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TECHNICAL PAPER

Study of PCDD/Fs distribution in fly ash, ash deposits, and bottom ash from a medical waste incinerator in China

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*Over the past decades in China, the number of medical waste incinerators (MWIs) has been rising rapidly, causing emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). In this study, samples of fly ash, ash deposits, and bottom ash from typical MWIs were analyzed for PCDD/Fs and their distribution characteristics. Results showed international toxic equivalent (I-TEQ) values in the range of 6.9–67 ng I-TEQ/g in fly ash and ash deposits, whereas the concentration in bottom ash was extremely low (only 1.33 pg I-TEQ/g), yet the generation of PCDD/Fs was mostly de novo synthesis in fly ash and ash deposits according to the ratio of PCDFs to PCDDs; the major distribution differences of PCDD/Fs in fly ash was manifested by the content of toxic furan 2,3,7,8-TCDF, but other toxic PCDD/Fs showed similar distribution. Other findings are that 2,3,4,7,8-PeCDF had the most contribution to TEQ concentration, and that the most abundant toxic furan congener is 1,2,3,4,6,7,8-HpCDF. Correlation analysis showed that there was no significant correlation between PCDD/Fs concentration and several other physical and chemical parameters.*

Implications: This paper is of interest because it presents the emission performances of PCDD/Fs in ash from medical waste incineration in China. PCDD/F contents in fly ash and ash deposits vary between 6.9 and 67.3 ng I-TEQ/g. However, the concentration in bottom ash was extremely low (only 1.33×10^{-3} ng I-TEQ/g). The fingerprints of PCDD/Fs in fly ash are almost similar, except for 2,3,7,8-TCDF. There is no marked correlation between PCDD/Fs and other physicochemical properties.

Supplemental Materials: Supplemental materials are available for this paper. Go to the publisher's online edition of the *Journal of the Air & Waste Management Association*.

Introduction

In 1977 Olie et al. first reported the detection of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in fly ash from municipal solid waste (MSW) incineration (Olie et al., 1977). Chen et al. compared the distribution characteristics of PCDD/Fs between different kinds of waste incinerators, which indicated that the total and toxic equivalent (TEQ) concentrations of dioxins in fly ash from mechanical grate furnaces were higher than those from fluidized bed units (Chen et al., 2004). Additionally, by means of analysis of PCDD/Fs in fly ash and bottom ash from various kinds of waste incinerators, distribution characteristics of normalized concentration were very similar, which showed PCDD/Fs might have the similar reaction mechanism (Yang et al., 2004). Grochowalski (1998) determined the PCDD/F concentration in bottom ash from 18 Polish medical waste incinerators (MWIs), and the levels ranged from 7.8 to 43 ng TEQ/g. Matsui et al. collected ash samples from MWIs, MSWIs, and small-scale domestic waste incinerators in Japan, and the concentrations of PCDD/Fs ranged from 1.9 to 7.0 ng TEQ/g from four MWIs, which were lower than those from the MSWI (8.1 ng TEQ/g) and sometimes higher than that from the domestic waste incinerator (2.1 ng TEQ/g) (Matsui et al., 2003). Mininni et al. conducted a series of experiments on a hospital and cemetery waste incineration plant in order to assess the emissions of PCDDs, PCDFs, and polycyclic aromatic hydrocarbons (PAHs), which indicated that PCDD/F concentration in fly ash samples (1.7–147 ng international toxic equivalents [I-TEQ]/g) were very much higher than in bottom ash samples (4–120 pg I-TEQ/g) (Mininni et al., 2007). Moreover, fly ash could catalyze the formation of PCDD/Fs, to a certain degree, in fly ash from the actual process of waste incineration, compared with the distribution characteristics of congeners in fly ash and flue gas (Shin and Chang, 1999). Comparing concentration and congener distribution of PCDD/Fs in flue gas and fly ash from three different sizes and technology of waste incineration systems, PCDD/F concentrations were related to burning conditions and running conditions of the flue gas treatment system, but congener distribution was just related to the flue gas treatment system (Kim et al., 2005). Furthermore, Wang et al. estimated the PCDD/F emission in fly ash from waste incineration industry during 2005 to 2020 in China, based on a number of PCDD/F test results in flue gas and fly ash from MSWIs and MWIs (Wang et al., 2005). They summarized that fly ash had a contribution

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rate of 76–90% to total PCDD/F emission from MSWIs, yet fly ash from MWIs accounted for up to 41–78%.

