm) sieve. Organic matter (OM) of the sediment samples was determined using potassium dichromate oxidation method (NAU,

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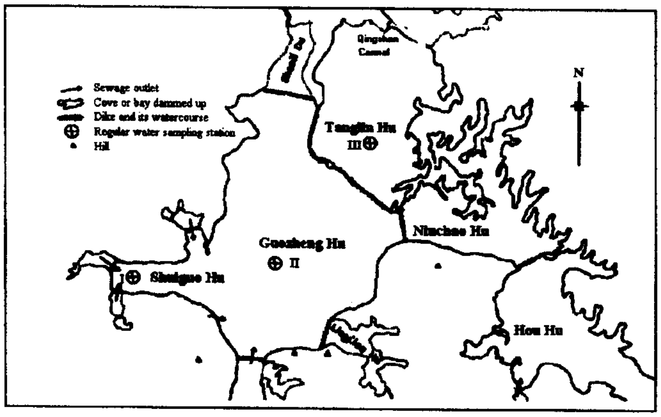

Figure 1. Map of Lake Donghu, showing the sampling sites.

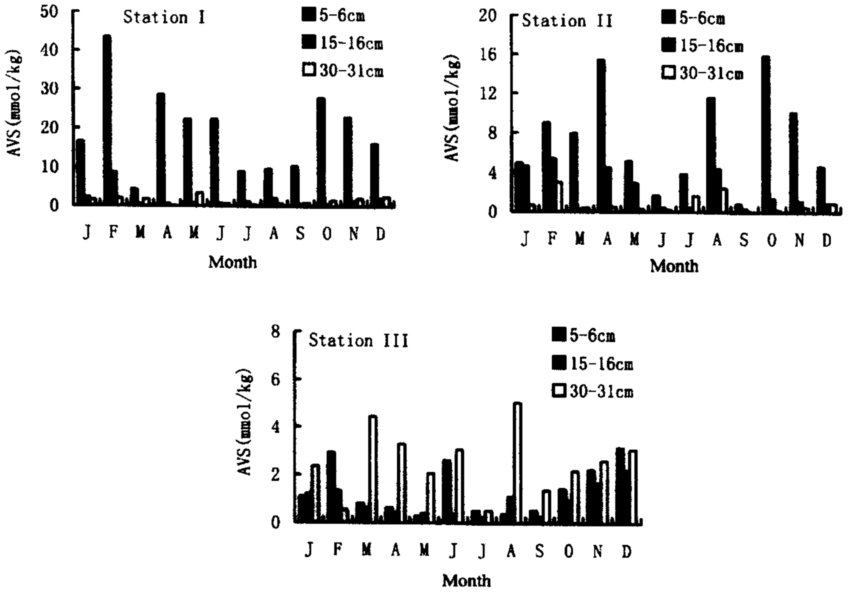

Figure 2. Seasonal variation of AVS concentrations in the sediments of the three stations in Lake Donghu in 2001.

1986). The analysis procedure of AVS and SEM in this research was modified from the cold-acid purge-and-trap technique described in detail by Di Toro et al (1990). A sodium sulfide standard was analyzed for quality assurance and calibration of the AVS apparatus. The concentrations of Cu, Pb, Cd, Ni, Co, Ag and Cr were analyzed on a graphite furnace atomic absorption spectrophotometer (Perkin Elmer-4100 ZL). The concentration of Zn were analyzed on flame AAS(WFX-1B). The recovery rate during the experimental procedure was checked

Table 1. Annual mean concentrations (mmol kg $^{-1}$ dry weight) (±standard deviation, SD) of AVS, acid extractable heavy metal, SEM and the SEM/AVS ratio in sediment cores of the three stations in Lake Donghu.

