Variance of mercury speciation in municipal sewage treatment plant: effects of mercury on the atmosphere

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Abstract

The speciation of mercury in various processing units of sewage treatment in autumn and winter were studied to understand the conversion and fate of mercury. The results show that the average concentrations of total mercury (THg) in the influent were 130.5 ± 69.8 ng/L and 231.3 ± 107.2 ng/L in autumn and winter, respectively, and the particulate mercury (PHg) was the main speciation (accounting for 59.3% and 86.9%, respectively). The proportion of dissolved mercury (DHg) increased after treatment, and the total removal efficiencies of THg were 78.9% and 90.8%, respectively. The release of mercury into the atmosphere during wastewater treatment was studied for the first time. The dissolved gaseous mercury (DGM) levels in the influent in autumn and winter were 0.60 ± 0.40 ng/L and 0.34 ± 0.21 ng/L, respectively. The estimated mercury from aeration was 3.94 kg per year in China. DGM will be released to the air if the sewage treatment plant is open-air. Closed sewage treatment and collection of waste gas treatment are necessary to reduce the influence of released mercury. Mercury releases into the atmosphere in the process of sewage treatment is one of the fates of mercury in sewage. Closed sewage treatment and collection of waste gas treatment are necessary to reduce the influence of released mercury. The reactive mercury (RHg) levels in the influents of autumn and winter were 1.28 ± 0.49 ng/L and 1.96 ± 0.43 ng/L, and these levels account for a small proportion of THg, only 1.7% and 0.8%. Hg^{2+} were released by the degradation of organic matter in the secondary biological treatment. The THg levels in dehydrated sludge were higher than those in biochemical sludge but lower than the maximum limit of THg in agricultural sludge.

1. Introduction

Hg, a highly toxic heavy metal element that causes health and environmental problems, has been a point of great concern for decades (Kyrre et al., 2017). With accelerated urbanization, municipal sewage treatment plants (MSTPs) have become a gathering place for domestic sewage. The mercury discharged from municipal sewage into the environment has been underestimated or even neglected, but in fact, it is an important part of China's anthropogenic mercury emissions (Liu et al., 2016; Hui et al., 2017). In the process of water treatment, species of mercury change and are redistributed in various phases to re-enter the environment. The total mercury released into the aquatic system through municipal sewage worldwide was approximately 16–81 t/a (Ullrich et al., 2001). In 2015, the analysis of the materials of 62 MSTPs in 24 cities in China showed that the amounts of THg released to the aquatic environment, soil and atmosphere from sewage were 23 t (17 t and 6.2 t from untreated and treated sewage, respectively), 120 t and 15 t, respectively (Liu et al., 2018). There are many mercury species in water (Ullrich et al., 2001); among them, DGM mainly exists as elemental mercury (Hg^0), which can be directly exchanged with the atmosphere; RHg mainly exists as free Hg^{2+} , which has high activity and can complex with inorganic ions or organic matter. Different mercury species have different environmental impact mechanisms and bioavailability for the environment due to their different physical and chemical properties. Only a small part of the mercury entering the sewage treatment plant is discharged with the effluent; most of it is absorbed by the activated sludge and discharged with the remaining sludge (Mao et al., 2016; Liu et al., 2018). The remaining sludge is used in agriculture, placed in landfills and incinerated (Takaoka et al., 2012; Pudasainee et al., 2013); then, mercury re-enters to the environment. Previous studies have shown that agricultural use of sludge brings large amounts of mercury into farmland (Kocman et al., 2017). However, the mercury released by sludge incineration contributes the most to mercury emissions from sewage treatment plants. In 2010, 12 t of Hg was emitted by municipal waste incineration (including sludge and other domestic waste) in China (Zhang et al., 2015), and 37 t of mercury was estimated by Tian et al. (Tian et al., 2012). It must be pointed out that burying mercury in the sludge in landfills is not entirely without negative consequences. Gaseous mercury from municipal solid waste in landfills is released into the atmosphere and groundwater, which has attracted people's attention for many years (Cheng and Hu, 2012; Zhu et al., 2013; Tao et al., 2017).