In general, numerous previous works have studied the distribution characteristics of PCDD/Fs in fly ash from MSWIs; however, research studes on emission performance of PCDD/Fs in flue gas and fly ash from MWIs, as important emission sources, are still very scarce. In addition, there are different characteristics of MWI compared with MSWI: small capacity, intermittent operation, and difficult to control the discharge of pollutants. In this paper, the emission performance of PCDD/Fs in fly ash from MWIs is analyzed, including distribution characteristics of PCDD/Fs in fly ash, ash deposits, and bottom ash, and factor analysis between physics and chemical parameters and dioxin levels, from a multistage rotary pyrolysis incineration system.

Materials and Methods

Sample collection

In this investigation, fly ash, ash deposits, and bottom ash samples were taken from MWIs. The sampling locations of the ash samples (BH-1-1–Slag-1-9 {AirPreh-1-2}) and the types of incinerators, including air pollution control devices, are shown in Table S1 (Ni et al., 2012). The flow chart of a medical waste multistage rotary pyrolysis incinerator system, from which fly ash samples (BH-1-1–Slag-1-9 {AirPreh-1-2}) were sampled, is shown in detail in Figure S1 (Ni et al., 2012).

PCDD/F analysis

Each ash sample was Soxhlet extracted with toluene during 24 hr, rotary evaporated, and spiked with ^{13}C-labeled 2,3,7,8-substituted PCDD/Fs (Wellington Laboratories, Ontario, Canada) as internal standards. Then the sample extract was cleaned up by multilayer silica gel column and subsequently fractionated by an activated carbon column, packed with 1 g activated carbon-dispersed silica gel (Kanto Chemical, Tokyo, Japan). The fraction containing PCDD/Fs was condensed to 1–2 ml, then gently blown dry with high-purity nitrogen. Thereafter, the solution was spiked with ^{13}C-labeled PCDD/Fs as recovery standards.

Concentrated samples were analyzed by high-resolution gas chromatography (HRGC)/high-resolution mass spectroscopy (HRMS) analysis using a JMS-800D (JEOL, Japan). Gas chromatographic separation proceeded on a capillary column (J&W Scientific, USA) using DB-5 (60 m length, 0.25 mm ID, 0.25 μm film thickness).

Results and Discussion

Concentrations of congeners in bottom ash, ash deposits, and fly ash

The distribution profiles of PCDD/Fs of ash samples (fly ash, ash deposits, and bottom ash) from different sections of a medical waste multistage rotary pyrolysis incinerator system are shown in Table 1. BH-1-1 and AirPreh-1-2 are a fly ash sample from the bag filter and an ash deposits sample from the heat-transfer surface of the air preheater, on the same day, and are similar in TEQ concentration of PCDD/Fs, but total concentration in fly ash surpasses that in ash deposits by 7%. However, as a result of no cleaning treatment for the heat-transfer surface before collecting fly ash, AirPreh-1-2 content cannot represent the running condition result on the same day, yet represents the result of long-term accumulation. Comparing the main elements of the two samples, it is obvious that there are significant differences in C, O, Cl, Ca, and Fe contents, because some fly ash will be deposited on the cross-sections to form ash deposits.

According to Table 1, the actual concentrations of PCDDs and PCDFs are 71.8–993 ng/g and 368–2,807 ng/g, respectively. However, actual concentrations of PCDD/Fs congeners in fly ash vary with a range of 440–3,800 ng/g, which is different from the result (183 ± 20.4 ng/g) (Cobo et al., 2009). Moreover, PCDD/F concentrations in BH-1-6, 7, which were sampled at different times on the same day, are the two highest ones. However, there was the phenomenon of burning bags due to excessive temperature of exhaust gas on the sampling date. Therefore, the incineration system might be running unstably or in poor condition, which led to a high concentration of PCDD/Fs attaching to fly ash. Moreover, PCDD/Fs levels in bottom ash are extremely low (290 pg/g), as shown in Table 1. While in agreement with the aforementioned assertion, in fly ash the levels of dioxins oscillate between parts per trillion and parts per billion, but in bottom ash the levels are usually about parts per trillion (Azkona and Tsotsos, 2000).

