PCDD/F Emission from Pharmaceutical Industries

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ABSTRACT

The emission levels and profiles of unintentionally formed polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) were comprehensively investigated in flue gases released from 16 regenerative thermal oxidizers (RTOs) belonging to 8 pharmaceutical industries (PIs) in China. The PCDD/F total concentrations and TEQ values with great variation, ranged from 0.148–9.051 ng m⁻³ and 0.008–0.255 ng I-TEQ m⁻³, respectively. Emission levels of most RTOs were lower than the emission standard of China (0.1 ng I-TEQ m⁻³), yet two were above 0.25 ng I-TEQ m⁻³. The PCDD/F concentrations in flue gases were in the order of HWIs > MSWIs > PIs. OCDD was identified to be the dominant congener in most RTOs, accounting for 21–71 wt%. In addition, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF and 1,2,3,4,7,8-HxCDF were effective TEQ indicators, especially for 2,3,4,7,8-PeCDF with a Pearson correlation coefficient of 0.995. The estimated annual emission amount (AE) of PCDD/Fs for PIs in this study was in the range of 0.435–11.016 mg I-TEQ year⁻¹, with an average of 2.65 mg I-TEQ year⁻¹. It was estimated that 19.96 g I-TEQ of PCDD/Fs were emitted from Chinese PIs to atmosphere in 2017. This is the first comprehensive investigation on the unintentional emissions of PCDD/Fs from PIs in China.

Keywords: Emission characteristics; PCDD/Fs; Annual emission (AE); Pharmaceutical industry (PI); Regenerative thermal oxidizer (RTO).

INTRODUCTION

Persistent organic pollutants (POPs) have received extensive attention for their high toxicities to environment and human. The Stockholm Convention on POPs, established by the United Nations Environment Program (UNEP), aims to minimize or eliminate both of the production and the use of POPs. Parties need to identify sources of POPs and to accurately compile lists of POPs emitted into the environment (Black *et al.*, 2012). Polychlorinated dibenzo-*p*-dioxins (PCDDs) and poly-chlorinated dibenzofurans (PCDFs) are formed unintentionally during chemical production and municipal solid waste incineration. PCDD/Fs as important components of POPs to which humans are exposed, have been proven to be carcinogenic, neurotoxic and immunotoxic (Tsai *et al.*, 2014; Hsieh *et al.*, 2018b; Hung *et al.*, 2018). The Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases was first published in 2003 and was amended for the second time in 2013. The source categories listed in the Toolkit are divided

into ten groups (Waste Incineration, Ferrous and Non-Ferrous Metal Production, Heat and Power Generation, Production of Mineral Products, Transport, Open Burning Processes, Production and Use of Chemicals and Consumer Goods, Miscellaneous, Disposal and Landfill, and Contaminated Sites and Hotspots) and five release sectors (air, land, water, product, and residue) (UNEP, 2013). In addition, it provided a method of calculating annual emission for each source, with vector and recommended emission factors applied in these calculations. Due to limited published data, emission factors of PCDD/Fs in flue gas from pharmaceutical industries (PIs) have not been provided in the Toolkit so far.

With extensive attention on public health, pharmaceutical industry (PI) has experienced fast growth and now plays an important role in the national economy in China (MIIT, 2016). At present, Chinese pharmaceutical market is the second largest market in the world (Wu and Hsu, 2018), which however puts significant concern of organic pollutants (e.g., PCDD/Fs) emission from PIs. In fact, due to its rapid development and considerable pollution (Lin, 2011; Wang *et al.*, 2011; Li *et al.*, 2014), PI has been regarded as one of the 12 key industries in Chinese national environmental protection plan.

