The variations of mercury in sediment profiles from a historically mercury-contaminated reservoir, Guizhou province, China

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ABSTRACT

Baihua Reservoir in Guizhou Province, China, experienced serious Hg contamination from Guizhou Organic Chemical Plant (GOCP) between 1971 and 1997. However, the biogeochemical cycling of Hg in this reservoir is not well studied. Sediment cores were collected in fall 2002, spring 2003 and in spring and fall 2004. THg and MeHg concentrations in all sediment profiles ranged from 0.26 to 38.9 mg/kg and from 0.5 to 27.5 μg/kg (d.w.), respectively. The distribution of THg in sediment cores was characterized by a few peaks, which may correspond to the Hg-containing wastewater discharge history of the GOCP. The average THg concentrations in sediments cores decreased from upstream to downstream due to the deposition of particulate Hg, which is the major form of Hg in water. THg and MeHg concentrations in pore water varied from 6.1 to 5860 ng/L and from 0.3 to 15.4 ng/L, respectively, which were significantly higher than levels in the overlying water column. Average diffusive flux from sediment to water is 1642 and 36 ng/m²/day for THg and MeHg. The spatial distribution of THg in pore water from upstream to downstream showed the same trend as the sediment, but MeHg in pore water did not show a declining pattern with distance from the GOCP. These results suggested that sediments experienced serious contamination of Hg, and the contaminated sediment is an important Hg contamination source to the overlying water.

1. Introduction

In natural aquatic systems mercury (Hg) concentrations in sediment are low; for example, in the Great Lakes concentrations vary from 0.002 to 0.03 mg/kg (Marvin et al., 2004). Generally, total Hg concentration in sediments range from 0.027 (Rémy et al., 2003) to 0.42 mg/kg (such as He, 2007; Jiang, 2005; Huggett et al., 2001). The global Hg burden (including Hg in sediment) is presently three times higher than that in pre-industrial times due to human activities (Mason et al., 1999). Hg contaminated sediment may pollute the water column, biota,

food chain and eventually threaten human health. In the 1950s, total Hg (THg) concentrations as high as 2000 mg/kg were detected in sediment near the overflow of the Chisso Chemical Plant in Minimata in Japan (Kitamura et al., 1960), and the Hg dispersed in the bay was bioaccumulated by fish and shellfish, and caused the notorious Minamata disease in humans (Ninomiya et al., 1995; Harada, 1995; Akagi et al., 1998; Harada et al., 1998).

Sediments play an important role in the biogeochemical cycling of Hg in the aquatic system. Sediments can be a sink and/or a secondary source of Hg contamination to the water

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body (Covelli et al., 1999). The distributions and concentrations of THg in sediment and pore water may have significant impacts on the distribution of Hg in the overlying water (Kim et al., 2004). Sediments are also considered the main site for Hg methylation (Furutani and Rudd, 1980) and thus are perceived as the major source of methylmercury (MeHg) to the water column and the aquatic food chain (Mason et al., 1999). Benthic chamber experiments conducted by Horvat et al. (1999) indicated only 74% of deposited Hg is retained in sediments. The diffusion and re-suspension of sediment Hg are important processes that affect Hg in water bodies, and subsequent accumulation of Hg by fish and shellfish.

Baihua Reservoir was seriously contaminated with Hg from the GOCP, but research concerning Hg biogeochemical cycling in the reservoir has not been conducted. The references show the concentration of THg is very high in surface sediment in Baihua Reservoir (the highest concentration is 33.5 and 62.1 mg/kg in 1992 and 1997, respectively) (Wang, 1993; Zhang, 2000), and the highest concentration of THg exceeds 0.53 mg/kg in wild fish in 1996, (Qu, 1999). There are no cases of human mercury poisoning, but current Hg distribution patterns in sediment and pore water profiles of the reservoir remain undocumented. As a part of the biogeochemical cycling study of Hg, the distribution pattern of THg and MeHg in sediment profiles and pore water of the sediment were for the first time measured, in order to estimate the Hg flux from sediment to water and to understand the Hg contamination status of the sediment in Baihua Reservoir.

