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Process tracing of PCDD/Fs from economizer to APCDs during solid waste incineration: Re-formation and transformation mechanisms

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ABSTRACT

The emission of PCDD/Fs is a crucial factor for the aggravation of the Not-In-My-Back-Yard (NIMBY) syndrome, especially for the incineration plants that fail to meet the emission standard. It is well known that physicochemical processes in the boiler can notably affect the discharge of dioxins, especially under transient, non-steady conditions. However, few studies paid attention to the important operational parameters that influence PCDD/Fs formation and transformation in the boiler when an incinerator is in its daily steady operation. In this study, 36 samples were analyzed to achieve process tracing of PCDD/Fs. The concentration, congener profile and vapor/solid partitions of PCDD/Fs from the economizer to air pollution control devices (APCDs) under two typical steady conditions were investigated. Results indicated that increasing air supply aggravated the formation of PCDD/Fs, disturbed the vapor/solid partitions, and triggered a substandard emission. Quantitative structure–activity relationship (QSAR) modeling was firstly performed for the formation mechanism and orbital energy factors were identified as dominating factors. Besides, the removal rates of PCDD/Fs significantly correlated with the saturated vapor pressure and proportions of different isomers. This study is beneficial for operators to optimize relevant operational parameters of the incineration plants so as to get rid of substandard problems.

1. Introduction

Wide concern has been continuously raised over the emission of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in municipal solid waste (MSW) incineration plants around the world. Incineration has been vastly promoted for solid waste treatment in China in recent years, and great efforts have been made to enhance the environmental performances of incineration plants. Periodic monitoring on PCDD/Fs carried out by the authorities has become an effective measure for environmental supervision on solid waste incineration and parameters such as furnace temperatures are required to be disclosed to ensure the decomposition of dioxin in the furnace (Lu et al., 2017; China MEE., 2020). Air pollution control devices (APCDs) such as activated carbon injection and bag filter (ACI + BF) have been widely adopted to guarantee the dioxin emission (Trivedi and Majumdar, 2013; Zhang et al., 2013; Ma et al., 2020). Still, quite a few incineration plants occasionally failed to meet the emission limit stated in the national standard, which aggravated the Not-In-My-Back-Yard (NIMBY) syndrome (Lu et al., 2019). The emission limit has been set by the toxicity equivalent quantity (TEQ) of the seventeen PCDD/F congeners with chlorine substitution in 2,3,7,8 positions.

Reasons for excessive emissions were partly unveiled in previous studies as follows. Firstly, the removal efficiency of ACI + BF is restricted by the quality and quantity of activated carbon, adsorption temperature, and filtration efficiency (Chi and Chang, 2005; Chi et al., 2006b; Kim et al., 2007; Tsiliyannis, 2018). Kim et al. (2007) found that the removal efficiency of ACI + BF was limited in the range of 94% to 99%, and an excessive injection of activated carbon could increase the PCDD/Fs emission by 60% on the contrary. Secondly, excessive formation of PCDD/Fs takes place in the post-combustion zone (Huang and Buekens, 1995; Nakahata and Mulholland, 2000; Hell et al., 2001). Lin et al. (2015) noted that PCDD/Fs concentrations at the outlets of superheater and economizer were respectively 10 and 66 times larger than those at the furnace outlet. Besides, quite a few researchers took note of increased PCDD/Fs due to drastic changes or instability of operational conditions. It is known that transient, non-steady conditions in the incineration system can induce dramatic concentrations of dioxins in the boiler with the occurrence of memory effects (Zimmermann et al., 2001), which could significantly increase

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PCDD/Fs concentration by 0.1–15 times (Trivedi and Majumdar, 2013). Dioxins accumulated in ash deposits in the furnaces and boilers were likely to cause high dioxin concentrations in the flue gas during the startup period (Tejima et al., 2007) and high concentrations of PCDD/Fs were indeed generated in the boilers under abnormal operating conditions (Gass et al., 2003; Hunsinger et al., 2003). In consequence of the above mentioned findings, physicochemical processes in the boiler can dramatically affect the discharge of PCDD/Fs.

