Emission Characteristics and Formation Pathways of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans from a Typical Pesticide Plant

Yufeng Ma¹, Xiaoqing Lin^{1*}, Zhiliang Chen¹, Tong Chen¹, Mingxiu Zhan², Shuaixi Xu³, Hailong Wu⁴, Xiaodong Li¹, Jianhua Yan¹

¹ State Key Laboratory for Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou 310027, China

² College of Metrology and Measurement Engineering, China Jiliang University, Hangzhou 310018, China

³ Zhejiang Electric Power Design Institute Co., Ltd., Hangzhou 310012, China

⁴ Environment Protection Bureau of Zhoushan, Zhoushan 316021, China

ABSTRACT

The emission characteristics and the formation pathways of the polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from a pesticide plant were well investigated. In the present study, the international toxic equivalent quantity (I-TEQ) value of the PCDD/Fs (0.087 ng I-TEQ Nm⁻³) in the flue gas at the outlet of stack can meet the emission limit (0.1 ng I-TEQ Nm⁻³). The I-TEQ value of the PCDD/Fs (3.25 pg I-TEQ g⁻¹) in the fly ash is much lower than the permitted standard for disposal in sanitary landfill sites (3.0 ng of I-TEQ g⁻¹). In addition, 1,2,3,4,6,7,8-HpCDD, OCDD and 1,2,3,4,6,7,8-HpCDF are the three main congeners in the PCDD/Fs for the outlet of both the secondary combustion chamber and the stack. 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD are the most dominant congeners for the PCDD/Fs from inlet of bag filter. PCDD/Fs may be formed through high temperature homogeneous synthesis and heterogeneous precursor synthesis in the flue gas. In addition, PCDD/Fs might be formed in bag filter via de novo synthesis. The main formation areas of PCDD/Fs are waste heat boiler and quenching/deacidification tower in this pesticide plant. The TEQ estimated emissions of PCDD/Fs reaches 9.3 g year⁻¹. These findings are helpful for further controlling the formation and emission of PCDD/Fs in pesticide plants, yet more studies are still required.

Keywords: Polychlorinated dibenzo-*p*-dioxins and dibenzofurans; Chemical plant; Emission characteristics; TEQ emission factor; Formation pathways.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), as major classes of persistent organic pollutants (POPs), have become serious problem threatening environment and human health (Tsai *et al.*, 2014; Hsieh *et al.*, 2018b; Hung *et al.*, 2018; Lee *et al.*, 2018) because of their properties such as neurotoxicity, carcinogenicity, immunotoxicity, and bioaccumulation. For the past decades, the international community has been trying to control the global pollution of POPs and to protect the environment and human health through the Stockholm Convention (Stockholm Convention 2001). There are 151 countries, including China, have joined the Convention to undertake the responsibility of reducing POPs, which requires studying and revealing the emission characteristics of PCDD/Fs in China.

The emission characteristics of PCDD/Fs from industrial and thermal processes have been studied for over 40 years (Olie *et al.*, 1977; Singh and Prakash, 2007; Mubeen *et al.*, 2017), identifying several major sources of PCDD/Fs (McKay, 2002) such as municipal solid waste incinerators (MSWI) (Wei *et al.*, 2016), cement kiln, the electric arc furnaces, and power plants (Tsai *et al.*, 2014; Hsieh *et al.*, 2018a; Xu *et al.*, 2018; Zhan *et al.*, 2018). In addition, advanced combustion technology and air pollution control devices (APCDs), including activated carbon injection and baghouse filter are widely used to control the emission of PCDD/Fs, meeting the limited standard (0.1 ng I-TEQ m⁻³) (GB18485-2014) (Lockwood and Ou, 1993; Karstensen, 2008; Shi *et al.*, 2008; Aurell and Marklund, 2009). The emission of each source is quite different because of the differences in scale, technology, air pollution control devices (APCDs), and the awareness of environmental protection. It is estimated that the total emission of PCDD/F from all Chinese sources was 9.1 kg TEQ in 2013. Steel and other metal production industries made the largest PCDD/F emission with 45.6%, followed by waste incineration,

* Corresponding author.

E-mail address: linxiaoqing@zju.edu.cn

power generation and heating. The total discharge of these three accounted for 81%.

However, emission characteristics from chemical plants, especially pesticide plants, are still obscure. In 2004, the emission of PCDD/Fs from chemical plants accounted for 2.6% of the total emissions. In recent years, due to the rapid increase of chemical plants constructed annually, emission of toxic pollutions from chemical plant has been given considerable attention (Xue *et al.*, 2006; Černá *et al.*, 2007; Hou *et al.*, 2013; Tan *et al.*, 2013). From an international perspective, with the in-depth development of economic globalization, the production of the pesticides in developed countries has been gradually shifted to developing countries. Approximately, in the past five years during 2013–2017, the production of pesticide in China has exceeded 3 million tons year⁻¹, and it is estimated that pesticide production will also be over 2.8 million tons in 2018 (National Bureau of Statistics of China, 2018). During the production of pesticides, persistent organic pollutants can be generated in huge amounts (Weber and Varbelow, 2013). The fine particles and organic chlorides (such as HCl, methyl chloride and so on) (Weber *et al.*, 2008a, b) in the flue gas significantly facilitate the production of PCDD/Fs generally through heterogeneous (solid-gas phases) reaction (200–400°C) and homogeneous (gas phase) reaction (500–800°C) (Choudhry *et al.*, 1982; Stanmore, 2004; Karstensen, 2008). De novo and precursor synthesis are two major pathways of the heterogeneous reaction. For the formation pathway, the PCDD/Fs are synthesized from carbon matrix through a series reactions of oxidation and chlorination (Iino *et al.*, 2000), while the precursor synthesis indicates that the PCDD/Fs are formed by the transformation of dioxin-like precursors on the particle surface with the assistant of metal catalysts (Addink and Olie, 1995). Besides, it has been demonstrated that the homogeneous reaction of PCDD/Fs synthesis is also associated with the precursors. The PCDD/Fs content in the flue gas from a municipal solid waste incinerator is highly related to the concentration of various possible precursors (Kaune *et al.*, 1994). However, the emission characteristics of PCDD/Fs in pesticide plants have not been investigated in detail, and the formation mechanisms have not yet been revealed by now.

