Emissions of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans from the Incinerations of Both Medical and Municipal Solid Wastes

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Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from the stack flue gases of four medical waste incinerators (MWIs) and ten municipal solid waste incinerators (MSWIs) were investigated. The mean PCDD/F concentrations in the stack flue gases of these MWIs and MSWIs is 0.521 ng I-TEQ Nm^{-3} and 0.0533 ng I-TEQ Nm^{-3}, respectively. In the stack flue gases of MWIs, OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDF were the major congeners, while in MSWIs, OCDD and 1,2,3,4,6,7,8-HpCDD were the major ones. The mean PCDD/F emission factors (20.1 μg I-TEQ ton-$waste^{-1}$) of the MWIs was about 210 times of magnitude higher than that of MSWIs, which was 0.0939 μg I-TEQ ton-$waste^{-1}$. In Taiwan, the annual emissions of PCDD/Fs from MWIs and MSWIs are 0.371 g I-TEQ $year^{-1}$ and 0.737 g I-TEQ $year^{-1}$, respectively. Although the contribution of PCDD/Fs from MWIs to the atmosphere was 50.3% of that from MSWIs, it should be noted that most MWIs are equipped with a low stack and are situated in the proximity of the residential area and PCDD/F emissions from MWIs could significantly affect its surrounding environment.

Keywords: PCDD/Fs, emission factor, incineration, municipal solid waste, medical waste

1. Introduction

After polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were discovered in the flue gases and fly ash of municipal solid waste incinerators (MSWIs) in 1977 (Olie et al., 1977), PCDD/Fs have become a serious issue in many countries, because of their toxicological effects and associated adverse health implications.

US EPA's Office of Research and Development (ORD) had developed the “Database of Sources of Environmental Releases of Dioxin like Compounds in the United States” (US EPA, 2001) to be a repository of PCDD/Fs emissions data from all

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known sources. It reveals that MSWIs released 64% and 38% of the total PCDD/F emission into the air in 1987 and 1995, respectively; medical waste incinerators (MWIs) released 20% and 16% of the total PCDD/F emission into the air in 1987 and 1995, respectively. In the United Kingdom, the total estimated emissions of PCDD/Fs into the atmosphere ranged from 560 to 1100 g I-TEQ year^{-1}; MSWIs dominated, contributing 460-580 g I-TEQ year^{-1}, an average of 63% to the total emissions. MWIs contributed 18-88 g I-TEQ year^{-1} in the UK (Eduljee et al., 1996). Despite source reduction measures (emissions fell to 220-660 g I-TEQ year^{-1} in 1999), MSWIs remain a significant source of PCDD/Fs to the atmosphere, contributing 460-580 g I-TEQ year^{-1}, an average between 30-50% of the total PCDD/Fs I-TEQ emissions (Alcock et al., 1999). Although emissions from MWIs are less than those from MSWIs, on-site MWIs cause special attention, mainly because of the typical hospital's proximity to a city (Lee et al., 1996).

PCDD/F emissions from most combustion processes are detected as a mixture of 75 PCDD and 135 PCDF congeners. The mixture can be translated into profiles, which represent the distribution of individual PCDD/Fs. These profiles may give a signature or fingerprint of the types of PCDD/Fs associated with particular incinerators and air pollution control devices (APCDs). The fingerprinting of PCDD/Fs has been interestingly applied in identification of sources, atmospheric transport and transformation studies and formation mechanism elucidation (Buekens et al., 2000).

Taiwan had adopted incineration as a mainstream technology for treating both municipal solid wastes and medical wastes, because of the country's high population density and rapidly increasing waste generation per capita. This study investigated four MWIs (H1 ~ H4) and ten MSWIs (M1 ~ M10). The congener profiles of PCDD/Fs in the stack flue gases of both MWIs and MSWIs are presented and compared. Furthermore, the emission factors of PCDD/Fs from the stack flue gases of MWIs and MSWIs were determined on the basis of the total weight of the waste. In Taiwan, the total quantities of PCDD/Fs emitted from the MWIs and MSWIs were estimated, compared and discussed.

