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Mercury speciation and emission from municipal solid waste incinerators in the Pearl River Delta, South China

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HIGHLIGHTS

- Mercury in the flue gas was measured for 8 municipal waste incinerators in China.
- Mercury concentration in flue gas differed as a function of incineration method.
- Gaseous oxidized mercury was the dominant form released.
- Air pollution control devices are important for reducing mercury emissions.
- Total emissions will increase as the amount of waste incinerated in China increases.

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ABSTRACT

The potential for Hg release during municipal solid waste incineration (MSWI) is attracting increased attention due to high volume of municipal waste being treated by incineration in China. Emission amounts have been estimated using emission factors developed for other countries. To fine tune our emission estimate total mercury (THg) and mercury speciation were measured using isokinetic sampling in eight plants, of which six used grate furnace combustor (GFC) and two circulation fluidized bed combustors (CFBCs). Results showed that average THg concentration (19.5 ± 13.6 μg/Nm^3) in flue gas at the facilities that used CFBC was significantly lower than that at those using GFC (51.4 ± 28.3 μg/Nm^3, $p = 0.002$). Gaseous oxidized mercury (GOM), gaseous elemental mercury (GEM, Hg^0), and particulate mercury (Hg^p) represented $95.5 \pm 3.8\%$, $4.1 \pm 3.9\%$ and $0.4 \pm 0.3\%$ in GFC, and $63.8 \pm 8.6\%$, $33.6 \pm 10.5\%$ and $2.6 \pm 1.9\%$ in CFBC, respectively. The measured average THg emission factor for the 8 MSWI plants was 208 ± 130 mg/t in the Pearl River Delta (PRD) region, with 217 ± 158 mg/t and 188 ± 17.7 mg/t were from GFC and CFBC, respectively. Using the average emission factor the estimated total mercury emissions from MSWI were 4.67 ± 2.91 t in China, and 770 ± 65.5 kg in the PRD region in 2010. Of these, 4240 ± 210 kg, 408 ± 231 kg and 14.8 ± 14.1 kg, and 688 ± 37 kg, 78.9 ± 40.6 kg and 3.2 ± 3.0 kg were GOM, Hg^0, and Hg^p, respectively. Mercury emissions will continue to increase as the amounts of MSW being incinerated increases.

1. Introduction

Gaseous elemental mercury (GEM, Hg^0) and oxidized mercury (GOM), as Hg(II) compounds, are the dominant mercury species in the atmosphere (Poissant et al., 2005; Valente et al., 2007). The residence time for Hg^0 is thought to be 0.5 to 2 years, and as such this pollutant can be globally dispersed through atmospheric transport (Schroeder and Munthe, 1998; Weiss-Penzias et al., 2003). Anthropogenic activities are currently the main mercury emission source (US EPA, 1997; UNEP, 2002). In China, anthropogenic mercury emissions were estimated to be 536 t in 1999, 605 t in 2000 and 800 t in 2005, with the latter accounting for 30% of global emissions (Streets et al., 2005; Pacyna et al., 2006, 2010). These values were estimated through industrial emission factors or coal consumption and do not take into account nonindustrial sources. To improve the accuracy of mercury emission estimates, emission factors need to be developed for nonindustrial sources (Zheng et al., 2011).

Municipal solid waste (MSW) disposal accounts for approximately 8% of the total anthropogenic mercury emissions worldwide (Pirrone et al., 2010). Although nonferrous metal smelting and coal combustion are the largest mercury emission sources in China, mercury emissions associated with MSW incineration need to be quantified because of the large amount of MSW produced and disposed of by incinerators. It has been suggested that municipal solid waste incineration (MSWI) should be considered in China's mercury control strategy (Cheng and Hu, 2010a, 2012).

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Total mercury (THg) emission from MSWI plants in China was estimated to be 10 t in 2003 (Wang et al., 2006). Waste is not classified and recycled in China, and Hg(II) forms could be produced from waste plastic, food residue, fluorescent lamps, or other sources (Wang et al., 1999; Abanades et al., 2002; Hu and Cheng, 2012). Oxidized forms of Hg are deemed to be a dominant mercury species emitted from MSWI plants (AMAP/UNEP, 2008). This species is easily deposited into soil, water and can be further transformed into methyl mercury (Ullrich et al., 2001; Cheng and Hu, 2012). Previous work suggested that THg concentrations in vegetable leaves near MSWI plants in China exceeded the Chinese National Health Standard (0.01 mg/kg) (Tang et al., 2005). With the current increase in solid waste generation, and waste incineration in China due to rapid economic growth and unprecedented urbanization, mercury emissions from waste incineration are of concern (Cheng and Hu, 2012). However, there are few reports of direct analysis of mercury emissions from waste incineration (Park et al., 2008; Kim et al., 2010).

The Pearl River Delta (PRD) in Guangdong province is one of the three most economically developed areas in China. A large number of domestic and industrial wastes are produced in association with economic development and a waste output growth rate of 10% has been estimated (SBGD, 2011). Due to lack of industrial and commercial land, the first MSWI plant in China was located in Shenzhen in 1988. In 2010, there were 104 MSWI plants in China, of which 16 plants were located in the PRD and accounted for 15% of the total number in China (MHURD, 2011). Using estimated emission factors, a recent paper suggested that mercury emissions from MSWI in the PRD region accounted for 21% of the THg emission, which was just below mercury emission from coal-fired combustion (28%) (Zheng et al., 2011). In this study, the authors used an average emission factor calculated from multiple locations (Shanghai of China, Europe and United States) (UNEP, 2005; Zhang et al., 2008; Trozzi et al., 2009) and a mercury speciation ratio of Hg^0:Hg^{2+}:Hg^p = 96:0:4.

