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Spatial distribution and methylation of mercury in a eutrophic reservoir heavily contaminated by mercury in Southwest China

Haiyu Yan [a], Qiuhua Li [c], Bo Meng [a], Cuiping Wang [d], Xinbin Feng [a,*], Tianrong He [d], Janusz Dominik [b,1]

[a] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, China
[b] Institute F.-A. Forel, University of Geneva, Route de Suisse 10, C.P. 416, CH-1290 Versoix, Switzerland
[c] Guizhou Mountain Environment Key Laboratory, Guizhou Normal University, China
[d] College of Resources and Environmental Engineering, Guizhou University, China

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ABSTRACT

In Baihua Reservoir (BHR), a Hg-contaminated and eutrophic reservoir in SW China, water and sediment samples were collected in June 2010 for the determination of Hg species, metal, major ion and nutrient concentrations. Using a stable isotope tracer technique, $^{202}HgCl_2$ and $Me^{198}HgCl$ were spiked into sediment cores to study methylation and demethylation processes. The inorganic Hg concentration range was 600–13,000 ng/g (dry weight, dw) in the top 10 cm of sediment; exceeding the local background concentration (260 ng/g, dw). Concentrations of Hg species in the water column and pore water were similar to non-Hg contaminated reservoirs in the same watershed. Dissolved total Hg(DHg)and dissolved methylmercury (DMeHg) (mean ± SD) in the pore water in BHR were 6.8 ± 3.1 and 0.27 ± 0.20 ng/L, respectively. Dissolved Hg, DMeHg and reactive Hg (RHg) in the water column were 2.3 ± 0.9, 0.23 ± 0.22, and 0.77 ± 0.17 ng/L, respectively. The vertical distributions of Hg species showed inorganic Hg and methylmercury (MeHg) concentrations peaked near the bottom of the water column, implying the impact of thermal stratification and eutrophic conditions on the production and distribution of Hg species in this reservoir. The methylation rate (<0.1%/day) in these sediments was lower and the demethylation rate (17.6%/day) was higher than those reported in other eutrophic reservoir studies.

1. Introduction

Mercury is a trace toxic metal that exists in the atmospheric, aquatic and soil systems. Methyl Hg is a highly neurotoxic Hg species and tends to accumulate and biomagnify in predatory fish in aquatic ecosystems. Chemical and mining industry discharges and coal burning emissions are major sources of Hg to aquatic environments (Wang et al., 2004). Methyl Hg concentrations in fish can reach very high concentrations as a result of methylation of inorganic Hg in the sediment and subsequent bioaccumulation of MeHg in the food chain (Bravo et al., 2010). Therefore, the methylation mechanisms of Hg in aquatic ecosystems are of particular concern in Hg research (Therriault and Schneider, 1998; Hylander et al., 2006; Carrasco et al., 2011).

Previous studies (Chen et al., 1996; Drott et al., 2008; Li et al., 2010; Feyte et al., 2012) have shown that Hg methylation is influenced by multiple factors, such as inorganic Hg, dissolved organic C (DOC), sulfide (S^{2-}), dissolved O_2 (DO), temperature (T), pH, and SO_4-reducing bacteria activity (SRB). Recently, eutrophication has been thought to have an important effect on methylation and biogeochemical cycling of Hg, because eutrophication may increase DOC and lower DO and thus could enhance Hg methylation (He et al., 2008; Gray and Hines, 2009; Wang et al., 2012). In addition, eutrophication can change other physical, chemical and biological parameters, such as nutrients, particle characteristics, Fe and bacteria in the water and sediments. All these characteristics are important factors influencing the Hg methylation process.

Baihua Reservoir (BHR) is a Hg-contaminated and eutrophic reservoir in SW China. The reservoir was severely contaminated with Hg released from the Guizhou Organic Chemical Plant (GOCP) from 1971 to 1997. Previous studies have shown total Hg (THg) to be as high as 38.9 mg/kg dry weight (dw) in the sediment profile, and up to 5860 and 153 ng/L in the pore water and water column, respectively (Wang, 1993; Yan, 2005; Yan et al., 2008). Despite the extremely high concentrations of THg in the water and sediments of BHR, the average concentrations of THg and MeHg in fish samples (wet weight, wt), including some carnivorous fish, were much lower than 300 ng/g (Yan, 2005; Yan et al., 2010; Liu et al., 2012). Although the distribution and transport of Hg species in the water and sediments of BHR have been studied previously, it remains unclear why Hg in fish is low. In 2009, a Sino-Swiss collaboration project was conducted, aiming to investigate the geochemical cycling of Hg species in this reservoir and to understand mechanisms leading to the low Hg concentration in fish. The recent research

* Corresponding author. Tel.: +86 5890356; fax: +86 5891356.
E-mail address: fengxinbin@vip.skleg.cn (X. Feng).
[1] Present address: Istituto di Scienze Marine – CNR, Venezia, Italy.

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suggested that the low fish Hg in BHR could be attributed to the low MeHg concentrations in the oxic layer of the water column and limited bioaccumulation of MeHg along the short food chains found in this reservoir (Liu et al., 2012). In this study, the distribution of Hg forms was further examined and the methylation processes in BHR investigated by the stable isotope tracer technique, with the objective of understanding the main factors that influence MeHg production, transport and fate.

2. Methods and materials

2.1. Study area

Baihua Reservoir (106°27′–106°34′ N, 26°35–26°42′ E) is located approximately 16 km NW of Guiyang, Guizhou Province, SW China. The reservoir is long and narrow, has an average water depth of 13 m, and has a mean water residence time of 1 month (Yan et al., 2010). Baihua reservoir is one of the reservoirs built on the Maotiao River and its closest neighboring reservoir is Hongfeng Reservoir (~20 km up stream). Besides the Maotiao River, there are three small seasonal streams flowing into the BHR; however, they make a limited contribution to its volume. The surface area of BHR (14.5 km^2) covers 0.77% of its watershed area. The reservoir has a typical karstic topography with limestone and dolomite being the dominant bedrock types. The watershed has dense vegetation cover and the major soil types are calcareous and yellow soil.

