Emission and removal of chlorinated aromatic compounds and PAHs in Municipal Waste Incinerator

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Introduction

Emission of PCDD/Fs and dioxin-like PCBs (dl-PCBs) from municipal waste incinerators (MWI) has caused much concern due to acute toxicity to human health. Previous studies indicated that there are two main PCDD/Fs formation pathways in MWIs, one is *precursor route*, which involves the surface-catalysed reaction of compounds such as chlorobenzenes (CBs) and chlorophenols (CPs), and the other is *de novo* synthesis, which is generally due to heterogeneous formation of macromolecular carbon structures (such as soot and polycyclic aromatic hydrocarbons (PAHs)) via oxidative breakdown[1 2]. Thus, investigation of chlorinated precursors (CBs and CPs) and PAHs is essential to better understand the formation potential of PCDD/Fs. In addition to PCDD/Fs and PCBs, hexachlorobenzene and pentachlorophenol are also listed on the Stockholm Convention. European Union (EU) and USEPA also list 15+1 PAHs and 16 PAHs, respectively, as hazardous chemicals. Some PAHs are well known as carcinogens, mutagens, and teratogens and pose serious threat to human health. Therefore, investigation of emission and distribution of chlorinated aromatic compounds (such as PCDD/Fs, PCBs, CBs and CPs) and PAHs from MWIs is not only important to study the relationship between PCDD/Fs and the precursors but also provides the information on the emission of hazardous pollutants from MWIs.

In this study, the concentration and distribution of chlorinated aromatic compounds and PAHs in flue gas at different sampling locations of an MWI in Taiwan are investigated. Moreover, the removal efficiencies of chlorinated aromatic compounds and PAHs achieved with APCDs are also evaluated.

Materials and methods

Information of MWI

The waste treated in this MWI is composed of 40% municipal waste and 60% industrial waste. The feeding rate of the waste is designed as 450 ton/day. The temperature of the furnace is higher than 900^{o}C during the normal operation and the APCDs in MWI include selective non-catalytic reduction (SNCR), semi-dry scrubber, activated carbon injection (ACI) and baghouse in series (Figure 1). The injection rates of lime slurry and activated carbon are 3 m^3/hr and 6.61 kg/hr, respectively. The sampling points were selected as inlet of semi-dry scrubber, inlet of baghouse and the stack. The information on flue gas at three sampling points is shown in Table 1

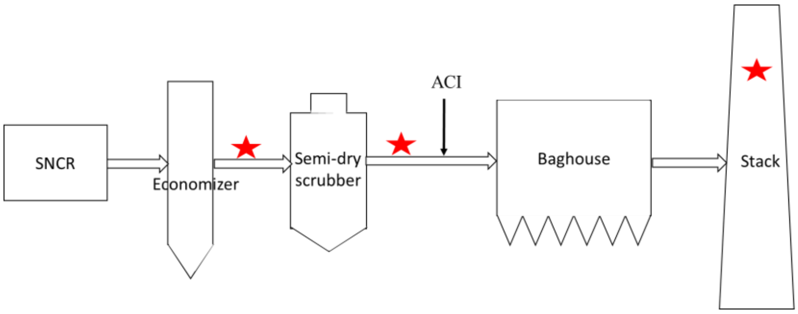

Figure 1. The air pollution control devices in the MWI (the star represents the sampling point)

Table 1. Parameters of flue gas at these sampling points in MWI

	inlet of semi-dry scrubber	*inlet of baghouse*	*stack*
Temperature(^{o}C)	237~243	152~161	143~154
Particulate matter (mg/Nm^3)	435.6	627.6	1.3
HCl (ppm)	300	N.A	19
O_2(%)	8.6~9.1	9.3~10.6	9.6~11.2
CO_2(%)	11.5~12.3	10.3~11.6	10.6~11.2

N.A：not available

Sampling of flue gas

The flue gas samples are collected by isokinetic sampling system (NCU-CS[3]) which has been proved effective for the capture of chlorinated aromatic compounds and PAHs in previous study. Particle-phase and gas-phase pollutants in flue gas collected by filter and XAD-2, respectively. The temperature and amount of XAD-2 are controlled at 20ºC and 70 g, respectively.