In this study, the samples of flue gas and fly ash are

collected from different positions in a pesticide plant. The main objective of this work is to study the emission characteristics and the formation pathways of PCDD/Fs in the pesticide plant. Specifically, the PCDD/Fs in the flue gas of cooling system is worthy of attention, which are the basis of emission control.

MATERIALS AND METHODS

Experimental Design

The experiments are conducted in a typical pesticide plant in eastern China, consisting of two main parts of directional conversion furnace and APCDs. The directional conversion furnace can also be referred to as Regenerative Thermal Oxidizer (RTO), which includes a two-stage directional converter. Phosphate mixture is rapidly dewatered and shaped in the first-stage directional converter and then free fall to the second-stage directional converter. Phosphate mixture is basically converted to crude phosphate in the second-stage directional converter. Meanwhile, the volatile organic compounds waste gas (HCl, methanol, chlorine, formaldehyde, triethylamine, methyl chloride, etc.) is continuously fed into the directional conversion furnace for treatment. The APCDs include the cyclone separator, the secondary combustion chamber, the waste heat boiler, the quenching/deacidification tower, and the baghouse filter. The emitted volatile organic compounds (VOCs) from the directional conversion furnace are burned out in the secondary combustion chamber for over 2 s at temperature of about 800°C. The quenching/deacidification tower is applied to remove acidic gas and to decrease flue gas temperature. Activated carbon is used to absorb PCDD/Fs from flue gas and then is collected in bag filter efficiently together with other particles. Following the flow of flue gas, the gas samples are collected at the outlet of the secondary combustion chamber (FG1), the inlet of the baghouse filter (FG2), and the outlet of the stack (FG3), respectively. The fly ashes (FA) are collected from the baghouse filter. The details of sampling position are shown in Fig. 1. Samples are stored in sealed plastic pots prior to analysis.

Three parallel samples are collected at each position to ensure the reliability of the results. The concentration of PCDD/Fs in the outlet of the second combustion chamber

Fig. 1. Scheme of sampling positions.

(FG1) can reflect the influence of combustion situation on the formation of PCDD/Fs. The regeneration of PCDD/Fs in cooling system can be studied by comparing the PCDD/Fs in FG2 (from the inlet of baghouse filter) to those in FG1. In addition, the removal efficiency of PCDD/Fs for baghouse filter can be identified by comparing FG3 (from stack) to FG2.

In this pesticide plant, the average volume of dry flue gas is $20000 \text{ Nm}^3 \text{ h}^{-1}$, the average moisture content in the flue gas is 35%, the average fly ash discharge rate is 3 kg h^{-1} , and the concentration of CO which is normalized to dry air at 11% of O_2 is $258.56 \text{ mg Nm}^{-3}$.

Sample Analysis

According to United States Environmental Protection Agency (U.S. EPA) Methods 23A and 1613 (EPA, 1994) to pretreat PCDD/Fs samples in the flue gas and fly ash, respectively. The fly ash needs to be soaked for 4 h in 2 mol L^{-1} hydrochloric acid with a solid/liquid ratio of $1 \text{ g } 40 \text{ mL}^{-1}$ to eliminate the metal salts in the fly ash before the cleanup procedure. The high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) on a 6890 Series gas chromatograph (Agilent, USA) coupled with a JMS-800D Ultrafocus mass spectrometer (JEOL, Japan) was used to identify and quantify the PCDD/Fs. A DB-5 ms ($60 \text{ m} \times 0.25 \text{ mm}$ inside diameter, $0.25 \text{ }\mu\text{m}$ film thickness) capillary column was used to separate the PCDD/F congeners. The detailed PCDD/Fs analysis can be found in other papers (Wu et al., 2012; Chen et al., 2017). The toxic equivalent quantity (I-TEQ) were calculated using Eqs. (1) and (2):

$$C_g = \frac{\sum_{i=1}^n \frac{C_{ni}}{V_{sdi}}}{n} \quad (1)$$

$$C_f = \frac{\sum_{i=1}^n \frac{C_{ni}}{M_{fi}}}{n} \quad (2)$$

where C_g is the average I-TEQ concentration of PCDD/Fs in the flue gas, C_{ni} is the I-TEQ value of PCDD/Fs in either gas or ash sample i (ng I-TEQ), V_{sdi} is the volume of flue gas for collecting sample i (m^3), C_f is the average I-TEQ concentration of PCDD/Fs in the fly ash (ng I-TEQ), M_{fi} is the mass of the fly ash conducted to PCDD/F analysis (g), and n is the number of parallel samples.

