The impact of eutrophication on the biogeochemical cycling of mercury species in a reservoir: A case study from Hongfeng Reservoir, Guizhou, China

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Eutrophication may affect the biogeochemical cycling of mercury in reservoir.

Abstract

The mercury distribution and speciation in the water column were investigated from November 2003 to September 2004. The distribution and concentrations of total mercury (THg) and particulate mercury (PHg) showed that algae had a large capacity to bind mercury in late spring (e.g. in May). It is shown that dissolved gaseous mercury (DGM) concentrations may also be affected by algae activities. The MeHg profile in the water column at a highly eutrophied site in Hongfeng Reservoir demonstrated that most of the MeHg was produced in the hypolimnion, whereas the MeHg profile pattern at another site with less eutrophication indicated that MeHg in water was largely ascribed to release from sediment. In September, the outflow of the reservoir was enriched with MeHg, which was 5.5 times higher than that in the inflows. The discharge of MeHg-concentrated water from the anoxic hypolimnion in the reservoir may pose a risk to downstream fauna.
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1. Introduction

Mercury accumulation in aquatic food chains is a global public health concern, because it is the predominant pathway of human exposure to methylmercury, which is one of the most toxic forms of mercury (e.g. Tchounwou et al., 2003). Understanding the cycling of mercury in the aquatic environment and its controlling factors is essential to comprehend the mechanism of mercury enrichment in aquatic food chains. Sources, trends, contents and distributions of Hg in water

are affected by local physiographic, geochemical, and water quality characteristics such as pH, redox conditions, dissolved organic carbon, etc. Eutrophication in aquatic systems, which can induce algal blooms, is also a public concern (e.g. Carpenter et al., 1998; Smith et al., 1999). Eutrophication can alter the water quality and the biogeochemical cycles of many elements, but until now the impact of eutrophication on the biogeochemical cycle of mercury species in aquatic systems is still unknown.

Eutrophication may play an important role in mercury transport and immobilization (e.g. Coelho et al., 2005). Eutrophication can produce a mass of macroalgae, which may represent a substantial reservoir of mercury in the aquatic

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system, as a result of its high growth rate and large capacity to bind trace metals (e.g. Radway et al., 2001). When macroalgae move with the water current and/or settle to sediment, the distribution of mercury can change in aquatic systems. More importantly, eutrophication can affect the chemical forms and bioavailability of mercury in water. Algal blooms alter re-dox potential and pH, and affect the concentrations of Fe and Mn compounds, and sulfur and carbon (e.g. Eggleton and Thomas, 2004). These changes strongly affect the chemical forms of mercury, which can determine the bioavailability of mercury in water. Fish in eutrophic lakes, however, were often found to contain less mercury than those in oligotrophic lakes. This phenomenon has been explained by the increasing algal biomass in eutrophic systems reducing mercury accumulation at higher trophic levels through the dilution of mercury in con-sumed algal cells (e.g. Pickhardt et al., 2002). Nevertheless, the impact of eutrophication on the methylation rate of mer-cury is also an issue deserving further study. The increased mi-crobial activities, the increased anaerobiosis, and the increased concentrations of fulvic acid resulting from eutrophication are likely to increase the methylation rate of mercury in the water column.

Hongfeng Reservoir, which was established in 1960 with a surface area of 57.2 km^2 and a volume of 6.01×10^8 m^3, is located near Qingzhen City, a suburb of Guiyang City, Guiz-hou Province, Southwestern China (Fig. 1). It was constructed for the purpose of hydroelectric power generation, flood con-trol, tourism, drinking-water supply, and fishery production. There are nearly two dozen factories in the drainage area of Hongfeng Reservoir, and a large volume of improperly treated wastewater has been discharged to the reservoir, which turned the reservoir into a polluted and eutrophic water body (Zhang, 1999). Episodes of high wastewater loading caused a series of serious environmental accidents in Hongfeng Reservoir (Zhang, 1999). Approximately 230,000 kg fish died in a few days because of contamination in 1994 (Zhang, 1999). The reservoir water turned black from organic matter and the bloom of a large quantity of aquatic organisms in 1995 (Zhang, 1999). About 500 people who drank water from the reservoir were diagnosed with arsenic poisoning in 1996 (Zhang, 1999). Large masses of algae (algal blooms) appeared in the reservoir in 1996 and 1997 (Zhang, 1999), and again in May 2004 in Houwu basin of the reservoir (Lu, 2004), one of our sampling sites. A large number of studies have been car-ried out to investigate the biogeochemical cycling of nutrients and eutrophication processes in the reservoir (e.g. Xiao and Liu, 2004; Liang et al., 2004).

The status of mercury contamination in the aquatic systems of Hongfeng Reservoir is still unknown. Besides the above-mentioned anthropogenic sources that discharge mercury to Hongfeng Reservoir, a large coal fired power plant (300 MW) situated on the southeast bank of the reservoir is also an important contamination source of mercury to the res-ervoir. In addition, a chemical plant is located in the vicinity of the city of Qingzhen. As mercury was used as a catalyst for the production of acetic acid in this plant until 1986, over 140 t of Hg was released into the environment from this factory and

a considerable amount of mercury was discharged into Baihua Reservoir which is connected to Hongfeng Reservoir through a channel (Horvat et al., 2003). Although this chemical plant is located at the downstream area of Hongfeng Reservoir, a con-siderable amount of mercury was also emitted into the atmo-sphere from this plant and may have deposited to the reservoir surface. Some of this atmospheric mercury may also have deposited to the rice fields around the reservoir, con-verted to MeHg, and entered into Hongfeng Reservoir with surface runoff. It is imperative to understand the biogeochem-ical cycling of mercury in Hongfeng Reservoir to better eval-uate mercury contamination to the food web in the reservoir.

Hongfeng Reservoir is located in an area with a serious acid rain problem due to coal combustion emissions (e.g. Zhou et al., 1997). The main bedrock types of the watershed are limestone and dolomite (Zhang, 1999). As a result, Hongfeng Reservoir is an alkaline reservoir which is also seasonally anoxic and eutrophic. The special characteristics of Hongfeng Reservoir provide us a good opportunity to understand the effects of eutrophication on the behavior of mercury in aquatic systems, and to understand the effect of acid precipitation on mercury cycling and enrichment in food chains in alkaline res-ervoirs. In this paper, we report the temporal and spatial distri-butions of different mercury species in the water column of the reservoir to better understand the effect of eutrophication on the distribution of mercury in the reservoir.

2. Methodology

2.1. Sampling sites

Two sampling sites in the reservoir, six sampling sites in the inflows and one sampling site in the outflow were chosen as shown in Fig. 1. The Houwu sampling site was situated in the south basin of the reservoir where the coal fired power plant was located on the southeast bank of the reservoir. A large fish farm was located in this area because of the higher water temperature caused by the discharge of hot water from the power plant. The Daba sampling site, which was close to the dam, was located in the north basin of the reser-voir, which received discharge from the chemical fertilizer plant. As the Daba sampling site is near the dam of the reservoir, the water level at Daba fluctu-ated markedly. Water depth was up to 32 m after water storage of the reservoir in autumn and winter, but decreased to 17 m after water discharge from the reservoir in spring and summer. Yangchang, Maxian, and Taohua rivers are the main water sources to Hongfeng Reservoir (Zhang, 1999). Due to contam-inations from wastewater, the Yangchang and Maibao rivers and the Fertilizer Plant Drain were more seriously contaminated than the Maxian, Taohua, and Houliu rivers (Zhang, 1999). The Maotiao River is the only outflow of the reservoir. The water discharged from Hongfeng Reservoir originates mainly from the deep water of the reservoir.