However, there are few studies that paid attention to the crucial operational parameters that influence PCDD/Fs formation and transformation in the boiler when an incineration plant is in its daily steady operation. Additionally, studies on the re-formation mechanism of PCDD/Fs downstream of the incinerator are mainly based on lab-scale experiments and theoretical speculations (Chi and Chang, 2005; Zhang et al., 2013; Pham et al., 2019; Yang et al., 2020), rather than full-scale demonstrations established on an MSW incineration plant. Therefore, it is necessary to investigate the mechanisms of PCDD/Fs formation on the basis of physicochemical processes occurring in the boiler under steady conditions with different operational parameters settled, in order to optimize the operation status of MSW incineration plants and then avoid the excessive discharge of pollutants.

Quantitative structure–activity relationships (QSAR) modeling methods may provide reliable insights into which aspect of the molecular structure influences the re-formation of PCDD/Fs, as they have been applied for effectively predicting the toxicity of different congeners and the photolysis half-life of PCDFs (Hu and Aizawa 2003; Niu et al. 2005; Gu et al., 2007). For instance, Kafafi et al. (1992) reported a structure–activity model of Ah binding with PCDD/Fs in virtue of molecular lipophilicities quantified by descriptors such as electronic energy gaps (E_d). Niu et al. (2005) found that increasing the number of chlorine atoms and E_d^2 values leaded to the increase of photolysis half-life values of PCDFs. However, these methods were rarely used to explore the formation and congener profile of PCDD/Fs (Nevalainen and Kolehmaine, 1994; Larsson et al., 2013; Palmer et al., 2018). Besides, the results of QSAR modeling on PCDD/Fs removal were sometimes controversial, as the sensitiveness of models to highly chlorinated isomers was hampered by the insufficiency of chemical and physical properties of similar isomers from the database (Pankow, 1987, 1994; Harner and Bidleman, 1998). While the removal rates of highly chlorinated isomers were deemed larger than lower chlorinated ones in some studies (Hung et al., 2011; Zhou et al., 2015b), others held the opposite viewpoints that the nonlinear models didn't fit well with highly chlorinated isomers (Chi and Chang, 2005; Chi et al., 2006b; Chang et al., 2009). Therefore, molecular descriptors with sufficient differences among PCDD/Fs isomers were used in this study.

In order to improve deficiencies of existing studies, this paper focuses on the re-formation and transformation of PCDD/Fs in the economizer (i.e., the rear part of the exhaust gas boiler) as well as removal mechanisms. Both vapor-phase and solid-phase PCDD/Fs at the inlet and outlet of the economizer were monitored and analyzed under two typical different steady conditions. The concentration, congener profile, and vapor/solid partition of PCDD/Fs were analyzed and the quantitative structure–activity relationship (QSAR) models were adopted to reveal the intrinsic influencing factors that determine the re-formation and removal of PCDD/Fs. This study may be beneficial for operators of incineration systems to get rid of substandard problems.

2. Materials and methods

2.1. Experimental design

A full-scale MSW incineration plant using a movable grate was selected to conduct this study, as the movable grate technology held about 80% market share in China (Lu et al., 2017). This incineration plant located in South China had a capacity of 750 tonnes per day and was put into operation in 2005 (see Fig. 1). The principle of "3T + E" was implemented to inhibit PCDD/Fs formation in the furnace. Soot in the boiler was discontinuously blown by shock waves. The APCDs consisted of selective non-catalytic reduction, semi-dry scrubbing and ACI + BF. The consumption of activated carbon was about 0.38 kg per tonne of solid waste.

