Evaluation of PCDD/F Congener Distributions between Gas and Particulate Phases in Flue Gases in MWI

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Introduction

The percentage of municipal solid wastes (MSW) being incinerated in Taiwan is expected to reach 90% by the year 2004. However, relevant studies indicate that the waste incineration process possibly emits various pollutants including CO, acid gases, particulate matter, heavy metals and PCDD/Fs into the atmosphere if not properly treated(1). To reduce PCDD/F emissions, waste incinerators are equipped with various types of air pollutant control devices (APCDs). Among the methods used, spraying of powdered activated carbon (PAC) into gas streams or installing a fixed-bed system to adsorb PCDD/Fs in waste gases is considered as the simplest one. Nevertheless, some problems exist in controlling PCDD/F emissions from municipal waste incinerators (MWIs) with activated carbon injection (ACI). The removal efficiencies of PCDD/F congeners achieved with ACI are not always consistent due to the difference of congeners in terms of vapor pressure, and different adsorbing capacities of the activated carbons used. Normally, lowly chlorinated PCDD/Fs can be easily adsorbed by activated carbon. Highly chlorinated PCDD/Fs are easier to adhere to the particles due to the lower vapor pressures and are harder to adsorb with activated carbon. Hence, understanding PCDD/Fs partitioning in gas/particulate phase is important in selecting and designing PCDD/F control equipment. To examine this important feature, this study was motivated to investigate the partitioning of PCDD/Fs in gas/particulate phase of MWI flue gas.

Experimental

The municipal waste incinerator (MWI) investigated in this study started to operate in 1995. It consists of three incinerating units, each with its own heat recovery system. The incinerator is equipped with cyclone (CY), dry lime sorbent injection systems (DSI) and bag filters (BF) for controlling acid gas and particulate emissions. In 1999 Taiwan government promulgated the PCDD/F emission limits for existing large-scale MWIs (0.1 ng-TEQ/Nm^3). The ACI technology was retrofitted in this MWI in March 1999 for reducing PCDD/F emission to meet the stringent standards. The PCDD/F sampling points and temperature variation of the MWI are schematically shown in Figure 1. To compare the temperature variation of APCDs with the distribution of gas/particulate phase PCDD/Fs, three sets of flue gases were sampled simultaneously before and after APCDs (bag filter) for evaluating the performance of the APCDs at different operation temperatures for reducing PCDD/F emissions. The flue gas conditions at two sampling points are listed in Table 2. The flue gas samples were collected with Graseby Anderson Stack Sampling System complying with USEPA Method 23A (2). The gas-phase sample was collected with XAD-2 resin while the particle bound samples were collected with a glass fiber filter. The glass fiber filter

(Whatman-1820 110 mm) used in this study has a collection efficiency better than 99.9 % on the test particles with a mean particle diameter of 1.0 μm at the flow rate below 300 L/min. To avoid the error caused by the dioxins bound to particulate matter, isokinetic sampling had to be conducted in order to collect a representative sample. The samples were analyzed for seventeen 2,3,7,8-substituted PCDD/F congeners with high resolution gas chromatography (HRGC) (Hewlett Packard 6890 plus)/high resolution mass spectrometer (HRMS) equipped with a fused silica capillary column DB-5 MS (60m x 0.25 mm x 0.25μm, Supelco). The mass spectrometer was operated with a resolution greater than 10,000 under positive EI conditions, and data were obtained in the selected ion monitoring (SIM) mode.