The GOCP is located ~18 km upstream of BHR and used Hg as a catalyst for producing acetic acid during the period 1970–1997. The discharge from the plant enters BHR through a small river (Zhujia River), which is joined by another small river at Dongmen Bridge, before flowing into Maotiao River (Fig. 1). The reported concentrations of THg in Zhujia River ranged from 250 to 1000 ng/L (Yan, 2005).

2.2. Sample collection

In June 2010, sediment, water and plankton samples were collected at three sites in BHR for measurements of Hg and ancillary variables. These three study sites (Y, M and D) were chosen to represent the upper, middle and lower reaches of the pelagic part of the reservoir (Fig. 1), respectively. The water depths at these three sites were 12, 16 and 20 m, respectively.

2.2.1. Water column samples

Water samples were collected using a 10-L Niskin sampler (at 0.5, 5, 6, 7, 8, 12, 14, 18 m depths, depending on site). A part of the water sample was filtered using a 0.45 μm membrane (Millipore) for the determination of DHg and DMeHg. The filters were then used for the analysis of chlorophyll a (Chl-a), particulate total Hg (PHg) and particulate methylmercury (PMeHg). For the analysis of DOC, water was filtered through a Whatman (GF/F) glass-fiber C-free filter. The unfiltered water samples were collected for reactive Hg–RHg, the abundance and species of plankton, and ancillary variables such as total P (TP), total N (TN), Chl-a, and total suspended solid (TSS).

The *T*, pH, DO, total dissolved solid (TDS), Chl-a, and Blue green algae – phycoerythrin (BGA) were also measured using *in situ* probes (YSI-6600V2, USA) at 0.5, 1 and 2 m depth, followed by intervals of 2 m.

2.2.2. Sediment samples

Since Hg methylation mainly takes place in the surface sediments, only the upper 10 cm were collected for this study. These

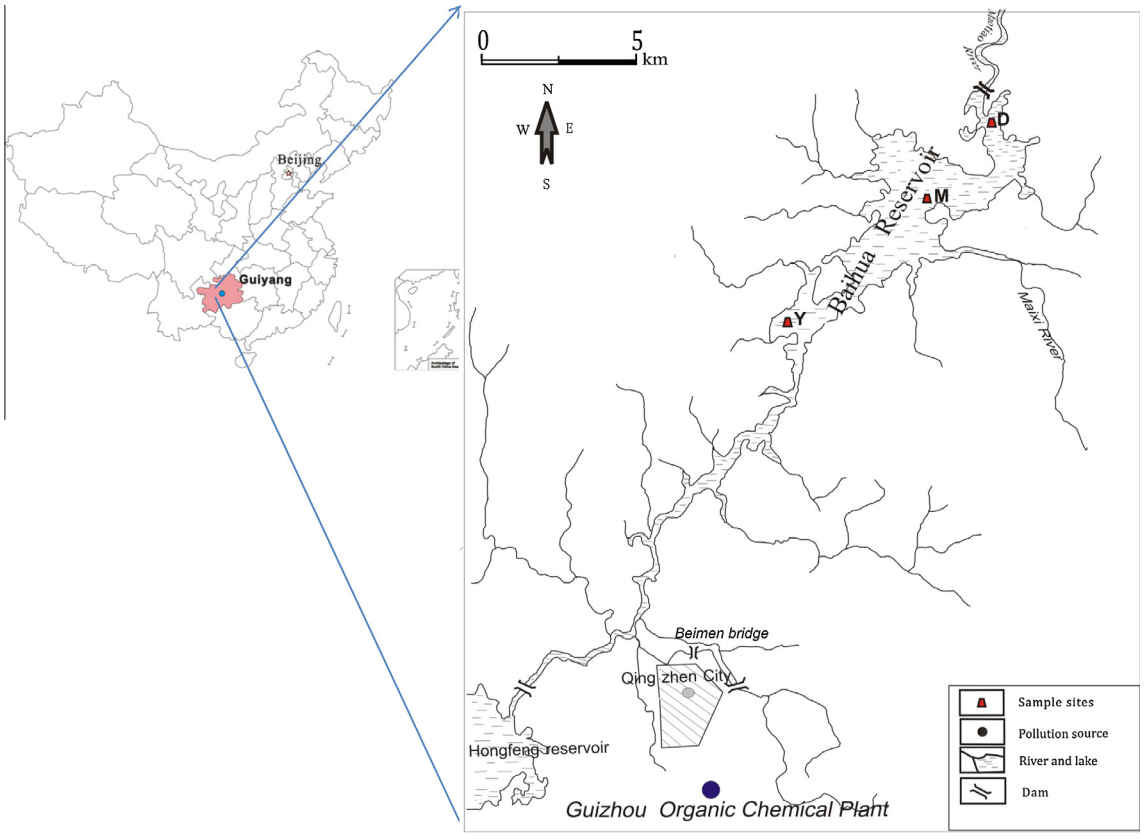

Fig. 1. Location of the study area and sampling sites in Baihua Reservoir.

sediments were collected using a gravity corer. The overlying water in the core tube was siphoned down to about 0.5–0.2 m above the sediment surface. It was filtered and preserved for the same analyses as described in Section 2.2.1. Within a few hours of collection, sediment cores were sectioned in an O_2-free glove box filled with N_2. Sediment samples were placed in centrifuge tubes, capped and sealed with parafilm. Following centrifugation, the samples were returned to the glove box where the pore water was filtered using 0.45 μm nitrocellulose filters and the filtrate was divided for DHg, DMeHg, and other analyses (such as DOC and S^{2-}). Two aliquots of the pore water were acidified with 0.5% (v/v) ultrapure HCl for DMeHg and DHg analysis. A third aliquot was treated with a 6% Zn-acetate solution to precipitate sulfides and then preserved in 0–4 °C prior to the quantification of dissolved S^{2-}. A fourth and fifth aliquot were obtained for the measurement of DOC and anions, respectively. The sixth aliquot was acidified with ultrapure HNO_3 for cation analysis.

