



# Mercury distribution in a typical shallow lake in northern China and its re-emission from sediment

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## ABSTRACT

Mercury (Hg) re-emission from sediment is an important process in the biogeochemistry cycles of Hg in the aquatic ecosystem. The contribution of Hg released from sediment to water remains unclear for some shallow lakes. Lake Nansi is a typical shallow lake in northern China that is divided into upper and lower lakes by a dam. The Hg species in the water profile and sediment were measured from two sampling sites in the lake. Nansi Lake was not markedly contaminated by Hg. The Hg profile in the sediment indicated that the demand for energy and the policy management in the catchment influenced the Hg accumulation in its sediment. On the basis of Fick's first law and the sedimentation rate, the diffusion flux of dissolved Hg from sediment to overlying water and the accumulation flux were estimated. According to one-year scale estimation, approximately 10%–13% the Hg in the sediments can be re-released into the overlying water. The Hg diffused from the sediment accounted for 7.9%–16% of the Hg in the overlying water. These results of this study improve the understanding of the sources of pollution in water and enable researchers to focus on the contribution of sediment to the pollution of water in shallow lakes.

## 1. Introduction

Mercury is released into the environment mainly in inorganic forms, and methylmercury (MeHg) can be formed by Hg methylation, which is mainly a microbial-mediated process (Hsu-Kim et al., 2018). Due to the bioaccumulation and biomagnification effects of MeHg, elevated Hg concentration in fish has been found in some lakes and new impoundment reservoirs. Fish have become the main Hg exposure route to people because they usually contain more MeHg than other food (Evans et al., 2005; Hylander et al., 2006; Mergler et al., 2007). Thus, there is increasing concern about Hg biogeochemistry in aquatic systems.

Sediment is an important component in aquatic systems, and numerous studies have shown that high amounts of Hg can accumulate in sediment, which acts as a sink for Hg (He et al., 2008; Haris et al., 2017). The re-emission of Hg from sediment is also an important part of

the biogeochemistry cycles of Hg in aquatic ecosystems. Some researchers have found that the diffusion of Hg from porewater to the overlying water should not be disregarded (Gill et al., 1999; Choe et al., 2004; Feng et al., 2011; Wang et al., 2012a). In the San Francisco Bay Delta, the sediment–water exchange flux was found to be as important as riverine transport, especially during dry months (Choe et al., 2004). In the Mediterranean Sea, total Hg (THg) and MeHg inputs from sediment to overlying water were measured at approximately 25% and 75% respectively of the THg and MeHg input from atmospheric deposition, rivers, and straits (Zagar et al., 2014). Therefore, the process of Hg exchange at sediment–water interfaces of lakes should be more accurately evaluated because this exchange is essential to understanding the influences of Hg in sediment on overlying water and aquatic organisms.

For shallow-water lakes, diffusion from sediment could be a more important source of contaminants than from terrestrial sources.

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According to the eutrophication research on Chinese shallow lakes, the internal phosphorus loading from their sediments accounted for as much as 54% of the increased water column total phosphorus during the prebloom period (Ding et al., 2018). Thus, to determine the internal Hg contribution to the overlying water could be very important for recognizing the Hg biogeochemical cycle in shallow lakes.

Nansi Lake is a typical shallow freshwater lake in northern China and is also an important reservoir for the East Line Project of Water Transfer from South to North in China (WTSNC). Studies have indicated that Hg concentration in the sediment and some inflow rivers of Nansi Lake were markedly higher than those of the environmental background, and the Hg concentration in sediment in the northern lake was higher than that in the southern lake, which was associated with the anthropogenic activities in the lake's catchment (Lv et al., 2014; Ren et al., 2018; Zhang et al., 2018). However, currently there is limited knowledge about the contribution of Hg from the sediment to the overlying water in Nansi Lake.

Therefore, the main objectives of this study were (1) to clarify the distribution of Hg species in water profiles and sediment cores, (2) to quantify Hg flux at the sediment–water interface, and (3) to evaluate the contribution of Hg from the sediment to the overlying water.

## 2. Materials and methods

### 2.1. Study area

Nansi Lake, in southwest Shandong province, is one of the largest freshwater lakes in China, with an area of 1266 km<sup>2</sup>, covering a catchment area of 31,700 km<sup>2</sup>. The catchment is in Shandong, Jiangsu, Henan, and Anhui provinces, while the lake water area is in Shandong province. In Chinese, Nansi Lake means “southern four sub-lakes,” which are interconnected. The four sub-lakes, from north to south, are Nanyang Lake, Dushan Lake, Zhaoyang Lake, and Weishan Lake, of which Weishan Lake is the largest.

Nansi Lake is approximately 120 km long from south to north, and 5–25 km wide from east to west. It is a plain, shallow lake, whose average depth is around 1.5 m. It is divided into an upper lake (including the Nanyang Lake, Dushan Lake, and the northern part of Zhaoyang Lake) and a lower lake (the south part of Zhaoyang Lake and the Weishan Lake) by a secondary dam constructed in Zhaoyang Lake in the 1960s. The areas of the upper and lower lakes are approximately 602 km<sup>2</sup> and 664 km<sup>2</sup> respectively. The main functions of Nansi Lake include water supply, flood control, irrigation, and aquaculture. As a part of the East Line Project of WTSNC, it also serves as water storage.

