



## PCDD/F Emissions from Hazardous Waste Incinerators in China

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### ABSTRACT

In order to investigate the dioxin emission levels of hazardous waste incinerators (HWIs), and estimate their emission factors to the atmosphere, flue gas samples were collected from 12 HWIs in China, and analyzed for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). Eleven HWIs are located in the south-eastern coastal areas of China, with rotary kilns being the most widely used type of incinerator (more than 50% of the units), followed by pyrolysis kilns. Eleven incinerators had their emission levels below the current standards in China, while only four facilities exhibited emission levels below the European Union's limits. The highest concentration of PCDD/Fs, at nearly 1 ng TEQ/Nm<sup>3</sup>, was in the flue gas collected from an HWI with a waste burning capacity of 5 ton/d. This result was significantly higher than the values found for the other 11 incinerators, and thus was due to the poor performance of air pollution control devices and the influence of memory effects caused by PCDD/Fs emissions related to the start-up of the incinerator. In addition, the high dioxin emissions of this HWI were related to its feeding wastes, which mainly consisted of chemical industry waste residue with high a chlorine content. The emission factors of PCDD/Fs from the HWIs examined in this work were in the range of 0.27–18 µg TEQ/ton hazardous waste, with an average value of 3.74 µg TEQ/ton hazardous waste. It is estimated that 5.0 g TEQ of PCDD/Fs was released from HWIs to the atmosphere in China in 2010, which is less than that seen in 2004. The results of principal component analysis and hierarchical cluster analysis show all the investigated HWIs can be assigned to three groups, as verified by the results of nonparametric statistics. OCDD, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HpCDF and OCDF are the main congeners in these three groups.

**Keywords:** PCDD/Fs; HWIs; Flue gas; Emission factors.

### INTRODUCTION

As the largest developing country, China generates huge amounts of hazardous waste every year, which has put severe pressures on the Chinese environment due to extraordinary economic growth, urbanization, and industrialization. Waste products generated from chemical industries or hospitals are both classified as hazardous waste in China (MEP, 2007). Incineration is an ultimate disposal means for hazardous wastes which cannot be safely deposited, reduced or recycled in a secured landfill site (Visvanathan, 1996). With respect to traditional hazardous waste disposal technologies, incineration incorporates weight and volume reduction, detoxification and energy recovery. At present, incineration has been demonstrated to be a priority disposal

method for hazardous waste in “the Nation Plan for Construction of Facilities for Disposal of Hazardous Wastes and Medical Wastes”, which was established by the National Development and Reform Commission and State Environmental Protection Administration of China (Chen *et al.*, 2008). As a result of increasing annual production of hazardous waste, the construction of HWIs has been booming in the mainland of China (Ma *et al.*, 2011; Wu *et al.*, 2012). However, PCDD/Fs emissions from HWIs have become a serious issue in China because of the public fear about dioxins, which are a group of persistent organic pollutants never intentionally produced but found as by-products in thermal industrial-chemical processes (Anderson *et al.*, 2002).

HWIs were catalogued as important potential emission sources of PCDD/Fs (Prashant *et al.*, 2008) and therefore, more attention is required for a better understanding of PCDD/Fs emissions from hazardous waste incineration. There is still a lack of detailed information on PCDD/Fs emissions from HWIs in China until now, although some PCDD/Fs emission data about medical waste incinerators (MWIs) have been reported (Gao *et al.*, 2009). PCDD/F

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emissions from the existing HWIs in China has become one of the most serious issues need to be solved by the Ministry of Environment Protection (MEP) of the People's Republic of China (NIP, 2007).

In order to get information on the environmental impact of HWIs, this study investigates the emission levels of PCDD/Fs from HWIs in China, and estimates their emission factors released into the atmosphere. Using principal component analysis (PCA) and hierarchical cluster analysis (HCA), the possible grouping of similar emissions were analyzed and the congener profiles were categorized in corresponding groups. Also a comparison of PCDD/Fs emission characteristics from several typical types of HWIs in mainland China is made.

