

THE IMPACTS OF ORGANIC MATTER ON THE DISTRIBUTION AND METHYLATION OF MERCURY IN A HYDROELECTRIC RESERVOIR IN WUJIANG RIVER, SOUTHWEST CHINA

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Abstract: To understand the impacts of organic matter on the geochemical processing of Hg in a hydroelectric reservoir, spatial and seasonal distributions of total mercury (THg) and methylmercury (MeHg) in both solid and liquid phases of sediment cores were investigated in the Wujiangdu Reservoir in Guizhou Province, China. Four sampling sites with different intensities of cage aquaculture activities were chosen and were evenly distributed from upstream to downstream of the Wujiangdu Reservoir. Elevated MeHg concentrations and the high percentage of MeHg in solid and liquid phases of the surface sediment demonstrated that the active Hg methylation process occurred downstream of the Wujiangdu Reservoir. In contrast, the absence of obvious peaks for MeHg in sediment from the upper reaches of the Wujiangdu Reservoir, consistent with low levels of organic matter, suggested that production of MeHg was limited. In sediment with high organic matter content, reduction occurred closer to the sediment surface, resulting in maximum MeHg concentration in these layers. The correlation between MeHg and organic carbon implied that organic matter content in the sediment originating from cage aquaculture activities can help to predict MeHg production rates in reservoirs, which could be used to assess possible MeHg contamination in a reservoir ecosystem. *Environ Toxicol Chem* 2016;35:191–199. © 2015 SETAC

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INTRODUCTION

As an extremely toxic pollutant, mercury (Hg) has received considerable attention because of its methylation, bioaccumulation, and biomagnification in aquatic food chains [1]. Reservoirs have been constructed worldwide for the purposes of hydropower generation, flood control, fisheries, and irrigation. An important environmental consequence of constructing reservoirs is methylmercury (MeHg) contamination in the food web of aquatic ecosystems [2–4]. Elevated levels of MeHg were observed in fish from newly constructed reservoirs in North America and northern Europe in the late 1970s and early 1980s [5]. Significantly increased Hg concentrations have also been found in Chinese fish from the Pengshui reservoir (within the Wujiang River) and the Gezhouba reservoir (within the Yangze River) [6,7]. Active MeHg production in newly built reservoirs following impoundment may persist for up to 10 yr [3]. Subsequently, the increased MeHg levels in fish from reservoirs may last for up to 30 yr [8]. The methylation of inorganic Hg (IHg) in waters and sediments constitutes a key role in the cycling of Hg in aquatic systems [9]. Previous studies have shown that parameters such as soil properties—including organic matter content and Hg concentration, the ratio of flooded area to total water surface area, water residence time, and primary productivity in the biota system—play an important role in net Hg methylation in reservoir systems [2]. Specifically, the decomposition of flooded vegetation and organic matter in soils may stimulate the microbial methylation of IHg to MeHg [4]. Given the decomposition of organic matter in submerged soil, the net Hg methylation rate decreases with the

increase in reservoir age [2–4]. However, the organic matter concentration in submerged soil is not a good indicator to predict an MeHg trend for fish in reservoirs, because both the amount and type of submerged organic matter can impact the production of MeHg in newly constructed reservoirs [10]. Despite the abundance of literature on the biogeochemical cycle of Hg in a reservoir ecosystem, the factors controlling Hg methylation processes in a reservoir are extremely complex and are far from being fully understood.

Because of sharply increasing demands for energy, China has built a great number of hydropower reservoirs. The total number of large dams in China has accounted for more than 50% of the total number in the world since 1982 [11]. The Wujiang River is the largest tributary of the upper Yangtze River. With the implementation of China's Go West Policy, numerous large reservoirs have been or are being constructed in Guizhou Province along the Wujiang River (Figure 1). Because of the increase in global demand for aquatic products, cage aquaculture activities are increasing rapidly and currently are the most prevalent use of water resources globally. Recently, the Food and Agriculture Organization of the United Nations estimated that food fish aquaculture production throughout the world had reached 70.5 million tonnes, with China accounting for as much as 62% of the total production in 2013 [12]. From 2002 to 2012, China was the largest fish exporter in the world [12]. In 2012, the aquaculture area of the lakes and reservoirs in China rose by 3.4% to 2.9×10^6 ha, which accounted for more than one-half of the fresh aquaculture area [13]. However, the impacts of cage aquaculture activities on Hg transportation and transformation in reservoirs in China are still unknown.

From the currently available data in the open literature, it can be confirmed that newly constructed Chinese reservoirs within the Wujiang River (such as Yinzidu, Suofengying, and Hongjiadu) were not active sites of net Hg methylation as a result of low organic matter concentrations in submerged