2. Materials and methods

2.1. Site description

Baihua Reservoir (106°27′–106°34′N, 26°35′–26°42′E) is situated 16 km northwest of Guiyang, the capital of Guizhou Province. The Maotiao River flowed in a SW to NE direction before it was flooded in 1966. Baihua Reservoir is a long and narrow (length 18 km, mean width 0.8 km) hydroelectric reservoir with a main input flow and only one output flow. The watershed is 1895 km^2, and the climate is subtropical rainy monsoon with an average annual rainfall of 1200 mm and annual mean temperature of 13.8 °C. Calcareous soil and yellow soil are typical soils in the watershed and vertical zoning changes with height. The terrain around Baihua Reservoir is highly vegetated. The total water surface area of Baihua Reservoir is 14.5 km^2, the average water depth is 12 m, and the average salinity and DOC concentrations are 0.2% and 0.3 mg/L, respectively (Yan, 2005). The organic matter (C) and total nitrogen (TN) concentrations in sediment are about 5% and 0.38%, respectively.
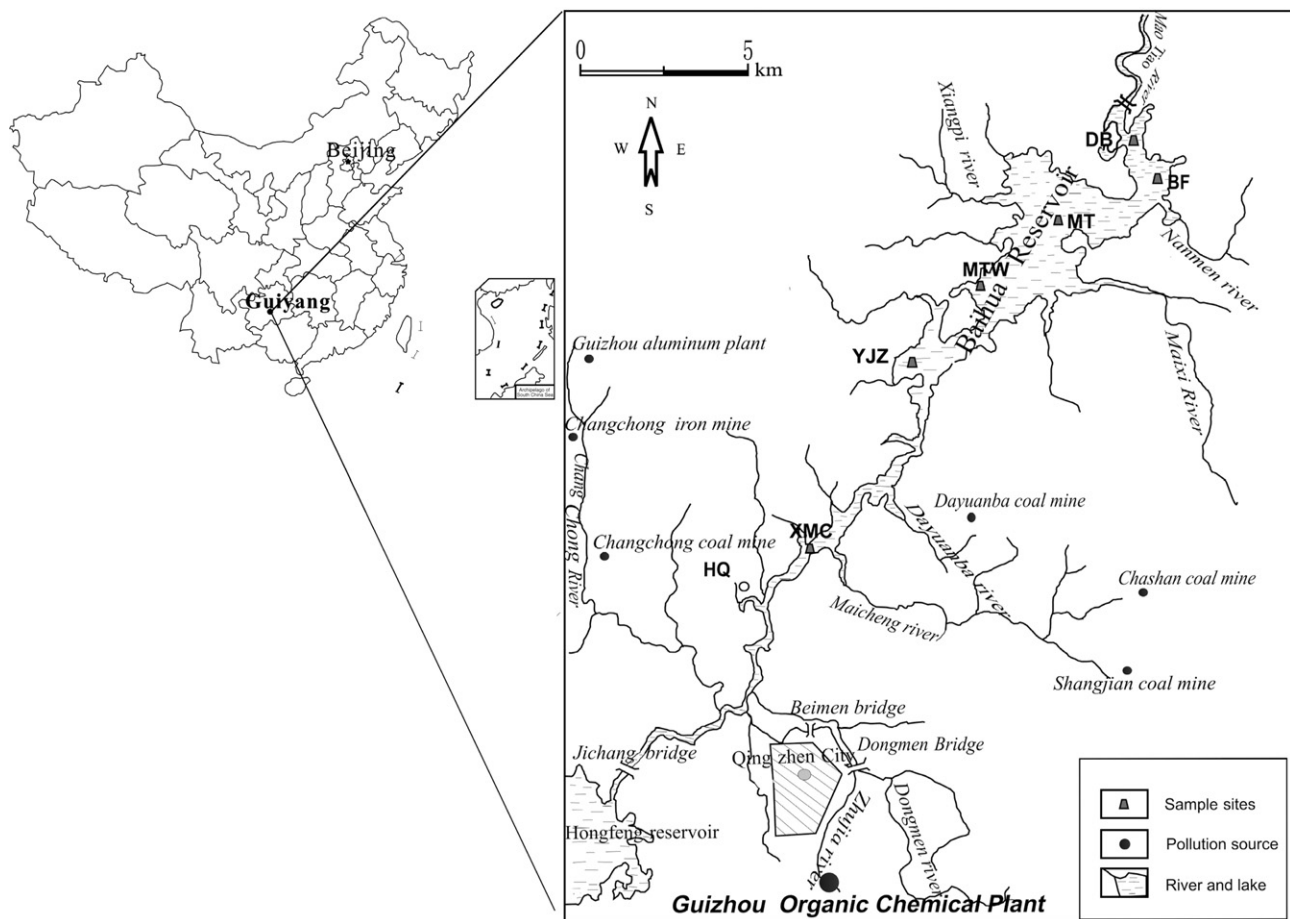

Fig. 1 – The locations of the sampling sites.

Between 1971 and 1997, Baihua Reservoir experienced serious Hg contamination from GOCP, which is the only factory in China that used metallic Hg as a catalyst to produce acetic acid. GCOP is located in the upper reach of the reservoir as shown in Fig. 1. Baihua Reservoir was built and impounded in 1966. From 1971 to 1985, 573 ton Hg was consumed by the plant. The wastewater from GOCP was directly discharged into Zhujia River without any treatment, and flowed into Baihua Reservoir by Dongmen Bridge; this seriously contaminated Baihua Reservoir and the surrounding environment. After 1985, a Hg removal device was used to prevent Hg discharging into Zhujia River. At present, total Hg concentrations in this river still range from 250 to 1000 ng/L (Yan, 2005). In addition, 7 small coal mines, one iron mine and Guizhou aluminum plant are situated at the upper reaches of the reservoir, and these may also be Hg contamination sources to the reservoir.

2.2. Sample collection

In order to understand the whole pattern of Hg contaminations in sediment of Baihua Reservoir, six representative sites, namely Xie-Mei-Chang (XMC) upstream, Yan-Jiao-Zhai (YJZ) upstream, Mei-Tu-Wan (MTW) in the middle reaches, Ma-Tou (MT)in the middle reaches, Beng-Fang (BF) downstream, and Da-Ba (DB) downstream were selected for sediment and pore water sampling from upstream to downstream as shown in Fig. 1. Sediment cores at sampling sites DB, BF, and YJZ were collected in November 2002, and sediment cores at XMC and MT were collected in March 2003 for the THg analysis. For MeHg, sediment cores at YZJ, MTW and BF were collected in August 2004. Even though HgT and MeHg profiles were not obtained in the same cores, this does not influence/bias our interpretation because all sediment cores were collected in the deepest parts of the reservoir. Sediment cores were taken by means of a gravity corer. At each sampling site, filtered water samples 10–20 cm above the sediment–water interface was collected into acid-cleaned borosilicate glass bottles (Millipore, Durapore® Membrane Filters). Sediment cores were sliced in situ in layers of 1 cm thickness for THg and 2 cm thickness for MeHg analysis. For MeHg, sediments samples were sliced and stored in acid-cleaned high-density polyethylene centrifuge tubes under anaerobic condition and sealed with parafilm®. All samples were stored in acid-cleaned high-density polyethylene centrifuge tubes and were transported to the lab and stored in the refrigerator (at 4 °C).