## METHODS

### Sample Collection

The flue gas samples were collected with an isostack sampler (M5, KNJ Engineering, South Korea) according to USEPA method 23A. The sample collection components included the glass fiber filters, in line with a condenser, the sorbent (XAD-2 resin) module and four impingers. The sampling standard ( $^{13}\text{C}_{12}$  labelled standard, Cambridge Isotope Laboratories, Inc., USA) was spiked into the XAD-2 resin before sampling of flue gas.

The flue gas samples were collected from 12 HWIs located in China, and Table 1 lists some information about these incinerators. Most of these are located in the south-eastern coastal areas of China, where the generation of hazardous wastes is much higher than in other areas due to the relatively rapid development of local economy. Ten of the investigated HWIs were along a coastal area (Tianjin, Shanghai, Zhejiang, Fujian and Guangdong Province). All HWIs are domestic-made with waste burning capacity ranging from 5 to 100 ton/d. Rotary kiln, pyrolysis kiln, fluidized bed are the main incineration technologies for hazardous waste disposal currently used in China. Different with other combustion process, pyrolysis is a starved air process with air levels less than the stoichiometric requirements for complete combustion (Li *et al.*, 1999). In pyrolysis, waste

organic compounds may undergo destructive distillation, or evaporation to form solid residues and combustible gas. In our survey, rotary kiln incineration technology is the most widely used (more than 50% of the units), followed by pyrolysis kiln. For rotary kiln facilities, the combustion temperature is in the range of 700–1200°C, and their capacities range from 15 to 100 ton/d with an average level of 33 ton/d. For pyrolysis facilities, the waste treatment capacities range from 5 to 36 ton/d, while the average disposal capacity at a level of 15 ton/d. The air pollution control devices (APCDs) consisted of semi-dry scrubber, activated carbon injection and fabric filter.

### PCDD/Fs Analysis and Quality Control

Sample extraction and purification methods were performed according to the USEPA method 1613 (Xu *et al.*, 2009). Briefly, the sample was spiked with 1 ng of  $^{13}\text{C}_{12}$ -labeled Internal Standards prior to Soxhlet extraction. The extract was then spiked with 1 ng of  $^{13}\text{C}_{12}$ -labeled Alternative Standard and was sequentially cleaned by acid/base extraction and multilayer silica gel and basic alumina columns. The final extract was concentrated to 20  $\mu\text{L}$  and spiked with 1 ng of  $^{13}\text{C}_{12}$ -labeled Recovery Standards prior to the analysis by HRGC/HRMS. The instrumental analysis was 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  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ) capillary column was used for separation of the PCDD/Fs congeners. The GC temperature program was optimized as follows: automatic splitless injection of 1  $\mu\text{L}$  at 150°C, initial oven temperature of 150°C for 1 min, then increased at 25 °C/min to 190°C held for 1 min, finally increased at 3 °C/min to 280°C and held for 20 min. The mass spectrometer was operated in the electron impact ionization mode using selected ion monitoring (SIM). The mass system was turned to a minimum resolution of 10,000 (10% valley) under positive EI conditions (38 eV electron energy).

Quality control and quantification method of PCDD/Fs analysis have been presented elsewhere (Yan *et al.*, 2008). The toxic 2,3,7,8-substituted PCDD/Fs (referred to as congeners) as well as tetra- to octa-chlorinated homologues

**Table 1.** Characteristics of the investigated HWIs in mainland of China.

|     | Facility type  | Capacity (ton/d) | Sampling times | Air Pollution Control Devices  |
|-----|----------------|------------------|----------------|--|
| H01 | Rotary kiln    | 50               | 3              | Semi-dry scrubber + activated carbon + Fabric filter                         |
| H02 | Rotary kiln    | 15               | 3              | Semi-dry scrubber + Fabric filter  |
| H03 | Rotary kiln    | 100              | 3              | Semi-dry scrubber + activated carbon + Fabric filter                         |
| H04 | Rotary kiln    | 37               | 3              | Semi-dry scrubber + Fabric filter  |
| H05 | Rotary kiln    | 20               | 3              | Semi-dry scrubber + activated carbon + Fabric filter                         |
| H06 | Fluidized bed  | 100              | 3              | Semi-dry scrubber + activated carbon + Fabric filter                         |
| H07 | Rotary kiln    | 10               | 3              | Semi-dry scrubber + Fabric filter  |
| H08 | Pyrolysis kiln | 5                | 3              | Semi-dry scrubber + activated carbon + Fabric filter                         |
| H09 | Rotary kiln    | 6                | 3              | Activated carbon + Fabric filter   |
| H10 | Pyrolysis kiln | 36               | 3              | Multi-tubular Cyclone + Semi-dry scrubber + activated carbon + Fabric filter |
| H11 | Rotary kiln    | 24               | 3              | Semi-dry scrubber + activated carbon + Fabric filter                         |
| H12 | Pyrolysis kiln | 5                | 3              | Semi-dry scrubber + Fabric filter  |