	AVS	Zn	Cr	Cu	Co	Ni	Pb	Ag	Cd	SEM	SEM/AVS
I_T	19.5(10.9)	2.43(1.03)	0.65(0.48)	0.46(0.21)	0.22(0.08)	0.14(0.11)	0.16(0.05)	0.005(0.004)	0.003(0.003)	4.06(1.42)	0.33(0.39)
I_M	1.7(2.3)	3.3(2.3)	0.43(0.26)	0.46(0.27)	0.28(0.13)	0.13(0.09)	0.12(0.05)	0.002(0.003)	0.002(0.002)	4.72(2.41)	5.07(3.84)
I_B	1.4(1.0)	3.00(2.77)	0.41(0.25)	0.26(0.17)	0.27(0.11)	0.12(0.10)	0.10(0.03)	0.002(0.003)	0.001(0.001)	4.18(2.81)	5.49(7.13)
II_T	7.6(5.0)	1.01(0.42)	0.59(0.76)	0.27(0.19)	0.25(0.1)	0.11(0.06)	0.11(0.05)	0.002(0.002)	0.002(0.001)	2.35(1.18)	0.56(0.58)
II_M	2.2(2.0)	1.05(0.69)	0.37(0.30)	0.27(0.17)	0.27(0.09)	0.11(0.05)	0.09(0.03)	0.001(0.001)	0.002(0.003)	2.17(0.98)	2.61(2.47)
II_B	0.9(1.0)	1.19(1.09)	0.42(0.48)	0.31(0.24)	0.3(0.11)	0.1(0.06)	0.11(0.04)	0.001(0.001)	0.001(0.001)	2.43(1.55)	6.39(6.50)
III_T	1.4(1.1)	1.93(2.11)	0.16(0.06)	0.51(0.54)	0.17(0.10)	0.11(0.07)	0.12(0.06)	0.002(0.002)	0.002(0.003)	3.01(2.18)	5.15(6.76)
III_M	0.9(0.6)	0.46(0.19)	0.23(0.08)	0.29(0.19)	0.18(0.09)	0.08(0.04)	0.08(0.03)	0.001(0.001)	0.002(0.002)	1.32(0.39)	2.49(1.89)
III_B	2.5(1.4)	0.46(0.23)	0.36(0.28)	0.28(0.14)	0.27(0.08)	0.11(0.07)	0.11(0.03)	0.002(0.004)	0.001(0.001)	1.59(0.60)	0.97(0.85)

I_T : The top (5-6 cm) sediment cores at Station I.
I_M : The middle (15-16 cm) sediment cores at Station I.
I_B : The bottom (30-31 cm) sediment cores at Station I.

Table 2. The vertical distribution of organic matter in the sediments of the three stations in Lake Donghu (mg/g).

Depth (cm)	0-2	2-4	4-6	6-8	8-10	10-12	12-14	14-16	16-18	18-20	20-22	22-24	24-26	26-28	28-30	30-32	32-34	34-36	36-38	38-40
Station I	65.0	65.6	38.3	44.1	29.4	24.0	22.3	22.7	21.4	19.0	19.7	17.5	17.1	21.2	17.5	13.8	17.5	20.8	19.4	20.1
Station II	41.3	45.8	19.9	19.4	17.4	17.4	19.2	19.9	19.4	17.9	18.5	18.5	18.8	24.0	22.9	25.1	28.2	22.9	27.3	26.8
Station III	29.9	30.1	31.3	27.9	29.0	21.0	18.5	18.1	16.1	15.4	16.1	15.9	16.1	17.0	20.3	15.6	16.5	16.5	19.9	19.4

by using a sodium solution with known concentration and appeared to be over 90%. For duplicate measurements, the relative standard deviations of the AVS-content and SEM-content were 9% and 4%, respectively. The detection limit of this method is approximately 0.5μmol g^{-1} (Di Toro et al. 1990).

