Correcting the gas and particle partitioning of PCDD/F congeners in the flue gas of an iron ore sinter plant

Yu-Chieh Kuo [a], Yu-Cheng Chen [a], Jeng-How Yang [a], Perng-Jy Tsai [a,b,*], Lin-Chi Wang [c,d,**], Guo-Ping Chang-Chien [c,d]

[a] Department of Environmental and Occupational Health, Medical College, National Cheng Kung University. 138, Sheng-Li Road, Tainan 704, Taiwan
[b] Department of Occupational Safety and Health, College of Public Health, China Medical University and Hospital, 91, Hsueh-Shih Road, Taichung 40402, Taiwan
[c] Department of Chemical and Materials Engineering, Cheng Shiu University. 840, Chengching Road, Kaohsiung 833, Taiwan
[d] Super Micro Mass Research and Technology Center, Cheng Shiu University. 840, Chengching Road, Kaohsiung 833, Taiwan

ARTICLE INFO

ABSTRACT

This study was aimed at developing an approach for correcting the gas and particle partitioning of PCDD/F congeners for samples collected from the flue gas of an iron ore sinter plant. An iron ore sinter plant equipped with an electrostatic precipitator (EP) and a selective catalytic reduction (SCR) was selected. Flue gas samples were collected at EP inlet, EP outlet and SCR outlet. Both particle- and gas-phase PCDD/Fs were analyzed for each collected sample. PCDD/F contents in EP ashes (EP$_{ash}$) were also analyzed and used to correct the gas and particle partitioning of PCDD/F congeners of the collected flue gas samples. Results show that PCDD/Fs in the flue gas were dominated by the gas-phase. Before correction, the removal efficiencies for the gas- and particle-phase PCDD/Fs for EP were −58.1% and 64.3%, respectively, and SCR were 39.4% and 83.9%, respectively. The above results were conflict with the expected results for both EP and SCR indicating the need for correcting the gas and particle partitioning of PCDD/F congeners for all collected flue gas samples. After correction, the removal efficiencies become more reasonable for EP (=4.22% and 97.7%, respectively), and SCR (=54.7% and 62.0%, respectively). The above results confirm the effectiveness of the approach developed by this study.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are toxic, persistent, lipophilic and stable-chemical compounds in the environment, and are known harmful to the human health [1]. Since PCDD/Fs were first discovered from the fly ash of a municipal solid waste incinerator (MSWI) [2], their emissions from various sources, such as MSWI [3], power generation [4,5], metallurgical process [6–8] and chemical process [9] have become a serious issue in the environmental science field. Among them, the iron ore sinter plant, one of the source categories listed in part II of Annex C under the Stockholm Convention, is considered as the most important PCDD/F emission source in many countries [6,8].

PCDD/Fs are semi-volatile in nature presenting in the forms of gas-phase and particulate-phase in the flue gas. For the control of PCDD/F emissions from iron ore sinter plant, various air pollution control devices (APCDs) are selected to decrease the emission levels of both gas- and particle-phase PCDD/Fs [10,11]. In principle, particle-phase PCDD/Fs in flue gases can be largely controlled by using a cyclone, bag filter or electrostatic precipitator (EP) [12]. On the other hand, the carbon injection system and selected catalytic reduction (SCR) are widely adopted to remove gas-phase PCDD/Fs [13]. Therefore, a better understanding to PCDD/F concentrations and their partitions in gas/particle phases would be helpful for evaluating the removal efficiencies of various installed APCDs.

In practice, the standard isokinetic sampling method, suggested by U.S. EPA [14] and European Committee for Standardization (CEN) [15], is commonly used in a duct/stack system to sample both the gas- and particle-phase PCDD/Fs simultaneously. During sampling, the particle-phase PCDD/Fs in the flue gas was collected by the filter mounted in the sampling train, and gas-phase fraction was collected by the subsequent sorbent. However, a potential bias might be introduced during the sampling which results in incorrect sampling results in both gas- and particle phase PCDD/Fs contents. For example, some gas-phase PCDD/Fs might be absorbed by particulate matters collected on the filter, or to the contrary, some
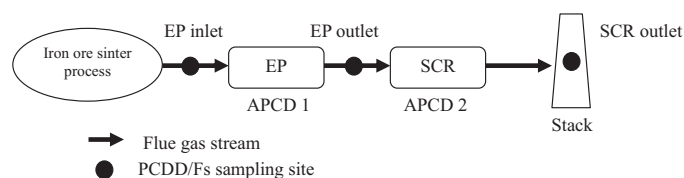
EP inlet   EP outlet   SCR outlet

Iron ore sinter process → EP → SCR → Stack

APCD 1   APCD 2

→ Flue gas stream
● PCDD/Fs sampling site

Fig. 1. Air stream diagram and the three PCDD/Fs sampling sites.

particle-phase PCDD/Fs might become gas-phase PCDD/Fs due to sampling time is usually longer than 3 h. In addition, the difference in temperature between the flue gas and sampling train might also result in the condensation of some gas-phase onto the particle-phase PCDD/Fs [16,17].