2.2. Sample collection and analysis

Unfiltered and filtered water samples from Hongfeng Reservoir were col-lected using trace metal clean protocols. Four sampling campaigns were con-ducted in November 2003, and February, May and September 2004, representing autumn, winter, spring and summer seasons, respectively, accord-ing to the local climate conditions. Water samples in the reservoir were taken from different depths throughout the entire water columns (0, 4, 8, 12, 16, 20, 24, 28, and 30 m), while only surface water was sampled in the inflows and outflow of the reservoir. The filtered samples were collected by filtering with a 0.45-μm filter (Millipore) on site. All water samples were filled in borosilicate glass bottles, then acidified with 0.5% HCl, double-bagged and
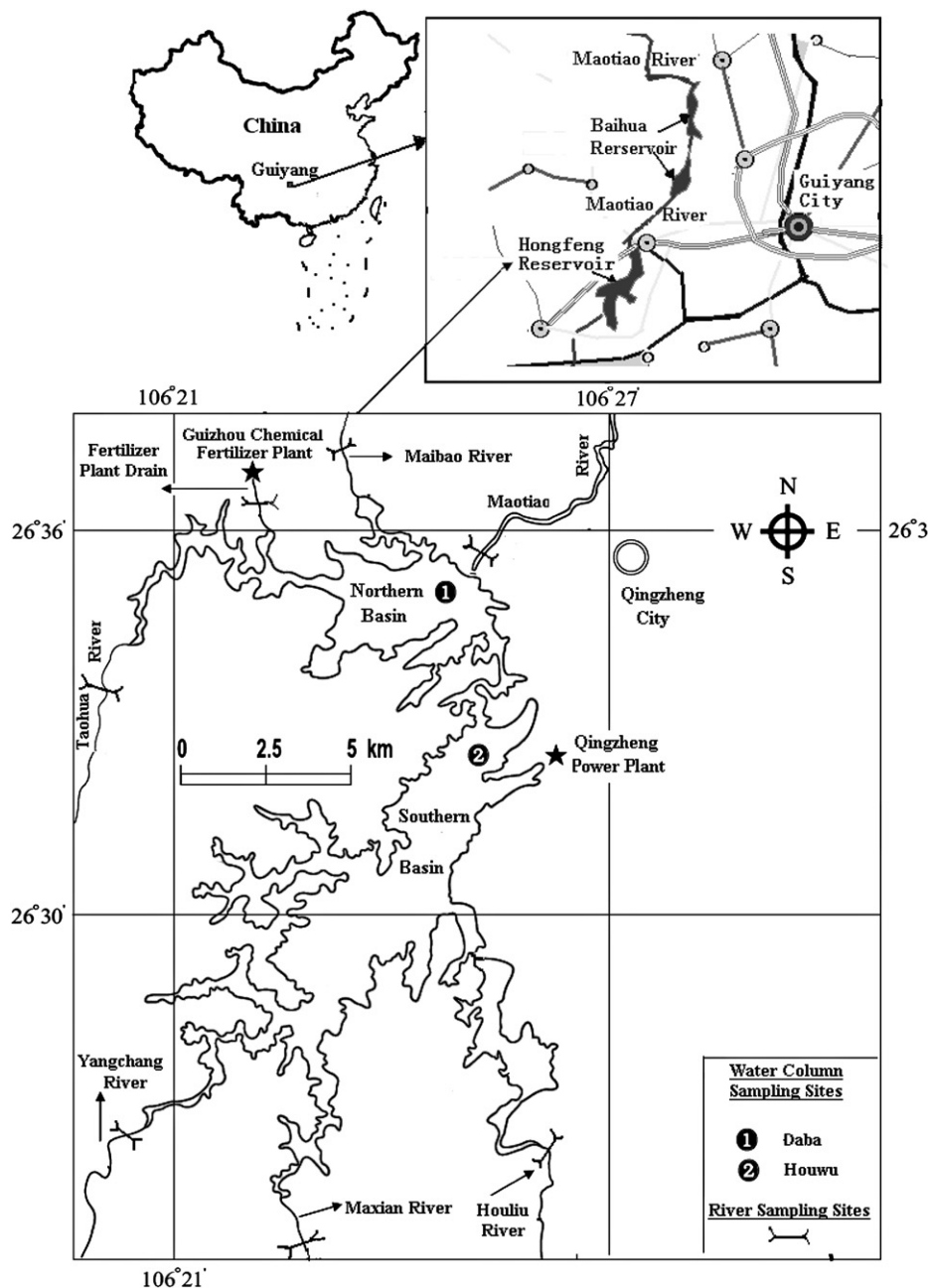
Fig. 1. Hongfeng Reservoir, China, showing location of sampling sites.

transported to the laboratory within 24 h, and then stored at 3–4 °C in the dark until analysis. All borosilicate glass bottles for collecting samples and analysis were cleaned by acid leaching, rinsing with ultrapure deionized water (18 MΩ cm) and heating for several hours in a muffle furnace at 500 °C.

Total Hg (THg), reactive Hg (RHg), dissolved Hg (DHg), dissolved gaseous mercury (DGM), total methylmercury (TMeHg), and dissolved methylmercury (DMeHg) were analyzed for each sample. The analytical methods used for Hg speciation in water have been described in detail elsewhere (Bloom and Fitzgerald, 1988; Bloom, 1989; Horvat et al., 1993; US EPA, 2001, 2002; Yan et al., 2003). All methods relied on cold vapor atomic fluorescence detection.

For THg and DHg, water samples were oxidized with 0.5% BrCl. After oxidation, $NH_2OH \cdot HCl$ was added to destroy the free halogens before adding stannous chloride ($SnCl_2$) to convert Hg(II) to volatile Hg(0). The resulting sample was then purged with Hg-free N_2 and Hg(0) was absorbed onto a gold trap (Bloom and Fitzgerald, 1988; Yan et al., 2003).

RHg was determined by addition of 20% $SnCl_2$ to unfiltered and acidified samples, followed by the purge/trap CVAFS method. The RHg determined would include mostly ionic (Hg^{2+}) plus DGM, labile organic fractions and Hg that was leachable from the particulate matter in the sample (Dalziel, 1995).

Dissolved gaseous mercury is composed primarily of Hg(0), so it was assumed that DGM was essentially Hg(0) in this study. Approximately 500 mL of a fresh water sample was purged with mercury-free nitrogen gas for 30 min and elemental mercury in the sample was trapped on a gold trap on site. The gold traps were taken to the laboratory for DGM determination within 12 h (Yan et al., 2003).

TMeHg and DMeHg concentrations in water were determined using the standard distillation−ethylation−GC separation−CVAFS technique (Bloom, 1989; US EPA, 2001). A 45-mL aliquot of acidified sample was placed in a fluoropolymer distillation vessel and the distillation was carried out at 125 °C under Hg-free N_2 flow until approximately 35 mL of water was collected in

the receiving vessel. The sample collected was adjusted to pH 4.9 with an acetate buffer and the Hg in the sample was ethylated in a closed 200-mL bubbler by the addition of sodium tetraethyl borate. The ethyl analog of CH_3Hg, $CH_3CH_3CH_2Hg$, was separated from solution by purging with N_2 onto a Tenax trap. The trapped $CH_3CH_3CH_2Hg$ was then thermally desorbed, separated from other mercury species by an isothermal GC column, decomposed to Hg(0) in a pyrolytic decomposition column (700 °C) and analyzed by CVAFS. All PTFE vials for distillation were cleaned by heating for 48 h in concentrated nitric acid (Horvat et al., 1993).