Results and discussion

Figure 2 shows the average PCDD/F concentrations in flue gas at different sampling points with temperature variation. Results of the flue gas sampling indicate that the PCDD/F concentrations are 3.82 ~4.61 ng-TEQ/Nm^3 at CY outlet and 0.146~0.507 ng-TEQ/Nm^3 at stack gas with different operation temperature, respectively. Since the flue gas temperatures (Set 1 to 3) at CY outlet are quite close (206~208 ^{0}C); the PCDD/F concentrations at this sampling point do not vary significantly. However, the PCDD/F concentrations at stack gases are quite different with the temperature variation (140~156 ^{0}C) of flue gases. The results prove that there is optimal operating temperature (Set 2) for PCDD/F removal with ACI. Figure 3 shows the PCDD/F gas/particulate phase distributions in the flue gas at different sampling points in MWI. Based on the gas/particulate phase distribution of PCDD/F congeners at CY outlet, PCDD/F congeners mostly distributed in gas phase (about 75% of the total PCDD/Fs). In stack gas, over 85% of PCDD/F congeners were distributed in gas phase. In addition, PCDF accounts for 50% in gas phase and 15% in particulate phase at the CY outlet and 65% in gas phase and 3.4% in particulate-phase PCDD/F at the stack. Previous study[3] indicates that semi -volatile organic compounds (SOCs) have been classified as compounds with vapor pressures between 10^{-11} and 10^{-4} atm and include the PCDD/Fs, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs). Besides, the fraction of SOCs (like PCDD/Fs) adsorbed to particles was mainly affected by the vapor pressures of those compounds. The vapor pressure of the organic compound increases as the temperature increases. That also results in lower fraction of PCDD/F congeners being adsorbed to particles. Figure 4 indicates that the temperature in flue gas decreases from CY outlet to stack (DSI: 173℃→BF: 150℃, Set 1). When the level of temperature variation in flue gas decreases intense ($\Delta T_{\%}$: -13.3%), the gas-phase PCDD/Fs likely to condense on particle surface in flue gas. Therefore, the activated carbon injected in DSI could not effectively remove gas-phase PCDD/Fs in flue gas (gas-phase PCDD/F removal efficiency is below 90%), and the distribution of particulate-phase PCDD/Fs is higher than that in gas phase. When the trend of temperature variation ($\Delta T_{\%}$: -5.2%) is smooth (DSI: 190℃→BF: 180℃, Set 3), the gas-phase PCDD/F will still distribute in gas phase and not easily condense on particles in flue gas. Therefore, the activated carbon injected could remove gas-phase PCDD/Fs in flue gas with a reasonable efficiency (gas-phase PCDD/F removal efficiency is over 90%). But the PCDD/F concentration of Set 2 emitted from stack is the lowest among those three operating temperatures. It might be attributed to the temperature variation that affects the particle removal efficiency (table 2). Hence, the particulate-phase PCDD/Fs will be the determining factor of the PCDD/F concentrations emitted from stack in the MWI investigated. In addition, the results demonstrate a positive correlation between the particulate-phase PCDD/F and particle concentration in flue gas. Based on the studies completed in other countries, certain correlation between particle and PCDD/F concentration is found[4]. Furthermore, Figure 5 indicates that as the chlorination level of PCDD/F congener increases, the removal efficiency of gas-phase

PCDD/Fs achieved with ACI decreases. Generally speaking, activated carbon could adsorb volatile organic pollutant effectively, lowly-chlorinated congener are of higher vapor pressure compared to highly-chlorinated congener and have higher tendencies to desorb from particles and be adsorbed by activated carbon(5). Figure 5 illustrates the decreasing removal efficiencies of gas-phase PCDD/F congeners with increasing chlorination with ACI technology. The removal efficiencies achieved with bag filters for particulate-phase PCDD/F and particle are close (98.5% and 99.8%, respectively). Since the PCDD is the major distributor (56%~62%) of particulate-phase PCDD/Fs; the removal efficiency of particulate-phase PCDD is higher than that in gas phase with ACI. The ACI technology can effectively remove gas-phase PCDD/Fs while it is almost ineffective in removing particulate-phase PCDD/Fs. The removal efficiency of APCDs for particles with small diameter (especially those with diameters of 0.1-1μm) is relatively low compared to that of large particles.

The results obtained from the flue gas sampling at different sampling points of a large-scale MWI indicate that the gas/particulate phase distributions of PCDD/Fs are mainly affected by the temperature variation. In addition, the results demonstrate that the gas/particulate phase distributions and removal efficiencies of PCDD/Fs in flue gases change closely with the chlorinated level of PCDD/F congeners.

