



Polychlorinated dibenzo-*p*-dioxins/dibenzofuran mass distribution in both start-up and normal condition in the whole municipal solid waste incinerator

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ABSTRACT

Although many researches focused on the polychlorinated dibenzo-*p*-dioxins/dibenzofuran (PCDD/F) emissions from stack, in the bottom ash and in the surrounding environment, researches focused on PCDD/F mass distributions in the whole incineration plant have seldom been addressed. This study determined PCDD/F emissions in the whole plant. A high-resolution gas chromatograph/high-resolution mass spectrometer was utilized for analyzing 17 PCDD/F species. Experimental results displayed that PCDD/Fs were formed during fly ash from super heater (SH), economizer (EC), semi-dryer absorber (SDA) and fabric filter (FF) was transferred to fly ash pit. Mass distribution ratios of PCDD/Fs in g I-TEQ (Toxicity Equivalency Quantity) per week from stack, SH, EC, SDA, FF, generation and bottom residue (BR) in start-up operations were 14.6%, 0.1%, 8.3%, 1.0%, 41.7%, 33.4% and 0.9%, respectively. Above results indicated that main PCDD/F source in the MSWI was from fly ash. However, the fly ash is easily controlled and PCDD/F emitted from stack flue gases will be difficult to be handled. Therefore, we should pay more attention on PCDD/F emission from flue gases especially from start-up procedure. Besides, fly ash should be controlled by sodium hypophosphite before being landfilled. MSWI did require further detoxification treatments for the solid residues and flue gases.

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1. Introduction

Waste-to-energy incineration was considered as a mainstream strategy for municipal solid waste management due to the lack of landfill spaces and the associated risks to water and soil. Besides, a landfill also gives risk to air because gas pollutants are formed by the reaction among wastes and then emit from the landfill. Approximately 85% of the waste volume and 60–75% of the mass of municipal solid waste incineration (MSWI) could be reduced [1,2]. In addition, MSWI could be located in the proximity of residential areas and generate electricity and/or heat from the energy content of municipal solid waste. Nevertheless, there are still negative impacts on the environment from MSWIs. Since polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) was first found in flue gases and in the fly ash of municipal solid waste incinerators (MSWIs) [3], extensive examinations on PCDD/Fs have been conducted due to their acute toxicity and the negative impacts on human health. Recent discussions of the possible mechanisms of PCDD/F formation have focused on two hypotheses: (1) Stieglitz et al. have suggested a de novo synthesis of PCDD/F from active

carbon particulates by gas–solid and solid–solid reactions with air, moisture, and inorganic chlorides, catalyzed by copper ions [4–6]. (2) Karasek and Dickson [7,8] have proposed that PCDD/F are formed from chloroaromatic precursors such as polychlorophenols and polychlorobenzenes by reactions which have been shown to occur by heterogeneous catalysis on the surface of fly ash particles at 250–400 °C.

There are many researches focused on the PCDD/F emissions from stack, in the bottom ash and in the surrounding environment [9–12]. However, there were only few researches focused on PCDD/F mass distributions in the whole plant have been reported. In 1992, Johnke concluded that the total PCDD/F emission factor was 211.6 µg I-TEQ ton-waste⁻¹ and the mass distribution of PCDD/Fs in the bottom ash, slag water, boiler ash, ESP (electrostatic precipitators) ash, scrubber water, filter cake and stack gas from the MSWI were 4.3%, 1.5%, 0.7%, 56.7%, 2.4%, 22.7% and 11.8%, respectively. Moreover, net 121.6 µg I-TEQ per waste was produced due to the incineration process [13]. Similar result was found. Giugliano et al. concluded that the total PCDD/F emission factor was 10.44 µg I-TEQ ton-waste⁻¹ and the mass distribution of PCDD/Fs in the slag, boiler ash, fabric filter ash, sludge and stack gas were 72.6%, 5.6%, 18.6%, 1.5% and 1.7%, respectively [14]. Recently, several studies have focused on the high PCDD/F emission during the start-up of incinerators [15–24]. In Taiwan, the elevated PCDD/F emissions

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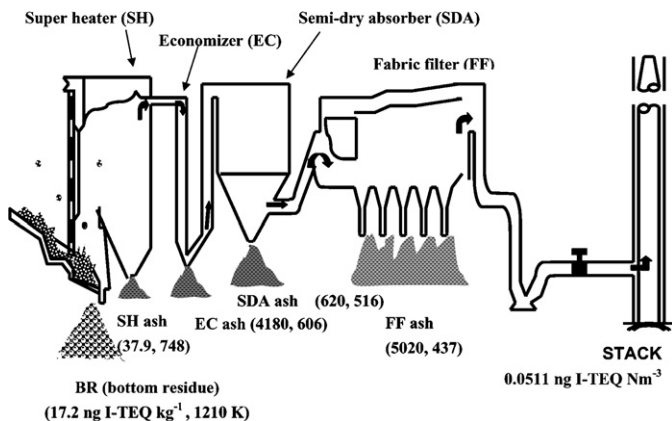


Fig. 1. The flow diagram of the KS MSWI.

of the MSWI during start-up could reach $96.9 \text{ ng I-TEQ Nm}^{-3}$ and still maintained a high PCDD/F emission (40 times higher than the Taiwan emission limit) even 18 h after the injection of activated carbon, indicating the memory effect. Moreover, the PCDD/F emission quantity from stacks resulted from the start-up was 2.35 times larger than that of a whole year's normal operations [15]. Therefore, mass distribution of PCDD/Fs extended to the MSWI under the start-up operation condition should be investigated.

In this study, the PCDD/F contents in the output residues and PCDD/F concentration in the stack gas from the MSWI were measured. Secondly, the PCDD/F congener profiles were compared and discussed. Finally, emission factor and mass distribution ratios of PCDD/Fs in the MSWI under the start-up operation condition were assessed.

