Characteristics of Congener Distributions and Removal Efficiencies of PCDD/Fs from Three Solid Waste Incinerators

Moo Been Chang and Kai Hsien Chi
Graduate Institute of Environmental Engineering, National Central University, Chungli, Taiwan
E-mail: mbchang@ncuen.ncu.edu.tw

Abstract
Partitioning of PCDD/F congeners between gaseous and particulate phases and removal efficiencies of the existing air pollution control devices (APCDs) for PCDD/Fs at three solid waste incinerators in Taiwan are evaluated via stack sampling and analysis. Three incinerators (two are municipal waste incinerators and one is industrial waste incinerator) investigated are equipped with activated carbon injection (ACI), selective catalytic reduction system (SCR) and fixed carbon bed (FCB), respectively as major PCDD/F control devices. The results obtained on gas/particulate partitioning in flue gases indicate that the particulate-phase PCDD/Fs accounted for 27.7%, 24.7% and 20.1% of the total PCDD/F concentrations at the outlets of cyclone (CY), electrostatic precipitator (EP) and wet electrostatic precipitator (WEP), for I-1, I-2 and I-3, respectively. In addition, the gas/particulate partitioning in flue gas after PCDD/Fs control devices is quite different in three incinerators, being affected by the removal efficiencies and mechanism with different APCDs. The average PCDD/F concentrations of stack gas are 0.17, 0.043 and 1.74 ng-TEQ/Nm$^3$ in those three incinerators, respectively. The average removal efficiency of PCDD/Fs achieved with ACI (I-1) reaches 95%, SCR system (I-2) reaches 99% and FCB (I-3) reaches 72%. Since ACI and FCB can only transfer the PCDD/Fs from gas-phase to particulate phase and SCR system can effectively destroy PCDD/F congeners in flue gas, SCR system could serve as a better PCDD/F control device for the solid waste incinerators.

Introduction
PCDD (Polychlorinated Dibenzo-p-dioxins) and PCDF (Polychlorinated Dibenzofurans) are commonly known as dioxin which has been listed as one of the persistent organic pollutants (POPs). Due to the different level of chlorination and positioning of chlorine atoms, there exist 210 congeners. Among them, 17 congeners with chlorine substitution in the 2,3,7,8 position are most toxic to the human being. Previous study$^{(1)}$ indicates that ambient PCDD/Fs originate mainly from waste incineration processes including municipal waste incinerators (MWIs), industrial waste incinerators (IWIs), electric arc furnaces (EAFs) and sinter plants. To examine this important feature, this article is motivated to investigate the partitioning of PCDD/Fs between gas/particulate phases of stack gas. In addition, we focus on the understanding of the partitioning and removal efficiency of PCDD/Fs of flue gases at several PCDD/F emission sources equipped with different air pollution control devices (APCDs).

