Characteristics of PCDD/F content in fly ash discharged from municipal solid waste incinerators

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ABSTRACT

Different from most previous studies with quantity-limited data, this paper presents PCDD/F content characterization in the fly ash discharged from sixteen large-scale commercial MSWIs. From the results with over hundreds of data using periodically sampling and analysis, it was found that the PCDD/F contents in the fly ash were from 9.07 to 46.68 ng/g, d.w., and if based on international toxicity equivalent quantity, they were from 0.78 to 2.86 ng I-TEQ/g, d.w. The higher chlorinated PCDDs likely dominated more than lower chlorinated PCDDs, but this tendency was not for PCDFs. The OCDD had the highest contribution to the total PCDD/F content, but if based on I-TEQ content, 2,3,4,7,8-PeCDF is the PCDD/F congener with the highest toxicity contribution. Moreover, the PCDD/F characteristic index (DCI) is suggested using the representative congener content of 2,3,4,7,8-PeCDF to characterize the fly ash. The DCI is $0.875 \pm 7.6\%$ for the fly ash discharged from the MSWI with the APCD assembly of SD, AC and BF. The findings obtained in this work provide overview information on the PCDD/F content characterization in fly ash. They will provide PCDD/F fingerprint information to distinguish from other PCDD/F sources, like steel refinery industry, hazardous waste incinerators, or cement kilns, and thus be applied to fly ash management in the environment.

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1. Introduction

In recent years atmospheric emissions from many thermal processes have been the subject of public concern. One of them is that combustion of organic matter leads to some toxic pollutant emissions. It is widely recognized that the combustion process in the presence of chlorine and metals is a major source of polychlorinated dibenzo-*p*-dioxin (PCDD), polychlorinated dibenzofuran (PCDF) and other toxicants released into the environment. All published reports confirm that the PCDD/F is a cancer hazard to people. It can cause immune system damage and interfere with the regulatory hormones [1–3]. A number of technical issues remain for mass-burn systems and further research is warranted. One of these issues is PCDD/Fs control, which seems to be a problem in early design plants. The issue of PCDD/F emissions continues to be major in permission applications and public relations. PCDD/F emits from municipal solid waste incinerator (MSWI) in the flue gases, the fly ash, and the bottom ash or slag. As a result, stringent regulations have been enforced with the aim of reducing the PCDD/F

emission into the environment. Previous researches also indicated that the PCDD/F content in fly ash could increase as the fly ash passes through air pollution control device (APCD) zone [4]. The APCD environment (e.g. temperature and oxygen concentration) may actually affect the PCDD/F content in fly ash. So far, the environmental protection agencies of many countries have classified MSWI fly ash as hazardous material or usually regulate it as hazardous waste because the PCDD/F content in the fly ash is over the regulation limit (e.g. 1.0 ng I-TEQ/g, Taiwan). It is required further treatment of MSWI fly ash before its disposal into final landfills [5]. Thereby, the fly ash control and management is an important issue of concern.

Some researches have investigated the PCDD/F content in the fly ash discharged from MSWIs. They have also conducted studies on the PCDD/F characteristics in the fly ash with available treatment technologies [6–10]. For example, Cains and Eduljess [11] indicated that most PCDD/F species would exist in ESP fly ash. The distribution ratio of PCDD/F species between stack and ESP was about 0.075–0.229. Chang and Chung [12] studied the PCDD/F content in MSW incinerated fly ash, and surveyed the PCDD/F levels in fly ash in major countries. They found that the PCDD/Fs in fly ash were in the range of 0.47–25.74 ng I-TEQ/g, and that fine fly ash particles usually have higher PCDD/F content than large fly ash particles.

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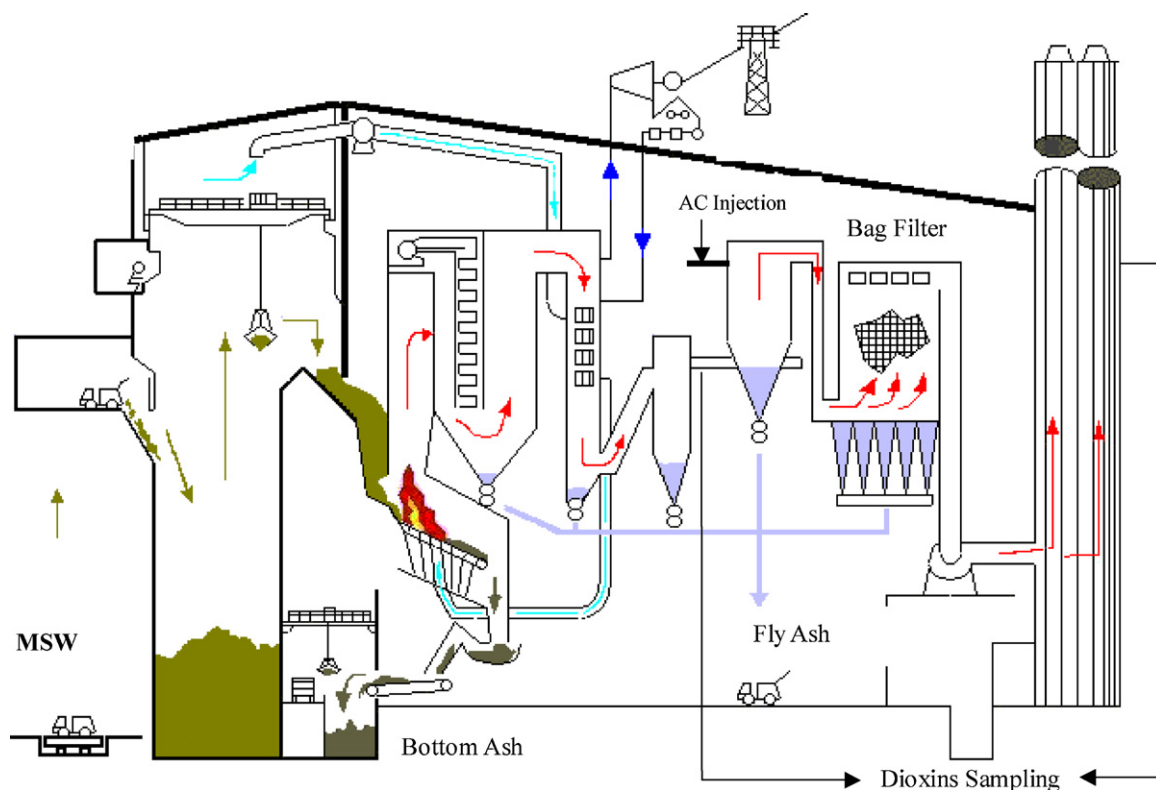 *E-mail address:* ymchang@ntut.edu.tw (Y.-M. Chang).