According to our best knowledge, previous studies have never been conducted to correct the gas and particle partitioning of PCDD/F congeners for flue gas samples collected from iron ore sinter plants. In the present study, an approach was proposed and the effectiveness of the proposed approach was assessed by examining the resultant removal efficiencies for all installed APCDs.

2. Theoretical background

The whole study was conducted in an iron ore sinter plant (raw mixtures feeding rate = $\sim$1000 t h^{-1}) installed with two APCDs, including an EP and followed by a SCR (V_2O_5–WO_3–TiO_2 system). Flue gas samples were collected from three selected sites, including the EP inlet, EP outlet and SCR outlet (i.e., at the stack area). Fig. 1 shows the air stream diagram, and Table 1 shows the basic information of the flue gas obtained from the above three selected sites. Since the all measured temperatures were consistently less than 200 °C indicating that the reformation of PCDD/Fs via the de novo syntheses might not be possible [18,19]. In addition, the particulate matter collected on the collection plates of EP is periodically removed by vibrator or rapper and transferred to EP ash hopper per every 5 s. The above short contact time suggest that the release of PCDD/Fs from the particle matter collected on EP to the flue gas (or the adsorption of PCDD/Fs of particle matter collected on EP from the flue gas) could be negligible. Therefore, it could be reasonably to assume that the PCDD/F contents containing in EP ashes ($C_{EP_{ash}}$; ng mg^{-1}) would be representative to those particle-phase PCDD/Fs for samples collected from any selected site. In the present study, the corrected PCDD/F concentration of the particle-phase (C'_p; ng Nm^{-3}) and gas-phase (C'_g; ng Nm^{-3}) for flue gases samples collected from any selected sampling site could be calculated as follows:

$$C'_p = \frac{C_{EP_{ash}} \times W_p}{V} \tag{1}$$

$$C'_g = \frac{C_g \times V + (C_p \times V - C_{EP_{ash}} \times W_p)}{V} \tag{2}$$

where V is the total sampling volume (Nm^3), W_p is the total weight of the collected particulate matter (mg), and C_g and C_p are the measured concentrations (ng Nm^{-3}) of the gas- and particle-phase PCDD/Fs for the collected flue gases sample, respectively.

3. Material and methods

3.1. Sampling strategy

For each selected sampling site, flue gas samples (n = 3) were collected by using a Graseby Anderson stack isokinetic sampling system. The sampling train is comparable to the U.S. EPA Modified Method 5, in which the particle- and gas-phase PCDD/Fs were collected by a glass fiber filter (Whatman-EPM 2000

110 mm) and an XAD-2 sorbent module, respectively. Prior to sampling, XAD-2 resin was spiked with PCDD/F surrogate standards prelabeled with isotopes, including $^{37}Cl_4$-2,3,7,8-TeCDD, $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, $^{13}C_{12}$-2,3,4,7,8-PeCDF, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF, and $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF. The mean volumes of flue gas sampled from the EP inlet, EP outlet and SCR outlet were 1.01, 2.28, and 3.10 Nm^3, respectively. In addition, EP ash samples were gathered simultaneously with the flue gas sampling. In order to obtain representative ash samples, ashes were collected every 30 min throughout the flue gas sampling to gain a total of about 100 g. The collected ashes were well-mixed. A total of 5 g ash of each collected ash sample was used for further PCDD/Fs analysis.

3.2. PCDD/Fs analysis

Analysis of PCDD/Fs for all collected flue gas samples and ash samples followed the U.S. EPA Modified Method 23 by an accredited laboratory in Taiwan. Seventeen PCDD/F congeners were analyzed. For each collected sample, it was first extracted for 24 h, and then the extract was concentrated, treated with concentrated sulfuric acid, and then followed by a series of sample cleanup and fractionation procedures. The eluate was concentrated to 1 mL, transferred to a vial, and then further concentrated to near dryness by using a nitrogen stream. PCDD/Fs were analyzed using a high-resolution gas chromatography (HP 6970)/high-resolution mass spectrometry (HRGC/HRMS) with a DB-5 capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific, CA, USA). Injections were done using the splitless mode with a column oven temperature program of 150 °C, 30 °C/min to 220 °C (5 min), 1.5 °C/min to 240 °C (5 min), than 15 °C/min to 310 °C (20 min). Injector and detector temperature were 250 °C and 310 °C, respectively. Helium was used as the carrier gas (1.2 mL min^{-1}). The HRMS (Micromass Autospec Ultimate) was equipped with a positive electron impact (EI+) source. The electron energy and source temperature were specified at 35 eV and 250 °C, respectively. The analyzer mode of the selected ion monitoring (SIM) was used with a resolution of 10,000.

Analysis of the serial dilution of PCDD/F standards showed that the method detection limits (MDL) of HRGC/HRMS was 0.299 – 3.26 pg. PCDD/F recovery efficiencies were determined by processing a solution containing with known PCDD/F concentrations through the same experimental procedure used for the samples. The recovery efficiency of PCDD/Fs varied from 75.3% to 103% with an average of 91.5%. The mean relative standard deviation (RSD) (%) of recovery efficiencies was 17.1% (range 16.1 − 21.5%). Blanks were analyzed using the same procedures as that of the recovery-efficiency tests about without adding the known standard solution before extraction. Analysis of blanks showed no significant contamination.