The [PCDF]/[PCDD] ratio is an important indicator to discriminate between the possible reaction routes for PCDD/Fs formation (Huang and Buekens, 1995); one is de novo synthesis

Table 1. PCDD/Fs concentration in fly ash and bottom ash of BH-1 series

	[PCDDs], ng/g	[PCDFs], ng/g	[PCDF]/[PCDD]	$\sum$PCDD/Fs A ng/g	TEQ-Conc. B ng I-TEQ/g	Ratios A/B
BH-1-1	155	870	5.16	1026	13.5	76.0
AirPreh-1-2	440	1652	3.65	2093	25.5	82.1
BH-1-3	561	1635	2.93	2196	25.5	86.1
BH-1-4	373	1265	3.36	1638	17.5	94.6
BH-1-5	71.8	368	4.89	440	6.90	64.8
BH-1-6	993	2807	2.89	3800	44.7	85.0
BH-1-7	452	1935	4.28	2388	67.3	35.5
BH-1-8	142	724	5.10	866	13.1	66.1
Slag-1-9	0.12	0.17	1.40	0.29	1.33×10^{-3}	218

(synthesize PCDD/Fs or precursors through surface catalytic reaction by C, O, H, Cl, etc. atoms on fly ash surface), and the other is precursor synthesis. When [PCDF]/[PCDD] > 1, the main route for PCDD/Fs formation is de novo synthesis, and the major products are furans. However, when [PCDF]/[PCDD] < 1, the main route is precursor condensation, and the main products are dioxins, which are condensed from chlorophenol, chlorobenzene, polycyclic aromatic hydrocarbons, and other precursors generated by incomplete combustion in the incineration system. In general, according to the design of furnace structure, and assuring the "3T" principles, which are high temperature, long residence time, and sufficient degree of turbulence, PCDD/Fs are mainly de novo synthesized in off-gas cooling process, as complete combustion after the second combustion chamber and a low concentration of precursors. The [PCDF]/[PCDD] ratios are generally higher than 2 in advanced incineration systems, and the ratios vary in the range of 2.89–5.16 in fly ash and ash deposits in this study, which indicates that de novo synthesis is the main reaction route.

Distribution of toxic congeners in fly ash and ash deposits

Fly ash samples were categorically analyzed by hierarchical cluster analysis, and then the distribution characteristics of PCDD/Fs were discussed according to the clustering results.

With respect to the similarity of concentration distribution of toxic PCDD/Fs in fly ash, the results of hierarchical cluster analysis of fly ash were divided into two major categories: One is BH-1-1 and BH-1-3–7, and the other is BH-1-8, yet the first category was divided into two parallel subclasses, which are BH-1-1, 4, 6, 7 and BH-1-3, 5. The distribution diagrams of TEQ concentration of toxic PCDD/Fs in three kinds of fly ash are shown in Figure 1a. The distribution is extremely similar within and between the subclasses: 2,3,4,7,8-PeCDF shows the highest fraction of toxic PCDD/Fs congeners, and another peak in total concentration is shown at 1,2,3,4,6,7,8-HpCDF. Lundin et al. also recognized that at the lower temperatures of the postcombustion zone, as the sampling condition in this study, the relative proportions of PCDD species increased, and HpCDD and OCDD species become the major species in the component profile of PCDDs, accounting for ∼60% of the total PCDD content (Lundin and Marklund, 2008).

According to clustering results, Figure 1b contrasted the normalized distribution of toxic PCDD/Fs, in order to make the fingerprint features of PCDD/Fs in fly ash more obvious. The main distributional differences register as toxic PCDFs, such as 2,3,7,8-TCDF, whereas the distribution of other toxic PCDDs/PCDFs is very similar. The common character as a whole has a connection in that the fly ash samples were all sampled from the same waste incinerator, while the difference was due to the fluctuation of combustion conditions, and to changes of composition and running conditions of the exhaust gas purification system. In addition, combustion conditions, such as the temperature in the combustion zone, have substantial effects on the concentration of PCDD/Fs, and on their degree of chlorination (Wikström, 1999), but not on the distribution of isomers within homologous series (Wehrmeier et al., 1998; Weber and Hagenmaier, 1999; Wikström et al., 1999; Mulholland and Ryu, 2001; Ryu et al., 2006).