Since the temperature and oxygen content in the economizer were generally regarded as crucial parameters that reflect operating performances, three sampling points located respectively at the inlet and outlet of the economizer (Q1 and Q2), and the inlet of the stack (Q3) were arranged. A 2-hour sampling process at a temperature below 400 °C was necessary for collecting sufficient masses of particles to accurately analyze the dioxin concentration of each

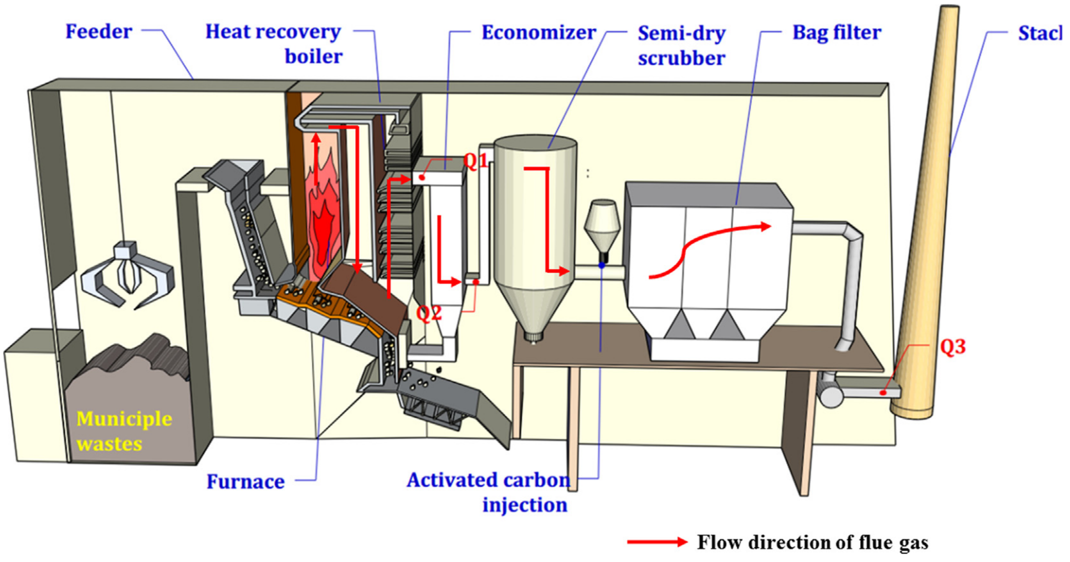

Fig. 1. Three sampling points in the selected waste incineration line. (Q1- the inlet of economizer; Q2- the outlet of economizer; Q3- the inlet of stack).

Table 1
Key operating parameters of the incineration system under two conditions.

Conditions		Furnace temperature (°C)	Temperature at Q1 (°C)	Temperature at Q2 (°C)	Oxygen content at Q2 (%)	Capacity (t/d)	Primary air (Nm^3/h)	Secondary air (Nm^3/h)
E1	Range	1130–1189	309–314	204–213	8.1–8.6	–	–	–
	Average	1168	311	208	8.3	628	32,859	9037
E2	Range	1042–1096	320–338	210–231	10.6–11.7	–	–	–
	Average	1070	327	225	11.1	590	33,269	9601

The sampling time for E1 was 10:47–12:47 AM, 1:34–3:34 PM, and 4:11–6:11 PM on the first day; while Q3 point that for E2 was 2:44–4:44 PM, 5:03–7:03 PM and 7:21–9:21 PM on the second day.

sample. And the flue gas temperature of Q1 and Q2 fluctuated exactly in a range of 309–338 °C and 204–231 °C in the process of the experiment (Table 1).

For this incineration system, the oxygen content in the economizer was commonly limited to 8%–11%, to maintain a balance between power generation efficiency and pollutant release. Besides, it is impossible to keep the oxygen content in the economizer on a constant level, even by holding the primary and secondary air unchanged. Therefore, only two typical steady conditions known as E1 and E2 were settled for the experiment. Key operating parameters of E1 and E2 were given in Table 1. E1 represented the daily status of the incineration plant. The oxygen content in the economizer was in the range of 8.1%–8.6% (averaged 8.3%), and the temperature of the inlet and outlet of the economizer respectively fluctuated at 311 °C and 208 °C. Sampling of PCDD/Fs in different phases in flue gas was simultaneously conducted at the three sampling points, with three samples in parallel at each point acquired.

