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The fate of mercury in municipal wastewater treatment plants in China: Significance and implications for environmental cycling

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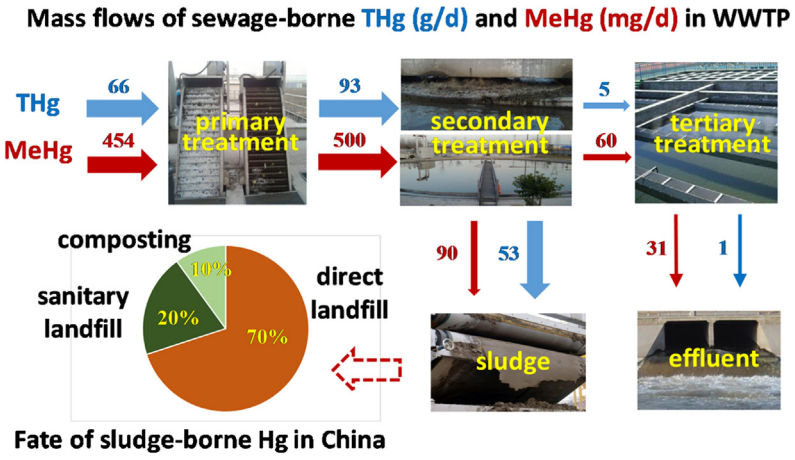
HIGHLIGHTS

- Provide much needed information for the role of WWTPs in Hg cycling in China.
- Quantify MeHg and THg in each step of WWTP for a better mass balance calculation.
- WWTP is an important sink of sewage-borne MeHg and THg.
- MeHg in sewage is mainly degraded while THg is transported to waste sludge.

GRAPHICAL ABSTRACT



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ABSTRACT

Municipal wastewater treatment plants (WWTPs) play an important role in controlling pollutant discharges to surface waters. Previous studies suggested that the removal of mercury (Hg) by WWTPs was strongly correlated with solid removal. However, conclusions regarding possible transformations of Hg species within WWTPs were not consistent across those studies. We characterized total Hg (THg) and methylmercury (MeHg) concentrations and loads in a WWTP located in Jiaozuo, China, to further understand Hg fate and transformations in WWTPs. THg and MeHg were primarily associated with wastewater solids, and removal of both were greater than 90%; concentrations in the sewage were $(2.0 \pm 2.7) \times 10^3$ ng/L and 7.5 ± 5.8 ng/L, respectively. A mass balance calculation revealed that 80% of the THg input to the WWTP ended up in the sewage sludge (SS), while more than 70% of the influent MeHg mass was degraded, indicating WWTPs are an important sink for sewage-borne Hg. THg and MeHg concentrations in SS were $(3.9 \pm 1.4) \times 10^3$ ng/g and 6.3 ± 2.3 ng/g, respectively, suggesting SS could be a significant source of THg and MeHg to the environment if not handled properly. The significance of sewage and SS in the biogeochemical cycling of THg and MeHg in China is discussed.

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1. Introduction

Mercury (Hg), as a global pollutant, has been a point of great concern for decades. In recognition of the adverse environmental and health effects of Hg, a global treaty, namely Minamata convention on Hg, was signed in 2013, calling for a great reduction in Hg production, usage, and emission/release. The United Nations Environment Programme (UNEP) Global Mercury Assessment 2013 established a preliminary inventory of anthropogenic Hg sources, including 1960 tons emitted to the atmosphere and more than 1000 tons released into waters in 2010 [1]. However, as the UNEP report points out, there are some sectors whose emission/release has not been quantified, most possibly because of lack of data [1]. Emission/release of Hg species from municipal wastewater treatment plants (WWTPs) is one of the missing pieces.

Collecting most of a city's domestic, commercial, industrial (with or without pre-treatment) wastewater, and rain water in some cases, WWTPs play important roles in the removal of particulate materials, organic matter, and nutrients from the influent liquid. Modern WWTPs are generally effective in the removal of Hg from sewage thus greatly reduce the amount of Hg discharging into the receiving waters [2–7]. However, recent studies have shown that, via discharge of effluent and sludge, WWTPs could be important point sources for micro-pollutants [8], such as pharmaceuticals, personal care products, steroids, polybrominated diphenyl ethers, as well as Hg compounds [2–4,9–12]. Mercury removed from the raw sewage is mainly transported to the waste sludge, which would be another potential source of Hg to the environment if disposed inappropriately [3,13]. The Hg loads carried by sewage and sewage sludge (SS) and their fate in each treatment step remain unclear. In addition, methylmercury (MeHg), a highly toxic form of Hg, has been detected in the raw sewage, effluent, and sludge of some WWTPs [2–6,14–16], indicating that WWTPs might be a source of MeHg to the environment. The few studies carried out on MeHg in WWTPs seem to be controversial. Goldstone et al. observed MeHg in the activated sludge of Whitlingham Sewage Treatment Plant but not in the raw sewage, thus claimed that in situ methylation of Hg occurred in the processes of wastewater treatment [2]. Methylation of Hg was also observed in a municipal WWTP contaminated by elemental Hg originated from the sealing apparatus [4]. On the other hand, a study conducted at San Jose/Santa Clara Water Pollution Control Plant revealed that only 1/3 of MeHg in the raw sewage could be recovered in the plant effluent and waste sludge, suggesting the occurrence of demethylation of MeHg during wastewater treatment processes [6]. WWTPs in other three cities were found to be effective in the removal of both THg and MeHg from the raw sewage [5,15,17], however, MeHg in the sludge was not analyzed thus the transformations and fate of Hg and MeHg were not clearly identified.

