

The impact of sulfate reduction on the distribution of methylmercury in reservoirs in the city of Guiyang

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Abstract In this paper, the relationship between sulfate reduction potential and mercury methylation potential was studied in the Aha, Baihua and Hongfeng reservoirs from Guiyang City. The methylmercury (MeHg) concentrations of lake water in the Aha Reservoir were greatly elevated as compared to those of the Hongfeng and Baihua reservoirs, which was correlated with its distinctly high SRB abundance, SO_4^{2-} , and S^{2-} concentrations. Among the three reservoirs, however, the highest MeHg was observed in the top several centimeters of pore water profile in the Hongfeng Reservoir where the lowest S^{2-} in pore water occurred. The distributions of MeHg in lake water and pore water showed the highest methylation potential occurred at water-sediment surface for the Aha Reservoir and the in the top several centimeters of sediments for the Hongfeng Reservoir. It is guessed that the highest mercury methylation only occurs at the sites with certain sulfide concentrations.

Key words sulfate reduction; methylmercury; sulfate-reducing bacterium; pore water; Hongfeng, Aha and Baihua reservoirs

1 Introduction

Previous researches reported elevated methylmercury (MeHg) concentrations in fish even in lakes located far from point pollution sources in Canada and the USA (Verta, 1990; Lindqvist et al., 1991). MeHg levels in fish and invertebrates in some lakes or marine systems were found to exceed state, federal, or international health guidelines (Chase et al., 2001). As a result, mercury contamination of aquatic systems should be a worldwide health concern (Clarkson, 1990; Fitzgerald and Clarkson, 1991).

There is considerable evidence from laboratorial experiments that methylation is carried out by sulfate-reducing bacteria (SRB) (e.g. Gilmour and Henry, 1991; Benoit et al., 1999), while relatively little attention has been paid to field investigation. Hines et al. (2004) observed that the distinct peaks of MeHg roughly were correlated with maxima in sulfate reducing activity at 5- and 15- cm depths in a bog lake.

Macalady et al. (2000), however, found that there was no significant relationship between sulfate reduction and mercury methylation in the Clear Lake. The positive correlation between SRB biomass and mercury methylation is interesting in light of previous works at the same sampling locations, which showed that sulfate reduction and mercury methylation potential are highly correlated at one of sampling sites, but weakly correlated at the other sites (Mack, 1998). In this paper, correlations between sulfate reduction potential and mercury methylation potential were studied in three important, yet polluted drinking water sources of Guiyang, Aha, Baihua and Hongfeng reservoirs.

The Aha Reservoir has been contaminated by small-sized or artisanal coal mining activities for many years. About 220 small coal mines were under operation in the catchments of the reservoir during the 1980s, and constantly discharged acid pollutants, SO_4^{2-} , Fe, and Mn into it (Bai, 2006). Since 1995, two water treatment plants have been built to purify the

inlet water of the Aha Reservoir by using lime neutralization and aeration oxidation. Even though measures were taken to clean the inlet water, the SO_4^{2-} contents in water of the reservoir still reach 303 mg/L (Luo, 2003). Most of the coal mines were not closed till 2011.

The Hongfeng Reservoir was constructed in 1960 with a surface area of 57.2 km² and a volume of $6.01 \times 10^8 \text{ m}^3$. It is located in an area with serious acid rain due to coal combustion emissions (Zhou Tao et al., 1997), and has the main bedrocks of the watershed of limestone and dolomite (Zhang Wei, 1999). There are nearly two dozen factories in its drainage area, and a large volume of improperly treated waste water has been discharged into the reservoir, which turned the reservoir into a polluted and eutrophic water body. As a result, the reservoir exhibits alkaline conditions with seasonally anoxic and eutrophic features.

The Baihua Reservoir (BHR) is a long and narrow reservoir with a surface area of 14.5 km² and an average water depth of 13 m. It has a typical karstic topography with the dominant bedrock types of limestone and dolomite (Zhang Wei, 1999). The Guizhou Organic Chemical Plant is located about 18 km upstream of BHR and used mercury as a catalyst for the production of acetic acid from 1970 to 1997 (Yan Haiyu et al., 2005).