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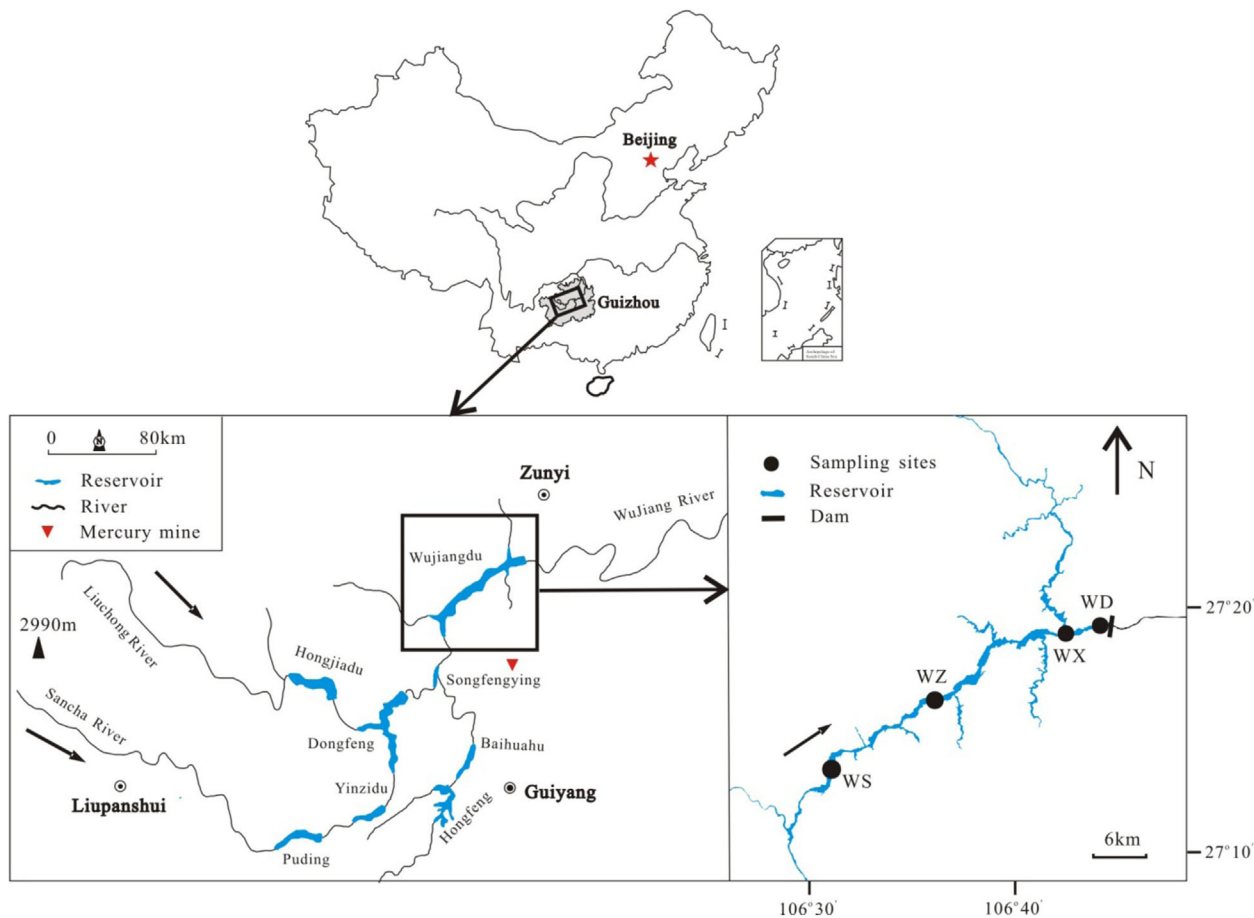


Figure 1. Study area and the locations of 4 sampling stations (sites WS, WZ, WX, and WD) in the Wujiangdu Reservoir on the Wujiang River in Guizhou Province, China.

soil [14,15]. In the older reservoirs within the Wujiang River (such as Puding and Dongfeng), however, the sediments act as net sinks of total Hg (THg) but as net sources for MeHg [16,17]. It seems clear that Hg methylation processes will be accelerated with increases in reservoir ages. The production of MeHg in reservoirs in the Wujiang River cannot be predicted using previous observations in North America and Europe, as the Hg methylation process is driven by a completely different mechanism in reservoirs in the Wujiang River [14–16,18]. Unfortunately, Hg methylation and its controlling factors in reservoirs in Wujiang River are still unclear.

To better understand the controlling factors of Hg methylation in reservoirs, the present study focused on the concentrations and distributions of different Hg species in sediment cores in the Wujiangdu Reservoir. Four sampling sites with different intensities of cage aquaculture activities were chosen. The primary objectives were to investigate the spatial and seasonal variations of Hg species in sediment cores in the Wujiangdu Reservoir, to further understand the influence of organic matter on Hg methylation in aquatic ecosystems, and to elucidate the relationship between cage aquaculture activities and MeHg production in reservoirs in the Wujiang River.

MATERIALS AND METHODS

Site descriptions

The Wujiangdu Reservoir is located in the lower branch of the Wujiang River, which is the largest tributary of the upper

Yangtze River (Figure 1). Four sampling stations spatially distributed from upstream to downstream of the Wujiangdu Reservoir were chosen, as shown in Figure 1. Site WS ($27^{\circ}13'27.8''\text{N}$, $106^{\circ}31'20.6''\text{E}$) is located in the upper stream of the reservoirs, site WZ ($27^{\circ}15'50.3''\text{N}$, $106^{\circ}36'04.1''\text{E}$) is in the middle, site WX ($27^{\circ}18'38.8''\text{N}$, $106^{\circ}42'44.2''\text{E}$) is downstream, and site WD ($27^{\circ}19'07.5''\text{N}$, $106^{\circ}44'54.6''\text{E}$) is adjacent to the dam (within $\sim 500\text{ m}$). Cage aquaculture activities conducted by local residents have been prominent downstream of the Wujiangdu Reservoir. No formal quantitative data on cage aquaculture activities are available. Detailed information concerning the Wujiangdu Reservoir is provided in the Supplemental Data.

Sample collection

Undisturbed water–sediment interface water samples and sediment cores approximately 30 cm long were collected in each season in 2007 using a custom-designed sampler [19]. All samples were collected following ultraclean sampling protocols. The interface water (5–10 cm above the sediment surface) in the core tube was siphoned, filtered into cleaned borosilicate glass bottles using a $0.45\text{-}\mu\text{m}$ filter (Millipore), and subsequently analyzed for dissolved total Hg concentrations (THg_f) and dissolved MeHg concentration (MeHg_f). The sediment cores were immediately sliced using a plastic cutter in an oxygen-free glove box under argon. The first 10 cm were sectioned at 1-cm intervals and the next 20 cm at 2-cm intervals. The sediment samples were placed in acid-cleaned 50-mL

plastic centrifuge tubes, capped, and sealed with Parafilm. All samples were transported in an ice-cooled container to the laboratory within 24 h and stored at 3 °C to 4 °C for further analysis.