The primary objectives of the present study were (1) to quantify the occurrence of THg and MeHg in the influent, effluent, and sludge in a typical WWTP in China, (2) to assess the transport, transformation, and fate of sewage-borne THg and MeHg in WWTPs through Hg speciation analysis and mass balance calculations considering both wastewater and sludge, and (3) to perform a preliminary estimation of the annual loads of THg and MeHg carried by sewage and SS and their fate in China. The results obtained in this study are important for a better understanding of the biogeochemical cycling of Hg in China, a country with the largest Hg production and usage in the world.

2. Experimental

2.1. Site description

Located in northwestern Henan Province, China, Jiaozuo is a medium-sized city with a population of 0.8 million. As one of the three municipal WWTPs, the Kangda WWTP collects domestic, commercial, and partial rain water from 4 districts of Jiaozuo city. Utilizing oxidation ditch (OD) processes, the plant was designed at a treatment capacity of 1.0×10^5 m^3/d.

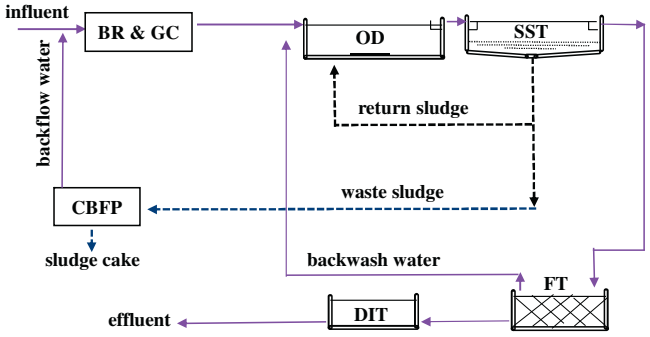

Fig. 1. Schematic of each treatment step used in the wastewater treatment plant dealt in this study. BR, GC, OD, SST, FT, DIT, and CBFP stand for bar rack, grit chamber, oxidation ditch, secondary settling tank, filter tank, disinfection tank, and continuous belt filter press, respectively.

As shown in Fig. 1, wastewater is conveyed to two parallel ODs and mixed with activated sludge after flowing through bar racks (BRs) and grit chambers (GCs) to eliminate large objects and grit. Surface aerators are installed at several positions of the ODs to aerate the mixed slurry of wastewater and activated sludge. After retaining in the ditches for 12 h, the mixed slurry of wastewater and activated sludge enters the secondary settling tanks (SSTs), where separation of water and sludge is accomplished. Effluent water from the overflow weirs of SSTs is transported to a set of filter tanks (FTs) to further remove suspended particulate materials, followed by chlorination in a disinfection tank (DIT) by adding chlorine dioxide. Backwash water of the FTs is conveyed back to the ODs. The final effluent of DIT is discharged to a local canal which finally leads to the Haihe River. The sludge obtained from the bottom of SSTs is split into two parts. Majority of the sludge (namely return sludge) is returned to the ODs to maintain a sufficient quantity of activated sludge in the ditches, while the rest of the sludge (namely waste sludge) is transported to a sludge treatment unit where two continuous belt filter presses (CBFPs) are used to separate water from sludge and finally produce sludge cake which contains about 80% of solid. Water produced by the CBFPs (backflow water) goes back to the GCs, while the sludge cake is transported to a sanitary landfill.

2.2. Sampling strategy, sample preparation, and analysis

Flow-proportional composite samples of wastewater and sludge were collected from the inlet and outlet of each operation unit during the year-round sampling campaign.

The water samples for THg and MeHg analysis were obtained by filling 500 mL pre-cleaned borosilicate glass bottles and preserved by adding 5 mL HCl (trace metal grade), while these for dissolved THg and MeHg were filtered (0.45 μm) before adding HCl. All water samples were double-bagged and kept on ice in a cooler until analysis.

The sludge samples from the ODs and SSTs were centrifuged on site. The supernatant was treated as water samples, while the pellet (and the sludge cake samples from CBFPs) was retained in the polypropylene centrifuge tubes and kept on ice in a cooler, freeze-dried upon arrival in the laboratory, ground into fine powder, and stored in a freezer (−20 °C).

Total Hg in the water and sludge samples was analyzed according to United States Environmental Protection Agency (USEPA) method 1631 [18]. The method detection limits (MDLs) were 0.5 ng/L and 0.3 ng/g as Hg for water and sludge samples, respec-