Dissolved organic carbon (DOC), total suspended particles (TSP), and water quality parameters such as pH, temperature (*T*), dissolved oxygen (DO), and total dissolved solid (TDS) were also measured. DOC was measured by the high-temperature combustion method (Cosovic et al., 2000). Water quality parameters such as *T*, DO, pH, and TDS were measured by a portable analyzer (Radiometer Analytical) on site. Chlorophyll and total dissolved phosphorous (TDP) concentrations in water samples were analyzed in February, April, June and August 2004. Chlorophyll was measured by spectrophotometric analysis of acetone-extracted filters (Jing and Tu, 1990). TDP was measured by potassium phosphate digestion followed by ammonium molybdate spectrophotometric analysis (China EPA, 2002).

Quality assurance and quality control of the analytical process were carried out using duplicates, method blanks, field blanks, and matrix spikes. Field blanks and duplicates were taken regularly (>10% of samples) throughout each sampling campaign. Detection limits were estimated as three times the standard deviation of the blank measurement and are, respectively, 0.004 ng/L for DGM, 0.02 ng/L for RHg, 0.10 ng/L for DHg, and 0.009 ng/L for DMeHg. The relative standard deviations (RSDs) on precision tests for the duplicate samples varied from 1.1 to 12.5% for MeHg analysis, and were <8% for inorganic mercury species analysis. Recoveries for matrix spikes were in the range of 88.2–110% for MeHg analysis, and 86.1–110.3% for inorganic mercury analysis.

3. Results and discussion

3.1. Physical and chemical characteristics of water

Fig. 2 shows the distributions of the main water quality parameters in Houwu and Daba basins. In the November and February campaigns, there were no discernable differences in water temperature, pH, and DO distributions in the water column, which demonstrated that the water in the reservoir was well mixed in the autumn and winter seasons. In the May sampling campaign, however, an anaerobic layer developed in the deep water. The pH and DO distributions showed significant differences in the vertical profiles. Both pH and DO were at maximum at the surface because of the algae bloom, but began to decrease in deep water because of stratification in the water column. In the September campaign, as the decomposing dead algae depleted dissolved oxygen, the concentration of DO decreased in the whole water column, especially in the hypolimnion. There was a sharp decrease in DO between 8 and 12 m depth, showing that the reservoir was well stratified.

Table 1 shows the distributions of pH and DO in the inflows and the outflow. The pH and DO were significantly lower in the outflow than in the inflows, indicating that water quality had been significantly changed by the reservoir.

Table 2 shows the seasonal vertical profiles of average total dissolved phosphorous and average chlorophyll at Houwu and Daba. TDP ranged from the detection limit to 0.32 mg/L. Concentrations of chlorophyll ranged from 1.01 to 45.9 µg/L. According to the OECD (Organization for Economic Cooperation and Development) standard for eutrophication in lakes, the average concentrations of chlorophyll at Houwu in February (16.9 µg/L), April (15.4 µg/L) and August (14.9 µg/L) exceeded the threshold for eutrophication (14.3 µg/L). The average total nitrogen (1.90 mg/L, data from EPA of Guizhou, China) at Houwu in 2004 also exceeded the threshold for eutrophication (1.5 mg/L).

The seasonal distributions of TSP and DOC at the two sampling sites are presented in Fig. 3. TSP concentrations were generally low, and ranged from 0.8 to 5.8 mg/L with an average concentration of 2.1 mg/L in all samples except May 2004 at Houwu. Due to the algae bloom, however, highly elevated average concentrations of TSP (up to 15.67 mg/L) were observed at Houwu in May 2004. DOC concentrations ranged from 1.74 to 3.23 mg/L, which were not as high as some bog lakes in North America (Hines et al., 2004).

The distributions of physical and chemical characteristics of water columns at Houwu and Daba showed spatial variation as there are many different internal and external contamination sources in Hongfeng Reservoir. During the warm season, the average concentrations of TSP, TDP, chlorophyll and DOC at Houwu were higher than those at Daba, while DO and pH in the hypolimnion at Houwu were lower than at Daba. These variations showed that eutrophication at Houwu was more developed than at Daba.

3.2. THg, DHg, and PHg in the water columns

Spatial and temporal distributions of THg and DHg at Houwu and Daba are presented in Fig. 4. THg concentrations changed from 2.49 to 13.9 ng/L with an average concentration of 6.89 ng/L. DHg concentrations ranged from 1.19 to 7.96 ng/L with an average of 3.98 ng/L. Mercury concentrations in water of Hongfeng Reservoir were distinctly higher than other natural waters reported in Europe and North America (e.g. Bloom et al., 2004; Sullivan and Mason, 1998). THg and DHg had no discernable vertical distribution trends throughout the whole water column in all sampling campaigns. However, there were spatial and seasonal variations of THg and DHg concentrations in the water column in the reservoir. This spatial variation suggested that the two basins of the reservoir were impacted by different mercury contamination sources. The highest average concentrations of THg and PHg were observed at Houwu in May 2004 (up to 11.43 and 5.95 ng/L, respectively) while lower average concentrations of THg and PHg (6.06 and 3.84 ng/L, respectively) were found at Daba at the same time. Similarly, the highly elevated average concentration of TSP also occurred in May at Houwu; TSP averaged 15.67 mg/L compared to 2.1 mg/L at Daba at the same time. This difference was attributed to the appearance of a great deal of algae at Houwu in May due to aquaculture activities and the input of wastewater enriched with N and P. The distribution of mercury also showed that macroalgae may have a capacity to bind mercury, and may represent a substantial pool of mercury in the aquatic system. The levels of total and dissolved mercury were relatively low in September compared with those in November and February. This seasonal distribution of
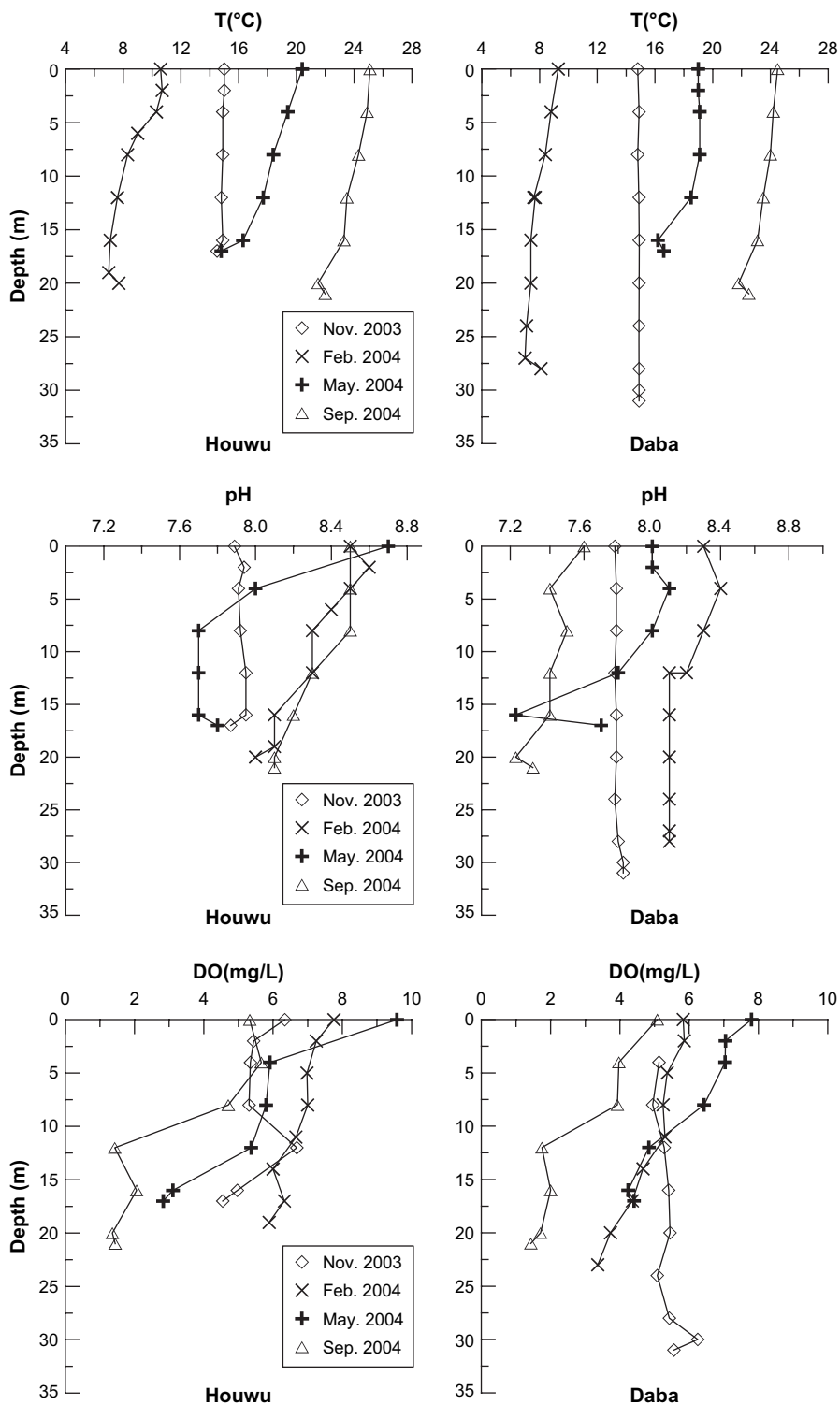
Fig. 2. Seasonal distributions of *T*, pH, and DO in Hongfeng Reservoir.