RESULTS AND DISCUSSION

Emission Characteristics of PCDD/Fs in Flue Gas

The Concentrations of PCDD/Fs in the Flue Gas

The I-TEQ value, the homologue distribution, the weight ratio of PCDF/PCDD and the weight average level of chlorination (Cl-PCDD/Fs) in the flue gas from different positions are shown in Table 1. The concentration and I-TEQ value of PCDD/Fs at the outlet of the secondary combustion chamber (FG1) are 0.69 ng m^{-3} and $0.056 \text{ ng I-TEQ m}^{-3}$, respectively, which shows that PCDD/Fs has been formed initially. As is well known, temperature and chlorine are the most critical factors for the formation of PCDD/Fs (Addink and Olie, 1995; Wikström et al., 2003), and PCDD/Fs are easily produced during incomplete combustion (Wikström et al., 2004). Some scholars investigated the homogeneous synthesis of PCDD/Fs in high-temperature areas of chambers, suggesting that pollutants of incomplete combustions (PIC) provide precursors and produce PCDD/Fs in the gas phase at the temperatures between $600\text{--}800^\circ\text{C}$ (Sidhu et al., 1995). The content of CO is one of the most important parameters reflecting the condition of combustion (Weber et al., 2002). The concentration of CO in the

Table 1. Concentration and distribution of 17 2,3,7,8-substituteds-PCDD/Fs in flue gas and fly ash.

	FG1	FG2	FG3	FA	Unit
$\sum \text{PCDDs}$	0.30	4.47	0.30	20.31	FG: ng m^{-3} FA: pg g^{-1}
$\sum \text{PCDFs}$	0.39	2.44	0.38	22.98	FG: ng m^{-3} FA: pg g^{-1}
$\sum \text{PCDD/Fs}$	0.69	6.92	0.68	43.29	FG: ng m^{-3} FA: pg g^{-1}
PCDF/PCDD ^a	1.31	0.55	1.28	1.13	/
PCDF/PCDD ^b	3.14	0.41	3.29	2.96	/
Cl-PCDD ^c	7.22	6.43	7.26	7.28	/
Cl-PCDF ^c	6.21	5.95	6.22	6.23	/
Cl-PCDD/Fs ^c	6.65	6.26	6.68	6.72	/
I-TEQ (11% oxygen)	0.056	1.412	0.087	3.25	FG: ng I-TEQ m^{-3} FA: pg I-TEQ g^{-1}
Stand. Dev. $\sum \text{PCDD/Fs}$	0.08	1.8	0.06	4.3	Duplicate experiments
Stand. Dev. TEQ	0.01	0.08	0.02	0.148	/

^a The concentration ratio of PCDF to PCDD.

^b The I-TEQ ratio of PCDF to PCDD.

^c Weight average chlorination level was calculated as follows:

$$\text{Cl} = \frac{\sum C_j \times n_j}{C} \quad (j = 4, 5, 6, 7, 8)$$

where C_j is the concentration of each 2,3,7, 8-substituted PCDD/Fs, n_j is the amount of chlorine atom of each 2,3,7,8-substituted PCDD/Fs; C is the total concentration of PCDD/Fs.

directional conversion furnace has reached $258.56 \text{ mg Nm}^{-3}$, indicating an incomplete combustion to some extent. PCDD/Fs produced at this position may be attributed to the formation of PCDD/Fs in high temperature gas phase conditions. The formation mechanism is that the precursors synthesize PCDD/Fs under high temperature conditions. The precursors are mainly derived from the organic chloride waste gas in the glyphosate mother solution, which is produced from the thermal reaction process of the directional conversion furnace. This is similar with other researchers who believe that precursors should be responsible for the homogeneous formation of PCDD/Fs under high temperature (600–1200K) (Zhang *et al.*, 2009; Pan *et al.*, 2013; Zhang *et al.*, 2014). We can see the proportion of PCDFs and PCDDs from Fig. 2. The PCDFs and PCDDs accounted for 57 and 43%, respectively, which means that more PCDF is generated at high temperature.

The concentration and I-TEQ value of PCDD/Fs in the flue gas at the inlet of the baghouse filter (FG2) are 6.92 ng m^{-3} and $1.412 \text{ ng I-TEQ m}^{-3}$, respectively, which shows that PCDD/Fs have been produced dramatically in the area (from the outlet of secondary combustion chamber to the inlet of baghouse filter). This area consists of a waste heat boiler with temperature range of 800–500°C and a quenching/deacidification tower with temperature range of 400–200°C. It is identified that high-temperature (500–800°C) homogeneous reaction mainly happening in gas phase leads to the formation of PCDD/Fs and their precursors (Yang *et al.*, 1998; Ryu *et al.*, 2006). Low temperature (200–400°C) catalytic heterogeneous routes, taking place at the surface of solid carbon (such as soot and charred materials) on fly ash particles and being catalyzed by some metal ions (such as Cu and Fe), usually have the largest contribution to the formation of PCDD/Fs (Benfenati *et al.*, 1991; Stanmore, 2004). This area is also rich in O, Cl and organochlorinated matters, which are the most important factors for the formation of PCDD/Fs and can significantly

influence the PCDD/F yields (Babushok and Tsang, 2003; Peng *et al.*, 2016). Some researchers have already discovered that the waste heat boiler plays a very important role in the formation of PCDD/F from municipal solid waste incinerator (MSWI) (Düwel *et al.*, 1990; Zhang *et al.*, 2018). The quenching/deacidification tower section covers the optimum temperature range (250–400°C), which is conducive to heterogeneous catalytic reactions and has been repeatedly accused of promoting the formation of PCDD/F (Wang *et al.*, 2010). Heterogeneous production of PCDD/Fs mainly includes (1) de novo synthesis, beginning from carbon matrix or polycyclic aromatic hydrocarbons (PAH) and (2) precursor pathways, beginning from chemicals with similar structure to PCDD/Fs. With the temperature range of 400–200°C in quenching/deacidification tower, the PCDD/Fs can mainly be formed through the rearrangement/condensation of precursors in the pesticide plant. This is different from municipal solid waste incinerators, in which de novo synthesis is considered to be the main formation pathway (Huang and Buekens, 2000; Zhan *et al.*, 2019). The ratio of PCDF to PCDD is related to the importance of de novo and precursor pathways, respectively (Altwick, 1996).