were identified based on isotope ratios within  $\pm 15\%$  of the theoretical values and signal to noise ratios of equal or greater than 2.5. Quantification of PCDD/Fs was performed by an isotope dilution method using relative response factors previously obtained from the five calibration standard solutions. A blank sample was analyzed for every batch of six samples, and a duplicate sample was analyzed for every two batches. Recoveries of internal standards, as determined against external standard, generally varied between 63 and 118%, and were all satisfied with the Method of USEPA 1613. Besides, the average limits of detection (LOD) varied between 0.040 and 0.324 pg/g from tetra- to octa-chloro PCDD/Fs, respectively. Toxic equivalents value (TEQ) was calculated by using the 2005 World Health Organization toxicity equivalency factors (WHO-2005-TEF). All data was reported with reference to standardized conditions, i.e. per normal cubic meter ( $\text{Nm}^3$ ) dry gas with 11% of  $\text{O}_2$ .

### Statistical Analysis

Principal component analysis (PCA) and hierarchical cluster analysis (HCA) were performed by using the SPSS 16.0 statistical package. Because there are only 12 HWIs were investigated in this study, the sample size is too small to use PCA and HCA. In order to eliminate the effects of data quality caused by the small sample, nonparametric statistics was used to test the correlation of PCDD/Fs emission in possible groups.

## RESULTS AND DISCUSSION

### Emission Levels of PCDD/Fs from HWIs

The 12 investigated HWIs exhibited a large variation in their PCDD/Fs emissions to the atmosphere (Table 2). The emission levels of PCDD/Fs ranged from 0.031 to 0.902 ng TEQ/ $\text{Nm}^3$ . The median concentration of PCDD/Fs was 0.227 ng TEQ/ $\text{Nm}^3$ , and the average emission level of 12 facilities was 0.273 ng TEQ/ $\text{Nm}^3$ . Eleven incinerators showed emission levels below current PCDD/Fs emission standard for HWIs in China (0.5 ng TEQ/ $\text{Nm}^3$ ) (Gao et al., 2009), while only four incinerators had the PCDD/Fs emission levels below the limit of 0.1 ng TEQ/ $\text{Nm}^3$  regulated by developed countries (Streibel et al., 2007). For one plant, H12, the concentration of PCDD/Fs in flue gas was nearly 1 ng TEQ/ $\text{Nm}^3$ . The high emissions of HWIs may result from poor performance of air pollution control devices and the influence of memory effect caused by start-up on PCDD/Fs emission of incinerators (Chi et al., 2006; Wang et al., 2007; Choi et al., 2008). In this research, the amount of activated carbon injection in H12 (0.05 g/ $\text{Nm}^3$  flue gas) is less than the average of other 11 incinerators (1.75 g/ $\text{Nm}^3$  flue gas). The HWIs with larger amount of activated carbon injection have lower dioxin emission. Another reason for high dioxin emission of this investigated HWI due to its feeding materials was chemical industry waste residue with high chlorine content. Gao et al. (2009) found that the concentration of PCDD/Fs in stack gas from HWIs in China ranged from 0.01–7.79 ng TEQ/ $\text{Nm}^3$ , which were higher than the emission levels from HWIs in Turkey and Spain (0.02–0.025 ng TEQ/ $\text{Nm}^3$  in average). Although many studies showed that

