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Formation and emission status of PCDDs/PCDFs in municipal solid waste incinerators in Korea

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Abstract

This study was carried out to examine the formation and the emission status of polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs) in the flue gases of commercial-scale municipal solid waste (MSW) incinerators, and thus to provide the engineering data for the reduction of PCDDs/PCDFs emitted from MSW incinerators. The formation concentrations of the PCDDs/PCDFs generated at the outlet of waste heat boilers (WHB) were in the range of 1.18–29.61 ng-TEQ/N m^3 (average 5.75 ng-TEQ/N m^3), while the emission concentrations at the stacks were in the range of 0.026–4.548 ng-TEQ/N m^3 (average 0.924 ng-TEQ/N m^3). Two major 2,3,7,8-substituted congeners were 2,3,4,7,8-PeCDF and 2,3,4,6,7,8-HxCDF, and their concentrations were up to 50% and 64% of total TEQ values at the outlet of WHB and the stack, respectively. From the results of multi-regression analysis, the formation concentration of PCDDs/PCDFs could be predicted as follows with the correlation factor of $r^2 = 0.962$: PCDDs/PCDFs (ng-TEQ/N m^3) $= 3.036$ (Cl) $+ 0.094$ (T_1) $- 0.472$ (Combustibles) $+ 0.059$ (CO) $- 0.039$ (THC) $-$ 3.366 (H) $+ 22.157$, where T_1 (°C) is the temperature at the outlet of the WHB. Cl, Combustibles and H are given as percentages and the others are in parts per million.

Keywords: Municipal solid waste incinerator; Waste heat boiler; Stack; Flue gas; PCDDs/PCDFs; Formation; Emission; Multi-regression analysis

1. Introduction

As of 1998, the incineration rate of municipal solid waste (MSW) incinerators in Korea was recorded to be about 5%. It will be increased up to about 15% in the year 2001 due to the lack of available landfill sites (Ministry of Environment, Republic of Korea, 1998).

However, the incineration-favored policy has faced the dioxin-emission problem as the construction activities of further commercial-scale incineration facilities are increased. Accordingly, the government has enforced a series of countermeasures such as the enactment of 0.1 ng-TEQ/N m^3 PCDDs/PCDFs emission standards (Ministry of Environment, Republic of Korea, 1999), management guidelines, financial assistance for the repair of incineration facilities, technical assistance for good combustion practice (GCP), designation of dioxin analysis agencies, etc. Through such a dioxin-control policy, the generation and emission concentrations of PCDDs/PCDFs at the MSW incinerators have been reduced. In this study, the formation and emission status of PCDDs/PCDFs at commercial-scale MSW incinerators with treatment capacity of above 200 ton/day were investigated through the year 1998 to provide the

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engineering data for reducing PCDDs/PCDFs emitted from MSW incinerators.

2. Material and methods

A total of nine commercial-scale MSW incinerators with treatment capacity of above 200 ton/day were selected to determine the characteristics of MSW before incineration and the formation and the emission concentrations of PCDDs/PCDFs during incineration. About two tons of MSW were analyzed every week for the past three years at the nine incineration sites in order to determine the density, the physical components, the calorific value and the elemental composition. PCDD/PCDF samplings were performed three times on each incineration site at the outlets of the WHBs and the stacks, simultaneously.

The Korean standard testing method for dioxins and furans (Ministry of Environment, Republic of Korea, 1996) was used for sampling, pretreatment and analysis. The concentrations of PCDDs/PCDFs were determined by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS: Micromass, Autospec Ultima) above 10,000 resolution with an SP-2331 column. Operation conditions of the HRGC/HRMS during PCDDs/PCDFs analysis are given in Table 1. Toxic equivalents as 2,3,7,8-TeCDD (TEQ) were calculated by using international toxicity equivalency factors (I-TEF).