Many studies have been conducted on the migration and removal efficiency of THg and methylmercury (MeHg) and the methylation of mercury in wastewater treatment processes (Balogh and Liang, 1995; Bodaly et al., 1998; Gbondo-Tugbawa et al., 2010; Li et al., 2014; Liu et al., 2018), focusing on dissolved mercury (DHg) and particulate mercury (PHg); no studies focused on DGM and RHg. In the natural water environment, Hg^{2+} can be reduced to Hg^0 by photoreduction and microbial reduction (Mason et al., 1995; Nascimento and Chartone-Souza, 2003; **Gonzalez-Raymat et al., 2017**); then, Hg^0 is released to the air. Since many microorganisms in the biological treatment decompose organic substances in sewage water, we speculate that elemental mercury will also be generated during this process, which will be released into the air through aeration. By studying the speciation of DGM, RHg, DHg, and PHg in the sewage treatment process, the possible conversion process and removal mechanisms of different mercury species were analysed to learn their possible impacts on the environment.

2. Materials And Methods

The samples were collected at the World Garden Water Purification Plant (WGWPP) in Qingdao, China. The WGWPP mainly receives domestic sewage from surrounding universities and residential areas; its sewage treatment capacity is 6000 m³/day. The anaerobic-anoxic-aerobic traditional activated sludge method and membrane filtration reactor (A²/O-MBR) are used. The main process configuration is shown in Fig. 1.

2.1. Sampling and storage

Sampling was performed for 5 consecutive days from October 30 to November 3 in 2019 and January 11 to 15 in 2020, representing autumn and winter samples, respectively. The sampling time was 9:00 am, and 7 water sampling points were set (A~G) along with 4 sludge sampling points (H~K), (Fig. 1). The temperature, pH and dissolved oxygen (DO) were measured at the same time. GEM was collected in aerobic tank(A) in autumn. SKC 5000 pump was used to collect the gas with a flow rate of 600 mL/min for 20 minutes. The Teflon tube was penetrated to about 50 cm from the water surface, and the GEM was finally trapped by a gold sand tube, a soda-lime tube was connected to remove water vapor and acidic gases. Three parallel samples were collected every day. Finally, GEM was measured by a cold atomic fluorescence system spectrometer (CVAFS, Model III, Brooks Rand Labs, USA). The similar details of the sampling methods and determination of GEM were given in (Chong et al., 2019)

After the wastewater samples were brought back to the laboratory in the dark, they were divided into 4 parts. One portion of the water was immediately used to measure DGM and RHg first. The second part was transferred to a 250-ml Teflon bottle, and trace-metal grade HCl was added for storage to measure THg. After 30 min of natural settlement, the supernatant water was filtered through a 0.45- μm cellulose acetate filter membrane. Then, the filtrate was transferred to a 250-ml Teflon bottle, and trace-metal grade HCl was added for storage to determine DHg, while sulfuric acid was added into another filtrate for storage to determine parameters, such as COD, TN and TP. The precipitated sludge samples were centrifugally dehydrated and lyophilized for preservation. After grinding through a 100-mesh sieve, the sludge was sealed and stored.

2.2. Sample analysis method

DGM in a 400-mL water sample was bubbled using mercury-free nitrogen at a flow rate of 350 mL/min for 30 min. Dissolved gaseous elemental Hg was adsorbed on a gold sand tube and then measured by a cold atomic fluorescence spectrometer (Brooksrand Lab, Model III) (Wang et al., 2017). SnCl_2 solution was added in the bubbler bottle to reduce the Hg^{2+} to Hg^0 , and then, Hg^0 was absorbed by the gold sand tube bubbling with mercury-free nitrogen at a flow rate of 350 mL/min for 30 min. The gold sand tube was heated to measure mercury by the cold atomic fluorescence spectrometer. This portion was RHg.

The unfiltered and filtered water samples were digested with nitrohydrochloric acid (HCl: HNO₃ = 3:1) at 98°C for 1 h to measure THg and DHg. Then, the digested water samples were measured according to the method of EPA1631 (USEPA, 2007). Briefly, 5 mL digested water was oxidized by bromine monochloride solution (BrCl). Then, hydroxylamine hydrochloride (NH₂OHCl) was used to reduce excess oxidant prior to quantification by tin chloride reduction. Mercury was determined by an atomic fluorescence spectrometer (Brooksrand Lab, Merx-T). The concentration of PHg was the difference between THg and DHg.

The chemical oxygen demand (COD), total nitrogen (TN), and total phosphorus (TP) in sewage were determined referring to "Water and Wastewater Monitoring and Analysis Method" (SEPA, 2002). The sludge sample was digested by nitrohydrochloric acid at 98°C for 1 h to determine the total mercury by atomic fluorescence photometer (AFS-920).