2. Experimental methods

2.1. Basic information about the selected MSWI

The stack samples and ash samples were collected from KS MSWI, located in southern Taiwan. There are four incinerators, each of which includes own heat recovery systems (350°C), selective non-catalytic reduction, dry scrubber ($250\text{--}230^\circ\text{C}$), activated carbon injection, fabric filter ($180\text{--}160^\circ\text{C}$) and stack. The treatment processes are the most common ones in Taiwan, which are recognized as the most effective technique for PCDD/F emission control. Operation of the KS MSWI began in 2000 and its total capacity is 1800 ton/day with lower heating value of $2500 \text{ kcal/kg-waste}$. The flow diagram of the KS MSWI was shown in Fig. 1.

2.2. Sample collection

The PCDD/F samples were collected isokinetically from the stack flue gas of the selected incinerators according to US EPA modified Method 23. The sampling train adopted in this study is comparable with that specified by US EPA Modified Method 5. Prior to sampling, XAD-2 resin was spiked with PCDD/F surrogate standards pre-labeled with isotopes, including $^{37}\text{C}_{14}\text{-}2,3,7,8\text{-TCDD}$ (tetrachlorodibenzo-*p*-dioxin), $^{13}\text{C}_{12}\text{-}1,2,3,4,7,8\text{-HxCDD}$ (hexachlorinated dibenzo-*p*-dioxin), $^{13}\text{C}_{12}\text{-}2,3,4,7,8\text{-PeCDF}$ (pentachlorinated dibenzofuran), $^{13}\text{C}_{12}\text{-}1,2,3,4,7,8\text{-HxCDF}$ (hexachlorinated dibenzofuran) and $^{13}\text{C}_{12}\text{-}1,2,3,4,7,8,9\text{-HpCDF}$ (heptachlorinated dibenzofuran). The recoveries of PCDD/F surrogate standards were 95–117%, and met the criteria within 70–130%. To ensure the free contamination of the collected samples, one trip blank and one field blank were also taken during the field sampling was conducted. Details are similar to that given in our previous work [19].

There are four incinerators at the KT MSWI. Therefore, the sampled incinerator was selected by random sampling for stack samples and ash samples. To obtain good representative ash samples, sampling was done according to regulation specified in ordinance NIEA R118.02B and also referred to Minnesota regulation 7035.2910 in US. In the sampling period, ash was collected directly from super heater (SH), economizer (EC), semi-dry absorber (SDA), fabric filter (FF) and bottom residue (BR). Above ash was weighed in order to calculate ash amounts. Then ash from SH, EC, SDA and FF was put back to transfer process and sent to fly ash pit. Ash from SH, EC, SDA and FF was mixed well in fly ash pit and the mixed ash was named FAP (fly ash pit) ash. Every 12 h for 3 days, about 200 g of samples were collected from the SH, EC, SDA, FF, FAP and BR for PCDD/Fs analysis. As a result, approximately 1.2 kg of samples was collected from the incinerator. The collected samples should be stored in properly sealed containers to eliminate the effects from air circulation and water. Appropriate labels should be used for the delivery of samples. A sampling report should also be supplied for the samples. Except for samples that were in solid state, all samples must be stored in the refrigerator with temperature maintained at 4 ± 1 . The ferrous and non-ferrous metals, glass and stone were removed and after well-mixing and diagonal sectioning, 600 g of different ash was retained. The samples were then spread out on a clean aluminum foil and naturally dried. The samples were then mixed thoroughly for the determination of PCDD/F analysis.

2.3. Analyses of PCDD/Fs

Analyses of stack flue gas followed the US EPA modified Method 23. Analyses of PCDD/Fs in the ash samples followed the US EPA modified method 1613A. All chemical analyses were carried out by the Super Micro Mass Research and Technology Center at Cheng Shiu University—the accredited laboratory in Taiwan for PCDD/F analyses. Prior to analysis, each collected sample was spiked with a known amount of the $^{13}\text{C}_{12}$ -labeled internal standard to the extraction thimble. Add toluene to fill the reservoir approximately 2/3 full. Adjust the heat source to cause the extractor to cycle 3 times/h. After being extracted for 24 h, the extract was concentrated, treated with concentrated sulfuric acid, and then followed by a series of sample cleanup and fractionation procedures, including multilayer silica gel column, alumina column and activated carbon chromatography. The eluate was concentrated to approximately 1 mL and transferred to a vial. The concentrate was further concentrated to near dryness, using a stream of nitrogen. Immediately prior to analysis, the standard solution for recovery checking was added to the sample. The recoveries of PCDD/F internal standards for the tetra-through hexachlorinated homologues were between 71% and 95%, and met the criteria within 40–130%, while that for the hepta and octachlorinated homologues were between 57% and 106%, and met the criteria within 25–130%. A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used in the PCDD/F analyses. The HRGC (Hewlett Packard 6970 Series gas, CA, USA) was equipped with a DB-5MS fused silica capillary column ($L = 60 \text{ m}$, $ID = 0.25 \text{ mm}$, film thickness = $0.25 \mu\text{m}$) (J&W Scientific, CA, USA) and with a splitless injection. Helium was used as the carrier gas. The HRMS (Micromass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI+) source. The analyzer mode of the selected ion monitoring (SIM) was used with resolving power at 10,000. The electron energy and source temperature were at 35 eV and 250°C , respectively. Details of the analysis could be found in our previous work [10,20]. The toxic equivalent quantity of PCDD/Fs is given by $\text{I-TEQ} = \sum \text{Xi} \times \text{li}$, where I-TEQ denotes the international toxic equivalent quantity, Xi represents the concentration of PCDD/F congeners, and li is the