Grate furnace combustor (GFC) and circulation fluidized bed combustor (CFBC) are the two main incineration technologies used for MSWI in the PRD region and China (http://www.cn-hw.net). The GFC consists of a combustor equipped with obliquely downward three level grates: the drying zone (about 600 °C), the combustion zone (600 to 1100 °C) and the burnout zone (1100 to 700 °C), and the waste is moved through the system by the interlocking motion between the grates. This technology has stable operating conditions and does not need coal added as auxiliary fuel. In a CFBC, a bed of quartz sand, combustion ash, or other sand-like material is suspended in an upward flowing airstream. The MSW after fragment is suspended or "fluidized" through the introduction of under fire air at a high pressure and flow rate. Waste-fired CFBC's typically operate at bed temperatures from 800 to 900 °C. Due to net caloric value and higher water content, the technology needs to add coal to improve the combustion temperature and keep stable burning (Shi et al., 2008). This technology is difficult to control and unstable operating conditions.

The purpose of this study was (1) to measure the concentrations of THg, GEM, GOM, particulate mercury (Hg^p) forms directly at 8 out of 16 MSWI plants in the PRD region; (2) to compare the mercury emission associated with GFC and CFBC technology; and (3) to estimate emission of THg and different mercury speciation from MSWI in the PRD and China. To our knowledge, this is one of the few reports on mercury speciation and emission factors from different types of MSWI plants in China.

2. Materials and methods

2.1. Locations

Flue gas samples were collected from eight MSWI plants (six plants using GFC technology and two plants using CFBC technology) in five cities (Guangzhou, Shenzhen, Foshan, Dongguan and Zhongshan) of the PRD from March 2010 to August 2011 (Fig. 1). All facilities had the following air pollution control devices (APCDs), semidry (lime slurry)/dry (lime power) scrubbing system for removing acidic gases, an activated carbon injection (ACI) system for capturing dioxins and heavy metals, followed by a downstream fabric bag filter (FF). This combination of devices is quite effective at removing mercury from the flue gas (Zhang et al., 2008). The MSWI technology and sampling details are summarized in Table 1. Flue gas was collected when the plants were operating at normal and stable conditions. Due to the lack of monitoring ports before the APCDs, flue gas prior to filtration was not collected. Samples were collected after APCDs before the stack or directly in the stack (Fig. 2, Table 2). Energy consumption, amount of solid waste incineration and flow rate of flue gas were surveyed or measured during each sampling period (Tables 1,2).

2.2. Sample collection and analysis

An Apex Stack Sampling System, complying with US EPA Method 5 and the Ontario Hydro Method (OHM) (ASTM D6784-02, 2008), was used as the sampling train. This method collects different forms of Hg using operationally defined methods. A total of eight impingers were included in the sampling train. Briefly, a sample was withdrawn from the flue gas stream isokinetically through a probe/filter system maintained at 120 °C, followed by a series of impingers in an ice bath. Particulate mercury was collected in the front half of the sampling train through a quartz fiber filter (Pall, 82.6 mm in diameter). Gaseous oxidized mercury (Hg(II) and Hg(I) forms) was collected in the first, second and third impingers containing 1 N aqueous potassium chloride (KCl) solution. Gaseous elemental mercury collected the last 4 subsequent impingers. The fourth impinger contained an aqueous solution of 5% *v*/*v* nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). The fifth, sixth, and seventh impingers contained an aqueous solution of 4% *w*/*v* potassium permanganate ($KMnO_4$) and 10% *v*/*v* sulfuric acid (H_2SO_4). The last impinger containing silica gel was provided to ensure the flue gas was thoroughly dried before exiting the impinger train and entering the pumps and dry gas meter. Before sampling, a flue gas analyzer (TH-880, Tianhong) was used to test the moisture content to ascertain if an additional empty impinger was required. When flue gas streams were sampled with high moisture content (>20%), an additional empty impinger between the KCl and HNO_3–H_2O_2 was used and the rinse was added to the preceding impinger (ASTM D6784-02, 2008).

Data for each incinerator was collected in triplicate in parallel. The total sampling time for a sample was 2 to 3 h according to collection volume of approximately 1.0 dry cubic meter flue gas, sampling time intervals were approximately 2 h. The collected samples were recovered and analyzed using a cold atomic absorption mercury analyzer (F732-S, Huaguang). To recover the samples all the connections and impingers were rinsed with 0.1 N HNO_3. For preservation 5% *w*/*v* $KMnO_4$ was added to the sample obtained from first four impingers until purple color remained, 10% *w*/*v* hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) was added to the last three impingers until purple color just faded, and a drop of 5% *w*/*v* $KMnO_4$ was added. Finally, 1 mL 5% *w*/*v* potassium dichromate ($K_2Cr_2O_7$) was added to all impingers to maintain the oxidation state. For analyses $NH_2OH{\cdot}HCl$ as a suitable reductant was added to reduce $K_2Cr_2O_7$. Mercury contents of the filter samples were directly analyzed without digestion by an automatic mercury analyzer (Hydra-C, Leeman)through direct combustion method (US EPA Method 7473 (US EPA, 2007)). All the data were converted according to dry flue gas with 11% O_2 in the standard state using following equation:

$$\rho = \frac{10\rho_s}{21-O_s}$$

where ρ is converted concentration of THg in the flue gas in the standard state, μg/Nm^3; O_s is the concentration of O_2 in the flue gas, %; ρ_s is concentration of THg in the flue gas in the standard state, μg/Nm^3.