All the samples were collected in acid-washed Teflon bottles (4 mol/L and 1% HCl treated successively in 60°C for at least 12 h) and stored double bagged. The glassware was soaked in 4 mol/L HNO₃ acid for more than 12 h, rinsed with deionized water, heated at 500 °C for 1 h, then sealed in a bag for use. Two blanks, 10% parallel and 2 spiked recovered samples, were measured to check the accuracy. The relative standard deviations (RSD) of the measurements of the parallel samples were all less than 10%, and the recovery rate was approximately 92%.

2.3 Modeled Hg Saturation and Flux

The saturation (S_a) values of DGM were calculated by the following formula

$$S_a = \frac{C_w H^*}{C_a}$$

(1)

C_w —DGM concentration in water, pg/L;

C_a —GEM concentration in the atmosphere, ng/m³;

H^* —dimensionless Henry's law constant, given by Andersson et al. (2008);

$$H^* = \exp\left(\frac{-2404.3}{T} + 6.92\right) \quad (2)$$

T is the water temperature in K.

Water/air flux of Hg was calculated using a thin film gas exchange model developed by (Wanninkhof and Rik, 1992) and the water/air exchange flux of Hg, F (ng·m⁻²·h⁻¹), was calculated using Eq. (3):

$$F = K_w \left(C_w - \frac{C_a}{H^*} \right) \quad (3)$$

K_w —the gas transfer velocity of a Hg⁰ in the water/air surface (cm·h⁻¹) and was calculated according to Eq. (4): (Wanninkhof and Rik, 1992)

$$K_w = 0.31 \times U_{10}^2 \times (Sc_{Hg}/600)^{-0.5} \quad (4)$$

U_{10} —the wind speed normalized to 10 m above water surface;

Sc_{Hg} —the Schmidt number for Hg, is defined as follows: $Sc_{Hg} = \nu / D_{Hg}$ (5)

ν —the kinematic viscosity ($\text{cm}^2 \cdot \text{s}^{-1}$) of freshwater;

D_{Hg} —the Hg diffusion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$) in freshwater, which was calculated by the molecular dynamics simulation, as described by (Kuss et al., 2009).

3. Results And Discussion

3.1. THg in sewage

In autumn, the average THg concentration in the influent was 130.5 ± 69.8 ng/L, ranging from 55.4 to 230.2 ng/L with 54% coefficient of variation (CV). In winter, the average THg concentration in the influent was 231.3 ± 107.2 ng/L, ranging from 83.6 to 335.8 ng/L with 46% CV (Fig. 2). THg in the raw sewage varied widely during the sampling period, which was similar to previous results (Bodaly et al., 1998; Gbondo-Tugbawa et al., 2010; Li et al., 2014), and was affected by the change of sewage sources. The THg concentration of sewage in the WGWPP was higher than that in the Winnipeg sewage treatment plant of Canada ($2 \sim 150$ ng/L) (Bodaly et al., 1998) but lower than the Onondaga County Metropolitan Wastewater Treatment Plant in New York (385 ± 287 ng/L) (Gbondo-Tugbawa et al., 2010) and the Jiaozuo No. 1 sewage treatment plant (1212 ± 598 ng/L) in China (Li et al., 2014). This difference between different plants is mainly related to the sources of sewage. The sewage of the WGWPP comes from surrounding universities and residential areas without industry sources; the COD values in the sewage were 225.1 ± 28.3 mg/L and 239.6 ± 36.3 mg/L in autumn and winter, respectively, resulting in a lower total mercury concentration in raw sewage. THg in winter was higher than that in autumn, which may be affected by higher the concentration of organic pollutants. The total amount of sewage treatment in winter was smaller than that in autumn and was affected by less bathing water.

Table 1
Correlation between mercury speciation content and sewage quality parameters

	T(°C)	pH	DO	COD	TN	TP	DHg	PHg	DGM	RHg	THg
T(°C)	1										
pH	-0.371*	1									
DO	-0.050	-0.352*	1								
COD	-0.226	0.674**	-0.565**	1							
TN	-0.200	0.810**	-0.451**	0.842**	1						
TP	-0.428	0.512	-0.815**	0.694**	0.526	1					
DHg	-0.017	0.504**	-0.453**	0.485**	0.590**	0.512	1				
PHg	0.066	0.628**	-0.354*	0.582**	0.746**	0.532	0.556**	1			
DGM	0.221	-0.061	-0.260	0.058	0.010	0.587*	0.150	0.069	1		
RHg	0.059	0.058	0.424*	-0.200	-0.155	-0.162	-0.224	-0.147	0.234	1	
THg	0.096	0.587**	-0.476**	0.565**	0.680**	0.587*	0.772**	0.934**	0.088	0.301	1
*. At the 0.05 level (two-tailed), the correlation is significant. **. At the 0.01 level (two-tailed), the correlation is significant.											