Table1. Basic information concerning MWIs and MSWIs

Incinerator	Capacity	APCDs
H1	160 kg hr^{-1}	QC, VS, PBS
H2	100 kg hr^{-1}	QC, VS, PBS
H3	120 kg hr^{-1}	QC, VS, PBS
H4	75 kg hr^{-1}	DS, FF, ACI
M1	900 tons day^{-1}	DS, ACI, FF
M2	900 tons day^{-1}	DS, ACI, FF
M3	900 tons day^{-1}	DS, ACI, FF
M4	1,200 tons day^{-1}	DS, ACI, FF
M5	1,350 tons day^{-1}	DS, ACI, FF
M6	1,800 tons day^{-1}	DS, ACI, FF
M7	900 tons day^{-1}	DS(ACI), FF
M8	1,350 tons day^{-1}	CY, DSI(ACI), FF
M9	1,350 tons day^{-1}	CY, DS, ACI, FF
M10	1,500 tons day^{-1}	EP(ACI), VS, PBS, SCR

ACI: Activated Carbon Injection; CY: Cyclone; DS: Dry Scrubber; DSI: Dry Sorbent Injection; EP: Electrostatic Precipitator; FF: Fabric Filter; SNCR: Selective Noncatalytic Reduction, QC: Quench Chamber; VS: Venturi Scrubber

2. Material and Method

2.1 Basic Information Concerning MWIs and MSWIs

Table 1 presents basic information concerning the four MWIs (H1 ~ H4) and ten MSWIs (M1 ~ M10) investigated here, including each capacity and APCDs in sequence. The operation type of all MWIs is intermittent while that of MSWIs is continuous.

Table 2. Mean PCDD/F concentration in the stack flue gases of MWIs and MSWIs

PCDD/Fs	H1	H2	H3	H4	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10
Total (ng Nm^{-3})	7.14	4.89	13.0	0.550	2.35	0.976	0.82	0.564	2.23	1.16	1.73	1.06	0.776	1.24
Mean (RSD, %)	6.40 (81.1%)				1.29 (47.5%)									
Total I-TEQ (ng I-TEQ Nm^{-3})	0.511	0.314	1.22	0.040	0.081	0.049	0.037	0.023	0.105	0.054	0.065	0.038	0.035	0.043
Mean (RSD, %)	0.521 (96.7%)				0.0533 (46.0%)									

2.2 Sampling

Three PCDD/F samples were collected from the stack flue gas for each MWI and ten PCDD/F samples for each MSWI according to US EPA modified Method 23. A sampling train adopted in this study is comparable with that specified by US EPA Modified Method 5. The company certified by the Taiwan EPA to sample PCDD/Fs in the stack flue gas performed the sampling. Prior to sampling, XAD-2 resin was spiked with PCDD/F surrogate standards pre-labeled with isotopes. Each stack flue gas sampling lasted for ~3 h. 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 given in Wang et al. (2003)

2.3 Analyses of PCDD/Fs

All chemical analyses were conducted by the only accredited laboratory, the Super Micro Mass Research and Technology Center in Cheng Shiu Institute of Technology, certified by the Taiwan EPA for analyzing PCDD/Fs. Each collected sample was spiked with a known amount of the internal standard prior to PCDD/F analysis. After being extracted for 24 h, the extract was concentrated, treated with concentrated sulfuric acid, and followed by a series of sample cleanup and fractionation procedures. Prior to analysis, the standard solution was added to the sample to ensure the recovery during the analysis process. A high-resolution gas chomatograph/high-resolution mass spectrometer (HRGC/HRMS) was used for PCDD/F analyses. The HRGC (Hewlett Packard 6970 Series, CA, USA) was equipped with a DB-5 fused silica capillary column (L = 60 m, ID = 0.25 mm, film thickness = 0.25 μm) (J&W Scientific, CA, USA), and with a splitless injection. The HRMS (Micromass Autospec Ultima, Manchester, UK) mass spectrometer 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 specified at 35 eV and 250°C, respectively. Details are given in Wang et al. (2003)

3. Results and Discussion

3.1 PCDD/F Concentrations in the Stack Flue Gases

Table 2 lists the mean PCDD/F concentrations in the stack flue gases of MWIs and MSWIs. The range of PCDD/F concentrations of the four MWIs is between 0.0403 and 1.22 ng I-TEQ Nm^{-3} (Mean : 0.521 ng I-TEQ Nm^{-3} , RSD: 96.7%), while that of the ten MSWIs is between 0.0237 and 0.105 ng