The water samples used for Hg analysis were stored in precleaned 200 mL borosilicate glass bottles and acidified upon collection to 0.5% v/v with sub-boiling distilled ultra-pure HCl acid. The borosilicate glass bottles were acid-cleaned followed by baking in a Muffle furnace at 500° C for 1 h. Samples for plankton analysis were preserved in a 3–5% formalin solution. All aqueous samples were stored at 0–4 °C prior to analysis, while solid sediment was stored in a freezer.

2.3. Analysis methods

2.3.1. Water and pore water

Concentrations of DHg in the water column, overlying water and pore water were measured using dual stage Au amalgamation and cold vapor atomic fluorescence spectrometry (CVAFS, Tekran model 2500), following sample preoxidation by 0.5% v/v BrCl, reduction by 0.2% v/v $NH_2OH{\cdot}HCl$ and $SnCl_2$, and pre-concentration of Hg^0 onto a Au trap with an aspirator. Concentrations of RHg in unfiltered water samples were determined according to USEPA method 1631e, (USEPA, 2002), after $SnCl_2$ addition and purging by Hg-free N_2. The PHg was measured using a thermal combustion method (AMA 254, Leco®) at Institute F.-A. Forel, University of Geneva, Switzerland. The DMeHg concentrations were determined using gas chromatography (GC)–CVAFS following USEPA Method 1630 (USEPA, 2001), after sample distillation and ethylation (Liang et al., 1994; Jiang et al., 2004). The PMeHg was determined by a HNO_3 leaching/CH_2Cl_2 extraction method, followed by ethylation, purging, and trapping onto Tenax® traps, and GC separation and detection by Tekran® (Model 2500, Tekran Inc., Ontario, Canada) (Horvat et al., 1993; Liang et al., 1994; He et al., 2004; Liu et al., 2012). The THg and TMeHg were obtained as the sum of dissolved and particulate forms of Hg and MeHg.

Anions and cations were measured using ICP-OES (Vista MPX, Varian, America) and IC (ICS-90, DIONEX, America) at the Institute of Geochemistry, the Chinese Academy of Sciences. The DOC was determined by high temperature catalytic oxidation (Li et al., 2008). The S^{2-} in the pore water samples was measured by the methylene blue method (Cline, 1969).

Analysis of TP, TN, and Chl-a were performed according to the methods described by Li and Han (2007). Briefly, TN and TP were determined after digesting with potassium persulfate, NH_4–N, NO_3–N, and PO_4–P were measured following a colorimetric procedure after filtering with 0.45 μm glass fiber filters. Analyses of these parameters were performed following the procedures outlined in the Chinese Standard Methods for Water Quality Analysis (GB3838-2002). Membranes for Chl-a analysis were steeped in 90% acetone solution for 24 h after being frozen and thawed repeatedly.

2.3.2. Sediment

Sediment samples were freeze-dried and homogenized before the analysis. Total Hg and MeHg in the sediments were determined at the Institute F.-A. Forel, University of Geneva, Switzerland. The THg was analyzed using a thermal combustion method (AMA 254, Leco®). The MeHg in solid matrix was extracted (Liu et al., 2012) using a HNO_3 leaching/CH_2Cl_2 extraction method, followed by ethylation, purging, trapping, GC separation (Bloom, 1989) and AFS detection (Model 2500, Tekran Inc., Canada). Loss on ignition (LOI%) was measured by heating the dried sediment samples at ~550 °C for 30 min. The TN and TP were measured using the national standard analysis method of total N and P in soil (GB9837-88, 1988, Qian et al., 1990).

2.4. QA/QC

In water samples, the detection limits for THg and MeHg, obtained from method blanks (blanks + 3 standard deviations), were 0.09 and 0.03 ng/L, respectively. Field blanks were similar to laboratory blanks indicating adequacy of the applied clean procedure of sampling. Since mean blanks for THg and MeHg were below 3.9% and 13% of the lowest measured concentrations in water samples, the results presented were not corrected for blanks. Because the measurements of MeHg required an extraction procedure, recovery was controlled with a matrix spike. The MeHg spike recovery was in the range of 89.2–103.1%. The relative differences between duplicate samples were always below 4.5% and 5.4% for THg and MeHg, respectively.

For sediments, detection limits were 0.07 and 0.003 ng/g dw for THg and MeHg, respectively. Accuracy, verified with reference materials, was satisfactory. For MESS-3 THg a concentration of 0.084 ± 0.001 mg/kg; $n = 3$ was obtained (certified THg concentration 0.091 ± 0.0009 mg/kg). For ERM CC580 a MeHg mean concentration of 70.6 ± 0.6 ng/g; $n = 7$ was obtained (certified value 70.2 ± 3 ng/g). The relative differences between duplicate samples were always below 14% and 20% for THg and MeHg, respectively.

2.5. Experiment and calculation of specific methylation and demethylation rate constants

For studying methylation and demethylation processes in sediment, two duplicate intact sediment cores were spiked carefully at 1-cm interval using a gas-tight syringe. The isotope-enriched $^{198}HgCl_2$ and $Me^{202}HgCl$ were pre-equilibrated with overlying water. The Hg spikes were added at concentrations of 10% and 100% of the ambient concentration for THg and MeHg in sediment, respectively (Gilmour et al., 1998).