Fig. 1. Sampling positions and schematic diagram of MSWI plant in northern Taiwan (designed capacity: 900 Mg/D).

Takasuga et al. [13] studied the formation of PCDD/Fs using dioxin-free ash as a catalyst and the relation with several chlorine-sources. Wilkström and Marklund [14] indicated that the most important variable for changes in PCDDs/PCDFs formation in fly ash or flue gas was disturbance in the combustion condition and not the variation in chlorine content in the feeding wastes. Zhou et al. [15] found that non-thermal plasma technology is capable of effectively destroying PCDD/F compounds in fly ash. The highest destruction efficiency reached 81% for the 2,3,7,8-TeCDD compound in fly ash. Misaka et al. [16] studied removal of PCDD/Fs and dl-PCBs in MSWI fly ash with PCDD/F content of 4.70 ng I-TEQ/g by heating under vacuum. Lundin and Marklund [17] indicated that the total amount of PCDD and PCDF increased as the temperature decreased in the post combustion zone. The increase was due to both adsorption to the fly ash and the formation of PCDD and PCDF. Chen et al. [18] studied the homologue distribution of PCDD/Fs in the fly ash emitted from incinerators. They also indicated that there is a strong correlation between the content of 2,3,4,7,8-PeCDF and the I-TEQ value of fly ash. Chang et al. [19] indicated that the fly ash discharged from municipal solid waste incinerators contained high PCDD/F content as well as heavy metals, and showed excellent treatment efficiency for the fly ash using thermal treatment with DC double arc argon plasma.

Recently, Taiwan local governments have gradually focused on PCDD/F inventory management strategies from air pollution to solid waste (e.g. fly ash), after they have well managed PCDD/F emissions from industrial stacks [19]. Solidification and then land-fill are now still the available treatment methods for fly ash in Taiwan, though some technology advances in the past years has dramatically demonstrated to decrease the PCDD/F levels in the fly ash and slag, like recent studies have shown that melting or plasma treatment of incinerator residues can reduce the PCDD/F levels by more than 95% [20–22]. However, it is still necessary to characterize the PCDD/F content in fly ash to avoid hazardous impact on the environment in long-term final disposal. Because the impact of haz-

ardous gaseous PCDD/Fs on the environment is more serious due to air transportation, numerous researches have studied PCDD/F emissions from stacks. Generally, only about 10% of the PCDD/F inventory comes from air pollution, including gaseous PCDD/Fs and suspended particular matter in flue gas. Most PCDD/Fs exist in the fly ash during the incineration process. The PCDD/F content in fly ash usually exceeds the national standards in Taiwan. Fly ash is regulated as a hazardous waste. Investigation into the PCDD/F content in fly ash is important for fly ash management in Taiwan. This paper presents the monthly data in 2008 to characterize the PCDD/F content in the fly ash discharged from the sixteen MSWIs in Taiwan. It is expected that these data will provide the PCDD/F fingerprint information to distinguish it from other PCDD/F sources, and thus be applicable to fly ash management.

2. Experimental methods

There are now twenty-four large MSWI facilities in operation in Taiwan. Of them, the sixteen MSWIs investigated in this study have similar incinerator types and APCD systems, assembly of semi-drying scrubber (SD), activated carbon injector (AC) and baghouse filter (BF) as listed in Table 1. The monthly samplings in the study were conducted in 2008, in which the sampling time interval was 3–4 weeks exclusively in the maintenance period. Fig. 1 shows the ash sampling position at the incineration plants. Typical ash samples were a mixture of the ashes collected from the boiler and bag filter. Fly ash mixture was collected at a weight of 20 kg or so from both boiler and baghouse conveyor drainers using regulated sampling tools. This fly ash was then reduced down to about 1.0 kg by well cross-mixing for laboratory analysis. Local legal-permitted companies carried out laboratory analysis for PCDD/Fs.

Fly ash sampling, cleanup, and quantification for PCDD/F analysis were conducted in accordance with the current Standard Protocols, in which analytical and sampling procedures are described in detail [Taiwan NIEA 119.00 & NIEA M801.11B,

Table 1
Incineration features for twenty MSWIs in Taiwan.

Incinerator plant	Year of operation beginning	Capacity (ton/D@24 h)	Incineration temperature (°C)	Feeding rate of activated carbon (mg/Nm³)
T1	1999	1800	850–980	60–121
T2	2001	1350	880–990	55–124
T3	1995	1350	750–1030	90–176
T4	1994	900	780–990	78–122
T5	2001	1350	750–960	55–98
T6	2001	900	790–950	60–120
T7	1995	900	780–960	89–168
T8	2000	900	760–1020	75–139
T9	2004	900	830–990	76–120
T10	2001	900	840–1010	87–145
T11	1998	300	840–980	102–185
T12	2001	900	790–1020	56–88
T13	1999	900	870–990	102–188
T14	2001	900	860–980	75–135
T15	2001	1350	830–970	98–134
T16	2006	600	770–960	54–89

Incinerator type: mass-burning, based on averaged yearly data. Air pollution control devices: SD + AC + BF; SD: semi-dry scrubber, AC: activated carbon injector, BF: baghouse filter.

similar to USEPA M23 & 8290]. In recent years, particularly with advances in analytical chemistry techniques, the measurement of PCDD/F contents has become easier and more reliable, particularly using high-resolution mass spectrometry and high-resolution gas chromatography (HRMS/HRGC). Following standard extraction and chromatographic cleanup, sample extract analyses were conducted to analyze PCDD/Fs with congeners using HRGC/HRMS after 48 h toluene extraction in a certified laboratory.

The HRGC used was a Hewlett Packard 6970 series gas chromatograph, where chromatographic separation was achieved with a DB-5 (J&W Scientific, CA, USA) fused-silica capillary column (60 m × 0.25 mm ID, 0.25 μm film thickness) with helium as the carrier gas in the splitless injection mode (1–2 μL). The temperature program for chromatographic separation was: 140–200 °C (1 min) at 20 °C/min, then at 3 °C/min to 300 °C and held isothermally for 20 min at 300 °C. Syringes for analyses were washed with two kinds of solvents: n-hexane and dichloromethane. The HRMS used was a Micromass Autospec Ultima (UK) mass spectrometer with a positive electron impact (EI+) source. The analyzer mode was selected ion monitoring (SIM). The electron energy was set at 35 eV, and the source temperature was set at 250 °C. An CTC A200S autosampler (CTC Analytics AG, GCPAL, Switzerland) was equipped with a pull-up speed of 55 μL/s and injection speed of 55 μL/s.