3. Results

As shown in Table 2, the moisture content of the MSW incinerated in Korea was 56% (w/w) on average (Kim, 1998). The major source of moisture in the MSW was food waste, which was one of three major physical components (food, paper, and plastics). The moisture content of food waste was as high as 67% with an average of 50% (w/w) in the MSW to total MSW. Consequently, the high heating value (HHV) and the low heating value (LHV) of the MSW were, on average, only 2,129 kcal/kg and 1,661 kcal/kg, respectively, although the average carbon value was 46% of the MSW.

The formation concentrations of PCDDs/PCDFs generated at the outlets of the WHBs were in the range of 1.18–29.61 ng-TEQ/N m^3 (average 5.75 ng-TEQ/N m^3) (Table 3), and the emission concentrations at the stacks were in the range of 0.026–4.548 ng-TEQ/N m^3 (average 0.924 ng-TEQ/N m^3) (Table 4). Congener profiles of 2,3,7,8-substituted congeners as TEQ values followed almost the same pattern in both formation and emission cases; the penta- and hexa-CDFs recorded the relatively higher TEQ values than the other 2,3,7,8-substituted congeners at similar ratios (Figs. 1 and 2). Two major 2,3,7,8-substituted congeners were 2,3,4,7,8-PeCDF and 2,3,4,6,7,8-HxCDF, and their TEQ values were 50% and 64% of the total TEQ values at the outlets of the WHB and the stack, respectively. The formation and the emission concentrations of PCDFs were about three and five times higher TEQ values than those of PCDDs, respectively; the formation and the emission ratios of PCDFs to PCDDs were 78:22 and 84:16, respectively. From the results of multi-regression analysis, the formation concentration of PCDDs/PCDFs could be predicted as follows with a correlation factor of $r^2 = 0.962$: PCDDs/PCDFs (ng-TEQ/N m^3) $= 3.036$ (Cl) $+0.094$ (T_1) -0.472 (Combustibles) $+ 0.059$ (CO) -0.039 (THC) $- 3.366$ (H) $+ 22.157$, where T_1 (°C) is the temperature at the outlet of the WHB (Fig. 3). The unit of Cl, Combustibles and H is percent, and the others are in parts per million.

4. Discussion

The low quality of the MSW, which had high moisture content and low calorific value, resulted in low incineration temperature and high generation of pollutants. Also, a lot of supplemental fuel was required to increase the inside furnace temperature and reduce pollutant generation. For better and cost-effective combustion of such a low-quality MSW, the recommended

Table 1
GC/MS analytical condition of PCDDs/PCDFs

Parameters	PCDDs/PCDFs
Injector	250°C
Column	SP-2331 (60 m × 0.32 mm ID × 0.2 μm)
Oven	120°C (3 min) → 10°C/min to 200°C (3 min) → 3°C/min to 265°C (15 min)
Carrier gas	He, 2.5 ml/min
Ionization	EI, 36 eV
Ion source	270°C
Resolution	>10,000
Monitoring	4 Function, SIM (selected ion monitoring)

Table 2
Characteristics of MSW incinerated in Korea[a]