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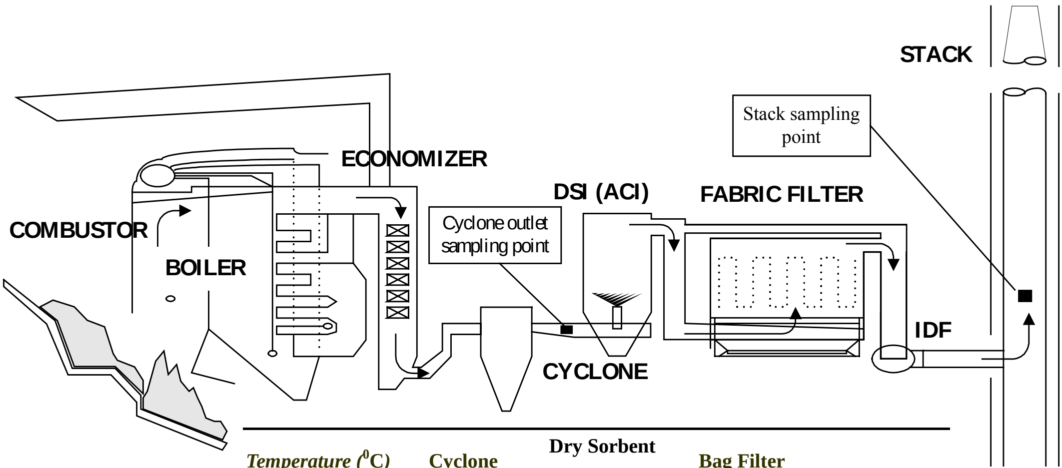
Table 1 The operating conditions of the MWI investigated.

Capacity (tons/day/incinerator)	**450**
Operating temperature ( )	**850-1,050**
Air pollution control device (APCD)	**Cyclone Dry Sorbent Injection (with Activated Carbon Injection) Bag Filter**
Stack height (m)	**120**
Flue gas flow rate (kNm^3/h/incinerator)	**96.6 ±2.7**
Injection rate of activated carbon	**50 mg/Nm^3**

Table 2 The condition of flue gas at different sampling points in two MWIs.

Location	Set 1		Set 2		Set 3	
	CY - outlet	Stack	CY - outlet	Stack	CY - outlet	Stack
Temperature ( )	206	138	208	144	207	156
Particulate matter (PM) concentration (mg/Nm^3)	921.2	3.6	741.3	1.2	800.3	2.6
PM Removal efficiency (%)	99.6		99.8		99.7	



Temperature (^{0}C) & Batch	Cyclone (CY)	Dry Sorbent Injection (DSI)	Bag Filter (BF)	Stack
Set 1	206	173	150	140
Set 2	208	182	160	144
Set 3	207	190	180	156

Fig.1 Sampling points and temperature variation of APCDs in MWI investigated.