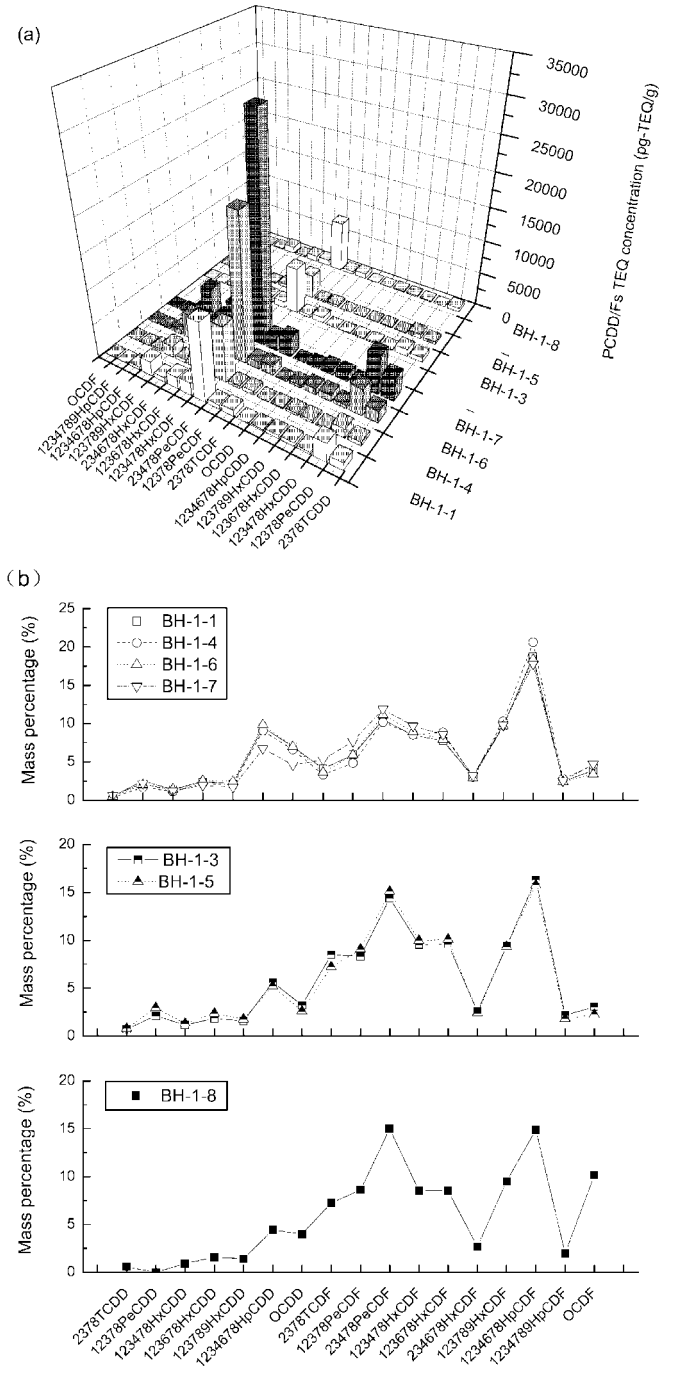

Figure 1. Distribution diagram of toxic PCDD/F concentrations in BH-1 ashes: (a) TEQ concentration; (b) mass percentage of total concentration.

An air preheater was located near the 500°C heat transfer surface, and the running temperature of the bag filter should be lower than 150°C, so ash deposits and fly ash were located at the foreside and rearward of the exhaust gas purification system, respectively. The concentration of ash deposits represents the result of an accumulative effect, so the concentration distribution in ash deposits had no necessary connection with that in fly ash

in logic. However, according to the comparison of toxic PCDD/Fs concentration between ash deposits and fly ash sampled in the same day, the formation mechanism of PCDD/Fs in ash deposits and the relationship of PCDD/Fs between ash deposits and fly ash can be concluded. The diagrams of toxic equivalent (TEQ) concentrations and total concentrations of toxic PCDD/Fs in AirPreh-1-2 and BH-1-3 are shown in Figure 2a.