mercury could be a result of wastewater contamination. In May and September, high runoff volume due to abundant precipitation diluted the concentration of mercury in water, whereas there was very little precipitation in February and November so that mercury concentrations in water were much higher.

PHg/THg ratios were high in May and September at 57 and 49%, respectively, while the PHg/THg ratio was only 26% in February. However, increased TSP was not observed in May and September except for high TSP at Houwu in May due to the algae bloom. Therefore, the proportion of PHg increased probably because of the increased fraction of organic particles, which can absorb more mercury than inorganic particles, in May and September. In September, however, DHg in the hypolimnion increased again, especially at Houwu, and the

Table 1
Dissolved oxygen (DO) and pH in the inflow and outflow rivers of Hongfeng Reservoir

Rivers	DO (mg/L)			pH		
	November 2003	May 2004	September 2004	November 2003	May 2004	September 2004
Maotiao	4.7	3.2	1.8	6.9	7.4	7.4
Maxian	8.0	8.4	5.4	8.1	7.9	8.0
Yangchang	8.5	8.9	6.7	8.0	7.6	7.9
Taohua	8.3	–	7.2	8.4		8.2
Houliu	7.4	8.3	5.3	7.8	7.6	7.6
Maibao	7.7	8.5	8.0	7.7	7.7	7.7
Fertilizer Plant Drain	7.6	5.5	5.3	7.6	8	7.5

Data from the February 2004 campaign are missing.

highest proportion was up to 82%. This is probably because the anaerobic decomposition of particulate organic matter in the hypolimnion resulted in an increase in dissolved organic matter in anoxic water which can absorb more mercury than chloride or hydroxide complexes (Coquery et al., 1997). Moreover, the dissolution of iron and manganese oxide in anoxic water probably could also contribute to the increase in dissolved mercury (Regnell et al., 2001).

3.3. DGM and RHg in the water column

For comparison between different vertical profiles of DGM, the samples of every vertical profile were always collected at midday as DGM concentrations in water, especially in surface water, are significantly affected by sunlight. DGM concentrations ranged from 0.02 to 0.11 ng/L during the four sampling campaigns (Fig. 5). DGM concentrations were highest at the water surface and decreased with depth. The average concentrations of DGM in September (0.08 ng/L at Daba; 0.07 ng/L at Houwu) were higher than those in February (0.04 ng/L at Daba; 0.05 ng/L at Houwu). This DGM distribution pattern is consistent with the hypothesis that photoreduction of Hg(II) complexes is the main source of Hg(0) formation in water, and temperature plays an important role in the photoreduction process. There was a sharp decrease in DGM concentrations at 8–12 m depth in September 2004. This suggested that the seasonal stratification may also affect the vertical DGM distribution. The lowest average DGM concentration (0.04 ng/L) was observed at Houwu in May instead of February, whereas the DGM concentration at Daba in May (0.08 ng/L) was as high as that in September. This suggested that other processes may also control DGM production. The lowest average DGM concentration observed

at Houwu in May can probably be attributed to the algae bloom, which can block sunlight. Early studies (e.g. Barkay et al., 1991) suggested that Hg^{2+} reduction was performed by bacteria and some eucaryotic microorganisms, such as algae. Ben-Bassat and Mayer (1987) found that the formation of Hg(0) decreased as a function of the inhibition of photosynthesis in cultures of the green algae chlorella.

The seasonal distribution patterns of RHg in the reservoir are presented in Fig. 5. RHg ranged from 0.14 to 2.17 ng/L with an average concentration of 0.64 ng/L. RHg concentrations at the water surface were lower than those at depth in all of the vertical profiles except at Daba in September. This was probably due to the intense particulate scavenging and/or biological reduction of Hg^{2+} near the water surface and subsequent release of Hg(0) to the atmosphere (Gill, 1986; Kim and Fitzgerald, 1986; Dalziel, 1995). The unusual high RHg at Daba in September may be related to contamination from the nearby chemical fertilizer plant. This possibility is supported by the very high RHg concentrations (up to 81.49 ng/L) observed in the Fertilizer Plant Drain, which was contaminated by the chemical fertilizer plant.

RHg decreased from subsurface to deep water in most of the vertical profiles, a pattern that may be related to the methylation of Hg^{2+} or the presence of S^{2-} in deep anoxic water. As RHg is the main species that could either be reduced to Hg(0) or methylated in a bacterially mediated process (Ullrich et al., 2001), reduction and methylation likely controlled RHg concentrations. However, the above-mentioned distribution patterns of RHg in the water column were not observed at Houwu in May and at Daba in February, probably as a result of contamination from the chemical fertilizer plant at Daba and the excessive algae at Houwu as discussed above.

3.4. Inorganic mercury species in the rivers

The concentrations of THg, DHg, RHg in the inflows and outflow during four campaigns are presented in Table 3. Relatively high concentrations of mercury were observed in the Yangchang and Maibao rivers and the Fertilizer Plant Drain, likely from both industrial and domestic wastewater sources of mercury in the drainage area of Hongfeng Reservoir. PHg, whose proportion to THg was 58, 64 and 84% in the

Table 2
Seasonal variations of average total dissolved phosphorous (TDP) and average chlorophyll over the entire water column at Houwu and Daba in 2004

