



Gas-Particle Partitioning of Polychlorinated Dibenzo-*p*-dioxins, Dibenzofurans, and Biphenyls in Flue Gases from Municipal Solid Waste Incinerators

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ABSTRACT

Gas-particle partitioning of polychlorinated dibenzo-*p*-dioxins, dibenzofurans (PCDD/Fs), and biphenyls (PCBs) was evaluated in flue gases emitted from two municipal solid waste incinerators. Total PCDD/Fs and dl-PCBs in the flue gas were presented, in decreasing order, within gas phases, particulate phases, and aqueous phases. PCDD/F concentrations in the flue gas ranged from 0.75 to 15 ng m⁻³, while in the particulate phase they ranged from 0.14 to 8.1 ng m⁻³. Dioxin-like (dl-) PCBs had concentrations of 0.18–28 ng m⁻³ in the flue gas, and 0.041–1.3 ng m⁻³ in the particulate phase. PCDD/F and dl-PCB levels were associated with specific size ranges of particles, increasing as particle size decreased. More than 54% (81%) of PCDD/Fs and 49% (79%) of dl-PCBs were associated with fine particles of less than 2.5 (10) μm-diameter. In addition, average levels of PCDD/Fs, PCBs, and dl-PCBs were 0.15 ± 0.11 ng m⁻³, 11 ± 11 ng m⁻³, and 0.21 ± 0.20 ng m⁻³, respectively. Levels of non-2,3,7,8-chlorinated PCDD/Fs were much higher than 2,3,7,8-chlorinated PCDD/Fs in PCDD/F homologue patterns. This suggests that more attention should be paid to non-2,3,7,8-chlorinated PCDD/Fs in the environment, given their potential to transform to more toxic species.

Keywords: PM_{2.5}; Haze; MSWIs; Gas-particle-water partitioning; Non-2,3,7,8-PCDD/Fs.

INTRODUCTION

Incineration is commonly used around the world as an effective, sanitary and practical method of waste disposal, leading to the establishment of more municipal solid waste incinerators (MSWIs) (Zhang *et al.*, 2014). A total of 50.1 million tons of municipal solid waste was incinerated in China in 2013 (a 33% increase over the last decade) (Han *et al.*, 2016a; Meng *et al.*, 2016), becoming an important emission source of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Xu *et al.*, 2009; Li *et al.*, 2012; Li *et al.*, 2016), as well as dioxin-like compounds such as polychlorinated biphenyls (PCBs) (Guo *et al.*, 2014). Concentrations of PCDD/Fs and PCBs released in flue gases from MSWIs primarily increase with increasing incineration temperature, and are typically adsorbed onto atmospheric particles (Cetin *et al.*, 2017). PCDD/Fs and PCBs emission from the incinerators had been proved to be harmful for human health (Yu *et al.*, 2016). Given the high frequency

of occurrence for serious haze-fog events and severe air pollution in China, characterizing the spatial distributions of such contaminants in the atmosphere, especially in the particulate phase, has become a focus of research.

PCDD/Fs and PCBs released from the flue gas can spread through air, soil, water bodies, sediments, and enter plant and animal systems through atmospheric deposition (Du *et al.*, 2011; Suryani R *et al.*, 2015; Chang *et al.*, 2016). They occur as both gas and particulate phases in the atmosphere. On undergoing gas-particle partitioning in the atmosphere, PCDD/Fs and PCBs tend to combine with particles and be deposited (Li *et al.*, 2008; Wu *et al.*, 2009; Zhang *et al.*, 2016; Zhu *et al.*, 2016). Fine particles (with aerodynamic diameter (D) less than 2.5 μm; PM_{2.5}) have longer atmospheric lifetimes in the atmosphere than larger ones, and a higher ability to adsorb and retain PCDD/Fs and PCBs, because of their larger specific surface areas and more porous surfaces (Zhu *et al.*, 2016).

Kaupp and McLachlan measured most PCDD/Fs in particles less than 2.9 μm in size (Kaupp and McLachlan, 2000). Chao *et al.* (2003) investigated the particle size distributions of PCDD/Fs in the atmosphere with D between 0.056 and 100 μm, and found over 80% of PCDD/Fs bound to fine particles (D < 2.0 μm). Most previous studies of PCBs focused on atmospheric distributions (Chrysikou

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et al., 2009; Chrysikou and Samara, 2009), and PCBs emitted as gas from various sources (Baek *et al.*, 2010). To date, there have been few studies of particle-bound PCBs and their size distributions. Some studies have reported polychlorinated naphthalene and polycyclic aromatic hydrocarbon distributions in different particle sizes; these compounds also are preferentially associated with smaller particles (Kaupp and McLachlan, 2000; Zhu *et al.*, 2016). Wei *et al.* detected high concentrations of low-chlorinated PCDD/Fs in smaller particles (Wei *et al.*, 2016). Yu *et al.* found that PM_{2.5} contributed most to haze formation in regions where the population suffers most adverse health effects (Yu *et al.*, 2014). And a strongly relationship between particulate matters in the atmosphere and some kinds of diseases was concluded (Zhu *et al.*, 2017). Such health effects appear to increase, as particle size decreases (Kurogawa *et al.*, 1998). Consequently, the size distribution properties of aerosol particles could reflect the characteristics of pollution (Yu *et al.*, 2017).

The persistence and lipophilicity enhance the ability of accumulation of PCDD/Fs and PCBs in the environment for many years (Chi *et al.*, 2016). Thus the existence of relatively non-toxic dioxin congeners (non-2,3,7,8-substituted PCDD/Fs) in the environment should also be considered. Some relevant studies have investigated the metabolizing effects of 1,2,3,4-TCDD (Hanioka *et al.*, 1994), 1,3,7,8-TCDD (Petroske *et al.*, 1997) and 1,2,7,8-TCDD (Hakk *et al.*, 2001) in rats. In particular, 1,2,3,4-TCDD induced the activities of metabolizing enzymes and enzyme proteins at different doses (Hanioka *et al.*, 1994). Hakk *et al.* (2001) detected 1,2,7,8-TCDD in all tissue types of the rat model. Petroske *et al.* (1997) found that 1,3,7,8-TCDD could be metabolized into 2-OH-1,4,7,8-TCDD and 3-OH-1,2,7,8-TCDD in rats. As a result, the presence of non-2,3,7,8-substituted PCDD/Fs could influence various functions in living organisms.