2 Methodology

Lake water, pore water, and sediment samples from the Aha, Baihua, Hongfeng reservoirs were collected in June 2012 using metal clean protocols (Fig. 1). The sampling sites were situated in Daba of Hongfeng Reservoir (HFDB), Matou of Baihua Reservoir (BHMT), Daba of Aha Reservoir (AHDB) and Changtang of Aha Reservoir (AHCT) (Fig. 1). Water samples were taken from different depths (0, 4, 8, 12, 16, 20, and 24 m). The filtered samples were collected by way of filtering with a 0.45 μm filter (Millipore) *in-situ*. All water samples were acidified using 0.5% HCl solution, stored at 3–4°C in the absence of light until analysis. The sediment cores were taken and sliced into 1 to 3 cm subsamples onsite. Pore water was extracted from the wet sediment within 48 hours by centrifugation at $3000 \text{ r} \cdot \text{min}^{-1}$ for 30 minutes *in-situ* at the bottom-water temperature (5°C), and then filtered through a 0.45 μm PVDF membrane (Millipore). The whole process was done in a nitrogen bag with gloves.

The total methylmercury (TMeHg) and dissolved methylmercury (DMeHg) in lake water and pore water were measured by distillation, followed by aqueous phase ethylation, precollection on a Tenax trap, isothermal gas chromatography and cold vapor atomic fluorescence detection (US EPA, 2001).

Sulfate reducing bacteria were enumerated by the Most Probable Number (MPN) method. Serial dilutions ranged from 10^{-3} to 10^{-8} with 3 replicates. The media enclosed in the bottles were supplied by Beijing Xinhua Company. 1 mL of water sample was directly injected into the bottles with the media. 10 g of sediment sample was dissolved into 100 mL oxygen-free and sterilized water bottle with Headspace Crimp Caps and Septa. Then, 1 mL of solution was injected into the media.

Sulfides in lake water and pore water were measured by the Methylene Blue method, and their contents were determined by Ion Chromatography. At the same time, suspended particles and water quality parameters such as pH, temperature, dissolved oxygen, and TDS were measured. Quality assurance and control of the process of analysis were carried by using duplicates, method blanks, and matrix spikes.

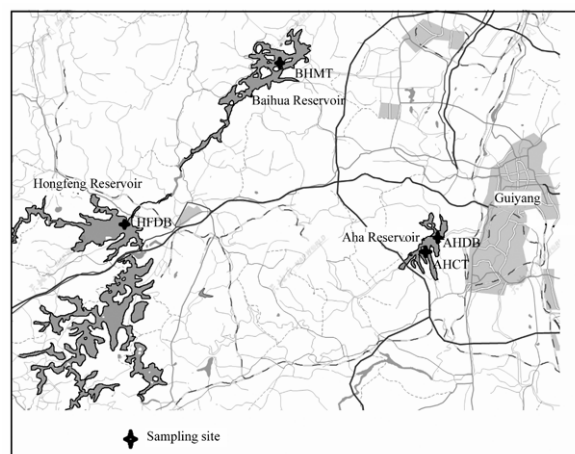


Fig. 1. Locations of sampling sites (AHDB, AHCT, BHMT and HFDB).

3 Results and discussion

3.1 Sulfate-reducing bacteria in lake water and sediments

Population density of sulfate-reducing bacteria in lake water and sediments is listed in Table 1. The samples were collected in consecutive days, starting with samples from the Aha Reservoir. At the beginning, the samples were diluted to 10^{-3} for AHDB and 10^{-4} for AHCT as the lake water has low SBR abundance. Unexpectedly, all bottles were filled with SRB in the next day. Then, the remaining samples were diluted to 10^{-6} . The SRB abundance of the Aha Reservoir cannot be obtained accurately, but it could be deduced that its value was higher than 9.5×10^3 for AHDB and 9.5×10^4 for AHCT according to the computational formula of the MPN method. Two values in the Aha Reservoir were distinctly higher than the val-

ues of lake water of the Baihua and Hongfeng reservoirs. There was no discernable difference in SRB distribution in sediments among the 3 reservoirs, and SRB contents in sediments of Aha were a little higher than those in the other reservoirs.