THg in the effluent of the superfine grid tends to be stable with average values of 73.3 ± 14.1 ng/L in autumn and 119.1 ± 68.5 ng/L in winter after a primary treatment, such as a coarse grid and regulating tank. The removal efficiencies of THg in the primary treatment process in autumn and winter were 43.4% and 48.5%, respectively. After the secondary biological treatment of wastewater, THg in water decreased by 64.3% and 84.1% in autumn and winter, respectively. Therefore, the removal of THg mainly occurred in the secondary biological treatment process. A large amount of activated sludge in the biochemical tank strongly adsorbs mercury (Gbondo-Tugbawa et al., 2010; Li et al., 2014; Liu et al., 2018), which leads to the migration of mercury from the aqueous phase to the surface of the activated sludge. The membrane filter can effectively separate sludge from water, so the removal of THg in water was significant. THg in the anaerobic, anoxic, and aerobic processes showed a general downward trend with the sewage treatment. In both seasons, THg in effluent increased slightly, possibly due to the introduction of a small amount of mercury when disinfecting with sodium hypochlorite (NaClO) in the clarification tank. There was a significant positive correlation between pH and THg (Table 1); mercury is more easily adsorbed at high pH. THg has a significant positive correlation with COD ($r = 0.565$, $P < 0.01$), TN ($r = 0.680$, $P < 0.01$), and TP ($r = 0.587$, $P < 0.05$), indicating that THg in sewage has a significant relationship with water pollution, mainly from organic pollutants in sewage.

The concentrations of THg in the effluent in autumn and winter were 27.5 ± 4.1 ng/L and 21.4 ± 4.0 ng/L, respectively, and the total removal efficiencies of THg were 78.9% and 90.8%, respectively. The removal efficiency of THg by the traditional activated sludge process in the Tangjiaqiao Wastewater Treatment Plant in Chongqing was 76.4% (Lu et al., 2008), while the removal rate of THg by the oxidation ditch process in the Jiaozuo No. 1 Wastewater Treatment Plant reached 98.2% (Li et al., 2014), which may be related with high influent THg. THg in the effluent was far lower than the maximum allowable concentration of 1000 ng/L pollutants in the Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant of China (GB18918-2002).

3.2 Change in mercury speciation in the sewage treatment process

3.2.1 DHg and PHg

In autumn, the average DHg concentration in influent was 50.3 ± 27.8 ng/L, ranging from 22.4 ~ 93.7 ng/L with 55% CV, while it was 24.1 ± 3.2 ng/L, ranging from 20.8 ~ 28.1 ng/L with 13.3% CV, in winter, which was lower and more stable (Fig. 3). DHg decreased from 24.1 ± 3.2 ng/L in influent water to 16.2 ± 3.3 ng/L in effluent from the superfine grid in winter, and the removal rate was 32.8%, but there was no significant decrease in autumn. The PHg/THg values were 59.3% and 86.9% in autumn and winter, respectively. PHg was the main speciation in the influent of the sewage treatment plant. High PHg in winter leads to high THg in the influent water. After the first stage treatment, PHg in autumn and winter decreased to 28.1 ± 15.1 ng/L and 102.9 ± 67.6 ng/L, respectively, and the removal rates were 64.9% and 50.3%. This observation indicated that the mercury in the sewage was mainly removed in the speciation of PHg with the particles in the sewage in this physical treatment process.