Table 2. TEQ values (pg TEQ/ $\text{Nm}^3$ ) of 17 substituted PCDD/Fs in 12 hazardous waste incinerators in China.

| Compound            | H01    | H02    | H03   | H04   | H05   | H06   | H07    | H08    | H09    | H10   | H11    | H12    |
|---------------------|--------|--------|-------|-------|-------|-------|--------|--------|--------|-------|--------|--------|
| 2,3,7,8-TCDD        | 15.21  | 14.43  | 1.73  | 4.48  | 22.11 | 2.2   | 6.63   | 10.03  | 50.76  | 6     | 17.82  | 26.95  |
| 1,2,3,7,8-PeCDD     | 35.58  | 29.86  | 8.81  | 13.47 | 13.65 | 4.48  | 29.29  | 24.43  | 117.1  | 11    | 45.98  | 84.85  |
| 1,2,3,4,7,8-HxCDD   | 1.83   | 2.16   | 1.09  | 0.86  | 0.54  | 0.66  | 6.54   | 2.48   | 8.89   | 0.4   | 5.46   | 5.24   |
| 1,2,3,6,7,8-HxCDD   | 2.56   | 2.71   | 1.63  | 1.45  | 1     | 0.75  | 6.38   | 2.83   | 13.97  | 0.8   | 8.5    | 6.8    |
| 1,2,3,7,8,9-HxCDD   | 1.64   | 2.49   | 1.25  | 0.94  | 1.01  | 0.66  | 5.99   | 2.17   | 11.23  | 0.6   | 4.59   | 5.5    |
| 1,2,3,4,6,7,8-HpCDD | 0.84   | 1.47   | 0.75  | 0.61  | 0.61  | 0.44  | 3.74   | 0.95   | 4.99   | 0.23  | 4.76   | 2.01   |
| OCDD                | 0.04   | 0.06   | 0.03  | 0.03  | 0.04  | 0.02  | 0.11   | 0.03   | 0.12   | 0.02  | 0.38   | 0.05   |
| 2,3,7,8-TCDF        | 9.43   | 14.37  | 1.64  | 4     | 33.32 | 1.81  | 6.65   | 13.38  | 28.41  | 10.4  | 21.43  | 81.96  |
| 1,2,3,7,8-PeCDF     | 3.72   | 19.17  | 0.59  | 1.29  | 2.97  | 0.65  | 3.32   | 4      | 7.06   | 1.65  | 4.81   | 25.94  |
| 2,3,4,7,8-PeCDF     | 106.95 | 108.37 | 14.51 | 18.69 | 33.07 | 10.54 | 160.5  | 108.63 | 110.02 | 20.1  | 98.62  | 457.87 |
| 1,2,3,4,7,8-HxCDF   | 10.2   | 22.25  | 5.26  | 4.84  | 4.1   | 2.59  | 36.79  | 25.77  | 30.54  | 3     | 29.38  | 78.89  |
| 1,2,3,6,7,8-HxCDF   | 9.3    | 147.92 | 3.68  | 5.9   | 4.02  | 2.25  | 18.28  | 17     | 31.7   | 3.2   | 20.34  | 56.85  |
| 2,3,4,6,7,8-HxCDF   | 10.95  | 43.68  | 5.23  | 5.6   | 4.52  | 2.47  | 49.23  | 23.98  | 35.58  | 2.9   | 26.77  | 52.72  |
| 1,2,3,7,8,9-HxCDF   | 1.81   | 49.22  | 0.95  | 1.37  | 1.26  | 0.46  | 7.23   | 2.67   | 6.8    | 0.8   | 3.48   | 4.79   |
| 1,2,3,4,6,7,8-HpCDF | 1.07   | 11.1   | 1.2   | 1.46  | 1.13  | 0.56  | 7.51   | 4.04   | 6.48   | 0.57  | 6.95   | 10.27  |
| 1,2,3,4,7,8,9-HpCDF | 0.25   | 2.14   | 0.29  | 0.2   | 0.58  | 0.09  | 1.93   | 0.43   | 1.09   | 0.07  | 1.09   | 0.94   |
| OCDF                | 0.03   | 0.05   | 0.03  | 0.04  | 0.05  | 0.01  | 0.15   | 0.03   | 0.1    | 0.02  | 0.23   | 0.08   |
| Total concentration | 211.41 | 471.45 | 48.65 | 65.24 | 124   | 30.64 | 350.27 | 242.87 | 464.84 | 61.77 | 300.57 | 901.71 |