Sediment samples were centrifuged for 30 min at 3000 r min⁻¹ at 5 °C to extract the porewater immediately after being transported to the laboratory. The porewater was then filtered through a 0.45- μ m disposable polycarbonate filter unit (Millipore) under argon in a glove box and placed in borosilicate glass bottles. Two sediment cores were collected at each sampling site: 1 for THg_f analysis in porewater and 1 for MeHg_f analysis. Subsequently, the freeze-dried sediment samples were ground and homogenized to a size of 150 meshes per inch with a mortar for solid-phase THg, MeHg, and organic matter concentration analysis. Precautions were taken to avoid any cross-contamination during the sample processing. The grinder was thoroughly cleaned after each sample processing. The powdered samples were subsequently packed into plastic dishes, sealed in polyethylene bags, and stored in a refrigerator within desiccators for further laboratory analysis.

All water samples were acidified on site to 0.5% (v/v) with ultrapure concentrated hydrochloric acid (HCl); the sample bottles were then capped, sealed with Parafilm, and stored in the refrigerator at 3 °C to 4 °C in the dark. Analyses of concentrations of Hg species in water samples were conducted within 28 d after sampling. The water content of the sediment samples was also estimated by weight loss.

Sample analyses

For THg analysis, 0.1-g to 0.2-g soil samples were prepared and digested using a mixture of HCl and HNO₃ (1:3, v/v). A suitable volume of an aliquot from digested samples was taken for THg analysis by cold vapor atomic fluorescence spectroscopy (CVAFS; Tekran 2500) preceded by BrCl oxidation, SnCl₂ reduction, purge, and thermo reduction of Hg [20]. Total Hg in water samples was quantified by using dual amalgamation CVAFS (Tekran 2500), following approved methodologies [20].

For MeHg analysis, 0.3 g to 0.4 g of sediment sample were prepared using CuSO₄-methanol/solvent extraction. Then the MeHg in samples was extracted with methylene chloride, back-extracted from the solvent phase into water and aqueous phase ethylation. Ethylated Hg species were purged onto a Tenax trap using N₂. These species were then thermally desorbed, isothermally separated by gas chromatography (GC), pyrolytically decomposed to Hg⁰, and analyzed by CVAFS (Brooks Rand model III) following method 1630 [21]. Water samples were quantified for MeHg using CVAFS (Brooks Rand model III) following distillation, aqueous phase ethylation, and isothermal GC separation [21].

Concentrations of IHg in sediment porewater and interface water were calculated as the difference between the concentrations of THg and MeHg in the sample [16]. The concentrations of organic matter in the sediment samples were analyzed using KCr₂O₇ (potassium dichromate) oxidation coupled with volumetric analysis.

Quality assurance and quality control

Quality control for THg and MeHg determination was conducted by method blanks, matrix spikes, duplicate, and certified reference material of sediment (GBW07305 and IAEA-405). The method detection limit ($3 \times \sigma$) was 0.02 ng L⁻¹ for THg and 0.01 ng L⁻¹ for MeHg in water samples. Limits of determination were 0.01 ng g⁻¹ for THg and 0.002 ng g⁻¹ for MeHg in sediment samples. The method blank was in each case

less than the detection limit. The relative standard deviations for duplicate sample analyses were <8.5% for THg and MeHg in water samples and were <7.8% for THg and MeHg in sediment samples. Recoveries for matrix spikes ranged from 87% to 113% and from 91% to 108% for THg and MeHg analysis in water samples. The average THg concentration of the geological standard of GBW07305 was 95 ± 7.0 ng g⁻¹ ($n = 15$), which is comparable with the certified value of 100 ± 20 ng g⁻¹. The average MeHg concentration of 5.3 ± 0.50 ng g⁻¹ ($n = 15$) was obtained from IAEA-405, with a certified value of 5.5 ± 0.53 ng g⁻¹.

Statistical evaluations were performed using SPSS 11.5 software. To reveal any relationship between the general sediment quality characteristics and Hg species, correlations between covariant sets of data were analyzed. The correlation coefficient (r) and test of significance (p) were computed for correlation analysis. Correlation was significant at 0.05 (1-tailed). Linear regression fits were also processed to model the relationship between organic matter content and MeHg concentration in sediments. In addition, Kolmogorov–Smirnov and Kruskal–Wallis tests were performed to compare significant differences between 2 or more independent datasets. Differences were significant at $p < 0.05$.

RESULTS AND DISCUSSION

General physical properties of sediment samples

Visual inspection of the sediment cores showed no macrofauna or signs of bioturbation. Samples mainly consisted of fine particles, whereas sand was virtually absent. Water content in sediment samples was the highest at the first 1 cm (WS, 80–85%; WZ, 79–87%; WX, 89–93%; WD, 91–93%) and then decreased gradually to 60% to 70% at the 4 sampling sites. The vertical profiles of organic matter content in sediment cores from the Wujiangdu Reservoir are shown in Figure 2. The annual average concentrations of organic matter in sediment cores were 2.9 ± 0.57%, 3.1 ± 0.77%, 4.8 ± 2.3%, and 5.1 ± 2.0% at sites WS, WZ, WX, and WD, respectively. Organic matter content in the sediments cores varied widely from 2.3% to 11% at WX, and from 2.7% to 11% at WD, but remained nearly monotonic at upstream sites (ranging from 2.2% to 5.2% at WS and from 2.2% to 5.5% at WZ). The maximum organic matter contents in sediment at the 4 sampling sites were observed at the surface sediment. Statistical analysis revealed that organic matter contents at depths of 1 cm to 5 cm in sediment were significantly higher than those in the corresponding sediment at depths of 6 cm to 30 cm across the 4 sampling sites (Kolmogorov–Smirnov test, $p < 0.01$). Furthermore, the organic matter contents in the first 1 cm of sediment at the downstream sites (WX and WD; ranging from 8.8% to 11%) were significantly higher than those at upstream sites (ranging from 3.7% to 5.5%) throughout the 4 sampling periods (Kolmogorov–Smirnov test, $p < 0.01$; Supplemental Data, Table S1). Temporal differences in organic matter content in sediment were not detected at any sampling site.