In autumn, both DHg and PHg decreased significantly in the anoxic tank, which was related to the larger volume and longer hydraulic retention time of the anoxic tank compared with the anaerobic tank. Activated sludge can absorb mercury from sewage, and most of the mercury was removed in the anoxic tank. However, DHg and PHg had no obvious change in the aerobic tank. After further membrane filtration, PHg in water was further reduced. During the whole secondary treatment process, DHg decreased from 49.6 ± 16.0 ng/L to 18.8 ± 6.1 ng/L with a removal efficiency of 62.1%, and PHg decreased from 28.1 ± 15.1 ng/L to 7.4 ± 4.9 ng/L with a removal efficiency of 73.7%. Therefore, the secondary biological treatment process had high removal efficiencies of both DHg and PHg. The concentrations of DHg and PHg in the final effluent were 21.0 ± 3.1 ng/L and 5.5 ± 2.3 ng/L respectively. The total removal efficiencies of DHg and PHg were 58.3% and 93.1%, respectively, similar to the results of Balogh (Balogh and Liang, 1995) and Gbondo-Tugbawa (Gbondo-Tugbawa et al., 2010). On the whole, DHg/THg showed an upward trend in autumn and winter from influent to effluent, which was similar to previous research (Lu et al., 2008) (Fig. 3). The DHg/THg ratio was higher in autumn; therefore, DHg was the main speciation of mercury in the wastewater treatment. In winter, although the PHg concentration of wastewater in the biological tank decreased obviously, PHg was much still higher than that of DHg in winter, in contrast to autumn. In winter, the water temperature was low (approximately 13°C); sludge bulking, poor sedimentation performance and high sludge particle content could lead to high PHg concentration, which was also the reason for the high THg in the biological tank. Some studies have found that sludge bulking caused by filamentous bacteria can be successfully induced when the operating temperature of the traditional process is below $14 \pm 1^\circ\text{C}$ (Gao et al., 2020); then, PHg decreased to 13.4 ± 10.3 ng/L after the membrane filter. The removal rates of DHg and PHg were 50% and 87%, respectively, in winter. Although DHg/THg also showed an upward trend in winter (Fig. 3B), in contrast to autumn, the PHg was always higher than that of DHg in the sewage treatment process, and the final effluent DHg/THg was 44.4%, which was higher than reported previously (Balogh and Nollet, 2008a) (mean 36%, 24%~49%); thus, PHg was the main mercury species in sewage in winter.

3.2.2 DGM and RHg

DGM is gaseous mercury dissolved in water, which is easily released into the air during aeration and water flow. The DGM levels in the influent were 0.60 ± 0.40 ng/L and 0.34 ± 0.21 ng/L in autumn and winter, respectively (Fig. 5), accounting for 0.5% and 0.15% of THg; these values were much higher than those of other natural water bodies (Table 2) (Feng et al., 2004; He et al., 2006; Ci et al., 2011; Ma et al., 2019) but lower than those of precipitation in the Xunyang mercury mining area (Ao et al., 2016).

Table 2
Concentrations of DGM and RHg in raw sewage and other water bodies.

Time	Location	Type	DGM/ng·L ⁻¹	RHg/ng·L ⁻¹	THg/ng·L ⁻¹	Reference
2019.10.30 ~ 11.3	WGWPP (Qing dao, China)	sewage	0.60 ± 0.40	1.28 ± 0.49	55.4 ~ 230.2	this article
2020.1.11 ~ 1.15	WGWPP (Qing dao, China)	sewage	0.34 ± 0.21	1.96 ± 0.43	83.6 ~ 335.8	this article
2012.7	Yellow Sea	sea	0.06 ± 0.01	1.08 ± 0.28	1.69 ± 0.35	(Ci et al., 2011)
2016.9 ~ 2017.6	Ruxi River (Chong qing, China)	river	—	0.21 ± 0.15	0.51 ~ 9.10	(Ma et al., 2019)
2014	Hongfeng Reservoir (Gui zhou, China)	reservoir	0.02 ~ 0.11	0.14 ~ 2.70	—	(He et al., 2006)
2003.3.27	Baihua Reservoir (Gui zhou, China)	reservoir	0.12	1.60	29.5	(Feng et al., 2004)
2012.7 ~ 2013.9	Xunyang mercury mining area (Shaan xi, China)	precipitation	3.8 ± 3.6	13.0 ± 9.0	48 ± 43	(Ao et al., 2016)

There was a slight decrease in the content after the primary treatment because part of the DGM was released to the air with the water flow. We found that the DGM levels in the anaerobic, anoxic and aerobic biochemical tanks were relatively high, especially in autumn; DGM in the anaerobic tank reached 2.48 ± 1.25 ng/L (Fig. 5A). The organic matter in water was decomposed under anaerobic conditions, and part of the mercury was transformed into Hg^0 by microorganisms (Robinson and Tuovinen, 1984). The dissolved oxygen was low in these three biochemical tanks; Hg^0 was apt to form under anaerobic conditions. Hg^0 was stable, and Hg^0 exchange between air and water was small under reduction conditions, resulting in high Hg^0 . The highest DGM concentration in the anaerobic tank indicated that more Hg^0 was produced under anaerobic conditions.