most of HWIs can meet the emission standard of 0.1 ng TEQ/Nm<sup>3</sup> in European countries (Karademir, 2004; Rivera-Austrui *et al.*, 2011), some researchers found this limit in stack gas was not accomplished due to a memory effect in the scrubber in Sweden (Lothgren *et al.*, 2005). On a global scale, the PCDD/Fs pollution of HWIs is very serious in many countries, especially in developing countries.

According to our research, incineration technologies should be further improved to reduce PCDD/Fs emissions. Given the operation situation of domestic HWIs in China, much more work and improvements need to be carried out in order to meet the present emission limits (0.5 ng TEQ/Nm<sup>3</sup>) and the more stringent regulations coming in the future (0.1 ng TEQ/Nm<sup>3</sup>).

#### Estimated Emission Factors of PCDD/Fs

The release of PCDD/Fs to air by flue gas is the predominant vector of dioxin emissions from hazardous waste combustion. The emission factors of 12 investigated HWIs in China were calculated based on the UNEP default emission factors of average flue gas rate of 7 500 Nm<sup>3</sup>/ton hazardous waste (TEQ below 0.1 ng/Nm<sup>3</sup>), 10 000 Nm<sup>3</sup>/ton hazardous waste (TEQ between 0.1 and 1 ng/Nm<sup>3</sup>) and 15000 Nm<sup>3</sup>/ton hazardous waste (TEQ between 1 and 20 ng/Nm<sup>3</sup>) (UNEP, 2005). According to these default values, the estimated emission factors of PCDD/Fs into the atmosphere from the 12 investigated HWIs in China were in the range of 0.269 to 17.732 µg TEQ/ton, with an average value of 3.736 µg TEQ/ton hazardous waste. In 2010, a total of 1344000 ton of hazardous wastes were incinerated in China, accounting for 74.2% of the annual disposal amount (MEP, 2010). Calculated with the average emission factor of 3.736 µg TEQ/ton, it was estimated that 5.0 g TEQ of PCDD/Fs was annual released from HWIs to the atmosphere in 2010. The annual production of PCDD/Fs from HWIs in 2010 was less than that from HWIs in 2004 (NIP, 2007), the same trend was found by Gao *et al.* (2009)

and Ni *et al.* (2009) in the surveys of PCDD/Fs emissions from medical waste incinerators (MWIs) and municipal solid waste incinerators (MSWIs). The underestimation of annual production of PCDD/Fs caused by waste incinerators possibly due to the lack of statistical emission data. The average emission factor calculated with only few TEQ values is insufficient to represent the emission conditions of PCDD/Fs from HWIs, MSWIs and MWIs in China, because of the large variation of PCDD/Fs concentration in stack gases. In order to understand and evaluate the contribution of PCDD/Fs from potential incineration emission sources in China comprehensively, more emission inventories should be carried out by scientists and government.

#### Congener Profiles of PCDD/Fs in Flue Gas

TEQ values of 17 substituted PCDD/Fs in 12 hazardous waste incinerators in China were showed in Table 2. The data revealed 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were the most abundant congeners.

Statistical methods such as PCA and HCA are commonly used by scientists as important tools on dioxin data analysis (Fiedler *et al.*, 1996; Cheng *et al.*, 2003). In this study, these two methods were applied to get a better understanding of PCDD/Fs congener distributions from HWIs in China. PCA was used to evaluate the potential variation and similarities of the PCDD/Fs congener patterns in different flue gas samples, the score plot of PCA shows the relative contributions of the 17 toxic PCDD/Fs congeners, as shown in Fig. 1. The HCA Dendrogram shows the similarities and differences between each hazardous waste incinerator (Fig. 2). Based on the two components extracted from PCA, the first principal component (PC 1) accounted for 60.75% of the total variance, and the second principal component (PC 2) accounted for 16.28% of the total variance. The score plot of PCA and the Dendrogram of HCA indicated that all the investigated HWIs can be assigned to three groups, and most of HWIs fell into Group