In this study, the PCDF/PCDD ratio is 0.55 for FG2, and the proportion of PCDDs reaches 65% (Fig. 2). One possible reason is that the precursor pathways become stronger at the quenching/deacidification tower and result in more production of PCDD than PCDF. Chlorophenols (CP) would produce the most abundant PCDD homologues through the rearrangement and condensation reactions (Chen *et al.*, 2018a, b; Ryu *et al.*, 2006; Zhang *et al.*, 2018). Another reason is that the presence of water vapor will increase the yield of PCDDs (Christelle *et al.*, 2007). The average moisture content in the flue gas is 35%. The formation of PCDDs will be facilitated at 300°C when water vapor is introduced into the flue gas stream (Stieglitz *et al.*, 1990; Christelle *et al.*, 2007). This feature is supposed to be further studied in pesticide plant.

Fig. 2. I-TEQ concentration of PCDD/Fs and the proportion of PCDD/Fs in the flue gases.

Activated carbon injection coupled with baghouse filters are effective for PCDD/Fs control (Hung *et al.*, 2011). Thus, the concentration of PCDD/Fs decreases sharply from 6.92 to 0.68 ng m⁻³ at the outlet of the stack (FG3) after going through the baghouse filters. Also, the I-TEQ value reduces from 1.412 to 0.087 ng I-TEQ m⁻³, which meets the Chinese emission limit of 0.1 ng I-TEQ m⁻³ for pesticide industry. The activated carbon adsorbs PCDD/Fs from flue gas but also provides additional reaction areas and carbon sources which might produce PCDFs via de novo synthesis in bag filters (Atkinson *et al.*, 2015; Bai *et al.*, 2017). The removal efficiencies of PCDD/Fs for both concentration and I-TEQ value are 90% (93% for PCDDs and 84% for PCDFs) and 94%, respectively, yet are lower than designed values (98% and 99%). The main reasons includes (1) the quality of activated carbon does not meet the requirements, (2) the activated carbon is not injected continuously, (3) the deficient operation of baghouse filters, and (4) the memory effects (Chen *et al.*, 2011). In addition, the ratio of PCDF/PCDD rises from 0.55 to 1.28, which can be attributed to either the promotion of de novo synthesis (in favor of PCDFs formation) (Atkinson *et al.*, 2015; Bai *et al.*, 2017) or the preferable absorption of PCDD by activated carbon. The latter speculation is supported by the fact that the vapor pressure of PCDD is lower than that of PCDF (Lin *et al.*, 2018; Chen *et al.*, 2019a) and the desorption enthalpy of PCDD is higher (Zhang and Buekens, 2016; Zhang *et al.*, 2018). This feature worth further studies by sampling PCDD/Fs from both gas and solid phases simultaneously in pesticide plant.

For controlling PCDD/Fs emission from this pesticide plant, some effective management strategies are proposed as: (1) increasing temperature to promote complete combustion in the secondary combustion chamber, (2) injecting the activated carbon with high quality continuously, (3) avoiding backflush in baghouse filter and reducing the air induced from the quenching part, (4) decreasing the residence time of flue gas in the quenching/deacidification tower, (5) trying to avoid shut-down of the furnace for mitigating the memory effect (Guo *et al.*, 2014).

Congener Profiles of PCDD/Fs in Flue Gas

The congener profiles of PCDD/Fs is useful for determining their sources and speculating on its underlying formation mechanisms (Zhao *et al.*, 2017). The congener profiles of 17 toxic 2,3,7,8-substituted PCDD/Fs in three flue gases are shown in Figs. 2 and 3, respectively. For PCDD/Fs in FG1 and FG3, the congener profiles exhibit the same distribution tendency. The percentage of PCDFs in the PCDD/Fs is 57 and 56% for FG1 and FG3, respectively. The reason has been illustrated in previous section of 3.1.1. Particularly, the proportion of PCDFs in the PCDD/Fs is merely 35% for FG2, indicating the dominant formation pathway of precursors synthesis. Specifically, 1,2,3,4,6,7,8-HpCDD, OCDD and 1,2,3,4,6,7,8-HpCDF are three main congeners in the PCDD/fs for FG1 and FG3, and the total percentage of them reaches 48%. OCDD has the biggest proportion among all congeners for FG1 and FG3. In addition, although 2,3,4,7,8-PeCDF does

not contribute a lot to the total concentration, it is the biggest component of the I-TEQ value (Fig. 3(b)). Also, the strong positive correlation between the concentration of 2,3,4,7,8-PeCDF and the I-TEQ value has been revealed (Fiedler *et al.*, 2010). The most abundant congeners found in FG2 are 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD. These four congeners account for 50% of total concentration. The major contribution to the I-TEQ value is 1,2,3,7,8-PeCDD, because of its relative abundance and high I-TEF of 0.5.

Discharging Characteristics of PCDD/Fs in the Fly Ash

Fly ash is classified as hazardous waste in many countries, including China, because of its high content of PCDD/Fs and heavy metals (Chen *et al.*, 2016; Chen *et al.*, 2019b; Zhiliang *et al.*, 2019). Therefore, special attention to fly ash from pesticide plant is both necessary and important for fly ash management. The concentration and I-TEQ of PCDD/Fs are 38.87–45.31 pg g⁻¹ (with an average value of 43.29 pg g⁻¹) and 2.75–3.33 pg I-TEQ g⁻¹ (with an average value of 3.25 pg I-TEQ g⁻¹), respectively. The I-TEQ values are far below Chinese limits for disposal in sanitary landfill sites (3 ng I-TEQ g⁻¹) (GB16889-2008). The order of magnitude of these values is less than those found in MSWI fly ashes (Bie *et al.*, 2007; Chang *et al.*, 2011). The diversification of PCDD/F contents in fly ash is caused by reactants (primary factor), incineration conditions and APCDs performance.