Distribution of PCDD/Fs in bottom ash

As shown in Figure 2b, PCDD/Fs concentration in bottom ash is quite low, and is lower than that in fly ash by approximately five orders of magnitude. There are marked differences of PCDD/Fs distribution between bottom ash and fly ash as follows: a few highly chlorinated toxic PCDD/Fs in bottom ash, and 1,2,3,6,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF accounted for the main part in TEQ concentration, while the most abundant congeners in total concentration are OCDD and OCDF. A complete agreement in the previous study was observed in that the main part of PCDDs in total concentration was OCDD in the bottom ash from MWIs, but HpCDFs contributed the most to PCDFs content, which may be due to the different composition and PCDFs levels of waste (Gidarakos et al., 2009).

Bottom ash is formed from waste that completely combusts through the rotary kiln and fluidized bed and is directly discharged from the high-temperature section. According to the analysis of main elemental and mineral composition, bottom ash is mainly composed of $CaCO_3$, $Ca(OH)_2$, and SiO_2, and the former two are formed with CaO released during combustion as the following reactions show, yet SiO_2 is the main ingredient of quartz sand, which is the fluidizing agent of the fluidized bed. As PCDD/Fs levels show, the PCDD/Fs in raw medical waste are almost broken down, and PCDD/Fs cannot be synthesized in a high-temperature environment like a furnace; thus, the PCDD/Fs content in bottom ash is extremely low. Evaluating bottom ash only by PCDD/Fs levels, it is safe enough.

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (1)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (2)$$

Distribution of PCDD/Fs in exhaust gas and fly ash

PCDD/Fs in flue gas from this incineration system were detected four times, numbered FG1–FG4, respectively. Humidity ratio, oxygen content, and average concentration of major conventional air pollutants at every sampling time are shown in Table 2, as well as PCDD/Fs contents. The sampling points were located after the bag filter. Off-gas samples are applied to compare and for reference, because fly ash and exhaust gas were not sampled at the same time.

As shown in Table 2, there is a significant change of PCDD/Fs concentration in exhaust gas, which indicates that combustion condition might fluctuate markedly, and the main formation route is de novo synthesis, based on the ratios of PCDFs to PCDDs. Comparison of toxic PCDD/Fs distribution between