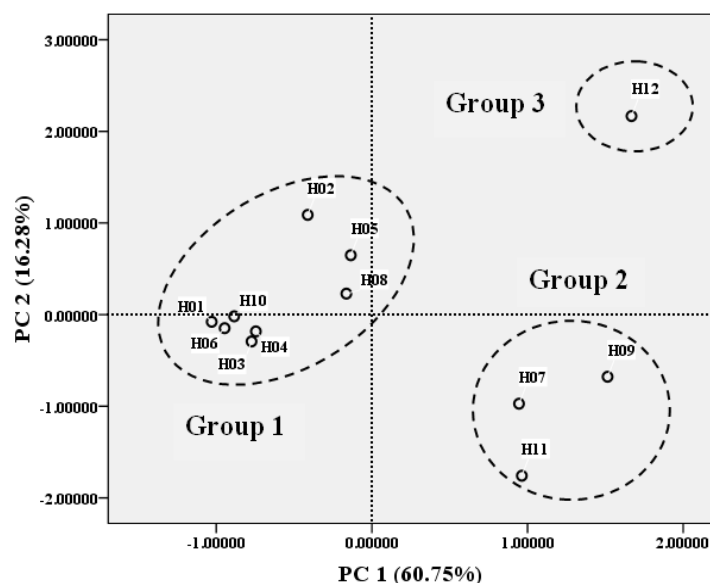
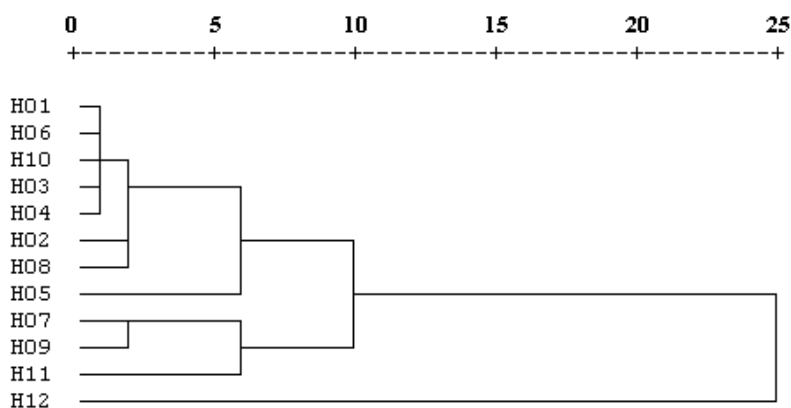


Fig. 1. Score plot of principal component analysis of 17 toxic PCDD/Fs emissions.



**Fig. 2.** Hierarchical tree plot of cluster analysis of the 12 hazardous waste incinerators.

1. Nonparametric statistics was used to test the correlation of PCDD/Fs emission in possible Group 1 and Group 2 (Group 3 absent due to only one variable). Spearman's rank correlation coefficient matrix of Group 1 and Group 2 were showed in Table 3 and Table 4. There is a very strong correlation between the PCDD/Fs emission of each group, especially in Group 2. The correlation coefficients of Group 2 are all higher than 0.7 and are significant at the 0.01 level. The results of nonparametric statistics verified well with the PCA and HCA.

Fig. 3 presents the congener profiles of PCDD/Fs in each group. The congener distributions were obtained by normalizing each congener to the total weight of all 2,3,7,8-substituted PCDD/Fs congeners. Some research results showed PCDD/Fs patterns in stack gas from HWIs are usually characterized by higher fractions of OCDF, 1,2,3,4,6,7,8-HpCDF, OCDD and OCDF (Aykan Karademir, 2004; Nuria Ferre-Huguet *et al.*, 2006). In this study, most of the samples fell into Group 1, and 2,3,4,7,8-PeCDF (14.97%) was the most abundant congener in Group 1, followed by 1,2,3,4,6,7,8-HpCDF (11.74%) and 2,3,7,8-TCDF (10.16%), which was similar to the report of PCDD/Fs emissions from medical waste incinerators in Antioquia, Colombia (Hoyos *et al.*, 2008). H07, H09 and H11 had emission levels below 0.5 ng TEQ/Nm<sup>3</sup> and fall into Group 2, 1,2,3,4,6,7,8-HpCDF was the most abundant congener (15.32%), and OCDD accounted for almost the same proportion (14.36%), which was similar to congener profiles of industry waste incinerators in previous study (Kao *et al.*,