Pretreatment and analysis of chlorinated aromatic compounds and PAHs

Both filter and XAD-2 adsorbent are spiked with isotopically labeled surrogate standards before sampling. The rinse was collected from washing the sampling tube with three kinds of solvents in the order of acetone, dichloromethane (DCM) and toluene. The filter, XAD-2 and the rinse of sampling tube were pretreated and analyzed following Taiwan NIEA A808.75B. The samples were fortified with 13C-labeld of PAHs and POPs as internal standard before extraction and then extracted by Soxhlet method which can be divided into two stages, DCM/hexane (1:1) used as solvent for the first stage and followed by toluene as the second stage. The extracts were concentrated respectively and then mixed homogenously. After that, the extract was separated into two fractions for clean up. One fraction in clean-up followed NIEA A808.75B for PCDD/Fs and PCBs analysis, and the other was eluted in sequence with 50 mL of n-hexane (discard) and 50 mL of n-hexane/DCM (5:1, v/v) (collected and concentrated) in the column that containing 10 g silica and 10 g aluminum for analysis of PAHs and other UPOPs. Finally, recovery standards were respectively added into the extracts and analyzed by HRGC/HRMS for 17 PCDD/Fs and 12 PCBs and HRGC/MS/MS for 4-8Cl PCN, 24 PAHs, 3-5Cl CPs, and 3-6Cl CBs.

Results and discussion

The mass concentrations of PCDD/Fs, PCBs, CPs, CBs and PAHs measured at three sampling points are shown in Figure 2. The results indicate that the concentrations of CBs, CPs and PAHs are much higher than those of PCDD/F and PCBs, which is consistent with previous study[3]. The PCDD/Fs and PCBs concentrations in stack gas are 0.04 and 0.028 ng TEQ/Nm^3, respectively, which meet the emission standard of PCDD/Fs promuglated by Taiwan EPA (0.1 ng-TEQ/Nm^3 for large-scale MWIs). Besides, the PAHs concentrations at these three locations are relatively high and the total concentration of 24 PAHs measured in stack is 1891 ng/Nm^3, which is significantly higher than chlorinated aromatic compounds. Furthermore, dominant congeners of PCDD/Fs are OCDD and OCDF, while PCB105 and PCB 118 are dominant species of PCBs in flue gas as shown in Figure 3. Interestingly, it has been found that PCB105 and PCB118 are the main PCBs congeners during combustion of industrial waste as repoted in previous study[4]. Hence, the operation of this MWI is more simiar to industrial waste incineration rather than municipal waste incineration. Furthermore, the main homolouge of CPs is TriCP, while PentaCB and HexaCB are the main CBs emitted from stack, which is consistent with previous study[5]. Figure 3 also indicates that that the main species of PAHs in these three sampling points is naphthalene, with the concentration higher than other PAHs by one order of magnitude. Moreover, it can be found that the concentrations of medium- and high- ring PAHs increase significantly after semi-dry scrubber.

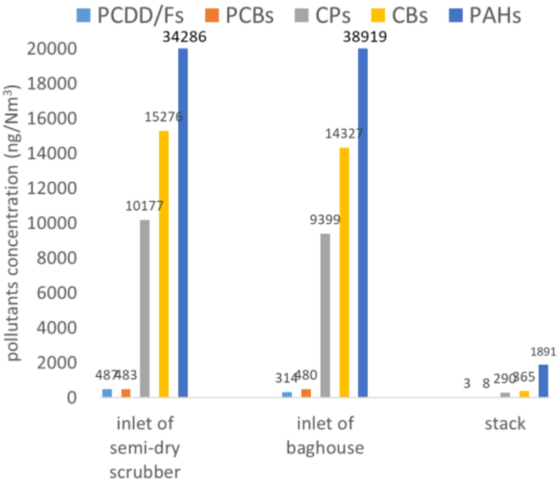

Figure 2. Concentrations of PCDD/Fs, PCBs, CPs, CBs and PAHs in flue gas at three sampling points

