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# Dioxin distribution characteristics and health risk assessment in different size particles of fly ash from MSWIs in China

Simiao Wu [a], Jizhi Zhou [a], Yun Pan [a], Jia Zhang [a], Lingen Zhang [a], Nobutoshi Ohtsuka [b], Mamoru Motegi [b], Shinichi Yonemochi [b], Kokyo Oh [b,*], Shigeo Hosono [b], Guangren Qian [a,*]

[a] School of Environmental and Chemical Engineering, Shanghai University, No. 99 Shangda Road, Shanghai 200444, PR China
[b] Center for Environmental Science in Saitama, 914 Kamitanadare, Kazo, Saitama 347-0115, Japan

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ABSTRACT

During the process of treating and recycling Municipal Solid Waste Incinerators (MSWIs) fly ash, polychlorinated dibenzo-p-dioxins (PCDD/Fs) and polychlorinated dibenzofurans (dl-PCBs) in fly ash may potentially mobilize in the atmosphere and be widely distributed in the environment because of the inevitable re-suspension. Thus, this work presents the distributions of PCDD/Fs and dl-PCBs in inhalable coarse particles (Dp10–2.5 (particle diameter in μm)), fine particles (Dp < 2.5) of fly ash and original fly ash from four MSWI plants in China. The results show that PCDD/Fs and dl-PCBs preferentially concentrated in Dp10–2.5 and Dp < 2.5. Their mass concentrations and TEQ were significantly higher than those in the original fly ash, but the distribution of PCDD/Fs congeners in Dp10–2.5 and Dp < 2.5 was close to that in the original fly ash. The main TEQ contribution included 1,2,3,7,8-PeCDD, 2,3,7,8-TeCDD in PCDDs and 2,3,4,7,8-PeCDF in PCDFs for Dp10–2.5, Dp < 2.5 fractions and the original fly ash. Furthermore, the mass and TEQ contribution of dl-PCBs was relatively low. In addition, compared with the fluidized bed, the samples from the grate-type furnaces had significantly lower dioxin concentrations. In terms of potential health risk, the non-carcinogenic risk of PCDD/Fs in Dp10–2.5 and Dp < 2.5 were estimated at $9.87 \times 10^{-1}$ to 4.81 and 1.19–7.95. For the carcinogenic risk of PCDD/Fs, both accumulation of Hazard Quotients (HQ) in Dp10–2.5 and Dp < 2.5 exceeded the threshold limit and should be considered as unacceptable risk for onsite workers. The above findings could provide data to support the risk management of MSWI fly ash during the process of recycle and disposal.



## 1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) are typically found in flue gas, bottom ash and fly ash generated by Municipal Solid Waste Incinerators (MSWIs). Since the past decades, some novel techniques have been developed to reduce the flue gas emission of PCDD/Fs (Caserini and Monguzzi, 2002; Finocchio et al., 2006; Ruokojärvi et al., 2004; Van Caneghem et al., 2014). Prior to stack emission, dioxins in flue gas are almost eliminated by active carbon powder adsorption and bag house filtration, so dioxins are enriched in the fly ash. According to previous reports, the dioxin concentrations of Chinese MSWI fly ash extended from 0.034 to 7.53 ng TEQ/g (Pan et al., 2013). This enrichment will further increase with more strict emission standards. PCDD/Fs are persistent environmental pollutants with high toxicity. However, many reports only focused on the spatial distribution of bulk fly ash, destruction and formation of PCDD/Fs and dioxin-like PCBs in combustion systems.

Based on the US EPA definition, particle matters include "inhalable coarse particles" with diameters ⩾ 2.5 μm and ⩽10 μm and "fine particles" with diameters ⩽ 2.5 μm (Kaupp and McLachlan, 2000; Kaupp and Michael, 1998; Lee et al., 2006; Ma et al., 2009). The PCDD/Fs, PCBs and PAHs contents of fine particles are higher than those of larger particles of fly ash. The finer particles have a significant effect on both the re-formation of chlorinated aromatic substance and the enrichment of dioxins.

In fact, MSWI fly ash is an aggregation of different particles. When fly ash is recycled and disposed, these fine particles appear to migrate into the atmosphere environment because of inevitable re-suspension. It is well known that the particle size is directly linked to its potential for causing health problems. Particle < 10 μm will be released into the air during the stabilization/solidification process under air disturbance. When workers in operation of these

* Corresponding authors.
*E-mail addresses:* o.kokyo@pref.saitama.lg.jp (K. Oh), grqian@shu.edu.cn (G. Qian).

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processes are exposed to the fine particles, 96% of these particles can pass through the alveolus and are deposited in the lung parenchyma (Chao et al., 2003). In addition, dioxins with a high concentration, which adhere on the fine particles because of the large specific surface area, will cause various health problems to the on-site workers and residents. Health-risk assessment indicate that the health risks for onsite workers in an industrial environment such as a sinter plant are significantly higher than those for residents living at residential and rural areas (Shih et al., 2008).

Thus, it is necessary to investigate the distribution of dioxins in finer particles of fly ash and their adverse health implications. Human health risk should be assessed particularly when the workers inevitably contact the fine particles that float in the atmosphere and enrich PCDD/Fs and dl-PCBs through re-suspension-inhalation, ingestion and hand-into-mouth (Kao et al., 2007; Ma et al., 2002). To our knowledge, there were few investigations about the detailed understanding of the distribution of dioxins in the various fractions of fly ash and their relative health risk.

This report was motivated to obtain more accurate data on the distributions and characteristics of PCDD/Fs and dl-PCBs content in inhalable and finer particles in comparison with the original fly ash. The relationship between the concentrations of PCDD/Fs and dl-PCBs in different particle sizes, as well as from different furnace types of municipal solid-waste incinerators was discussed, too. In addition, the potential human health risk was evaluated by using the total TEQ concentrations of PCDD/Fs and distribution information on re-suspended MSWI fly ash.