Table 1
PCDD/F concentration in the stack flue of the selected MSWI (ng Nm⁻³)

ng Nm ⁻³	Stack flue (n = 23)		
	Range	Mean	R.S.D. (%)
2,3,7,8-TeCDD	0.000775–0.00755	0.00259	61.5
1,2,3,7,8-PeCDD	0.00306–0.0178	0.00886	48.8
1,2,3,4,7,8-HxCDD	0.00397–0.0228	0.0109	50.8
1,2,3,6,7,8-HxCDD	0.0100–0.0661	0.0299	54.1
1,2,3,7,8,9-HxCDD	0.00544–0.0346	0.0155	51.2
1,2,3,4,6,7,8-HpCDD	0.0643–0.490	0.213	54.0
OCDD	0.034–0.919	0.340	64.7
2,3,7,8-TeCDF	0.00429–0.0584	0.0190	75.1
1,2,3,7,8-PeCDF	0.00722–0.0462	0.0222	51.1
2,3,4,7,8-PeCDF	0.0125–0.0859	0.0388	50.9
1,2,3,4,7,8-HxCDF	0.00943–0.0553	0.0306	45.6
1,2,3,6,7,8-HxCDF	0.0126–0.0655	0.0350	48.7
1,2,3,7,8,9-HxCDF	0.000596–0.0200	0.00446	90.2
2,3,4,6,7,8-HxCDF	0.0176–0.110	0.0516	49.7
1,2,3,4,6,7,8-HpCDF	0.0351–0.265	0.110	52.1
1,2,3,4,7,8,9-HpCDF	0.00785–0.0608	0.0240	64.1
OCDF	0.0208–0.317	0.0906	75.2
PCDDs	0.149–1.49	0.621	57.5
PCDFs	0.158–0.968	0.426	48.4
PCDDs/PCDFs	0.618–2.80	1.58	40.2
Total PCDD/Fs	0.337–2.19	1.05	48.8
PCDDs (ng I-TEQ Nm ⁻³)	0.00504–0.0267	0.0151	44.9
PCDFs (ng I-TEQ Nm ⁻³)	0.0120–0.0692	0.0360	46.4
PCDDs/PCDFs	0.302–0.629	0.448	23.3
Total PCDD/Fs (ng I-TEQ Nm ⁻³)	0.0171–0.0904	0.0511	44.4

R.S.D., relative standard deviation.

international toxic equivalent factor of each PCDD/F congener (I-TEF) [20].

3. Results and discussion

3.1. PCDD/F concentration and congener profile in the stacks of the selected MSWI

Twenty-three samples were collected from the stack flue gases of the MSWI in period of 2003–2006 under normal operation conditions for PCDD/F analysis. The PCDD/F concentration normalized to the dry flue gas conditions of 273 K and 11% O₂ in the stack flue of the selected MSWI was shown in Table 1. The range of total PCDD/F concentration was from 0.337 to 2.19 ng Nm⁻³. The averaged total PCDD/F concentration was 1.05 ng Nm⁻³ (relative standard deviation (R.S.D.) = 48.8%). The PCDDs/PCDFs ratio was 1.58 indicating that the main PCDD/Fs in the stack of the MSWI were PCDDs. For toxic equivalent, the range of total PCDD/F equivalent concentration was from 0.0171 to 0.0904 ng I-TEQ Nm⁻³. The averaged PCDD/F equivalent concentration was 0.0511 ng I-TEQ Nm⁻³ (R.S.D. = 23.3%) which was lower than regulation (0.1 ng I-TEQ Nm⁻³). The ratio of PCDD equivalent to PCDF equivalent was 0.448 indicating that the main toxic equivalent in the stack of the MSWI was PCDFs. PCDD/F congener profiles in the stack of the municipal waste incinerator were shown in Fig. 1. The mean five PCDD/Fs were OCDD (32.5%, 0.340 ng Nm⁻³), 1,2,3,4,6,7,8-HpCDD (20.3%, 0.213 ng Nm⁻³), 1,2,3,4,6,7,8-HpCDF (10.5%, 0.110 ng Nm⁻³), OCDF (8.65%, 0.0906 ng Nm⁻³) and 2,3,4,6,7,8-HxCDF (4.93%, 0.0516 ng Nm⁻³).

3.2. PCDD/F contents in different ash of the MSWI

Ash samples of the MSWI were sampled 15 times in period of 2003–2006 under normal operation conditions and a total 90 samples were collected for PCDD/Fs measurement. The PCDD/F contents in the samples were shown in Table 2. The averaged PCDD/F

contents for ash samples from the bottom residue, super heater, economizer, semi-dryer absorber, fabric filter and fly ash pit (FAP) were measured to be: 284 (R.S.D. = 49.2%), 544 (R.S.D. = 72.3%), 126,000 (R.S.D. = 109%), 16,900 (R.S.D. = 123%), 58,700 (R.S.D. = 84.4%) and 71,600 ng kg⁻¹ (R.S.D. = 65.5%), respectively; 17.2 (R.S.D. = 92.9%), 37.9 (R.S.D. = 60.3%), 4180 (R.S.D. = 72.5%), 620 (R.S.D. = 82.3%), 5020 (R.S.D. = 100%) and 6410 ng I-TEQ kg⁻¹ (R.S.D. = 125%), respectively. The ratios of toxic PCDDs/PCDFs in ash from BR, SH, EC, SDA, FF and FAP were 0.728, 0.509, 0.916, 0.712, 0.618 and 0.582, respectively. It could be seen that the ratio values were all less than 1.0. It indicated that the main toxic PCDD/Fs in ash from BR, SH, EC, SDA, FF and FAP were PCDFs. The PCDD/F contents was very low in the BR and SH because the temperature in super heater and combustion chamber were ~460 °C and 910 °C which is not within the favorable range for PCDD/F formation (250–400 °C). However, the PCDD/F contents in EC ash was much higher than that in BR and SH ash because the economizer was operating at ~335 °C, which is within the favorable range for PCDD/F formation. Therefore, the temperature of equipments should be avoided operating within the favorable range for PCDD/F formation (250–400 °C).