In addition, the pressure faced by the PI for

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environmental protection keeps increasing, especially with the employment of the Law Emission Standard of Air Pollutants for Pharmaceutical Industry Chemical Synthesis Products Category (DB33, 2016). The PI is one of the heavily polluting industries because a wide variety of hazardous chemicals are used as raw materials (Dos Santos and Biundo, 1999; Priya and Philip, 2015; Gao *et al.*, 2019). In order to minimize or eliminate VOCs in exhaust gases, technologies such as chemical spray adsorption, plasma, biotrickling filtration, activated carbon adsorption, condensation, incineration, have been adopted by many PIs (Balasubramanian *et al.*, 2012; Wu *et al.*, 2015; Hu *et al.*, 2016). Among them, incineration is widely used due to the high removal efficiency and long service life. Regenerative Thermal Oxidizer (RTO) is one of the incineration facilities. However, chlorine contained in exhaust gases can result in the formation of PCDD/Fs during incineration (Dyke *et al.*, 2007; UNEP, 2013). There are many studies on the PCDD/Fs emission in thermal processes such as waste incineration and steel industry (Kuo *et al.*, 2011; Wang *et al.*, 2014; Mubeen *et al.*, 2017; Xu *et al.*, 2018; Zhan *et al.*, 2018). However, there are little or no researches on the emission of PCDD/Fs from the RTO in PIs. According to the statistics of the National Bureau of Statistics of China, the number of pharmaceutical manufacturing industry in China increased from 5,926 in 2011 to 7,532 in 2017, with a growth rate of 27% in five years (National Bureau of Statistics of China, 2017). It is clear that PI is a very important potential source for PCDD/F emission, and it is necessary to conduct a comprehensive study to identify the emission characteristics of PCDD/Fs from RTO, thus to provide basic data for controlling PCDD/Fs from PI in future.

RTO has been widely applied for controlling VOCs with a heat recovery rate up to 95% (Bannai *et al.*, 2006; Vij, 2006). The RTO system decomposes the organics in exhaust gases into carbon dioxide and water by high-temperature oxidation and then recovers the heat, thereby achieving the dual purposes of both environmental protection and energy conservation (Bannai *et al.*, 2006; Chang and Chern, 2009). In RTO technology, from the perspective of energy saving, the exhaust gas is gradually preheated during the flow through the regenerative ceramic bed to the combustion chamber, and the operation output is maximized through a series of cyclic operations. In each cycle, VOC-contaminated gas flows through the hot bed (as a preheater) to increase its temperature, then completes oxidation in the combustion chamber and eventually releases most of its heat to the cold bed, which acts as a thermal energy storage device. High heat recovery reduces fuel requirements and saves operating costs (Amelio and Morrone, 2007). The reaction equation for the degradation of organic matters in the combustion chamber of RTO is as follows:

In order to update the Toolkit (2013 version), and to fill

up the research gaps, this study aims to estimate annual emission amount base on investigating the emission levels and profiles of PCDD/Fs in flue gases released from eight typical pharmaceutical industries (PIs) in China. Principal component analysis (PCA) is utilized to analyze the differences and similarities between congener patterns of all samples. In addition, the correlations between TEQ and mass concentrations of PCDD/Fs are examined by linear regression. This work will facilitate the management of PCDD/F emissions from PIs and help to predict congener profiles and average concentrations.

MATERIALS AND METHODS

Sample Collection

The flue gas samples were collected from 16 facilities belonged to 8 pharmaceutical industries (PIs), and the information about facilities are shown in Table 1. All PIs are equipped with RTO to treat VOCs.

Flue gas samples were collected with isostack sampler (TCR TECORA, Italy) according to U.S. EPA Method 23a. The sampling box composed of a glass fiber filter, 5 impingers (1 silica gel, 2 empty, and 2 water) and a resin. The collection lasts 2–3 h for each sample according to the national standard coded as HJ 77.2-2008. Before sampling, the $^{13}C_{12}$ -labelled EDF-4054 with 100 ng mL⁻¹ in nonane as sampling standard was spiked to XAD-2 resin. The EDF-4055 served as a recovery standard for PCDD/Fs, and $^{13}C_{12}$ -labelled EDF-4053 served as extraction standard. Three parallel samples were collected for each point and the mean value was determined.

Sample Analysis and Statistical Methods

The flue gas samples were transferred to the Soxhlet to extract more than 16 hours together with $^{13}C_{12}$ labeled PCDD/Fs internal standard and toluene. Then the colored samples were washed repeatedly with sulfuric acid until transparent. The purification procedure for PCDD/Fs analysis was carried out using two columns, namely multi-layer silica gel column (15 mm ID × 30 cm, elution with 100 mL of n-hexane) and basic alumina column (15 mm ID × 30 cm, 1st elution with 100 mL of n-hexane and 2nd elution with a 1:1 mixture of n-hexane and dichloromethane).