For accurate determination of MeHg concentrations, all spiked samples were divided into two parts (duplicate sediment cores were treated in the same manner). One part was frozen in liquid N_2 immediately, representing $t = 0$ days (t_0). The other part was put back at the water/sediment surface and incubated at *in situ* temperature for 48 h, representing $t = 2$ days (t_2). Then the incubation was stopped by freezing in liquid N_2. The formation of $Me^{198}HgCl$ and the decrease in $Me^{202}HgCl$ were measured using a GC–ICP-MS system following the ethylation-purge-trap method (Gilmour et al., 1998; Mao et al., 2008). The rates of Hg methylation and MeHg demethylation were calculated according to the standard method (Hintelmann et al., 1995, 2000), assuming that (1) both Hg methylation and MeHg demethylation follow first-order kinetics; (2) back reactions of newly added spikes are negligible; and (3) the bioavailability of added spikes remains constant throughout the experiment.

3. Results and discussion

3.1. Physical and chemical parameters of water column

3.1.1. Standard water quality parameters

A decreasing trend from the surface to the bottom of the water column was observed for all parameters (except TDS) at all three sampling sites (Fig. 2). All parameters showed an inflexion point at 6 m depth due to thermal stratification of water in summer, with the thermocline located at 5–6 m depth. The pH of water was neutral-alkaline (7.5–8.7), as in other reservoirs in Guiyang (Feng et al., 2011). The highest BGA occurred at 0.5 m depth with 2–4 × 10^4 cells/mL and showed a decreasing trend from Y, through M to D sites.

3.1.2. Phytoplankton, nutrients and TSS in water column

The maximum Chl-a concentrations were observed in surface water (46.5, 37.1 and 31.7 μg/L) with average concentrations of 38 ± 8, 27 ± 9 and 21 ± 9 μg/L (n = 3) within the top 6 m depth at the Y, M and D sites, respectively (Fig. 3). Among the 62 species of phytoplankton found in BHR, the three most abundant species were Cyanophyta (60%), Bacillariophyta (24%), and Chlorophyta (12%) (Fig. 4). Pyrrophyta, Euglenophyta and Cryptophyta represented about 6%. In the upper 8 m water layer, Cyanophyta made up to 70%. The abundance of phytoplankton showed a maximum value at the surface for the M and D sites, but at 6 m depth for the Y site. The maximum concentrations of TN and NO_3–N were observed at 5–8 m depth. The NH_4–N concentrations were highest in deeper water (10–14 m) although at site D a maximum was observed at 6 m. The highest TP concentrations occurred below 8 m depth. The concentrations of TP, TN, NO_3–N and NH_4–N, averaged by combining data from the three sampling sites, were 0.09, 1.10, 0.26, and 0.25 mg/L, respectively, with ranges of 0.04–0.22, 0.65–2.09, 0.04–0.57 and 0.03–1.44 mg/L, respectively. The NO_3–N concentrations were higher at the M site than at the D and Y sites, while NH_4–N concentrations were highest at the D site. The PO_4–P was usually detected only below 8 m with concentrations increasing with depth and reaching 113, 182, and 61 μg/L at sites Y, M and D, respectively.

3.1.3. Ions and DOC in water

The concentrations of K^+ and SO_4^{2-} showed only small variations in the water column at three sites (Fig. 5). During this survey, K^+ and SO_4^{2-} concentrations decreased slightly from the thermocline to the hypolimnion. Sulfate concentrations were similar to those observed in other reservoirs located in the same watershed in Guizhou province (He, 2007; Meng, 2011). The concentrations of DOC in water were about 2–3.5 mg C/L and have remained relatively consistent for the past decade (Yan, 2005).

3.2. Hg in water and pore water

3.2.1. Hg speciation and concentration in water profiles

3.2.1.1. RHg, DHg, PHg and THg in water. The THg concentrations in water overlying sediments were up to 40, 46 and 10 ng/L at sites Y, M and D, respectively, largely exceeding the concentrations in the

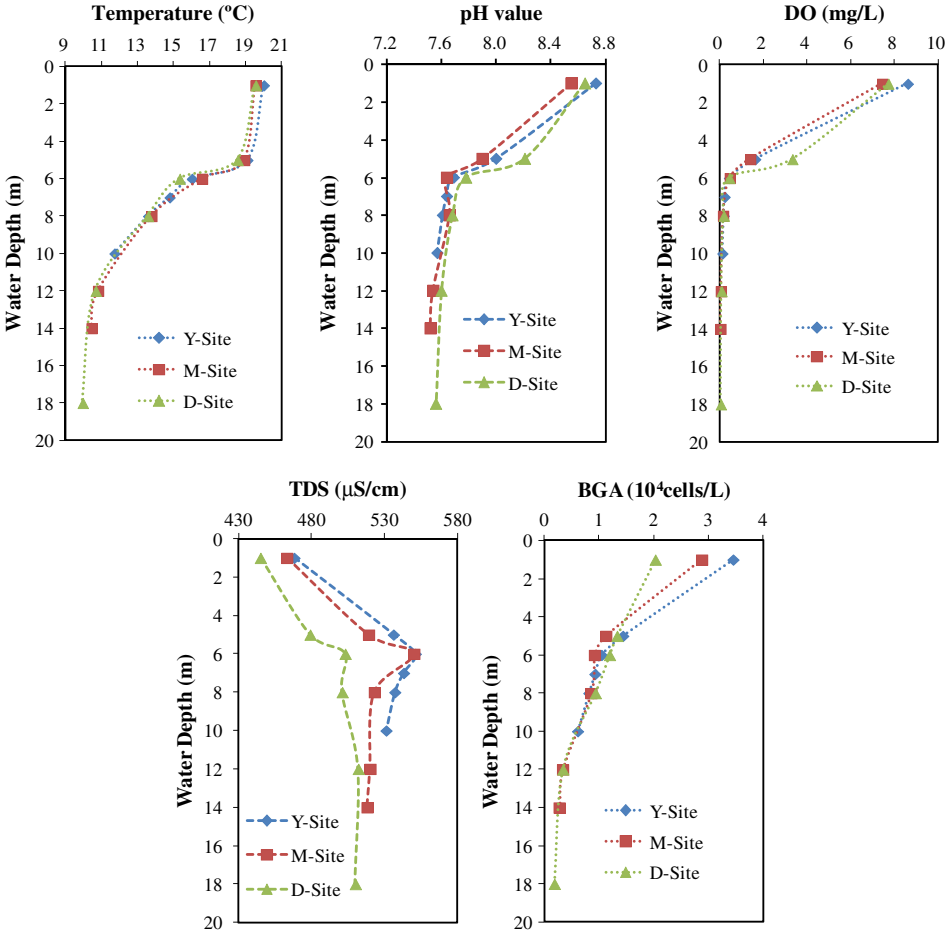

Fig. 2. Profiles of water quality parameters at three sites (DO – dissolved O_2, TDS – conductivity, BGA – blue–green algae) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