The PCDD/F contents decreased in the SDA, the averaged value observed was 620 ng I-TEQ kg⁻¹. In SDA, the temperature dropped quickly and calcium carbonate was added to the flue gas that lowered the PCDD/F content although SDA was operating at ~255 °C, which is still within the favorable range for PCDD/F formation (250–400 °C). The measured PCDD/F content in the FF ash was measured as 5020 ng I-TEQ kg⁻¹ and it showed a growing trend was observed. There were two effects resulted in the observed rising trend for PCDD/Fs. One was PCDD/Fs were captured by the active carbon in the FF even though the operation temperature of the FF was only ~165 °C. The other was the duration that fly ash stayed in the FF was also longer compared to other components in the incinerator. Finally, the PCDD/F content in the FAP, where the fly ash from the SH, EC, SDA and FF were collected, was 6410 ng I-TEQ kg⁻¹. Similar observations were reported. The PCDD/F content in solid waste mixture from electrostatic precipitator and fabric filter (8700 ng I-TEQ kg⁻¹) was higher than that in both fabric filter (790 ng I-TEQ kg⁻¹) and electrostatic precipitator (7870 ng I-TEQ kg⁻¹) [21]. Furthermore, PCDD/F content in ash almost increased along the flow path for the flue gas [14,22].

In Taiwan, based on hazardous waste regulations introduced on 14 December 1995, the upper limit for total PCDD/Fs is 1000 ng I-TEQ kg⁻¹, lower than that in Japan (3000 ng I-TEQ kg⁻¹). The regulation of PCDD/F contents in Taiwan was more restrictive. Thus, according to the present data, total PCDD/F content in ash from the EC, FF and FAP exceeded the legal limit. In Taiwan, the government policy for incineration residues advocates their reuse as road sub-bases or secondary building materials. Therefore, the transportation system for fly ash, transferred from different units to the FAP in the past, should be corrected. Ash with less than total PCDD/F limit, such as that from the SH, SDA and BR, can be collected and transferred to the FAP and reused. Ash exceeding total PCDD/F limit, such as that from the EC and FF, should be collected separately and be controlled by sodium hypophosphite [23] before being land-filled. Wang et al. concluded that the reductive dechlorination with 10% (w/w) sodium hypophosphite has shown high detoxification efficiencies of 99.4% and 99.3% at 350 °C and 450 °C, respectively, and as well as the dechlorination efficiencies about 98.7% [23].

3.3. PCDD/F congener profiles in different ash

PCDD/F congener profiles in different ash and stack flue from the municipal waste incinerator were shown in Fig. 2. In fly ash, the main five peaks were OCDD (156–63,200 ng kg⁻¹, 27.9–50.2%), 1,2,3,4,6,7,8-HpCDF (90.7–16,000 ng kg⁻¹, 12.7–16.7%), OCDF

Table 2
PCDD/F contents in different ashes of the MSWI (ng kg⁻¹)

ng g ⁻¹	BR (n = 15)		SH (n = 15)		EC (n = 15)	
	Mean	R.S.D. (%)	Mean	R.S.D. (%)	Mean	R.S.D. (%)
2,3,7,8-TeCDD	0.330	74.9	1.49	63.3	72.7	62.2
1,2,3,7,8-PeCDD	1.05	64.6	4.84	62.2	362	69.1
1,2,3,4,7,8-HxCDD	1.39	86.3	4.01	62.3	532	97.0
1,2,3,6,7,8-HxCDD	2.27	69.7	6.51	67.5	1300	110
1,2,3,7,8,9-HxCDD	1.88	64.0	5.20	63.8	908	103
1,2,3,4,6,7,8-HpCDD	27.3	87.5	50.0	77.1	17,100	114
OCDD	106	78.5	156	83.7	63,200	120
2,3,7,8-TeCDF	2.39	38.2	11.0	78.9	252	71.1
1,2,3,7,8-PeCDF	2.76	29.4	14.4	92.8	616	72.4
2,3,4,7,8-PeCDF	4.81	39.0	24.8	78.6	1110	80.1
1,2,3,4,7,8-HxCDF	5.66	33.4	21.0	84.9	1820	87.5
1,2,3,6,7,8-HxCDF	5.69	37.0	22.5	87.9	2080	90.0
1,2,3,7,8,9-HxCDF	1.20	93.4	2.41	75.9	360	147
2,3,4,6,7,8-HxCDF	8.50	55.3	28.9	67.0	3310	96.0
1,2,3,4,6,7,8-HpCDF	38.3	42.7	90.7	72.1	16,000	97.4
1,2,3,4,7,8,9-HpCDF	5.68	59.8	10.2	60.4	1910	94.6
OCDF	68.5	59.2	90.0	135	15,000	97.7
PCDDs	141	78.4	228	78.3	83,400	118
PCDFs	143	43.3	316	76.3	42,400	94.8
PCDDs/PCDFs	992	74.0	841	42.7	1850	25.7
Total PCDD/Fs	284	49.2	544	72.3	126,000	109
PCDDs (ng I-TEQ g ⁻¹)	8.66	137	10.1	66.3	2020	94.2
PCDFs (ng I-TEQ g ⁻¹)	8.57	54.2	27.8	67.7	2150	65.4
PCDDs/PCDFs	728	93.7	509	98.2	916	63.4
Total PCDD/Fs (ng I-TEQ g ⁻¹)	17.2	92.9	37.9	60.3	4180	72.5
ng g ⁻¹	SDA (n = 15)		FF (n = 15)		FAP (n = 15)	
	Mean	R.S.D. (%)	Mean	R.S.D. (%)	Mean	R.S.D. (%)
2,3,7,8-TeCDD	12.9	58.1	149	158	124	94.1
1,2,3,7,8-PeCDD	58.5	74.0	577	150	691	111
1,2,3,4,7,8-HxCDD	65.9	102	524	133	893	130
1,2,3,6,7,8-HxCDD	146	142	1190	115	1650	118
1,2,3,7,8,9-HxCDD	122	142	863	113	1210	109
1,2,3,4,6,7,8-HpCDD	1800	142	9210	92.6	12,200	101
OCDD	8310	137	16,300	61.4	21,900	59.3
2,3,7,8-TeCDF	50.2	60.9	859	149	692	98.7
1,2,3,7,8-PeCDF	106	70.1	1570	155	1160	106
2,3,4,7,8-PeCDF	189	86.5	2500	151	2310	114
1,2,3,4,7,8-HxCDF	267	106	2240	134	2390	76.3
1,2,3,6,7,8-HxCDF	292	100	2590	132	2770	73.7
1,2,3,7,8,9-HxCDF	47.8	208	319	174	348	97.9
2,3,4,6,7,8-HxCDF	449	101	3270	108	4050	74.0
1,2,3,4,6,7,8-HpCDF	2250	129	7880	89.7	9770	55.2
1,2,3,4,7,8,9-HpCDF	254	101	1450	88.2	1730	58.9
OCDF	2500	98.7	7100	87.7	7770	61.3
PCDDs	10,500	136	28,900	75.9	38,700	77.0
PCDFs	6400	103	29,800	97.8	33,000	59.3
PCDDs/PCDFs	1370	27.9	1110	46.6	1200	34.6
Total PCDD/Fs	16,900	123	58,700	84.4	71,600	65.5
PCDDs (ng I-TEQ g ⁻¹)	277	97.7	1920	101	2730	145
PCDFs (ng I-TEQ g ⁻¹)	343	77.7	3100	112	3690	111
PCDDs/PCDFs	712	49.4	618	69.1	582	45.1
Total PCDD/Fs (ng I-TEQ g ⁻¹)	620	82.3	5020	100	6410	125