The purified extracts were detected by high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) interfaced with a 6890 Series gas chromatograph (Agilent, USA) coupled with a JMS-800D mass spectrometer (JEOL, Japan). A capillary column DB-5 ms (60 m × 0.25 mm I.D., 0.25 μm film thickness) was applied to separate the PCDD/F congeners. Samples were injected in a splitless mode at an injector temperature of 280°C and at an initial column temperature of 90°C. The mean recoveries of the standards for PCDD/Fs ranged from 65 to 120%, which were within the acceptable range of 25–150%. And all data were obtained in the selected ion monitoring (SIM) mode. The toxic equivalents (I-TEQ) values for PCDD/Fs were calculated by using international toxicity equivalency factor (ITEF). Statistical analyses of PCDD/Fs were carried out by IBM SPSS Statistics

Table 1. Information of the investigated facilities in China.

	Combustion temperature (°C)	Stack temperature (°C)	Flue gas rate (m ³ h ⁻¹)	Exhaust gas main components	APCDs
R1	750–850	65	12,100	Methanol, vinyl chloride, isobutylene, phenols, ketones, etc.	Cooling tower + alkali scrubber
R2	750–850	66	12,400	Methanol, vinyl chloride, isobutylene, phenols, ketones, etc.	Cooling tower + alkali scrubber
R3	750–850	65	16,000	Vinyl chloride, isobutylene, phenols, ketones, etc.	Cooling tower + alkali scrubber
R4	750–850	68	15,000	Vinyl chloride, isobutylene, phenols, ketones, etc.	Cooling tower + alkali scrubber
R5	820–850	75	13,100	Methanol, formaldehyde, cyanide, isopropylene	Cooling tower + alkali scrubber
R6	820–850	75	13,200	Methanol, formaldehyde, cyanide, isopropylene	Cooling tower + alkali scrubber
R7	820–850	76	11,100	Dichloromethane, acetone, ethanol, ammonia	Cooling tower + alkali scrubber
R8	820–850	76	10,900	Dichloromethane, acetone, ethanol, ammonia	Cooling tower + alkali scrubber
R9	820–850	74	11,200	Methanol, chlorine, formaldehyde, methyl chloride	Cooling tower + alkali scrubber
R10	820–850	74	12,800	Methanol, chlorine, formaldehyde, methyl chloride	Cooling tower + alkali scrubber
R11	820–850	72	10,800	Methanol, methyl chloride, polychlorohexene	Cooling tower + alkali scrubber
R12	820–850	72	12,600	Methanol, methyl chloride, polychlorohexene	Cooling tower + alkali scrubber
R13	820–850	68	12,100	Methanol, formaldehyde, dichloromethane	Cooling tower + alkali scrubber
R14	900–1100	140	16,000	HCl, methanol, chlorine, formaldehyde, triethylamine, methyl chloride	Cooling with deacidification tower + activated carbon with fabric filter
R15	800–900	67	11,100	Chloroform, ether, ethanol, dichloromethane, organic amine	Cooling tower + alkali scrubber
R16	800–900	67	10,800	Chloroform, ether, ethanol, dichloromethane, organic amine	Cooling tower + alkali scrubber

(Version 24). The congener profiles were assessed by Principal component analysis (PCA) with results represented by scores and a loading plot.

RESULTS AND DISCUSSION

Emission Levels of PCDD/Fs in Various RTOs

The concentration and I-TEQ value of PCDD/Fs in flue gases of 16 RTOs are shown in Fig. 1 and are summarized in Table 2 in detail. The concentration range of PCDDs is 0.038–0.600 ng m⁻³, with an average of 0.227 ng m⁻³ and a medium value of 0.189 ng m⁻³, both of which are much lower than those of PCDFs (range of 0.073–1.390 ng m⁻³, average value 0.370 ng m⁻³, medium value 0.220 ng m⁻³). The concentration of PCDD-homologues generally increases with the rising of their degree of chlorination, which is not the case of PCDF-homologues. The concentration range of PCDD/Fs is 0.148–9.051 ng m⁻³, with an average of 0.563 ng m⁻³ and a medium value of 0.334 ng m⁻³, and the corresponding range of the I-TEQ value is 0.008–0.255