### 2.2. Sampling methods

In August 2016, we selected two water and sediment sample collection sites in Nansi Lake. One was in the middle of Dushan Lake, and marked as Dushan (DS); the other was in the middle of Weishan Lake, and marked as Weishan (WS) (Fig. 1).

Overlying water samples were taken by hydrophore at both DS and WS. For dissolved Hg and total Hg analysis, both filtered and unfiltered water samples were collected in borosilicate glass bottles. All the bottles were thoroughly pre-cleaned by acid leaching; ultrapure, deionized water washing; and purifying in a muffle furnace at 500 °C (He et al., 2008; Feng et al., 2011). The filtered water samples were filtered with a 0.45 μm filter membrane (0.45 μm MF-Millipore membrane filters [Millipore Sigma, USA]) on site. We added 0.4% v/v hydrochloric acid to the water samples to analyze the Hg. Dissolved organic carbon (DOC) samples were stored in brown reagent bottles that were pre-cleaned. All onsite water samples were marked with labels, double bagged, taken back to the laboratory, and stored at 4 °C.

Sediment cores were collected by gravity corers, with the core 39 cm and 36 cm long for DS and WS, respectively. The underlying water were collected from the top of the sediment core tube. And the

water samples were treated in the same procedure as the overlying water samples. The sediment cores were sectioned at 1 cm intervals. All onsite samples were stored in 50 mL centrifuge tubes and quickly transported to the laboratory in coolers. The wet weights of all samples were measured. Then the samples were centrifuged at 3000 rpm for 30 min to extract porewater. The porewaters were filtered by 0.45 μm Millipore filter membranes and stored in pretreated clean colorimetric tubes. To them, we added 0.4% v/v hydrochloric acid, placed them in a double-packed bag, and stored them in a refrigerator (He et al., 2008; Feng et al., 2011). We freeze-dried the sediment samples, weighed them by dry weight, removed stones and biological residues, ground them in a mortar, and sieved them through 0.150 mm mesh sieves before chemical analysis.

### 2.3. Sample analysis

To the water samples, the THg and dissolved Hg (DHg) are the Hg in unfiltered water and filtered water samples, respectively. For the analysis of THg or DHg in water samples, we analyzed the overlying water and porewater samples following US EPA Method 1631, which is BrCl oxidation and SnCl<sub>2</sub> reduction followed by a purge and trap with a gold trap, and analysis by cold vapour atomic fluorescence spectrometry (CVAFS) (He et al., 2008; Feng et al., 2011).

For the analysis of THg in the sediment, samples were measured by thermal decomposition and Zeeman atomic absorption spectrometry (Lumex RA-915 Plus and PYRO-915+ pyrolysis unit) (Sholupov et al., 2004).

To the water samples, the total MeHg (TMeHg) and dissolved MeHg (DMeHg) are the MeHg in unfiltered water and filtered water samples, respectively. To determine their MeHg concentration, overlying water samples were analyzed following the US EPA Method 1630, with distillation, aqueous ethylation with NaB(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> followed with a purge and trap with a Tenax trap, and analysis by CVAFS (He et al., 2008; Feng et al., 2011). For the analysis of MeHg in the sediment samples, sediment samples were pretreated with CuSO<sub>4</sub>–HNO<sub>3</sub> leaching and CH<sub>2</sub>Cl<sub>2</sub> extraction and back extraction, and then the MeHg was analyzed with aqueous ethylation with NaB(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> followed by a purge and trap with a Tenax trap, and analysis by CVAFS (Liang et al., 2004; Yan et al., 2008).

The water temperature, total dissolved solids (TDS), and pH were measured in situ with a DZB-718 portable multi-parameter analyzer (Shanghai INESA Scientific Instrument Co. Ltd., China). DOC in the water samples was analyzed in the laboratory by a High TOC II analyzer (Elementar, Germany). Total carbon (TC) in the sediment was analyzed in the laboratory by the CHNS Element Analyzer (Elementar, Germany).

### 2.4. Quality control and quality assurance

To the water samples, we applied THg and MeHg standard matrix spikes and matrix spike duplicates. The recoveries for matrix spikes were in the range of 98%–105% for THg, and those were in the range of 73%–91% for MeHg. The relative standard deviation for sample duplicates was less than 10%.

The certified sediment reference material (IAEA-405) and sample duplicates were used for sediment analytical quality control. The measured concentrations of THg and MeHg of the IAEA-405 reference material were 758 ± 16 ng/g (SD, n = 6) and 5.02 ± 0.18 ng/g (SD, n = 6) respectively, consistent with the certified value (810 ± 30 ng/g for THg and 5.49 ± 0.36 ng/g for MeHg).