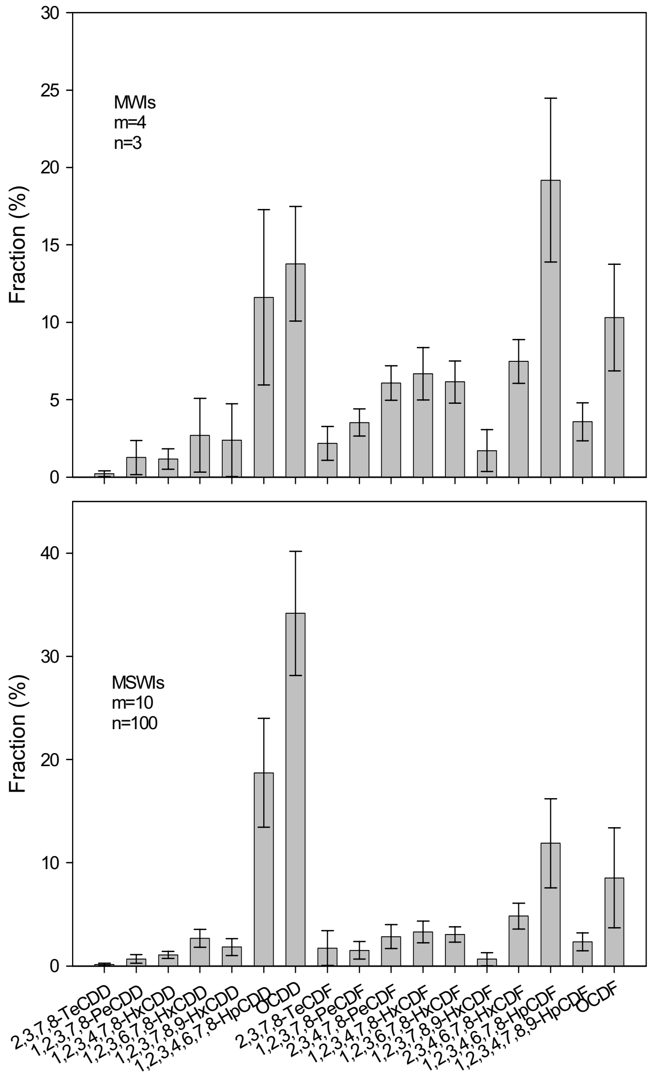

Figure 1. Congener profiles of seventeen 2,3,7,8 chlorinated substituted PCDD/Fs in the stack flue gas of MWIs and MSWIs

Table 3. Mean PCDD/F emission factors and theircorresponding relative standard deviations (RSD) of these four MWIs

PCDD/Fs	H1	H2	H3	H4
2,3,7,8-TeCDD	0.138	0.276	1.50	0.0738
1,2,3,7,8-PeCDD	2.52	1.11	14.1	0.199
1,2,3,4,7,8-HxCDD	2.81	1.52	10.5	0.216
1,2,3,6,7,8-HxCDD	4.79	2.47	34.1	0.414
1,2,3,7,8,9-HxCDD	4.45	1.68	29.2	0.273
1,2,3,4,6,7,8-HpCDD	24.8	15.3	97.3	2.60
OCDD	44.6	26.2	50.1	3.48
2,3,7,8-TeCDF	7.04	2.18	12.2	0.506
1,2,3,7,8-PeCDF	16.2	4.04	15.6	0.652
2,3,4,7,8-PeCDF	22.2	9.66	29.6	1.16
1,2,3,4,7,8-HxCDF	33.7	9.53	21.3	1.09
1,2,3,6,7,8-HxCDF	30.0	8.96	19.5	1.10
1,2,3,7,8,9-HxCDF	11.3	4.15	0.804	0.0302
2,3,4,6,7,8-HxCDF	33.8	14.3	22.6	1.24
1,2,3,4,6,7,8-HpCDF	89.1	37.0	43.5	3.27
1,2,3,4,7,8,9-HpCDF	14.3	7.86	9.17	0.456
OCDF	42.3	24.9	22.1	1.56
Total (μg/ton-waste)	384	171	433	18.3
Mean (RSD, %)	252 (66.3%)			
Total I-TEQ (μg I-TEQ/ton-waste)	27.5	11.0	40.7	1.34
Mean (RSD, %)	20.1 (75.1%)			

I-TEQ Nm^{-3} (Mean : 0.0533 ng I-TEQ Nm^{-3} , RSD: 46.0%).