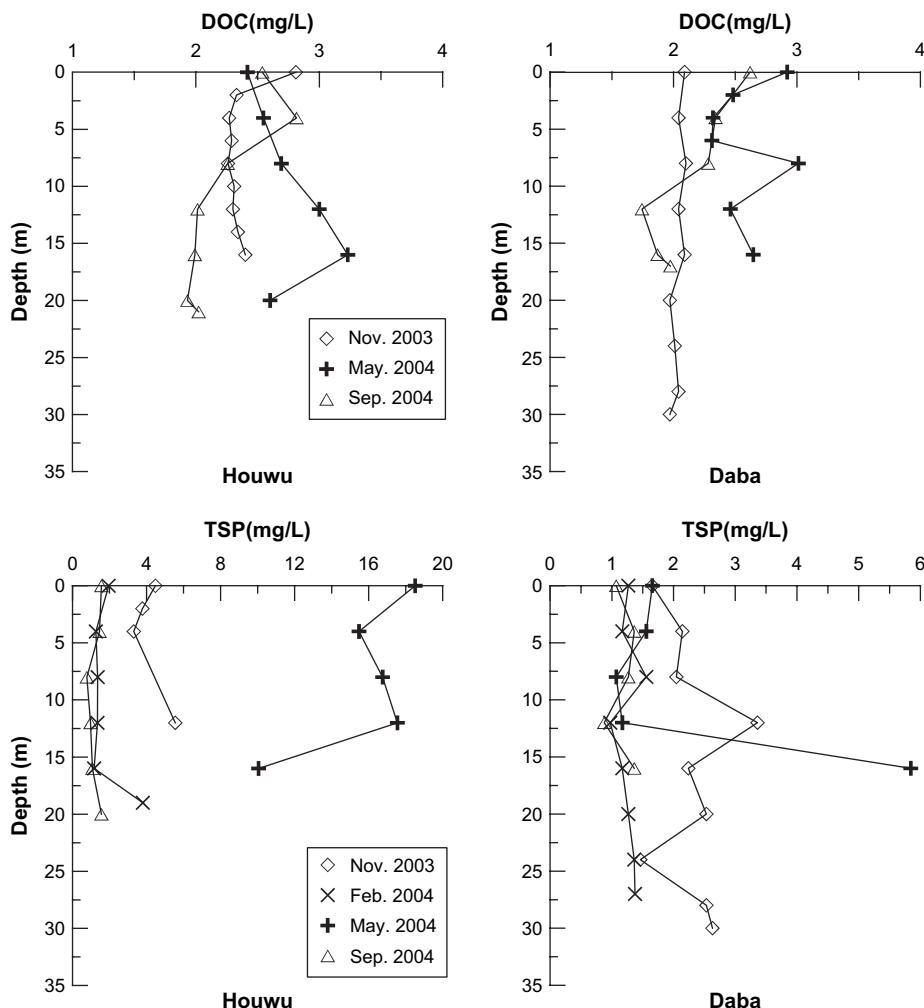| Parameters	Sampling sites	February	April	June	August
Chlorophyll (μg/L)	Houwu	16.97	15.40	11.09	14.92
	Daba	10.92	7.42	8.74	13.66
TDP (mg/L)	Houwu	0.015	0.02	0.094	0.086
	Daba	0.014	0.01	0.025	0.038

Fig. 3. Seasonal distributions of DOC and TSP in Hongfeng Reservoir.

Yangchang and Maibao rivers and the Fertilizer Plant Drain, respectively, contributed most of the THg to these rivers. THg and DHg concentrations in the outflow were much lower than those in the contaminated inflows. Water flows were not measured in this study, but we estimated rough annual inputs and outputs of mercury species based on average concentrations of mercury species in the four campaigns and long-term average annual flows of the rivers reported by Zhang (1999) (Table 4). These estimates suggest that more than 50% of the THg from the inflows was removed by the reservoir, and most of this THg was predicted to be buried in sediments.

3.5. TMeHg and DMeHg in the water column

The seasonal distributions of MeHg in water column are shown in Fig. 6. An analysis of variance showed that there were no statistically significant differences ($F = 3.01$, $p = 0.059$) between the TMeHg distributions in the water column at both sampling sites in the May, November and February campaigns. TMeHg concentrations in these campaigns varied

from 0.05 to 0.33 ng/L and increased slightly with depth in the water column in the February and November campaigns.

MeHg concentrations in the September campaign were statistically elevated compared to the other three sampling campaigns ($F = 9.48$, $p < 0.001$). The highest value of 0.92 ng/L occurred at Houwu and was 2.5 times higher than the highest value in other seasons. There was a distinct vertical distribution pattern of MeHg in the water column. TMeHg increased from 0.15 ng/L at the surface to 0.92 ng/L in the hypolimnion at Houwu, while TMeHg increased from 0.08 at the surface to 0.81 ng/L in the bottom water at Daba. There was a sharp increase in TMeHg concentrations at the depth of 8–12 m, which corresponded to a sharp decrease in dissolved oxygen concentrations at the same depth. Spatial and temporal distributions of MeHg showed that MeHg increased significantly in the hypolimnion in September, especially at the Houwu site.

MeHg content in water is influenced by a wide variety of environmental factors, such as total and reactive mercury content, temperature, redox potential, pH, and the inorganic and organic solutes in waters (Ullrich et al., 2001). However, these factors cannot be viewed independently of each other, as they often interact, forming a complex system of synergistic
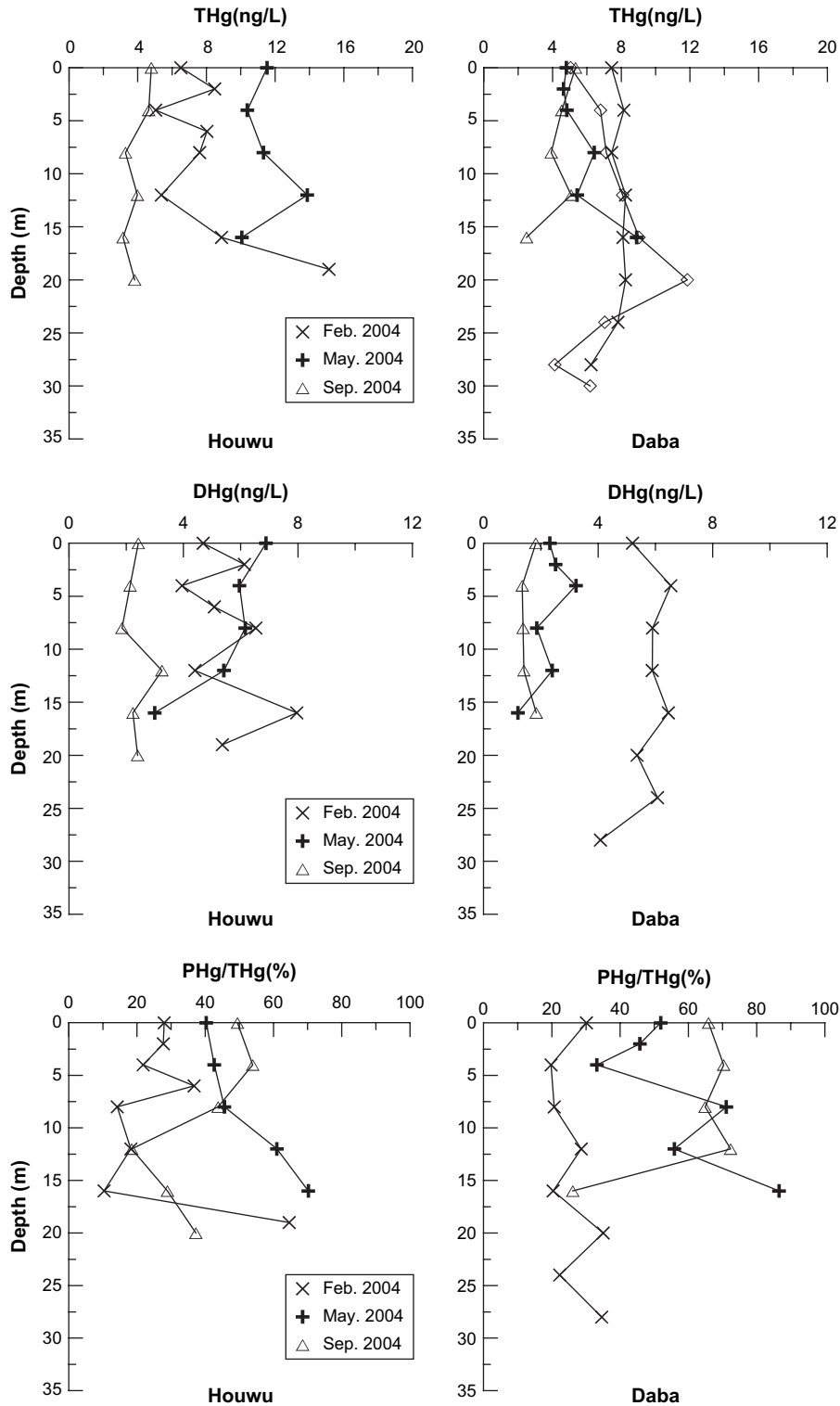
Fig. 4. Seasonal distributions of THg and DHg in Hongfeng Reservoir.