### 2.5. Accumulation flux of Hg in sediment

We calculated the annual deposition of Hg from water to sediment by (Covelli et al., 2008)

$$M_{Hg-sed} = \rho_s \times V_{sed} \times C_{sed} \times (1 - \phi), \quad (1)$$

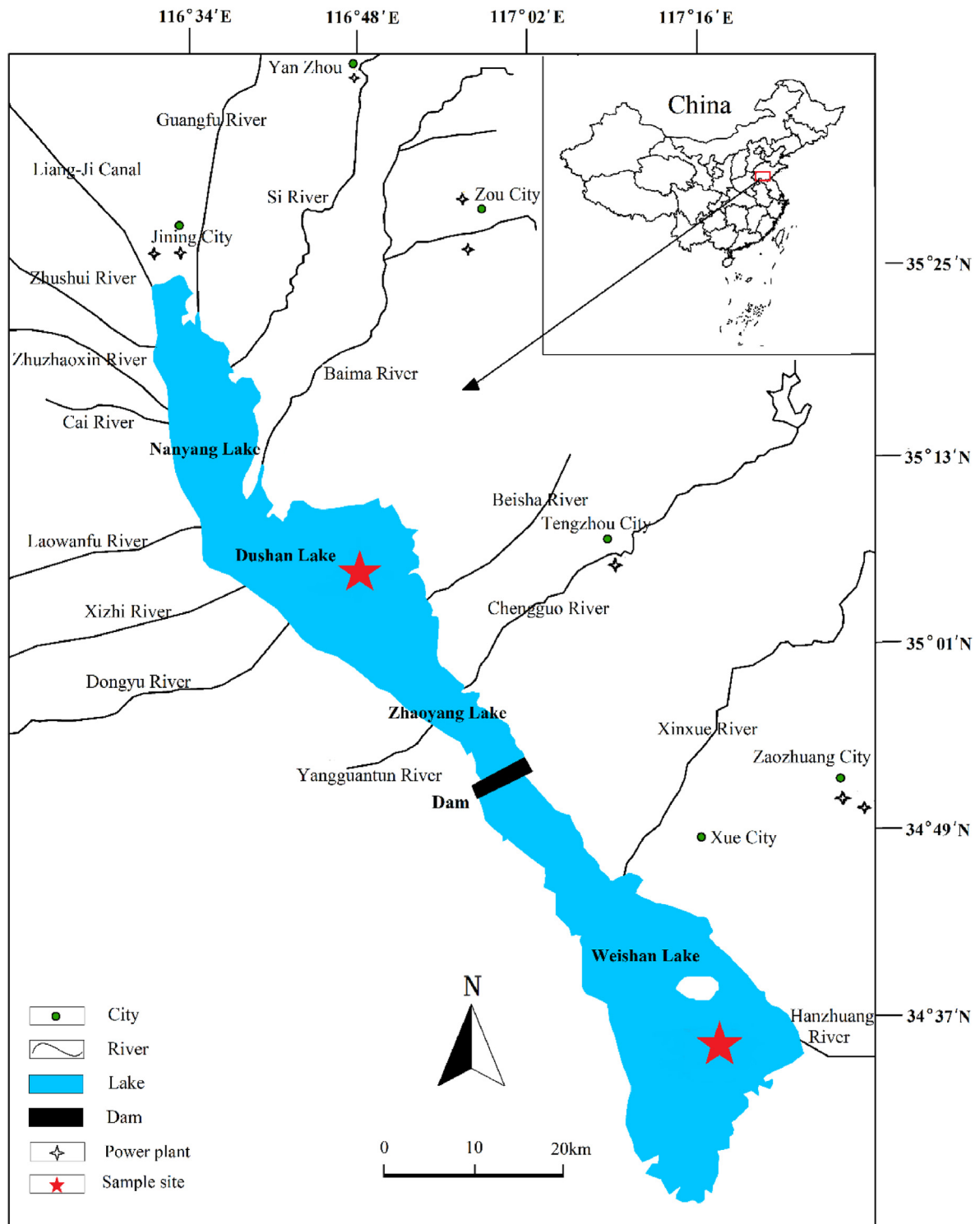


Fig. 1. Nansi Lake study area and sampling sites.

where  $M_{Hg-sed}$  is the accumulation flux of THg that entered the sediment ( $ng/cm^2/yr$ ),  $\rho_s$  is the dry density of the sediment ( $g/cm^3$ ),  $V_{sed}$  is the annual deposition rate ( $cm/yr$ ),  $C_{sed}$  is the Hg concentration in the surface sediment ( $ng/g$ ), and  $\phi$  is the sediment porosity (%).

Dry density ( $\rho_s$ ) and porosity ( $\phi$ ) was calculated by (Covelli et al., 2008)

$$\rho_s = \frac{M_{s1} \times V}{1 + MC} \tag{2}$$

and

$$\phi = \frac{M_w / \rho_w}{(M_{s2} / \rho_s) + (M_w / \rho_w)}, \tag{3}$$

where  $M_{s1}$  is the weight of wet sediment (g),  $M_{s2}$  is the weight of dry sediment (g),  $V$  is the volume of wet sediment ( $cm^3$ ),  $MC$  is the moisture content (%),  $M_w$  is the loss of water weight after sediment drying (g), and  $\rho_w$  is the water density ( $g/cm^3$ ).