Experimental
The sampling conditions of I-1, I-2 and I-3 are listed in Table 1. The flue gases were sampled simultaneously before and after APCDs for evaluating the performance of the APCDs for reducing PCDD/F emissions in three incinerators. All 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. 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) /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 1 shows the average PCDD/F concentrations in flue gases at different sampling points. Results of the flue gas sampling indicate that the average PCDD/F concentrations are 3.93 ng-TEQ/Nm³, 7.89 ng-TEQ/Nm³ and 6.05 ng-TEQ/Nm³ at CY, EP and WEP outlet, respectively. Besides, the average PCDD/F concentrations in stack gases are 0.17 ng-TEQ/Nm³, 0.043 ng-TEQ/Nm³ and 1.74 ng-TEQ/Nm³ in I-1, I-2 and I-3, respectively. In I-2, the PCDD/F concentration in flue gas at EP outlet was 134.1 ng/Nm³. It was significantly higher than that at CY and WEP outlet (50.6 ng/Nm³ and 49.7 ng/Nm³, respectively) of I-1 and I-3. The high PCDD/F concentration measured at EP outlet was attributed to the de novo synthesis since the operating temperature of EP was 233°C which was within the de novo synthesis temperature window. Figure 2 shows the PCDD/F gas/particulate phase distributions in the flue gas at different sampling points in three wastes incinerators. PCDD/Fs are mostly distributed in gas phase (about 72.3% of the total PCDD/Fs) at CY outlet in I-1. In stack gas of I-1, over 90% of PCDD/Fs congener was distributed in gas phase. In I-2, the gas-phase PCDD/Fs account for 75.3% of the total PCDD/Fs at EP outlet, and the particulate-phase PCDD/Fs account for about 70% of the total PCDD/Fs at the stack. In I-3 PCDD/Fs are mostly distributed in gas phase (about 80.3% of the total PCDD/Fs) at WEP outlet. In stack gas of I-3, over60% of PCDD/Fs congener was distributed in particulate phase. Figure 3 shows the PCDD/F removal efficiencies in flue gas with ACI and the average removal efficiencies could reach 95% with ACI in I-1. Besides, the results indicate 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 adsorbs volatile organic pollutant effectively; the lowly-chlorinated congeners are of higher vapor pressure compared to highly-chlorinated congeners and have higher tendencies to exist as gaseous form and be adsorbed by activated carbon. Figure 4 shows that the removal efficiency of PCDD/Fs in gas phase (99.5% to 99.8%) is higher than that in particulate phase (96.5% to 98.2%) in I-2. The trend matches with the results compiled in other countries (1). In general, the WS system could remove a part of the particulate matter in the flue gas. So the WS could remove the particulate phase PCDD/Fs in the meantime. Figure 5 shows the PCDD/F removal efficiencies in flue gas within FCB and the average removal efficiencies could reach 72% in I-3. In general, FCB could not remove particulate-phase PCDD/Fs. The FCB installed in I-3 even increases the particulate-phase PCDD/Fs possibly due to the attrition of granular activated carbon with the FCB. Hence, the distribution of particulate-phase PCDD/Fs is higher than that in gas phase in stack gas of I-3. But FCB could adsorb gas-phase PCDD/Fs effectively (60% to 87%), and the trends of chlorination level and removal efficiency of gas-phase PCDD/Fs are the same with that in I-1. Furthermore, ACI is usually followed by BF which has a higher particle
removal efficiency than FCB. That also results in different gas/particulate partitioning of PCDD/F congeners in flue gas after APCDs.

Although both APCDs are operated with high temperatures (>150℃), gas/particulate distributions of PCDD/Fs in stack gases found in I-1 and I-2 are quite different. In I-2, the operating temperature at SCR is higher than 200℃, but the distribution of particulate-phase PCDD/Fs is higher than that in gas phase. It might be caused by the fact that operating at high operating temperature (over 200℃), SCR could effectively remove gas-phase PCDD/Fs in flue gas. Therefore, the distribution of gas-phase PCDD/Fs in I-2 is much lower than that in I-1. Overall, this study has confirmed that gas/particulate phase distribution of PCDD/F congeners in flue gas is affected by the operating temperature of APCDs and removal mechanism.

Acknowledgements
The authors gratefully acknowledge the financial support provided by the National Science Council of the Republic of China (NSC 92-EPA-Z-008-002 and NCU-ITRI 930302).

References

Table 1  The condition of flue gases at different sampling points in three incinerators.

<table>
<thead>
<tr>
<th>Location</th>
<th>I-1</th>
<th>I-2</th>
<th>I-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY-outlet Stack</td>
<td>EP-outlet Stack</td>
<td>WEP-outlet Stack</td>
<td></td>
</tr>
<tr>
<td>Temperature (℃)</td>
<td>202</td>
<td>138</td>
<td>221</td>
</tr>
<tr>
<td>CO₂ (%)</td>
<td>10.9</td>
<td>8.6</td>
<td>11.7</td>
</tr>
<tr>
<td>O₂ (%)</td>
<td>9.9</td>
<td>11.2</td>
<td>9.1</td>
</tr>
<tr>
<td>Particulate matter (PM) concentration (mg/Nm³)</td>
<td>770</td>
<td>1.2</td>
<td>8.52</td>
</tr>
<tr>
<td>PM Removal efficiency (%)</td>
<td>99.8 (DSI+ACI+BF)</td>
<td>90.3 (WS+SCR)</td>
<td>54.9 (FCB)</td>
</tr>
</tbody>
</table>
Figure 1  Variation of PCDD/F concentration in gas/particulate phases at different sampling points in three incinerators

\( G = \text{gas phase} \quad P = \text{particulate phase} \quad T = \text{gas + particulate phase} \)
Figure 2  Partitioning of PCDD/Fs in gas/particulate phases at CY, EP and WEP outlet and stack gas of three incinerators
Removal efficiency (%)