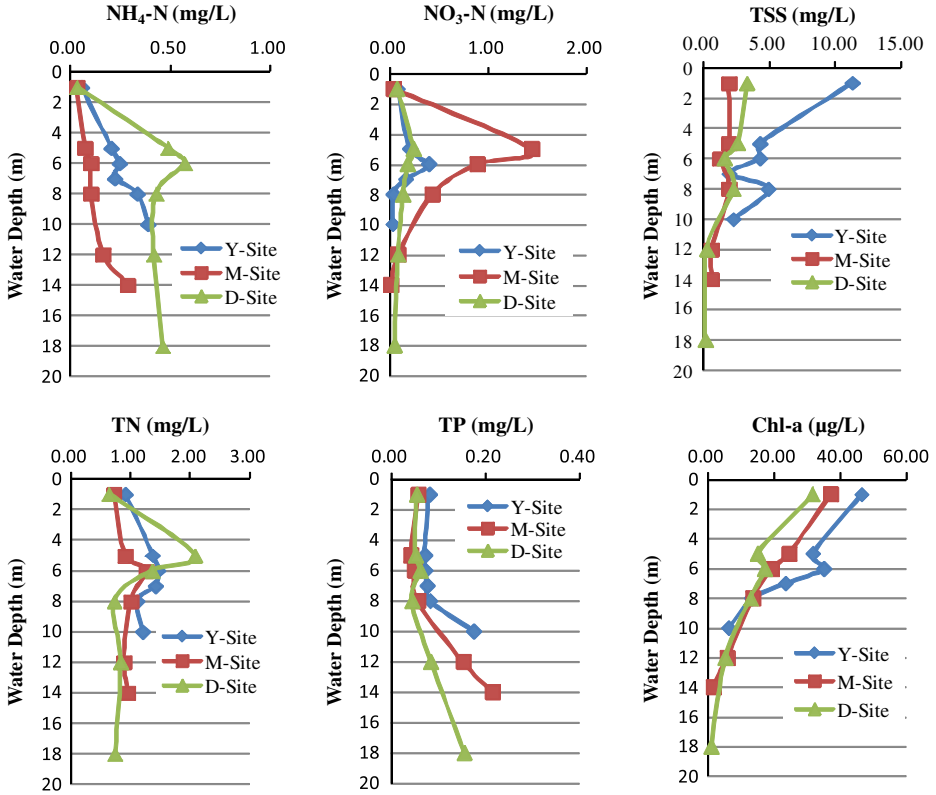

Fig. 3. Total suspended solid (TSS), Chl-a and nutrient concentrations in water columns.

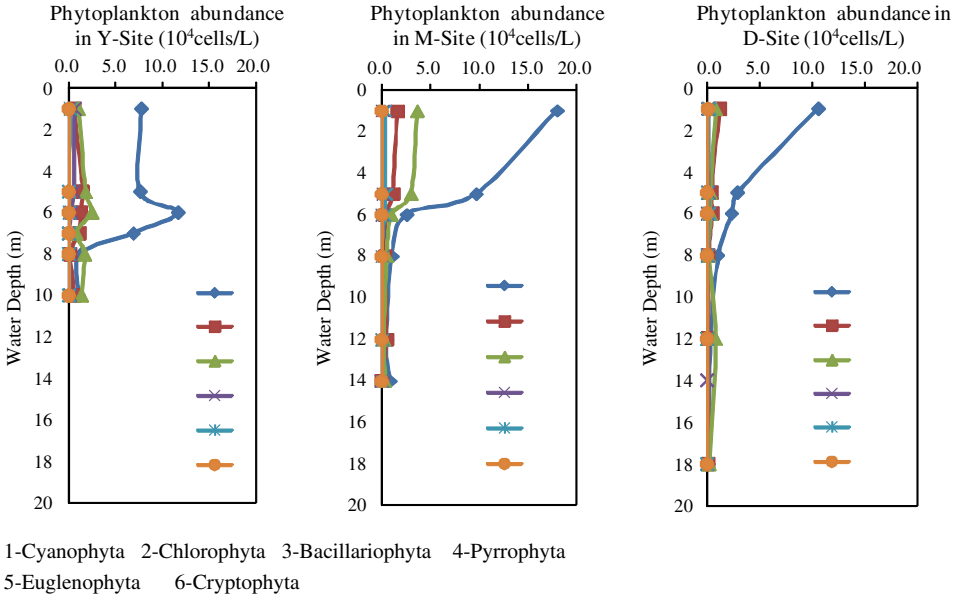

Fig. 4. Phytoplankton abundance in water columns.

water columns. The percentage of PHg in THg in overlying water was 82%, 93% and 63% for sites Y, M and D, respectively. The main reason for this was the re-suspension of surface sediment.

Compared to the previous study in which the average RHg, DHg, PHg and THg were 2.5, 10, 12 and 22 ng/L, respectively (Yan, 2005), all Hg species in water were lower in this survey (Fig. 6a), with the concentrations (average ± SD for three sites combined) being 0.77 ± 0.17, 2.2 ± 0.9, 1.9 ± 1.0 and 4.1 ± 1.3 ng/L for RHg, DHg, PHg and THg, respectively. These Hg concentrations approximate to natural lakes or Hg non-contaminated aquatic systems (He et al., 2008; Zhang et al., 2009; Jeremiason et al., 2009). The reduction in Hg concentrations in BHR could be attributed to the elimination or decrease of wastewater discharge from the pollution sources, including the discharge control of GOCP, which abated Hg input to BHR.