## 2.6. Diffusion flux of Hg from sediment to overlying water

The diffusion flux of Hg from sediment porewater to overlying water is usually modelled based on Fick's first law. The calculation equations are (Gill et al., 1999; Muresan et al., 2007)

$$F = - \left( \frac{\phi D_w}{\theta^2} \right) \frac{\partial C}{\partial x} \quad (4)$$

and

$$\theta^2 = 1 - \ln \phi^2, \quad (5)$$

where  $F$  (ng/m<sup>2</sup>/d) is the flux of DHg with concentration  $C$  at depth  $x$ ,  $C$  (ng/L) is the concentration of DHg in the overlying water or porewater,  $x$  (cm) is the overlying water and porewater depth,  $\theta$  is the sediment tortuosity,  $\phi$  is the sediment porosity, and  $D_w$  is the diffusion coefficient of the solute of interest in the water without the presence of the sediment matrix. The  $D_w$  value is for the inorganic Hg, which was set at  $9.5 \times 10^{-6}$  cm<sup>2</sup>/s (Gill et al., 1999).

## 2.7. Statistical analysis

All the data were analyzed using Microsoft Excel 2016, IBM SPSS 22.0, and Origin Pro 8.5 for Windows (OriginLab, USA), which included correlation analysis and variance analysis. The sampling map was drawn based on ArcGIS 10.0 software (Esri, USA).

## 3. Results and discussion

### 3.1. THg and MeHg concentrations in overlying water

As shown in Table 1, there was no appreciable difference in the water quality parameters between the surface and bottom waters at the sampling sites. The pH ranged from 7.8 to 8.8 overall, which showed that the water was alkaline, whereas the DOC and total dissolved solids in DS were  $49.01 \pm 0.82$  mg/L and  $641 \pm 8$  mg/L respectively, which were slightly higher than those in WS (DOC,  $36.39 \pm 1.02$  mg/L; total dissolved solids,  $421 \pm 1$  mg/L).

The THg concentration in the overlying water varied from 2.95 to 6.83 ng/L overall, and the TMeHg concentration varied from 0.16 to 0.23 ng/L overall. The Hg concentration is much lower than the 50 ng/L specified by the surface waters environmental quality standard (GB3838-2002) issued by Ministry of Ecology and Environment of the People's Republic of China. For both sites, the THg, TMeHg, DHg, and DMeHg concentrations in the bottom water were higher than those in the surface water. Natural physical processes (waves and wind) and anthropogenic activities (shipping, fishing, etc.) would make the Hg in sediment re-emit to the water through resuspension (Lund-Hansen et al., 1999; Morgan et al., 2012; Woszczyk et al., 2014). Moreover, the fact that the amount of DHg in the bottom water was slightly higher than that at the surface indicates that diffusion from sediment to water might play an important role in influencing the amount of Hg in bottom

water.

Mercury concentrations at both sites show that the THg concentration in DS was slightly higher than that of WS. For both depths in DS, the average ratio of DHg to THg was 44.2%. For WS it was 68.2%. This indicates that DS had mainly particulate-bound Hg and WS had mainly dissolved Hg. Twenty-nine rivers flow into the upper lake, and most of them were contaminated by Hg (Zhang et al., 2018). Mercury may have been carried by particulates discharged into the lake and then gradually settled with the direction of water flow. However, the DMeHg concentrations between DS and WS were not significant, indicated that DMeHg was not affected by the particulates.

Compared with other areas (Table 2), the THg concentration in the water of Nansi Lake was higher than that of some natural waters in China's Tibetan plateau, in Europe, and in North America. Nansi Lake's THg concentration was similar to that of some lakes in south-western China that are in Hg-enriched areas, such as Hongfeng Reservoir and the Puding Reservoir, but much lower than Taihu Lake and Dianchi Lake, which are human-influenced hypereutrophic lakes. The MeHg concentrations found in this study were similar to those in waters from Hg-enriched areas and hypereutrophic lakes. MeHg accounted for 3.4%–6.0% of THg in the overlying water, which was similar to most water in China and foreign remote areas, indicating that the Hg methylation levels in Nansi Lake were relatively low.

### 3.2. Total mercury in sediment cores

THg concentrations in sediment cores from DS and WS were  $38.03 \pm 12.34$  (18.10–71.90) ng/g and  $37.76 \pm 22.19$  (17.30–88.10) ng/g respectively. The THg levels were lower than those of most lakes that were contaminated by Hg or located in Hg-enriched areas (Table 3).

Generally, the history of the Hg deposition was reflected in the sediment profiles. THg concentrations in DS and WS sediment profiles showed increasing trends from the bottom to the surface of the sediment. Previous studies have shown that the sedimentation rates in Duanshan Lake and Weishan Lake were 3.5 mm/yr and 4.2 mm/yr, respectively (Sun et al., 2017). According to the sedimentation rate, the estimated annual accumulation fluxes and sedimentary sequences at both sites showed an increasing trend since the 1950s (Fig. 2). The annual accumulation fluxes of the DS and WS ranged from 0.18 to 9.05 ng/cm<sup>2</sup>/yr and 0.1–10.37 ng/cm<sup>2</sup>/yr respectively. Fig. 2 shows that the accumulation flux after the year 2000 was 10–80 times higher than that before 1950; this might be attributed to the recovery of local economic vitality and the increase in energy demands.