On the noon of the second day, the operating condition was changed by increasing the air supply by 2.3% (E2). As a result, not only was the oxygen content turned up to 10.6%–11.7% (averaged 11.1%), but the average temperature has also been raised by about 10 °C. After the operating condition became stable, the sampling at three points started. Two types of operating conditions and three sampling points led to 6 sets of sampling in all, and three samples were composited in each set of sampling, and each sample was used for detecting the concentration and congener profile of PCDD/Fs in both solid and gas phases. Thus, a total of 36 samples with known congener partitions in gas/solid phases would be obtained.

2.2. Sampling and analysis

PCDD/Fs in flue gas were collected through a sampler (X1-APIS, MEGA, Italy) following the Chinese Standard (HJ 77.2–2008). Isokinetic sampling was adopted at Q2 and Q3 points, while constant flow sampling was adopted at Q1 point due to the large flow rate fluctuations (>10%). For flue gas sampling, vapor-phase was collected by the XAD-2 resin while the solid-phase was collected with a fiber glass filter, and condensate water was collected with a brown glass bottle at the same time. ^{37}Cl -labelled internal standards were added to resin before sampling and the recoveries of PCDD/Fs standards varied from 71.1% to 131.7%. The collection time of each flue gas sample lasted for two hours. The gas-phase and condensate water phase were analyzed together, but the solid-phase was pretreated and analyzed separately.

The pretreatment of samples also followed the standard HJ 77.2–2008, and the procedures mainly included spiking $^{13}C_{12}$-labelled internal standards, Soxhlet extraction, cleanup with multilayer silica gel column and basic-alumina column, and spiking $^{13}C_{12}$-labelled recovery standards. A high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) (Waters, AutoSpec Premier) with a fused silica capillary column DB-5 MS (60 m × 0.25 mm × 0.25 μm) was used to analyze the purified samples. These recoveries standards varied from 48.1% to 129.8%, which were consistent with the Chinese Standard. Additionally, the concentrations of PCDD/Fs were normalized to dry air of 11% O_2 under 101.3 kPa and 0 °C.

2.3. QSAR modeling

The multiple linear regression method was used to analyze the formation, partitioning and removal mechanisms of PCDD/Fs. According to existing studies (Nevalainen and Kolehmaine, 1994; Iino et al., 2001; Li et al., 2011), three categories of molecular descriptors were used for QSAR modeling (Table S1): (i) Four basic descriptors that refer to chemical bonds including -CH, -CCl, C**, and C*-O-C* (successively denoted by f_1, f_2, f_3, f_4); (ii) Four structural amendment factors that refer to Cl-position-specific preferences (successively denoted by n_a, n_b, n_c, n_d); and (iii) three orbital energy factors that refer to the highest occupied molecular orbital energy, lowest unoccupied molecular orbital energy, and their energy gap (successively denoted by E_H, E_L, dE). For example, the molecular orbital structure of 1,2,3,7,8,9-HxCDF is much different from its isomers (Fig. S1), and the difference can be reflected by the molecular orbital energy gap. The multicollinearity of these eleven descriptors could be solved by stepwise linear regression using SPSS or R Studio.

3. Results and discussion

3.1. PCDD/Fs concentration, congener profile, and partition

The PCDD/Fs concentrations and vapor/solid partitions from three sampling points under two operating conditions are presented in Fig. 2 and Table S2. Solid-phase PCDD/Fs prior to the economizer (i.e., Q1 point) had a proportion of more than 80% under two conditions, in contrast with the result in which vapor-phase PCDD/Fs dominated (Chi et al., 2006b). Such a reverse result was probably determined by the quantity of particles in flue gas. When the particles were preliminary removed by an “extra” cyclone in Chi’s study, the solid-phase PCDD/Fs were reduced simultaneously. It was attractive that the PCDD/Fs concentrations decreased by half in the economizer (53.1% under E1 condition and 50.6% under E2 condition), mainly because densely deployed tubes in the economizer blocked the particles in gas flow (Nemathaga et al., 2008). Furthermore, when increasing the air supply by 2.3% while waste-feeding capacity and other parameters remained stable, the formation and emission of PCDD/Fs had been aggravated. Specifically, the mass (TEQ) concentration of PCDD/Fs respectively increased by 42.4% (49.7%), 50.1% (17.5%), and 117.2% (101.3%) at three sampling points. The unbalanced increased rates at Q2 point indicated that the congener profile of PCDD/Fs in the economizer had changed. In addition, with the change of the operating condition, the mass proportions of solid-phase PCDD/Fs increased by 11.9% at Q1 point but decreased by 44.6% at Q2 point, implying that the vapor/solid partition in the economizer also changed.