Horizontally, the average concentrations of THg in the water column decreased from 5.3 ± 0.9 ng/L at site Y to 4.3 ± 0.6 ng/L at site M and 2.6 ± 0.3 ng/L at site D, indicating the effect of an

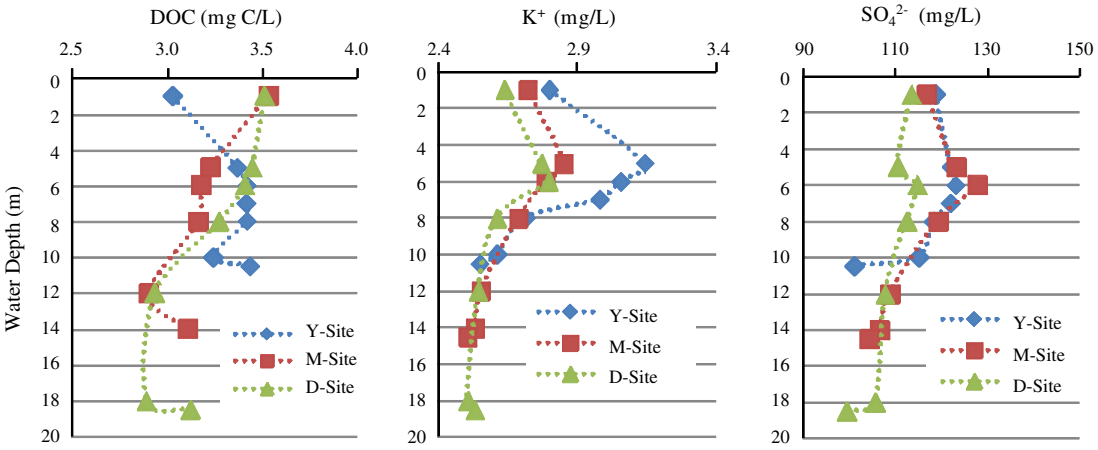

Fig. 5. Dissolved organic C (DOC), K^+, SO_4^{2-} concentrations in water columns.

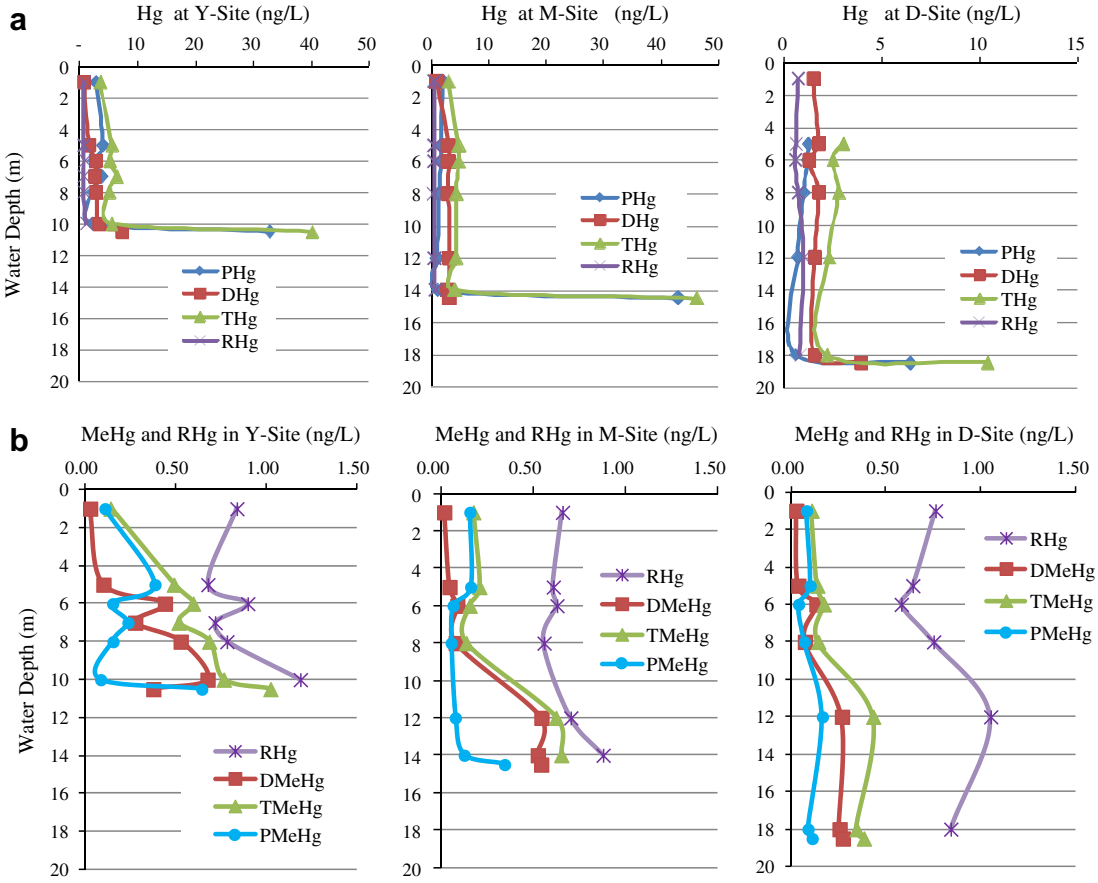

Fig. 6. Mercury species concentration in water columns (see text for species abbreviations).

upstream pollution source of Hg. Similar patterns existed for RHg, DHg and PHg.