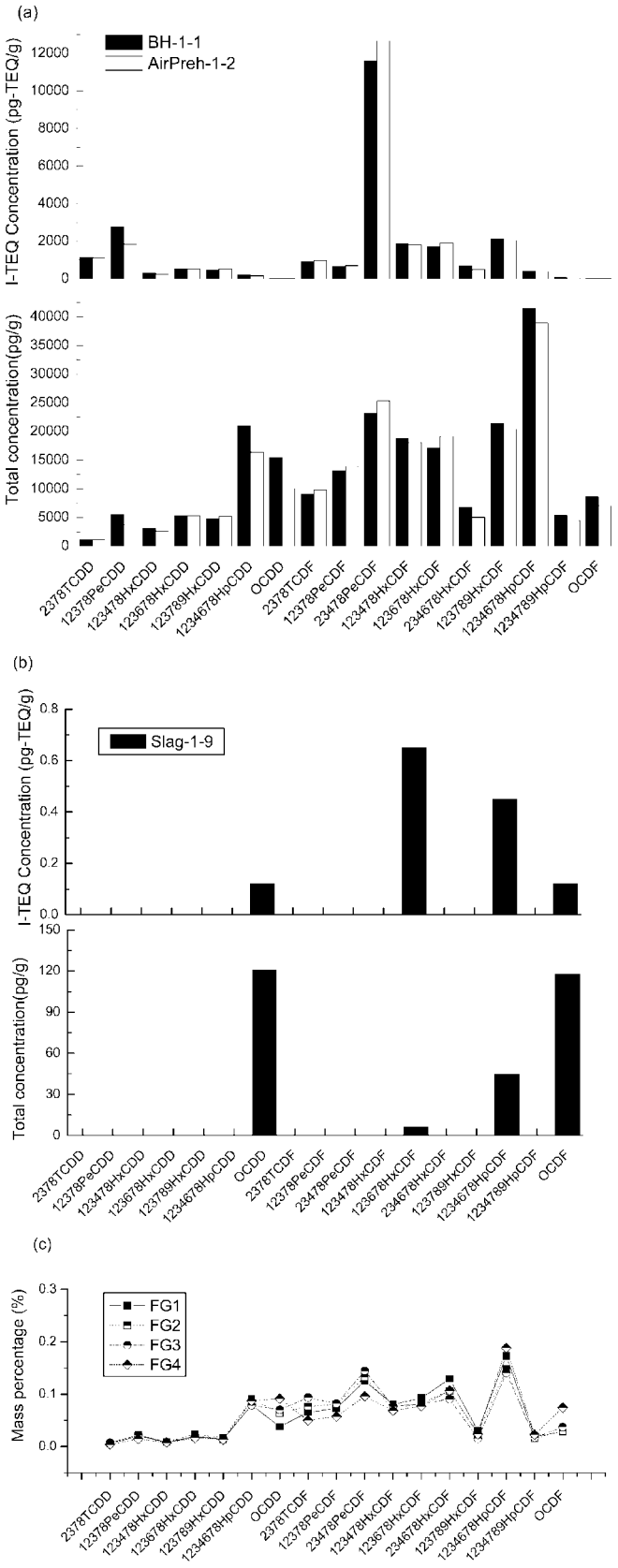

Figure 2. Concentration distribution of toxic PCDD/Fs of (a) ash deposits, (b) bottom ash, and (c) flue gas.

Table 2. Average contents of major components and PCDD/F concentrations in flue gas

	H_2O, %	CO_2, %	O_2, %	CO, mg/Nm^3	SO_2, mg/Nm^3	NO_x, mg/Nm^3	HCl, mg/Nm^3	[PCDDs], ng/Nm^3	[PCDFs], ng/Nm^3	[PCDF]/[PCDD]	$\sum$ PCDD/Fs, ng/Nm^3	TEQ-Conc., ng-ITEQ/Nm^3
F1	10.9	4.75	11.4	115	224	99.7	217.1	15.36	68.15	4.44	83.51	10.72
F2	6.85	4.99	11.8	127	340	135	175.0	3.87	12.82	3.31	16.69	2.19
F3	6.40	3.61	13.7	33.2	641	137	102.9	4.11	14.49	3.53	18.60	2.55
F4	11.4	0.39	18.7	244	174	26.8	232.0	2.13	6.93	3.26	9.06	0.92

fly ash and exhaust gas is shown in Figure 2c; the overall distribution is very similar, which indicates that the most abundant PCDD/Fs congeners in total concentration are 2,3,4,7,8-PeCDF and 1,2,3,4,6,7,8-HpCDF, respectively, but there are differences in distribution of single toxic PCDD/Fs, such as the marked different distribution of hexachlorodibenzofurans.

Statistical analysis on factors affecting PCDD/F content in fly ash

Toxic PCDD/Fs concentration in fly ashes from MWIs, MSWIs, and hazardous waste incinerators (HWIs) in published literature is analyzed. According to the results of cluster analysis of PCDD/Fs in fly ash, all fly ash can be classified into four categories, and the distribution of normalized concentrations are shown in Figure 3 (Hagberg et al., 2005; Kim et al., 2005). From the distribution profiles, distribution characteristics of toxic PCDD/Fs can be visually identified; that is, furans contents are higher than dioxins contents in the two groups just described, and the following two sets are in reverse. Most furans in fly ash originate from the cooling