3.3. Data analysis

Concentrations of gas- and particle-phase PCDD/Fs (C_g and C_p), and total PCDD/Fs (C_t; defined as the sum of C_g and C_p) for samples obtained from the three selected sampling sites were determined. In addition, the PCDD and PCDF concentrations ($C_{t\text{-PCDD}}$ and $C_{t\text{-PCDF}}$) in C_t were also determined in order to know its composition. To better describe both environmental and health impacts arising from PCDD/F emissions, the international toxic equivalent quantity (I-TEQ) was also used to characterize the measured C_t. The carcinogenic potency of the total I-TEQ for each measured C_p was determined as the sum of I-TEQs of the 17 PCDD/Fs congeners ($C_{t\text{-I-TEQ}}$, ng I-TEQ Nm^{-3}).

The corrected PCDD/F concentrations of the particle-phase (C'_p) and gas-phase (C'_g) were calculated using Eqs. (1) and (2), respectively. The above results were used to calculate the removal

Table 1
The characteristics of the flue gases at the EP inlet, EP outlet and SCR outlet.

Condition	EP inlet (mean ± SD)	EP outlet (mean ± SD)	SCR outlet (mean ± SD)
O_2 (%)	13.7 ± 0.1	13.8 ± 0.1	13.8 ± 0.1
CO_2 (%)	7.8 ± 0.1	7.7 ± 0.1	7.9 ± 0.1
Temperature (°C)	125 ± 10	117 ± 1	173 ± 1
Moisture content (%)	4.94	5.10	15.6
Speed of flue gas (m s^{-1})	15 ± 1	17 ± 0.1	18 ± 0.1
Particulate matter (PM) concentration (mg Nm^{-3})	1034 ± 212	23.8 ± 9.2	10.8 ± 7.0

efficiencies of PCDD/Fs (including both gas- and particle-phase PCDD/Fs) for the installed EP and SCR, respectively.

4. Results and discussion

4.1. Measured PCDD/F concentrations and their characteristics

Table 2 shows the concentrations of C_g, C_p, C_{t-PCDD}, C_{t-PCDF}, C_t, and $C_{t-I-TEQ}$ for samples collected from the EP inlet, EP outlet and SCR outlet. For samples collected from the EP inlet, C_p was higher than that of C_g $C_{t-PCDFs}$ were higher than that of $C_{t-PCDDs}$ with a mean $C_{t-PCDFs}/C_{t-PCDDs}$ ratio 8.20. For the EP outlet, C_p was quite similar to that of C_g $C_{t-PCDFs}$ was 8.51 times in magnitude higher than that of $C_{t-PCDDs}$. The mean C_t and $C_{t-I-TEQ}$ were 7.08 ng Nm^{-3} and 1.07 ng I-TEQ Nm^{-3}, respectively. For the SCR outlet, ~78.7% of C_t was contributed mostly by the gas-phase PCDD/Fs. The $C_{t-PCDFs}/C_{t-PCDDs}$ ratio was 5.34. The mean C_t and $C_{t-I-TEQ}$ were 2.70 ng Nm^{-3} and 0.357 ng I-TEQ Nm^{-3}, respectively. The above results are similar to those reported by Wang et al. [11], and Anderson and Fisher [20]. In principle, concentrations measured from the upstream sampling site should be higher than that of downstream sampling site due to the removal efficiencies of the installed APCDs. In the present study, C_p, C_{t-PCDD}, C_{t-PCDF}, C_t, and $C_{t-I-TEQ}$ did share the same trend as: EP inlet > EP outlet > SCR outlet. However, a totally different trend found in C_g (i.e., EP outlet > EP inlet > SCR outlet) suggests that the needs to correct the gas and particle partitioning for the collected flue gas samples.

Fig. 2 shows the congener profiles of the seventeen 2,3,7,8-substituted PCDD/Fs (mean and SD) obtained from the flue gas collected at the three designated sampling sites. The top three abundant congeners for samples collected from the EP inlet, presented in sequence, were 2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8-HpCDF, and 2,3,7,8-TeCDF, accounting for 15.5%, 14.9%, and 14.1% total PCDD/F emissions, respectively. For the EP outlet, 2,3,7,8-TeCDF, 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDF were the top three dominant congeners, accounting for 17.6%, 17.6% and 12.3% of the total PCDD/F emission, respectively. The above result is comparable to that obtained in the stack flue gases of sinter plant with EP but without SCR [8]. For the SCR outlet, OCDD, 2,3,7,8-TeCDF and 2,3,4,7,8-PeCDF were the three most abundant congeners, accounting for 17.6%, 13.5% and 12.9% emissions of total PCDD/Fs. The above results were similar to that obtained in the stack flue gases of sinter plant with EP and SCR [8].