With regard to energy consumption in the Nansi Lake region, coal is the main source of energy and accounts for two-thirds of its total energy consumption. Large thermal power plants, such as the Jining (Jining city), Tengzhou (Zaozhuang city), Zouxian (Jining city), and Shiliquan power plants (Zaozhuang city) are in the Nansi Lake basin area. The Tengzhou power plant was built in the 1950s, and the other power plants were built during the 1970s and 1980s. Hg emissions from coal

**Table 1**  
Water quality parameters and Hg concentration in Nansi Lake.

Sample site	Depth (m)	pH	DOC <sup>a</sup> (mg/L)	TDS <sup>b</sup> (mg/L)	THg <sup>c</sup> (ng/L)	TMeHg <sup>d</sup> (ng/L)	DHg <sup>e</sup> (ng/L)	DMeHg <sup>f</sup> (ng/L)
Dushan	0	7.8	49.59	636	4.76	0.18	2.09	0.10
	1.5	8.1	48.43	645	6.83	0.23	3.04	0.12
Weishan	0	8.3	37.11	420	2.95	0.16	1.98	0.08
	1.0	8.8	35.67	422	3.49	0.21	2.42	0.13

<sup>a</sup> Dissolved organic carbon.

<sup>b</sup> Total dissolved solids.

<sup>c</sup> Total mercury.

<sup>d</sup> Total methylmercury.

<sup>e</sup> Dissolved mercury.

<sup>f</sup> Dissolved methylmercury.

**Table 2**  
Mercury concentrations in the waters of Nansi Lake and other regions.

Study area	THg (ng/L)	MeHg (ng/L)	MeHg/THg (%)	Description	Reference
Hongfeng Reservoir, China	5.05 to 8.88	0.06 to 0.08	6.8 ± 3.3	Eutrophic lake	He et al. (2008)
Puding Reservoir, China	1.00 to 11.74 (2.74 ± 2.07)	0.19 to 0.51	9.0 ± 4.5	Local in Hg-enriched area	Zhang et al. (2009)
Aha Reservoir, China	2.14 to 16.64	0.03 to 0.90	4.0 to 9.1	Contaminated by coal mining activities	Feng et al. (2011)
Baihua Reservoir, China	4.1 ± 1.3	0.36 ± 0.23	–	Contaminated by chemical plant	Yan et al. (2013)
Dianchi Lake, China	18 to 46 (30 ± 8.0)	0.15 to 0.40 (0.24 ± 0.08)	0.22 to 1.5	Hypereutrophic lake	Wang et al. (2012b)
Taihu Lake, China	6.3 to 83 (28 ± 18)	0.04 to 0.31 (0.14 ± 0.05)	0.12 to 3.5	Hypereutrophic lake	Wang et al. (2012a)
38 lakes in Tibetan Plateau, China	3.82 ± 6.75	–	–	Background	Li et al. (2015)
Lake Balaton, Hungary	1.4 to 6.5	0.08 to 0.39	3 to 5.6	Background	Nguyen et al. (2005)
Four lakes in French Alps	0.1 to 4.34	0.002 to 0.009	< 2	Background	Marusczak et al. (2011)
131 lakes across New York State, US	0.25 to 7.71	0.03 to 3.6	–	Background	Simonin et al. (2008)
Three lakes in Quebec, Canada	1.39 to 1.78 <sup>a</sup>	0.036 to 0.087 <sup>a</sup>	–	Background	Surette et al. (2006)
Mackenzie River Basin, Canada	0.11 to 2.82	0.02 to 0.16	4.2 ± 2.1	Background	Evans et al. (2005)
Nansi Lake, China	2.95 to 6.83	0.16 to 0.25	3.4 to 6.0	–	This study

<sup>a</sup> Reported as DHg and DMeHg in Surette et al. (2006).

combustion account for a large portion of the anthropogenic releases in the environment (Wang et al., 2010). Previous studies have shown that 74.3% of the Hg in coal can be released into the atmosphere during boiler coal combustion in China (Wang et al., 2000). According to the *Statistical Yearbook of Zaozhuang City*, the production of electricity in 1980 was  $1.51 \times 10^5$  kWh, which was approximately 1000 times higher than that in 1952 ( $1.57 \times 10^2$  kWh), and the production has continued to increase (Zhanzhuang City Bureau of Statistics, 2016). The power generation was consistent with the increase in the accumulation rate in the sediment, indicating that coal combustion may be an important reason for the clear increase in Hg in the Nansi Lake sediment.

Also, since the “Reform and Opening-up Policy” in China was implemented in 1978, more industries have developed around Nansi Lake. Previous studies have found that the main inflow rivers and the soil around the Nansi Lake catchment have been contaminated by Hg, especially in industrial zones (Ren et al., 2018; Zhang et al., 2018). Thereby, Hg from anthropogenic emissions enters the environment through atmospheric deposition and runoff, resulting in an increase in Hg in Nansi Lake sediment, especially after 1980. However, the rate of Hg concentration and accumulation flux slowly decreased after 2010, which might be attributed to improvements in the ecological environment and rapid expansion of clean energy production during China's 12th five-year plan (2011–2015). Controlling particulate matter, SO<sub>2</sub>, and NO<sub>x</sub> emissions from coal-fired power plants was a key goal during that time. To reduce atmospheric Hg emissions, coal-fired power plants were requested to install air pollution control devices, such as de-NO<sub>x</sub> and flue gas desulfurization systems, both of which have high Hg removal efficiency (Wang et al., 2012).