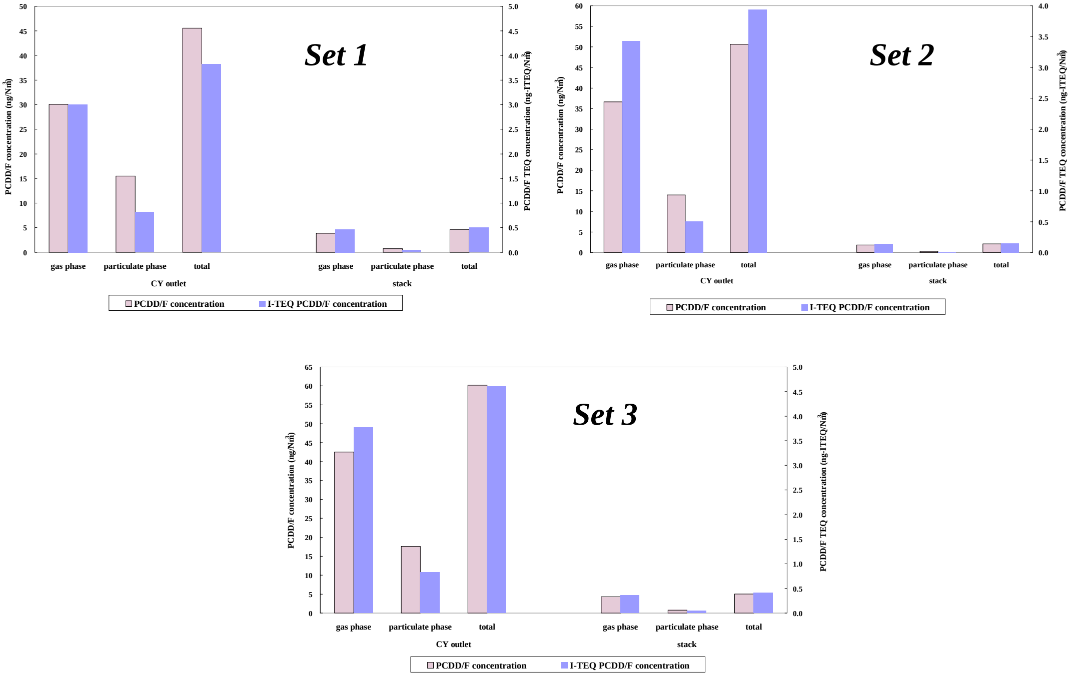


Fig. 2 Variation of PCDD/F concentration in gas/particulate phases at different sampling points in the MWI investigated.

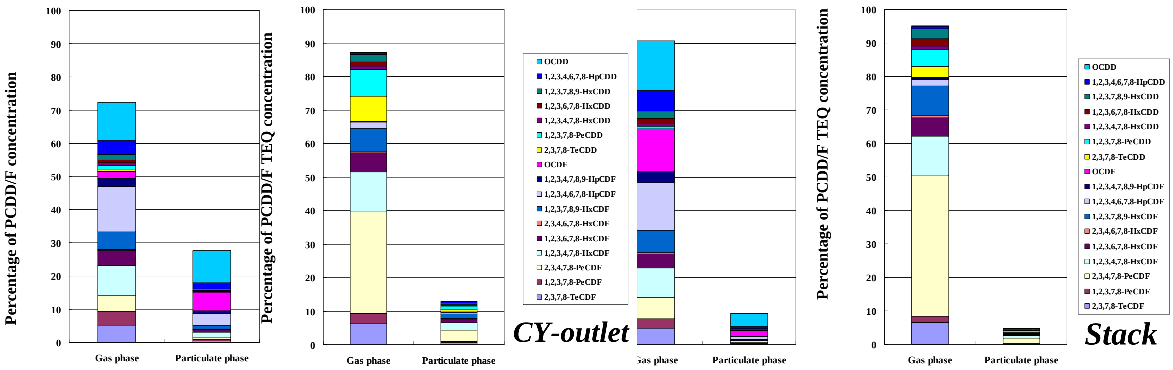


Fig. 3 Average partitioning of PCDD/Fs in gas/particulate phases at cyclone outlet and stack gas of the MWI investigated (n=12).