The aim of our present study is to determine the gas-particle-water partitioning of PCDD/Fs and PCBs in the flue gas emitted from typical MSWIs. In addition, concentrations of non-2,3,7,8-substituted gas-phase PCDD/Fs were measured. To the best of our knowledge, this study provides

the first extensive data set showing size-specific particle distributions of PCDD/Fs and PCBs in flue gases. Such data expand our current understanding of their transportation within the environment, and the relationships between sources and sinks of PCDD/Fs and PCBs. It is imperative to determine the concentrations and size-specific distributions of PCDD/Fs and PCBs in various emission sources to provide reliable baselines for atmospheric monitoring.

MATERIAL AND METHODS

Sampling

Two typical MSWIs (A and B) with furnace incinerators were selected in this study. Both of them have treatment capacities of 600 tons of solid waste per day. A series of flue gas samples (25) were collected from June 2015 to July 2016 with size separated particulate sampler, which was an Isostack Basic isokinetic sampling system and a low volume aerosol sampler (TCR sampler; Tecora Corp., Milan, Italy) (Ba *et al.*, 2009; Du *et al.*, 2010). Thus, the gas phase, particulate phase, and water fractions were collected simultaneously. Five sample sets (S1–S5) were collected. S1 and S2 were collected from MSWI A (before and after updating its bag filter, respectively), while S3, S4 and S5 were from MSWI B. The volume of each air sample was about 4 m³ and each condensed water sample was around 60 mL. In each set, one gas phase fraction was collected using the Isostack Basic isokinetic sampling system equipped with resin and three particulate phase fractions ($D > 10 \mu\text{m}$; $10 \mu\text{m} \geq D > 2.5 \mu\text{m}$; and $D \leq 2.5 \mu\text{m}$) were collected using the low volume aerosol sampler, equipped with one quartz fiber filter to collect particles between 2.5 and 10 μm ; the other two particulate fractions were wiped down with absorbent cotton (Fig. 1). It was difficult to accurately weigh particles adsorbed onto the filter or cotton, as they were lightweight. As a result, concentrations of PCDD/Fs and PCBs in particles were calculated based on the volume of sampled flue gas. The sampling flow rate was constant at 16.5 L min⁻¹. Before and after sampling, the filters for collecting particle samples were weighed to reading precision. All parts of the sampler were cleaned with methanol, acetone

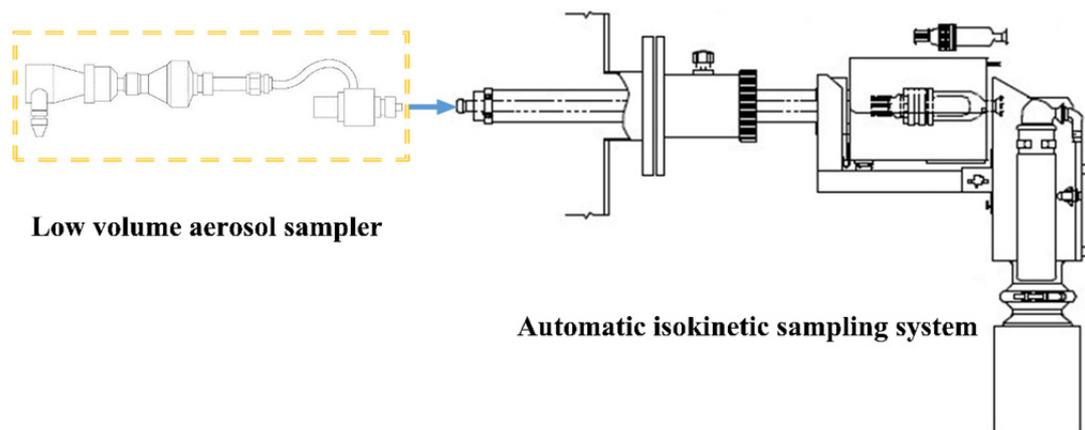


Fig. 1. Schematic diagram showing the Isostack Basic isokinetic sampling system, equipped with a low volume aerosol sampler.

and dichloromethane successively after sample collection. Samples were wrapped in aluminum foil, sealed in PVC bags, and stored in a refrigerator at -18°C until analysis.

Analytical Procedures

Samples were analyzed for PCDD/Fs and PCBs using US EPA Method 1613 and 1668A (Hu *et al.*, 2013; Han *et al.*, 2016b). Briefly, gas and particulate phase samples were extracted with 250 mL of toluene (pesticide grade) using Soxhlet extraction for 24 h. Condensed water samples were extracted with 90 mL of dichloromethane (30 mL for each repetition). Each sample was spiked with ^{13}C -labeled solutions of EPA-1613LCS and EPA-1668LCS (Wellington Laboratories, Guelph, Canada) as internal standards, before extraction. The extract was concentrated to a small volume and applied to a multilayer silica column and a basic alumina column to separate PCDD/Fs from PCBs. The final extract was concentrated to 20 μL under nitrogen flow and spiked with ^{13}C -labeled PCDD/F injection standards EPA-1613IS and EPA-1668IS (Wellington Laboratories, Guelph, Canada), before instrument analysis. PCDD/Fs and PCBs analyses were performed using high-resolution gas chromatography (HRGC; Agilent 6890 high resolution gas chromatograph; Agilent Technologies, Santa Clara, CA, USA) and high resolution mass spectrometry (Autospec Ultima high resolution mass spectrometer; Waters, Milford, MA, USA). The GC oven program for PCDD/F analysis was as follows: held at 160°C for 2 min, increased at a rate of $5^{\circ}\text{C min}^{-1}$ to 220°C (held 16 min), increased at a rate of $4^{\circ}\text{C min}^{-1}$ to 235°C (held 7 min), and increased at a rate of $5^{\circ}\text{C min}^{-1}$ to 330°C (held 1 min). The GC oven program for PCB analysis was as follows: held at 80°C for 2 min, increased at a rate of $15^{\circ}\text{C min}^{-1}$ to 150°C , increased at a rate of $2.5^{\circ}\text{C min}^{-1}$ to 270°C (held 3 min), and increased at a rate of $15^{\circ}\text{C min}^{-1}$ to 330°C (held 1 min). Simultaneously, non-2,3,7,8-substituted gas-phase PCDD/Fs in samples were determined based on retention times and the order of peaks after Fishman *et al.* (Fishman *et al.*, 2011). A total of 132 PCDD/Fs were detected, including 17 different 2,3,7,8-substituted PCDD/Fs in the gas phase (Supporting Information, Table S1).