Parameters	Incinerator									
	HWD	DD	CW	ID	MD	JD	SS	PC	SK	Mean
Density (ton/m^3)	0.36	0.46	0.30	0.39	0.46	0.30	0.40	0.24	0.45	0.37
Moisture (%)	65.90	62.61	54.65	55.13	48.70	48.17	48.61	65.74	55.75	56.14
Combustibles (%)	29.61	32.59	36.83	34.42	38.79	41.38	43.43	28.57	38.81	36.05
Ash (%)	4.49	4.80	8.52	10.45	12.51	10.45	7.96	5.69	5.44	7.81
Total (%)	100	100	100	100	100	100	100	100	100	100
Plastics (%)	10.70	18.30	15.12	13.79	14.69	27.85	14.45	9.36	13.66	15.32
Paper (%)	13.20	12.50	22.59	17.18	30.90	19.60	19.27	17.23	29.11	20.18
Food (%)	67.00	51.90	42.87	58.52	31.25	44.51	50.23	60.85	41.70	49.87
Wood (%)	1.90	1.05	3.55	2.82	8.51	0.84	6.88	3.62	6.58	3.97
Textile (%)	2.60	12.45	3.96	3.90	4.12	1.21	4.58	3.40	5.49	4.63
Metals (%)	2.30	2.02	3.55	1.23	5.00	3.15	2.01	2.01	0.53	2.42
Non-metals (%)	2.30	1.78	8.36	2.56	5.53	2.84	2.58	3.53	2.93	3.60
Total (%)	100	100	100	100	100	100	100	100	100	100
HHV (kcal/kg)	1,649	1,818	2,165	1,972	2,189	2,996	2,363	1,705	2,306	2,129
LHV (kcal/kg)	1,146	1,312	1,689	1,523	1,774	2,542	1,918	1,216	1,831	1,661
C (%)	47.50	45.82	50.70	54.50	38.91	47.59	44.38	40.47	44.21	46.01
H (%)	6.68	7.34	7.45	6.35	5.91	7.41	6.88	6.14	6.61	6.75
O (%)	38.93	37.73	30.36	25.19	38.15	30.18	36.91	40.79	39.93	35.35
N (%)	1.77	1.50	1.98	2.60	1.24	1.74	2.08	2.28	1.42	1.85
S (%)	0.30	0.22	0.30	0.30	0.43	0.23	0.20	0.24	0.09	0.26
Cl (%)	0.33	2.59	0.69	0.61	2.86	2.40	1.59	4.40	2.29	1.97
Ash (%)	4.49	4.80	8.52	10.45	12.51	10.45	7.96	5.69	5.44	7.84
Total (%)	100	100	100	100	100	100	100	100	100	100

[a] *Note*: HHV – high heating value; LHV – low heating value.

approach was to reduce the moisture content and make the quality and the size of MSW homogenized and uniform prior to supplying the MSW to the furnace for reaching a stable combustion condition.

During the investigation, the formation concentration of PCDDs/PCDFs in PC incinerator was recorded to be five times higher than the average of 5.748 ng-TEQ/N m^3 in 1998. Thus, the generation status of PCDDs/PCDFs in the furnace of PC incinerator was investigated in 1999.

The result showed that PCDDs/PCDFs at the outlet of furnace were generated in the range of 0.31–1.71 ng-TEQ/N m^3 (average 1.001 ng-TEQ/N m^3 (Jung et al., 1999). If one compared these furnace-outlet results of 1999 to the WHB-outlet results of 1998, it could be guessed that PCDDs/PCDFs were severely synthesized in the WHB when the flue gas was cooled down.

Meanwhile, multi-variable regression analysis was performed to predict the formation concentration of PCDDs/PCDFs at the outlet of the WHB with the 50 or more variables such as physico-chemical properties of the MSW incinerated, operation parameters of incinerator, first and second air rate supplied, and the others related to incineration. Of course, there are some controversies on the correlation (Finkelstein et al., 1990; Addink and Olie, 1995; Karasek, 1995; Huang and Buekens, 1995; Thuß and Herzschuh, 1995; Olie et al., 1998) between PCDDs/PCDFs and some parameters such as CO, SO_2, O_2, H_2O, chlorine, etc. Huang and Buekens (1995) indicated that such terms as O_2, HCl, F.A. (fly ash), SO_2 and CO had the possibility of participating in dioxin formation reaction as a result of multiple regression analysis. However, Thuß and Herzschuh (1995) indicated that the correlation between PCDDs/PCDFs and CO is not significant or at least weaker than that between PCDDs/PCDFs and other aromatic compounds. As a consequence of this investigation, it could be deduced that the formation concentration of PCDDs/PCDFs had low correlation with most of variables, but had positive correlation with Cl content of MSW, temperature at the outlet of WHB and CO concentration in the flue gas.