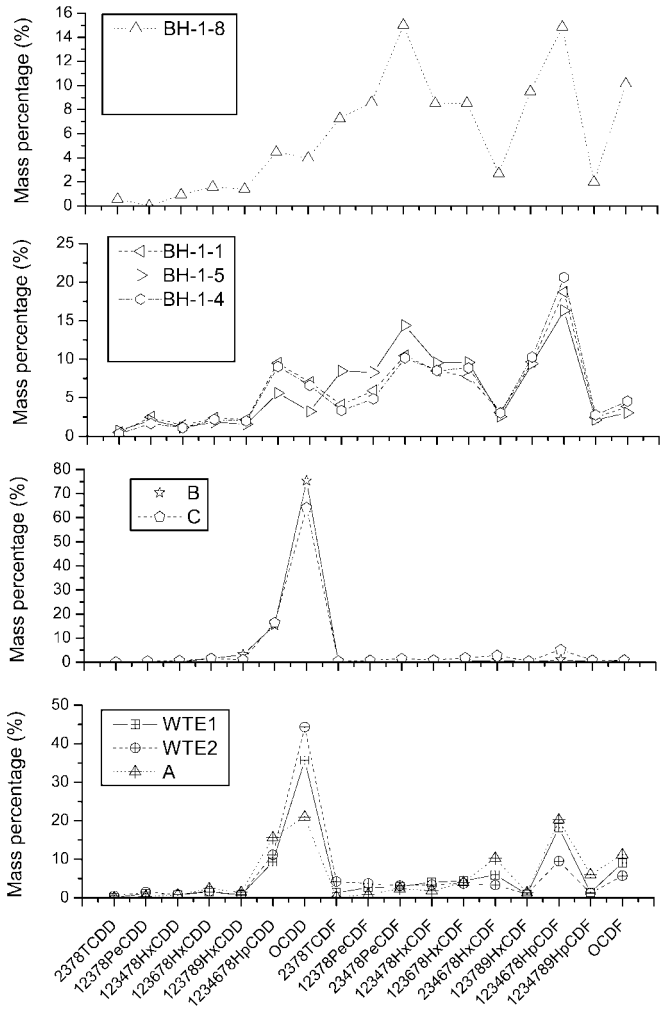

Figure 3. Comparison of toxic PCDD/Fs distribution in cluster fly ash: A, B, and C are fly ashes from a MSWI (Kim et al., 2005), and WTE1 and WTE2 are fly ashes from chlorinated organic reagents and waste appliance incineration (Hagberg et al., 2005).

stage of flue gas, which reveals that in this stage furans were de novo synthesized. As Ryu et al. indicated, while PCDF species predominate over PCDD species in a temperature-independent fashion, this could be an indication of that phenol condensation is an important formation mechanism (Ryu and Mulholland, 2005), which is a kind of de novo synthesis. As a result, in order to control PCDD/F emissions effectively, PCDD/F synthesis must be inhibited in the cooling phase of flue gas.

Principal components analysis (PCA) was applied to analyze the possible effects on PCDD/F formation by various indicators of physical and chemical parameters of fly ash. In Figure 4a, Cl and Fe contents are positively correlated with PCDD/Fs concentration, but relations with any other parameters are not evident. However, Cl and Fe contents are negatively correlated with PCDD/Fs concentration, as shown in Figure 4b. Additionally, the relations between other parameters and PCDD/F concentration in Figure 4b are in close agreement with that in Figure 4a. Parameters related to other in both physical and chemical parameters are C content and specific surface area, as well as Ca content and pH value.

Bivariate multivariable correlation statistical analysis figures are applied using SPSS 13 to determine the existing relationships between the already-mentioned parameters, as shown in Table 3 (Zhang, 2004). There is no marked correlation between PCDD/

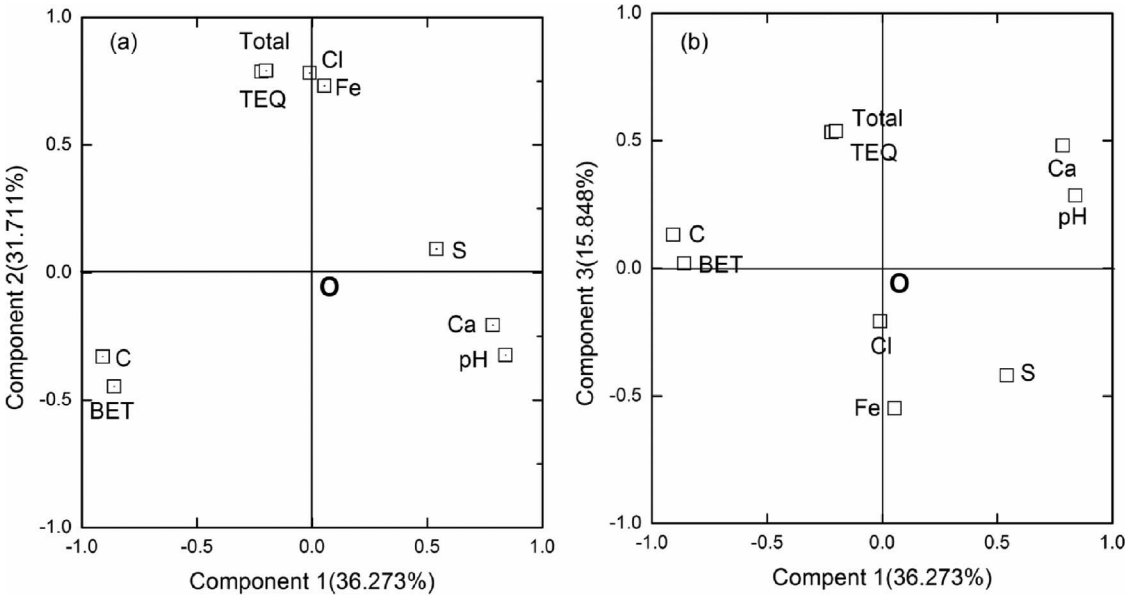

Figure 4. The scatter gram of load (TEQ and Total represent TEQ concentration and total concentration of PCDD/Fs, respectively, and BET is specific surface area).

