The Behaviors and Relationships of PCDD/Fs and Chlorobenzenes in the Whole Process of One Municipal Solid Waste Incinerator

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ABSTRACT

We examined the characteristics of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and chlorobenzenes (CBzs) in the flue gas and fly ash of a municipal solid-waste incinerator in four locations: the outlet of the furnace, the outlet of the high-temperature superheater, the inlet of the semi-dry scrubber and the stack after air pollution control device (APCD) processing. Both PCDD/Fs and CBzs were mostly formed at low temperatures. The dominant PCDD/Fs generated in the gaseous phase were 23478-PeCDF and TCDF, and 124-TrCBz was the major CBz in both the gaseous and solid phase. More PCDD/Fs were found in the solid phase with the decrease of temperature, while CBzs exhibited the opposite trend. Furthermore, activated carbon with a low surface area and mesoporous volume showed low flue gas removal efficiencies for PCDD/Fs and CBzs in the flue gas. The fraction of PCDD/Fs in the solid phase largely decreased when the flue gas passed through the fabric filter. Additionally, the memory effects of the aged filters increased the fractions of 234678-HxCDF, 1234678-HpCDF and 1234678-HxCDD. Most important, the relationships between PCDD/Fs and CBzs in the flue gas and fly ash were analyzed, respectively. In the gaseous phase, most of the CBzs displayed high correlation coefficients with PCDD/Fs, especially 123-TrCBz ($R^2 > 0.8$). In the solid phase, low correlation coefficients were found between CBzs and PCDD/Fs except for 135-TrCBz and 123-TrCBz ($R^2 = 0.8$). A remarkable correlation was also found between 124-TrCBz in the flue gas and PCDD/Fs in the fly ash. We conclude that TrCBzs may be regarded as the best indicator for PCDD/Fs in both flue gas and fly ash.

Keywords: Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans; Chlorobenzenes; Emission characteristic; Correlations; Gas-solid distribution.

INTRODUCTION

With the development of society, there have been numerous municipal solid waste incinerators, up to 220 in 2015 (China National Bureau of Statistics, 2015). Therefore, waste incineration, as the efficient disposal for waste reduction, becomes more and more significant. As is known waste incineration could induce varieties of emission pollutants. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are the typical pollution formed in the processes of municipal solid waste incinerators (MSWIs). Previous studies concentrate on PCDD/Fs emissions (Lee et al., 2003; Kao et al., 2006; Streibel et al., 2007; Ni et al., 2009). Other chlorinated aromatic hydrocarbons, such as chlorobenzenes (CBzs), chlorophenols, and polycyclic aromatic hydrocarbons (PAHs), are also major organic pollutants (Takaoka et al., 2003; Oh et al., 2007; Li et al., 2016a; Han et al., 2017). CBzs are important pollutants concerned due to their close relationships with the formation and emissions of PCDD/Fs. They reveal high emission levels in the flue gas and also are one of the major precursors for PCDD/F formation (Yang et al., 2012; Zhou et al., 2015). Moreover, CBzs could also be good indicators for PCDD/Fs. Real-time measurements, such as resonance-enhanced multi-photon ionization (REMPI) with time of flight mass spectrometry (TOFMS), could be used to characterize rapid responses in trace aromatic emissions from stationary and mobile sources (Wang et al., 2012; Gullett, 2013). CBzs could be detected efficiently to achieve
near-online monitoring of PCDD/Fs depending on good correlations between them (Kuribayashi et al., 2005; Gullet et al., 2011). It is much more significant in incinerators with unstable operation conditions resulting in high emission levels of PCDD/Fs. The online monitoring technology can be used to detect PCDD/Fs in time, and then diagnose the operation conditions and adjust the operating parameters.

The relationships among PCDD/Fs and other organic pollutants in the stack gas could be found in several studies (Kaune et al., 1998; Yoneda et al., 2002; Gullet et al., 2011; Zhou et al., 2015). In our previous researches, detailed characteristics and relationships between PCDD/Fs and CBzs in the stack gas from several typical circulating fluidized bed incinerators, compared with chlorophenols, PAHs and other common inorganic pollutants, have also been discussed (Wang et al., 2017, b). However, these studies only concentrate on the final emission levels of MSWIs and cannot give a comprehensive knowledge of target compounds in the whole process. Previous research on behaviors of CBzs related PCDD/Fs is about cement plants, the concentrations and operation process of which are much different from MSWIs (Li et al., 2016b). The knowledge of CBzs related to PCDD/Fs in whole process of Chinese waste incinerators is significantly needed.