Table 3 shows seventeen 2,3,7,8-substituted PCDD/Fs containing in EP$_{ash}$ and particles collected from the three designated sampling sites. For EP ash, the mean mass content for total PCDD/Fs was 4.74 ng/g. The PCDD/PCDF ratio was 0.219 indicating that EP ash was dominated by PCDFs. On the other hand, totally different results were found in our measured results. Here, the mean total PCDD/F contents and PCDD/PCDF ratios for the EP inlet, EP outlet and SCR outlet were 10.0, 419, and 128 ng/g, and 0.134, 0.145, and 0.253, respectively. Again, the above results confirm that measuring PCDD/F contents in particles for samples collected from the three designated sampling sites could be incorrect. Fig. 3 shows the content of the seventeen 2,3,7,8-substituted PCDD/Fs in EP$_{ash}$ and particles collected from the three designated sampling sites. For EP$_{ash}$, the top three abundant congeners

were 1,2,3,4,6,7,8-HpCDF, OCDD and 2,3,4,7,8-PeCDF. But different top three abundant congeners can be found in the EP inlet (1,2,3,4,6,7,8-HpCDF, 2,3,4,7,8-PeCDF, and 1,2,3,4,7,8-HxCDF), the EP outlet (1,2,3,4,6,7,8-HpCDF, 2,3,4,7,8-PeCDF, and 1,2,3,4,7,8-HxCDF), and the SCR outlet (1,2,3,4,6,7,8-HpCDF, 2,3,4,7,8-PeCDF,
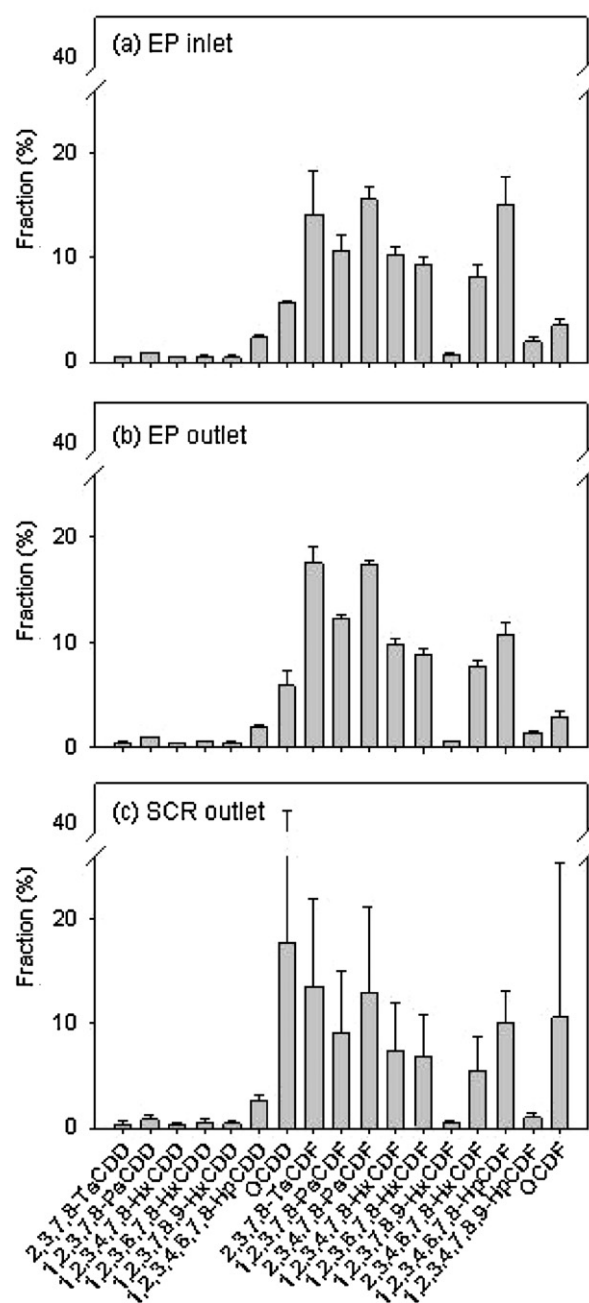

Fig. 2. The congener profiles of PCDD/Fs in the flue gases for samples collected from the EP inlet, EP outlet and SCR outlet (fraction of total PCDD/F mass concentration).

Table 2
The measured concentrations (mean ± SD) of C_g, C_p, C_t, $C_{t\text{-PCDD}}$, $C_{t\text{-PCDF}}$, and $C_{t\text{-I-TEQ}}$ for samples collected from the EP inlet, EP outlet and SCR outlet and their corresponding mean removal efficiencies for EP and SCR.