In the lab, sediment samples were centrifuged at 3500 rpm for 25 min at 4 °C. After being filtered through 0.22 μm membrane filter (Millipore, polyvinylidene difluoride), pore water samples were preserved with 0.4% (v/v) ultra pure HCl in acid-clean borosilicate glass tubes and stored at 0–4 °C until analysis. Field blanks were also prepared by adding Milli-Q water in sampling tubes. Collection, storage, and preservation of samples followed US EPA Method 1631 (2001). All glassware was cleaned by washing using DDW after having been boiled in warm hydrochloric acid for 2 h (HCl:H$_2$O = 1:1, V/V). Pore water samples were analyzed within 2 weeks after sample collection. Solid phase samples were freeze-dried and homogenized with mortar and pestle, then sieved through a 75 μm sieve to remove coarse particles and biologic debris before THg and MeHg analysis.

2.3. Analytical methods

THg measurement in sediments was performed by reduction with stannous chloride solution following oxidation by acid digestion (Li et al., 2005). The digestion procedure required approximately a 200 mg dry weight (d.w.) sample. The sample was placed inside a 25 mL glass tube covered with a glass ball, and 5 mL DDW and 5 mL aqua regia were added in turn, digested at 95 °C for 5 min. After that, 1 mL BrCl solution (27 g of reagent grade KBr and 38 g reagent grade KBrO$_3$ are dissolved in 2.5 L of low-Hg HCl) was added continuously to digest at 95 °C for 30 min. After cooling, the sample reacted for an additional 24 h and 0.2 mL NH$_2$OH·HCl solution (25 g of reagent grade NH$_2$-OH·HCl is dissolved in 100 mL DDW) was added in the sample. Then, THg was determined using cold vapor atomic fluorescence spectrometry (CVAFS). Limit of detection was 0.01 ng/g for THg analysis, which was calculated based on 3 times the standard deviation of blank measurements. The digestion tubes were cleaned by extensive acid washing.

THg analyses in water samples were completed within 2 weeks after sampling according to the U.S. EPA Method 1631 (2001). Mercury in water samples was oxidized using 0.5 mL BrCl/100 mL sample. After oxidation, 0.2 mL NH$_2$OH·HCl/100 mL water sample 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, and then was detected using dual stage gold amalgamation method and CVAFS detection.

MeHg in samples was measured using GC-CVAFS detection (Glas-Col TM568; Tekran Model 2500). MeHg in pore water was analyzed using distillation, ethylation, and GC-CVAFS detection followed US EPA Method 1630 (2001). MeHg in water was measured following EPA method 1630 (USEPA, 2001). An aliquot of 45 mL sample (pore water diluted with DDW) was placed in a fluoropolymer distillation vessel and the distillation was carried out at 125 °C until approximate 35 mL of water was collected in the glass receiving vessel. The sample collected was adjusted to pH 4.9 with an acetate buffer and Hg in the sample was ethylated in a closed 200-mL bubbler by the addition of sodium tetraethyl borate. The ethyl analog of CH$_3$Hg, CH$_3$CH$_3$CH$_2$Hg, was separated from solution by purging with pure nitrogen gas onto a Tenax trap. The trapped CH$_3$CH$_3$CH$_2$Hg was then thermally desorbed, separated from other Hg species by an isothermal GC column, decomposed to Hg(0) in a pyrolytic decomposition column (700–800 °C) and then carried into the cell of a cold vapor atomic fluorescence spectrometer (CVAFS) for detection.

Analysis of MeHg in solid sediment was performed following the procedure developed by Liang et al. (2004). Approximately 0.3 g of sediment was placed into a 50-mL centrifuge tube. 1.5 mL of 1 M CuSO$_4$, 7.5 mL of 3 M HNO$_3$ and 10 mL of CH$_2$Cl$_2$ was added. The tube was closed and shaken for 30 min. 5 mL of the CH$_2$Cl$_2$ layer was pipetted into another 50-mL centrifuge tube after the tube was centrifuged at 3000 rpm for 30 min. About 40 mL of double-deionized water was added to the tube. The tube was heated at 45 °C in a water bath until no visible solvent was left in the tube and the remaining liquid was then purged with nitrogen for 8 min in a water bath at 80 °C to remove solvent residue. The sample was brought to 50 mL with double-deionized water before an appropriate volume (generally 15 mL) of the sample was transferred to a

borosilicate bubbler for methyl Hg analysis following the procedure described previously.

Quality control for the THg determinations was addressed with method blanks, blank spikes, matrix spikes, certified reference materials (GBW07305, IAEA405), and blind duplicates. The average THg concentration of the geological standard of GBW07305 were 0.10±0.01 mg/kg (N=6), which is comparable with the certified value of 0.10±0.02 mg/kg. The percentage of recoveries of spiked samples ranged from 91 to 112% for THg in sediment samples. The relative percentage difference was <0.6% for THg analysis in sediment samples. The average MeHg concentration of 5.45±0.50 ng/g (n=6) was obtained from IAEA405 with the certified value of 5.49±0.53 ng/g. Limit of detection was 0.003 ng/g for MeHg in sediment sample. The average percentage of recovery on spiked samples was 97.9% for MeHg in water samples. The relative percentage difference was <4.5% for total Hg in water and pore water samples.