The characteristics of PCDD/Fs and CBzs in flue gas and fly ash at the outlet of furnace, outlet of high temperature superheater, inlet of semi-dry scrubber and stack after APCD, which were marked with 1# to 4#, respectively. The positions of sample sites are shown in Fig. 1. And the temperature and oxygen contents in different sites are in Table 1(b). Several common pollutant emission levels in the experiment are also shown in Table 1(c). Samples from four sites were collected simultaneously, as one group of data. Six groups were collected.

All samples were collected for approximately 2.0–4.0 m³ in 120–180 min using an isokinetic sampler (KNJ, Korea) according to U.S. EPA Method 23 (U.S. EPA, 1995). Each sample had two parts: the filter for particulate phase targets and the XAD-2 resin for gaseous phase targets. Furthermore, fly ash from the fabric filter was also sampled at the same time with the sampling of flue gas.

Sample Treatment and Analysis

The collected flue gas samples were extracted stepwise with methylene chloride and toluene and the extracts were concentrated separately to avoid losses of semi-volatile compounds (Oh et al., 2007). After extraction, aliquots of the samples were taken for PCDD/Fs and chlorobenzene analysis. Fly ash samples (1 g) were extracted and analyzed according to U.S. EPA Method 1613 (U.S. EPA, 1994).

The PCDD/Fs cleanup procedure and analysis were performed according to U.S. EPA Method 23 (U.S. EPA, 1995).

### METHODS

**Sample Collection**

The experiment was performed in a typical circulating fluidized bed (CFB) municipal waste incinerator in China, with a capacity of 450 tonnes of waste per day. The air pollution control device (APCD) used in this incinerator includes selective non-catalytic reduction (SNCR) for NOx control, semi-dry scrubber for acid gas control, and fabric filter with activated carbon (AC) injection for particulate matter (PM) and PCDD/Fs control. The CFB MSWI with APCD system has been working for over four years. Detailed information about it could be found in Table 1(a).

The characteristics of PCDD/Fs and CBzs at four important positions of MSWI were investigated, namely outlet of furnace, outlet of high temperature superheater, inlet of semi-dry scrubber and stack after APCD, which were marked with 1# to 4#, respectively. The positions of sample sites are shown in Fig. 1. The temperature and oxygen contents in different sites are in Table 1(b). Several common pollutant emission levels in the experiment are also shown in Table 1(c). Samples from four sites were collected simultaneously, as one group of data. Six groups were collected.

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<table>
<thead>
<tr>
<th>Table 1. Information of the investigated MSWI and experiment.</th>
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<tr>
<td><strong>(a) MSWI</strong></td>
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<tr>
<td>Capacity (tonnes day⁻¹)</td>
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<tr>
<td>Furnace temperature (°C)</td>
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<tr>
<td>Rated evaporation capacity(tonnes h⁻¹)</td>
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<td>Air pollution control device</td>
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<td>boiler load (tonnes h⁻¹)</td>
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<td><strong>(b) sampling conditions</strong></td>
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<tr>
<td>1#</td>
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<td>2#</td>
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<td>3#</td>
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<td>4#</td>
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<tr>
<td><strong>(c) common pollutant emissions, mg Nm⁻³, 11%O₂</strong></td>
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<tr>
<td>carbon monoxide</td>
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<td>NOx</td>
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Identification and quantification of PCDD/Fs were performed by HRGC/HRMS on a 6890 Series gas chromatograph (Agilent, USA) and coupled to a JMS-800D mass spectrometer (JEOL, Japan). A DB-5ms (60 m × 0.25 mm I.D., 0.25 µm film thickness) capillary column was used for separation of the PCDD/Fs congeners. The temperature of column in used method stay at 150°C for 1 min. And it firstly rises to 190°C at the rate of 25°C min⁻¹ and secondly increase to 280°C at the rate of 3°C min⁻¹. Finally, the column stays at 280°C for 20 min.