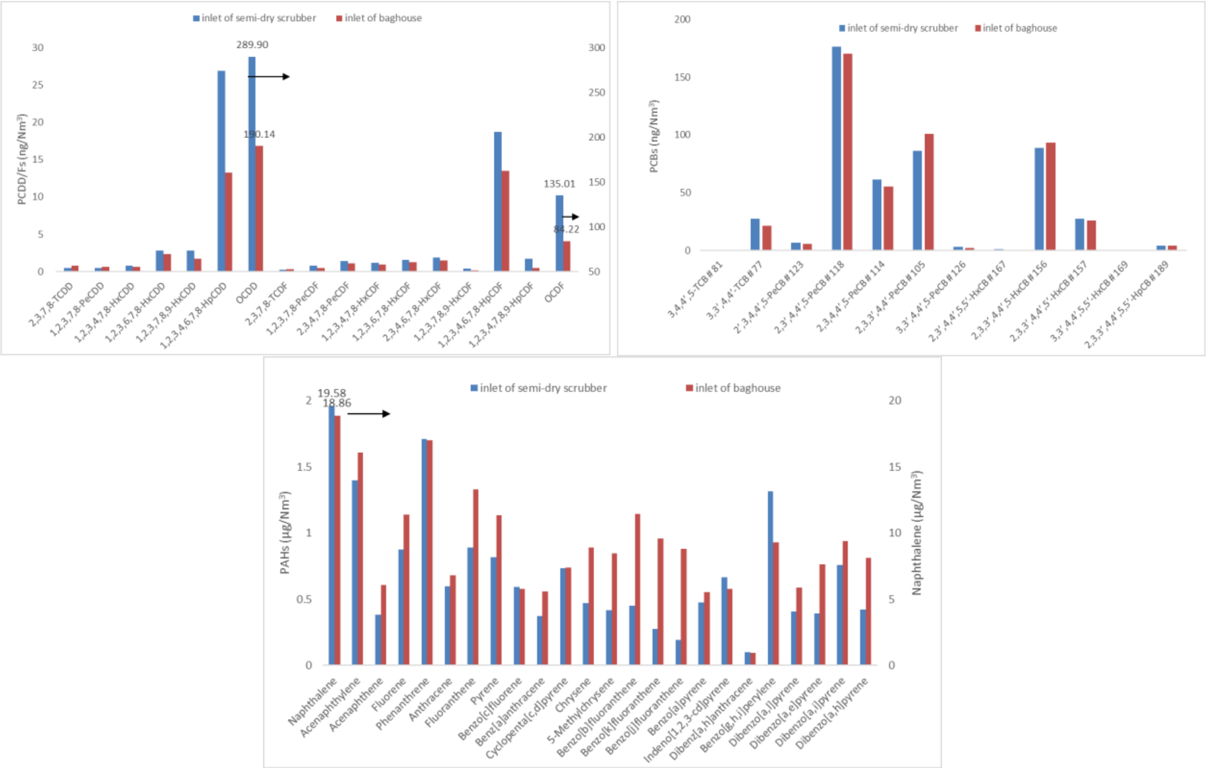

Figure 3. Concentrations of PCDD/Fs, PCBs and PAHs congeners in inlet of semi-dry scrubber and inlet of baghouse, respectively

The removal efficiencies of chlorinated aromatic compounds and PAHs achieved with semi-dry scrubber and ACI + baghouse are shown in Figure 4 The results indicate that the removal efficiencies of chlorinated compounds achieved with ACI+baghouse are significantly higher than those achieved with semi-dry scrubber. It is because air pollutants existing in both gas phase and particle phase in flue gas can be simultaneously removed by ACI + baghouse via adsorption and filtration, respectively. Besides, the removal efficiency of PCDD/Fs (36%) achieved with semi-dry scrubber is significantly higher than those of other chlorinated aromatic compounds and PAHs (1%-6%). It is attributed to the fact that the removal of highly chlorinated PCDD/Fs, which are dominant congeners in the flue gas at inlet of semi-dry scrubber, are significantly higher than those of low chlorinated PCDD/Fs, as shown in Figure 3. However, the results indicate that PAHs concentration increased slightly in semi-scrubber. Previous study indicates that the major formation mechanisms of PAHs are pyrolysis and pyrosynthesis process. In pyrolysis, the macromolecular aromatic compounds are broken into fragments to form PAHs. The temperature range of PAHs formation are from 200°C to 1000°C and high–molecular-weight PAHs are formed at relatively low temperature while low-molecular-weights PAHs are dominant at high temperature [6]. As shown in Figure 3, higher concentrations of medium- and high- ring PAHs are measured at the outlet of semi-dry scrubber than low-ring PAHs. Therefore, PAHs may be generated in the semi-dry scrubber within the temperature ranging from 150 to 250°C. Besides, the PCDD/Fs concentration decreased slightly after the semi-dry scrubber. It is suggested HCl as the chlorine source for PCDD/Fs formation is effectively removed by slurry injection and the removal efficiency of HCl achieved with semi-dry scrubber is 93.6%.