To identify the sinks of PCDD/Fs and PCBs in the flue gas, the Hybrid Single-Particle Lagrangian-Integrated Trajectory (HYSPPLIT) model (established by National Oceanic and Atmospheric Administration) was used to simulate forward trajectories of emission sources, know to release PCDD/Fs and PCBs (Han *et al.*, 2016).

Quality Assurance and Quality Control

Validation of our analysis method for PCDD/Fs was assessed using measures for repeatability, reproducibility, accuracy, and sensitivity. The repeatability and reproducibility of instruments and our method were evaluated using standard deviations of replicate analyses. The difference between observed and theoretical peak areas of PCDD/Fs was used as a measure of accuracy. One laboratory blank was analyzed in each batch of the samples. Sensitivity was estimated using both the limit of detection (LOD) and limit of quantification (LOQ). The LODs of the PCDD/Fs and PCBs ranged from 0.07 to 2.65 pg m^{-3} and from 0.12 to

3.49 pg m^{-3} , respectively. The sample recoveries of PCDD/Fs (PCBs) were between 42.9 (25.6%) and 141% (109%), which meet the requirements for their trace analysis. The concentrations of PCDD/Fs and PCBs with values below their LOD (less than 5%) were assigned concentrations of half their LOD values. In this study, toxic equivalency values (TEQs) for the 17 different 2,3,7,8-substituted PCDD/Fs and 12 dl-PCBs were quantified using their respective World Health Organization toxic equivalency factors (WHO₂₀₀₅-TEF) (Pan *et al.*, 2010).

RESULTS AND DISCUSSION

Concentrations of 2,3,7,8-PCDD/Fs and PCBs in Flue Gases

The specific contribution of PCDD/Fs and dl-PCBs to different particle fractions, phases, and condensed water in the flue gas samples is shown in Fig. 2.

The total concentrations of PCDD/Fs in the flue gas ranged from 0.75 to 15 ng m^{-3} , with an average concentration of 6.5 ng m^{-3} (giving TEQ of $0.59\text{ ng TEQ m}^{-3}$). Total concentrations of dl-PCBs in the flue gas were in the range of 0.18 – 28 ng m^{-3} , with an average concentration of 11 ng m^{-3} (giving TEQ of $0.08\text{ ng TEQ m}^{-3}$). Concentrations of indicator PCBs ranged from 66 to 1415 ng m^{-3} , having a mean concentration that was 67 times that of dl-PCBs. Although PCDD/F concentrations were lower than levels of dl-PCBs, the average TEQ of PCDD/Fs were 7.4 orders higher than dl-PCBs.

Total PCDD/Fs and dl-PCBs in the flue gas were presented, in decreasing order, within gas phases, particulate phases, and aqueous phases. The total concentrations of PCDD/Fs in gas phases were in the range of 0.53 – 7.1 ng m^{-3} , with a mean concentration of 4.1 ng m^{-3} . In particles, PCDD/Fs ranged from 0.14 to 8.1 ng m^{-3} , with a mean concentration of 2.2 ng m^{-3} . In contrast, dl-PCBs in gas phases were in the range of 4.4 – 28 ng m^{-3} , with a mean concentration of 11 ng m^{-3} ; while in the particulate phase, dl-PCBs ranged from 0.041 to 1.3 ng m^{-3} , with a mean concentration of 0.33 ng m^{-3} . Indicator PCBs in gas phases were in the range of 34 – 1403 ng m^{-3} , with a mean concentration of 608 ng m^{-3} ; while in the particulate phases, they ranged from 7.6 to 674 ng m^{-3} , with a mean concentration of 147 ng m^{-3} . Indicator PCBs in sample set S1 had highest concentrations in the particulate phase.

Total concentrations of PCDD/Fs in condensed water samples were in the range of 0.94 – 16 ng L^{-1} , with a mean concentration of $4.9 \pm 6.2\text{ ng L}^{-1}$ (giving TEQ of $0.40 \pm 0.36\text{ ng TEQ L}^{-1}$). The dl-PCBs in condensed water samples ranged from 0.72 to 16 ng L^{-1} , with a mean concentration of $5.4 \pm 6.7\text{ ng L}^{-1}$ (giving TEQ of $0.06 \pm 0.09\text{ ng TEQ L}^{-1}$). The average TEQ of PCDD/Fs were 6.7 times higher than dl-PCBs. Indicator PCBs in condensed water samples ranged from 2.6 to 842 ng L^{-1} , with a mean concentration of $289 \pm 347\text{ ng L}^{-1}$. Converting PCDD/F and PCB concentrations in condensed water into volume concentrations of the flue gas, yielded average levels of PCDD/Fs, PCBs and dl-PCBs that were $0.15 \pm 0.11\text{ ng m}^{-3}$, $11 \pm 11\text{ ng m}^{-3}$, and $0.21 \pm 0.20\text{ ng m}^{-3}$, respectively.