From the results obtained in this study, the distribution of 17 toxic congeners in fly ash is shown in Fig. 4(a). OCDD contributes the most (24 %) to the total PCDD/Fs concentration. Other congeners with higher proportion are 1,2,3,4,6,7,8-HpCDD (15%), 1,2,3,4,6,7,8-HpCDF (12%) and 2,3,4,6,7,8-HxCDF (10%). Because of the different vapor pressure of PCDD/Fs congeners, higher chlorinated congeners may be more dominant than others in the fly ash for PCDDs, but the trend of PCDFs is not obvious. Normally, higher chlorinated congeners with lower vapor pressures have higher solid phase fractions at a specific temperature (Chang *et al.*, 2011). In term of I-TEQ, the distribution of 17 toxic congeners in fly ash is shown in Fig. 4(b). It is obvious that the highest contribution (38%) to I-TEQ value is 2,3,4,7,8-PeCDF, which is agree with results from municipal solid waste incinerators (Wang and Gao, 2007). The PCDF/PCDD ratio is a general and practical indicator for identifying PCDD/F features. The I-TEQ ratio of PCDF to PCDD is 2.96 (Table 1), indicating a much more contribution for I-TEQ value by PCDFs than by PCDDs in the fly ash from pesticide plants.

TEQ Estimated Emissions of the Investigated Pesticide Plant

The formula for calculating the TEQ estimated emissions of PCDD/Fs is:

$$T = C_g \times V_g + C_a \times V_a \quad (3)$$

where T is the TEQ estimated emissions of PCDD/Fs, g year⁻¹. C_g is the PCDD/Fs concentration in the flue gas,

Fig. 3. Congener profile of 17 2,3,7,8-substituted-PCDD/Fs in flue gas (a-PCDD/F mass distribution; b-PCDD/F TEQ values distribution).

g m^{-3} . V_g is the volume of flue gas, $\text{m}^3 \text{ year}^{-1}$. C_a is the PCDD/F concentration in the fly ash (filter ash), g kg^{-1} , and V_a is the fly ash discharge rate, kg year^{-1} .

The TEQ estimated emissions was calculated based on PCDD/Fs in fly ash and in flue gas, while the PCDD/Fs in the slag was not involved. In this plant, the volume of the flue gas was $20000 \text{ Nm}^3 \text{ h}^{-1}$, and the fly ash discharge rate was 3 kg h^{-1} . Therefore, the TEQ estimated emissions of PCDD/Fs was 9.3 g year^{-1} during normal condition in this plant. However, the total TEQ estimated emissions of PCDD/Fs in all chemical industry is 102.4 g in China in 2004 by the PCDD/Fs inventory (Plan, 2007). One possible reason is that the monitoring data of PCDD/Fs was scarce, in 2004, limited by the level of analysis and cost.

CONCLUSION

This study investigated the emission characteristics and the formation pathways of the PCDD/Fs in both flue gas and fly ash in different position of a pesticide plant. The results are as follows:

- (1) Incomplete combustion facilitates PCDD/Fs formation within secondary combustion chamber. PCDD/Fs concentration and I-TEQ value in flue gas at the outlet of secondary combustion chamber (FG1) reach 0.69 ng m^{-3} and $0.056 \text{ ng I-TEQ m}^{-3}$. The PCDF/PCDD ratio of 1.31 indicates the preferable formation of PCDF than PCDD during high temperature synthesis.
- (2) The main formation areas of PCDD/Fs are waste heat

Fig. 4. Congener profile of 17 2,3,7,8-substituted-PCDD/Fs in fly ash (a-PCDD/F mass distribution; b-PCDD/F TEQ values distribution).

boiler and quenching/deacidification tower in this pesticide plant. The concentration and I-TEQ value of PCDD/Fs in the flue gas increase sharply at the inlet of the baghouse filters (FG2). The PCDF/PCDD ratio of 0.55 indicates the major formation pathways of rearrangement and condensation of precursors.

- (3) The I-TEQ value ($0.087 \text{ ng I-TEQ m}^{-3}$) in flue gas at outlet of stack meets the Chinese emission limit of $0.1 \text{ ng I-TEQ m}^{-3}$ with the utilization of activated carbon injection coupled with baghouse filter. The major contribution to the I-TEQ value is 1,2,3,7,8-PeCDD.
- (4) The I-TEQ value of PCDD/Fs ($3.25 \text{ pg I-TEQ g}^{-1}$) in fly ash is much lower than both that in MSWI fly ashes and Chinese emission limits ($3 \text{ ng I-TEQ g}^{-1}$). The I-TEQ is contributed by PCDFs far more than PCDDs for the

fly ash from pesticide plants. Some management strategies have been proposed for controlling PCDD/Fs in pesticide plant.

- (5) The TEQ estimated emissions of the investigated pesticide plant reaches 9.3 g year^{-1} in the pesticide plant.

ACKNOWLEDGEMENTS

This study was supported by the national key research and development program of China (2018YFB0605200) and the Fundamental Research Funds for the Central Universities (2019FZA4010). In addition, the authors thank the samples collected by Hong Yu and appreciate Bei Chen (Dioxin Analysis Laboratory of Zhejiang

University) for her help with pretreatment of samples for dioxin quantitative analysis and HRGC/HRMS instrument operation.