The mean recoveries of standards for PCDD/Fs range from 55 to 125%, which are all within the acceptable 25 to 150% range. The toxic equivalent values (TEQs) of PCDD/Fs were calculated with the international toxic equivalent factors (I-TEFs) (Bhavsar et al., 2008) according to standard for pollution control at the municipal solid waste incinerators in China. All the concentrations are normalized to dry air, 1.01 × 10⁵ kPa, and 237 K.

Pre-treatment of CBzs was depicted in detail by Yan (2012). GC-ECD (GC 6890N, Agilent, USA) with a DB-5 column (30 m × 0.25 mm × 0.25 µm) is used to analyze CBzs, with a heating rate of 10°C min⁻¹ to 220°C.

**RESULTS AND DISCUSSION**

**The Concentration of PCDD/Fs and CBzs**

The concentrations and TEQ values of PCDD/Fs in the four investigated sites were calculated. It is obvious that the concentrations and TEQ values of PCDD/Fs at the outlet of furnace (1#, 830°C) and high temperature superheater (2#, 560°C) were rather lower than those before the semi-dry scrubber (3#, 220°C) and after the whole APCD (4#, 148°C). At the former two sites the concentrations of PCDD/Fs were 2.09 and 1.34 ng Nm⁻³, respectively. The corresponding TEQ values were 0.26 and 0.21 ng Nm⁻³, respectively. It should be noted that the concentrations of PCDD/Fs before the semi-dry scrubber reached up to 767.7 ng Nm⁻³ and the TEQ values reached up to 79.2 ng Nm⁻³. The temperature at the sampling position was the primary factor affecting the different PCDD/Fs concentrations. As is known, PCDD/Fs could originate directly from the waste and also be generated in the combustion system through the homogeneous pathway (500–800°C) and heterogeneous pathway (200–450°C) (Stanmore, 2004; Altarawneh et al., 2009). In full scale
CFB MSWIs the incoming PCDD/Fs from the waste are effectively destroyed during the incineration, regardless of their concentrations because of the high temperature (850–1000°C) in the furnaces (Van Caneghem et al., 2012). The high temperature, enough retention time, combustion chamber turbulence and proper excess air coefficient ensured that fewer PCDD/Fs were generated during waste combustion in the furnace. Therefore, the concentrations of PCDD/Fs at the outlet of furnace were low. The temperatures from the outlet of furnace to the outlet of superheater were in the range of homogeneous pathway. The concentrations of PCDD/Fs at the two sites were very similar. The fact indicated that the formation of PCDD/Fs in the high temperature process is very limited. Amounts of PCDD/Fs were generated in the flue gas at the inlet of scrubber. It was about 400 times higher than that of the high temperature process. The result confirmed that the low temperature process is the primary route of PCDD/Fs formation, proved in previous research both in laboratory and pilot scale experiments (Everaert and Baeyens, 2002; Van Caneghem et al., 2012).

The distributions of PCDD/Fs in the gaseous and solid phase were also studied. As shown in Fig. 2, the concentrations of PCDD/Fs in the gaseous phase were similar to that in the solid phase during the high temperature process (1# and 2#, 560–830°C). While at the semi-dry scrubber inlet, namely the “end” formation site of the MSWI system, the concentrations of PCDD/Fs in the solid phase were up to 658.8 ng Nm–3. And the gas phase part occupied 108.9 ng Nm–3 of PCDD/Fs, only 14% of the total concentrations. The available particle properties, the temperature and the relative humidity all affect the distributions of semi-volatile organic compounds between the gas and solid phases (Lohmann and Jones, 1998). From the furnace outlet to the scrubber inlet with a decrease of temperature, PCDD/Fs generated preferred to exist in the solid phase (Chi et al., 2005). The concentration in the solid phase at the scrubber inlet was 600 times higher than that in the stack. The result in this study was also higher than other data before the APCD in some studies (Chi et al., 2005, 2006a). It perhaps resulted from large amounts of ashes, or particulate matters existing in this MSWI, which could promote PCDD/Fs formation in the low temperature process with high concentrations of PCDD/Fs.

The concentration variations of chlorobenzenes from 1# to 3# were the same as that of PCDD/Fs, shown in Fig. 1. At the outlet of furnace (1#) and high temperature superheater (2#) the total concentrations of CBzs were lower than 10 µg Nm–3. While at the scrubber inlet the concentrations increased by 12 times up to 120.0 µg Nm–3, which were also higher than results before varieties of APCDs in other MSWIs (Takaoka et al., 2003; Oh et al., 2007; Yang et al., 2012). It is found that chlorobenzenes were also generated majorly during the low temperature process, with the similar formation trend to PCDD/Fs proved in studies (Yan et al., 2010).