Our field investigation showed that cage aquaculture activity was absent at site WS, appeared to be sporadic at site WZ, and was pervasive across sites WX and WD. Because of the high intensity of cage aquaculture activity downstream of the Wujiangdu Reservoir, fish food and feces were potentially the main sources of organic matter input to downstream sediments, which also resulted in higher primary productivity compared with upstream of the Wujiangdu Reservoir (Supplemental Data). The organic matter content ranged from 2% to 5% in

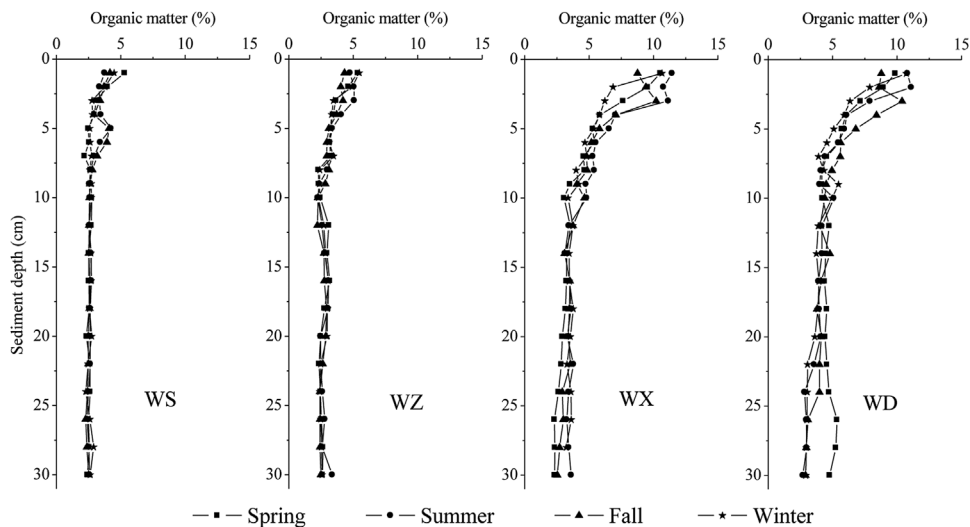


Figure 2. Distributions of organic matter in sediment profiles of the 4 sampling stations (sites WS, WZ, WX, and WD) in the Wujiangdu Reservoir, Guizhou Province, China.

submerged soils in the Wujiangdu Reservoir catchment [15], which was comparable with the mean (range) values of organic matter in sediment at sampling sites WS. Therefore, it is reasonable to believe that organic matter in sediment upstream of the Wujiangdu Reservoir was mainly derived from the watershed, such as soil erosion and surface runoff input, with little contribution from the autochthonous sources.

Distribution of mercury species in sediment cores

The distribution patterns of THg concentrations in sediment profiles are illustrated in Figure 3. Overall, no discernible seasonal trends in THg distribution were observed in the sediment profiles of the Wujiangdu Reservoir during our sampling periods. However, an obvious spatial variation was observed between site WS and other sampling sites. The concentrations of THg in sediment cores at sites WZ, WX, and WD exhibited a very narrow range ($106\text{--}494\text{ ng g}^{-1}$), whereas those at site WS ranged widely, from 128 ng g^{-1} to 1376 ng g^{-1} . Furthermore, the vertical distributions of THg in sediment cores

of the Wujiangdu Reservoir showed little variation, with the exception of sharp peaks at the depth of 10 cm to 15 cm at WS close to the inflow of the Wujiangdu Reservoir. The solid-phase THg record can be used to reconstruct the evolution of the anthropogenic Hg deposition. As shown in Figure 1, site WS is located downstream from an Hg mining area. Therefore, the sharp peaks at depths of 10 cm to 15 cm in sediment cores throughout the 4 sampling periods indicated a direct input from the point source nearby (previous Hg mining activity).

The annual average THg concentrations in sediment cores were $389 \pm 259\text{ ng g}^{-1}$, $238 \pm 69\text{ ng g}^{-1}$, $300 \pm 85\text{ ng g}^{-1}$, and $268 \pm 74\text{ ng g}^{-1}$ at sites WS, WZ, WX, and WD, respectively. These values were comparable with the background level of THg (260 ng g^{-1}) in soil in Guizhou Province [22]. Generally, uncontaminated sediments in reservoirs or lakes have been suggested to have mean THg concentrations ranging from 50 ng g^{-1} to 300 ng g^{-1} in the study region [23]. The average THg concentration in sediment collected from sites WZ, WX, and WD suggested that sediment cores at the middle and

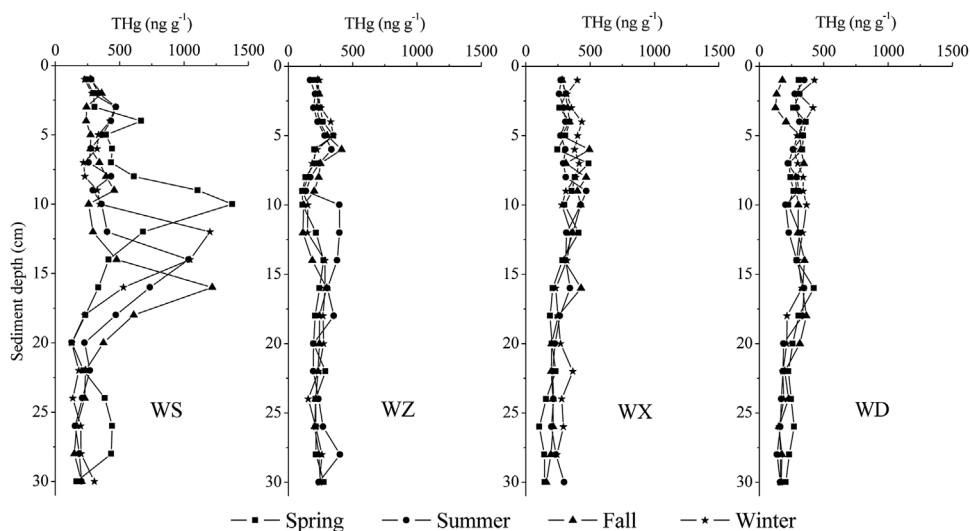


Figure 3. Distributions of total mercury (THg) in sediment profiles of the 4 sampling stations (sites WS, WZ, WX, and WD) in the Wujiangdu Reservoir, Guizhou Province, China.