REFERENCES

- Addink, R. and Olie, K. (1995). Mechanisms of formation and destruction of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in heterogeneous systems. *Environ. Sci. Technol.* 29: 1425–1435.
- Altwick, E.R. (1996). Formation of PCDD/F in municipal solid waste incinerators: Laboratory and modeling studies. *J. Hazard. Mater.* 47: 137–161.
- Atkinson, J.D., Hung, P.C., Zhang, Z., Chang, M.B., Yan, Z. and Rood, M.J. (2015). Adsorption and destruction of PCDD/Fs using surface-functionalized activated carbons. *Chemosphere* 118: 136–142.
- Aurell, J. and Marklund, S. (2009). Effects of varying combustion conditions on PCDD/F emissions and formation during MSW incineration. *Chemosphere* 75: 667–673.
- Babushok, V.I. and Tsang, W. (2003). Gas-phase mechanism for dioxin formation. *Chemosphere* 51: 1023–1029.
- Bai, S.T., Chang, S.H., Duh, J.M., Sung, F.H., Su, J.S. and Chang, M.B. (2017). Characterization of PCDD/Fs and dioxin-like PCBs emitted from two woodchip boilers in Taiwan. *Chemosphere* 189: 284–290.
- Benfenati, E., Mariani, G., Fanelli, R. and Farneti, A. (1991). Synthesis and destruction of PCDD and PCDF inside a municipal solid waste incinerator. *Chemosphere* 23: 715–722.
- Bie, R., Li, S. and Wang, H. (2007). Characterization of PCDD/Fs and heavy metals from MSW incineration plant in Harbin. *Waste Manage.* 27: 1860–1869.
- Černá, M., Kratěnová, J., Žejglicová, K., Brabec, M., Malý, M., Šmíd, J., Crhová, Š., Grabic, R. and Volf, J. (2007). Levels of PCDDs, PCDFs, and PCBs in the blood of the non-occupationally exposed residents living in the vicinity of a chemical plant in the Czech Republic. *Chemosphere* 67: S238–S246.
- Chang, Y.M., Fan, W.P., Dai, W.C., Hsi, H.C., Wu, C.H. and Chen, C.H. (2011). Characteristics of PCDD/F content in fly ash discharged from municipal solid waste incinerators. *J. Hazard. Mater.* 192: 521–529.
- Chen, C.C., Yang, X.Y. and Chang, G.P. (2011). Influence of memory effect caused by aged bag filters on the stack PCDD/F emissions. *J. Hazard. Mater.* 185: 1148–1155.
- Chen, Z., Mao, Q., Lu, S., Buekens, A., Xu, S., Wang, X. and Yan, J. (2017). Dioxins degradation and reformation during mechanochemical treatment. *Chemosphere* 180: 130–140.
- Chen, Z., Lin, X., Lu, S., Li, X., Qiu, Q., Wu, A., Ding, J. and Yan, J. (2018a). Formation pathways of PCDD/Fs during the co-combustion of municipal solid waste and coal. *Chemosphere* 208: 862–870.
- Chen, Z., Tang, M., Lu, S., Ding, J., Qiu, Q., Wang, Y. and Yan, J. (2018b). Evolution of PCDD/F-signatures during mechanochemical degradation in municipal solid waste incineration filter ash. *Chemosphere* 208: 176–184.
- Chen, Z., Lin, X., Lu, S., Li, X. and Yan, J. (2019a). Suppressing formation pathway of PCDD/Fs by S-N-containing compound in full-scale municipal solid waste incinerators. *Chem. Eng. J.* 359: 1391–1399.
- Chen, Z., Lu, S., Tang, M., Ding, J., Buekens, A., Yang, J., Qiu, Q. and Yan, J. (2019b). Mechanical activation of fly ash from MSWI for utilization in cementitious materials. *Waste Manage.* 88: 182–190.
- Chen, Z.L., Lu, S.Y., Mao, Q.J., Buekens, A., Chang, W., Wang, X. and Yan, J.H. (2016). Suppressing heavy metal leaching through ball milling of fly ash. *Energies* 9: 524.
- Choudhry, G.G., Choudhry, G.G., Hutzinger, O. and Hutzinger, O. (1982). Mechanistic aspects of the thermal formation of halogenated organic compounds including polychlorinated dibenzo-*p*-dioxins. Part V: Hypotheses and summary. *Toxicol. Environ. Chem.* 5: 295–309.
- Christelle, B., Shawn, R., Dennis, T., Abderrahmane, T. and Gullett, B.K. (2007). Formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from a mixture of chlorophenols over fly ash: Influence of water vapor. *Environ. Sci. Technol.* 41: 850–856.
- Düwel, U., Nottrodt, A. and Ballschmiter, K. (1990). Simultaneous sampling of PCDD/PCDF inside the combustion chamber and on four boiler levels of a waste incineration plant. *Chemosphere* 20: 1839–1846.
- Fiedler, H., Lau, C. and Eduljee, G. (2010). Statistical analysis of patterns of PCDDs and PCDFs in stack emission samples and identification of a marker congener. *Waste Manage. Res.* 18: 283–292.
- Guo, C.J., Wang, M.S., Lin, S.L., Mi, H.H., Wang, L.C. and Chang-Chien, G.P. (2014). Emissions of PCDD/Fs and PCBs during the cold start-up of municipal solid waste incinerators. *Aerosol Air Qual. Res.* 14: 1593–1604.
- Hou, H., Zhao, L., Zhang, J., Xu, Y.F., Yan, Z.G., Bai, L.P. and Li, F.S. (2013). Organochlorine pesticides and polychlorinated biphenyls in soils surrounding the Tanggu Chemical Industrial District of Tianjin, China. *Environ. Sci. Pollut. Res.* 20: 3366–3380.
- Hsieh, Y.K., Chen, W.S., Zhu, J. and Huang, Q. (2018a). Characterization of polychlorinated dibenzo-*p*-dioxins and dibenzofurans of the flue gases, fly ash and bottom ash in a municipal solid waste incinerator. *Aerosol Air Qual. Res.* 18: 421–432.
- Hsieh, Y.K., Chen, W.S., Zhu, J., Wu, Y.J. and Huang, Q. (2018b). Health risk assessment and correlation analysis on PCDD/FS in the fly ash from a municipal solid waste incineration plant. *Aerosol Air Qual. Res.* 18: 734–748.
- Huang, H. and Buekens, A. (2000). Chemical kinetic modelling of PCDD formation from chlorophenol catalysed by incinerator fly ash. *Chemosphere* 41: 943–951.
- Hung, N.T., Ting, H.W. and Chi, K.H. (2018). Evaluation of the relative health risk impact of atmospheric PCDD/Fs in PM_{2.5} in Taiwan. *Aerosol Air Qual. Res.* 18: 2591–2599.
- Hung, P.C., Lo, W.C., Chi, K.H., Chang, S.H. and Chang, M.B. (2011). Reduction of dioxin emission by a multi-