The concentrations of CBzs in the low temperature process (from 2# to 3#) rose by about 20 times. The concentrations of PCDD/Fs rose dramatically by about 500 times. It was much easier for low temperature process of the MSWI system to promote PCDD/Fs formation. It is also noticed that concentrations of CBzs before the APCD were always 100–1000 times higher than that of PCDD/Fs, same as the results in previous research (Takaoka et al., 2003; Yang et al., 2012). At the outlet of furnace and high-temperature superheater the gas–solid distributions of CBzs were similar to PCDD/Fs, while at the inlet of semi-dry scrubber the distributions became different. The gaseous phase still dominated in total CBz concentrations (Fig. 2), similar to the previous investigation (Han et al., 2017). The result revealed the different effects of temperature and existing particles on gas–solid distributions of CBzs and PCDD/Fs. It might be due to the much different vapor pressures (Pankow, 1994a, b; Chi et al., 2006b).

**The Emissions of PCDD/Fs and CBzs**

The characteristics of PCDD/Fs and CBz formation were analyzed according to the results from the furnace outlet to the semi-dry scrubber inlet. And the final emission results in flue gas after the fabric filter with AC injection

![Fig. 2. The gas and solid phase distributions of PCDD/Fs and CBz concentrations.](image-url)
(4#) revealed the removal ability of the APCD. In Fig. 1 it could be seen that both concentrations and TEQ values of PCDD/Fs decreased. The average removal efficiencies of PCDD/Fs concentrations and TEQ values were 85.1% and 78.5%, respectively. However, the final emission levels of PCDD/Fs were still higher than the standard in China. The fabric filter with AC injection played a major role in controlling PCDD/Fs. AC can absorb PCDD/Fs in the gaseous phase and then be removed through the filter with the solid phase parts. Among the six samples collected PCDD/Fs in the solid phase were found to be all removed dramatically, with average 99% of removal efficiency. As shown in Fig. 3(a), the removal efficiencies of TEQ in the gaseous phase among four samples were changeable in the range of 6–56%. And the concentrations and TEQ values of PCDD/Fs even increased obviously in other two samples. It was rather different from the solid phase results. The final emission levels of PCDD/Fs were influenced by the semi-dry scrubber, AC injection and fabric filter. Fabric filters work and remove dioxins associated with particles and any vapors that adsorb to the particles (McKay, 2002). Amounts of ashes and particulate matters were removed successfully. Therefore, the removal efficiencies in the solid phase were always good. The decrease of the gaseous PCDD/F concentrations depends on the injection of a hydrated lime or Ca(OH)$_2$-slurry in the semi-dry scrubber and AC injection. The effects in the semi-dry scrubber is limited (Hung et al., 2016). And the efficiency of AC is obviously influenced by varieties of factors, such as adsorbent characteristics, temperature, dosing rate, residence time during entrained flow and fly ash concentrations (Lu et al., 2013; Zhou et al., 2016). In this research the function of AC was very limited. The characteristics of AC used was analyzed. Rather low BET surface area (96.87 m$^2$ g$^{-1}$) and mesopore volume (0.1 cm$^3$ g$^{-1}$) were found. The AC used in this MSWI was not useful and good enough, compared with some AC experiments with 99% of removal efficiency (Everaert et al., 2003; Zhou, 2016). It directly resulted in the low reduction of PCDD/Fs. It is emphasized that proper and superior AC species play an important role in PCDD/Fs emission control.

Besides, the fly ash/soot deposited in the air pollution control system could result in the memory effect (Cunliffe and Williams, 2009; Li et al., 2011; Trivedi and Majumdar, 2013). The fly ash acts as an adsorption matrix for PCDD/Fs formation and subsequent desorption into the flue gas stream. The aged APCD system in this MSWI, especially the aged fabric filters contaminated over years, could also cause the PCDD/F memory effect. The increase of PCDD/Fs seriously affected the final emission levels in the flue gas to conform the standard. That should be the primary reason why the emission levels in flue gas were even higher than that before the APCD system.