2006). In group 3 (H12), 2,3,4,7,8-PeCDF was the most abundant congener (21.30%), the result was concordant with the research of Spanish scientists (Ferre-Huguet *et al.*, 2006). Although there are differences in the PCDD/Fs fingerprint in Groups 1, 2 and 3, the fractions of OCDD, 2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8-HpCDF and OCDF showed they were main congeners in three groups, respectively. Compared with other results, the congeners fraction of flue gas samples in our study were typical HWI gas profile with a dominant homologue of PCDFs and relatively low PCDDs.

It has been reported that the homologue patterns of flue gas were similar from various thermal processing facilities, including MSWIs, HWIs, MWIs and automobiles, where PCDF levels were higher than PCDDs (Hagenmaier *et al.*, 1994; Oh *et al.*, 1999), but a large variation of congener patterns was observed among different incineration sources. From Fig. 3 and other previous study, we can see that HWIs and MSWIs exhibited different congener distributions of PCDD/Fs in stack gas. In MSWIs, the congener profile of flue gas was dominated by OCDD and 1,2,3,4,6,7,8-HpCDF, followed by 1,2,3,4,6,7,8-HpCDF and OCDF (Yan *et al.*, 2008). High fraction of OCDD, 2,3,7,8-TCDF and 1,2,3,4,6,7,8-HpCDF were observed from congener profiles of PCDD/Fs in flue gas of MWIs (Gao *et al.*, 2009), which coexists the similarities and differences compared with the results of this study. The possible factors affecting the congener distributions of PCDD/Fs in incinerators can be combined into three categories: the types of incinerator, waste composition, and the types of APCD. The formation

**Table 3.** Spearman's rank correlation coefficient of Group 1.

|     | H01     | H02     | H03     | H04     | H05     | H06     | H08     | H10     |
|-----|---------|---------|---------|---------|---------|---------|---------|---------|
| H01 | 1.000   | 0.608** | 0.701** | 0.775** | 0.691** | 0.784** | 0.684** | 0.789** |
| H02 | 0.608** | 1.000   | 0.515*  | 0.625** | 0.380   | 0.507*  | 0.422   | 0.475   |
| H03 | 0.701** | 0.515*  | 1.000   | 0.941** | 0.696** | 0.971** | 0.703** | 0.900** |
| H04 | 0.775** | 0.625** | 0.941** | 1.000   | 0.767** | 0.949** | 0.782** | 0.926** |
| H05 | 0.691** | 0.380   | 0.696** | 0.767** | 1.000   | 0.723** | 0.993** | 0.674** |
| H06 | 0.784** | 0.507*  | 0.971** | 0.949** | 0.723** | 1.000   | 0.725** | 0.944** |
| H08 | 0.684** | 0.422   | 0.703** | 0.782** | 0.993** | 0.725** | 1.000   | 0.674** |
| H10 | 0.789** | 0.475   | 0.900** | 0.926** | 0.674** | 0.944** | 0.674** | 1.000   |

\* Correlation is significant at the 0.05 level (2-tailed).

\*\* Correlation is significant at the 0.01 level (2-tailed).

**Table 4.** Spearman's rank correlation coefficient of Group 2.

|     | H07     | H09     | H11     |
|-----|---------|---------|---------|
| H07 | 1.000   | 0.809** | 0.868** |
| H09 | 0.809** | 1.000   | 0.745** |
| H11 | 0.868** | 0.745** | 1.000   |

\* Correlation is significant at the 0.05 level (2-tailed).