RESULTS AND DISCUSSION

Seasonal variations of AVS levels in the sediments of the three stations are presented in Figure 2. AVS level in the top (5-6cm) layer was much higher than in the middle (15-16cm) and the bottom (30-31cm) layers at Stations I and II. AVS maxima in the top layer were over 40 mmol/kg ds. (Station I), 15 mmol/kg d.s. (Station II), but AVS concentrations in the middle and bottom layers were less than 5 mmol/kg d.s. The temporal variation of AVS was greater in the top sediments than in the middle and bottom sediments. In the top layer of Station I, a nearly constant AVS level of approximately 10 mmol/kg d.s. was observed from July to September, whereas AVS level increased from October to June. At Station II, seasonal AVS patterns were similar to those at Station I, but the AVS level was lower. However, at Station III, AVS level in the bottom layer (30-31cm) was higher than those in the top and the middle layers during most months. With little seasonal variation, AVS concentration (annual mean) in the bottom sediment was 2.5±1.4 mmol/kg d.s. Generally, AVS maximum is reached during summer due to summer oxygen depletion in the hypolimnion (Howard and Evans, 1993; Lawra et al., 2001). However, in the shallow Lake Donghu, AVS concentration was generally low in summer, perhaps due to different mechanisms. Thus, metals in the sediment of shallow lakes are expected to be potentially more toxic in summer than in the other seasons.

Heavy metal concentrations in the top, middle and bottom sediments at the three stations are shown in Table 1. The concentrations were in the order of Zn>Cr>Cu>Co>Ni≈Pb>>Ag≈Cd. Among heavy metals, Zn, Cr and Cu were the dominating species, accounting for nearly 90% of SEM. At Stations I and II, SEM levels in the top layer were nearly constant during the year, and the SEM level (annual mean) did not differ significantly among the top, middle and bottom layers. However, at Station III, SEM concentration (annual mean) was significantly higher in the top layer (3.01±2.18 mmol/kg d.s.) than in the middle (1.32±0.39 mmol/kg d.s.) and bottom layers (1.59±0.60 mmol/kg d.s.). Comparison of transects between the three stations revealed variation between and within stations, indicating positive relationships between both depth and AVS concentration, and OM and AVS concentration. The AVS profiles in cores of Stations I and II (Figure 3) showed a maximum concentration at about 5-cm depth, and then a drop-down to a low level. On the contrary, the AVS profile in cores of Station III showed AVS peak between 10 cm and 20 cm depths.

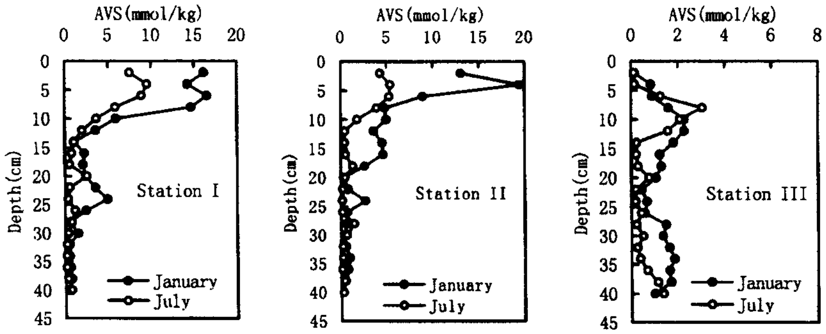

Figure 3. The vertical distribution of AVS in the sediments of Lake Donghu.