The change of total CBz concentrations after APCD was different from the change of total PCDD/Fs in Fig. 1. The average concentrations of total CBz after APCD went up. The decrease of total PCDD/Fs in this MSWI was primarily due to the removal of solid phases though the fabric filter, while chlorobenzenes were mostly present in gas phase. The removal efficiency of CBzs by fabric filter was limited. Among the former samples both PCDD/Fs and CBzs in gaseous phase were reduced through the APCD. But the removal efficiencies of CBzs were different from that of gas-phase PCDD/Fs in Fig. 3(b). Only in one sample the removal efficiency of CBzs was similar to that of PCDD/Fs. There seem to be no clear comparison results between the removal efficiencies of gaseous PCDD/Fs and CBzs. In the last two samples (Sample 5 and 6) CBzs increased with the increase of PCDD/Fs in the gaseous phase. The variation trends of CBzs and gaseous PCDD/Fs were similar through the APCD, but the efficiencies for PCDD/Fs and CBzs were different. The semi-dry scrubber and AC injected in APCD could also affect the concentrations of CBzs. Due to the temperature on formation of CBzs (Yan et al., 2010), CBzs could possibly be generated at the semi-dry scrubber. The micropore volume of diameter less than 2 nm in AC...
was the key factor governing the adsorption capacity of CBzs (Inoue and Kawamoto, 2008). The micropore volume of AC (< 0.1 cm$^3$ g$^{-1}$) in this MSWI used was further lower than mesopore volume, resulting in negative effects on chlorobenzenes. It is hard to say the definitive effects of APCDs on CBzs in this study and it need more attentions and studies.

**PCDD and PCDF Concentration**

In all samples including the gas phase and solid phase in Fig. 4, PCDF concentrations were higher than PCDD concentrations. The ratio of PCDFs and PCDDs was always higher than 1. During the low temperature process before the semi-dry scrubber inlet, both PCDD and PCDF concentrations in the gaseous phase and solid phase had an upsurge. PCDFs in the gaseous and solid phase and PCDDs in the solid phase were all raised by over 200 times, while PCDDs in the gaseous phase were only raised by 44 times. It revealed that the principal formation in this MSWI was the generation of PCDFs. Furthermore, PCDD/Fs were mostly generated in the solid phase, and much more PCDFs than PCDDs were generated in the gaseous phase. The conclusions also accorded with the variation of the ratio of PCDFs and PCDDs. From Sample Site 1# to 3#, the ratio came up to 8.29 in the gaseous phase while the ratio in the solid phase was only 2.12.

After the APCD system, in the gaseous phase PCDDs still had an increment of 28.7% but PCDFs nearly did not change, while in the solid phase both PCDDs and PCDFs dropped down dramatically, by 99.9% and 99.8%, respectively. The ratio of PCDFs and PCDDs in the gaseous phase declined from 8.29 to 6.52 but in the solid phase the ratio nearly did not change (from 2.12 to 2.77). The results show that PCDDs were generated more in the gaseous phase when the flue gas went through this APCD system and both PCDDs and PCDFs were removed similarly in solid phase.

**Homologue Concentrations of PCDDs and PCDFs**

Fig. 5 shows specific PCDD/F congener profiles in the flue gas in the whole MSWI system. At the outlet of the furnace (Fig. 5(a)), OCDD, 1234678-HpCDF, 23478-PeCDF and OCDF were the dominant congeners in the gaseous phase, occupying 17.0%, 12.6%, 12.1%, and 12.0%, respectively. OCDD, 1234678-HpCDF, and OCDF were also the dominant congeners in the solid-phase, with the fraction of 17.7%, 19.5% and 16.6%, respectively. Compared with the results at the furnace outlet, after the high temperature process at the superheater outlet (Fig. 5(b)) the gaseous phase fractions
of 2378-TCDD and 2378-TCDF increased obviously. The fraction of 2378-TCDD went up from 0.9% to 9.2% and the fraction of 2378-TCDF went up from 4.3% to 11.8%. In the solid phase tetra- to hexa-PCDFs had a significant increment while 2378-TCDD, 1234678-HxCDD and OCDD decreased.

After the low temperature formation process in the flue gas (Fig. 5(c)) the profiles changed a lot. 23478-PeCDF and TCDF increased dramatically to be the dominant gaseous PCDD/Fs. HpCDD had the highest concentration among PCDDs. Conversely in the solid phase OCDD and HpCDD had high fractions of concentrations among PCDDs, about 18.1% and 8.0%, respectively. Highly chlorinated PCDDs, especially OCDD, were transferred much more easily to the solid phase with the decreasing temperature of flue gas from the superheater to the inlet of APCD.