Type of data	Type of concentration	EP inlet (ng Nm^{-3})	Removal efficiency of EP (%)	EP outlet (ng Nm^{-3})	Removal efficiency of SCR (%)	SCR outlet (ng Nm^{-3})
Measured data	C_g	2.22 ± 1.20	−58.1	3.51 ± 0.709	39.4	2.12 ± 1.57
	C_p	10.1 ± 2.39	64.3	3.57 ± 1.36	83.9	0.575 ± 0.709
	C_t	12.3 ± 1.62	42.4	7.08 ± 2.07	62.6	2.70 ± 2.26
	$C_{t\text{-PCDD}}$	1.33 ± 0.152	44.0	0.745 ± 0.147	43.0	0.425 ± 0.284
	$C_{t\text{-PCDF}}$	10.9 ± 1.47	41.8	6.34 ± 1.93	64.2	2.27 ± 2.29
	$C_{t\text{-I-TEQ}}$	1.69 ± 0.239	36.9	1.07 ± 0.320	66.4	0.357 ± 0.407

Table 3
Contents (mean ± SD) of seventeen 2,3,7,8-substituted PCDD/Fs in EP$_{ash}$ and particle collected from the three sampling sites.

Samples	Content (ng g^{-1})			
	PCDD/Fs	PCDFs	PCDDs	PCDF/PCDD
EP$_{ash}$	4.74 ± 0.591	3.89 ± 0.483	0.850 ± 0.115	4.58
EP inlet	10.0 ± 2.83	8.84 ± 2.54	1.18 ± 0.291	7.49
EP outlet	419 ± 298	366 ± 263	53.2 ± 35.0	6.88
SCR outlet	128 ± 91.3	108 ± 87.1	19.9 ± 5.06	5.43

and 2,3,7,8-TeCDF). The above results further support the measured data might not reflect the true gas and particle partitioning of PCDD/F congeners of the collected flue gas samples.

4.2. The removal efficiencies of PCDD/Fs for the installed EP and SCR based on the measured data

Table 2 also shows the removal efficiencies of C_g, C_p, $C_{t\text{-PCDD}}$, $C_{t\text{-PCDF}}$, C_t, and $C_{t\text{-I-TEQ}}$ for the installed EP and SCR based on measured data. For EP, the resultant average removal efficiencies were −58.1%, 64.3%, 44.0%, 41.8%, 42.1%, and 36.9%, respectively. In principle, EP is used for the removal of particulate matters from the flue gas. Its removal efficiency is usually greater than 90% for all particle bound PCDD/Fs congeners [22]. Obviously, the above value was much higher than that found in the present study (i.e., 64.3%). In addition, it should be noted that a quite unreasonable removal efficiency for the gas-phase PCDD/Fs was obtained from the present study (i.e., −58.1%). The above negative result suggests that part of PCDD/Fs of particle-phase could be released and become gas-phase during sampling.

For SCR, the average removal efficiencies of C_g, C_p, $C_{t\text{-PCDD}}$, $C_{t\text{-PCDF}}$, C_t, and $C_{t\text{-I-TEQ}}$ were 39.4%, 83.9%, 43.0%, 64.1%, 62.6%, and 66.4%, respectively. To date, SCR units have been widely used for the controls of NO$_x$ and PCDD/Fs simultaneously in various combustion processes. Usually, the removal efficiency for gas-phase PCDD/Fs in the flue gas is greater than 95% [23,24]. However, unreasonably removal efficiencies were found in the present study for the gas-phase PCDD/Fs (39.4%) and particle-phase PCDD/Fs (83.9%). The above results further confirm our previous inference (i.e., part of particle-phase PCDD/Fs could be released during sampling and were converted to gas-phase PCDD/Fs).

In this study, the re-formation of PCDD/Fs (due to de novo synthesis) might not be possible at three designated sampling sites

because the measured flue gas temperatures were consistently below 200 °C [18,19] (see Table 1). Therefore, the removal efficiencies of EP and SCR in both gas-phase PCDD/Fs and particle-phase PCDD/Fs found in the present study could be doubtful. In other words, correcting the partitions of gas/particle phase PCDD/Fs for PCDD/F samples collected from the three selected sampling sites are necessary to have a better understanding the removal efficiencies of the installed APCDs.

4.3. Correcting the partitions of gas/particle phase PCDD/Fs

Table 4 shows the concentrations of PCDD/Fs (i.e., C'_g, C'_p, $C'_{t\text{-PCDD}}$, $C'_{t\text{-PCDF}}$, C'_t, and $C'_{t\text{-I-TEQ}}$) after being corrected by our proposed approach. For the EP inlet, C'_g was higher than that of C'_p. $C'_{t\text{-PCDF}}$ was higher than that of $C'_{t\text{-PCDD}}$ with a $C'_{t\text{-PCDD}}/C'_{t\text{-PCDF}}$ ratio 0.122. The mean C'_t and $C'_{t\text{-I-TEQ}}$ were 12.3 ng Nm^{-3} and 1.69 ng Nm^{-3}, respectively. For the EP outlet, C'_g was much higher than that of C'_p. $C'_{t\text{-PCDF}}$ was 8.51 times in magnitude higher than that of $C_{t\text{-PCDDs}}$. The mean C_t and $C_{t\text{-I-TEQ}}$ were 7.08 ng Nm^{-3} and 1.07 ng I-TEQ Nm^{-3}, respectively. For the SCR outlet, ~98.2% of C'_t was mainly contributed by the gas-phase PCDD/Fs. The $C_{t\text{-PCDFs}}/C_{t\text{-PCDDs}}$ ratio was 5.34. The mean C_t and $C_{t\text{-I-TEQ}}$ were 2.70 ng Nm^{-3} and 0.357 ng I-TEQ Nm^{-3}, respectively.