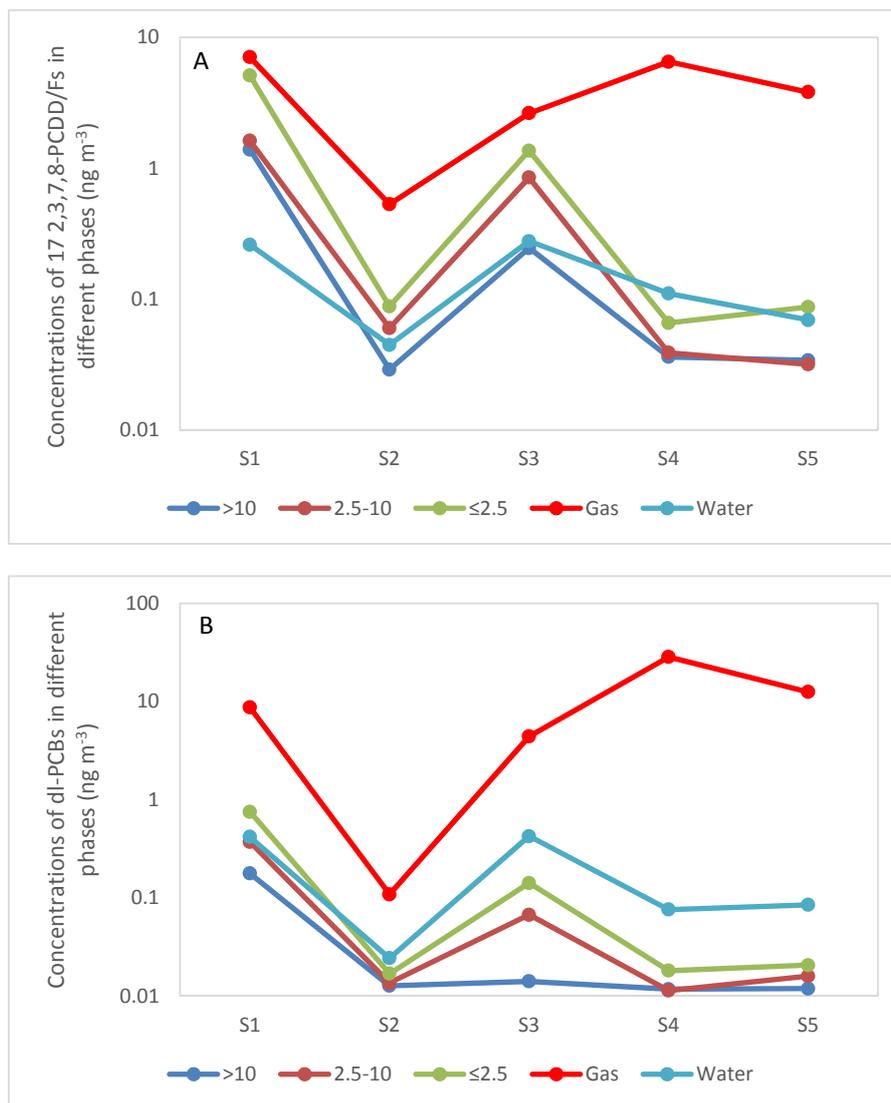


Fig. 2. Concentrations of PCDD/Fs (A) and dl-PCBs (B) in different phases of the flue gas.

Gas-Particle-Water Partitioning of 2,3,7,8-PCDD/Fs and PCBs

PCDD/Fs and PCBs occurred in largest proportions in the gas phases, based on their whole gas-particle-water partitioning distribution characteristics. Concentration contributions of PCDD/Fs and dl-PCBs in different phases to the total PCDD/Fs and dl-PCBs in the flue gas are described in Figs. 3(A) and 3(B). In addition, the profiles of the sum total of 2,3,7,8-PCDD/Fs and PCBs, based on their chlorine atoms, are depicted in Figs. 3(C) and 3(D).

The average contribution of PCDD/Fs in gas, particle, and water fractions to the sum total of 17 different 2,3,7,8-PCDD/Fs in the flue gas were 71%, 26%, and 3.2%, respectively. Proportions of dl-PCBs in gas, particle, and water fractions to total dl-PCBs in the flue gas were 86%, 8.4%, and 5.4%, respectively. PCDD/Fs and dl-PCBs were mainly presented in the gas phases in all sample sets, except for sample set S1. PCDD/Fs in gas phases in S1 accounted for 46%, which was slightly smaller than for particulate phases (53%). Meanwhile, PCDD/Fs in the gas

phases in S2 were 3 times that in the particulate phases. It is possible that updating the bag filter at MSWI A, improved dust removal efficiency, specifically reducing the emission of PCDD/Fs in fine particles, post-S1 sampling. Likewise, PCDD/Fs and dl-PCBs obviously decreased in the condensed water fraction of S2 compared with S1. PCDD/Fs and dl-PCBs in gas and particulate phases from sample sets S3, S4, and S5 were similar.

Congener profiles of 2,3,7,8-PCDD/Fs and PCBs were also investigated to evaluate gas-particle-water partitioning of PCDD/Fs and PCBs in the flue gas. As shown in Figs. 3(C) and 3(D), less chlorinated PCDD/Fs (TCDD/Fs and PeCDD/Fs) were more common in gas phases (above 60%), while higher chlorinated ones (HxCDD/Fs, HpCDD/Fs, and OCDD/Fs) occurred equally in both gas and particulate phases. All chlorinated PCBs, including TrCBs, TeCBs, PeCBs, HxCBs, and HpCBs mainly occurred in the gas phases, accounting for more than 70%. However, PCDD/Fs and PCBs in the water fraction were below 10%.