3.   Results and discussion

3.1.   Sedimentary environment description

As a canyon reservoir, the sediment depth of Baihua Reservoir varied from the upstream to the downstream. The sediment depth was 15, 28–34, 28, 24, 25 and 18–32 cm at XMC, YJZ, MTW, MT, BF and DB, respectively. XMC is 1.5 km from Baihua Reservoir water inlet. The average water flow at the HQ site was about 20–30 m^3/s with a width only about 50 m at HQ site (Zhang, 1999), so no sediment was found at the bottom. Between HQ to XMC, the strong flow rate and narrow riverway disrupted settlement of particulates, this led to the thinnest sediment at this site. At YJZ site, the wider surface water area and lower flow rate led to higher deposition of suspending solid particulate matter, forming the thickest sediment layer. In addition, the input of wastewater from small coal mines increased the sediment thickness. Downstream sediment deposition rates decreased gradually from YJZ to DB. At MT, BF and DB site, the sediment columns included both the flooded soil and sediment, which can be distinguished by physical and chemical characteristics such as such as color, granularity.

Since the reservoir was built in 1966, the sediment core only covered a maximum of 36 to 38 years. It is very difficult to correctly date the sediment cores with such a young age using Pb^{210} or other dating methods. However, we can use the information of the thickness of the sediment and assume that the sedimentation rates were constant at each sampling site to simply date the sedimentation rate at MT, BF, and DB sites. The average sedimentation rate was 0.20 g cm^{-2} a^{-1} in Baihua Reservoir, which was higher than in natural lakes (it was 0.046 g cm^{-2} a^{-1} in Erhai Lake in Yunnan province). However, it is also possible that incomplete profiles due to sediment erosion at the upper stream sites may have also occurred.

3.2.   THg and MeHg in sediment

Compared with aquatic systems impacted by point or non-point sources, sediment THg concentrations are all very high. Concentrations ranged from 0.26 to 38.9 mg/kg, with an
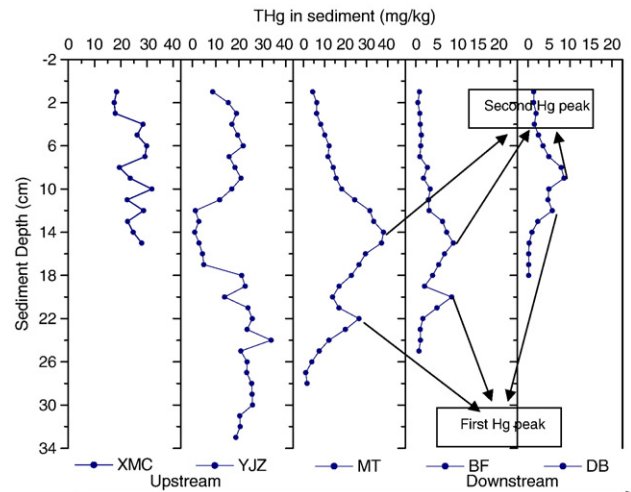

Fig. 2 – The vertical distribution of THg in sediment profiles.

average concentration of 12.9 mg/kg (d.w.) in Baihua Reservoir (as shown in Fig. 2). Generally, in lakes with non-point source contamination, THg concentrations may range from 0.05 to 0.3 mg/kg dry weight (d.w.), while THg concentration can reach 10 μg/kg in some Hg contaminated aquatic systems (i.e. Anirudh et al., 2003; Jacek and Janusz, 2003). In Guizhou province, the background level of THg in soil is about 0.26 mg/kg (d.w.) (Wang et al., 1992). In the same river basin as Baihua Reservoir, He (2007) found the average concentration of THg in sediment from non-point sources contaminated area including Hongfeng Reservoirs was 0.39 mg/kg, while MeHg levels ranged from 2.4 to 3.4 μg/kg (d.w.). French et al. (1999) reported the average concentration of THg in sediment was 39 ng/g in 34 reservoirs in Newfoundland, Canada, and MeHg was 3.89 ng/g in two adjacent reservoirs (Lake Gordon and Lake Pedder) in southwest Tasmanian (Bowles et al., 2003). Hintelmann and Wilken (1995) reported the maximum value for sediment THg in the Elbe River, which was polluted by chlor-alkali and acetaldehyde plants, reached 12 mg/kg (d.w.), with an average THg content of ~8 mg/kg (d.w.). THg in solid sediment ranged from 0.6 to 12 mg/kg in Tagus Estuary, Portugal, which was also polluted by the effluent of a chlor-alkali industry (Canário et al., 2003).