3.2 Sulfide and sulfate in lake water and pore water

The spatial distributions of SO_4^{2-} and S^{2-} in the three reservoirs are shown in Figs. 2 and 3. SO_4^{2-} in

lake water of the Aha Reservoir is distinctly higher than that in the Baihua and Hongfeng reservoirs, while SO_4^{2-} in pore water of Aha is just a little higher than that in the other reservoirs. SO_4^{2-} in pore water of the Hongfeng Reservoir is on average, but S^{2-} in pore water is lowest. On the contrary, SO_4^{2-} in pore water of the Baihua Reservoir is low, but S^{2-} in pore water is as high as that in the Aha Reservoir. This spatial variation suggested sulfate-reducing activity in the sediments at the HFDB sampling site is weaker than that at other sampling sites.

Table 1 Population densities of SDR in lake water and sediments

	AHDB0		AHCT0		BHMT0	10	HFDB0	10
Lake water (cell/mL)	AHDB8	>	AHCT8	>	BHMT8	10	HFDB8	4.5×10^3
	AHDB12	9.5×10^3	AHCT12	9.5×10^4	BHMT12	45	HFDB16	4.5×10^3
	interface		interface		interface	2.5×10^4	interface	9.5×10^3
Sediment (cell/g)	AHDB1	9.5×10^4	AHCT1	4.5×10^5	BHMT1	9.5×10^4	HFDB1	9.5×10^4
	AHDB3	9.5×10^4	AHCT3	2.5×10^5	BHMT3	4.5×10^4	HFDB3	2.5×10^4
	AHDB5	4.5×10^4	AHCT5	9.5×10^4	BHMT5	-	HFDB5	9.5×10^4
	AHDB7	4.5×10^4	AHCT7	9.5×10^4	BHMT7	4.5×10^4	HFDB7	9.5×10^4
	AHDB9	9.5×10^4	AHCT9	9.5×10^4	BHMT9	9.5×10^4	HFDB9	2.5×10^4

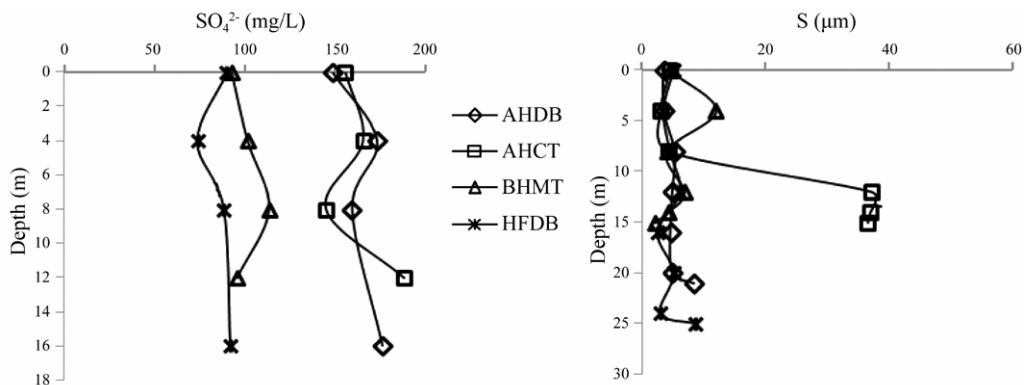


Fig. 2. Distributions of SO_4^{2-} and S^{2-} in lake water of the Aha, Baihua and Hongfeng reservoirs.

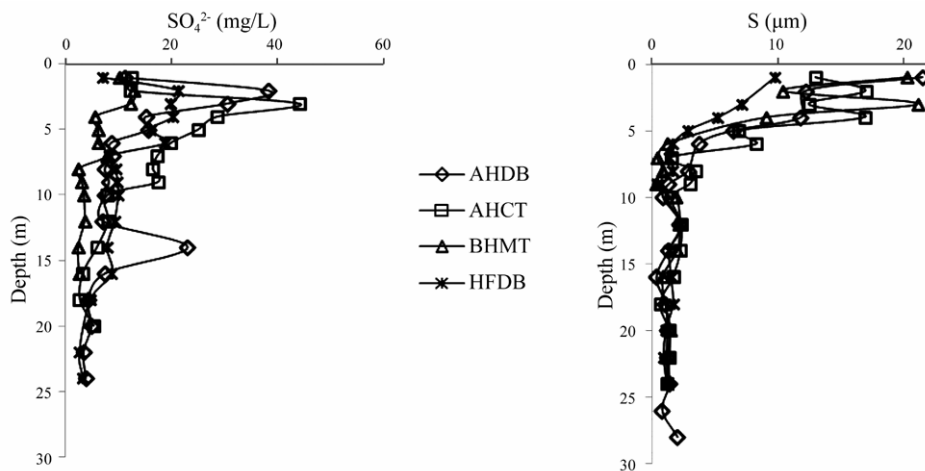


Fig. 3. Distributions of SO_4^{2-} and S^{2-} in pore water of the Aha, Baihua and Hongfeng reservoirs.