R.S.D., relative standard deviation.

(90.0–15,000 ng kg⁻¹, 10.8–16.5%), 1,2,3,4,6,7,8-HpCDD (50.0–17,100 ng kg⁻¹, 9.18–17.1%) and 2,3,4,6,7,8-HxCDF (28.9–4050 ng kg⁻¹, 2.63–13.4%) in fly ash. In bottom ash, the main five peaks were OCDD (106 ng kg⁻¹, 37.4%), OCDF (68.5 ng kg⁻¹, 24.1%), 1,2,3,4,6,7,8-HpCDF (38.3 ng kg⁻¹, 13.5%), 1,2,3,4,6,7,8-HpCDD (27.3 ng kg⁻¹, 9.63%) and 2,3,4,6,7,8-HxCDF (8.50 ng kg⁻¹, 2.99%). In stack flue, the main five peaks were OCDD (0.340 ng Nm⁻³, 32.5%), 1,2,3,4,6,7,8-HpCDD (0.213 ng Nm⁻³, 20.3%), 1,2,3,4,6,7,8-HpCDF (0.110 ng Nm⁻³, 10.5%), OCDF (0.0906 ng Nm⁻³, 8.65%) and 2,3,4,6,7,8-HxCDF (0.0516 ng Nm⁻³, 4.93%). It could be seen that PCDD/F congener profiles were similar to each other and similar to

that in stack. The main five species were OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, OCDF and 2,3,4,6,7,8-HxCDF.

3.4. Emission factor of PCDD/Fs in the MSWI

The emission factor (μg ton-waste⁻¹) of PCDD/Fs in the stack of the MSWI was calculated by using the PCDD/F concentration, air flow rate and the waste amount combusted in the incineration of the MSWI. The emission factor (μg ton-waste⁻¹) of PCDD/Fs in different ash was calculated by using the ash amount generated in incineration of municipal solid waste, the PCDD/F