When the flue gas went through the APCD (Figs. 5(c)–5(d)), the profiles of PCDD/Fs did not change remarkably. 23478-PeCDF had the highest level among the PCDD/F congener in the gaseous phase. The APCD has no obvious removal selectivity of different chlorinated PCDD/Fs. The result is similar to the previous research before and after one wet scrubber (Takaoka et al., 2003). In contrast, after the APCD the fractions of 234678-HxCDF, 1234678-HpCDF and 1234678-HxCDD increased. This was because the PCDD/Fs with higher chlorination levels in the raw flue gases were more difficult to be adsorbed by activated carbon. They would gradually accumulate on the aged filters, and then were released to the flue gas. The result is similar to facts due to the memory effects of aged bag filters in other research (Li et al., 2011).
Homologue Concentrations of Chlorobenzenes

At the four sampling sites of this MSWI system, the concentrations of TrCBzs were higher than that of other homologues, shown in Fig. 6. And the concentrations of chlorobenzenes went down with the increase of chlorination. The APCD did not affect the homologue profiles of chlorobenzenes. This result was the same with that of PCDD/Fs.

Further analysis on the isomers in Fig. 6 revealed that 124-TrCBz nearly dominated in all chlorobenzenes especially when the PCDD/Fs concentrations were low (< 0.3 ng Nm⁻³). The fact was different from the result that 123-TrCBz was the highest one in previous research (Wang et al., 2017a, b) when the concentrations of PCDD/Fs were high. Observably, the concentrations of TeCBzs and PCBzs at the inlet of semi-dry scrubber increased obviously. It revealed that TeCBzs and PCBzs were majorly generated through the low-temperature heterogeneous pathway.

Correlations between PCDD/Fs and Chlorobenzenes

Given the rather lower concentrations of PCDD/Fs and CBzs at high-temperature sampling sites (1# and 2#), the correlations were only analyzed at 3# and 4#. These results would reflect the dominant formation and the final emission from this MSWI.

Analysis among Different PCDD/Fs and CBz Homologues

Statistical methods, principal component analysis (PCA) and hierarchical cluster analysis (HCA) were used to evaluate the relationships among congener patterns of 17 toxic PCDD/Fs and tri- to hexa-chlorobenzenes. The PCA “objects” were each sample run and the “variables” were each compound’s concentration, performed on normalized concentrations of PCDD/Fs and CBzs. HCA was conducted with Ward’s method and the data were standardized by z-score.

At the inlet of semi-dry scrubber, 17 gaseous toxic PCDD/Fs and gaseous CBzs were analyzed in Fig. 7(a). Based on the two components extracted from PCA, the first principal component (p[1]) accounted for 89.4% of the total variances and the second principal component (p[2]) accounted for 7.5%. 2378-TCDF stated closely to all the CBzs detected, revealing a closer correlation with CBzs. From HCA analysis result it was also found that all the compounds could be divided into two clusters. 2378-TCDF and all CBzs were in one cluster and other PCDD/Fs in another cluster. Furthermore, TrCBzs were most closely related to 2378-TCDF among all CBzs. However, the relationships among solid-phase PCDD/Fs and CBzs were poor in Fig. 7(b). All the 17 toxic PCDD/Fs stated further from all CBzs in the PCA result. PCDD/Fs and CBzs were divided in different clusters in the HCA dendrogram. 124-TrCBz and 1235/1245-TeCBz were more closely related to PCDD/Fs according to the shorter rescaled distances in the HCA dendrogram.

Rare CBzs and PCDD/Fs were present in the solid phase based on the emission results (4#). The total concentrations were analyzed in Fig. 7(c). The first principal component still accounted for high fraction, 79.1%. According to the PCA and HCA results, all the compounds could be divided into three clusters. Cluster 1 included TeCBzs, PCBz, HCBz and 124-TrCBz. Cluster 2 included 123-TrCBz, 135-TrCBz, 2378-TCDD and 2378-TCDF. The rest of PCDD/Fs were included in Cluster 3.

Both before and after the APCD, TrCBzs were more closely related to PCDD/Fs than other CBzs, consistent with previous research (Kuribayashi et al., 2005; Gullett et al., 2011; Guo et al., 2014). TrCBz should be concerned as the best indicator of PCDD/Fs.