Fig. 4 shows the ratios of the C_p to C_t for samples collected from three designated sampling sites (denoted as the measured data), and their corresponding corrected values based on the approach proposed by the present study. For all measured data, the ratios of the gas-phase PCDD/Fs to total PCDD/Fs consistently decreased as the number of substituted chlorine atoms in both PCDD and PCDF homologues increased for the sampling data. The same trend can also be seen in the corrected data. The above results might because the increase in chlorination levels would result in the decrease in

Table 4
The corrected concentrations (mean ± SD) of C'_g, C'_p, C'_t, $C'_{t\text{-PCDD}}$, $C'_{t\text{-PCDF}}$, and $C'_{t\text{-I-TEQ}}$ of the EP inlet, EP outlet and SCR outlet and their corresponding mean removal efficiencies for EP and SCR.

| Type of data	Type of concentration	EP inlet (ng Nm^{-3})	Removal efficiency of EP (%)	EP outlet (ng Nm^{-3})	Removal efficiency of SCR (%)	SCR outlet (ng Nm^{-3})
Corrected data	C'_g	7.33 ± 1.01	4.91	6.97 ± 2.07	62.0	2.65 ± 2.26
	C'_p	4.95 ± 1.39	97.7	0.113 ± 0.0141	54.7	0.0512 ± 0.00638
	C'_t	12.3 ± 1.62	42.4	7.08 ± 2.07	61.9	2.70 ± 2.26
	$C'_{t\text{-PCDD}}$	1.33 ± 0.150	44.0	0.745 ± 0.147	43.0	0.425 ± 0.284
	$C'_{t\text{-PCDF}}$	10.9 ± 1.47	41.8	6.34 ± 1.93	64.2	2.27 ± 2.29
	$C'_{t\text{-I-TEQ}}$	1.69 ± 0.239	36.9	1.07 ± 0.320	66.4	0.357 ± 0.407
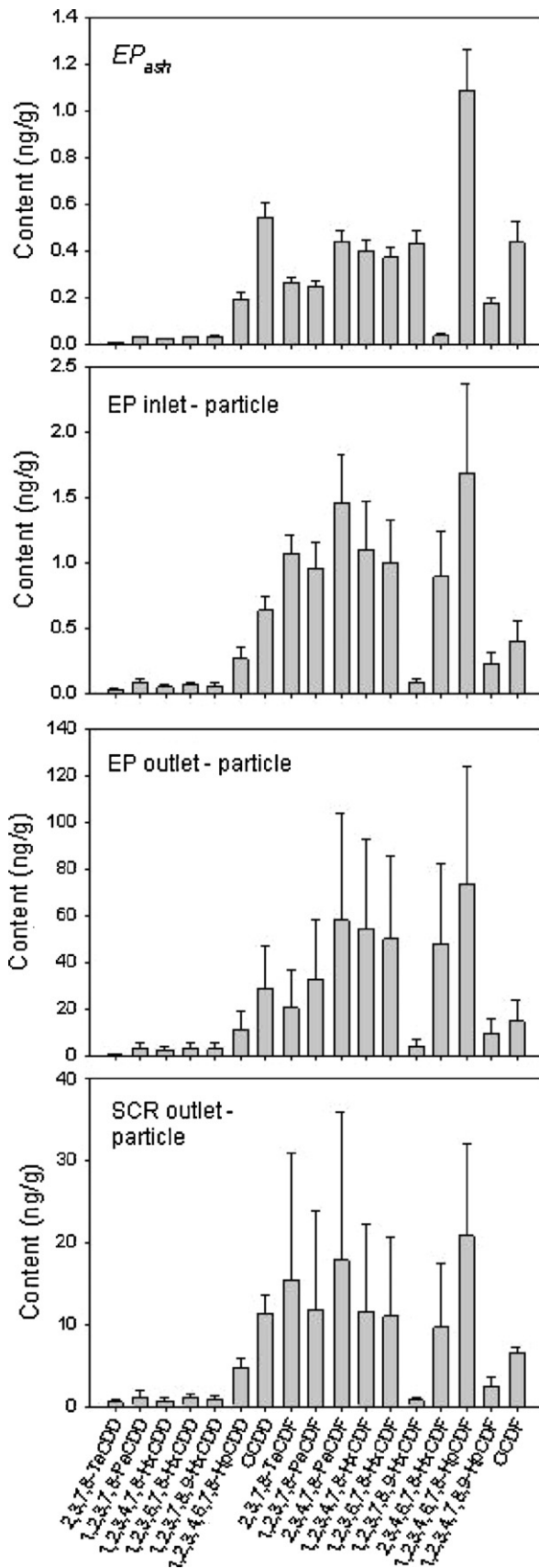
Fig. 3. The mean contents of 17 PCDD/F congeners containing in EP$_{ash}$, and particles collected from the flue gas of the EP inlet, EP outlet and SCR outlet.
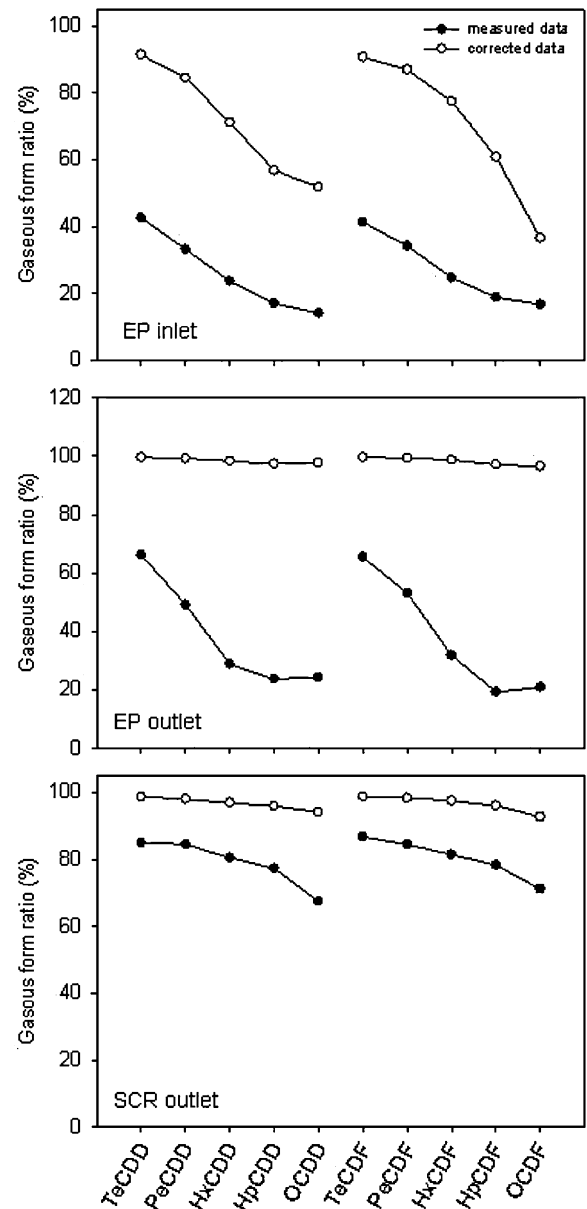