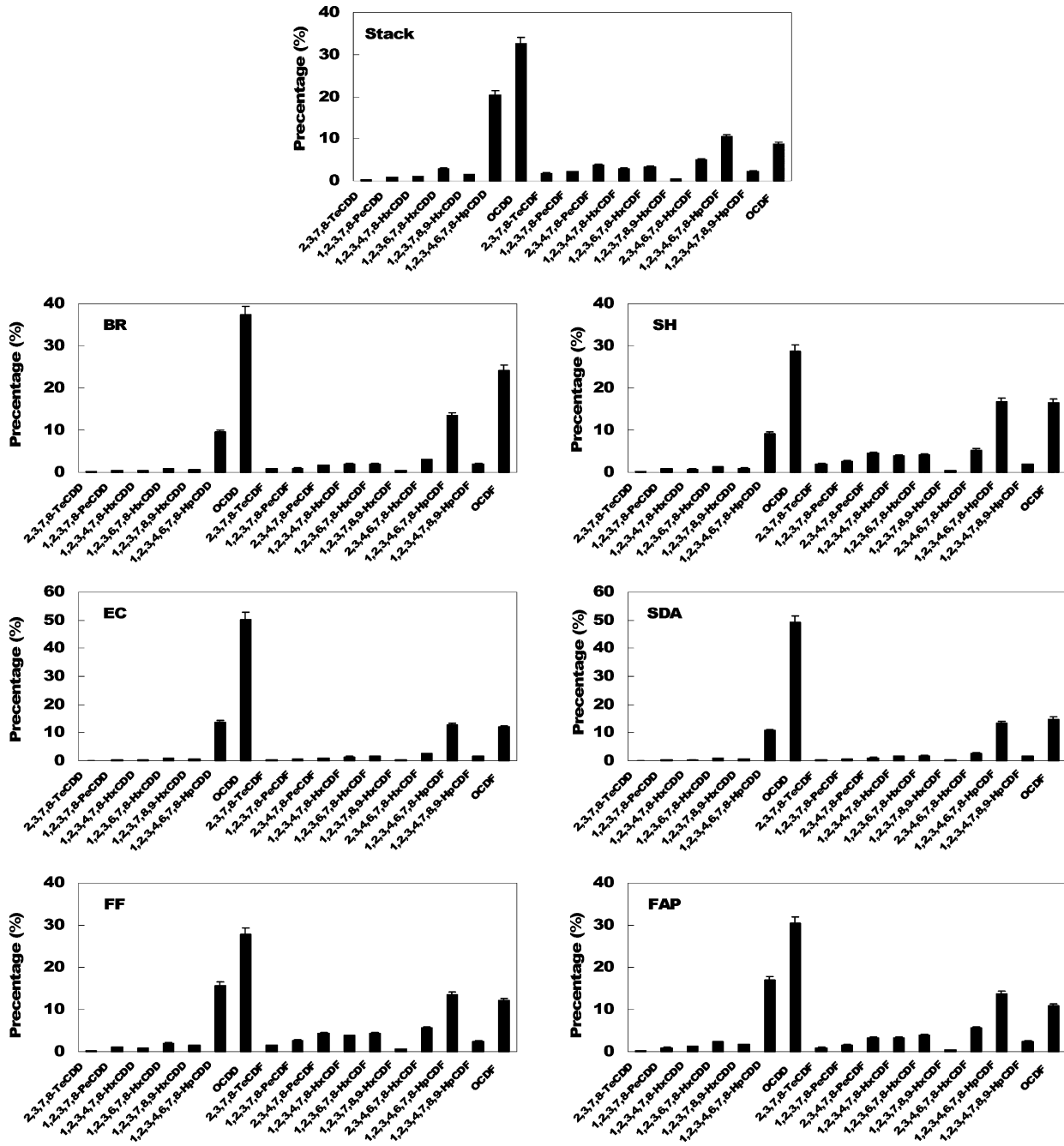


Fig. 2. PCDD/F congener profiles in different ashes from the MSWI.

content in different ash and the waste amount combusted in the incineration of the MSWI. Emission factor was shown in Table 3. The total PCDD/Fs emission factors were stack (8.47 $\mu\text{g ton-waste}^{-1}$; 0.454 $\mu\text{g I-TEQ ton-waste}^{-1}$), BR (58.2 $\mu\text{g ton-waste}^{-1}$; 3.54 $\mu\text{g I-TEQ ton-waste}^{-1}$), SH (4.40 $\mu\text{g ton-waste}^{-1}$; 0.306 $\mu\text{g I-TEQ ton-waste}^{-1}$), EC (961 $\mu\text{g ton-waste}^{-1}$; 31.9 $\mu\text{g I-TEQ ton-waste}^{-1}$), SDA (100 $\mu\text{g ton-waste}^{-1}$; 3.66 $\mu\text{g I-TEQ ton-waste}^{-1}$), FF (1870 $\mu\text{g ton-waste}^{-1}$; 160 $\mu\text{g I-TEQ ton-waste}^{-1}$) and FAP (3610 $\mu\text{g ton-waste}^{-1}$; 323 $\mu\text{g I-TEQ ton-waste}^{-1}$), respectively. Theoretically the PCDD/F emission factor in FAP should be equal to summation of that in SH, EC, SDA and FF because fly ash from SH, EC, SDA and FF were transferred to fly ash pit. However, it is interesting that total PCDD/F emission factor in FAP

(3610 $\mu\text{g ton-waste}^{-1}$; 323 $\mu\text{g I-TEQ ton-waste}^{-1}$) was higher than summation of that in SH, EC, SDA and FF (2940 $\mu\text{g ton-waste}^{-1}$; 195 $\mu\text{g I-TEQ ton-waste}^{-1}$). In other words, the PCDD/Fs might be formed (674 $\mu\text{g ton-waste}^{-1}$; 128 $\mu\text{g I-TEQ ton-waste}^{-1}$). Similar results were found in other researches [21,24]. Future investigation is needed to make sure how PCDD/Fs formed during the transfer process or within the fly ash pit. Although the temperature was maintained at about 150–170 $^{\circ}\text{C}$ in order to prevent steam formation when the fly ash was transferred from different equipments to the FAP, this is not the optimal temperature for PCDD/F formation. However, PCDD/Fs might be formed during the transfer process or within the fly ash pit. As a result, the temperature should be maintained at a level of

Table 3
PCDD/F emission factor in the selected MSWI ($\mu\text{g ton-waste}^{-1}$)