According to statistics, although China's total energy consumption has increased, the proportion of coal consumption decreased by 1%–2% per year in the past five years, and the dust emission in Zaozhuang City dropped significantly from  $3.8 \times 10^4$  tons in 2014 to  $4.5 \times 10^3$  tons in 2016 (Zhanzhuang City Bureau of Statistics, 2016). Therefore, the

anthropogenic activities and environmental protection policies during various time periods might have caused the variation characteristics of Hg in Nansi Lake.

### 3.3. Methylmercury in sediment cores

Fig. 3 shows that MeHg concentrations in DS and WS sediments were  $0.36 \pm 0.18$  ng/g (0.12–1.01 ng/g) and  $0.33 \pm 0.19$  ng/g (0.15–1.03 ng/g) respectively. These results show that the MeHg concentrations in both sampling sites were slightly lower than those of most lakes in the world (Table 3). Generally, the MeHg/THg ratio in uncontaminated sediment was approximately equal to the relative rates of Hg methylation (Sunderland et al., 2004). In our study, the proportion of MeHg in sediments ranged from 0.4% to 1.8%, which is consistent with many lakes in China, showing a low Hg methylation rate (Table 3).

For both sites, a higher MeHg/THg ratio appeared at the sediment surface, which is consistent with previous studies that methylation of Hg generally takes place in the upper layer or subsurface zones (He et al., 2008; Feng et al., 2009). The formation of MeHg is limited by microbial activity, the partitioning between the solid/adsorbed and the aqueous phases, electron donors form and redox conditions. (Gilmour et al., 1992; King et al., 2001; Jiang et al., 2015; Zhu et al., 2018). In this study, TC concentration closely correlated with MeHg ( $P < 0.01$ ) in the sediment in both lakes, indicating that carbon is an important factor affecting the production process of MeHg. Carbon may supply energy and electron donors to bacteria and potentially contribute to Hg methylation. Also, the partition coefficient ( $K_d$ ) of THg between the solid and aqueous phases is determined by the THg concentration in the sediment divided by the DHg concentration in the porewater (reported as  $\log K_d$ ). This coefficient can reflect the migration ability of Hg<sup>2+</sup> between the liquid and solid phases and influence the Hg methylation rate (Zhu et al., 2018). In this study, the decreased  $\log K_d$  (which means

**Table 3**  
Mercury concentrations in the sediments of Nansi Lake and other regions.

Study area	THg (ng/g)	MeHg (ng/g)	MeHg/THg (%)	Reference
Hongfeng Reservoir, China	220 to 580	0.61 to 6.24	0.2 to 1.8	He et al. (2008)
Lake Taihu, China	12 to 470	0.2 to 0.96	0.5 to 1.5	Wang et al. (2012a)
Dianchi Lake, China	99 to 580 (290 ± 120)	0.43 to 2.95 (1.2 ± 0.68)	< 1	Wang et al. (2012b)
Aha Lake, China	160 to 252	0.2 to 7.2	–	Feng et al. (2011)
Lakes in Voyageurs National Park, USA	102 to 364	–	–	Wiener et al. (2006)
Lake Balaton, Hungary	9 to 160	0.07 to 0.84	0.2 to 1.0	Nguyen et al. (2005)
Palude Maggiore, Italy	742 ± 157	1.14 ± 0.20	0.1 to 0.2	Dominik et al. (2014)
Nansi Lake, China	17.30 to 88.10 (38.15 ± 17.55)	0.12 to 1.01 (0.33 ± 0.19)	0.4 to 1.8 (0.9 ± 0.3)	This study

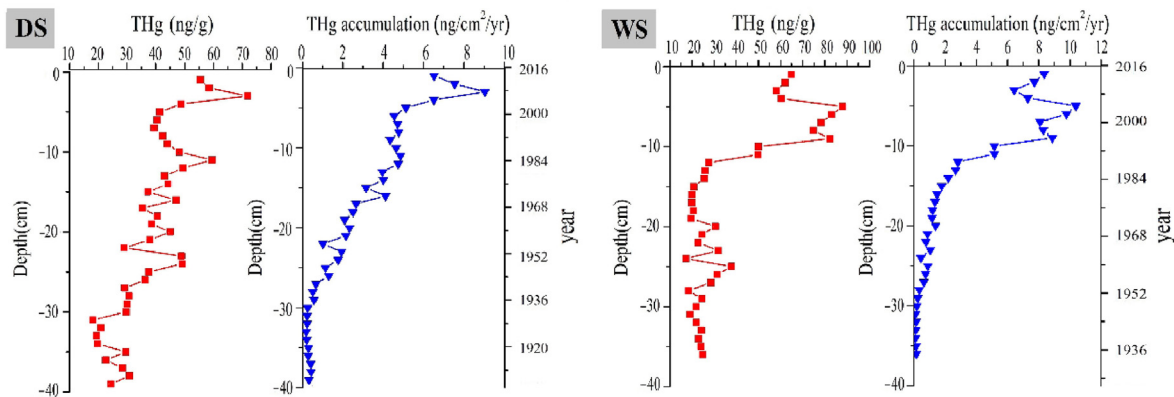


Fig. 2. THg concentration and estimated accumulation influx in sediment.

the increase in THg solubility) in the surface layer was consistent with the MeHg/THg ratio, indicating that the solubility of THg also affected the methylation of Hg in both sites.