The average concentration of DGM in the three biological tanks was 0.86 ± 0.47 ng/L during winter, and this concentration was significantly higher than that in the influent. However, there was no significant difference among them, which was different from the case in autumn. In winter, the average water temperature was 13°C, and the lower water temperature was not conducive to the reduction of divalent mercury because the activity of anaerobic microorganism decreased with the decrease of water temperature. Previous studies have shown a minimum DGM release at the lowest temperature (Kristin A Sullivan, 1998). Moreover, DGM release was affected by the decrease of the inflow of wastewater treatment plant and the small load of sewage treatment in winter. The DGM in the effluent of the membrane filter decreased because of the release of DGM into the air under aeration. The final DGM levels of the effluent were 0.48 ± 0.22 ng/L (autumn) and 0.16 ± 0.06 ng/L (winter), which decreased by 20% and 47% compared with the influent, respectively.

To verify whether DGM continues to be produced in the biochemical tanks, the sewage in the three biological tanks was continuously bubbled for 2.5 h, and the released DGM was measured every 0.5 h during the period (Fig. 4). The amount of DGM produced gradually decreased over 2.5 h, and it remained stable after 1.5 h but was still produced after 2.5 h. Therefore, DGM was produced continuously by some microbial activities under continuous nitrogen conditions. The DGM amount produced in the aerobic tank water was larger than that in the anaerobic and anoxic tanks; therefore, the formation of DGM was more favourable under the aerobic conditions.

The RHg levels in autumn and winter were 1.28 ± 0.49 ng/L and 1.96 ± 0.43 ng/L respectively, accounting for 1.7% and 0.8% of THg in the influent. The RHg/THg in the atmospheric precipitation of the Xunyang mercury mining area in Shaanxi Province was approximately 27% (Ao et al., 2016), while Ci et al. found that the RHg/THg in the Yellow Sea reached 63.9% (Ci et al., 2011), but the Baihua Reservoir was 5.4% (Feng et al., 2004). The low RHg/THg ratio in wastewater was due to the large amount of organic compounds in the wastewater. Hg^{2+} combines with organic or inorganic ligands to form complexes, resulting in a low content of divalent mercury. The chelate of DOC can combine with Hg^{2+} to inhibit the reducibility of mercury (Rolfhus and Fitzgerald, 2001). The decrease in RHg in the superfine grid effluent may be due to the removal of Hg^{2+} with the particulate matter. Secondary biological treatment can greatly reduce COD, TN, TP, etc., and Hg^{2+} was released from the organic and inorganic complexes. This can effectively explain the phenomenon of increased RHg in the membrane filter effluent after the secondary biological treatment. According to the correlation analysis, there was a positive correlation between RHg and DO ($r = 0.424$, $P < 0.05$). The increase in RHg in the final effluent may be caused by the oxidation of partially dissolved mercury when sodium hypochlorite was added for disinfection. In general, RHg in sewage increased after treatment by the sewage treatment plant.

These significant differences show that, in autumn, there was no significant difference in DGM among other units, except for the anaerobic tanks, although there was higher DGM in the biological tanks (Fig. 5A). The RHg in the effluent was significantly different from the other units. In winter, significant differences occurred in DGM between other non-biological tanks and the three biological tanks (Fig. 5B). There was large difference of RHg in the water treatment process from the error bars, which might be related to the small volume of sewage treated. The RHg was lower in the biological tanks compared with the other processes, although there was no significant difference of RHg among most treatment processes.