Table 3. Correlation coefficient between PCDD/Fs and other physical and chemical parameters in fly ash

	TEQ	Total	BET	C	S	Cl	Ca	Fe	pH
TEQ	1	0.998	−0.119	0.039	−0.146	0.421	−0.120	0.290	−0.241
		(0.000)	(0.713)	(0.903)	(0.652)	(0.173)	(0.709)	(0.360)	(0.451)
Total	**0.998**	1	−0.140	0.022	−0.140	0.421	−0.103	0.294	−0.226
	(0.000)		(0.665)	(0.945)	(0.664)	(0.173)	(0.749)	(0.354)	(0.480)
BET	−0.119	−0.140	1	**0.965**	−0.365	−0.339	−0.568	−0.411	−0.551
	(0.713)	(0.665)		**(0.000)**	(0.244)	(0.280)	(0.054)	(0.184)	(0.063)
C	0.039	0.022	**0.965**	1	−0.442	−0.287	**–0.581**	−0.380	**–0.596**
	(0.903)	(0.945)	**(0.000)**		(0.150)	(0.365)	**(0.047)**	(0.224)	**(0.041)**
S	−0.146	−0.140	−0.365	−0.442	1	0.089	0.171	0.233	0.362
	(0.652)	(0.664)	(0.244)	(0.150)		(0.783)	(0.594)	(0.466)	(0.247)
Cl	0.421	0.421	−0.339	−0.287	0.089	1	−0.126	0.493	−0.445
	(0.173)	(0.173)	(0.280)	(0.365)	(0.783)		(0.696)	(0.103)	(0.147)
Ca	−0.120	−0.103	−0.568	**–0.581**	0.171	−0.126	1	−0.437	**0.766**
	(0.709)	(0.749)	(0.054)	**(0.047)**	(0.594)	(0.696)		(0.155)	**(0.004)**
Fe	0.290	0.294	−0.411	−0.380	0.233	0.493	−0.437	1	−0.276
	(0.360)	(0.354)	(0.184)	(0.224)	(0.466)	(0.103)	(0.155)		(0.385)
pH	−0.241	−0.226	−0.551	**–0.596**	0.362	−0.445	**0.766**	−0.276	1
	(0.451)	(0.480)	(0.063)	**(0.041)**	(0.247)	(0.147)	**(0.004)**	(0.385)	

Notes: Total is the total concentration of PCDD/Fs. BET is specific surface area. C, S, Cl, Ca, and Fe are carbon, sulfur, chlorine, calcium, and iron contents in fly ash. The boldface in the table highlights the maximum coefficient of the column data.

Fs and other physical and chemical parameters. Specific surface area is positively correlated with C content and weakly negatively correlated with Ca content and pH value. Moreover, this revealed a weak negative correlation between Ca content and C content, as well as a strongly positive correlation between pH value and Ca content.

Conclusion

This study worked on the emission performances of PCDD/F congeners in fly ash, ash deposits, and bottom ash from medical waste incineration. PCDD/F concentrations in fly ash and ash deposits samples varies in the range of 6.9–67.3 ng I-TEQ/g, whereas the concentration of bottom ash was extremely low (only 1.33 pg I-TEQ/g). The [PCDF]/[PCDD] ratios indicate that de novo synthesis is the main reaction route. The fingerprints of PCDD/Fs are almost similar in all fly ash samples, except the main difference of 2,3,7,8-TCDF. Statistical analysis shows no marked correlation between PCDD/Fs and other physical and chemical parameters. Specific surface area is positively correlated with C content and weakly negatively correlated with Ca content and pH value. Bottom ash from the presented type of MWI in this paper is characterized with very low PCDD/Fs content.

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