5. Conclusion

- The formation concentrations of PCDDs/PCDFs generated at the outlets of waste heat boilers were in the range of 1.18–29.61 ng-TEQ/N m^3 (average 5.75 ng-TEQ/N m^3), while the emission concentrations

Table 3
Formation concentrations of PCDDs/PCDFs at the outlet of the WHBs in MSW incinerators

2,3,7,8-Substituted congeners ($ng\text{-}TEQ/N\ m^3$)		Incinerator										
		MD	CW	PC	HWD	DD	SK	JD	SS	IS	Mean	(%)
1	2,3,7,8-TCDD	0.029	0.079	0.583	0.040	0.028	0.433	0.038	0.159	0.186	0.175	3.04
2	1,2,3,7,8-PeCDD	0.085	0.089	1.569	0.071	0.091	0.693	0.065	0.336	0.285	0.365	6.35
3	1,2,3,4,7,8-HxCDD	0.018	0.012	0.457	0.019	0.031	0.123	0.017	0.072	0.048	0.088	1.54
4	1,2,3,6,7,8-HxCDD	0.100	0.024	1.420	0.055	0.084	0.360	0.066	0.081	0.098	0.254	4.42
5	1,2,3,7,8,9-HxCDD	0.043	0.019	0.809	0.030	0.041	0.259	0.033	0.108	0.071	0.157	2.73
6	1,2,3,4,6,7,8-HpCDD	0.080	0.018	0.958	0.041	0.060	0.278	0.047	0.124	0.082	0.188	3.26
7	OCDD	0.018	0.006	0.210	0.009	0.009	0.075	0.016	0.025	0.016	0.042	0.74
	Total PCDDs	0.373	0.247	6.006	0.265	0.344	2.221	0.282	0.905	0.786	1.269	22.09
8	2,3,7,8-TCDF	0.030	0.048	0.495	0.058	0.050	0.122	0.024	0.127	0.135	0.121	2.11
9	1,2,3,7,8-PeCDF	0.034	0.031	0.597	0.021	0.032	0.098	0.027	0.069	0.054	0.107	1.86
10	2,3,4,7,8-PeCDF	0.854	0.461	11.074	0.499	0.886	1.621	0.541	1.909	0.967	2.090	36.37
11	1,2,3,4,7,8-HxCDF	0.162	0.066	1.667	0.053	0.106	0.252	0.094	0.199	0.125	0.303	5.27
12	1,2,3,6,7,8-HxCDF	0.308	0.139	2.823	0.118	0.198	0.539	0.191	0.476	0.278	0.563	9.80
13	2,3,4,6,7,8-HxCDF	0.734	0.139	4.438	0.117	0.199	0.511	0.336	0.690	0.270	0.826	14.37
14	1,2,3,7,8,9-HxCDF	0.078	0.024	0.580	0.016	0.015	0.086	0.050	0.076	0.035	0.107	1.86
15	1,2,3,4,6,7,8-HpCDF	0.223	0.068	1.515	0.031	0.053	0.238	0.119	0.207	0.097	0.283	4.93
16	1,2,3,4,7,8,9-HpCDF	0.059	0.007	0.277	0.005	0.007	0.033	0.026	0.039	0.017	0.052	0.91
17	OCDF	0.042	0.004	0.136	0.001	0.001	0.010	0.013	0.015	0.007	0.025	0.44
	Total PCDFs	2.524	0.987	23.598	0.919	1.547	3.510	1.421	3.807	1.985	4.478	77.91
	Total PCDDs/PCDFs	2.894	1.232	29.610	1.183	1.892	5.732	1.701	4.713	2.771	5.748	100.00