Only seventeen PCDD/F surrogates with higher toxic equivalent factors, like tetra-chlorinated dibenzo-p-dioxins (TeCDDs) were analyzed. Other PCDD/F surrogates like polychlorinated biphenyls, or coplanar were not included and studied in this work because they are not regulated in the Taiwan pollution standards. The international toxic equivalent quantity (I-TEQ) as 2,3,7,8-TCDD was calculated using international toxicity equivalency factors (I-TEF). Quality criteria were based on quality control (QC) and quality assurance (QA) application measures such as analysis of a blank sample covering the complete analytical procedure [23].

3. Results and discussion

As other investigations found, the patterns of normalized distribution for PCDD/F congeners exhibited characterization similarities in many effluents though they are dependent on many variables such as waste characterization, incineration conditions, APCD systems and incinerator types. A series of monthly sampling and PCDD/F concentration analysis from sixteen commercial MSW incineration plants were carried out under well-defined QA/QC

requirement in this work. The results and discussion are presented as follows:

3.1. PCDD/F Contents in fly ash

Table 2 lists the annual-average data of PCDD/Fs for the sixteen MSWIs in 2008. It was found that the PCDD/Fs in the fly ash discharged from the sixteen MSW incinerators were from 46.48 ng/g to 9.07 ng/g, and 23.53 ng/g on average (SD = 10.24, N = 16). If based on international toxicity equivalent quantity, they were from 2.87 ng I-TEQ/g to 0.78 ng I-TEQ/g (as listed in Table 3), and 1.87 ng I-TEQ/g on average (SD = 0.57, N = 16). The order of magnitude of these values is likely consistent with those found in Asia area [16,18], but more than those found in American or Europe Area [24–26].

The variation in PCDD/F contents in fly ash resulted from waste compositions, incineration performance and APCD conditions [27]. The former would be the major effect. In fact, it is necessary to know the PCDD/F content variation due to waste composition. In this work, MSW properties were collected from Taiwan EPA information center, including physical composition, approximate analysis (moisture, combustible matter and ash), ultimate analysis and heating value [28,29].

Table 4 lists the annual data for the characteristics of MSW generated from Taiwan during October 2008 to September 2009. The data is the average results of MSW generated in Taiwan, not the case study of one incinerator. About 95% of the MSW (on a dry basis) is comprised of organic or combustible materials (categorized by paper, wood/garden trimmings, cloth, plastics, food waste, rubber/leather, and others). The remaining 5% is non-combustible materials (categorized by metal, glass, ceramic and other inert materials). In general, plastic waste and cloth (textile) waste are the major components in Taiwan MSW. In addition, the organic chlorine content in the refuse varied from 0.04% to 0.63% (average 0.26%).

3.2. Distribution of PCDD/F congeners

From the results obtained in this work, the distribution profiles of the original contents of 17 major PCDD/F congeners are macroscopically similar, as shown in Fig. 2. The OCDD had the highest contribution to the total PCDD/F content, and its contribution percentage to total PCDD/F content ranged from 51.5% to 23.8% (average 35.7%). Other congeners with higher percentage in order are 1,2,3,4,6,7,8-HpCDD (13.4%), 2,3,7,8-TeCDF (10.0%), and 2,3,4,7,8-PeCDF (9.2%). It was found that the higher chlorinated PCDDs likely dominate more than lower chlorinated PCDDs in the fly ash, but the tendency was not obvious for PCDFs.

Many factors affect PCDD/F congener distribution in fly ash. One of them is the activated carbon, because fly ash generated in Incineration partly comes from AC. In general, the AC is applied in three ways, i.e., entrained flow or called activated carbon injection, fixed bed and moving bed adsorption. In most cases, powder activated carbon (PAC) is injected upstream of the baghouse filter and accumulates on the filter bag surface, and flue gases are made to pass through the AC and residual dust layer. Therefore, the vapor/solid-phase PCDD/Fs and particulate matter in the raw gas of the MWIs can both be removed in the meantime, and hence become a part of fly ash. Besides the properties and quantity of AC particles in flue gas, the chemical properties of PCDD/F congeners are also important to PCDD/F characterization in fly ash. In addition, PCDD/F molecular equilibrium between solid and vapor-phases in the flue gas is another effect, which relates to the vapor pressures of the PCDD/F congeners. In certain conditions at a given temperature, it is likely a linear function of the saturation vapor pressure. Generally lower chlorinated congeners with higher vapor pressures have higher gaseous fractions at a specific temperature

Table 2
Average PCDD/F congener original concentration for each MSWI plant (ng/g).