downstream of the Wujiangdu Reservoir have not been severely impacted by Hg contamination. However, the mean THg concentration in sediment at site WS was higher than the background level of THg in soil in the study region [22], and the elevation of the average THg concentration in sediment at WS resulted from the sharp peak at the depth of 10 cm to 15 cm in the sediment profile. Overall, the THg concentrations in sediment observed in the Wujiangdu Reservoir were much higher than those observed in North America and northern Europe. For example, French et al. [24] reported that the mean THg concentration in sediment collected from 34 reservoirs in Newfoundland, Canada, was 39 ng g^{-1} .

In comparison with the distribution patterns of THg in sediment profiles, different vertical and spatial trends of MeHg in sediment cores were observed (Figure 4). The spatial distribution of MeHg concentrations in sediment reveals that the MeHg concentrations were relatively higher at the middle and downstream of the Wujiangdu Reservoir (sites WZ, WX, and WD) compared with upstream (site WS) of the Wujiangdu Reservoir. Statistically significant differences in MeHg levels in sediment were found among sites WS, WZ, WX, and WD throughout the 4 sampling periods (Kruskal–Wallis test, $p=0.001$). Furthermore, MeHg concentrations in sediment collected from sites WX and WD were significantly higher than those from sites WS and WZ (Kolmogorov–Smirnov test, $p=0.003$). These observations suggested considerably different net Hg methylation among sites WS, WZ, WX, and WD.

The percentage of THg as MeHg (MeHg%) is recognized as an indicator of net Hg methylation in substrates [25]. Generally, MeHg concentrations accounted for approximately 1.0% to 1.5% of THg in sediments, and this ratio tended to be lower (typically $<0.5\%$) in estuarine environments [26]. However, the MeHg% in sediment in the Wujiangdu Reservoir reached up to 2.8%, 2.9%, and 4.2% at sites WZ, WX, and WD, respectively (Supplemental Data, Table S1), which were much higher than those in the greater depth of sediment cores as well as other reservoirs in the same area [23]. Moreover, the highest MeHg% values were all observed at the surface sediment at sites WZ, WX, and WD throughout the 4 sampling periods, indicating that active net Hg methylation occurred in this sediment layer. However, MeHg% fluctuated throughout the sediment cores at

site WS in each season, with the highest value (1.5%) observed at the depth of 4 cm in the fall. The major differences among the 4 sampling sites are that both water depth and organic matter content in the sediment increases from upstream to downstream of the Wujiangdu Reservoir. The distribution patterns of MeHg and MeHg% in sediment cores were mirrored by the organic matter content in sediment throughout the sampling sites, suggesting that relatively high production of MeHg is related to high organic matter content in sediment. Moreover, the regression analyses yielded significantly positive correlations when MeHg versus organic matter content in sediment was plotted for each of the sampling sites (Supplemental Data, Figure S1), further implying that sediment organic matter plays an important role in the methylation of THg in the Wujiangdu Reservoir. Pearson correlation coefficients between MeHg concentrations and organic matter concentrations in sediment at site WS ($r=0.52$) were much lower compared with site WZ ($r=0.77$), site WX ($r=0.75$), and site WD ($r=0.70$). It seems that other factors apart from organic matter content may also control MeHg production in the sediment at site WS. This relationship between MeHg concentration and organic matter in sediment has also been observed by other researchers [16,27]. However, there was no such significant correlation between MeHg and THg concentrations in sediment, which is in agreement with a previous study [28]. This indicated that THg concentration is not a useful indicator for predicting MeHg concentrations in the Wujiangdu Reservoir.

The absence of an obvious peak for organic matter in surface sediment at site WS in all seasons, consistent with the low levels of MeHg, suggested that the production of MeHg in this sediment layer is limited. As described previously, watershed soil erosion and surface runoff may be the primary source of organic matter to the sediment at site WS. Bishop and Lee [29] reported that the strong association of Hg with humic matter implies the watershed transport of Hg. Therefore, we have suggested that transport of terrestrial organic matter with surface runoff could be an important source of MeHg to sediment at site WS [14,15]. The remarkably higher values of MeHg and MeHg% at a depth of 4 cm at site WS also implied the existence of additional factors controlling MeHg production at that site.