3.3 Methylmercury in lake water and pore water

The distributions of MeHg in the water column are shown in Fig. 4. TMeHg concentrations range from 0.10 to 0.58 ng/L with an average concentration of 0.22 ng/L in the Baihua Reservoir and from 0.04 to 0.47 ng/L with an average concentration of 0.17 ng/L in the Hongfeng Reservoir. Both TMeHg and DMeHg concentrations increase slightly with depth of the water column at the sampling sites of the Hongfeng and Baihua reservoirs.

MeHg concentrations in lake water at the sampling sites of the Aha Reservoir are distinctly elevated compared to those in the other reservoirs. The highest value of 3.09 ng/L is observed at AHDB and is 6.5 times higher than the highest value at the HFDB sampling site. There is a distinct vertical distribution pattern of MeHg in the water column at the two sampling sites of the Aha Reservoir. TMeHg increases from 0.05 ng/L on the surface to 3.09 ng/L in the water-sediment interface at the AHDB sampling site, while TMeHg increases from 0.22 ng/L at the surface to 1.51 ng/L in the water-sediment interface at AHCT.

Shown in Fig. 5 are the profiles of MeHg in pore water at the four sampling sites. MeHg concentrations are generally low, and vary from 0.06 to 0.92 ng/L at AHDB and AHCT. The highest values of both pore water profiles are lower than the values at the water-sediment surface of water columns at the two sampling sites. This result shows that the highest methylation potential in the Aha Reservoir occurred at the water-sediment interface of water column. MeHg concentrations in pore water range from 0.08 to 2.97 ng/L at the HFDB sampling site of the Hongfeng Reservoir. Higher values are observed in the upper 6 cm of the profile, and the highest value of 2.97 ng/L is 7 times the highest value in the water column. This shows that the highest methylation potential in the Hong Reservoir occurred in the top several centimeters of sediment core. The peaks of MeHg in Baihua not only appear in the top several centimeters, but also at 14 cm. This is probably because the Baihua Reservoir is seriously contaminated by mercury from Guizhou Organic Chemical Plant.

Variations in MeHg concentrations in the Aha and Hongfeng reservoirs are probably related to different pollutants in the two reservoirs. The Aha Reservoir has been contaminated by AMD for many years. The distribution of sulfide, sulfate ions and SRB in the reservoirs suggests that SRB and sulfate reduction potential are higher in the Aha Reservoir. It is generally believed that Hg methylation is predominantly a microbially mediated process. And some studies have shown that methylation is carried out by sulfate-reducing bacteria in the water column (Watras et al.,

2005; Eckley et al., 2005). In lake water, MeHg contents are distinctly high in the Aha Reservoir, corresponding to the highly elevated abundance of SRB in the Aha Reservoir. MeHg contents in pore water, however, show no same distribution trend; On the contrary, distinctly high MeHg contents are observed at the HFDB site. Berman and Bartha (1986) observed that MeHg levels in sediments were initially in direct proportion to sulfide concentrations, but declined sharply beyond the contents of some sulfides. From Fig. 3, the contents of sulfides in the top several centimeters in the Aha reservoir are much higher than those in the Hongfeng Reservoir, which may decrease Hg^{2+} , thus inhibiting MeHg formation in sediments. MeHg contents are usually highest in the oxic/anoxic boundary layer in sediments or hypolimnetic waters of seasonally stratified lakes and reservoirs (Watras et al., 1995). Watras et al. (1995) proposed that zones of Hg methylation and SO_4^{2-} reduction followed the oxic/anoxic boundary in both the water column and sediments. In present study, all the four sampling sites lie in the seasonally stratified reservoirs, and oxic/anoxic layer should be in hypolimnetic waters in summer. However, the highest mercury methylation potential occurred in different layers in the two reservoirs. It is proposed that the highest mercury methylation potential probably controlled sulfate reducing process. The highest mercury methylation just occurs at the site where sulfides reach a certain concentration. Sulfide contents are too high, which will reduce Hg^{2+} . Sulfide contents are too low, which shows that sulfate reducing activity is weak. Mercury methylation potential will decrease in the two situations. It is necessary to study this process in more detail in the future.