PCDD/Fs (ng/g)	MSWI Plant															
	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14	T15	T16
2,3,7,8-TeCDD	0.1101	0.0701	0.0556	0.0153	0.0436	0.0231	0.0265	0.0229	0.0741	0.0724	0.0791	0.0672	0.0051	0.0147	0.0354	0.1236
1,2,3,7,8-PeCDD	0.1524	0.2451	0.2002	0.1488	0.1843	0.1642	0.0939	0.1616	0.2511	0.2784	0.2032	0.1799	0.1341	0.3395	0.3365	0.6238
1,2,3,4,7,8-HxCDD	0.1915	0.0901	0.2068	0.0481	0.1921	0.0553	0.1149	0.2236	0.2555	0.2585	0.1315	0.1431	0.0552	0.0351	0.1490	0.3831
1,2,3,6,7,8-HxCDD	0.4934	0.1731	0.6299	0.1121	0.5212	0.1438	0.2321	0.6656	0.5015	0.4211	1.2428	0.2185	0.2353	0.0793	0.5566	0.6983
1,2,3,7,8,9-HxCDD	0.3729	0.1521	0.4749	0.0838	0.3721	0.0978	0.1751	0.4187	0.3805	0.3819	0.2906	0.2062	0.1674	0.3552	0.3541	0.5835
1,2,3,4,6,7,8-HpCDD	4.2231	1.1960	4.7767	1.0575	4.5399	1.2885	2.5586	4.7097	4.3907	3.4855	2.8541	1.9151	2.0448	0.7375	5.5684	6.3189
OCDD	16.9101	2.7111	11.444	3.3711	9.3899	5.7603	11.306	8.2293	16.617	12.169	4.9276	7.0909	4.1466	2.8558	4.5604	23.9361
2,3,7,8-TeCDF	1.0101	1.6212	2.3421	1.3602	2.8173	5.6801	2.7329	3.0766	1.5041	2.1811	1.4585	0.7195	1.2864	1.3682	1.4183	2.6343
1,2,3,7,8-PeCDF	1.2200	1.2721	1.3643	1.1203	1.3957	1.1912	2.1825	1.9322	1.5360	2.7251	0.6827	0.5613	1.0595	0.1301	1.2374	1.2076
2,3,4,7,8-PeCDF	3.2201	1.8930	2.2359	2.9693	1.9311	2.8162	1.2893	1.1917	2.2866	2.3475	1.4464	2.3511	0.9397	0.5047	1.1809	2.7167
1,2,3,4,7,8-HxCDF	0.9478	0.3690	0.5099	0.1695	0.6949	0.2245	0.3579	0.5813	0.9151	1.2921	0.7150	0.7858	0.1101	0.1554	0.2843	1.7655
1,2,3,6,7,8-HxCDF	0.2406	0.4221	0.586	0.1897	0.8032	0.2632	0.3764	0.7046	1.0353	1.4247	0.8412	0.8692	0.1446	0.1945	0.3519	1.0446
1,2,3,7,8,9-HxCDF	1.8302	0.2051	1.4559	1.1473	0.741	0.2243	0.2462	0.9898	0.9561	0.9332	1.6936	1.5466	1.2107	0.6508	1.3698	1.4920
2,3,4,6,7,8-HxCDF	1.8258	0.4192	0.6779	0.2065	1.1528	0.2999	0.5048	0.9322	1.2305	1.7568	0.8098	0.8391	0.2241	0.3075	0.4506	0.4590
1,2,3,4,6,7,8-HpCDF	1.0551	0.2371	0.3601	0.2599	1.9735	0.8773	1.3381	0.2224	0.5603	2.0523	2.1347	1.2707	0.5956	1.0766	0.9606	0.4623
1,2,3,4,7,8,9-HpCDF	1.4406	0.1621	0.3227	0.0893	0.5277	0.1711	0.2604	0.4084	0.7017	0.9446	0.4157	0.3961	0.0989	0.1896	0.1562	1.3650
OCDF	0.5647	0.1170	0.1747	0.0544	0.3618	0.1028	0.1187	0.3044	0.3357	0.4311	0.2356	0.2057	0.0615	0.0763	0.1147	0.6684
Total (ng/g)	35.8085	11.3551	27.8176	12.4030	27.6419	19.3836	23.9143	24.775	33.5318	33.1553	20.1620	19.3660	12.5195	9.0708	19.0851	46.4827
Standard deviation[a]	3.3456	2.1342	5.6712	3.8901	7.8911	2.2213	8.3412	6.7122	9.3412	6.1232	3.4512	6.7511	4.3352	1.6540	3.2314	6.2134

[a] Based on 12 samples ($N = 12$) of total PCDD/F content (ng/g) for each MSWI plant.

Table 3
Average PCDD/F congener toxicity-equivalent concentration for each MSWI plant (ng I-TEQ/g).

PCDD/Fs (ng I-TEQ/g)	MSWI plant															
	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14	T15	T16
2,3,7,8-TeCDD	0.1101	0.0701	0.0556	0.0153	0.0436	0.0231	0.0265	0.0229	0.0741	0.0724	0.0791	0.0672	0.0050	0.0147	0.0354	0.1236
1,2,3,7,8-PeCDD	0.0762	0.1226	0.1001	0.0744	0.0922	0.0821	0.0470	0.0808	0.1256	0.1392	0.1016	0.0900	0.0671	0.1698	0.1683	0.3119
1,2,3,4,7,8-HxCDD	0.0192	0.0090	0.0207	0.0048	0.0192	0.0055	0.0115	0.0224	0.0256	0.0259	0.0132	0.0143	0.0055	0.0035	0.0149	0.0383
1,2,3,6,7,8-HxCDD	0.0493	0.0173	0.0630	0.0112	0.0521	0.0144	0.0232	0.0666	0.0502	0.0421	0.1243	0.0219	0.0235	0.0079	0.0557	0.0698
1,2,3,7,8,9-HxCDD	0.0373	0.0152	0.0475	0.0084	0.0372	0.0098	0.0175	0.0419	0.0381	0.0382	0.0291	0.0206	0.0167	0.0355	0.0354	0.0584
1,2,3,4,6,7,8-HpCDD	0.0422	0.0120	0.0478	0.0106	0.0454	0.0129	0.0256	0.0471	0.0439	0.0349	0.0285	0.0192	0.0204	0.0074	0.0557	0.0632
OCDD	0.0169	0.0027	0.0114	0.0034	0.0094	0.0058	0.0113	0.0082	0.0166	0.0122	0.0049	0.0071	0.0041	0.0029	0.0046	0.0239
2,3,7,8-TeCDF	0.1010	0.1621	0.2342	0.1360	0.2817	0.5680	0.2733	0.3077	0.1504	0.2181	0.1459	0.0720	0.1286	0.1368	0.1418	0.2634
1,2,3,7,8-PeCDF	0.0610	0.0636	0.0682	0.0560	0.0698	0.0596	0.1091	0.0966	0.0768	0.1363	0.0341	0.0281	0.0530	0.0065	0.0619	0.0604
2,3,4,7,8-PeCDF	1.6101	0.9465	1.1180	1.4847	0.9656	1.4081	0.6447	0.5959	1.1433	1.1738	0.7232	1.1756	0.4699	0.2524	0.5905	1.3584
1,2,3,4,7,8-HxCDF	0.0948	0.0369	0.0510	0.0170	0.0695	0.0225	0.0358	0.0581	0.0915	0.1292	0.0715	0.0786	0.0110	0.0155	0.0284	0.1766
1,2,3,6,7,8-HxCDF	0.0241	0.0422	0.0586	0.0190	0.0803	0.0263	0.0376	0.0705	0.1035	0.1425	0.0841	0.0869	0.0145	0.0195	0.0352	0.1045
1,2,3,7,8,9-HxCDF	0.1830	0.0205	0.1456	0.1147	0.0741	0.0224	0.0246	0.0990	0.0956	0.0933	0.1694	0.1547	0.1211	0.0651	0.1370	0.1492
2,3,4,6,7,8-HxCDF	0.1826	0.0419	0.0678	0.0207	0.1153	0.0300	0.0505	0.0932	0.1231	0.1757	0.0810	0.0839	0.0224	0.0308	0.0451	0.0459
1,2,3,4,6,7,8-HpCDF	0.0106	0.0024	0.0036	0.0026	0.0197	0.0088	0.0134	0.0022	0.0056	0.0205	0.0213	0.0127	0.0060	0.0108	0.0096	0.0046
1,2,3,4,7,8,9-HpCDF	0.0144	0.0016	0.0032	0.0009	0.0053	0.0017	0.0026	0.0041	0.0070	0.0094	0.0042	0.0040	0.0010	0.0019	0.0016	0.0137
OCDF	0.0006	0.0001	0.0002	0.0001	0.0004	0.0001	0.0001	0.0003	0.0003	0.0004	0.0002	0.0002	0.0001	0.0001	0.0001	0.0007
Total (ng I-TEQ/g)	2.6332	1.5667	2.0964	1.9796	1.9807	2.3010	1.3543	1.6173	2.1711	2.4640	1.7155	1.9367	0.9699	0.7809	1.4210	2.8663
Standard deviation	2.1541	0.1235	0.3185	0.3125	0.2254	0.1785	0.2196	0.2547	0.4086	0.3235	0.1542	0.3342	0.1521	0.0652	0.1312	0.2218