ng I-TEQ m⁻³, with an average of 0.056 ng I-TEQ m⁻³ and a medium value of 0.055 ng I-TEQ m⁻³. The average I-TEQ of PCDD/Fs from this study is several orders of magnitude lower than values reported from secondary zinc production in Vietnam (3.440 ng I-TEQ m⁻³) and from municipal solid waste incineration in China (0.228 ng I-TEQ m⁻³) (Li *et al.*, 2017; Pham *et al.*, 2019), and is the same order of magnitude as those from municipal solid waste incineration in northern China (Zhu *et al.*, 2018). Fourteen RTOs show emissions below the current PCDD/F emission standard for pharmaceutical industry chemical synthesis products category in China (0.1 ng I-TEQ m⁻³) (DB33, 2016). But for two RTOs (i.e., R15 and R16), the I-TEQ concentration of PCDD/Fs in flue gases is 0.249 and 0.255 ng I-TEQ m⁻³, respectively, which are much higher than emission standard. The wide range of PCDD/Fs in flue gases indicates the necessity of special attentions for pollution control. Application of flue gas purification systems usually exhibits acceptable effect for reduction of PCDD/F emission. Activated carbon injection coupled with baghouse filters

Fig. 1. (a) Mass and (b) I-TEQ concentration of PCDD/Fs in the flue gas of 16 RTOs.

are effective for PCDD/Fs control (Hung *et al.*, 2011). Due to the low temperature of flue gases in R05 and R06 (Table 1), activated carbon injection coupled with baghouse filter can efficiently reduce the discharge of PCDD/Fs after the flue gases are reheated.

Considering the great variation of PCDD/F concentrations in flue gases, the average is not enough to represent the emission levels of PCDD/Fs from PIs, MSWIs and HWIs in China. Fig. 2 demonstrates some statistical parameters for flue gas samples from PIs, MSWIs and HWIs in China. The MSWIs and HWIs data are from the studies of Gao *et al.* (2009) and Zhu *et al.* (2018). The figure shows that the average value of PIs is higher than that of MSWIs, but the percentile 50 for PIs is lower than the percentile 25 for

MSWIs, indicating that PIs are generally characterized by lower emission levels than MSWIs in China. It is obvious that the percentile 25 for HWIs is much higher than the percentile 75 for either PIs or MSWIs. Therefore, the concentration of PCDD/Fs in flue gas is in the order of HWIs > MSWIs > PIs.

Congener Profiles of PCDD/Fs in Flue Gases

The PCDF/PCDD weight ratio is usually applied to roughly distinguish the major formation pathway of PCDD/Fs as: de novo synthesis (PCDF/PCDD > 1) or precursor formation (PCDF/PCDD < 1) (Luijk *et al.*, 1994; Ni *et al.*, 2009; Zhao *et al.*, 2017). As shown in Fig. 1 (Mass), the proportion of PCDF in 12 RTOs flue gases marks much

Table 2. Concentration and distribution of seventeen 2,3,7,8-substituted PCDD/Fs in flue gases of the 16 RTOs.