Correlations between PCDD/Fs and CBzs

The detailed correlations between PCDD/Fs and CBzs of the flue gas from the scrubber inlet were analyzed in the gaseous phase and solid phase separately. According to the results calculated in Table.2, in the gaseous phase most of chlorobenzenes showed high correlation coefficients with PCDD/Fs, especially 123-TrCBz, significant at 0.01 level.
Fig. 7. Principal component analysis and hierarchical cluster analysis of PCDD/Fs and CBzs (A1: 135-TrCBz, A2: 124-TrCBz, A2: 123-TrCBz, B1: 1235/1245-TeCBz, B2: 1234-TeCBz, C: PCBz, D: HCBz T1-T17: 2378-TCDD, 12378-PeCDD, 123478-HxCDD, 123678-HxCDD, 123789-HxCDD, 1234678-HpCDD, OCDD, 2378-TCDF, 12378-PeCDF, 23478-PeCDF, 123478-HxCDF, 1234789-HpCDF, OCDF).
APCD. The coefficient of determination was up to 0.9. demonstrated in this investigation. 123-TrCBz still remained and TEQ was 0.95. The same fact (Fig. 8) was also found the best correlation coefficient between 135-TrCBz 295.1 ng g–1, nearly 3 times higher than that in the flue gas. concentrations of PCDD/Fs in the fly ash reached up to rather high concentrations of PCDD/Fs. In this MSWI the PCDD/Fs was 0.89 (Gullet among all CBzs, 124-TrCBz was still the pollutant with appropriate correlations (R2 = 0.8) with PCDD/Fs, significant Table 2. However, 135-TrCBz and 123-TrCBz still revealed the highest concentration. The differences between PCDD/Fs (two-tailed); 1234-TeCBz, significant at 0.01 level (two-tailed); and PCBz, significant at 0.05 level (two-tailed). 123-TrCBz revealed rather high coefficients of determination (R2 > 0.8) with TEQ in the gaseous phase, as shown in Fig. 8. Even in the linear regression which has been widely used in practical applications, R2 could be up to 0.89. Both before and after the APCD 123-TrCBz always had a good correlation with gaseous PCDD/Fs. The correlations between PCDD/Fs and CBzs in the solid phase were not as good as that in the gaseous phase in Table 2. However, 135-TrCBz and 123-TrCBz still revealed appropriate correlations (R2 = 0.8) with PCDD/Fs, significant at 0.1 level (two-tailed). It provided a thought that indicators, such as 123-TrCBz, could be applied for predicting the results of PCDD/Fs both in gas phase and solid phase. A comprehensive formation result of PCDD/Fs in the MSWI could be monitored online through it. The results in the stack after the APCD reflect the final emission levels of PCDD/Fs from the MSWI, which is seriously controlled by the government standard. Previous studies have proved that TrCBz has pretty good correlations with PCDD/Fs as significant indicators. Kuribayashi developed a vacuum ultra-violet single-photon ionization ion trap time-of-flight mass spectrometer system for real-time monitoring of TrCBzs as PCDD/Fs indicators (Kuribayashi et al., 2005). Gullet found that the correlation coefficient between 124-TrCBz and I-TEQ was 0.85, and the correlation coefficient between 124-TrCBz and concentrations of PCDD/Fs was 0.89 (Gullet et al., 2011). Guo et al. (2014) found the best correlation coefficient between 135-TrCBz and TEQ was 0.95. The same fact (Fig. 8) was also demonstrated in this investigation. 123-TrCBz still remained a good correlation with PCDD/Fs in the stack gas after the APCD. The coefficient of determination was up to 0.9.