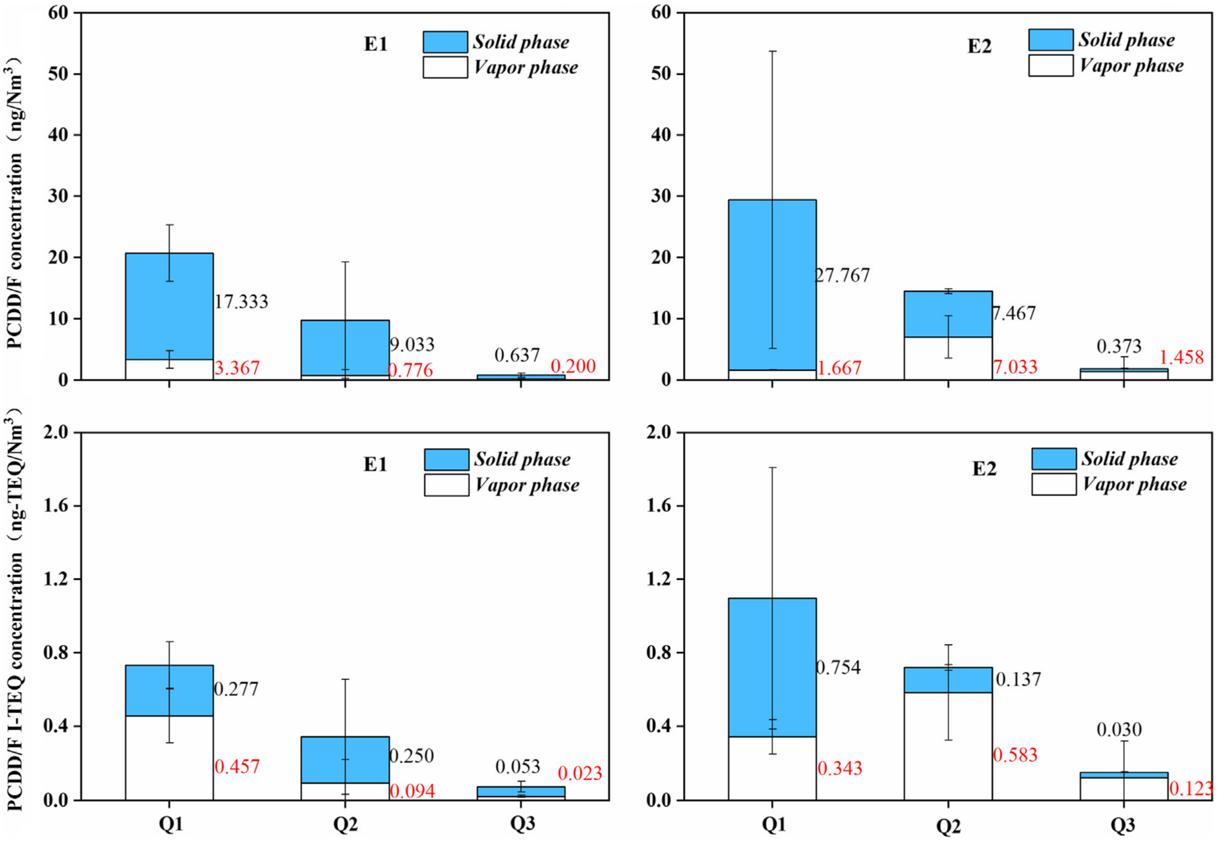

Fig. 2. Variation of vapor/solid partitions of PCDD/Fs at three sampling points.