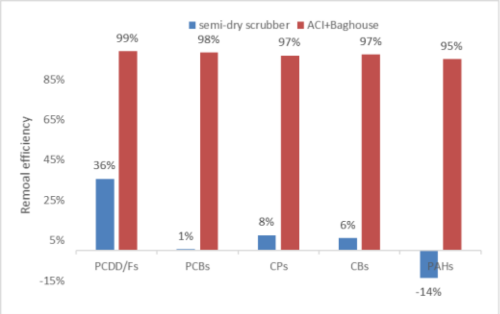

Figure 4. Removal efficiencies of chlorinated aromatic compounds and PAHs achieved with semi-dry scrubber and ACI + baghouse, respectively.

Figure 5 shows the gas/particle phase partitioning of chlorinated aromatic compounds and PAHs in flue gas of the MWI. It indicates that the percentage of PCDD/Fs in particle phase is higher than that in gas phase. It is attributed to the fact that the dominant congeners of PCDD/Fs are highly chlorinated PCDD/Fs (OCDD and OCDF) with lower vapor pressures and have a higher tendency to associate with particles. Furthermore, the percentage of CPs and CBs in gas phase is significantly higher than that in particle phase due to higher vapor pressures. However, the percentage of PAHs in particle phase increases after semi-dry scrubber, suggesting that some PAHs are deposited on particle. As shown in Figure 3, the medium- and high- ring PAHs which have lower vapor pressures tend to be adsorbed on particles with the semi-dry scrubber. Besides, the percentages of PCDD/Fs, PCBs, CPs, CBs and PAHs in gas phase decrease significantly after ACI + baghouse, implying that the main removal mechanism of ACI + baghouse for these pollutants is adsorption[7].

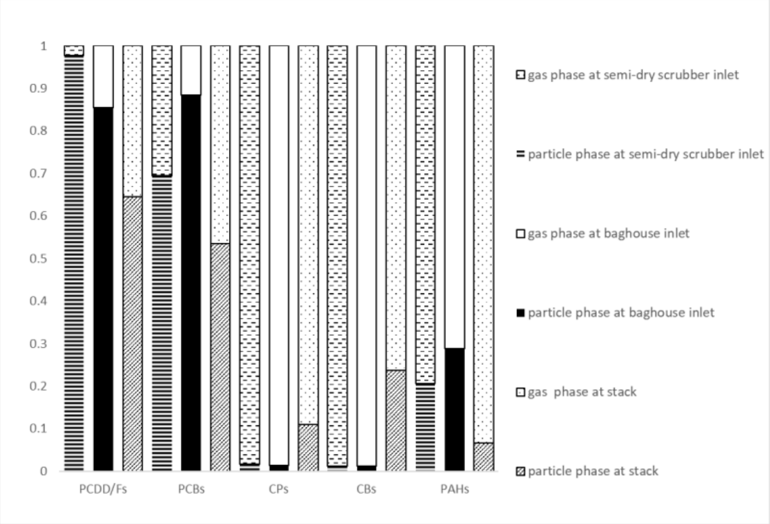

Figure 5. Comparison of gas/particle partitioning of chlorinated aromatic compounds and PAHs in flue gas at different sampling points

Acknowledgements

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References:

1. Environmental and Safety Services for Environment Australia, (1999)
2. Fujimori, T, Nishimura, K, Oshita, K, Takeda, N, Takaoka, M (2014) *AEROSOL AIR QUAL RES*. 14(4): 1131-1141
3. Wang, TJ , Chen, T, Lin, BB, Lin, XQ, Zhan, MX, Li, XD (2017) *RSC Adv.* 7 (70): 44309-44318
4. Moussaoui, Y, Tuduri, L, Kerchich, Y, Meklati, BY, Eppe, G (2012) *Chemosphere.* 88(3): 270-277
5. Peng, YQ , Chen, JH, , Lu, SY, Huang, JX, ,Zhang, MM, Buekens, A, Li, XD, Yan, JH (2016) *Chem Eng J* 292 ,398-414
6. Li, C, Zhang, X, Gao, X, Qi, S, Wang, Y(2019) *Int. J. Environ. Res. Public Health* 16(8), 13684
7. Abdel-Shafy, H.I., Mansour, M.S.M., (2016) *Egyptian Journal of Petroleum* 25(1) :107-123