and antagonistic effects. 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). Methylation rates appear to be enhanced under anaerobic conditions because of increased

activity of anaerobic sulfate-reducing bacteria. In our investigation, TMeHg had a strong negative relationship with DO, with a Pearson correlation coefficient of -0.81 ($n = 78$, $p < 0.0001$). As pH, DOC and salinity in all samples varied only within a narrow range, no significant correlations between methylmercury and these parameters were observed.
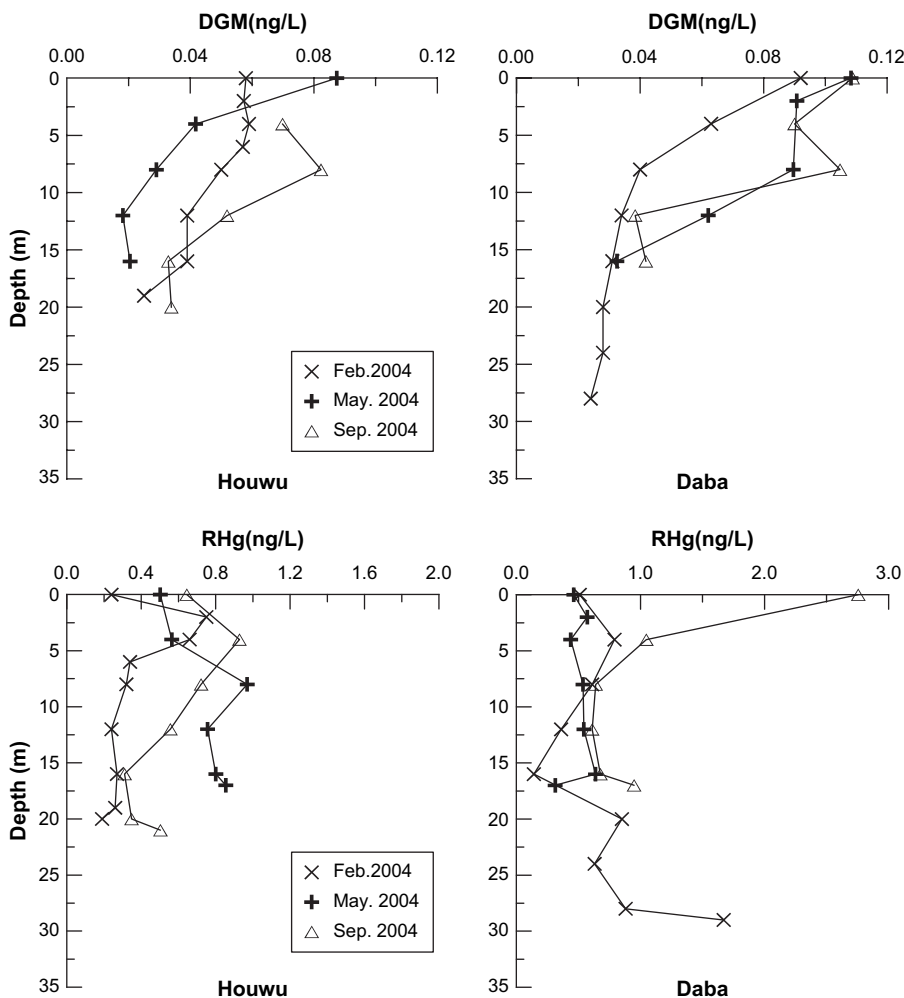
Fig. 5. Seasonal distributions of DGM and RHg in Hongfeng Reservoir.

Many studies have shown that increased MeHg in the hypolimnion is related to increased methylation rates and/or the accumulation of settling particulate matter, instead of the release of MeHg from sediments (e.g. Regnell and Ewald, 1997; Verta and Matilainen, 1995). Gilmour and Henry (1991) suggested that both low pH and negative redox potential, which are common to anoxic hypolimnia, not only increase methylation rates but also decrease demethylation rates resulting in a net increase in MeHg. Eckley et al. (2005) showed that methylation rates in hypolimnetic waters were sufficient to account for the observed accumulation of MeHg in hypolimnetic water during summer in two pristine Wisconsin lakes. Some studies also showed that the accumulation of settling particulate matter from the epilimnion, such as hydrous ferric and manganese oxides which can bind MeHg, and their dissolution in the hypolimnion contributed to the high concentration of MeHg

Table 3
Seasonal variations of Hg concentrations in the rivers in November 2003, February, May and September 2004

Rivers	THg (ng/L)				DHg (ng/L)				RHg (ng/L)			
	November	February	May	September	November	February	May	September	November	February	May	September
Maotiao (outlet)	9.92		3.64	5.19	3.41		1.61	3.70	1.92		0.60	0.93
Maxian	6.70	4.04	6.69	2.14	3.90	2.28	5.03	1.58	0.19	0.20	0.11	0.53
Yangchang	37.5	25.8	15.2	15.1	19.1	16.2	4.54	2.70	8.51	1.27	0.61	0.54
Taohua	4.51	2.96		2.21	3.99	2.67		1.34	0.32	0.24		0.21
Houliu	6.87	11.35	15.9	5.45	4.33	5.47	6.07	1.94	0.35	0.41	0.14	1.01
Maibao	121	9.02	27.5	46.7	25.3	6.91	11.2	4.67	0.33	0.24	0.64	1.55
Fertilizer Plant Drain	175	178	352	233	32.4	40.0	33.7	26.1	62.8	56.3	54.3	81.9

Table 4
Average concentrations of THg, DHg and RHg in the inflows and outflow of Hongfeng Reservoir during four campaigns and their estimated contribution to annual Hg input and output

Rivers	Annual discharge (10^6 m^3)	THg (ng/L)	DHg (ng/L)	RHg (ng/L)	Annual input or output of THg (g)	Annual input or output of DHg (g)	Annual input or output RHg (g)
Maotiao (outflow)	819	6.3	2.9	1.2	5599	2862	941
Maxian (inflow)	167	4.9	3.2	0.26	819	535	43
Yangchang (inflow)	400	23.4	10.7	2.7	9521	4432	1092
Taohuayuan (inflow)	131	3.2	2.7	0.26	421	348	34
Houliu (inflow)	58.7	9.9	4.5	0.48	607	287	28
Maibao (inflow)	31.5	51.2	12.0	0.69	1629	379	22
Fertilizer Plant Drain (inflow)	31.5	234.4	33.1	71.7	7404	1056	2262
Sum of the inflows	819	–	–	–	20,402	7038	3481
Difference: input minus output					14,803	4177	2540