Based on 12 samples ($N = 12$) of total PCDD/F content (ng I-TEQ/g) for each MSWI plant.

Table 4
Typical annual data of characteristics for the feeding MSW studied in this work.

Items	Composition	Physical composition (wt.%)		Moisture	Ash		Combustible wet base	High heating value (HHV)		Low heating value (LHV)		Chemical element wet base						
		Dry base (%)	Wet base (%)	(%)	Dry base (%)	Wet base (%)	(%)	Dry base Kcal/kg	Wet base Kcal/kg	Dry base Kcal/kg	Wet base Kcal/kg	C (%)	H (%)	N (%)	O (%)	S (%)	Org.Cl (%)	(C/N)
Combustibles	1.Paper	13.84	19.13	56.47	12.29	5.35	38.18	3712	1616	3241	1411	19.79	2.45	0.52	14.12	1.04	0.27	38.06
	2.Cloth/textile	19.33	21.31	45.41	12.94	7.06	47.52	4011	2189	3585	1957	25.64	2.84	1.74	16.89	0.00	0.42	14.74
	3.Wood/garden trimmings	17.92	18.58	41.97	13.65	7.92	50.11	3852	2235	3443	1998	25.72	2.91	1.20	20.14	0.07	0.06	21.43
	4.Food waste	12.73	16.39	53.29	9.47	4.42	42.29	1205	563	787	368	14.72	1.82	1.06	24.59	0.06	0.05	13.89
	5.Plastics	22.03	14.75	10.14	6.72	6.04	83.82	7221	6489	6722	6041	54.47	8.11	2.05	18.12	0.44	0.63	26.57
	6.Lether/rubber	5.23	4.37	27.95	17.77	12.80	59.25	3645	2626	3272	2357	30.57	3.81	3.92	19.98	0.92	0.04	7.80
	7.other organics	3.58	2.19	1.40	9.61	9.48	89.12	4128	4070	3810	3757	45.83	5.73	2.82	33.67	0.75	0.32	16.25
Incombustible	8.Metals	0.89	0.55	2.40	100	97.60	0	0	0	0	0	–	–	–	–	–	–	–
	9.glass	1.76	1.09	2.85	100	97.15	0	0	0	0	0	–	–	–	–	–	–	–
	10.Ceramic	1.79	1.09	1.22	100	98.78	0	0	0	0	0	–	–	–	–	–	–	–
	11.Sand/stone and inert	0.90	0.55	1.71	100	98.29	0	0	0	0	0	–	–	–	–	–	–	–
Overall*		100.00	100.00	39.83	15.95	9.59	50.58	4062	2444	3647	2195	26.82	3.40	1.40	18.36	0.34	0.26	19.16

Bulk density 214 kg/m³ (2006.10–2007.09 average*).

as compared to the highly chlorinated ones. Since activated carbon can effectively remove gas-phase PCDD/Fs and it is ineffective in removing particle-bound PCDD/Fs, the partitioning of these compounds plays a significant role in the PCDD/F congener distribution in the fly ash.

Smolka and Schmidt [30] presented a theoretical and experimental study on the partitioning of PCDD/Fs in the flue gas at low temperatures before and after an AC filter. They reported that the gaseous fraction was higher before the AC unit and that the gaseous fraction increased as the vapor pressure increases, in compliance with theoretical results showing higher gas/particle ratios for lower chlorinated PCDD/Fs. This means that highly volatile congeners were adsorbed comparatively more strongly than lower volatile ones. Higher chlorinated PCDD/F congeners have lower vapor pressures, and thus more easily condensed into fly ash. Therefore, it would explain why the highly chlorinated PCDD congeners dominate in the fly ash as found in this study, but the explanation is difficult for PCDF congeners. Maybe, it needs more information and investigation on the issue in the near future. Based on I-TEQ, Fig. 3 shows the distribution profiles of 17 major PCDD/F congeners. This indicates that the PCDD/F congener with the highest contribution percentage is 2,3,4,7,8-PeCDF and it ranged from 75.0% to 32.3% and 51.5% on average.

3.3. Distribution of PCDD/F homologues

Basically, the major effects on homologue distribution are the chlorine in feeding waste and chemical stability of the PCDD/F homologue formed during incineration. Other effects would be chemical composition in fly ash, like carbon and catalytic heavy metals [31]. PCDD/F homologue distribution represents chlorination degree of PCDD/F molecular, and thus characterizes the PCDD/F toxicity. As shown in Fig. 4, the results found that highly chlorinated homologues were dominant for PCDDs, but lowly chlorinated homologues were dominant for PCDFs, where the homologues of TeCDD, PeCDD, HxCDD, and etc. indicate sum of each isomers. This result was likely consistent with those found by Chang and Huang [4] and Chen et al. [18]. The possible reason is that PCDDs with high chlorination would be more stable due to a more symmetrical molecular structure, e.g. OCDD is more chemically stable than PeCDD. The OCDD had the highest contribution to the total PCDD/F content, and its contribution percentage to total PCDD/F content ranged from 51.5% to 23.8% (average 35.7%). Other homologues with higher percentage in order were PeCDF (15.2%), HpCDD (13.5%) and HxCDF (13.0%). However, based on I-TEQ, the PCDD/F homologue with the highest contribution percentage is PeCDF and it ranged from 83.1% to 33.2% and 54.7% on average, as shown in Fig. 5. This reveals that the major source of PCDD/F toxicity comes from PeCDF homologue due to its relatively higher concentration quantity and toxicity factor.