Clearly, gas phase PCDD/Fs and dl-PCBs released to the

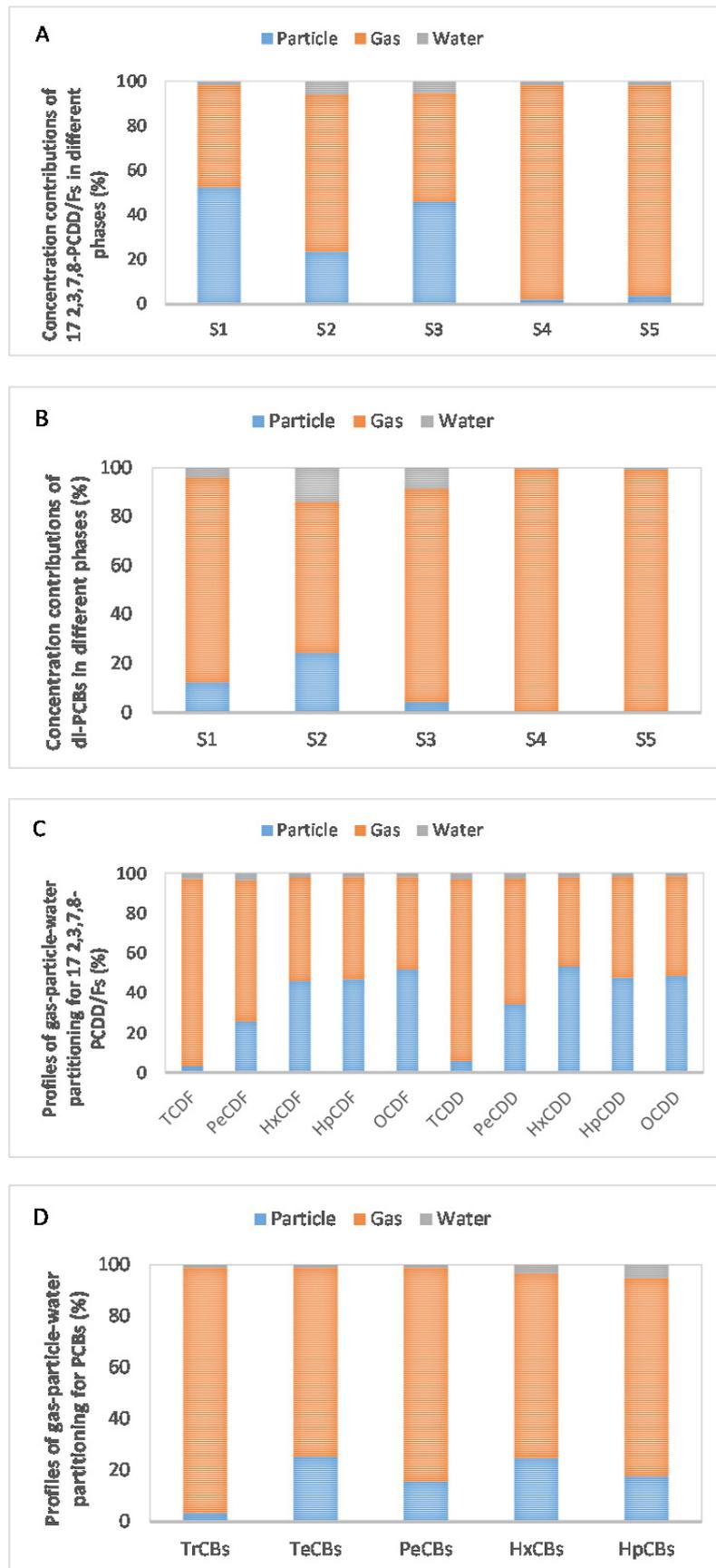


Fig. 3. Concentration contributions of PCDD/Fs (A) and dl-PCBs (B) to different phases and profiles of gas-particle-water partitioning for PCDD/F (C) and PCB (D) congeners.

ambient air are more easily photodegraded than particulate phases, contributing to a greater extent to haze formation (Chao *et al.*, 2003). However, it is clearly necessary to investigate PCDD/Fs and dl-PCBs in all phases to assess their environmental and health impacts.

Particle Size Distributions of 2,3,7,8-PCDD/Fs and PCBs

Concentrations of PCDD/Fs and dl-PCBs in particulate matter having diameters less than 10 μm (PM_{10}) ranged from 0.10 to 6.7 ng m^{-3} (with a median of 0.15 ng m^{-3}) and from 0.03 to 1.1 ng m^{-3} (with a median of 0.04 ng m^{-3}), respectively. This accounts for more than 81% and 79% of the total particulate matter. In the $\text{PM}_{2.5}$ fraction, the PCDD/F level was in a range of 0.07–5.1 ng m^{-3} , and was 0.02–0.75 ng m^{-3} for dl-PCBs. For particles larger than PM_{10} , the mean and median concentrations of PCDD/Fs (dl-PCBs) were 0.35 (0.05) and 0.04 (0.01) ng m^{-3} , respectively. Indicator PCBs in particles with different diameters showed no significant variation. Levels of indicator PCBs in particle fractions larger than PM_{10} , $\text{PM}_{2.5-10}$, and $\text{PM}_{2.5}$ were 50, 46, and 51 ng m^{-3} , respectively. Clearly, more PCDD/Fs and dl-PCBs were present in smaller sized particles. The $\text{PM}_{2.5}$ fraction made the highest contribution of more than 54% (49%) of PCDD/Fs (dl-PCBs) to the particulate phase. The $\text{PM}_{2.5}/\text{PM}_{10}$ ratios in this study were 0.67 ± 0.07 and 0.62 ± 0.06 for PCDD/Fs and dl-PCBs, respectively. Such high levels of PCDD/Fs and dl-PCBs can be attributed to primary emissions from the MSWIs.

Particle size distributions of PCDD/F and dl-PCB concentrations and TEQs in samples collected in this study are shown in Fig. 4. The TEQ of PCDD/Fs and dl-PCBs in different particle sizes shows a similar trend in all sample sets, increasing gradually with decreasing size of particles. In $\text{PM}_{2.5}$, the mean concentrations of PCDD/Fs and dl-PCBs were $0.10 \pm 0.14 \text{ ng TEQ m}^{-3}$ and $0.005 \pm 0.008 \text{ ng TEQ m}^{-3}$, respectively. For $\text{PM}_{2.5-10}$, the PCDD/F mean concentration was $0.02 \pm 0.03 \text{ ng TEQ m}^{-3}$, while the mean concentration of dl-PCBs was $0.002 \pm 0.003 \text{ ng TEQ m}^{-3}$. In PM_{10} , the mean concentrations of PCDD/Fs and dl-PCBs were $0.13 \pm 0.17 \text{ ng TEQ m}^{-3}$ and $0.006 \pm 0.01 \text{ ng TEQ m}^{-3}$. For particles larger than PM_{10} , PCDD/F and dl-PCB mean concentrations were $0.01 \pm 0.02 \text{ ng TEQ m}^{-3}$ and $0.0004 \pm 0.0006 \text{ ng TEQ m}^{-3}$. Thus, the TEQ contributions of PCDD/Fs were dozen times higher than dl-PCBs.