It is well known that fly ash from the APCD contains rather high concentrations of PCDD/Fs. In this MSWI the concentrations of PCDD/Fs in the fly ash reached up to 295.1 ng g–1, nearly 3 times higher than that in the flue gas. This rate will increase with higher removal efficiency of injected AC. The concentrations of CBzs in the fly ash were also detected. The total concentrations of CBzs were only 3.1 µg g–1, much lower than that in the flue gas. Among all CBzs, 124-TrCBz was still the pollutant with the highest concentration. The differences between PCDD/Fs and CBzs in the fly ash resulted from the different adsorptive capacities of activated carbon. Obviously, fly ash is a serious pollution source of PCDD/Fs from MSWIs. Previous research concentrates only on how to monitor PCDD/Fs in the flue gas in time (Zhou et al., 2015). It is also necessary to monitor PCDD/Fs in the fly ash through several rapid methods. Streibel stated PCDD/Fs concentrations in electrostatic precipitator ash and boiler ash had weak correlation with indicators in the flue gas (Streibel et al., 2007). Different from their result, chlorobenzenes in the stack gas were found to have remarkable correlations with PCDD/Fs in fabric filter ash from this MSWI shown in Table 3. It revealed gaseous phase pollutants in the stack gas were further correlated with fly ash than that in the flue gas before the APCD. And the correlations revealed not to be positive but to be negative, since pollutants in fly ash were removed from gaseous phase through the fabric filter. 124-TrCBz was found to be sufficiently correlated to PCDD/Fs in the solid residues.

It gives a further thought that TrCBzs could be used as the indicator parameter for monitoring the total PCDD/Fs emitted from MSWIs, both in the flue gas and fly ash.

**CONCLUSION**

The characteristics of PCDD/Fs and CBzs in the flue gas and fly ash at the outlet of the furnace, at the outlet of the high-temperature superheater, at the inlet of the semi-dry scrubber and in the stack after APCD processing in one MSWI in China were studied. Both the PCDD/Fs and CBzs were formed mostly at low temperatures, especially the PCDD/Fs. The dominant PCDD/Fs generated in the gaseous phase were 23478-PeCDF and TCDF, whereas they were 1234678-HpCDF and TCDF in the solid phase. 124-TrCBz was the major CBz in both the gaseous and solid phase.

Prior to reaching the semi-dry scrubber at the inlet of the APCD, more PCDD/Fs were found in the solid phase as the temperature decreased, while CBzs exhibited the opposite trend. When the flue gas went through the APCD, pollutants in the solid phase largely decreased due to the fabric filter. However, activated carbon with a low surface area and mesoporous volume showed low removal efficiencies for gaseous PCDD/Fs and CBzs. Furthermore, the memory
Fig. 8. Correlation between 123-TrCBz and TEQ. (a) gas phase at scrubber inlet, (b) solid phase at the scrubber inlet, and (c) total TEQ in stack gas.

Table 3. Parson Coefficients between chlorobenzenes in flue gas and PCDD/Fs in fly ash.

<table>
<thead>
<tr>
<th></th>
<th>135-TrCBz</th>
<th>124-TrCBz</th>
<th>123-TrCBz</th>
<th>1235/1245-TeCBz</th>
<th>1234-TeCBz</th>
<th>PCBz</th>
<th>HCBz</th>
</tr>
</thead>
<tbody>
<tr>
<td>total concentrations</td>
<td>-0.249</td>
<td>-0.891</td>
<td>-0.671</td>
<td>-0.641</td>
<td>-0.622</td>
<td>-0.524</td>
<td>-0.502</td>
</tr>
<tr>
<td>total TEQ</td>
<td>-0.196</td>
<td>-0.759</td>
<td>-0.624</td>
<td>-0.466</td>
<td>-0.465</td>
<td>-0.327</td>
<td>-0.284</td>
</tr>
</tbody>
</table>

*Significant at 0.01 level (two-tailed); †significant at 0.05 level (two-tailed); ‡significant at 0.1 level (two-tailed).

effects of the aged filters caused increased fractions of 234678-HxCDF, 1234678-HpCDF and 1234678-HxCDD.

In the gaseous phase, most of the CBzs showed high correlation coefficients with PCDD/Fs, especially 123-TrCBz ($R^2 > 0.8$). In the solid phase, poorer correlations were found between CBzs and PCDD/Fs in the flue gas. However, 135-TrCBz and 123-TrCBz still displayed good correlations ($R^2 = 0.8$) with the PCDD/Fs. The concentrations of PCDD/Fs in the fly ash of the fabric filters were nearly 3 times higher than those in the flue gas. A remarkable correlation was also found between gaseous 124-TrCBz in the stack gas and PCDD/Fs in the fabric filter ash.

The comprehensive analysis shows that TrCBzs may be regarded as the best indicators of PCDD/Fs in both flue gas and fly ash for comprehensively monitoring the total PCDD/Fs emitted by MWSIs.

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