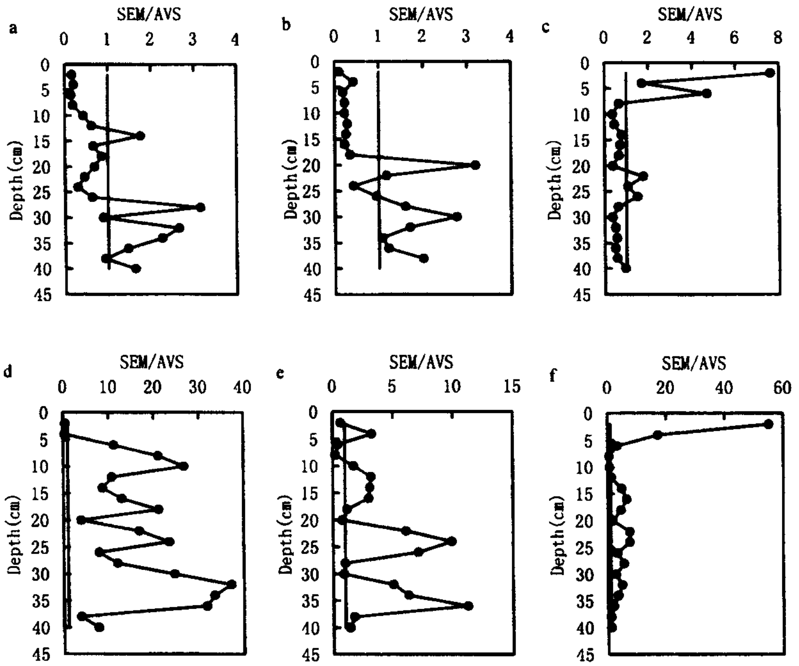

Figure 4. The vertical distribution of SEM/AVS ratios in the sediments of Lake Donghu (a-Station I, January; b-Station II, January; c-Station III, January; d-Station I, July; e-Station II, July; f-Station III, July).

The vertical distribution of organic matter in the sediments of the three stations is shown in Table 2. Significant linear relationships ($P<0.05$) were observed between organic matter and AVS at all the stations (Table 3). There was closer relationship between OM and AVS in the sediment with high concentration of OM than with low concentration of OM, and AVS/OM ratio (slope) was in the order of Stations I > II > III. This indicates that organic matter exerted great effects on the distribution of AVS in the sediment.

Table 3. Linear regression coefficients between AVS and OM for equation AVS = constant + slope×OM (Boldface words indicate significant linear relationship at the 95% confidence level, N=20.).

Stations	constant	slope	r	p
I	-0.084	0.006	**0.9091**	0.001
II	-0.048	0.004	**0.5218**	0.018
III	-0.017	0.002	**0.4579**	0.042

There have been many reports on the vertical variations of AVS concentrations in sediment, and generally concentrations are lower in the surface layer than in the bottom layer of the sediments, and AVS peaks between 10 – 20 cm sediment, probably resulting from the bioturbation of benthic organisms (Howard and Evans, 1993; Leonard et al., 1993; Van den Berg et al., 1998; Besser et al., 1996; Mackey and Mackay, 1996). In the present study, however, AVS in the sediments of the eutrophic Stations I and II was the highest in the surface layer (0 – 6 cm) and then decreased sharply with increased depth. This may be attributed to the high flux of organic matter to the sediments. Firstly, in aquatic systems, the production of AVS is mediated by sulfate-reducing bacteria (SRB), which reduce inorganic sulfate to sulfide (Oenema, et al., 1990). These organisms require a metabolizable carbon source. The sediments of Stations I and II were covered by sullage, and organic matter in the top layer of the sediments were as high as 65mg/g at Station I, 45mg/g at Station II. Thus, the higher concentration of AVS may due to the great difference of carbon (including sulfur) input between upper and lower sediments. Secondly, low redox condition (<-100mv) is necessary for SRB to have an optimal growth (Howard et al., 1993). Probably, with reduction of abundant organic matter, the surface sediment became anoxic, and oxidation of AVS by bioturbation or oxygen transfer from overlying water into surface sediment was relatively difficult. The sediments at Station I show more anoxic than other stations because of the sewage outlets to Shuiguohu subarea (Station I) (Yang et al., 1992). Thus, reduced inorganic sulfur products tend to be accumulated in the top layer of sediments with anoxic condition in hypertrophic lakes like Lake Donghu, while generally it is usually in deeper sediment (10 – 20 cm) in mesotrophic lakes. In a Taiwan river, Ell-Ren River, a similar vertical distribution of AVS was found under absolutely anoxic and highly heavy-metal contaminated environment in the sediments (Yu et al., 2001). Therefore, high organic matter flux in hypertrophic lake exerts significant influences on vertical AVS profile of sediments, shifting AVS peak from 10 – 20 cm depths into the surface sediment.