3.2 Congener Profiles

The congener profiles of the 2,3,7,8-substituted PCDD/Fs were selected as the signatures of the MWIs and MSWIs. Figure 1 shows the congener profiles of the "dirty" seventeen PCDD/Fs (mean±SD) detected from the stack flue gases of MWIs and MSWIs. Each selected congener was normalized by reference to the total weight of all 2,3,7,8-congeners. The variable "m" represents the number of incinerators while the variable "n" represents the number of total stack flue gas samples. In the stack flue gases of MWIs, OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDF were the major congeners, while in MSWIs, OCDD and 1,2,3,4,6,7,8-HpCDD were the major ones. The congener profiles of MWIs and MSWIs are similar to those presented in other research (US EPA, 1998).

3.3 Emission Factors

Table 3 and table 4 list the mean PCDD/F emission factors from the stack flue gases of MWIs and MSWIs, respectively. The mean PCDD/F emission factors of the four MWIs is 20.1 μg I-TEQ ton-waste^{-1} (Range: 1.34 μg I-TEQ

Table 4. Mean PCDD/F emission factors and their RSD of these ten MSWIs

PCDD/Fs	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10
2,3,7,8-TeCDD	0.0059	0.0066	0.0033	0.0005	0.0071	0.0022	0.0038	0.0040	0.0026	0.0027
1,2,3,7,8-PeCDD	0.0239	0.0167	0.0108	0.0057	0.0256	0.0124	0.0178	0.0113	0.0092	0.0114
1,2,3,4,7,8-HxCDD	0.0480	0.0176	0.0173	0.0095	0.0405	0.0211	0.0309	0.0185	0.0155	0.0161
1,2,3,6,7,8-HxCDD	0.160	0.0432	0.0288	0.0269	0.110	0.0425	0.0812	0.0439	0.0442	0.0413
1,2,3,7,8,9-HxCDD	0.117	0.0251	0.0215	0.0162	0.0558	0.0384	0.0412	0.0240	0.0191	0.0347
1,2,3,4,6,7,8-HpCDD	1.11	0.324	0.179	0.188	0.720	0.274	0.632	0.332	0.296	0.310
OCDD	1.60	0.654	0.399	0.368	1.38	0.454	1.09	0.910	0.524	0.741
2,3,7,8-TeCDF	0.0556	0.0372	0.0106	0.0096	0.158	0.0447	0.0239	0.0175	0.0152	0.0131
1,2,3,7,8-PeCDF	0.0191	0.0613	0.0217	0.0158	0.063	0.0178	0.0453	0.0277	0.0256	0.0217
2,3,4,7,8-PeCDF	0.0519	0.0882	0.0407	0.0361	0.126	0.0365	0.0827	0.0476	0.0507	0.0516
1,2,3,4,7,8-HxCDF	0.106	0.0894	0.0463	0.0344	0.123	0.0654	0.0904	0.0432	0.0414	0.0487
1,2,3,6,7,8-HxCDF	0.0896	0.0900	0.0481	0.0335	0.136	0.0421	0.095	0.0459	0.0455	0.0555
1,2,3,7,8,9-HxCDF	0.0167	0.0059	0.0275	0.0154	0.0200	0.0099	0.0086	0.0036	0.0029	0.0030
2,3,4,6,7,8-HxCDF	0.148	0.113	0.0926	0.0613	0.225	0.0572	0.150	0.071	0.0652	0.119
1,2,3,4,6,7,8-HpCDF	0.191	0.329	0.219	0.209	0.471	0.133	0.391	0.156	0.151	0.310
1,2,3,4,7,8,9-HpCDF	0.0608	0.0628	0.0559	0.0179	0.0887	0.0357	0.0827	0.0317	0.0253	0.0611
OCDF	0.0837	0.273	0.199	0.0800	0.217	0.104	0.314	0.104	0.0734	0.345
Total (μg ton-waste^{-1})	3.88	2.24	1.42	1.13	3.97	1.39	3.18	1.89	1.41	2.19
Mean (RSD, %)	2.27 (46.4%)									
Total I-TEQ (μg I-TEQ ton-waste^{-1})	0.134	0.112	0.0645	0.0475	0.187	0.0647	0.121	0.0678	0.0642	0.0764
Mean (RSD, %)	0.0939 (46.4%)									