Generally, many factors control Hg methylation, such as sulfur (King et al., 2001; Benoit et al., 1999a,b), pH (Wiener et al., 2006; Kamman et al., 2004), organic matter (Aiken et al., 2003; Haitzer et al., 2003), iron (Mehrotra and Sedlak, 2005; Warner et al., 2003), Hg "aging" (Gilmour et al., 2006; Orihel et al., 2006) and type and activity of bacteria (Munthe et al., 2007), therefore, there are differences in MeHg distribution in sediments among different aquatic systems. Baihua Reservoir was seriously polluted by Hg, but the net methylation rate is low (MeHg/THg % about 0.12%). This suggests that the speciation and spatial distribution of Hg species within a contaminated sediment system with many non-point contamination sources are controlled by complex processes. For methylmercury, its concentration and distribution pattern in sediment can be related with the chemical speciation of mercury in different depth sediment (Castelle et al., 2007).
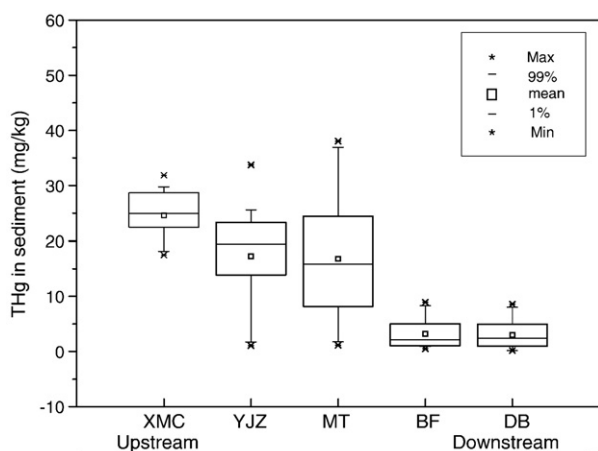
Fig. 3 – The horizontal distribution of THg in sediment cores.

Fig. 4 – The vertical distribution of MeHg in sediment profiles.

3.2.1. Vertical and horizontal patterns of THg

The vertical distribution patterns of THg in sediment profiles are shown in Fig. 2. The vertical distribution patterns show historical Hg contamination in the Baihua Reservoir, which is related to sewage drainage from the GOCP. In non-point source contamination sediment systems of North America, the vertical profiles for THg show a 2 to 4 times increase in surface sediment compared to the deep sediment representing the pre-industrial mercury deposition (Engstrom et al., 1994). Based on background levels of 0.3 mg/kg, two high peaks of THg concentration exist in the middle sediment layers, which are 15 to 129 times higher than the background concentration for Baihua Reservoir (the average value of THg was 43 times the background concentration for all 5 sites) (Fig. 2).

According to the production records of the GOCP, the annual usage of acetic acid increased each year from 1971 to 1975, and the untreated Hg-containing wastewater was directly discharged into Dongmen River, and then flowed into Baihua Reservoir. Statistical information (Qu, 2004) reported a 50% decrease in the acetic acid production in 1976 compared with that in 1975, which presumably corresponded with the first peak of THg in 3 of 5 vertical profiles (Fig. 2). From 1977 to 1985, acetic acid production increased sharply, and wastewater without treatment was discharged into the surrounding environment. Investigation data showed about 41.7 ton Hg entered the surrounding environment from 1977 to 1985 (Qu, 2004), and this made Hg levels in sediment rise sharply, which corresponded with the second high peak in all vertical profiles (Fig. 2). In 1985, this plant applied a new technology called 'the active carbon tower' (FT) to reduce Hg release to the environment from wastewater, and the amount of Hg discharged to the reservoir decreased sharply between 1985 and 1997. Since then, Hg levels in sediment were relatively low, because this plant stopped producing acetic acid using Hg technology. XMC sites did not show the double peaks due to high water flow velocities, and the strong re-suspension by hydrodynamic turbulence (Wang, 1993). This distribution pattern did not exist clearly at YJZ site due to human activity disturbance.

The horizontal distribution of THg in sediment is shown in Fig. 3. For non-point source contaminated reservoirs, no ob-
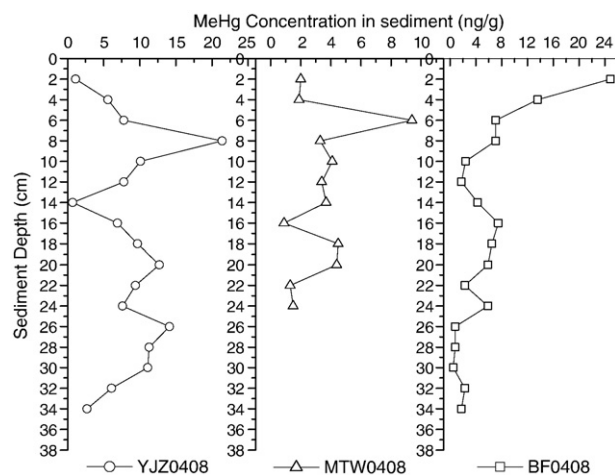
vious spatial differences of THg concentrations were observed in sediment levels from upstream to downstream (the average THg ranged from 0.3 to 0.6 mg/kg) (He et al., 2008). However, in a point source contaminated system, Hg content in sediment was higher upstream and declined with distance from the pollution source, similar to Minamata Bay (Kitamura et al., 1960). Baihua Reservoir is a canyon reservoir, and the major Hg pollution source (namely the GOCP) is located upstream (Fig. 1). Since most Hg in wastewater was bound to particulate matter, more Hg will likely deposit upstream than downstream. This pattern was observed in Baihua Reservoir (Fig. 3), where there was a declining trend in sediment THg concentrations from upstream to downstream. In downstream sites such as BF and DB, THg concentrations declined by 60% and 87% compared to upstream sediment, respectively. The average THg concentration reached 24.6 mg/kg at XMC, whereas it was 3.1 mg/kg at BF and DB. As a whole, the average THg concentrations in sediment profiles were 24.6 (ranging from 17.5 to 31.9) mg/kg at XMC, 17.3 (ranging from 1.1 to 33.7) mg/kg at YJZ, 16.8 (ranging from 1.1 to 38.9) mg/kg at MT, 3.2 (ranging from 0.5 to 8.9) mg/kg at BF, and 2.9
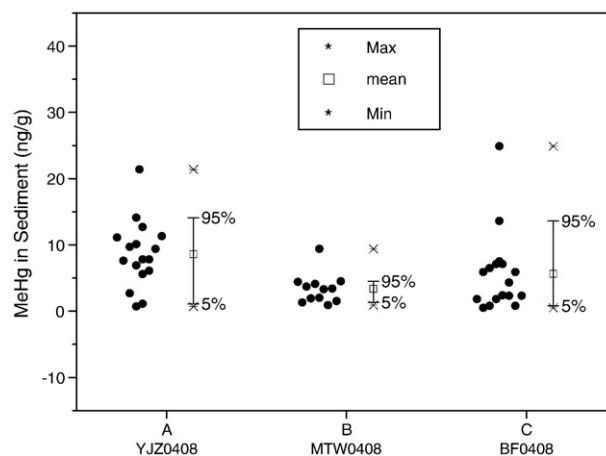