in deep water (Meili, 1997). Other studies indicated that the increased MeHg was mostly derived from the release of MeHg from sediments, especially at highly contaminated sites (e.g. Furutani and Rudd, 1980). Moreover, many studies indicated that MeHg release flux from sediments increased with decreased pH and DO (e.g. Ullrich et al., 2001). The highest values of total and dissolved MeHg at Houwu in September were not at the sediment–water interface. This
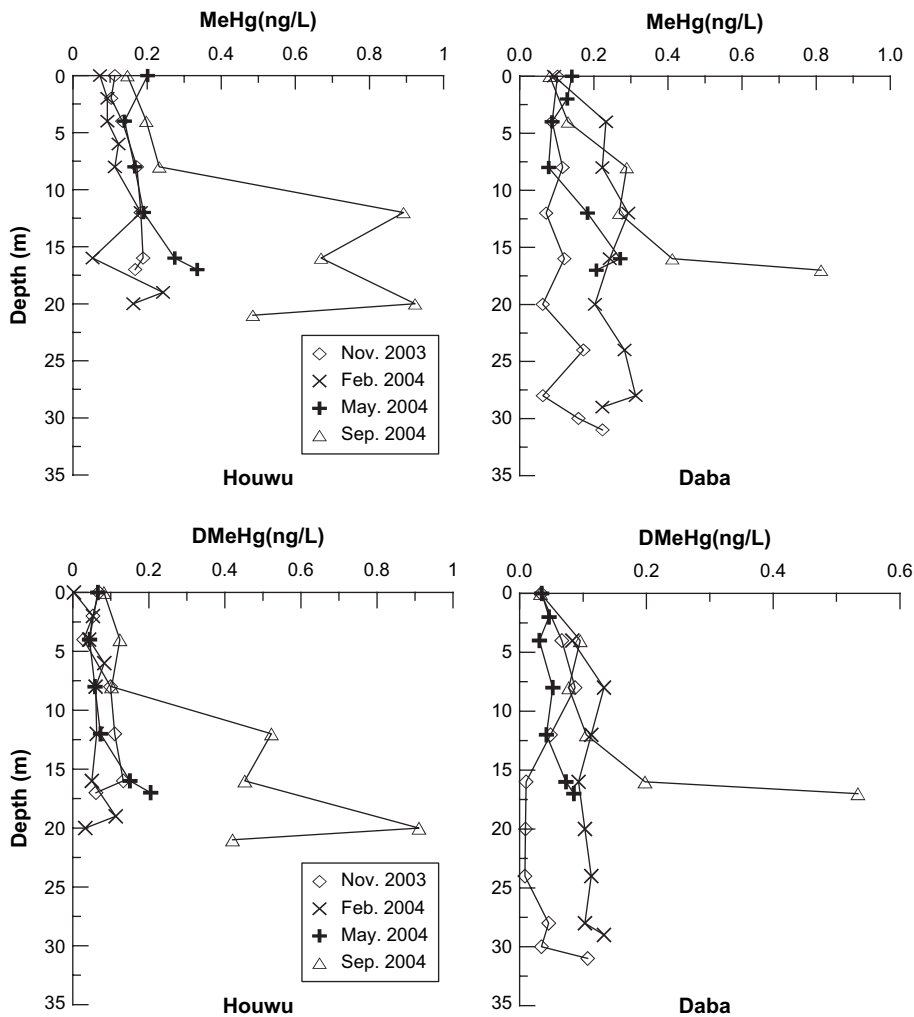

Fig. 6. Seasonal distributions of TMeHg and DMeHg in Hongfeng Reservoir.

suggested that MeHg in the water column did not come from the release of MeHg in sediment, but from in situ methylation in anoxic water. At Daba in September, however, MeHg showed a strong increasing gradient toward the sediment, which indicated that MeHg released from sediment had a strong impact on the MeHg depth profile at Daba.

Despite the MeHg increase in deep water at Daba in September, the Wilcoxon rank sum test showed that MeHg concentrations in Houwu were much higher than those in Daba at the same depths in September ($p < 0.05$), especially in the hypolimnion layer (Fig. 6). This finding suggests that MeHg was being formed in the hypolimnion layer at Houwu in September. The decomposition of a large volume of algae induced by high nutrient concentrations at Houwu led to low DO and pH, which may have accelerated Hg methylation.

No statistical difference in the proportions of DMeHg to TMeHg in water was observed in the November, February, and May campaigns; the average value was about 43%. In September, however, the proportion of DMeHg increased significantly, to an average of 65%, and a maximum of 98% at 20 m depth at Houwu. The proportion of DMeHg was also elevated (73%) in the outflow of the reservoir, which is hypolimnion water. Eckley et al. (2005) and Baeyens and Meuleman (1998) also observed an elevated proportion of DMeHg in the hypolimnion of seasonally stratified lakes. Hydrous ferric and manganese oxides and organic particles have large capacities for binding both MeHg and Hg(II). On one hand, under anoxic conditions, mercury methylation rates increased significantly resulting in an increase in MeHg concentrations. On the other hand, the dissolution of oxides and anaerobic decomposition of particulate organic matter possibly resulted in an increase of the DMeHg proportion in the hypolimnion (Regnell et al., 2001).

TMeHg concentrations in water at Houwu basin were statistically higher than those at Daba basin in all campaigns except for the February campaign (Wilcoxon rank sum test, $p < 0.05$). The average TMeHg concentrations at Houwu in May, September, and November were 0.22, 0.50, and 0.15 ng/L, respectively, while the corresponding values at Daba were 0.16, 0.34, and 0.12 ng/L, respectively. In February, however, MeHg at Daba (0.23 ng/L) was higher than that at Houwu (0.13 ng/L). The different contamination sources could be responsible for this seasonal and spatial variation. At Houwu, the main contamination source was aquaculture activities. At Daba, the main contamination sources were the chemical fertilizer plant and domestic wastewater inputs.

The fish farms at Houwu basin contributed a great amount of N and P to the water, resulting in more algae than at Daba. The decomposition of algae caused DO and pH to decrease, which favoured the methylation of mercury. In winter, the contamination at Houwu lessened significantly with the reduction of activity at the fish farm, but the contamination at Daba remained high because the pollutants were derived from the chemical fertilizer plant and domestic wastewater. RHg at Daba (0.72 ng/L) was also higher than that at Houwu (0.36 ng/L), while DO at Daba (4.9 mg/L) was lower than that at Houwu (6.7 mg/L) in February. All of these factors could result in a higher mercury methylation rate at Daba in winter.

3.6. MeHg in rivers

Table 5 shows the seasonal distribution of MeHg in the rivers discharging to Hongfeng Reservoir. MeHg concentrations were relatively greater in the Maxian, Houliu, and Yangchang rivers in May than in other seasons. These rivers are the main water sources to the reservoir and are affected by agriculture activities. No significant differences were observed between MeHg concentrations in inflows and the outflow in all campaigns except for the September campaign. In September, however, the outflow of the reservoir was rich in MeHg, and the concentration was 5.5 times higher than the average value in the inflows. This MeHg-enriched water from the anoxic hypolimnion represented the discharge from the reservoir. Though the stability of this MeHg in the more oxidizing environment of the outflow river is uncertain, it poses a potential risk to the ecosystem below the reservoir.

4. Conclusions

Hyper-eutrophication in Hongfeng Reservoir, which resulted in algae blooms and deterioration of water quality, affected the concentrations and distributions of mercury species in the reservoir. Macroalgae had a large capacity to bind mercury, and represented a substantial pool of mercury in the aquatic system. The formation of Hg(0) decreased, probably also because these macroalgae blocked out sunlight and inhibited photosynthesis. Most importantly, hyper-eutrophication resulted in lower DO and higher DOC, thus accelerating the formation of MeHg in the hypolimnion especially in summer. Hongfeng Reservoir was a large net sink of total mercury, but a net source of MeHg. The MeHg-enriched water

Table 5
Seasonal distribution of methylmercury in the inflows and outflow of Hongfeng Reservoir (ng/L)

Rivers	Outflow	Inflows					
	Maotiao	Maxian	Yangchang	Taohua	Houliu	Maibao	Fertilizer Plant Drain
November	0.138	0.180	0.155	0.096	0.111	–	0.212
February	–	0.102	0.143	0.091	0.156	0.134	0.235
May	0.164	0.186	0.207	–	0.244	0.103	0.062
September	1.022	0.121	0.178	0.077	0.159	0.140	0.110

discharged from the anoxic hypolimnion in the reservoir may pose serious risks to the ecosystem downstream of the reservoir.