$\mu\text{g ton-waste}^{-1}$	Stack flue					Bottom ash
	Stack					BR
2,3,7,8-TeCDD	0.0241					0.0676
1,2,3,7,8-PeCDD	0.0792					0.216
1,2,3,4,7,8-HxCDD	0.0824					0.286
1,2,3,6,7,8-HxCDD	0.241					0.465
1,2,3,7,8,9-HxCDD	0.119					0.386
1,2,3,4,6,7,8-HpCDD	1.60					5.61
OCDD	2.40					21.8
2,3,7,8-TeCDF	0.194					0.491
1,2,3,7,8-PeCDF	0.208					0.565
2,3,4,7,8-PeCDF	0.355					0.987
1,2,3,4,7,8-HxCDF	0.274					1.16
1,2,3,6,7,8-HxCDF	0.305					1.17
1,2,3,7,8,9-HxCDF	0.0497					0.245
2,3,4,6,7,8-HxCDF	0.450					1.74
1,2,3,4,6,7,8-HpCDF	0.954					7.86
1,2,3,4,7,8,9-HpCDF	0.223					1.17
OCDF	0.923					14.1
PCDDs	4.54					28.8
PCDFs	3.94					29.4
Total PCDD/Fs	8.47					58.2
PCDDs ($\mu\text{g I-TEQ ton-waste}^{-1}$)	0.126					1.78
PCDFs ($\mu\text{g I-TEQ ton-waste}^{-1}$)	0.328					1.76
Total PCDD/Fs ($\mu\text{g I-TEQ ton-waste}^{-1}$)	0.454					3.54
$\mu\text{g ton-waste}^{-1}$	Fly ash					FAP
	SH	EC	SDA	FF	Generation	
2,3,7,8-TeCDD	0.0121	0.555	0.0764	4.75	0.885	6.28
1,2,3,7,8-PeCDD	0.0391	2.76	0.345	18.4	13.3	34.9
1,2,3,4,7,8-HxCDD	0.0324	4.06	0.389	16.7	23.9	45.1
1,2,3,6,7,8-HxCDD	0.0526	9.95	0.860	38.1	34.2	83.2
1,2,3,7,8,9-HxCDD	0.0420	6.93	0.719	27.5	25.6	60.8
1,2,3,4,6,7,8-HpCDD	0.404	130	10.6	294	181	616
OCDD	1.26	482	49.1	521	49.3	1100
2,3,7,8-TeCDF	0.0890	1.92	0.296	27.4	5.16	34.9
1,2,3,7,8-PeCDF	0.116	4.70	0.623	50.0	3.17	58.7
2,3,4,7,8-PeCDF	0.200	8.46	1.11	79.9	26.9	117
1,2,3,4,7,8-HxCDF	0.169	13.9	1.57	71.6	33.4	121
1,2,3,6,7,8-HxCDF	0.182	15.9	1.72	82.7	39.2	140
1,2,3,7,8,9-HxCDF	0.0195	2.75	0.282	10.2	4.34	17.6
2,3,4,6,7,8-HxCDF	0.233	25.3	2.65	104	71.6	204
1,2,3,4,6,7,8-HpCDF	0.733	122	13.3	251	105	493
1,2,3,4,7,8,9-HpCDF	0.0824	14.6	1.50	46.3	25.0	87.5
OCDF	0.728	115	14.8	227	35.2	392
PCDDs	1.85	637	62.1	921	329	1950
PCDFs	2.55	324	37.8	951	345	1660
Total PCDD/Fs	4.40	961	100	1870	674	3610
PCDDs ($\mu\text{g I-TEQ ton-waste}^{-1}$)	0.0816	15.4	1.64	61.1	59.4	138
PCDFs ($\mu\text{g I-TEQ ton-waste}^{-1}$)	0.225	16.4	2.03	98.9	68.3	186
Total PCDD/Fs ($\mu\text{g I-TEQ ton-waste}^{-1}$)	0.306	31.9	3.66	160	128	323

105–110°C to prevent formation of PCDD/Fs and save energy as well.

According to Table 3, emission factor of total PCDD/Fs in FAP was equal to generation plus summation of that in SH, EC, SDA and FF. It could be seen that 674 $\mu\text{g ton-waste}^{-1}$ of PCDD/Fs formed which was 18.7% of total PCDD/F emission factor in FAP, respectively. Furthermore, 128 $\mu\text{g I-TEQ ton-waste}^{-1}$ of PCDD/Fs formed which was 39.4% of total PCDD/F emission factor in FAP. The total PCDD/F emission from the MSWI was 3680 $\mu\text{g ton-waste}^{-1}$ and 327 $\mu\text{g I-TEQ ton-waste}^{-1}$. Distribution ratios of PCDD/Fs in $\mu\text{g ton-waste}^{-1}$ of fly ash, bottom ash and stack flue were 98.2%, 1.58% and 0.23%, respectively. Distribution ratios of PCDD/Fs in $\mu\text{g I-TEQ ton-waste}^{-1}$ of fly ash, bottom ash and stack flue were 98.8%, 1.08% and 0.14%, respectively. The above results indicated

that the main PCDD/F source in the MSWI was fly ash accounting for 98–99% of total PCDD/F emission in the MSWI. Similar results were found by Johnke and Stelzner [13] and Giugliano et al. [14]. The above results indicated that MSWIs did require further detoxification treatments for the solid residues despite the highly efficient destruction behaviour evaluated, resulting in a total PCDD/F release to be considered rather low (8.47 $\mu\text{g ton-waste}^{-1}$; 0.454 $\mu\text{g I-TEQ ton-waste}^{-1}$).

3.5. Annual and weekly amount of PCDD/Fs emitted from the MSWI under start-up operation condition

The emission amount ($\mu\text{g year}^{-1}$) of PCDD/Fs in the stack of the MSWI was calculated by using its PCDD/F emission fac-

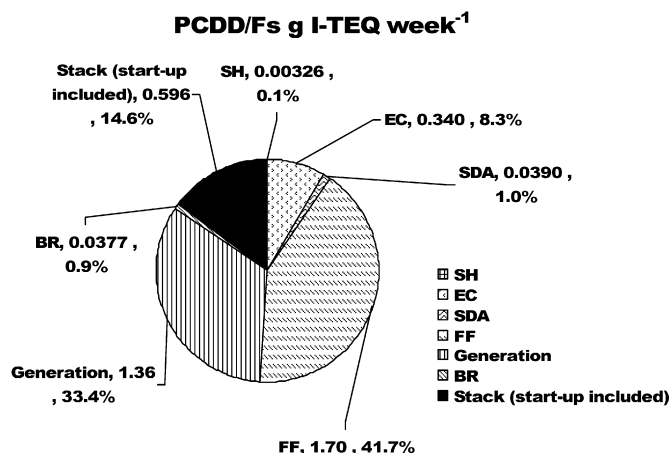


Fig. 3. PCDD/F mass distribution in the whole MSWI (start-up included).