3.4. Estimation of Hg exchange flux at sediment–water interface

When the Hg concentration in sediment porewater is higher than that in overlying water, the porewater is a potential source of Hg, which can diffuse to the overlying water (Gill et al., 1999). In our study, the DHg concentration in the surface porewater of sediment ranged from 1.5 to 12.42 ng/L, which was 2.7–3.2 times higher than that of the

overlying water, indicating that there was an obvious Hg exchange flux between the sediment and the water. On the basis of Fick's first law, the diffusion fluxes of DHg from sediment to overlying water in DS and WS were 22.93 ng/m<sup>2</sup>/d and 23.06 ng/m<sup>2</sup>/d respectively. The result shows that the diffusion fluxes of Hg from the sediment were similar in both sample sites but lower than those of Dianchi Lake (210–230 ng/m<sup>2</sup>/d) and North Taihu Lake (410–960 ng/m<sup>2</sup>/d) (Wang et al., 2012a, 2012b). We took the surface area of Nansi Lake under normal water storage as the direct exchange area between its sediment and overlying water and took the upper and lower portions of Nansi Lake as the exchange areas of DS and WS respectively. The deposition area of upper lake is

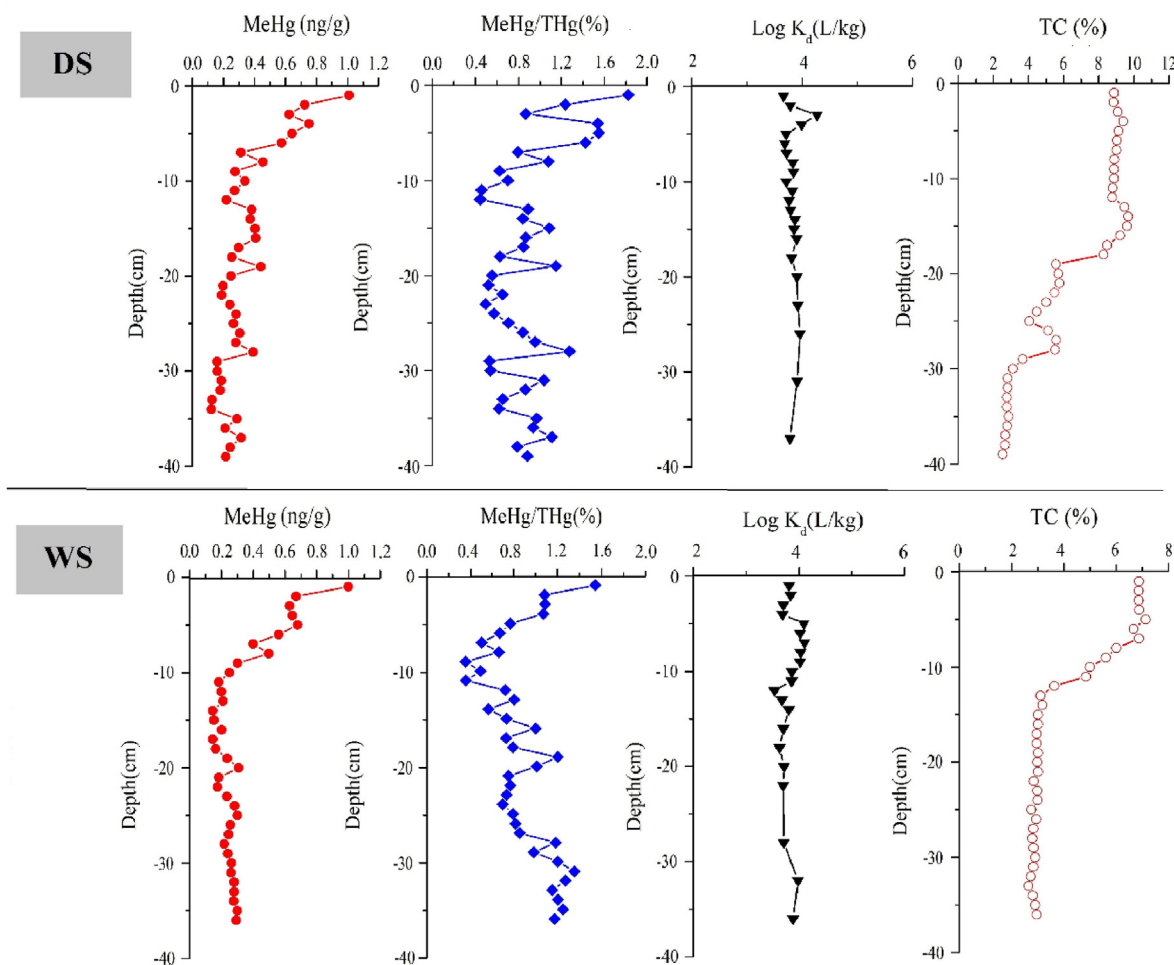


Fig. 3. MeHg concentration, MeHg/THg ratio, log  $K_d$  of THg, and total carbon in DS and WS sediments at various sediment depths.