Fig. 4. Ratios of gas-phase PCDD/Fs to the total PCDD/Fs for samples collected at the EP inlet, EP outlet and SCR outlet calculated based on measured data and corrected data.

vapor pressures of PCDD/F homologues. On the other hand, the ratios obtained from the measured data were lower than that of the corrected data indicating that gas-phase PCDD/Fs were absorbed onto the particulate matter collected on the filter during sampling. For the SCR outlet, the ratios obtained from the measured data were much closer to that of corrected data, comparing with the corresponding results obtained from both the EP inlet and EP outlet. The above result might because the decrease in the concentrations in both particulate matter and gas-phase PCDD/Fs of the flue gas after passing through the EP and SCR. As a result, the effect of sampling artifact on the partitions of gas/particle phase PCDD/Fs in the flue gas became not so significant for the SCR outlet.

4.4. The removal efficiencies of PCDD/Fs for EP and SCR based on corrected data

As shown in Table 4, the mean corrected removal efficiencies of C_g' and C_p' for EP have been improved respectively as 4.91% and 97.7%

which are more reasonable than the corresponding uncorrected values (i.e., −58.1% and 64.3%, Table 2). For SCR, the mean corrected removal efficiencies of C'_g and C'_p were 62.0% and 54.7%, respectively (Table 4). In comparison with the corresponding uncorrected values (i.e., 39.4% and 83.9%, Table 2), the corrected values obviously become much acceptable. The above results support that the correcting approach proposed by the present study might be applicable for correcting the gas/particle partitioning of PCDD/F congeners for flue gas samples collected from the iron ore sinter plant.

However, it should note that the developed approach only good for all collected samples were free from de novo synthesis of PCDD/Fs. If the flue gas temperatures could be higher than 250 °C, the developed approach should be used with caution. In addition, sizes of particles collected from the EP inlet, EP outlet and SCR outlet could be different from that of EP ashes. Therefore, their PCDD/F contents could be varied from that of EP ashes even de novo synthesis of PCDD/Fs was not possible. In the present study, our assumption (i.e., the PCDD/F contents containing in EP ashes would be representative to those particle-phase PCDD/Fs for samples collected from any selected site) might result in the corrected removal efficiencies of PCDD/Fs for EP and SCR somewhat different from the corresponding true values. Considering directly measuring particle-phase PCDD/Fs for samples collected from any selected site is still impossible at this stage, the methodology proposed by the present study, at least, can provide a convenient way for better estimations.