In freshwater systems with a high organic C input, the relatively low diffusive input of SO_4 from the water column to the sediments often narrows the depth interval over which SO_4 reduction takes place (Capone and Kiene, 1988). In our study, AVS concentration was maximized within a depth interval of about 4~6 cm in sediment with a sufficient organic carbon and relatively low concentration of SO_4 (about 4 mg/L). The close linear relationships between organic content and AVS confirmed the great effect of organic matter on the distribution of AVS in the sediment, which was more significant at the hypertrophic Station I.

Table 4. The correlation between SEM and AVS in the sediments in Lake Donghu (Boldface words indicate significant linear relationship at the 95% confidence level, N=40.).

	Zn	Cr	Cu	Ni	Co	Pb	Ag	Cd
AVS-I	-0.1061	**0. 7129**	0.2885	**0.5658**	-0.1775	0.2403	**0.6973**	**0.5885**
AVS-II	0.3111	**0.4114**	0.0319	**0.4330**	-0.2082	-0.2196	**0.7786**	**0.4201**

Significant linear relationships ($P<0.05$) were observed between trace metals (Cr, Ni, Ag, Cd) and AVS at Stations I and II (Table 4), indicating that these elements (Cr, Ni, Ag, Cd) were associated to the AVS phase in the sediments more than other metals. No significant correlation ($P<0.05$) was observed between trace metals and AVS at Station III, probably due to low AVS concentrations in the sediments. AVS is a reactive pool of solid-phase sulfide that is available to bind with metals and hence reduce bioavailability of metals. The relation between toxicity of heavy metals and the SEM/AVS ratio has been intensively studied for divalent metals (such as Cd, Cu, Ni, Pb, Zn) and also for a monovalent metal (silver). This does not imply that sulfide has no effect on the toxicity of other metals. In fact, AVS is able to reduce the toxicity of other metals and metalloids that form metal sulfides less soluble than iron and manganese monosulfides in sediments (Wang et al., 1999). But the toxic tests of these metals (such as Co and Cr) in the presence of AVS are absent. Recent studies (Mackey et al., 1996; Lawra et al., 2001) implicitly indicate that Cr can displace the iron in FeS and rapidly bind to AVS with strong affinity. However, Morse et al. (1999) indicate that sulfide do not easily react with Cr (III) that is dissolved or on solid oxide phases. Our results show that there was a closer relationship between SEM-Cr and AVS in the sediment with high AVS (Station I, r=0.7129) than in the sediment with low AVS (Station II, r=0.4114) while SEM-Cr level did not differ significantly in both stations. Because Cr is strongly influenced by complex redox reaction pathways rather than simple substitution reactions (Morse et al., 1999), it seems likely that Cr tends to adsorb on, or coprecipitate with iron sulfide phases in an anoxic environment more than a slight anoxic environment. Ag and Cd can form very strong insoluble metal sulfides, and shows significant relation with AVS in our study. It seems that bioavailability of Ag and Cd is controlled by AVS more strongly than other metals. The lack of correlation between AVS and Cu and Co in our study might be due to the presence of discrete metal sulfide phases (e.g., CuS, CoS) in the zone of AVS precipitation, which does not dissolve in 1M HCl completely (Cooper and Morse, 1998).

Vertical changes in the SEM/AVS ratio in the sediments of the three stations are shown in Figure 4. The depth where the SEM/AVS ratios were less than one varied spatially and temporally. Generally, this ratio was much greater in July than in January at all the stations, indicating that metals in the sediments are more potentially toxic in the summer than in the winter. SEM/AVS ratio also changed in different depths at the same station. At Stations I and II, SEM/AVS ratio was much greater in the bottom sediment than in the top sediment, while the reverse was found at Station III. This suggests that sulfides in the top sediments of Station I and II were sufficient to bind the metals.

Our study showed that there were two different patterns of AVS distribution in sediments, probably due to different organic content in the sediments. High organic matter flux shifted AVS peak into the surface sediment at the more eutrophic Stations I and II. Cr, Cd and Ag are likely controlled by AVS more strongly than other metals in anoxic sediments.

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