	R01	R02	R03	R04	R05	R06	R07	R08	unit
TCDD	0.002	0.002	0.004	0.004	0.001	0.000	0.001	0.001	ng m ⁻³
PeCDD	0.003	0.005	0.005	0.006	0.001	0.000	0.002	0.004	ng m ⁻³
HxCDD	0.005	0.011	0.027	0.020	0.002	0.001	0.015	0.026	ng m ⁻³
HpCDD	0.009	0.014	0.067	0.048	0.005	0.003	0.023	0.041	ng m ⁻³
OCDD	0.019	0.027	0.056	0.250	0.140	0.214	0.049	0.388	ng m ⁻³
Σ PCDDs	0.038	0.059	0.160	0.328	0.148	0.218	0.089	0.460	ng m ⁻³
TCDF	0.045	0.012	0.023	0.014	0.003	0.002	0.004	0.004	ng m ⁻³
PeCDF	0.045	0.020	0.049	0.053	0.011	0.011	0.033	0.047	ng m ⁻³
HxCDF	0.032	0.028	0.157	0.156	0.042	0.057	0.145	0.206	ng m ⁻³
HpCDF	0.012	0.018	0.162	0.147	0.010	0.007	0.077	0.107	ng m ⁻³
OCDF	0.005	0.011	0.050	0.190	0.007	0.005	0.021	0.013	ng m ⁻³
Σ PCDFs	0.140	0.089	0.440	0.559	0.073	0.081	0.280	0.378	ng m ⁻³
Σ PCDD/Fs	0.177	0.148	0.600	0.887	0.221	0.299	0.369	0.838	ng m ⁻³
PCDF/PCDD ^a	3.7	1.5	2.8	1.7	0.5	0.4	3.1	0.8	/
PCDF/PCDD ^b	5.1	1.5	3.3	3.6	6.1	18.1	7.6	5.7	/
Cl-PCDD/Fs ^c	5.6	6.4	6.6	7.1	7.3	7.4	6.5	7.1	/
I-TEQ	0.023	0.015	0.040	0.044	0.008	0.009	0.032	0.052	ng I-TEQ m ⁻³
	R09	R10	R11	R12	R13	R14	R15	R16	unit
TCDD	0.001	0.001	0.001	0.001	0.003	0.002	0.011	0.013	ng m ⁻³
PeCDD	0.001	0.001	0.003	0.004	0.007	0.008	0.068	0.044	ng m ⁻³
HxCDD	0.007	0.006	0.009	0.011	0.050	0.044	0.086	0.087	ng m ⁻³
HpCDD	0.016	0.012	0.014	0.017	0.138	0.099	0.081	0.119	ng m ⁻³
OCDD	0.035	0.120	0.061	0.053	0.112	0.145	0.024	0.072	ng m ⁻³
Σ PCDDs	0.600	0.141	0.089	0.086	0.311	0.298	0.270	0.335	ng m ⁻³
TCDF	0.002	0.003	0.010	0.014	0.018	0.015	0.218	0.202	ng m ⁻³
PeCDF	0.012	0.016	0.029	0.031	0.047	0.058	0.435	0.436	ng m ⁻³
HxCDF	0.051	0.078	0.076	0.049	0.159	0.169	0.440	0.523	ng m ⁻³
HpCDF	0.026	0.022	0.028	0.030	0.119	0.110	0.077	0.206	ng m ⁻³
OCDF	0.021	0.015	0.017	0.035	0.027	0.031	0.007	0.025	ng m ⁻³
Σ PCDFs	0.111	0.135	0.159	0.156	0.370	0.382	1.178	1.390	ng m ⁻³
Σ PCDD/Fs	0.172	0.275	0.248	0.245	0.681	0.681	1.448	1.726	ng m ⁻³
PCDF/PCDD ^a	1.8	1.0	1.8	1.8	1.2	1.3	4.4	4.1	/
PCDF/PCDD ^b	3.9	4.6	4.3	3.4	2.6	3.3	3.5	4.7	/
Cl-PCDD/Fs ^c	6.8	7.0	6.6	6.6	6.6	6.7	5.5	5.8	/
I-TEQ	0.012	0.016	0.021	0.020	0.048	0.051	0.249	0.255	ng I-TEQ m ⁻³

^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:

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

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.

higher than that of PCDD (R13 > R14 > R02 > R04 > R11 > R12 > R09 > R03 > R07 > R01 > R16 > R15 > 55%), partially indicating de novo synthesis as the main pathway for PCDD/F formation in these RTOs. The proportion of PCDF and PCDD is similar in R08 and R10, indicating that de novo synthesis and precursor formation have the similar contribution on the formation of PCDD/F. For R05 and R06, the proportion of PCDD is much higher than that of PCDF (R06 > R05 > 55%), indicating that the precursor formation is the major pathway for PCDD/F formation in

these two RTOs. In terms of I-TEQ concentration, the proportion of PCDF much higher than that of PCDD as in Fig. 1 (I-TEQ), indicating that PCDF is the main contributor to TEQ value in all RTOs flue gases. The detailed congener profiles of PCDD/Fs in flue gases are presented in Fig. 4 (Mass) and Fig. 5 (I-TEQ).