tor (g I-TEQ ton-waste⁻¹) and annual amount of municipal solid waste (ton year⁻¹). The emission amount (g year⁻¹) of PCDD/Fs in different ash was calculated by using its PCDD/F emission factor ($\mu\text{g ton-waste}^{-1}$) and annual amount of municipal solid waste (ton year⁻¹) as well. According to statistical data, the mean annual amount of municipal solid waste in the MSWI during 2003–2006 is 5.54×10^5 ton. Therefore, the total emission amount of PCDD/Fs from stack, BR, SH, EC, SDA, FF and generation were 0.252, 1.96, 0.170, 17.7, 2.03, 88.6 and 70.9 g I-TEQ year⁻¹, respectively, by directly adopting the mean emission factors that were obtained from this study. The PCDD/F emission quantity from stacks resulted from the start-up was 2.35 times larger than that of a whole year's normal operations [15]. Therefore, total emission amount of PCDD/Fs from the stacks in this MSWI was 0.844 ($=0.252 \times (2.35 + 1)$) g I-TEQ year⁻¹ with considering the start-up. Mass distribution ratios of PCDD/Fs in g I-TEQ year⁻¹ from stack, SH, EC, SDA, FF, generation and BR in start-up operations were 0.5%, 0.1%, 9.7%, 1.1%, 48.6%, 38.0% and 1.1%, respectively. The above results displayed that the main PCDD/F source in the MSWI was from fly ash and the contribution of increase at start-up is negligible in whole year. Therefore, the weekly amount (g I-TEQ week⁻¹) of PCDD/Fs in the stack of the MSWI was calculated. The result showed that the total emission amount of PCDD/Fs from stack, BR, SH, EC, SDA, FF and generation were 0.00484, 0.0377, 0.00326, 0.340, 0.0390, 1.70 and 1.36 g I-TEQ week⁻¹. Besides, total emission amount of PCDD/Fs from the stacks in this MSWI was 0.596 ($=0.00484 \times (52 \times 2.35 + 1)$) g I-TEQ week⁻¹ with considering the start-up operations. Therefore, mass distribution ratios of PCDD/Fs in g I-TEQ week⁻¹ from stack, SH, EC, SDA, FF, generation and BR in start-up operations were 14.6%, 0.1%, 8.3%, 1.0%, 41.7%, 33.4% and 0.9%, respectively (Fig. 3). It could be seen that the main PCDD/F source in the MSWI was from fly ash (~85%) although start-up procedure was 2.35 times larger than that of a whole year's normal operations. The above results indicated that main PCDD/F source in the MSWI was from fly ash. However, the fly ash is easily controlled and PCDD/F emitted from stack flue gases will be difficult to be handled. Therefore, we should pay more attention on PCDD/F emission from flue gases especially from start-up procedure.

4. Conclusions

Experimental results displayed that the averaged PCDD/F equivalent concentration was 0.0511 ng I-TEQ Nm⁻³. The averaged PCDD/F contents for ash samples from the bottom residue, super heater, economizer, semi-dryer absorber, fabric filter and

fly ash pit were measured to be: 17.2, 37.9, 4180, 620, 5020 and 6410 ng I-TEQ kg⁻¹, respectively. The total PCDD/Fs emission factors were stack ($8.47 \mu\text{g ton-waste}^{-1}$; $0.454 \mu\text{g I-TEQ ton-waste}^{-1}$), BR ($58.2 \mu\text{g ton-waste}^{-1}$; $3.54 \mu\text{g I-TEQ ton-waste}^{-1}$), SH ($4.40 \mu\text{g ton-waste}^{-1}$; $0.306 \mu\text{g I-TEQ ton-waste}^{-1}$), EC ($961 \mu\text{g ton-waste}^{-1}$; $31.9 \mu\text{g I-TEQ ton-waste}^{-1}$), SDA ($100 \mu\text{g ton-waste}^{-1}$; $3.66 \mu\text{g I-TEQ ton-waste}^{-1}$), FF ($1870 \mu\text{g ton-waste}^{-1}$; $160 \mu\text{g I-TEQ ton-waste}^{-1}$) and FAP ($3610 \mu\text{g ton-waste}^{-1}$; $323 \mu\text{g I-TEQ ton-waste}^{-1}$), respectively. Theoretically the PCDD/F emission factor in FAP should be equal to summation of that in SH, EC, SDA and FF because fly ash from SH, EC, SDA and FF were transferred to fly ash pit. In other words, the PCDD/Fs might be formed ($674 \mu\text{g ton-waste}^{-1}$; $128 \mu\text{g I-TEQ ton-waste}^{-1}$). As a result, the temperature of transmission system should be maintained at a level of 105–110 °C to prevent formation of PCDD/Fs and save energy as well. Recently, several studies have focused on the high PCDD/F emission during the start-up of incinerators. Therefore, the total emission amount of PCDD/Fs from stack, BR, SH, EC, SDA, FF and generation were 0.596, 0.0377, 0.00326, 0.340, 0.0390, 1.70 and 1.36 g I-TEQ week⁻¹ with considering the start-up operations, respectively. Mass distribution ratios of PCDD/Fs in g I-TEQ week⁻¹ from stack, SH, EC, SDA, FF, generation and BR in start-up operations were 14.6%, 0.1%, 8.3%, 1.0%, 41.7%, 33.4% and 0.9%, respectively. It could be seen that the main PCDD/F source in the MSWI was from fly ash although start-up procedure can generate ~60% of the PCDD/F emissions from stacks for one whole year of normal operations. The above results indicated that main PCDD/F source in the MSWI was from fly ash. However, the fly ash is easily controlled and PCDD/F emitted from stack flue gases will be difficult to be handled. Therefore, we should pay more attention on PCDD/F emission from flue gases especially from start-up procedure. Besides, fly ash should be controlled by sodium hypophosphite before being landfilled. MSWI did require further detoxification treatments for the solid residues and flue gases.

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