## 2. Materials and methods

### 2.1. Preparation of particulate matter in fly ash

The bulk fly ashes were collected from four municipal solid waste incineration plants in China. The basic information and parameters of the 4 MSWIs are listed in Table 1. In the four bulk fly ash samples, fine particles with diameter (Dp) ranges from 10 to 2.5 μm (Dp10–2.5) and <2.5 μm (Dp < 2.5) were separated. The concentration of dioxins and their health risk in fine particles Dp10–2.5 and Dp < 2.5 are discussed in the current working comparison with those of the bulk fly ash sample.

The separation procedure of fly ash was carried out by an air sampler (AN-200) equipped with a plastic bag as big as 1.0 $m^3$ in volume in lab. Prior to the separation, 1 kg of fly ash particulate was suspended in the plastic bag manually shaken. Then, the suspended fly ash went through the air sampler with a vacuum pump at the flow rate of 28.3 L/min. Dp10–2.5 and Dp < 2.5 fractions from the bulk fly ash samples was collected in the air sampler with two filters which pore size was 10 μm and 2.5 μm respectively. The size of filter was 80 mm in diameter. In identical sampling conditions, i.e., identical temperature (20 °C), relative humidity (50%) and atmospheric pressure to the working environment condition of on-site workers. After collection, the fly ash samples (bulk fly ash, Dp10–2.5, and Dp < 2.5) were weighed at a constant temperature. The mass percentage of Dp10–2.5 and Dp < 2.5 was 26% and 11% in the total bulk fly ash, respectively (Zhou et al., 2015).

### 2.2. Chemical analysis of dioxins

Dioxins analyses were conducted at the Center for Environmental Science in Saitama, Japan. The samples were extracted in Soxhlet according to JISK 0312 2005. Prior to the extraction: $^{13}C_{12}$-labeled PCDDFs and dl-PCB cleanup spikes (seventeen 2,3,7,8-chlorine-substituted PCDD/Fs and twelve dl-PCBs; Wellington Laboratories) were added. The extraction was first treated with concentrated sulfuric acid and subsequently with 44% sulfuric-acid-impregnated silica gel (Wako Pure Chemical Industries), and column chromatography was performed with 10% silver-nitrate-impregnated silica gel (Wako Pure Chemical Industries). Thereafter, the solution was loaded into an active-carbon-dispersed silica-gel column (Kanto Chemical), washed with hexane, and eluted with toluene. The toluene solution was concentrated, and $^{13}C_{12}$-labeled syringe spikes (eight compounds selected from tetra- to heptachlorinated dibenzofurans and biphenyls; Wellington Laboratories) were added to the concentrated solution.

Concentrations of PCDD/Fs and dl-PCBs were determined using high-resolution GC/MS (HP-6890 (Agilent Technologies, Wilmington, DE) + JMS-800 (JEOL, Tokyo, Japan)) with 1 mL/min of Helium as the carrier gas. Tetra–Hexa PCDD/Fs were used "CP-Sil88 for dioxins", Hepta–Octa PCDD/Fs and dl-PCBs were used DB-5 ms for capillary column. The GC/MS interface and injector temperature were set at 280 °C and 290 °C, respectively. The GC temperature program was performed as follows: 130 °C (2 min) to 210 °C (0 min) at 20 °C/min, subsequently to 300 °C at 3 °C/min, and maintained at 300 °C for 4 min (total: 40 min). The MS was operated in the selected ion-monitoring (SIM) mode with a mass resolution of >10,000 (Lock mass, PFK), and the electron impact ionization energy was 38 eV with an ion-source temperature of 280 °C (Pan et al., 2013).

Dioxins in the operational blank samples were of negligible levels. The recovery of the cleanup spikes was satisfactory, and the average recovery rates for PCDDs, PCDFs and dl-PCBs were 91 ± 10%, 88 ± 10% and 89 ± 8%, respectively. The concentrations below the detection limits were considered to be zero. Thus, the precision and credibility of the dioxin analysis data were notably high with strict management of dioxin detection.

### 2.3. Health risk quantification

The risk assessment of onsite worker exposure to PCDD/Fs in Dp10–2.5, Dp < 2.5 fractions and in the bulk fly ash were calculated using the USEPA methodology (EPA, 1996). In this scenario, three exposure routes were considered to assess the possible environmental exposure to PCDD/Fs, which includes inhalation, dermal absorption and ingestion (Fig. S1). The exposure parameters are listed in Table S1.

For the non-carcinogenic risk, the average daily doses obtained through inhalation ($CDI_{inh}$), skin contact ($CDI_{dermal}$), and ingestion ($CDI_{ing}$) are calculated as follows:

$$CDI_{inh} = \frac{C \times InhR \times EF \times ET \times ED}{PEF \times AT \times BW} \quad (1)$$

**Table 1**
Basic information and parameters concerning on the 4 MSWIs.

| Sample no. | Furnace type | Capacity (ton/d) | Air pollution control device | Location |
|---|---|---|---|---|
| FA1 | CFB[a] | 3 units × 200 | Semidry purification system + bag filter | Shandong (Northeast of China) |
| FA2 | CFB[a] | 2 units × 400 | Semidry neutralization reaction + AC[b] + bag filter | Hangzhou (East of China) |
| FA3 | Grate-type | 1000 | Semidry purification system + AC + bag filter | Shanghai (East of China) |
| FA4 | Grate-type | 1500 | Urea + AC + hydrated lime + bag filter | Shanghai (East of China) |

[a] CFB: circulating fluidized bed.
[b] AC: activated carbon.

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