As a multivariate statistical method, principal component analysis (PCA) is frequently used in environmental science to reduce the dimensionality of a data set. PCA is commonly applied to analyze the similarities and differences between

Fig. 2. PCDD/Fs statistical results of flue gas samples from PIs, MSWIs (Gao *et al.*, 2009) and HWIs (Zhu *et al.*, 2018) in China.

distribution patterns of PCDD/Fs for flue gas samples in all facilities, and to reveal the sources of PCDD/Fs (Fiedler *et al.*, 1996; Gao *et al.*, 2009; Jin *et al.*, 2009; Liu and Liu, 2009). In the present study, this method is adopted to get a better understanding of PCDD/F-congener distributions from RTOs in China. PCA was performed on standardized PCDD/F-congeners data using IBM SPSS Statistics (Version 24). The score plot of PCA presenting the relative contributions of seventeen 2,3,7,8-substituted congeners is demonstrated in Fig. 3. The first principal component (PC1) accounts for 62.26% of the total variance, and the second principal component (PC2) accounts for 17.39% of the total variance. The score plot of PCA indicates that all of the investigated RTOs can be divided into three groups, and most RTOs belong to Group 3. PCDD/Fs in Group 3, including R04, R05, R06, R08, R09, R10, R11, R12 and R14, are strongly associated with PC1 derived from the correlative matrix. R01, R15 and R16 in Group 1 are associated with PC2 derived from another kind of matrix. For Group 2 involving R02, R03, R07 and R13 is associated with both PC1 and PC2, which might be due to the different distribution patterns of PCDD/Fs.

Congener profiles of each group are showed in Fig. 4. For Group 1, 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDF and 2,3,7,8-TCDF are three most abundant congeners (accounting for 51, 45 and 38% in R01, R15 and R16, respectively), indicating that high-chlorinated PCDFs are less than the low-chlorinated PCDFs. This result is different from that from municipal solid waste incinerators (Choi *et al.*, 2008), but is similar to the results of Group 3 in the report of (Ni *et al.*, 2009) and that of G33 in the report of (Yoon *et al.*, 2017), who studied the PCDD/F emission in flue gases from municipal solid waste and medical waste incinerators, respectively. R15 and R16 with

high emission of 0.25 ng I-TEQ m⁻³ belong to Group 1. Congener 2,3,4,7,8-TCDF is the most abundant one (16 and 15%) in these two RTOs, which is similar to the results of (Hoyos *et al.*, 2008), who investigated the emission of PCDD/Fs from medical waste incinerators in Antioquia. For Group 2, 1,2,3,4,6,7,8-HpCDF, 2,3,4,6,7,8-HxCDF, OCDD and 1,2,3,4,6,7,8-HpCDD are four most abundant congeners (accounting for 51, 52, 55 and 60% in R02, R03, R07 and R13, respectively), which is similar to the results of Group 2 in the report of (Ni *et al.*, 2009) and that of Group 3 in the report of (Gao *et al.*, 2009), who studied the PCDD/F emission in flue gases from municipal solid waste and hospital waste incinerators. The distribution of other congeners is uniform. 9 out of 16 RTOs belong to Group 3, and OCDD is the most abundant congener (21–71%), which is similar to the result of Group 1 in the report of (Gao *et al.*, 2009). Most samples in this paper fall into same group, indicating that the congener profiles of PCDD/Fs are less influenced by the types of exhaust gases and APCDs. Some scholars believe that the chlorine concentration plays a significant role in deciding the formation mechanisms and congener profiles of PCDD/Fs in flue gases (Wang *et al.*, 2003). When the chlorine concentration is higher than a threshold, PCDD/Fs are formed from PAHs through de novo synthesis, and the formation rates of PCDFs exceed those of PCDDs. When the chlorine concentration is lower than a threshold, the chlorine is used to form chlorophenols, which are primary precursors of PCDD/Fs and produce much more PCDDs than PCDFs (Wilhelm *et al.*, 2001; Wang *et al.*, 2003; Ryu and Mulholland, 2005). In this study, (Table 1) the content of chlorine in the exhaust gases treated by R05 and R06 is less than that of the other facilities. This is the main reason that the proportion of PCDD exceeds 60%.

Fig. 3. Score plot of principal component analysis of seventeen 2,3,7,8-substituted-PCDD/F emissions.