The special, combined changes of PCDD/Fs concentration, congener profile, and vapor/solid partition in the economizer can be further decomposed and analyzed step by step as below:

(i) The obstruction and phase migration of PCDD/Fs in the economizer. The obstruction could be visually proved by the amount of particle matter at the sampling fiber filters. The amount of particle matter at Q1 point was higher than that at Q2 point (Fig. S2). As PCDD/Fs tended to distribute in the solid phase, tubes in the economizer could block particles and PCDD/Fs. Solid-phase PCDD/Fs at Q2 point were respectively obstructed by 48.5% and 73.1% under E1 and E2 conditions, while vapor-phase PCDD/Fs at Q2 point were respectively obstructed by 76.9% and −327.5%. The negative obstruction rate of vapor-phase PCDD/Fs (i.e., −327.5%) under E2 condition indicated that the deposited PCDD/Fs could be released and transformed into vapor-phase PCDD/Fs. Such release was dynamic and unstable, influenced by temperature or flow velocity of flue gas. As long as gas flows existed in the tubes, this kind of release would be persistent. A stronger flush of gas caused by larger velocity and higher temperature aggravated this release, as the flow velocity and temperature of flue gas increased respectively by 13.2% and 5%. In other words, this release might be called "adsorptive memory effect", meaning that previously formed PCDD/Fs which were adsorbed on deposited particles transformed into the flue gas (Trivedi and Majumdar, 2013).

(ii) The disturbance caused by changing the operating condition. Changing the operating condition from E1 to E2 increased the flow velocity by 13.2%, the oxygen content by 2.3%, and the gas temperature by 16℃ in the economizer, causing a series of disturbances in PCDD/Fs concentration and vapor/solid partition. Firstly, the larger flow velocity washed more ash deposits from heat exchange tubes and brought a higher concentration of solid-phase PCDD/Fs to the economizer. Solid-phase PCDD/Fs in the economizer, meanwhile, could be released and transformed into vapor-phase PCDD/Fs. Secondly, the higher oxygen content benefited Deacon Reaction by providing more active chlorine for the re-formation of PCDD/Fs (Zhang et al., 2017). Lastly, a higher temperature might enhance the re-formation of PCDD/Fs (McKay, 2002) and accelerate the release of deposited PCDD/Fs into the flue gas. As a combined result, solid-phase PCDD/Fs decreased by 73.1% but vapor-phase PCDD/Fs increased by 327.5% in the economizer under E2 condition, which might be attributed to the memory effect in the economizer.

(iii) The variation of the congener profile and vapor/solid partition. As seen in Fig. 3, highly chlorinated congeners always dominated the mass concentration of PCDD/Fs, although they were subordinate in the TEQ concentration due to their small toxicity equivalence factors (TEFs). For instance, HxCDFs and HpCDFs occupied 63%–87% of PCDFs, while HxCDDs and HpCDDs occupied 69%–99% of PCDDs under E1 and E2 conditions. However, 2,3,4,7,8-PeCDF, the TEF of which is 0.5, has the largest proportion in the TEQ concentration, which is similar to the existing studies (Chi et al., 2006a; Li et al., 2017; Lei et al., 2018; Palmer et al., 2018). Moreover, at Q1 point, the ratios of PCDDs to PCDFs were 4.0 and 2.4 under E1 and E2 conditions, suggesting that the *de novo* reactions which often cause the ratios of PCDDs to PCDFs <0.2 (Zhou et al., 2015a) almost didn't take place. Then at Q2 point, the ratios of PCDDs to PCDFs decreased to 1.6 and 1.1, respectively. Lastly at Q3 point, the ratios of PCDDs to PCDFs decreased to 0.6 and 0.5, respectively, suggesting that PCDDs were easier to be removed by APCDs. Furthermore, from the perspective of vapor/solid partition, solid-phase PCDD/Fs dominated the mass concentration but vapor-phase PCDD/Fs dominated the TEQ concentration, revealing that highly chlorinated congeners with lower saturated vapor pressures (Chi and Chang, 2005; Chi et al.,