3.3 Hg release to the air

3.3.1 Generation of GEM in aerobic tank

GEM in water is easily released into the atmosphere under aeration. In view of the continuous aeration of air into the aerobic tank in the secondary biological treatment, we speculated that a considerable amount of gaseous mercury will be generated at this stage. As shown in Fig. 6, the average GEM concentration in aerobic tank air was 6.34 ± 0.49 ng/m³, ranging from 4.28 to 9.02 ng/m³. The average concentration of GEM in Qingdao was 2.18 ng/m³ during autumn (Nie et al., 2020). The aeration rate of the air-blower was stable at 14.2 m³/min. After subtracting the original GEM from the air, GEM production was 18.1 ng/m³ by aeration according to the average sewage treatment capacity (4708 m³/d) of WGWWP. Therefore, 3% of mercury in the raw sewage was released into the air by aeration. GEM in aerobic tank of a large sewage treatment plant (Maidao) in Qingdao was also measured, and the average GEM concentration was 15.45 ± 4.11 ng/m³, ranging from 11.49 to 22.67 ng/m³ (Fig. 6). In the same way, according to the daily aeration rate (38800 m³/h) and water treatment capacity (140984 m³/d), Maidao sewage treatment plant GEM production was 102 ng/m³ in aeration tank. By the end of 2019, China's urban sewage treatment plants have a treatment capacity of 1.77×10^8 m³/d, with a total treatment capacity of 5.32×10^{10} m³/a (MEE, 2019). Supposed that two-thirds are large-scale like Maidao MSTP and one-third are small-scale like WGWWP, we can estimate that the direct emission of mercury from aeration is 3.94 kg per year in China.

3.3.2 Estimate Hg Saturation and Flux of DGM

Based on the atmospheric GEM (2.18 ng/m³ and 2.30 ng/m³ during autumn and winter, respectively) in Qingdao in 2018 (Nie et al., 2020) and the average wind speed during the sampling period (5.63 m/s and 5.17 m/s), we estimated the S_a and flux of Hg by the formulas mentioned in 2.3. Since the aeration tank is aerated, flux estimation is not performed here. The high S_a (1) indicates that the DGM in water was oversaturated and the higher the value, the easier

the release to the atmosphere. As shown in Table 3, under the assumption the waste water treatment plant was open-air, the average water/air Hg fluxes were $71.6 \pm 36.7 \text{ ng}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $29.4 \pm 13.6 \text{ ng}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ in autumn and winter respectively, much higher than that the natural water bodies (Feng et al., 2004; Ci et al., 2011; Wang et al., 2017) because of the higher DGM. Lower DGM concentration and lower wind speed in winter make mercury released to air less significant than in autumn. When the tanks were covered by shelters and waste air was collected, the released mercury might be removed by the treatment materials partly. However, mercury was released to the air in waste water treat plant without shelters could not be ignored. At present, there are still many open-air sewage treatment plants in the world. If the waste air released was not treated, much mercury will be released to the air which was also an important sink for mercury in sewage. Most sewage treatment plants are located in or near densely populated urban areas, therefore, closed sewage treatment and collection of waste gas treatment are necessary to reduce the influence of released mercury.

Table 3
DGM saturation (Sa) and fluxes of sewage in various processing units in autumn and winter

		influent	SG effluent	Anaerobic	Anoxic	MF effluent	effluent	average
Sa	autumn	76.4 ± 50.9	45.8 ± 26.7	315.8 ± 159.2	124.8 ± 52.2	44.6 ± 28.0	61.1 ± 28.0	111.4 ± 57.5
	winter	33.6 ± 20.7	17.8 ± 6.9	88.9 ± 45.4	86.9 ± 41.5	28.6 ± 7.9	15.8 ± 5.9	45.3 ± 21.4
Flux ^a	autumn	48.9 ± 32.4	29.1 ± 16.7	204.1 ± 102.6	80.3 ± 33.2	28.2 ± 17.5	39 ± 17.5	71.6 ± 36.7
($\text{ng}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	winter	21.7 ± 13.1	11.2 ± 3.9	58.4 ± 29.5	57.1 ± 26.9	18.4 ± 4.6	9.8 ± 3.3	29.4 ± 13.6

Note: a, Flux was estimated under the assumption the waste water treatment plant was open-air.