However, the detail description regarding the PCDD/F congener or homologue formation in fly ash would not be more addressed from these results obtained in this paper, which just aims on the characteristics of the PCDD/F content based on annual-averaged data with an overview point on fly ash management. Therefore, these relevant issues derived in this paper, like the difference of PCDD/F congener formation in fly ash, may need more intensive study in the near future.

3.4. PCDDs/PCDFs ratio

So far, the difference of information mechanism between PCDDs and PCDFs in not clear because their chemical reaction and formation stability are more complex than the theoretical explanation during high thermal process. However, the PCDDs/PCDFs ratio would be a rough and practically useful index to identify the
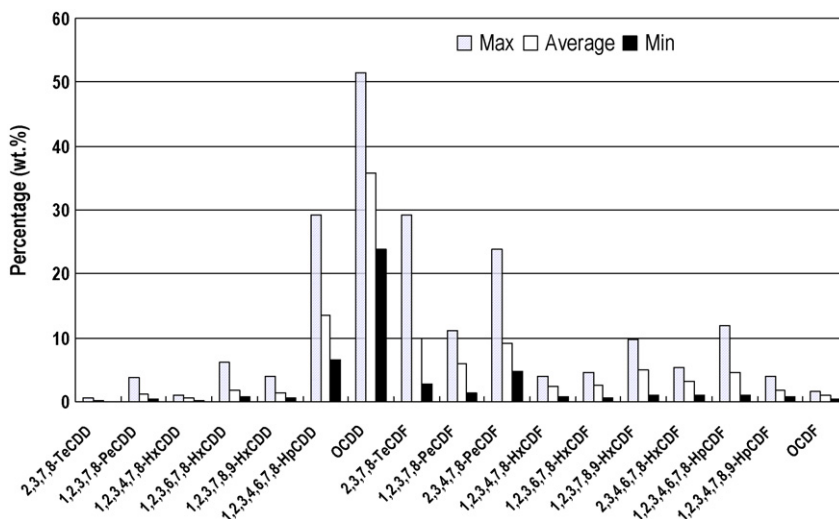
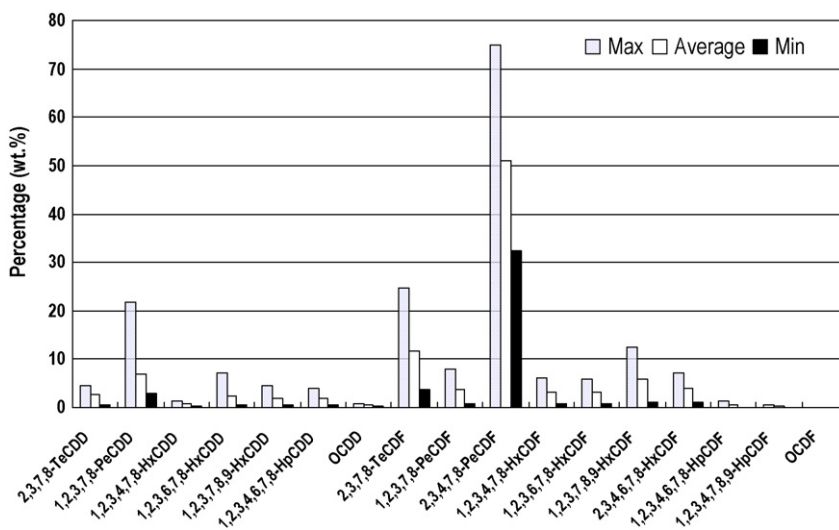**Fig. 2.** Content distribution of PCDD/F congeners (averaged for 16 MSWIs).

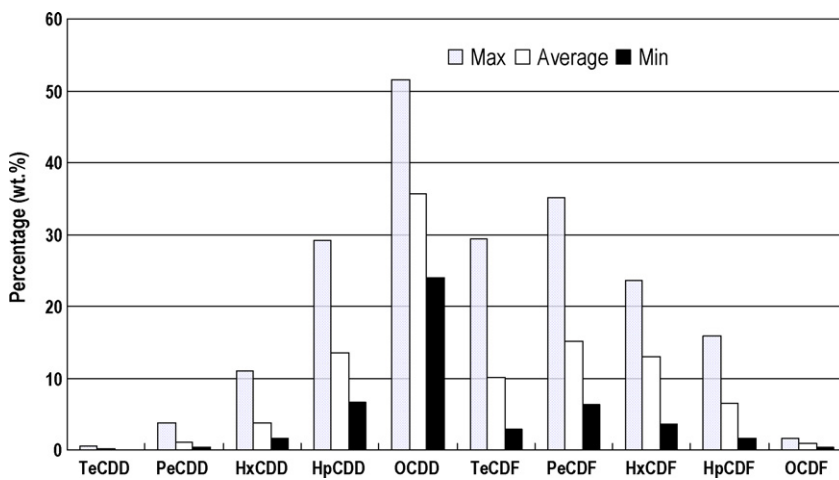**Fig. 3.** Content distribution of PCDD/F congeners—I-TEQ (averaged for 16 MSWIs).

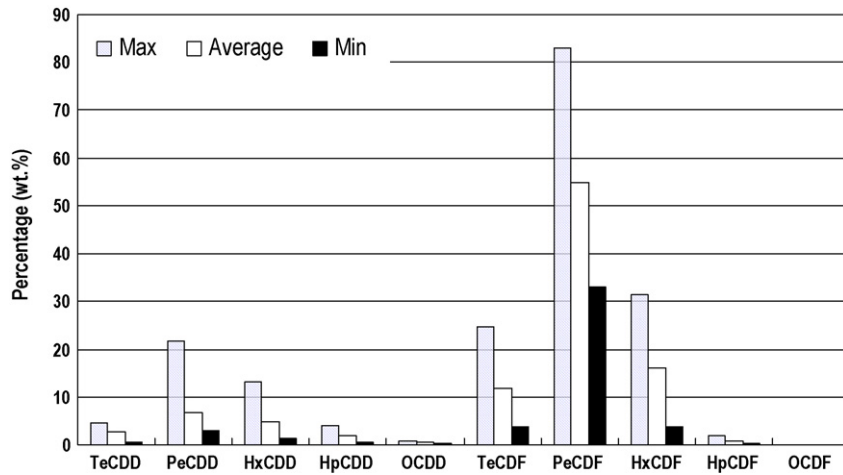**Fig. 4.** Content distribution of PCDD/F homologues (averaged for 16 MSWIs).