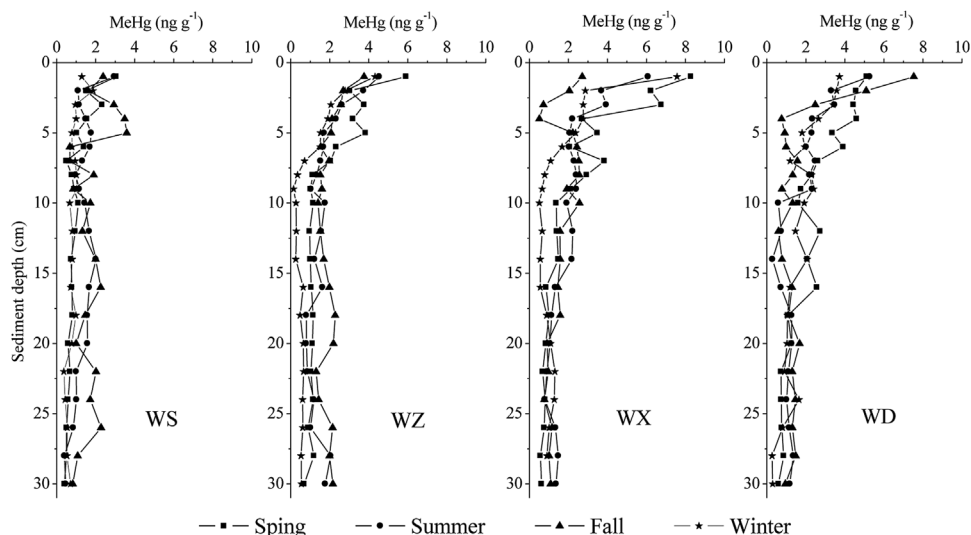


Figure 4. Distributions of methylmercury (MeHg) in sediment profiles of the 4 sampling stations (sites WS, WZ, WX, and WD) in the Wujiangdu Reservoir, Guizhou Province, China.

Studies in North America have implied the presence of active MeHg production in newly constructed reservoirs and concluded that enhanced Hg methylation may last for more than 30 yr after impoundment [2–4]. Methylation rates of Hg decreased with the age of the reservoir, as a result of the decomposition of organic matters in flooded soil [2–4]. The present study shows that the reservoirs located in southwestern China may have Hg biogeochemical dynamics that are different from reservoirs in Europe and North America. The organic matter content in submerged soil [15] was much lower than the organic matter concentrations (which varied from 30% to 50%) in submerged soil from the boreal forest or wetland in North America and Europe [2,4]. The major source of organic matter in the newly constructed reservoirs in the Wujiang River is mainly derived from the watershed input, with little autochthonous contribution because of the low primary productivity [14,15]. Recent studies have concluded that the low organic matter content in the submerged upland soil of the Wujiang River Basin may inhibit methylating microorganisms or at least decrease their rate of metabolism [14,15]. Therefore, because of the low organic matter content in submerged soil, the newly constructed reservoirs (such as Suofengying, Hongjiadu, and Yinzidu) in the Wujiang River did not show a net production of MeHg in the reservoir systems.

Phytoplankton-derived organic matter, along with fish food and feces, were potentially the most significant sources of organic matter input to surface sediments of the downstream Wujiangdu Reservoir [14]. This may imply that the organic matter in surface sediment originating from cage aquaculture activities in the Wujiangdu Reservoir were easily decomposed by microorganisms that mediated Hg methylation processes in the sediments. It is well known that organic matter in sediment plays an important role in the methylation of IHg [30]. Numerous studies have shown elevated MeHg concentrations in sediments along with elevated organic matter content [31], which is attributed to the stimulation effect of organic nutrients on microbial methylation activity. Cossa and Gobeil [32] postulated that increased oxygen consumption during organic matter degradation causes progressively more anoxic conditions at the sediment–water interface, which may lead to active methylation.

In our previous study [14], the vertical profiles for pH and dissolved oxygen in the water column of the Wujiangdu Reservoir were documented. In brief, the water was slightly acidic in the bottom stratum, as a result of the formation of organic acids in the sediment. Moreover, explicit deficiencies of dissolved oxygen were persistent in the bottom water of sites WX and WD throughout the sampling seasons but were less pronounced at site WX and were absent at site WS. It is generally accepted that an aquatic environment with low dissolved oxygen and pH favors net Hg methylation [26]. Intensive cage aquaculture has contributed to the high primary productivity downstream of the Wujiangdu Reservoir. The contribution of organic matter to sediment from cage aquaculture is the key factor that would explain the different rates of MeHg production among sites WS, WZ, WX, and WD.

Moreover, it is accepted that the supply of oxygen to the surface sediment tends to decrease with increasing water depth, which became greater from upstream to downstream of the Wujiangdu Reservoir [14]. Therefore, the limit of the oxygen supply to the epilimnion of the water column may also play an important role in influencing the variation of sedimentary MeHg production in the Wujiangdu Reservoir [33]. The lower levels of MeHg at WS compared with the other sampling sites suggests

that the influence on Hg methylation of organic matter originating from catchment runoff and soil erosion may be minor.

The MeHg concentrations in sediment cores at sites WZ, WX, and WD showed definite maxima just below the water/sediment interface and decreased with depth throughout the 4 sampling periods, unlike the concentrations found at WS. This is in a good agreement with the previous observation that MeHg concentration often reached a maximum value in the anaerobic surface sediments and then sharply declined with increasing sediment depth [34]. The MeHg concentrations fluctuated throughout the sediment cores at site WS over the 4 seasons, which could be explained by the greater amount of river erosion and surface runoff acting as potential sources of MeHg. Previous studies have also observed a seasonal variation of maximum MeHg concentrations in the sediment profile. Feng et al. [16] reported that MeHg concentrations in sediment cores were the highest in July and the lowest in December. However, Bloom et al. [34] found a sharp peak in MeHg concentrations in sediment in early spring, following by a decrease in the other seasons. Seasonal variations in MeHg production and demethylation are controlled by numerous factors, such as temperature, seasonal change in productivity/nutrient supply, pH, and redox conditions [26]. As discussed in section *General physical properties of sediment samples*, the amount of seasonal input of fresh organic matter to the sediment surface is relatively minor in comparison with the total amount of organic matter already existing in the sediment; consequently, temporal differences in sediment organic matter were not seen in the present study. Therefore, organic matter content in sediment alone could not explain the seasonal variations of MeHg in the surface sediment. We speculated that seasonal variation in redox conditions in the surface sediment of the Wujiangdu Reservoir may play an important role in controlling the temporal trend of MeHg [16]. Other factors may also affect the methylation process, and further work is urgently needed.