References

[1] A. Schecter, L. Birnbaum, J.J. Ryan, J.D. Constable, Dioxins: an overview, Environ. Res. 101 (2006) 419–428.
[2] K. Olie, P.L. Vermeulen, O. Hutzinger, Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in The Netherlands, Chemosphere 6 (1977) 455–459.
[3] L.C. Wang, G.P. Chang-Chien, Characterizing the emissions of polybrominated dibenzo-*p*-dioxins and dibenzofurans from municipal and industrial waste incinerators, Environ. Sci. Technol. 41 (2007) 1159–1165.
[4] L.F. Lin, W.J. Lee, H.W. Li, M.S. Wang, G.P. Chang-Chien, Characterization and inventory of PCDD/F emissions from coal-fired power plants and other sources in Taiwan, Chemosphere 68 (2007) 1642–1649.
[5] L.C. Wang, W.J. Lee, W.S. Lee, G.P. Chang-Chien, Emission estimation and congener-specific characterization of polybrominated diphenyl ethers from various stationary and mobile sources, Environ. Pollut. 158 (2010) 3108–3115.
[6] R.E. Alcock, R. Gemmill, K.C. Jones, Improvements to the UK PCDD/F and PCB atmospheric emission inventory following an emissions measurement programme, Chemosphere 38 (1999) 759–770.
[7] W.S. Lee, G.P. Chang-Chien, L.C. Wang, W.J. Lee, K.Y. Wu, P.J. Tsai, Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from stack flue gases of electric arc furnaces and secondary aluminum smelters, J. Air Waste Manag. Assoc. 55 (2005) 219–226.
[8] L.C. Wang, Y.F. Wang, H.C. Hsi, G.P. Chang-Chien, Characterizing the emissions of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) from metallurgical processes, Environ. Sci. Technol. 44 (2010) 1240–1246.
[9] P.S. Kulkarni, J.G. Crespo, C.A.M. Afonso, Dioxins sources and current remediation technologies – a review, Environ. Int. 34 (2008) 139–153.
[10] E. Guerriero, A. Guarnieri, S. Mosca, G. Rossetti, M. Rotatori, PCDD/Fs removal efficiency by electrostatic precipitator and wetfine scrubber in an iron ore sintering plant, J. Hazard. Mater. 172 (2009) 1498–1504.
[11] L.C. Wang, W.J. Lee, P.J. Tsai, W.S. Lee, G.P. Chang-Chien, Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from stack flue gases of sinter plants, Chemosphere 50 (2003) 1123–1129.
[12] A. Karademir, M. Bakoglu, F. Taspinar, S. Ayberk, Removal of PCDD/Fs from flue gas by a fixed-bed activated carbon filter in a hazardous waste incinerator, Environ. Sci. Technol. 38 (2004) 1201–1207.
[13] H.W. Li, L.C. Wang, C.C. Chen, X.Y. Yang, G.P. Chang-Chien, E.M.Y. Wu, Influence of memory effect caused by aged bag filters on the stack PCDD/F emissions, J. Hazard. Mater. 185 (2011) 1148–1155.
[14] U.S. EPA Modified Method 23: Determination of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans from stationary sources. In Code of federal regulations, U.S. Environmental Protection Agency, Washington, D.C., 2001, Title 40, Part 60, Appendix A.
[15] European Standard EN 1948: Stationary source emissions – determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 1: Sampling of PCDDs/PCDFs, Part 2: Extraction and clean-up of PCDDs/PCDFs, and Part 3: Identification and quantification of PCDDs/PCDFs. European Committee for Standardization: Brussels, Belgium, 2006.
[16] A. Cavallaro, L. Luciani, G. Ceroni, I. Rocchi, G. Invernizzi, A. Gorni, Summary of results of PCDD analyses from incinerator effluents, Chemosphere 11 (1982) 859–886.
[17] K.H. Chi, M.B. Chang, Evaluation of PCDD/F congener partition in vapor/solid phases of waste incinerator flue gases, Environ. Sci. Technol. 39 (2005) 8023–8031.
[18] R. Addink, D. Drijver, K. Olie, Formation of polychlorinated dibenzo-*p*-dioxins/dibenzofurans in the carbon/fly ash system, Chemosphere 23 (1991) 1205–1211.
[19] M. Lasagni, E. Collina, M. Tettamanti, D. Pitea, Kinetics of MSWI fly ash thermal degradation. 1. Empirical rate equation for native carbon gasification, Environ. Sci. Technol. 34 (2000) 130–136.
[20] D.R. Anderson, R. Fisher, Sources of dioxins in the United Kingdom: the steel industry and other sources, Chemosphere 46 (2002) 371–381.
[22] A. Karademir, M. Bakoglu, S. Ayberk, PCDD/F removal efficiencies of electrostatic precipitator and wet scrubbers in izaydas hazardous waste incinerator, Fresenius Environ. Bull. 12 (2003) 1228–1232.
[23] R. Weber, T. Sakurai, H. Hagenmaier, Low temperature decomposition of PCDD/PCDF, chlorobenzenes and PAHs by TiO$_2$-based V$_2$O$_5$-WO$_3$ catalysts, Appl. Catal. B: Environ. 20 (1999) 249–256.
[24] P. Liljelind, J. Unsworth, O. Maaskant, S. Marklund, Removal of dioxins and related aromatic hydrocarbons from flue gas streams by adsorption and catalytic destruction, Chemosphere 42 (2001) 615–623.