4 Conclusions

In this paper, the relationship between sulfate reduction potential and mercury methylation potential were studied in the Aha, Baihua and Hongfeng reservoirs located in the suburbs of Guiyang City. The SRB abundance, SO_4^{2-} , and S^{2-} in the Aha Reservoir are much higher than the values in the Baihua and Hongfeng reservoirs while there are no discernable differences in distributions of SRB contents, SO_4^{2-} and S^{2-} in sediment and pore water except for much lower S^{2-} in pore water of the Hongfeng Reservoir. MeHg concentrations at the sampling sites of the Aha Reservoir are distinctly elevated compared to the other 2 sampling sites while much higher MeHg were observed in pore water in the Hongfeng Reservoir. The distributions of MeHg in lake water and pore water showed that the highest methylation potential occurred at the water-sediment surface of the Aha Reservoir and in the top several centimeters of sediment of the

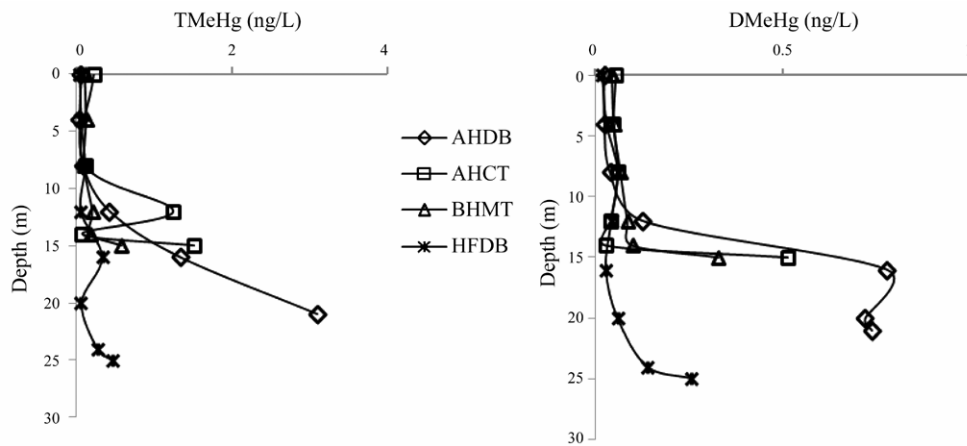


Fig. 4. Distributions of methylmercury in lake water of the Aha, Baihua and Hongfeng reservoirs.

Hongfeng Reservoir. The highest mercury methylation potential probably controls sulfate reducing process. The highest mercury methylation just occurs at the site where sulfides reach a certain concentration. Sulfide contents are too high, which will reduce Hg^{2+} . Sulfide contents are too low, which shows that sulfate reducing activity is weak. Mercury methylation potential will decrease in the above two situations. It is necessary to study this process in more detail in the future.

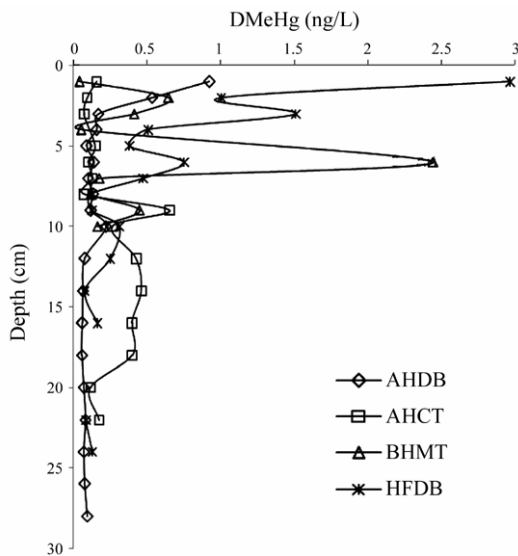


Fig. 5. Distributions of methylmercury in pore water of the Aha, Baihua and Hongfeng reservoirs.

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