Although a number of studies have investigated the concentrations of various sized PCDD/Fs in the atmosphere (Oha *et al.*, 2002; Sharma and Maloo, 2005; Barmpadimos *et al.*, 2012; Lee *et al.*, 2016), few have described the gas-particle partitioning of dl-PCBs. This is relevant because the processes of transportation and deposition of particles are determined by particle size (Chao *et al.*, 2003). To compare our results with other studies, the concentrations of PCDD/Fs and dl-PCBs in particles of various diameters in the flue gas are compared with values for particulate matter in the atmosphere. Generally, other studies found that substance loading on particles increases, with decreasing particle size. The results obtained in our study are consistent with such studies (Zhang *et al.*, 2015), since higher levels of PCDD/Fs and dl-PCBs were detected in smaller particle sizes. Lee *et*

al. (2016) reported much higher concentrations of $\text{PM}_{2.5}$ and PCDD/Fs in the ambient air of Xiaogang area, in southern Taiwan, with heavy industrial activities than local urban and rural areas. This suggests that flue gases emitted from MSWIs are an important emission source of PCDD/Fs and dl-PCBs to the atmosphere.

Profiles of 2,3,7,8-Chlorinated and Non-2,3,7,8-Chlorinated PCDD/Fs

Both PCDD/Fs and dl-PCBs have potential for long-range atmospheric transport. Generally, the toxic effects caused by PCDD/Fs were higher than for dl-PCBs, especially for gas-phase PCDD/Fs (Fig. 4). Most studies focused on the toxicities of 17 2,3,7,8-substituted PCDD/F congeners (Xu *et al.*, 2013; Cai *et al.*, 2016), while few studies have looked at non-2,3,7,8-chlorinated PCDD/Fs due to lack of data of toxicity.

Fishman *et al.* (2011) evaluated 136 PCDD/Fs in their study. Based on their results, a high number of gas-phase PCDD/F congeners were measured in this study (Table S1). Not all these PCDD/Fs were detected in other phases of our sampling sets. Total concentrations of 132 gas-phase PCDD/Fs in sample sets S1, S2, S3, S4, and S5 were 16.2, 1.01, 10.2, 127, and 107 ng m^{-3} , respectively. Similarly, concentrations of 17 different 2,3,7,8-substituted PCDD/Fs in sample sets S1, S2, S3, S4, and S5 were 7.06, 0.53, 2.63, 6.50, and 3.81 ng m^{-3} , respectively. This indicates that levels of non-2,3,7,8-chlorinated PCDD/Fs were much higher than 2,3,7,8-chlorinated PCDD/Fs. The homologue distributions of gas-phase non-2,3,7,8-chlorinated PCDD/Fs in our samples are described using box plots in Fig. 5.

Low-chlorinated PCDD/Fs accounted for higher proportions in samples than highly chlorinated ones; this can be correlated with the number of congeners. TCDF contributed 46% to total PCDD/F concentrations, of which non-2,3,7,8-chlorinated PCDD/Fs were critical components (Fig. 5(A)). Likewise, PeCDF and TCDD concentrations in total PCDD/F concentrations were high, but not in the 2,3,7,8-chlorinated PCDD/F component. TCDF compounds, 1,3,4,6-TCDF, 1,2,4,6-TCDF, 1,3,4,7-TCDF, 1,3,7,8-TCDF, and 1,2,4,7-TCDF were eluted simultaneously, contributing most (20.7%) to samples, followed by compounds 1,3,6,9-TCDF and 1,2,3,7-TCDF (11.1%), and finally 2,3,6,7-TCDF and 3,4,6,7-TCDF (9.30%). In the case of PeCDFs, 1,2,3,6,8-PeCDF/1,3,4,7,8-PeCDF/1,2,4,7,8-PeCDF was the most abundant homologue, accounting for 26.5%, followed by 2,3,4,6,7-PeCDF/1,2,3,6,9-PeCDF (12.9%). In the case of TCDD, 1,3,7,9-TCDD and 1,3,6,8-TCDD contributed 23.1% and 15.4% to total TCDD concentrations, respectively. To understand the relationships between 2,3,7,8-substituted PCDD/Fs and non-2,3,7,8-chlorinated compounds in our samples, the ratios of non-2,3,7,8-chlorinated PCDD/Fs and 2,3,7,8-chlorinated PCDD/Fs, except for OCDDs and OCDFs, are shown in Fig. 5(B). These ratios clearly show higher non-2,3,7,8-chlorinated PCDD/F levels than 2,3,7,8-chlorinated PCDD/Fs, especially for TCDDs, TCDFs, and PeCDFs.

According to the calculations for bond dissociation energy, 2-C and 3-C bonds in the PCDD/F structures are