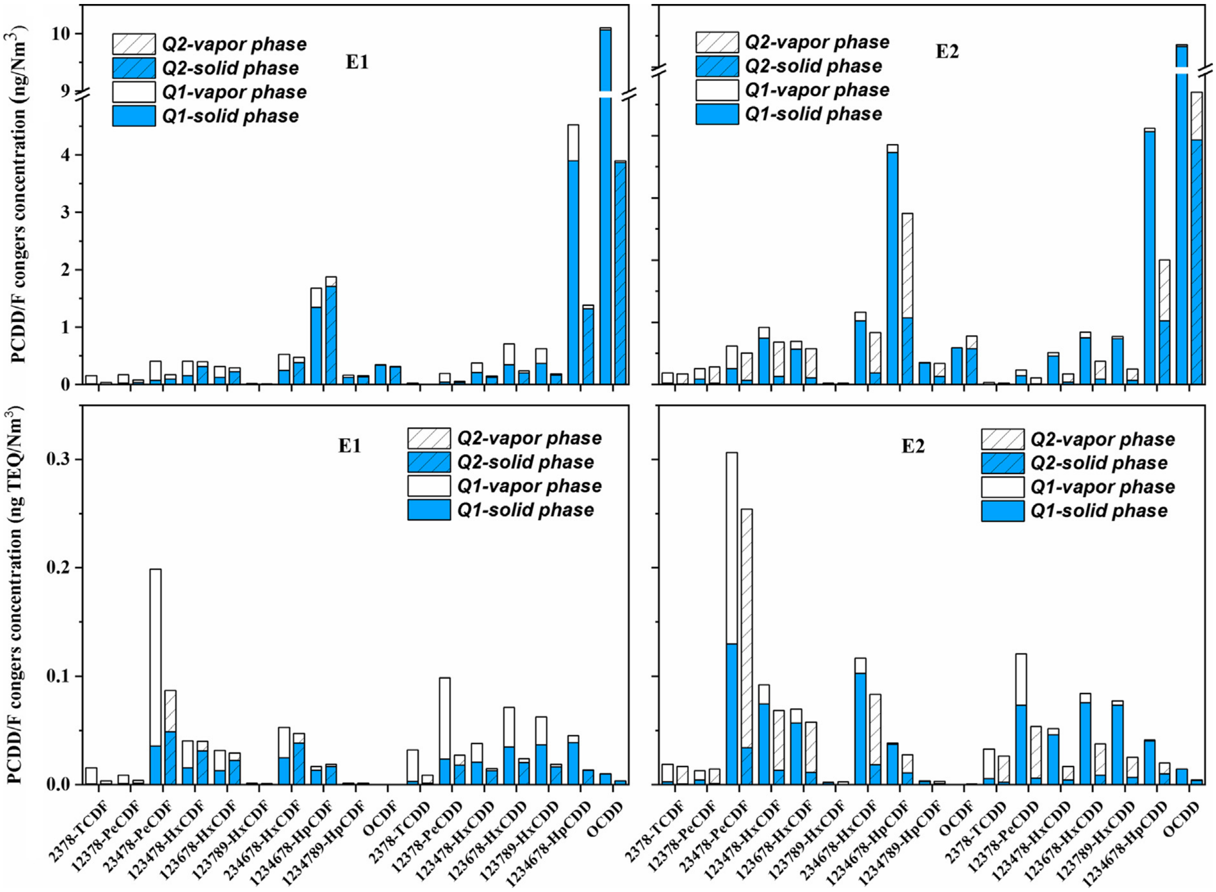

Fig. 3. The PCDD/F isomer concentrations and vapor/solid partitions at Q1 point and Q2 point.

2006b) were more concentrated in the solid phase. PCDDs were also mainly concentrated in the solid phase, which was in accordance with their lower saturated vapor pressure.