The RHg concentrations are usually low in aquatic systems, accounting for less than 15% of THg. The average percentage of RHg as THg was 15% at the Y and M sites, but 30% at site D. The RHg concentrations (average 0.77 ± 0.17 ng/L) showed a slightly increasing trend from the upper to bottom water layers. In the surface water at sites Y and M, a large part of DHg was RHg, but the percentage of DHg as RHg declined with depth. One possible reason could be that the diffusion of DHg from sediments was important, at least at sites Y and D, where strong DHg concentration gradients between overlaying water and the hypolimnion were observed. But at greater distance from the sediment/water interface, the DHg can be influenced by interacting with particles as the THg in the hypolimnion showed only small variations with depth.

The RHg can be considered as a bioavailable Hg form and thus a high proportion of RHg would favor methylation. In Fig. 6b, the similarity in the distribution patterns of RHg and DMeHg indicates that more bioavailable RHg would increase methylation, and RHg or RHg/DHg% could be used to indicate the potential methylation rate. At the Y and M sites, the RHg distribution pattern was similar to that at the D site, but the DMeHg/RHg ratio in the oxic layer was

much lower than in the anoxic layer. This result suggests that anoxic conditions are favorable for methylation when RHg is in sufficient supply, or the demethylation rate is higher in the oxic layer than in the anoxic one.

3.2.1.2. MeHg species in water column and factors affecting methylation. For the whole reservoir, the average DMeHg, PMeHg and MeHg concentrations in the water column were 0.23 ± 0.22, 0.13 ± 0.08 and 0.36 ± 0.23 ng/L, respectively. These concentrations were slightly lower than previously observed in this system (Yan et al., 2003; Yan, 2005), but still higher than those determined for other reservoirs in the same watershed (Yao et al., 2010; Feng et al., 2011).

In a horizontal direction, the average concentrations of MeHg were 0.55 ± 0.22, 0.33 ± 0.24 and 0.22 ± 0.13 ng/L at Y, M and D site, respectively. These concentrations were higher than in other non-Hg-polluted reservoirs in the same watershed (He et al., 2008; Zhang et al., 2009; Feng et al., 2009). The horizontal distribution trend of MeHg in BHR is different from reservoirs with non-point source Hg inputs where the highest MeHg concentrations are usually observed at sites close to the dam (Meng, 2011). In the BHR water column, the highest MeHg concentration was observed upstream rather than in the dam area, due to Hg input from an upstream point source.

The vertical profiles (Fig. 6b) suggested that methylation mainly occurs in the anoxic layer in bottom water during water stratification. In the upper 5 m of the water column, 72% to 89% of MeHg was present as PMeHg, as compared to less than 40% in the anoxic hypolimnion. The MeHg concentration peaked at the bottom. The average percentage of MeHg as THg (i.e. %MeHg) was 8%, with a range of 2–19% in the water column at all sites. The percentage of dissolved Hg as DMeHg (i.e. %DMeHg) was higher in bottom water (17–20%). This suggests the methylation rate is faster in the bottom water than in the oxic water, or part of DMeHg diffused from the sediments into the bottom water. The high Hg methylation, as indicated by %MeHg and %DMeHg, in bottom water could be related to the abundance of RHg which is bioavailable and favors the methylation of Hg. This explanation is consistent with the similar vertical distribution pattern of RHg and DMeHg found in BHR as shown in Fig. 6b.

Previous studies have shown that DOC (e.g. the concentration and molecular size of DOC) plays an important role in Hg methylation (Belzile et al., 2008; Graham et al., 2012). The net methylation increases with DOC concentrations if DOC is within the range of 5–30 mg/L. But DOC can also inhibit Hg methylation at concentrations of <5 mg/L (Watras et al., 1995) or more than 30 mg/L (Babiarz et al., 2001, 2003; Benoit et al., 2001; Simonin et al., 2008). In BHR, the concentration of DOC fluctuated slightly, within a narrow range of 2.9–3.5 mg/L (mean ± SD of 3.3 ± 0.33 mg/L) for the whole reservoir. No statistically significant correlations were found between DMeHg and DOC suggesting that organic matter is perhaps not the main factor influencing the Hg methylation process in BHR.

3.2.2. Effect of geochemical factors on dissolved Hg in pore water

Compared to the results from 2003 to 2004, pore water DMeHg concentrations in the upper 3 cm sediment were one tenth of that previously measured (Yan et al., 2008), but similar to the non-point source contaminated reservoirs in the same watershed (He et al., 2008; Feng et al., 2009, 2011; Zhang et al., 2009). The DHg in the overlying water was lower than that in pore water extracted from the top 3 cm of sediment at all sampling sites, indicating that sediment was an important source of total Hg in the reservoir water (Table 1). The DMeHg concentration in overlying water at Y site was lower than that in the upper 3 cm of the sediment pore water, suggesting the diffusion of DMeHg from sediment. However, at the M and D sites, DMeHg in the overlying water was similar to its pore water counterpart. This stands in contrast to the inorganic Hg gradient, suggesting a strong flux from sediment pore water. While DOC in the pore water was about three times the value in the overlying water and the water column, DMeHg concentrations in the pore water, overlying water and water column are similar, suggesting again that organic matter is perhaps not the main factor influencing the Hg methylation process in BHR.

Table 1
Dissolved Hg (DHg), dissolved methylmercury (DMeHg), dissolved organic C (DOC), S^{2-} and SO_4^{2-} in pore water and overlying water (OW).

Depth (cm)	DHg (ng/L)	DMeHg (ng/L)	DOC (mg/L)	S^{2-} (μM)	SO_4^{2-} (mg/L)
OW–Y	7.4	0.38	3.4	0.11	101.1
Y 0–3	8.4	0.61	9.3	0.34	11.9
Y 3–6	5.2	0.31	9.2	0.11	11.4
Y 6–9	5.7	0.10	8.9	0.12	10.0
OW–M	3.2	0.54	4.5	0.23	104.5
M 0–3	7.8	0.56	10.7	2.31	12.0
M 3–6	4.0	0.34	11.7	0.13	10.0
M 6–9	2.0	0.06	8.2	0.10	6.1
OW–D	4.0	0.27	3.1	0.24	99.6
D 0–3	13	0.22	13.0	3.92	17.5
D 3–6	7.5	0.15	9.5	0.45	18.9
D 6–9	8.3	0.12	0.1	0.10	9.8

Overlying water (OW) was collected in sediment cores just above water/sediment interface at sites Y, M and D.