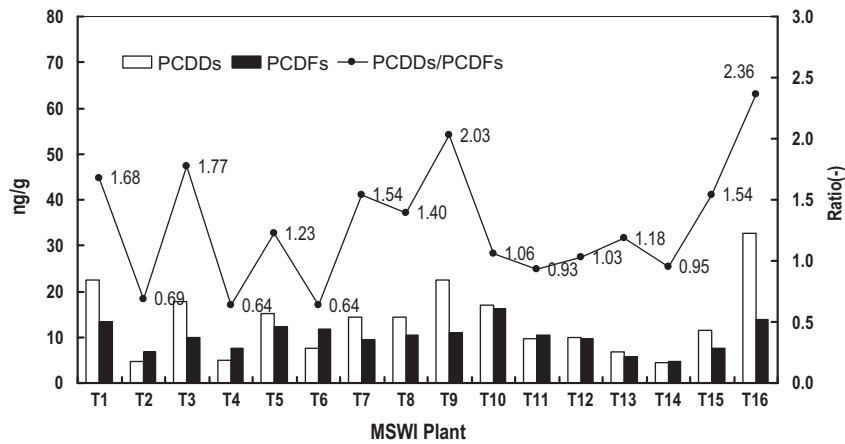**Fig. 5.** Content distribution of PCDD/F homologues—I-TEQ (averaged for 16 MSWIs).

Fig. 6. PCDD/F contents and ratios of PCDDs/PCDFs for sixteen MSWIs.

PCDD/F characteristic. The study found that PCDD compounds constituted more than PCDF compounds. On average, the PCDD compounds constituted 58.7% of the total PCDD/F content. The ratio of PCDDs/PCDFs based on original content is averaged 1.42 (ranged from 0.64 to 2.36) as shown in Fig. 6. However, the ratio of PCDDs/PCDFs based on I-TEQ becomes smaller. It is averaged 0.22 (ranged from 0.45 to 0.07) as shown in Fig. 7. This is equivalent that the PCDD compounds constituted 18.1% of total PCDD/F toxic

equivalent quantity. The results indicate that the PCDD/F quantity is contributed by PCDDs more than PCDFs, but PCDD/F toxicity is contributed by PCDFs more than PCDDs for the fly ash discharged from MSWIs.

Only scattered data of the PCDDs/PCDFs ratio for fly ash are presently published on the available academic journal papers. In comparison with limited data, the PCDDs/PCDFs ratio obtained in this work is likely consistent with those indicated by Shin and
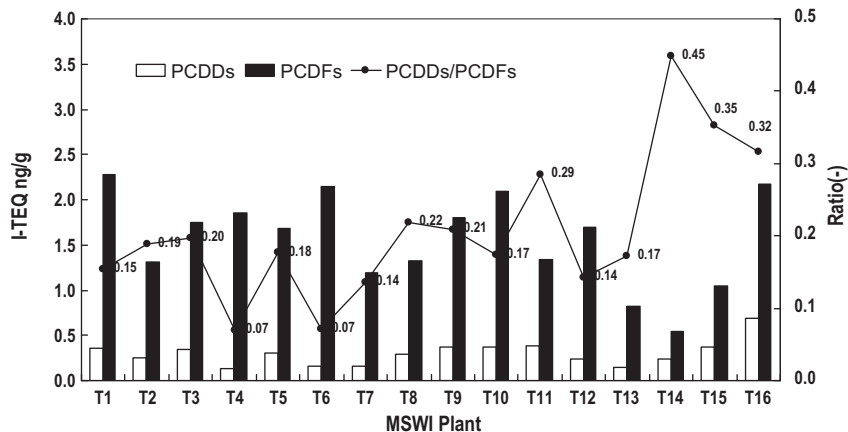

Fig. 7. PCDD/F contents and ratios of PCDDs/PCDFs for sixteen MSWIs (Based on I-TEQ)
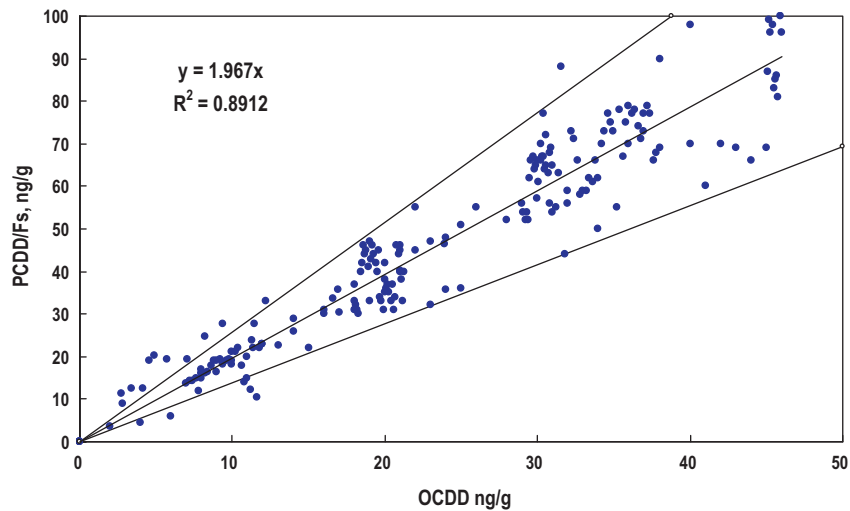
Fig. 8. Correlation between total PCDD/F contents and original OCDD contents

Chang [32] and Chen et al. [18]. In fact, distribution of PCDD/F congeners or homologues in fly ash is quite complicated and may be associated with the formation within different processes (isomer formation of PCDD/Fs from precursors or De novo synthesis). The significantly higher ratio of PCDDs/PCDFs is observed in T16 as shown in Fig. 6. It is believed that it is also affected by the different PCDD/F formation mechanism in the waste combustion process.