Table 4
Emission concentrations of PCDDs/PCDFs at the stacks of MSW incinerators

2,3,7,8-substituted congeners (ng-TEQ/N m^3)		Incinerator										
		MD	CW	PC	HWD	DD	SK	JD	SS	IS	Mean	%
1	2,3,7,8-TCDD	0.002	0.003	0.011	0.007	0.002	0.005	0.084	0.036	0.027	0.020	2.14
2	1,2,3,7,8-PeCDD	0.004	0.002	0.025	0.030	0.005	0.008	0.234	0.137	0.036	0.053	5.78
3	1,2,3,4,7,8-HxCDD	0.001	0.000	0.006	0.010	0.001	0.001	0.043	0.031	0.007	0.011	1.21
4	1,2,3,6,7,8-HxCDD	0.002	0.001	0.018	0.024	0.003	0.003	0.132	0.070	0.015	0.030	3.23
5	1,2,3,7,8,9-HxCDD	0.002	0.001	0.009	0.017	0.002	0.002	0.061	0.040	0.008	0.016	1.70
6	1,2,3,4,6,7,8-HpCDD	0.001	0.001	0.012	0.017	0.003	0.001	0.035	0.040	0.014	0.014	1.48
7	OCDD	0.000	0.000	0.002	0.002	0.000	0.000	0.004	0.008	0.004	0.002	0.25
	Total PCDDs	0.012	0.009	0.084	0.107	0.015	0.021	0.592	0.362	0.111	0.146	15.79
8	2,3,7,8-TCDF	0.000	0.001	0.011	0.006	0.002	0.004	0.063	0.006	0.025	0.013	1.43
9	1,2,3,7,8-PeCDF	0.000	0.001	0.008	0.004	0.001	0.002	0.064	0.018	0.013	0.012	1.33
10	2,3,4,7,8-PeCDF	0.007	0.010	0.164	0.129	0.027	0.039	2.137	0.788	0.271	0.397	42.95
11	1,2,3,4,7,8-HxCDF	0.001	0.001	0.019	0.016	0.004	0.003	0.131	0.067	0.039	0.031	3.39
12	1,2,3,6,7,8-HxCDF	0.002	0.003	0.044	0.036	0.009	0.007	0.371	0.194	0.097	0.085	9.17
13	2,3,4,6,7,8-HxCDF	0.002	0.003	0.074	0.041	0.008	0.009	1.056	0.399	0.175	0.196	21.22
14	1,2,3,7,8,9-HxCDF	0.001	0.000	0.009	0.006	0.001	0.001	0.049	0.025	0.019	0.012	1.34
15	1,2,3,4,6,7,8-HpCDF	0.000	0.001	0.019	0.011	0.003	0.002	0.072	0.071	0.051	0.026	2.78
16	1,2,3,4,7,8,9-HpCDF	0.000	0.000	0.002	0.002	0.000	0.000	0.011	0.010	0.012	0.004	0.47
17	OCDF	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.002	0.007	0.001	0.15
	Total PCDFs	0.014	0.020	0.350	0.252	0.056	0.068	3.956	1.580	0.709	0.778	84.21
	Total PCDDs/PCDFs	0.026	0.029	0.434	0.359	0.070	0.088	4.548	1.942	0.820	0.924	100

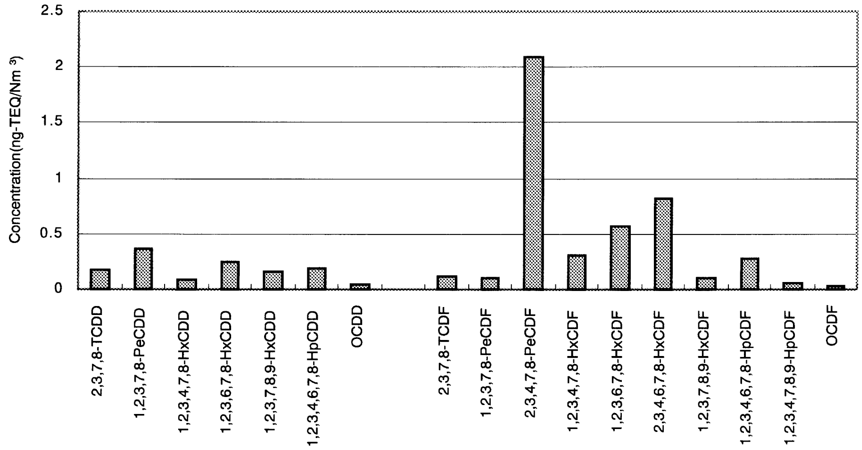

Fig. 1. Congener profile of 2,3,7,8-PCDDs/PCDFs at the outlet of the WHB.