The concentrations of S^{2-} were similar to these determined in some other reservoirs such as the Salmon Falls Creek Reservoir (SFCR) in the USA (less than 1 μM) (Gray and Hines, 2009), but lower than in the Wujiang reservoir, where sulfide ranged from 5 to 8 μM (unpublished data). The DMeHg/DHg ratio (Table 1) was lower (average is 4.3% with a range of 1.5–8.5%) than in the SFCR reservoir (about 12%) and the Wujiang Reservoir (14–21%).

The positive correlation between DHg and SO_4^{2-} in pore water was significant ($p < 0.05$, $r = 0.73$, $n = 9$). Sulfate was an order of magnitude higher in overlaying water than in pore water indicating a massive reduction of SO_4^{2-} in sediments. Since the concentrations of S^{2-} in pore water were relatively low the precipitation of Fe sulfides and possibly cinnabar (HgS) could explain the correlation between DHg and SO_4^{2-}. Less complete reduction of SO_4^{2-} would imply less precipitation of HgS and thus more DHg in pore water. No significant correlation is found between DMeHg and other parameters.

3.2.3. THg and MeHg in sediment

The THg and MeHg concentrations in the sediment were 590–12,700 and 4.1–10.0 μg/kg, with the mean ± SD being 3700 ± 390 and 6.1 ± 2.1 μg/kg in the upper 9 cm sediment, respectively (Table 2). The sediments were heavily contaminated with Hg, as these THg concentrations largely exceeded the local background level of about 200 μg/kg (He et al., 2008). The THg concentrations showed a descending trend with the increasing distance from the Hg pollution source. High THg concentrations in the sediment resulted from the wastewater discharge from GOCP, which contained high Hg. The THg in the sediment from 9 cm depth to the top layer, displays a declining trend. This was likely caused by the shutdown of GOCP in 1997, which decreased Hg inputs to BHR (Yan et al., 2008).

The MeHg concentrations in BHR sediment were slightly higher than in natural lakes or unpolluted reservoirs (He et al., 2008; Zhang et al., 2009; Feng et al., 2011). The highest MeHg concentrations in sediment were generally found at Site M. In addition, a

Table 2
Total Hg (THg), methylmercury (MeHg), methylation and demethylation parameters and ancillary variables in sediments.

Depth (cm)	THg (μg/g dw)	MeHg (ng/g dw)	MeHg/THg (‰)	LOI (%)	W/C (%)	M/C ($\times10^{-3}$ d^{-1})	D/C ($\times10^{-2}$ d^{-1})	N/M (ng g^{-1} d^{-1})
Y 1–3	5.0	8.7	1.7	14.5	64.6	0.07	78	−3.1
Y 4–6	6.3	4.9	0.8	14.3	61.7	0.01	30	−1.6
Y 7–9	12	6.2	0.5	14.0	60.2	0.06	35	−2.6
M 1–3	1.8	6.5	3.6	15.9	70.0	−0.4	−75	8.7
M 4–6	2.2	5.3	2.4	16.3	67.1	0.7	−77	10
M 7–9	2.8	10	3.7	16.4	63.3	0.1	94	−2.1
D 1–3	0.6	4.8	8.1	15.5	66.3	1.0	55	−1.4
D 4–6	0.7	4.0	5.4	15.8	65.4	−0.2	6.4	−0.5
D 7–9	1.4	4.1	2.9	16.6	63.1	−1.5	12	−3.1

W/C – water content %.
M/C – methylation coefficient ($\times10^{-3}$ d^{-1}).
D/C – demethylation coefficient ($\times10^{-2}$ d^{-1}).
N/M – net methylation (ng g^{-1} d^{-1}).
N/M – THg × M/C-MeHg × D/C.

highly elevated MeHg concentration (8.7 ng/g) was found at site Y near the sediment/water interface (0–3 cm depth).

Generally, the subsurface sediments should have relatively high %MeHg in lakes or reservoirs due to high organic matter and bacterial activity (Feng et al., 2009). The %MeHg is often used as an indicator of the net methylation rate (e.g. Sunderland et al., 2006). In this study, values of %MeHg fluctuated throughout the core (Table 2) within the range 0.05–0.81% (mean of 0.32%), with higher values occurring in the upper 0–3 cm than in 6–9 cm layer. In addition, %MeHg in the sediment of BHR was lower (average 0.3% with a range of 0.1–0.8%) than those found in other eutrophic reservoirs (0.3–5%) (Gray and Hines, 2009). The lower %MeHg suggests that despite the high nutrients and organic matter concentrations the methylation rate is relatively low in this eutrophic reservoir.

Some studies have suggested that organic matter shows significant positive correlation with MeHg in sedimentary environment (Ramalhosa et al., 2006; Graham et al., 2012). In this study, LOI% in sediment was similar for the top 9 cm of the sediment. No significant positive correlation of LOI% or DOC with %MeHg was found in sediment in BHR.

In general, weaker methylation (<0.1%/day) was found compared to the demethylation process in sediment (17.6%/day). The maximum MeHg concentration and net Hg methylation were present at site M, implying active Hg methylation there (Table 2). Sites D and Y showed limited methylation, but strong Hg demethylation potentials. As a result, MeHg concentrations for the samples collected from D and Y sites were quite low (especially for site D) when compared to site M. Bacterial activity could be a major factor for Hg methylation in this reservoir, as in other water bodies (Bravo et al., 2009). Therefore, SRB abundance in sediment needs to be measured in future research.

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