- layer reactor with bead-shaped activated carbon in simulated gas stream and real flue gas of a sinter plant. *Chemosphere* 82: 72–77.
- Iino, F., Imagawa, T. and Gullett, B.K. (2000). Dechlorination-controlled polychlorinated dibenzofuran isomer patterns from municipal waste incinerators. *Environ. Sci. Technol.* 34: 3143–3147.
- Karstensen, K.H. (2008). Formation, release and control of dioxins in cement kilns. *Chemosphere* 70: 543–560.
- Kaune, A., Lenoir, D., Nikolai, U. and Kettrup, A. (1994). Estimating concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the stack gas of a hazardous waste incinerator from concentrations of chlorinated benzenes and biphenyls. *Chemosphere* 29: 2083–2096.
- Lee, Y.Y., Hou, W.C., Zhu, J. and Wang, W. (2018). Wet deposition of PCDD/Fs in Taiwan. *Aerosol Air Qual. Res.* 18: 2600–2611.
- Lin, X., Chen, Z., Lu, S., Zhang, S., Zhang, M., Li, X. and Yan, J. (2018). Emission characteristics of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from the co-combustion of municipal solid waste in a lab-scale drop-tube Furnace. *Energy Fuels* 32: 5396–5404.
- Lockwood, F.C. and Ou, J.J. (1993). Review: Burning refuse-derived fuel in a rotary cement kiln. *Proc. Inst. Mech. Eng., Part A* 2017: 65–70.
- McKay, G. (2002). Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review. *Chem. Eng. J.* 86: 343–368.
- Mubeen, I., Lin, X., Buekens, A., Cao, X., Lu, S., Tang, M. and Yan, J. (2017). PCDD/F formation in milled fly ash: Metal chloride catalysis. *Aerosol Air Qual. Res.* 17: 2858–2866.
- National Bureau of Statistics of China (2018). <http://www.stats.gov.cn/>
- NIP (National Implementation Plan) (2007). The People's Republic of China National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants. <http://www.pops.int/>
- Olie, K., Vermeulen, P.L. and Hutzinger, O. (1977). Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in The Netherlands. *Chemosphere* 6: 455–459.
- Pan, W., Zhang, D., Han, Z., Zhan, J. and Liu, C. (2013). New insight into the formation mechanism of PCDD/Fs from 2-chlorophenol precursor. *Environ. Sci. Technol.* 47: 8489–8498.
- Peng, Y., Chen, J., Lu, S., Huang, J., Zhang, M., Buekens, A., Li, X. and Yan, J. (2016). Chlorophenols in municipal solid waste incineration: A review. *Chem. Eng. J.* 292: 398–414.
- Ryu, J.Y., Choi, K.C. and Mulholland, J.A. (2006). Polychlorinated dibenzo-*p*-dioxin (PCDD) and dibenzofurans (PCDF) isomer patterns from municipal waste combustion: Formation mechanism fingerprints. *Chemosphere* 65: 1526–1536.
- Shi, D.Z., Wu, W.X., Lu, S.Y., Chen, T., Huang, H.L., Chen, Y.X. and Yan, J.H. (2008). Effect of MSW source-classified collection on the emission of PCDDs/Fs and heavy metals from incineration in China. *J. Hazard. Mater.* 153: 685–694.
- Sidhu, S.S., Maqsood, L., Dellinger, B. and Mascolo, G. (1995). The homogeneous, gas-phase formation of chlorinated and brominated dibenzo-*p*-dioxin from 2,4,6-trichloro- and 2,4,6-tribromophenols. *Combust. Flame* 100: 11–20.
- Singh, S. and Prakash, V. (2007). Toxic Environmental Releases from Medical Waste Incineration: A Review. *Environ. Monit. Assess.* 132: 67–81.
- Stanmore, B.R. (2004). *The formation of dioxins in combustion systems*. Elsevier Inc., New York, pp. 398–427.
- Stieglitz, L., Zwick, G., Beck, J., Bautz, H. and Roth, W. (1990). The role of particulate carbon in the de-novo synthesis of polychlorinated dibenzodioxins and-furans in fly-ash. *Chemosphere* 20: 1953–1958.
- Tan, B., Wang, T.Y., Pang, B., Zhu, Z.Y., Wang, D.H. and Lü, Y.L. (2013). Pollution characteristics and health risk assessment of atmospheric volatile organic compounds (VOCs) in pesticide factory. *Huan Jing Ke Xue* 34: 4577.
- Tsai, Y.A., Mao, I.F., Chi, K.H., Chang, M.B., Feng, C.C., Lin, C.H., Hung, P.C. and Chen, M.L. (2014). Health risk from exposure to PCDD/Fs from a waelz plant in Central Taiwan. *Aerosol Air Qual. Res.* 14: 1310–1319.
- Wang, M.S., Chen, S.J., Lai, Y.C., Huang, K.L. and Chang-Chien, G.P. (2010). Characterization of persistent organic pollutants in ash collected from different facilities of a municipal solid waste incinerator. *Aerosol Air Qual. Res.* 10: 391–402.
- Wang, W. and Gao, X.B. (2007). PCDD/Fs distribution in MSWI fly ash and identification of the indicated isomer. *Huan Jing Ke Xue* 28: 445.
- Weber, R., Sakurai, T., Ueno, S. and Nishino, J. (2002). (2002). Correlation of PCDD/PCDF and CO values in a MSW incinerator—indication of memory effects in the high temperature/cooling section. *Chemosphere* 49: 127–134.
- Weber, R., Gaus, C., Tysklind, M., Johnston, P., Forter, M., Hollert, H., Heinisch, E., Holoubek, I., Lloydsmith, M. and Masunaga, S. (2008a). Dioxin- and POP-contaminated sites—contemporary and future relevance and challenges. *Environ. Sci. Pollut. Res.* 15: 363.
- Weber, R., Tysklind, M. and Gaus, C. (2008b). Dioxin - contemporary and future challenges of historical legacies. *Environ. Sci. Pollut. Res.* 15: 96–100.
- Weber, R. and Varbelow, H.G. (2013). Dioxin/POPs legacy of pesticide production in Hamburg: Part 1—securing of the production area. *Environ. Sci. Pollut. Res.* 20: 1918–1924.
- Wei, G.X., Liu, H.Q., Zhang, R., Zhu, Y.W. and Xu, X. (2016). Mass concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and heavy metals in different size fractions of hospital solid waste incinerator fly ash particles. *Aerosol Air Qual. Res.* 16: 1569–1578.
- Wikström, E., Ryan, S., Touati, A., Telfer, M., Tabor, D. and Gullett, B.K. (2003). Importance of chlorine speciation