The I-TEQ congener profiles are presented in Fig. 5. Except for R05 and R06, 2,3,4,7,8-PeCDF is the largest contributor for I-TEQ for other 14 RTOs, accounting for 27–50%. Li *et al.* (2017) and Hsieh *et al.* (2018a) also found that 2,3,4,7,8-PeCDF was the biggest contributor in MSWIs and MWIs, suggesting that it should be regarded as a major factor for PCDD/Fs control. For R05 and R06, the largest contributor for I-TEQ is 1,2,3,6,7,8-HxCDF (accounting for 31 and 40%, respectively), followed by 2,3,4,7,8-PeCDF (accounting for 27 and 24%, respectively). This is because that 1,2,3,6,7,8-HxCDF is the second abundant congener with relatively high TEF of 0.1.

Correlations between TEQ and Congeners

TEQ indicators have been widely applied for the real-time monitoring of PCDD/F emissions in MSWIs (Liu *et al.*, 2013). Thus, linear regression is performed to examine the correlations between TEQ and mass concentrations of PCDD/F-congeners in flue gases of PIs, and the results are shown in Table 3. The results present positive correlations ($R^2 > 0.5$) between TEQ and 12 congeners except for 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF and OCDF. Three PCDD/Fs congeners (1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF and 1,2,3,4,7,8-HxCDF) exhibits high correlation with TEQ with R^2 of 0.970, 0.995 and 0.977, respectively. This suggests that these three congeners could be regarded as TEQ indicators and applied for real-time monitoring of PCDD/F emissions from PIs (Fig. 6), especially for 2,3,4,7,8-PeCDF ($R^2 = 0.995$). Also, the strong correlation between the concentration of 2,3,4,7,8-PeCDF and the I-TEQ value has been revealed by (Fiedler *et al.*, 2010). Besides, TEQ indicators of municipal solid waste incineration (MSWI) and medical waste

incineration (MWI) were analyzed by (Li *et al.*, 2017; Zhu *et al.*, 2018), indicating that OCDF and 1,2,3,4,7,8,9-HpCDF were effective indicators in flue gas of MSWI plants, while 1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8-HxCDF were effective indicators for MWI plants.

Estimated Annual Emission Amount of PCDD/Fs

A large number of researchers in recent years have estimated annual emissions (AE) of PCDD/Fs from thermal industrial processes, such as woodchip boilers (Bai *et al.*, 2017), MSWIs and MWIs (Gao *et al.*, 2009; Li *et al.*, 2017), cement kilns (Conesa *et al.*, 2016; Zou *et al.*, 2018), metallurgical plants (Hu *et al.*, 2013), etc. But there are few reports on the annual emissions of PCDD/Fs in the PI and the current (UNEP, 2013) PCDD/F inventory toolkit also does not introduce PI sources. Therefore, the annual emission of PCDD/Fs obtained in this study would be a useful supplement for inventory toolkit of PCDD/Fs.

The formula for calculating the AE of PCDD/Fs is:

$$AE = C \times GF \times OT \times n \times 10^{-9} \quad (2)$$

where AE is annual emissions (g I-TEQ year⁻¹), C is the TEQ concentration of PCDD/Fs in flue gas (ng I-TEQ m⁻³) GF is the flue gas flowrate (m³ h⁻¹), OT is the average operating time (4000 h year⁻¹), and n is the estimated number of RTOs in China.

In this study, the annual emissions of PCDD/Fs from flue gases of 16 RTOs are shown in Table 4. The annual emission of 16 RTOs ranges from 0.435 to 11.016 mg I-TEQ year⁻¹, with a mean value of 2.65 mg I-TEQ year⁻¹. About 7532 Pharmaceutical manufacturing enterprises are recorded in China in 2017 (National Bureau of Statistics of China, 2017).

Fig. 4. Mass of seventeen 2,3,7,8-substituted-PCDD/Fs congeners profile in flue gas of three groups.

Fig. 5. TEQ of seventeen 2,3,7,8-substituted-PCDD/Fs congeners profile in flue gas from 16 RTOs.

Table 3. Correlations between TEQ and PCDD/Fs.