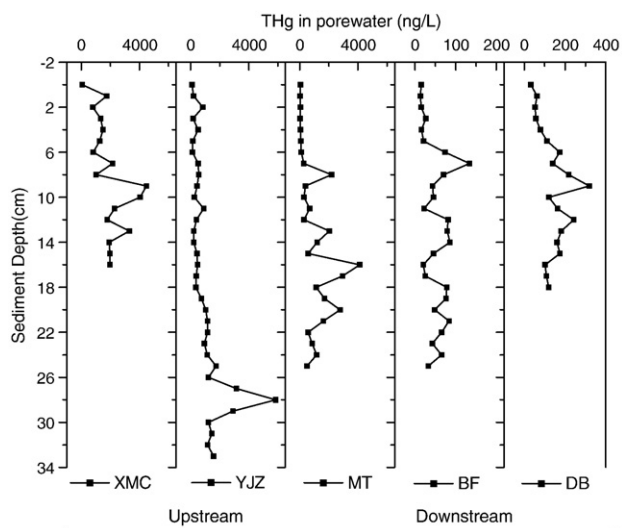Fig. 5 – The horizontal distribution of MeHg in sediment cores.

Fig. 6 – The vertical distribution of THg in pore water.

Fig. 8 – The vertical distribution of MeHg in pore water.

(ranging from 0.2 to 8.6) mg/kg at DB, respectively. Obviously, THg concentrations at the downstream sites (at BF and DB) were much lower than those at upstream sites. At the same time, high THg concentrations existed at the HQ entrance due to flow (Yan, 2005).

3.2.2. Vertical and horizontal patterns of MeHg

As a whole, MeHg concentrations ranged from 0.50 to 27.5 μg/kg(d.w.) and the mean level was 6.1±5.2 μg/kg (average±SD) in the Baihua Reservoir, which exceeded the local background level of 0.2 to 8.4 μg/kg in the adjacent Hongfeng reservoir (He, 2007). The vertical profiles of MeHg in sediment are shown in Fig. 4. Peak MeHg values showed an irregular distribution instead of a peak value between 0 and 10 cm depth, similar to other regional non-point source contaminated reservoirs (Jiang, 2005; He, 2007; Qian, 2007; Bai, 2006).

In YJZ and MTW, the maximum concentration was at 6–8 cm depth and the MeHg concentration was less than 5 μg/kg from 0 to 4 cm depth. However, a MeHg concentration peak was located in surface sediment at BF. According to water quality parameters,
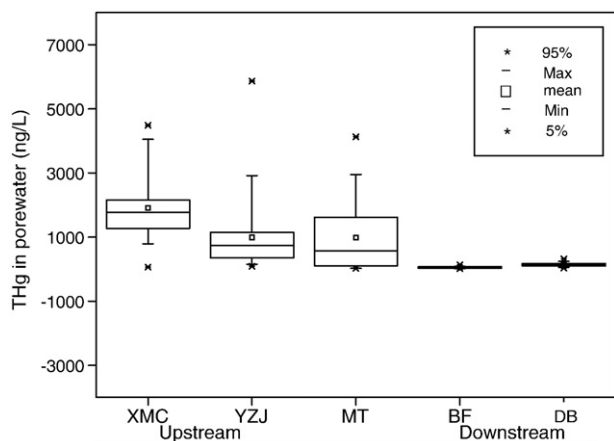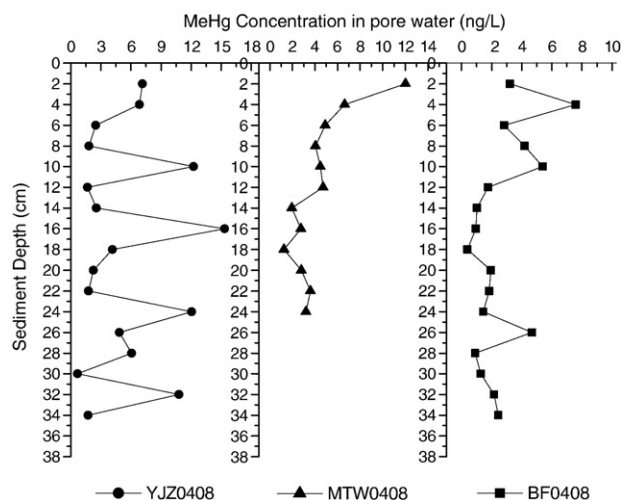
dissolved oxygen (DO) concentrations were 3.1, 1.6 and 1.1 mg/L in water–sediment interface at YJZ, MTW and BF, respectively. Therefore, one possible reason was that the low DO value at BF increased methylation of Hg in surface sediment (Fig. 5).