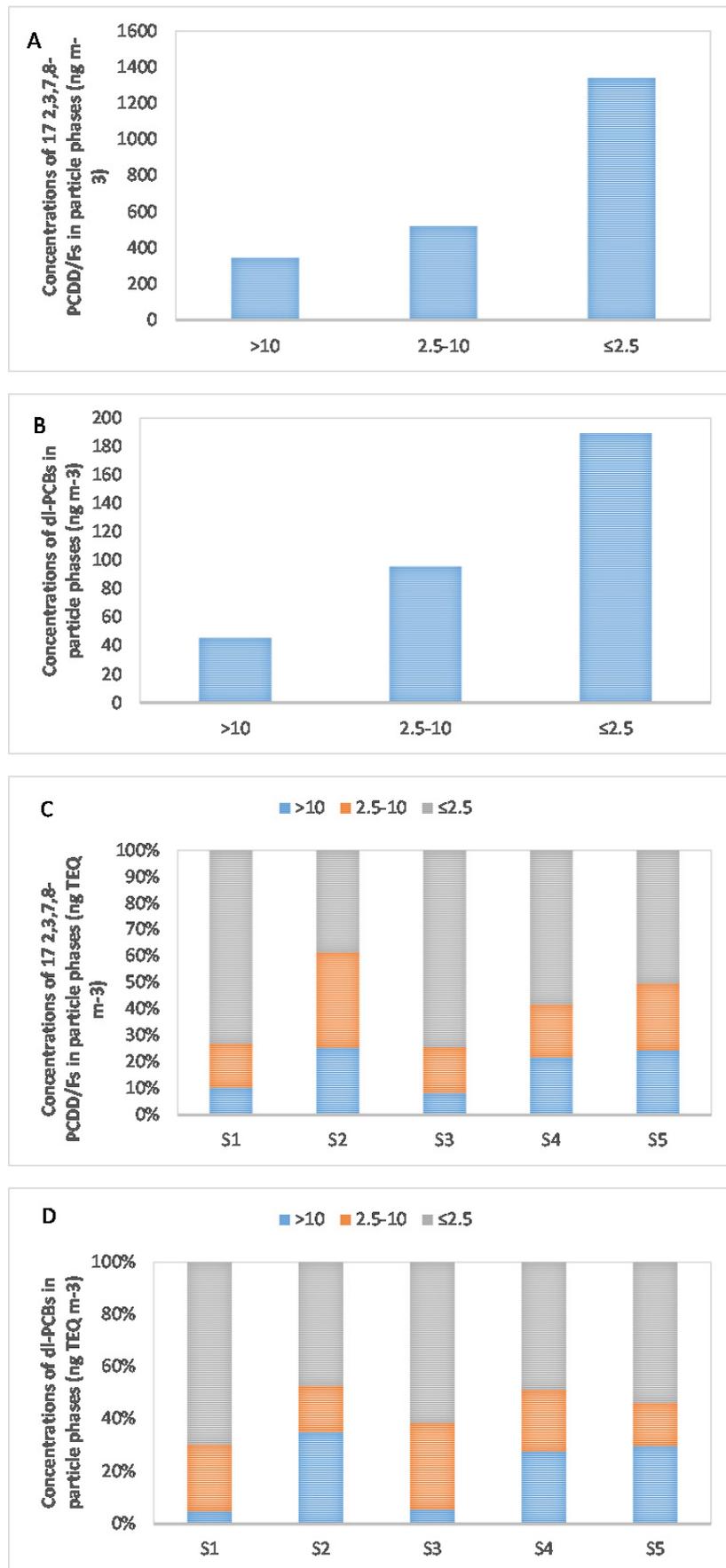


Fig. 4. Concentrations and TEQ of PCDD/Fs (A and C) and dl-PCBs (B and D) in different particle fractions.

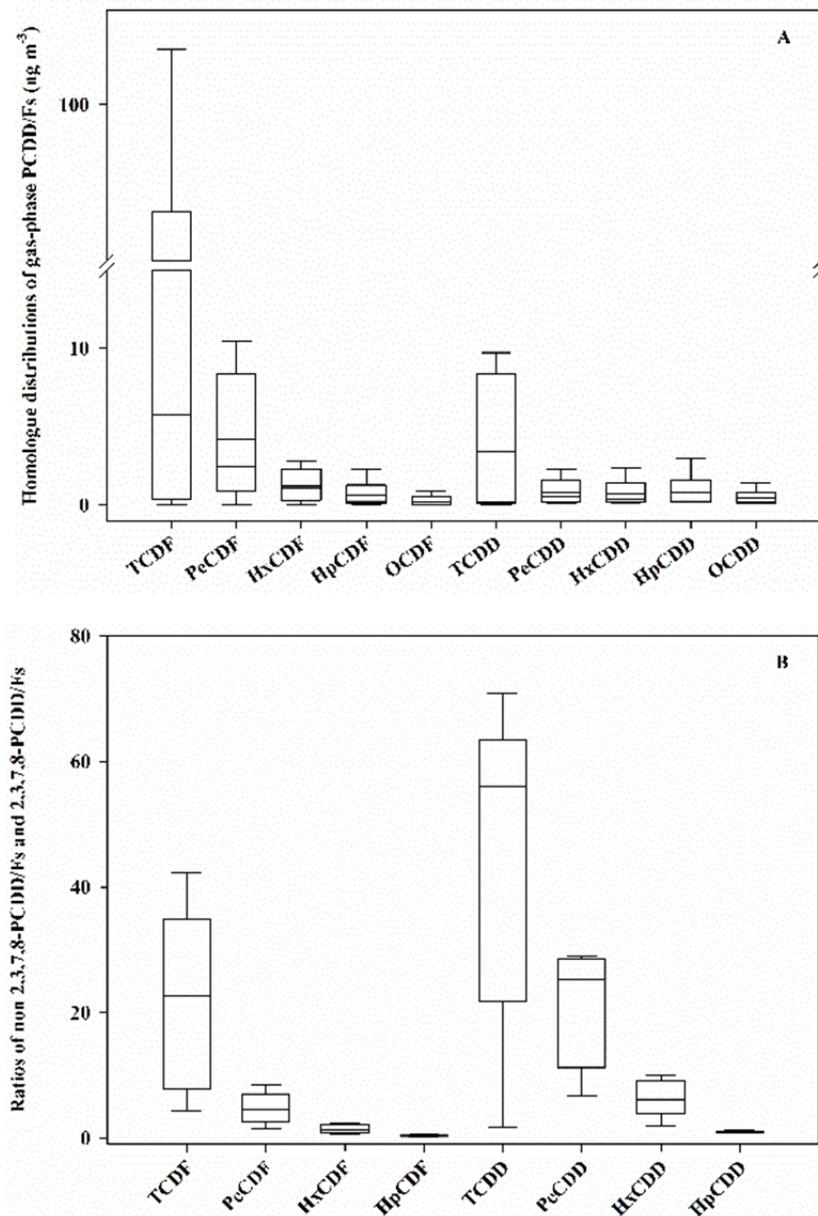


Fig. 5. Total concentrations of non-2,3,7,8-chlorinated versus 2,3,7,8-chlorinated PCDD/Fs in gas-phase samples.

more easily chlorinated (Han *et al.*, 2015). This suggests that the non-2,3,7,8-chlorinated PCDD/F compounds described above could be easily chlorinated to 2-C-Cl and 3-C-Cl forms. Non-2,3,7,8-chlorinated PCDD/Fs may be converted to 2,3,7,8-chlorinated PCDD/Fs by microorganisms over time, given that they are more stable in the environment. Therefore, greater attention should be paid to non-2,3,7,8-chlorinated PCDD/Fs, given their high levels in the atmosphere, and their potential health risks to humans on transformation. Furthermore, non-2,3,7,8-chlorinated PCDD/Fs could provide a theoretical model for reduction of emissions of 2,3,7,8-chlorinated PCDD/Fs.