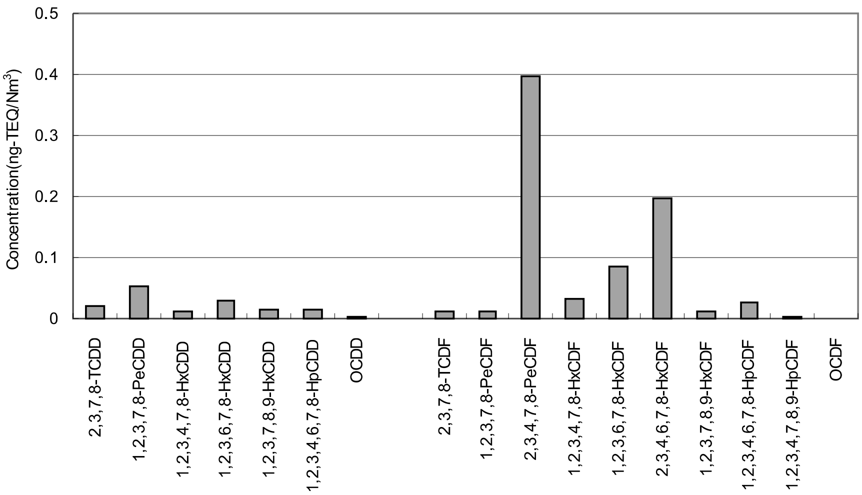

Fig. 2. Congener profile of 2,3,7,8-PCDDs/PCDFs at the stacks of MSW incinerators.

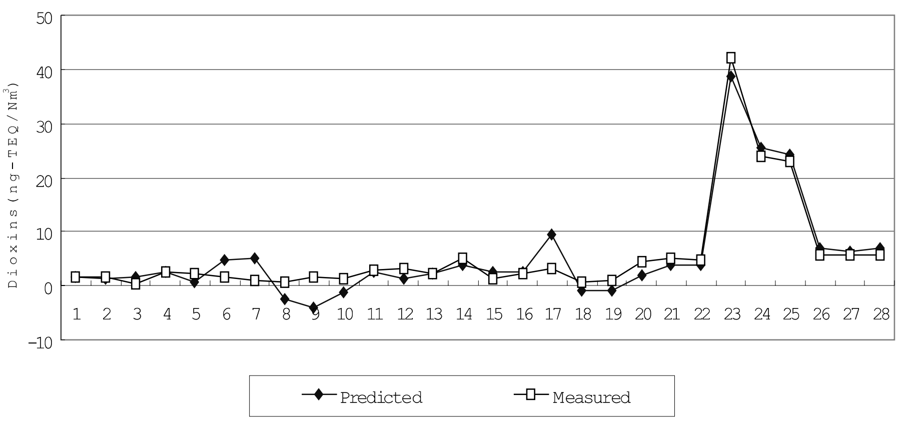

Fig. 3. Comparison of formation concentration measured and predicted at the outlet of the WHB.

at the stacks were in the range of 0.026–4.548 ng-TEQ/N m^3 (average 0.924 ng-TEQ/N m^3).

- Two major 2,3,7,8-substituted congeners were 2,3,4,7,8-PeCDF and 2,3,4,6,7,8-HxCDF, the TEQ values of which were 50% and 64% of the total values at the outlet of the WHB and the stack, respectively.
- As a result of multi-regression analysis, the formation concentration of PCDDs/PCDFs at the outlet of WHB could be predicted with a correlation factor of $r^2 = 0.962$ as follows: PCDDs/PCDFs (ng-TEQ/N m^3) $= 3.036\,(\mathrm{Cl}) + 0.094\,(T_1) - 0.472$ (Combustibles) $+ 0.059\,(\mathrm{CO}) - 0.039\,(\mathrm{THC}) - 3.366(\mathrm{H}) + 22.157$, where T_1 (°C) is the temperature at the outlet of the WHB, and the unit of Cl, Combustibles and H is percent and the others are in parts per million.
- The formation concentration of PCDDs/PCDFs had positive correlation with Cl content of MSW, temperature (°C) at the outlet of WHB and CO concentration in the flue gas.

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