3.5. PCDD/F characteristic index (DCI)

A PCDD/F index by a representative congener is useful to quantitatively characterize the PCDD/F toxicity of fly ash. It would be expected to provide the practical information for distinguishing from other PCDD/F sources, and even as a key component for enrich factor in risk assessment for fly ash management. Based on these results from over hundreds of statistic data obtained in this work, the OCDD was found to be the greatest contributor to the total PCDD/F content in fly ash. As shown in Fig. 8, the total PCDD/F content in fly ash is likely a function of the OCDD content as follows:

$$\left(\frac{\text{Total PCDD}}{\text{F content, ng/g}}\right) = 1.967x(\text{OCDD content, ng/g})R_2 = 0.8912 \tag{1}$$

It appears that the experimental data is not consistent across correlation (1) because there is a square correlation coefficient of 0.8912 and the data disperses within a range of 30% deviation from the regression equation. Although OCDD is the congener with a maximum concentration in both the fly ash and flue gas due to its chemical stability, the I-TEF of OCDD is relatively low (I-TEF = 0.01). In other hand, the 2,3,4,7,8-PeCDF is the greatest contributor to the I-TEQ value in fly ash. It is worth changing focus to the toxicity quantity, the relationship between the 2,3,4,7,8-PeCDF concentration and I-TEQ value in the fly ash as in previous researches [33]. As shown in Fig. 9, the I-TEQ value in fly ash would be expressed as follows:

$$\left(\frac{\text{Total PCDD}}{\text{F content, ng I-TEQ/g}}\right)$$

$$= 1.142x(2, 3, 4, 7, 8 - \text{PeCDF content, ng/g}) R_2 = 0.9765 \tag{2}$$

Statistically, the square correlation coefficient becomes 0.9765, and there is a standard error of 7.6% for this correlation if submitted under a 95% probability. The correlation shows that the data collected from these experiments disperses within a reasonable range of deviation from the regression equation as shown in Fig. 9, which shows the comparison between correlation results and the exper-
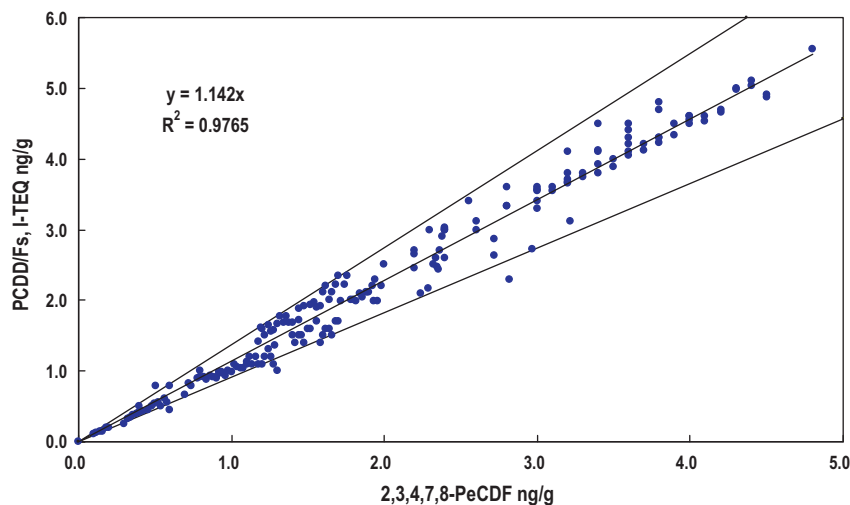

Fig. 9. Correlation between total I-TEQ contents and original 2,3,4,7,8-PeCDF contents

imental data obtained in this work. As far as is known, reviewing the previous researches on such correlations, only Chen et al. [18] proposed a similar correlation between the PCDD/F toxicity and PeCDF concentration in fly ash. In comparison with that suggested by Chen et al. [18], Eq. (2) is more reliable because it is based on enough practical data (over hundreds of samples), but few (only six) samples adopted by Chen et al. [18]. Hence, the strong correlation between the 2,3,4,7,8-PeCDF content and total PCDD/F I-TEQ content in fly ash is found and of much new interest to the managers. It is concluded that the PCDD/F characteristic index can be defined as:

$$DCI = \frac{(2,3,4,7,8 - PeCDF\ content,\ ng/g)}{(Total\ PCDD/F\ content,\ ng\ I - TEQ/g)} \quad (3)$$

It is suggested using the representative congener of 2,3,4,7,8-PeCDF to characterize the fly ash. For the cases in this study, the DCI is 0.875 with ±7.6% if submitted under 95% probability. It will be applied to characterize the fly ash discharged from the MSWI with the APCD assembly of SD, AC and BF.

4. Conclusion

Different from most previous studies on the PCDD/F concentrations with quantity-limited data, the results obtained from over hundreds of PCDD/F data using periodically sampling and analysis show that the PCDD/F contents in the fly ash discharged from sixteen large-scale commercial MSW incinerators were from 9.07 to 46.68 (23.53 on average) ng/g, d.w., and If based on international toxicity equivalent quantity, they were from 0.78 to 2.86 (1.87 on average) ng I-TEQ/g, d.w. The higher chlorinated PCDDs likely dominated more than lower chlorinated PCDDs, but this tendency was not for PCDFs. The OCDD had the highest contribution to the total PCDD/F content and its contribution percentage to the total PCDD/F content ranged from 23.8% to 51.5% (average 35.7%). Other congeners with higher percentage in order were 1,2,3,4,6,7,8-HpCDD (13.4%), 2,3,7,8-TeCDF (10.0%), and 2,3,4,7,8-PeCDF (9.2%). Based on the I-TEQ content, 2,3,4,7,8-PeCDF is the PCDD/F congener with the highest contribution percentage, ranging from 32.3% to 75.0% and 51.1% on average. The ratio of PCDDs/PCDFs based on the original content ranged from 0.64. to 2.36 (average 1.42). The PCDD compounds constituted 58.7% of the total PCDD/F content, but 18.1% based on I-TEQ.

Because the greatest contributor to the I-TEQ content in fly ash is the 2,3,4,7,8-PeCDF, the PCDD/F characteristic index is suggested using the representative congener content of 2,3,4,7,8-PeCDF to characterize the fly ash. The DCI is 0.875 ± 7.6% for the fly ash discharged from the MSWI with the APCD assembly of SD, AC and BF. This result provides PCDD/F fingerprint information to distinguish from other PCDD/F sources, such as the steel refinery industry, hazardous waste incinerators, or cement kilns. With more periodic field data than other previous researches, the findings obtained in this work reasonably elucidate the characterization of PCDD/F content in fly ash.

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