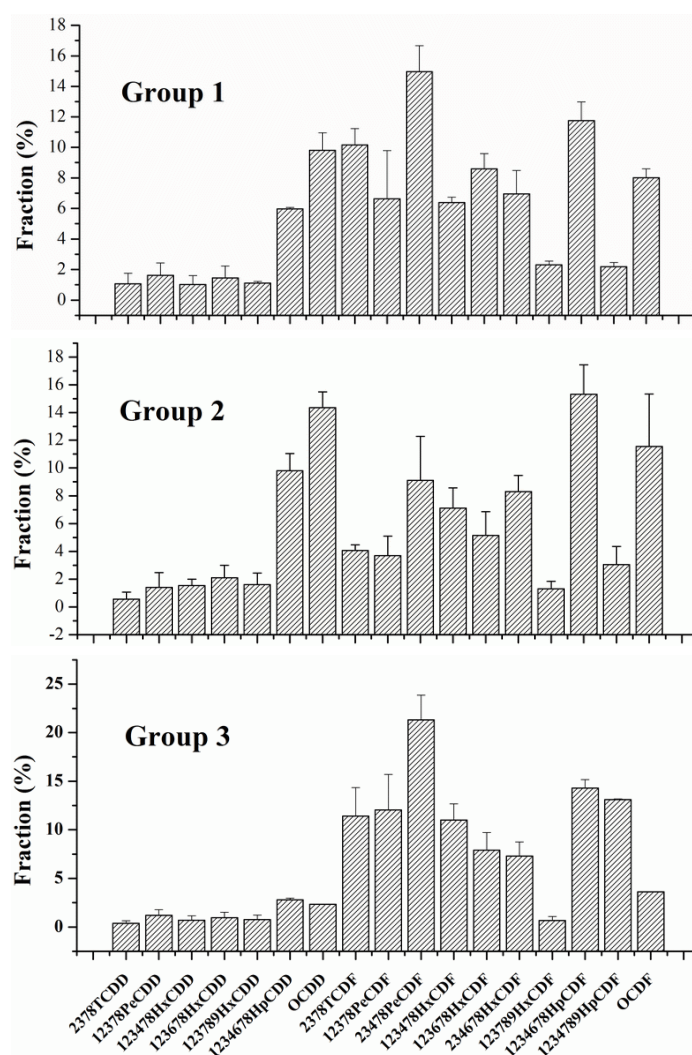
\*\* Correlation is significant at the 0.01 level (2-tailed).

mechanisms of PCDD/Fs are influenced first by whether the chlorine content in the feeding waste is over or below the threshold value then by other factors, which furnaces and APCDs represent (Wang *et al.*, 2003). The chlorine content in the waste plays an important role in determining the congener profiles and formation mechanisms of PCDD/Fs in flue gas (Wang *et al.*, 2003). When the chlorine level in the waste was below a threshold value at 0.8–1.1%, the chlorine was used to chlorinate the non-substituted phenol to produce chlorophenols, which are important precursors of PCDD/Fs and generate more PCDDs than PCDFs (Wang *et al.*, 2003; Ryuand Mulholland, 2005). When the chlorine content exceeds this threshold value, PCDD/Fs

are formed from many products of incomplete combustion (PICs) like PAHs through de novo synthesis, and the formation rates of PCDFs are higher than those of PCDDs (Wilhelm *et al.*, 2001; Wang *et al.*, 2003).

## CONCLUSIONS

In this study, the investigated HWIs exhibited a large variation of PCDD/Fs emissions to the atmosphere (0.036–1.182 ng TEQ/Nm<sup>3</sup>). Although one HWI had emission levels above the current standard in China, most of them can meet the emission standard. The emission factors of PCDD/Fs to the atmosphere were in the range of 0.27–18 µg TEQ/ton hazardous wastes. It was estimated that 5.0 g TEQ of PCDD/Fs was annually released from HWIs to the atmosphere in China in 2010. Combined PCA and HCA with nonparametric statistics, the 12 investigated HWIs can be divided into three groups, and most of them belonged to Group 1. The fractions of OCDD, 2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8-HpCDF and OCDF indicate they are main congeners in three groups, although there are differences in the PCDD/Fs fingerprint in Groups 1, 2 and 3.

**Fig. 3.** Congener distribution of PCDD/Fs in each group from hazardous waste incinerators.

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