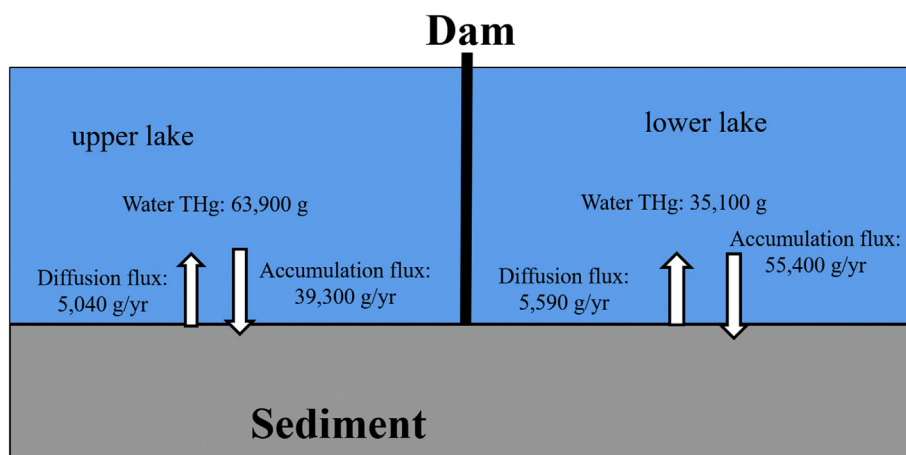


Fig. 4. Exchange of THg at sediment–water interface in Nansi Lake. Hollow arrows represent the Hg mass balance between overlying water and sediment.

approximately 602 km<sup>2</sup> and of lower lake is approximately 664 km<sup>2</sup>. Therefore, the total diffusion amount of Hg from sediment to the overlying water was 10,600 g/yr, with 5040 g/yr in the upper lake and 5590 g/yr in the lower lake.

Mercury deposition flux from water to sediment can also be estimated. Based on the THg concentrations in the surfaces of their sediment, the deposition fluxes of the sediments were 6.53 ng/cm<sup>2</sup>/yr in DS and 8.43 ng/cm<sup>2</sup>/yr in WS, and the total accumulations of Hg were 39,300 g/yr in DS and 55,400 g/yr in WS. The results show that 10%–13% of THg in the sediment could then be released into the overlying water, (Fig. 4). The results also show that the exchange process of the sediment–water interface should not be neglected, and sediment can be an important source of Hg in overlying water.

To estimate the relative contribution of Hg from sediment to overlying water at the sediment–water interface, we assumed the water and Hg species to be in instantaneous equilibrium. The quantity of water stored in the upper and lower lakes of Nansi Lake can be obtained from the Rainwater Information System of Shandong Hydrological Bureau (<http://www.sdswj.cn/>). At the time of this study, the quantities were approximately  $11.04 \times 10^9$  m<sup>3</sup> and  $10.9 \times 10^9$  m<sup>3</sup>, respectively. According to the THg concentration in overlying water, the results show that there were approximately 63,900 g and 35,100 g Hg in the upper and lower lakes respectively. It can be estimated that the diffusion from sediment accounted for 7.9% and 16% of the Hg in the water respectively, in which the time partition was calculated by year. The result reflects the important role of the diffusion of Hg at sediment–water interface in shallow lakes. Moreover, our estimate is probably lower than the actual concentration because shallow lakes are more susceptible to hydraulic disturbance, such as wave action and water transport. Therefore, although there are large uncertainties due to the limited data, our study highlights the importance of the potential risk to overlying water of Hg in sediment.

Methylmercury is produced principally in surficial sediment by Hg methylating microorganisms (Schaefer and Morel, 2009; Hu et al., 2013). Therefore, MeHg in sediment can be released to the overlying water, increasing its concentration in the water. However, the rate of its diffusion needs to be studied further.

#### 4. Conclusions

Nansi Lake was not markedly contaminated by Hg. The THg concentration and accumulation flux in the sediment indicated that the demand for energy and the policy management influenced the Hg accumulation in its sediment. The source of the Hg might have been regional emissions due to coal consumption. The accumulation rate has markedly increased at both collection sites since the 1950s; that increase is related to the increase in energy demand due to the recovery of

the local economy. However, the declining trend of the Hg concentration in recent years might be due to the strict control of pollutant emissions.

The MeHg concentration and the MeHg/THg ratio in water and sediment were relatively low. Total carbon and the solubility of THg in the solid or liquid phase could affect the MeHg concentration in sediment.

At the sediment–water interface, 10%–13% of THg in the sediment can be diffused into the overlying water in the year level. The diffusion from sediment accounted for 7.9%–16% of Hg in lake water, which reflected the important role of the re-emission of Hg in sediment. There are large uncertainties due to the limited data, but our study highlights that sediment in shallow lakes can be an important source of Hg in overlying water.

#### CRedit authorship contribution statement

**Liyuan Yang:** Data curation, Writing - original draft, Supervision. **Wei Zhang:** Methodology, Data curation, Writing - original draft. **Mingyi Ren:** Methodology, Investigation. **Feifei Cao:** Methodology, Investigation. **Fengfeng Chen:** Investigation, Visualization. **Yutao Zhang:** Visualization. **Lihai Shang:** Conceptualization, Methodology, Supervision, Writing - review & editing.

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