- on de novo formation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. *Environ. Sci. Technol.* 37: 1108–1113.
- Wikström, E., Shawn, R., Abderrahmane, T., Dennis, T. and Gullett, B.K. (2004). Origin of carbon in polychlorinated dioxins and furans formed during sooting combustion. *Environ. Sci. Technol.* 38: 3778–3784.
- Wu, H.L., Lu, S.Y., Li, X.D., Jiang, X.G., Yan, J.H., Zhou, M.S. and Wang, H. (2012). Inhibition of PCDD/F by adding sulphur compounds to the feed of a hazardous waste incinerator. *Chemosphere* 86: 361–367.
- Xu, S., Chen, T., Li, X., Yan, J. and Cen, K. (2018). Behavior of PCDD/Fs, PCBS, CBZS and PAHS during thermal treatment of various fly ash from steel industry. *Aerosol Air Qual. Res.* 18: 1008–1018.
- Xue, N., Zhang, D. and Xu, X. (2006). Organochlorinated pesticide multiresidues in surface sediments from Beijing Guanting reservoir. *Water Res.* 40: 183–194.
- Yang, Y., Mulholland, J.A. and Akki, U. (1998). Formation of furans by gas-phase reactions of chlorophenols. *Symp. (Int.) Combust.* 27: 1761–1768.
- Zhan, M., Wang, T., Yang, J., Ji, L., Zhou, G., Chen, T., Li, X. and Lin, X. (2018). The behaviors and relationships of PCDD/Fs and chlorobenzenes in the whole process of one municipal solid waste incinerator. *Aerosol Air Qual. Res.* 18: 3134–3146.
- Zhan, M.X., Xu, S., Cai, P., Chen, T., Lin, X., Buekens, A. and Li, X. (2019). Parameters affecting the formation mechanisms of dioxins in the steel manufacture process. *Chemosphere* 222: 250–257.
- Zhang, M. and Buekens, A. (2016). De novo synthesis in iron ore sintering. *Int. J. Environ. Pollut.* 60: 111–135.
- Zhang, M., Buekens, A. and Li, X. (2018). Characterising boiler ash from a circulating fluidised bed municipal solid waste incinerator and distribution of PCDD/F and PCB. *Environ. Sci. Pollut. Res. Int.* 25: 22775–22789.
- Zhang, Q., Qu, X., Wang, H., Xu, F., Shi, X. and Wang, W. (2009). Mechanism and thermal rate constants for the complete series reactions of chlorophenols with H. *Environ. Sci. Technol.* 43: 4105–4112.
- Zhang, Y., Zhang, D., Gao, J., Zhan, J. and Liu, C. (2014). New understanding of the formation of PCDD/Fs from chlorophenol precursors: A mechanistic and kinetic study. *J. Phys. Chem. A* 118: 449–456.
- Zhao, Y., Zhan, J., Liu, G., Zheng, M., Jin, R., Yang, L., Hao, L., Wu, X., Zhang, X. and Wang, P. (2017). Evaluation of dioxins and dioxin-like compounds from a cement plant using carbide slag from chlor-alkali industry as the major raw material. *J. Hazard. Mater.* 330: 135–141.
- Zhiliang, C., Minghui, T., Shengyong, L., Buekens, A., Jiamin, D., Qili, Q. and Jianhua, Y. (2019). Mechanochemical degradation of PCDD/Fs in fly ash within different milling systems. *Chemosphere* 223: 188–195.

Received for review, April 25, 2019

Revised, May 23, 2019

Accepted, May 25, 2019