Distribution of mercury species in sediment porewater

The seasonal and spatial distributions of IHg_f and MeHg_f in porewater in the Wujiangdu Reservoir are shown in Figures 5 and 6. The distribution patterns of porewater IHg_f were completely different from those of porewater MeHg_f in the Wujiangdu Reservoir and were more variable than THg concentrations in the sediment solid phase. This is in agreement with our previous study [16] showing that concentrations of IHg_f in vertical profiles of porewater varied randomly without discernible trends throughout the 4 sampling sites over each season. However, IHg_f concentrations in porewater were generally higher than those in the interface water, implying that the sediment was an important source of IHg to the water column. Moreover, IHg_f concentrations in porewater in summer were significantly higher than those in the other seasons for all sampling sites (Kolmogorov–Smirnov test, $p < 0.01$), indicating that the IHg in sediment tended to exist in the liquid phase during summer. The seasonal trend of IHg_f in sediment porewater may be explained by the increased solubility of IHg under anoxic conditions in the summer [35]. However, the partition of Hg into solid and aqueous phases is physically, chemically, or biologically controlled, and hence is affected by a number of environmental parameters such as pH, temperature, redox conditions, and bioturbation [26].

Similar to the distribution patterns of MeHg in the solid phase, MeHg_f concentrations in porewater varied widely: from 0.15 ng L⁻¹ to 3.1 ng L⁻¹, from 0.15 ng L⁻¹ to 5.3 ng L⁻¹, from

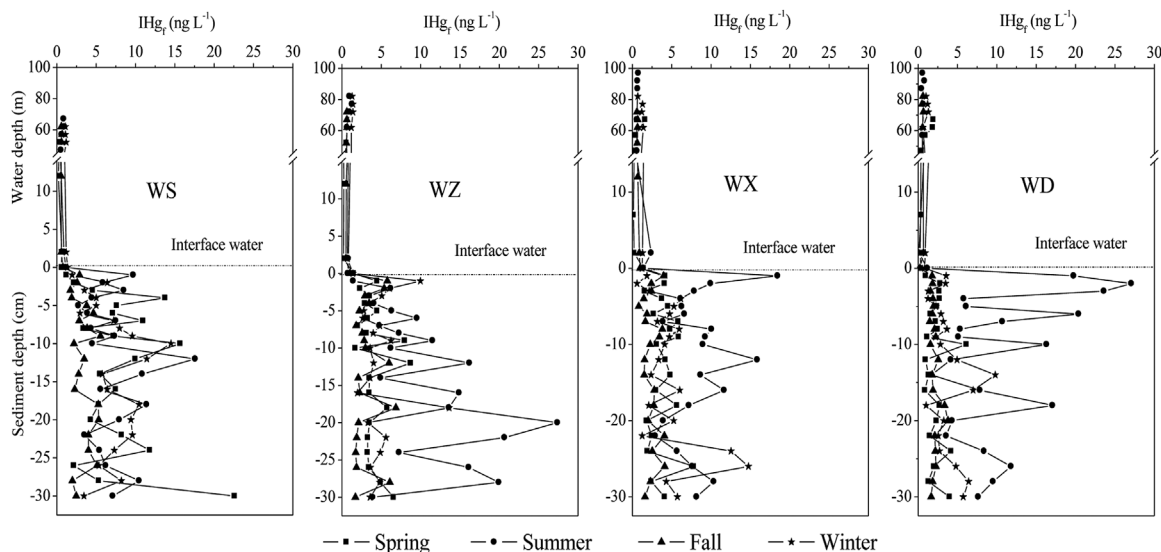


Figure 5. Distributions of dissolved inorganic mercury (IHg_f) in water column and sediment porewater of the 4 sampling stations (sites WS, WZ, WX, and WD) in the Wujiangdu Reservoir, Guizhou Province, China.

0.21 ng L^{-1} to 7.3 ng L^{-1} , and from 0.15 ng L^{-1} to 2.3 ng L^{-1} at sites WZ, WX, WD, and WS, respectively. The levels of MeHg_f in porewater generally represented the highest concentration at the surface sediment at sites WZ, WX, and WD throughout the 4 sampling periods, typically coinciding with peak concentrations of MeHg in the solid phase, and then declined gradually with depth. This again suggested that active net Hg methylation occurred in the surface sediment. Moreover, considerably different levels of net Hg methylation among sites WS, WZ, WX, and WD were further confirmed by a significant difference in porewater MeHg_f at the surface layer (Supplemental Data, Table S2). The seasonal distribution of MeHg_f in porewater showed that the MeHg_f concentrations in spring and summer were significantly higher than those in fall and winter (Kolmogorov–Smirnov test, $p < 0.001$) at sites WZ, WX, and WD. In comparison, MeHg_f fluctuated throughout the sediment cores at site WS, without any clear distribution trends. Previous studies have shown that oxic and alkaline conditions

generally favor sediment uptake of MeHg , whereas anoxic and acidic conditions favor MeHg release [26]. The solubility of MeHg in sediment in an anoxic environment can be increased as a result of the formation of soluble sulfide complexes [35]. Therefore, it is reasonable to assume that water characteristics in a stratified reservoir could be an important factor controlling the distribution of MeHg_f in sediment between the solid and liquid phases. Hence, we believe that seasonal distributions of MeHg_f in porewaters at sites WX, WZ, and WD may be linked with redox condition changes as a result of the seasonal stratification of the Wujiangdu Reservoir [36].

It is clear that MeHg_f concentrations in interface water at all sampling sites were much lower than those in the porewater in surface sediment throughout the 4 sampling periods, with the data at WD in fall and winter being an exception (Supplemental Data, Table S2). The slope of the MeHg_f in the vertical profile of the surface sediment porewater and the interface water showed a positive diffusion of MeHg from sediment to the water column.