Given that levels of PCDD/Fs are close to the LOD in the particulate phase, non-2,3,7,8-chlorinated PCDD/Fs were only detected in one particulate sample (PM_{2.5} in S1). The total concentration of non-2,3,7,8-chlorinated PCDD/Fs

in fine particles was 11.2 ng m⁻³, while 2,3,7,8-chlorinated species had concentrations of 5.11 ng m⁻³. This trend was similar for compounds found in the gas phase, where levels of non-2,3,7,8-chlorinated PCDD/Fs were much higher than 2,3,7,8-chlorinated PCDD/Fs, especially for TCDDs, TCDFs, and PeCDDs, having ratios of 140, 45.4, and 26.7, respectively.

Relationship between Haze-Fog and PCDD/F and dl-PCB Levels in Flue Gases

Since 2013, serious haze-fog events caused by aerosols, especially PM_{2.5}, have occurred frequently in China. These events are related to high emissions of atmospheric contaminants. Such events play a critical role in environmental and human health (Qiao *et al.*, 2015; Fu and Chen, 2017). Haze-fog episodes form through complex

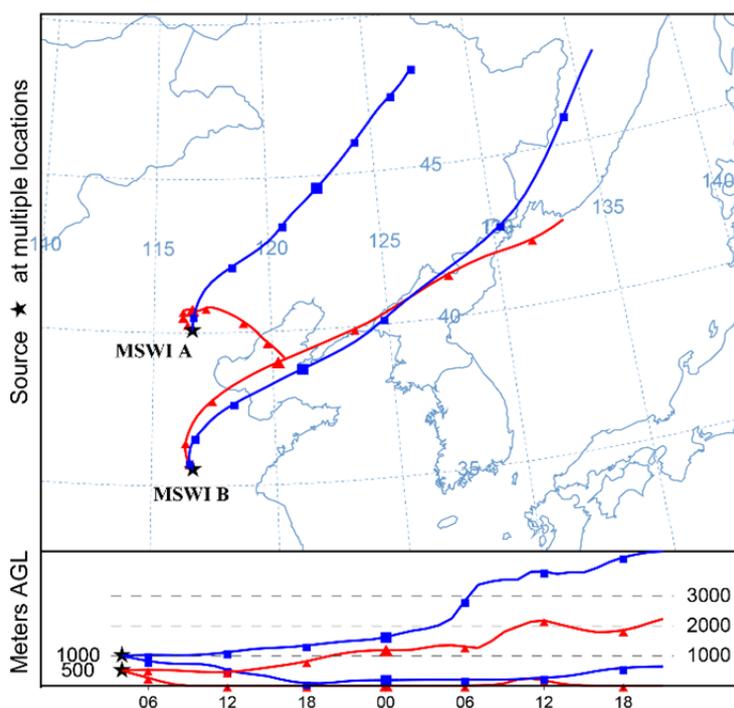


Fig. 6. Forward trajectories of PCDD/Fs and dl-PCBs emitted from two municipal solid waste incinerators (MSWIs A and B).

atmospheric reactions. In particular, water content in the atmosphere is an important factor contributing to the formation of haze-fog. In addition, emission sources, secondary aerosol formation, regional particulate transport, and adverse meteorological conditions contribute to serious haze-fog events (Fu and Chen, 2017). Some studies have shown that MSWIs are an important emission source of $PM_{2.5}$ (Yan *et al.*, 2016), given that the fine particles they release to the atmosphere are slow to decompose (Chao *et al.*, 2003).

We simulated the forward trajectories of PCDD/Fs and dl-PCBs emitted from the two MSWIs of this study (Fig. 6). Flue gas at two different heights (500 m and 1000 m) was simulated using ground meteorological data for 120 h (5 d) in the HYSPLIT model. Our simulations showed that air masses with high pollution levels move towards northeastern regions. Although transport paths of PCDD/Fs and dl-PCBs at 500 m and 1000 m were different, their forward trajectories all dissipated over the heavily polluted northeastern plain. This pollution clearly contributes to the formation of haze-fog episodes. In this case, PCDD/Fs and dl-PCBs move away from their emission sources, suggesting that MSWIs should be located at safe distances from high-density population areas to prevent adverse effects on environment and human health.

CONCLUSIONS

The concentrations and gas-particle-water partitioning of PCDD/Fs and PCBs were investigated in MSWI flue gases. (1) Total PCDD/Fs and dl-PCBs in the flue gas were presented, in decreasing order, within gas phases, particulate phases, and aqueous phases. Total concentrations of

PCDD/Fs in the flue gas ranged from 0.75 to 15 $ng\ m^{-3}$ and dl-PCBs (indicator PCBs) in the flue gas were in the range of 0.18–28 (66–1415) $ng\ m^{-3}$. (2) Average percentages of PCDD/Fs in gas, particle, and water components to the sum total of 17 2,3,7,8-PCDD/Fs in the flue gas were 71%, 26%, and 3.2%, respectively; while dl-PCBs in gas, particles, and water components to total dl-PCBs in the flue gas were 86%, 8.4%, and 5.4%, respectively. (3) PCDD/Fs and dl-PCBs increased with decreasing particle size and were highest in $PM_{2.5}$, contributing more than 54% (49%) of PCDD/Fs (dl-PCBs) to the particulate phase. (4) Concentrations of non-2,3,7,8-chlorinated PCDD/Fs were much higher than 2,3,7,8-chlorinated PCDD/Fs and low-chlorinated PCDD/Fs accounted for higher proportions than highly chlorinated PCDD/Fs.

CONFLICTS OF INTEREST

None declared.

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SUPPLEMENTARY MATERIAL

Concentrations of 132 gas-phase PCDD/Fs in sample sets S1–S5 are described in Table S1 in the Supporting Information. Supplementary data associated with this article

can be found in the online version at <http://www.aaqr.org>.

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