In middle and bottom layers at YJZ and MTW, the high MeHg content was attributed to high THg level. The MeHg profiles showed a similar distribution pattern of THg at BF (two peak values in middle layer and straight-line pattern with the low MeHg content). This indicated the MeHg came from the methylation of inorganic Hg in middle layer.

Compared to other reservoirs in the region, MeHg in sediment of Baihua is approximately 2–6 fold higher than those in Hongfeng reservoir (the average value is 2.7 μg/kg) (He, 2007), and in Wujiangdu and Dongfeng reservoirs (the average value is less than 2 μg/kg) (Jiang, 2005). The average MeHg content was 8.3±3.9, 3.4±2.3 and 3.4±2.5 (mean±SD) μg/kg (d. w.) from YJZ, MTW to BF, respectively. MeHg did not show a decreasing pattern as THg, because the methylation process was affected by both environmental conditions and THg content. Although the THg concentration was lower at BF than at MTW, the low redox conditions in surface sediment increased the methylation rate.

3.3. THg and MeHg in pore water

THg and MeHg concentrations were very high in pore water in Baihua Reservoir, which reflected the polluted sediment system. THg concentrations ranged between 6.1 and 5860 ng/L and the average level reached 815 ng/L in the whole reservoir. MeHg contents ranged from 0.30 to 15.4 ng/L with an average concentration of 4.82 ng/L in pore water, while the THg and MeHg levels are very low in pore water in non-point source contaminated reservoir. For example, the average THg and MeHg in pore water are 23.2±8.4 and 1.60±1.1 ng/L in summer in Hongfeng Reservoir, respectively (He et al., 2008). This demonstrated the pore water is also seriously contaminated with Hg in Baihua Reservoir.

The adsorption of Hg in solid phase and liquid phase of sediment is a complex physical–chemical process. Organic
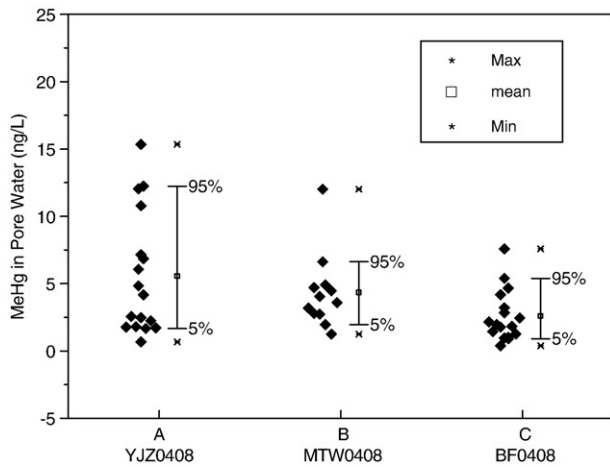

Fig. 7 – The horizontal distribution of THg in pore water.

Fig. 9 – The horizontal distribution of MeHg in pore water.

matter, clay minerals and oxides of iron and manganese all adsorb Hg in sediment. Other factors, such as the concentration gradient (Jiang, 2005), temperature (Kotnik et al., 2002; Bodaly et al., 1993), pH value (Miskimmin et al., 1992; Steffan et al., 1988), oxide potential (Ramamoorthy et al., 1982) and so on can also affect the Hg distribution in pore water. Due to nearby small coal mines, the nutrient salts (TP concentration is from 800 to 3000 mg/kg) (Wu et al., 1996) in sediment, and Fe (0.26 mg/L), Mn concentrations (from 0.56 to 1.16 mg/L) in water–sediment interface are all high in Baihua Reservoir (Bai et al., 1995), which may affect the solid-liquid equilibrium of Hg between sediment and pore water.

3.3.1. Vertical and horizontal patterns of THg

The vertical distribution patterns of THg in pore water are shown in Fig. 6. At DB, MT and BF, THg concentrations in pore water show a declining pattern in surface sediment. It is possible that Hg input declined year by year, which affected the diffusion of pore water Hg into the water column. Due to the impact from coal mines waste, the distribution patterns for THg in pore water at XMC and YJZ were some what different from other sites.

In Baihua Reservoir, THg concentrations in pore water of surface sediment were significantly higher than THg concentrations in the overlying water (Yan, 2005). The re-suspension of particulates in surface sediment may be also an important Hg source to the water column (especially, for bottom water). Re-suspended sediments with high Hg levels are also a potential threat for aquatic biota living on organic matter from the surface sediments.

Fig. 7 shows the average THg concentrations in pore water decreased with distance from the GOCP. In downstream sites such as BF and DB, Hg levels were relatively low. However, the average THg concentration at DB was slightly higher than at BF. The main reason was that BF was an important aquaculture area, where organic matter concentrations in sediment were much higher than at the DB site (Yan, 2005), and more Hg was therefore absorbed in organic particulate phases at BF than that at DB. XMC is located 1.5 km from HQ, where Hg-containing wastewater from the GOCP was discharged into Zhujia River and crossed Dongmen Bridge, and eventually flowed into Baihua Reservoir. Although

GOCP stopped discharging Hg contaminated wastewater in 1997, Hg concentrations were still relatively higher at XMC than those at the other four sites. On one hand, high Hg concentrations in sediment resulted in the high Hg concentrations in pore water. On the other hand, the re-suspension of sediment due to the dynamic flow of water stimulated the transformation of Hg from solid phase to dissolved phase.