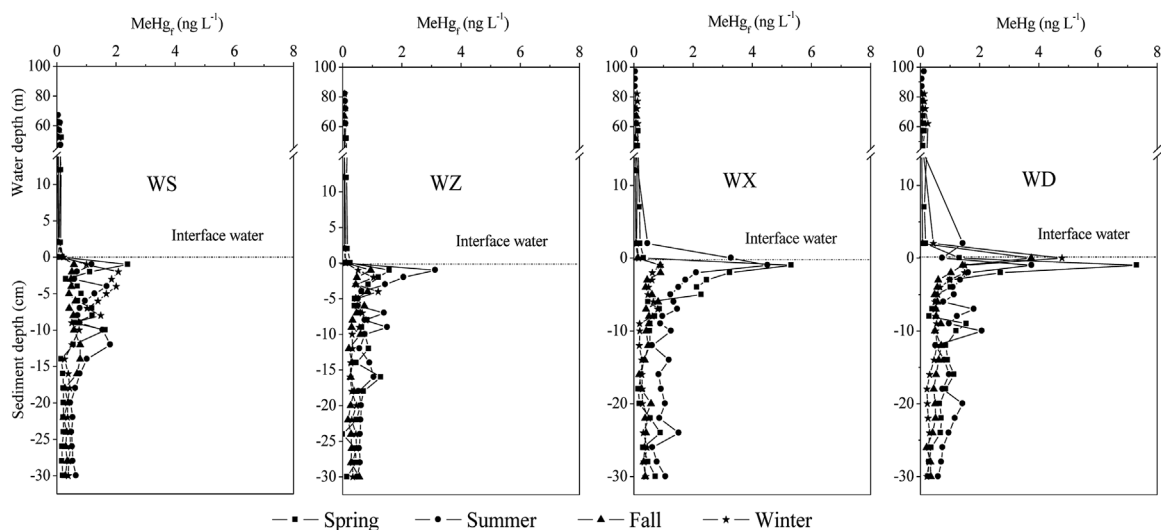


Figure 6. Distributions of dissolved methylmercury (MeHg_f) in water column and sediment porewater of the 4 sampling stations (sites WS, WZ, WX, and WD) in the Wujiangdu Reservoir, Guizhou Province, China.

The concentration of MeHg in sediment porewater is usually much higher than that in the overlying water column [26]. However, the MeHg_f values in the interface water during fall and winter at site WD were approximately 2.5 to 3 times higher than those in the porewater at the surface sediment. Moreover, it is interesting to note that the concentration of MeHg_f in bottom water (95 m) at WD during the summer was clearly higher than that in the interface water (sediment–water interface) as well as the overlying water, which agreed with a previous observation that MeHg levels in hypolimnetic waters of seasonally stratified reservoirs generally increase during summer stratification [37]. These results imply that Hg methylation is much more active above the sediment–water interface at WD during fall and winter.

There are 2 possible ways that MeHg could contribute to the peak levels of MeHg_f in the water column: in situ production controlled by redox chemistry or the settling of particulate matter containing MeHg [38]; and diffusion or resuspension, or both, of MeHg from underlying sediments [39]. The increased decomposition of organic matter in summer results in a more anoxic condition at surface sediments and hypolimnetic waters or interface water, which favors net Hg methylation [26]. Decreased dissolved oxygen concentrations and low pH in hypolimnetic water were detected during the summer at site WD [14]. Therefore, we speculate that the elevated MeHg concentrations in interface water during fall and winter, as well as in bottom water during summer at site WD, not only were the result of the redox-controlled release of MeHg from bottom sediments or the accumulation of settling particulate matters, but also were related to in situ Hg methylation in anoxic water [40]. Obvious MeHg concentration peaks in these layers suggest that net MeHg production occurred in both the surface sediment and anoxic water layers (the bottom and interface waters). Maximum methylation rates usually occurred at the boundary between oxidized and anoxic conditions, which may vary seasonally and frequently coincide with the sediment–water interface at site WD in the Wujiangdu Reservoir.

Elevated MeHg concentrations combined with elevated MeHg% in solid and aqueous phases of the surface sediment demonstrated that the active Hg methylation processes occurred downstream of the Wujiangdu Reservoir. The active Hg methylation processes were triggered by elevated levels of organic matter in the sediment. The temporal trends of MeHg concentrations in sediment were probably dependent on seasonal variation of redox conditions in the surface sediment of the Wujiangdu Reservoir. In contrast, the absence of obvious peaks for MeHg in sediment upstream of the Wujiangdu Reservoir, which is consistent with the low levels of organic matter in the sediment, suggests that the production of MeHg is limited at this site. Soil erosion and surface runoff through the catchment were the primary sources of MeHg to the sediment upstream of the Wujiangdu Reservoir. In sediments with high organic matter content, the anoxic conditions occurred close to the sediment surface and resulted in the maximum MeHg concentration in these layers. We demonstrate that both the surface sediment and the hypolimnetic water were the net sources of MeHg to the water column in the Wujiangdu Reservoir, which may pose a potential threat to the reservoir system and downstream aquatic ecosystems. The present study demonstrates that organic matter in the surface sediment from cage aquaculture in the Wujiangdu Reservoir was easily decomposed. Consequently, net MeHg production was principally governed by the supply of fresh organic matter to the sediment and the anoxic conditions therein. The correlation

between MeHg and organic carbon implies that organic matter in sediment originating from cage aquaculture can help to predict MeHg production rates in a reservoir, which could be used to assess possible MeHg contamination in a reservoir ecosystem. The present study may provide decision-makers with information to make informed decisions on the management of cage aquaculture in reservoirs to reduce MeHg contamination of the ecosystem.

Supplemental Data—Supplemental Data are available on the Online Wiley Library at DOI: 10.1002/etc.3181.

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Data availability—The data can be obtained from the corresponding author, X. Feng (fengxinbin@vip.skleg.cn).

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