3.4 THg in sludge (STHg)

After treatment in each unit, only a small part of the mercury was discharged with the effluent; most of the mercury entered the activated sludge and was discharged with the remaining sludge (Gilmour and Bloom, 1995; Balogh and Nollet, 2008b). The STHg levels in the biochemical tanks were $0.80 \pm 0.12(0.57 \sim 1.01) \text{ mg/kg}$ in autumn and $0.88 \pm 0.14(0.57 \sim 1.09) \text{ mg/kg}$ in winter (Fig. 7), and these values were not significantly different. STHg in the secondary sedimentation tank of the Jiaozuo No. 1 sewage treatment plant was $4.86 \pm 0.52 \text{ mg/kg}$, and the THg in its influent reached $1212 \pm 598 \text{ ng/L}$ (Li et al., 2014). The THg levels in the pressure filtration sludge and influent of the Metropolitan Wastewater Treatment Plant in St. Paul, Minnesota (USA) were 0.65 mg/kg and 174 ng/L , respectively (Balogh and Nollet, 2008b), which was similar to the results of our study. Therefore, high STHg is related to high THg in sewage. The STHg in the biochemical tank was relatively stable (variation coefficients were 14.8% and 15.9%, respectively), which may be due to the higher sludge age (20 d), stronger buffering capacity, or back-flow of sludge. STHg in the anaerobic tank was slightly higher than that in the anoxic and aerobic tanks, which was affected by the higher THg in the water of anaerobic tank (Fig. 2). The STHg levels in dewatered sludge were $1.45 \pm 0.10 \text{ mg/kg}$ in autumn and $1.65 \pm 0.08 \text{ mg/kg}$ in winter, which was significantly higher than those in the biochemical sludge. The decomposition of organic matter in the sludge during dehydration caused a concentration effect (Lu et al., 2008). THg in dewatered sludge was lower than the maximum limit of total mercury for the agricultural use of sludge in Discharge Standard of Pollutants for Municipal Wastewater Treatment Plants (DSPMWTP, GB18918-2002) (alkaline and neutral soil $\leq 15 \text{ mg}\cdot\text{kg}^{-1}$, acid soil $\leq 5 \text{ mg}\cdot\text{kg}^{-1}$); therefore, the sludge can be used in agriculture.

4. Conclusion

The concentrations of THg in the influent of the sewage treatment plant varied greatly from 55.4 to 230.2 ng/L in autumn and 83.6 to 335.8 ng/L in winter. The influent THg was higher in winter. However, the effluent levels in autumn and winter were 27.5 ± 4.1 ng/L and 21.4 ± 4.0 ng/L, respectively. The removal efficiencies of THg were 78.9% and 90.8%. The removal of THg mainly occurred in the secondary biological treatment process. THg content was significantly correlated with the content of organic pollutants in sewage.

The ratios of PHg/THg were 59.3% and 86.9% in autumn and winter, respectively. Therefore, PHg was the main mercury speciation in the influent, and the removal rate was relatively high in the primary physical treatment process. DHg/THg generally showed an upward trend following sewage treatment; DHg and PHg were the main mercury species in the sewage treatment process in autumn and winter, respectively. PHg contributed greatly to the removal of THg.

The influent DGM levels in autumn and winter were 0.60 ± 0.40 ng/L, 0.34 ± 0.21 ng/L respectively. DGM increased in the biochemical tanks affected by microbial action. The estimated mercury from aeration was 3.94 kg per year in China. DGM will be released to the air if the sewage treatment plant is open-air. Closed sewage treatment and collection of waste gas treatment are necessary to reduce the influence of released mercury. RHg accounted for a small proportion of THg and was released by decomposition of the organic matter in the secondary biological treatment.

The STHg levels in the biochemical tanks were 0.80 ± 0.12 mg/kg in autumn and 0.88 ± 0.08 mg/kg in winter. The STHg content of the biochemical tanks was relatively stable. The THg level in the dewatered sludge was higher than that of biochemical sludge because the decomposition of organic matter in the sludge during dehydration caused a concentration effect of THg.

Declarations

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Authors' contributions

Yunpeng Li: conceptualization, investigation, methodology, software, formal analysis, data curation, writing (original draft preparation), writing (review and editing) and visualization.

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Conflict of interest

The authors declare that they have no competing interests.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

All data generated or analysed during this study are included in this published article.

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Figures

Figure 1

Schematic diagram of the process configuration and sampling points at the World Garden Water Purification Plant. The blue line is the sewage flow direction. The brown line is the sludge flow direction.

Figure 2

THg concentration of different processing units in the sewage treatment plant. A represents autumn and B represents winter.

Figure 3

DHg and PHg concentrations and their proportions of THg in sewage of various processing units. A represents autumn and B represents winter.

Figure 4

The relationship between the amount of DGM released from the biological sewage tanks and the continuous bubbling time.

Figure 5

Variance of DGM and RHg in various processing units of sewage treatment. A represents autumn and B represents winter.

Figure 6

GEM concentration in aerobic tank of WGPP in 2019 and Maidao sewage treatment plant in 2020.

Figure 7

THg concentration in sludge from sludge production units in autumn and winter.