3.3.2. Vertical and horizontal patterns of MeHg

In Baihua Reservoir, the MeHg concentration profile in pore water is different in three sites (Fig. 8). MeHg content obviously fluctuated from surface to bottom in pore water at YZJ and the maximum value (15.4 ng/L) located at 16 cm depth. The MeHg content is about 7 ng/L in 0–4 cm depth pore water at YZJ. The MeHg concentration distribution alternated between high and low from 8 to 34 cm depth. One possible reason is that the methylation processes occurred at the middle or bottom part of the sediment, while another possibility is that the MeHg peaks could be relics of former inputs and/or be conserved due to limited demethylation (Castelle et al., 2007). The MeHg peaks occurred in between 0 and 10 cm depth, and the maximum values are 12.0 and 7.2 ng/L in MTW and BF, respectively. The maximum MeHg concentration in Baihua Reservoir is 10–20 fold higher than in Hongfeng Reservoir (He, 2007), but is comparable to that in Wujiangdu Reservoir (11.03 ng/L) and Dongfeng Reservoir (11.85 ng/L) (Jiang, 2005). However, the MeHg concentration profiles are different among the three sites in Baihua Reservoir.

The distribution pattern of MeHg in pore water showed a decreasing trend with distance from the GOCP (Fig. 9). The MeHg concentrations are 5.6±4.5, 4.4±2.8 and 2.6±1.9 ng/L (mean±STDEV) at YJZ, MTW and BF, respectively. MeHg levels showed a decreasing trend with the increasing direction from the pollution source (the GOCP). Compared with these unpolluted reservoirs in the same area, MeHg in pore water is similar or slightly higher. According to a study by Jiang (2005), the MeHg concentrations varied from 0.25 to 11.85 ng/L with an average value of 3.29 ng/L and from 0.09 to 11.03 ng/L with an average value of the 1.65 ng/L in Dongfeng and Wujiangdu Reservoir in July, respectively.

3.4. The diffusion fluxes of THg and MeHg of the sediments/water interface

Transfer and diffusion from sediment to water include molecular diffusion, hydraulic disturbance and bioturbation. Here, molecular diffusion is an important way to transfer solutes from sediment to overlaying water (especially for MT and DB sites). The diffusion flux of THg and MeHg between sediment and water was estimated using the measured concentration gradient and Fick's first Law (Berner, 1980):

$$\text{Fd} = -\Phi \cdot D_w \cdot dc/dz \qquad (1)$$

$$D_w = D_0 \cdot \Phi^2 \qquad (2)$$

Where Fd is the diffusive flux (ng·m^{-2} d^{-1}), Φ is the sediment porosity, dc/dz is the gradient of Hg in the bottom water and pore water in surface sediment (1–2 cm), D_w and D_0 are the diffusion coefficient in water and ideal solution, respectively.

According to Wan et al. (1990), the sediment porosity is 0.93 in 0–4 cm in Hongfeng Reservoir which is an adjacent reservoir to Baihua Reservoir and has a similar sedimentary environment. Thus, here we choose Φ as 0.93. D_0 is 9.5×10^{-6} and 1.3×10^{-5} cm^2/s for THg and MeHg, respectively (Gill et al., 1999). The Hg content in bottom water refers to the average THg and MeHg content in water–sediment interface (Yan, 2005).

Based on those data mentioned above, the average diffusion flux value is 1642 and 36 ng m^2/day for THg and MeHg from sediment to water, respectively. The MeHg flux is similar to Hongfeng and Wujiang Reservoir, but the THg flux is two orders of magnitude higher than that in Hongfeng Reservoir (Jiang, 2005; He, 2007). This suggests that sediment is an important inorganic Hg source for overlying water and the net methylation rate is low in the sediment.

4. Conclusions

The sediments and pore water of Baihua Reservoir still contain high concentrations of Hg, although the major contamination source stopped discharging Hg contaminated wastewater to the reservoir, and no measures were taken to eliminate Hg from the sediment. The vertical distribution of Hg in sediment profiles at most sampling sites reflected the history of Hg discharge from the GOCP. Hg concentrations in surface sediments decreased significantly because of the fact that the GOCP stopped using Hg to produce acetic acid in 1997. As a whole, the average THg and MeHg concentrations in sediment cores decreased from the upstream to downstream due to the deposition of particulate Hg, which is the major form of Hg in natural aquatic systems. Sediment pore water also contained elevated Hg concentrations, which may be an important Hg contamination source to the overlying water column. The maximum THg concentrations in pore water also occurred in the middle part of the sediment cores. Similar to sediment, THg in pore water showed the declining pattern with increasing distance from the GOCP. Our data suggested that (1) the sediment suffers from serious contamination of Hg and the contaminated sediment is an important Hg contamination source to the overlying water; (2) THg input and/or concentration are not the only factors controlling MeHg concentration in sediment. In addition, further studies are needed to address the impact of sediment to Hg distribution in water column and accumulation of Hg in biota in Baihua Reservoir. The parameters that may affect methlylation and demethlylation processes should be measured in sediment and pore water (such as pH value, sulfur, type and activity of bacteria, iron) to understand the methlylation process in sediment further.

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