PCDD/Fs congeners	Regression equation	R ²
2,3,7,8-TCDD	18.63034x + 0.01272	0.56589
1,2,3,7,8-PeCDD	4.0266x + 0.01504	0.92624
1,2,3,4,7,8-HxCDD	12.78202x - 0.01182	0.65924
1,2,3,6,7,8-HxCDD	5.51695x - 0.00846	0.91304
1,2,3,7,8,9-HxCDD	7.58613x - 0.00929	0.86372
1,2,3,4,6,7,8-HpCDD	1.11029x + 0.0069	0.38919
OCDD	-0.11872x + 0.06894	0.02346
2,3,7,8-TCDF	1.11006x + 0.01506	0.94922
1,2,3,7,8-PeCDF	1.25572x + 0.01039	0.97041
2,3,4,7,8-PeCDF	1.00197x + 0.00865	0.99527
1,2,3,4,7,8-HxCDF	1.66566x - 0.00659	0.97707
1,2,3,6,7,8-HxCDF	1.65907x - 0.02333	0.95116
1,2,3,7,8,9-HxCDF	5.42991x - 0.02187	0.91635
2,3,4,6,7,8-HxCDF	1.18787x - 0.00165	0.52623
1,2,3,4,6,7,8-HpCDF	0.82586x + 0.00683	0.31612
1,2,3,4,7,8,9-HpCDF	4.15231x + 0.00143	0.31969
OCDF	-0.06918x + 0.05793	0.00154

With an average annual emission of 2.65 mg I-TEQ year⁻¹, it is estimated that 19.96 g I-TEQ of PCDD/Fs is discharged to atmosphere in 2017 in China. The annual emission amount of PCDD/F is larger than that from MSWIs in 2015 in China (14.58 g I-TEQ) (Zhu *et al.*, 2018). However, the calculated mean value in this study is not enough to reflect emission amount exactly because of the limited data. More emission data from PIs are required to evaluate the potential emission amount of PCDD/Fs from PI in China in future.

CONCLUSIONS

This is the first study to comprehensively characterize PCDD/F emissions in flue gases from 16 RTOs belonged

to 8 pharmaceutical industries (PIs) in China. The emission concentration of PCDD/Fs ranges from 0.148 to 9.051 ng m⁻³ and the TEQ ranges from 0.008 to 0.255 ng I-TEQ m⁻³, with a large variation. The emissions from 14 out of 16 RTOs are lower than the new standard in China (0.1 ng I-TEQ m⁻³). But the emissions from the other two RTOs are higher than the standard, indicating that incineration technologies of pharmaceutical industry ought to be further enhanced. The concentration of PCDD/Fs in flue gases are in the order of HWIs > MSWIs > PIs. Base on PCA results, 16 RTOs could be divided into three groups, and 9 out of 16 belong to Groups 3. OCDD (21–71%) is the most abundant congeners in this group. R15 and R16 belonging to Group 1 have emissions above 0.25 ng I-TEQ m⁻³, and are characterized as high content of 2,3,4,7,8-PeCDF (15 and 16%).

Fig. 6. Correlations between TEQ and three PCDD/Fs congeners (a, b, and c).

Table 4. Annual emission amount of PCDD/Fs from 16 RTOs in China.

Facilities	TEQ (ng I-TEQ m ⁻³)	AE (mg I-TEQ year ⁻¹)
R01	0.023	1.126
R02	0.015	0.726
R03	0.040	2.554
R04	0.044	3.161
R05	0.008	0.435
R06	0.009	0.470
R07	0.032	1.386
R08	0.052	2.309
R09	0.012	0.533
R10	0.016	0.701
R11	0.021	1.071
R12	0.020	0.988
R13	0.048	2.307
R14	0.051	4.056
R15	0.249	10.943
R16	0.255	11.016

1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF and 1,2,3,4,7,8-HxCDF are effective TEQ indicators, especially for 2,3,4,7,8-PeCDF with R^2 of 0.995. The estimated annual emission amount (AE) of PCDD/Fs are in the range of 0.435 to 11.016 mg I-TEQ year⁻¹, with a mean value of 2.65 mg I-TEQ year⁻¹. It is estimated that 19.96 g I-TEQ of PCDD/Fs is discharged to atmosphere in 2017 in China.

ACKNOWLEDGEMENTS

This study was supported by the national key research and development program of China (2018YFB0605200), China Postdoctoral Science Foundation (2018M642429), the National Natural Science Foundation of China (51621005 and 51706201) and the Fundamental Research Funds for the Central Universities (2019FZA4010).

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Received for review, June 3, 2019

Revised, August 20, 2019

Accepted, August 26, 2019