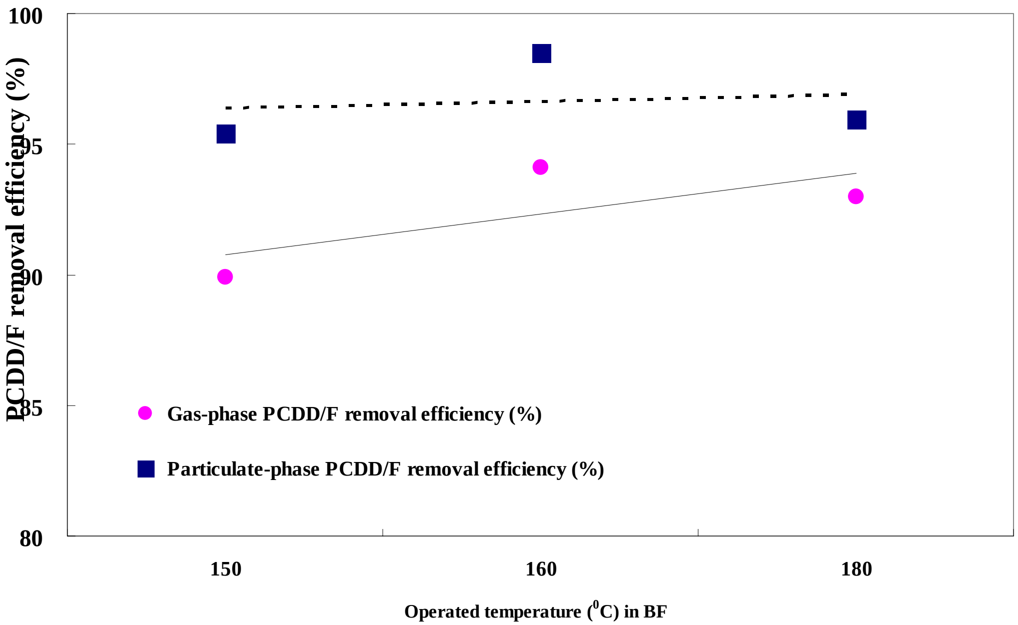


Fig. 4 Comparison of gas/particulate phase PCDD/F removal efficiencies with temperature variation

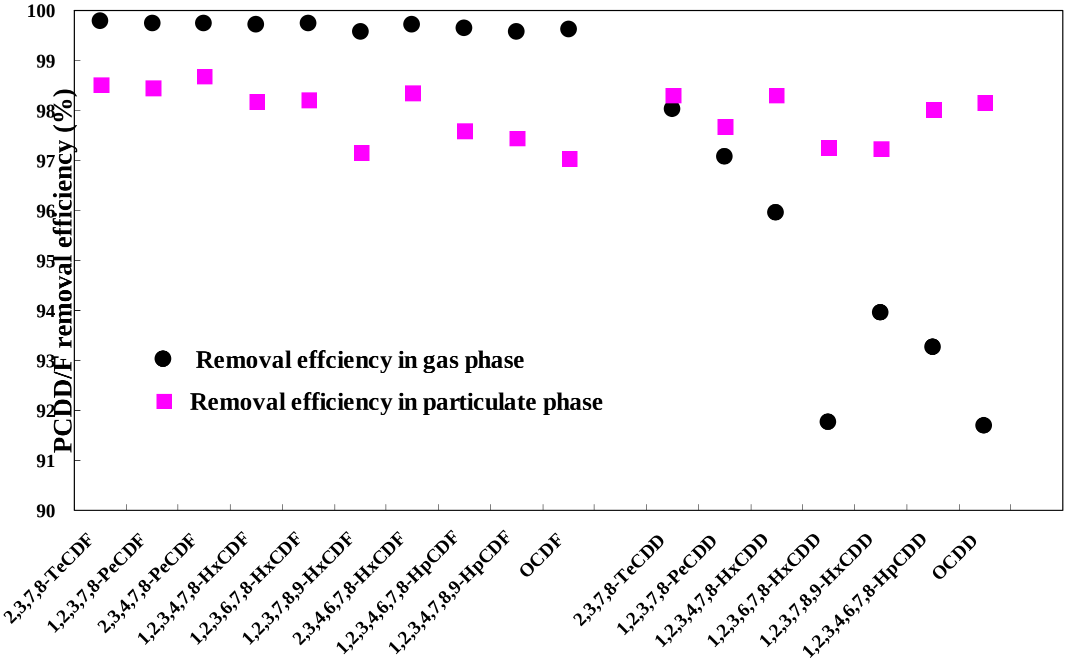


Fig. 5 Removal efficiencies of PCDD/F congeners in gas and particulate phases in flue gas with ACI+BF in MWI.