ton-waste^{-1} ~ 40.7 μg I-TEQ ton-waste^{-1}, RSD: 75.1%), while that of the ten MSWIs is 0.0939 μg I-TEQ ton-waste^{-1} (Range: 0.0475 μg I-TEQ ton-waste^{-1} ~ 0.187 μg I-TEQ ton-waste^{-1}, RSD: 46.4%). These emission factors were based on total weights of waste, excluding fuel. The mean PCDD/F emission factors (20.1 μg I-TEQ ton-waste^{-1}) of the MWIs was about 210 times of magnitude higher than that of MSWIs, which was 0.0939 μg I-TEQ ton-waste^{-1}. It is resulted from that MWIs are typically small-scale incinerators, with low combustion efficiency, and without advanced APCDs; most importantly, PVC is a major constituent in the feed waste stream for incineration. The emission factors of MWIs and MSWIs (new plants) in the United Kingdom were 20-200 and 0.8 μg I-TEQ ton-waste^{-1}, respectively (Eduljee et al., 1996). These values were higher than those obtained here.

3.4 Annual Emissions of PCDD/Fs from MWIs and MSWIs

The annual emissions of PCDD/Fs are estimated by the following formula (US EPA, 1998).

$$E_{total} = \sum E_{tested,i} + \sum E_{untested,i} = \sum E_{tested,i} + \sum (EF_i * A_i)_{untested}$$

where: E_{total} = annual emissions from all facilities (g I-TEQ year^{-1}); $\sum E_{tested,i}$ = annual emissions from all tested facilities in class *i*; $\sum E_{untested,i}$ = annual emissions from all untested facilities in class *i*; EF_i = mean emission factor of tested facilities in class *i*; A_i = activity measure for untested facilities in class *i*.

According to statistical data (Taiwan EPA, 2003) and operational records of each tested facility, in Taiwan, annual emissions of PCDD/Fs from MWIs and MSWIs are calculated as 0.371 g I-TEQ year^{-1} and 0.737 g I-TEQ year^{-1}, respectively. The confidence of these reported values are medium or high, especially for MSWIs because their tested percentage is very high. Although the contribution of PCDD/Fs from MWIs to the atmosphere was 50.3% of that from MSWIs, it should be noted that most MWIs are equipped with a low stack and are situated in the proximity of the residential area and PCDD/F emissions from MWIs could significantly affect its surrounding environment.

4. Conclusions

The mean PCDD/F concentrations in the stack flue gases of these four MWIs and ten MSWIs is 0.521 ng I-TEQ Nm^{-3} and 0.0533 ng I-TEQ Nm^{-3}, respectively. In the stack flue gases of MWIs, OCDD,1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDF were the major congeners, while in MSWIs, OCDD and 1,2,3,4,6,7,8-HpCDD were the major ones. The mean PCDD/F emission factors (20.1 μg I-TEQ ton-waste^{-1}) of the MWIs was about 210 times of magnitude higher than that of MSWIs, which was 0.0939 μg I-TEQ ton-waste^{-1}. It is resulted from that MWIs are typically small-scale incinerators, with low combustion efficiency, and without advanced APCDs; most importantly, PVC is a major constituent in the feed waste stream for incineration.

In Taiwan, the annual emissions of PCDD/Fs from MWIs and MSWIs are 0.371 g I-TEQ year^{-1} and 0.737 g I-TEQ year^{-1}, respectively. Although the contribution of PCDD/Fs from MWIs to the atmosphere was 50.3% of that from MSWIs, it should be noted that most MWIs are equipped with a low stack and are situated in the proximity of the residential area and PCDD/F emissions from MWIs could significantly affect its surrounding environment.

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