References

Ben-Bassat, D., Mayer, A.M., 1987. Reduction of mercury chloride by Chlorella: evidence for a reducing factor. Physiologia Plantarum 40, 157–162.

Baeyens, W., Meuleman, C., 1998. Behavior and speciation of mercury in the Scheldt estuary (water, sediments and benthic organisms). Trace Metals in the Westerschelde Estuary. Hydrobiologia 336, 63–79.

Barkay, T., Turner, R.R., Vandenbrook, A., Liebert, C., 1991. The relationship of Hg(II) volatilization from freshwater pond to the abundance of *mer* genes in the gene pool of the indigenous microbial community. Microbial Ecology 21, 151–161.

Bloom, N.S., Moretto, L.M., Scopece, P., Ugo, P., 2004. Seasonal cycling of mercury and monomethyl mercury in the Venice Lagoon (Italy). Marine Chemistry 91, 85–99.

Bloom, N.S., Fitzgerald, W.F., 1988. Determination of volatile mercury species at the picogram level by low temperature gas chromatography with cold-vapor atomic fluorescence detection. Analytica Chimica Acta 208, 151–161.

Bloom, N.S., 1989. Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection. Canadian Journal of Fisheries and Aquatic Sciences 46, 1131–1140.

Coquery, M., Cossa, D., Sanjuan, J., 1997. Speciation and sorption of mercury in two macrotidal estuaries. Marine Chemistry 58, 213–227.

Coelho, J.P., Pereira, M.E., Duarte, A., Pardal, M.A., 2005. Macroalgae response to a mercury contamination gradient in a temperate coastal lagoon (Ria de Aveiro, Portugal). Estuarine, Coastal and Shelf Science 65, 492–500.

China EPA, 2002. Methods and Guidance for the Analysis of Water and Wastewater. China Environmental Sciences Press, Beijing (in Chinese).

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Applications 8 (3), 559–568.

Cosovic, B., Ciglenecki, I., Vilicic, D., Ahel, M., 2000. Distribution and seasonal variability of organic matter in a small eutrophied salt lake. Estuarine, Coastal and Shelf Science 51, 705–715.

Dalziel, J.A., 1995. Reactive mercury in the eastern North Atlantic and southeast Atlantic. Marine Chemistry 1995, 307–314.

Eckley, C.S., Watras, C.J., Hintelmann, H., 2005. Mercury methylation in the hypolimnetic waters of lakes with and without connection to wetlands in northern Wisconsin. Canadian Journal of Fisheries and Aquatic Sciences 62, 400–411.

Eggleton, J., Thomas, K.V., 2004. A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events. Environment International 30, 973–980.

Furutani, A., Rudd, J.W., 1980. Measurement of mercury methylation in lake water and sediment samples. Applied and Environmental Microbiology 40, 770–776.

Gill, G.A., 1986. On the Marine Biogeochemistry of Mercury. Ph.D. thesis, University of Connecticut, 230 pp.

Gilmour, C.C., Henry, E.A., 1991. Mercury methylation in aquatic systems affected by acid deposition. Environmental Pollution 71, 131–169.

Hines, N.A., Brezonik, P.L., Engstrom, D.R., 2004. Sediment and porewater profiles and fluxes of mercury and methylmercury in a small seepage lake in northern Minnesota. Environmental Science and Technology 38, 6610–6617.

Horvat, M., Nolde, N., Fajon, V., Jereb, V., Logar, M., Lojen, R., Jacimovic, R., Falnoga, I., Qu, L.Y., Faganeli, J., Drobne, D., 2003. Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China. Science of the Total Environment 304, 231–256.

Horvat, M., Liang, L., Bloom, N.S., 1993. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part 2: water. Analytica Chimica Acta 282, 153–168.

Jing, X., Tu, Q.Y., 1990. Criteria for Investigation of Lake Eutrophication, second ed. China Environment Science Press, Beijing.

Kim, J.P., Fitzgerald, W.F., 1986. Sea–air partitioning of mercury in the equatorial Pacific Ocean. Science 231, 1131–1133.

Liang, X.B., Zhu, J.M., Liu, C.Q., 2004. Enzymatic and microbial degradation of organic matter in Lake Hongfeng, Guizhou Province, China. Chinese Journal of Geochemistry 23, 81–88.

Lu, D.Q., 2004. Green Algal Attack in Hongfeng Reservoir. Guizhou Metropolitan News.

Meili, M., 1997. Mercury in lakes and rivers. Metal Ions in Biological Systems 34, 21–25.

Pickhardt, P.C., Folt, C.L., Chen, C.Y., Klaue, B., Blum, J.D., 2002. Algal blooms reduce the uptake of toxic methylmercury in freshwater food webs. Proceedings of the National Academy of Sciences of the United States of America 99 (7), 4419–4423.

Regnell, O., Hammar, T., Helgee, A., Troedsson, B., 2001. Effects of anoxia and sulfide on concentrations of total and methyl mercury in sediment and water in two Hg-polluted lakes. Canadian Journal of Fisheries and Aquatic Sciences 58 (3), 506–517.

Regnell, O., Ewald, G., 1997. Factors controlling temporal variation in methyl mercury levels in sediment and water in a seasonally stratified lake. Limnology and Oceanography 42 (8), 1784–1795.

Radway, J.C., Wilde, E.W., Whitaker, M.J., Weissman, J.C., 2001. Screening of algal strains for metal removal capabilities. Journal of Applied Physiology 13, 451–455.

Smith, V.H., Tilman, G.D., Nekola, J.C., 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine and terrestrial ecosystems. Environmental Pollution 100, 179–196.

Sullivan, K.A., Mason, R.P., 1998. The concentration and distribution of mercury in Lake Michigan. Science of the Total Environment 213, 213–228.

Tchounwou, P.B., Ayensu, W.K., Ninashvili, N., Sutton, D., 2003. Environmental exposure to mercury and its toxicopathologic implications for public health. Environmental Toxicology 18, 149–175.

United States Environmental Protection Agency, 2002. Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (Method 1631, Revision E). EPA-821-R-02–019.

United States Environmental Protection Agency, 2001. Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS (Method 1630). EPA-821-R-01–020.

Ullrich, S.M., Tanton, T.W., Abdrashitova, S.A., 2001. Mercury in the aquatic environment: a review of factors affecting methylation. Critical Reviews in Environmental Science and Technology 31 (3), 241–293.

Verta, M., Matilainen, T., 1995. Methylmercury distribution and partitioning in stratified Finnish forest lakes. Water, Air and Soil Pollution 80, 585–588.

Watras, C.J., Morrison, K.A., Kent, A.D., Price, N., Regnell, O., Eckley, C., Hintelmann, H., Hubacher, T., 2005. Sources of methylmercury to a wetland-dominated lake in northern Wisconsin. Environmental Science and Technology 39, 4747–4758.

Xiao, H.Y., Liu, C.Q., 2004. Discrimination between extraneous nitrogen input and interior nitrogen release in lakes. Science in China, Series D: Earth Sciences 47, 813–821.

Yan, H.Y., Feng, X.B., Shang, L.H., Tang, S.L., Qiu, G.L., 2003. Speciation analysis of ultra trace levels of mercury in natural waters. Journal of Instrumental Analysis 22 (5), 10–13.

Zhang, W., 1999. Environmental Characters and Eutrophication in Hongfeng Reservoir and Baihua Reservoir. Guizhou Technological Publishing, Guiyang.

Zhou, T., Gu, T.H., Zhao, C., 1997. Weather study about acid rain process in Guiyang. Guizhou Weather 21 (3), 23–25.