(iv) The concentration variation of isomers. As obviously shown in Fig. 3, the concentrations of 1,2,3,7,8-PeCDF, 1,2,3,7,8,9-HxCDF, and 1,2,3,4,7,8,9-HxCDF were always lower than their isomers, while the dominance of 1,2,3,4,6,7,8-HpCDF and OCDD was reported (Ma et al., 2020). However, less attention has been paid to the reason of the variation of isomer concentrations in the existing studies, though it can be explained by the formation of PCDD/Fs from precursors in quantum mechanical studies (Zhang et al., 2008; Qu et al., 2009; Zhang et al., 2010). Since the dominating chlorophenol precursors, including 2,4,6-trichlorophenol and 2,4-dichlorophenol, are more likely to generate PCDD/Fs with chlorine atoms in 2, 3, 6, and 8 positions through the way of homogeneous gas-phase formation (Zhang et al., 2010), PCDD/F isomers with more chlorine atoms in 2,3,6, and 8 positions would occupy larger proportions. This phenomenon revealed that PCDD/Fs prior to the economizer might probably derive from the homogeneous gas-phase formation in the high temperature zone downstream of the incinerator. It was consistent with the review of Stanmore and B.R. (2004), but different to other studies (Shaub and Tsang, 1983; Huang and Buekens, 1995; Lu, 2004).

3.2. QSAR modeling for PCDD/Fs re-formation and transformation

The concentration variation of PCDD/Fs isomers can be explained with the aid of QSAR modeling. Influence factors can be attributed to the molecular descriptors, which are associated with the chlorinated positions, and molecular orbital energy, as PCDD/Fs in this study were more likely to derive from the re-formation occurring in the downstream zone of the incinerator. Thus, eleven available molecular descriptors were taken as independent variables in the QSAR modeling, while the concentrations, vapor-phase concentrations, and vapor/solid partitions of PCDD/Fs isomers were respectively taken as dependent variables. Stepwise linear regression was used for eliminating the multicollinearity of multiple molecular descriptors. Isomer concentrations of each single samples (n = 12 × 17) and their average values (n = 4 × 17) were used for the exploitation. The results of QSAR modeling for PCDD/Fs re-formation and transformation are represented in Table 2. Several intrinsic features can be concluded from Table 2.

(i) The variance within groups (i.e., three single samples) influenced the model precision. The R^2 values (i.e., goodness of fit) of regression models on the basis of average values were general better than those based on single monitoring values, because the average values balanced the fluctuation of single monitoring values.

(ii) The obstruction of tubes could be neutralized by the switch of the operating condition. When taking the isomer concentration or the vapor/solid distribution coefficients of isomer as the dependent variable, the R^2 values of regression models in E1-Q1 situation and E2-Q2 situation were larger than those in the other two situations. It suggested that isomer concentrations and vapor/solid distribution coefficients in E1-Q1 situation were not yet disturbed by the obstruction of tubes, and the disturbance caused by the change of operating conditions from E1 to E2 might be weakened by memory effects. It also indicated that the change of operating conditions would go against the goal of meeting the emission limit, though increasing air supply was beneficial for

Table 2
The results of QSAR modeling for PCDD/Fs re-formation and transformation.

Situations	**Modeling on the basis of single monitoring values**				**Modeling on the basis of average values of each three samples**			
	n	**Regression models**	R^2	***p*-value**	***n***	**Regression models**	R^2	***p*-value**
***y* denotes isomer concentrations**								
E1-Q1	51	$y = 1.511^{*} f_3 + 1.904^{***} n_a + 0.550^{***} dE - 6.529$	0.616	<0.001	17	$y = 1.968^{***} n_a - 0.487^{*} E_H - 5.349^{**}$	0.620	<0.001
E1-Q2	51	$y = -0.620^{***} f_1 + 0.197^{**} dE + 0.319$	0.295	<0.001	17	$y = -0.508^{*} f_1 - 0.318 n_a - 0.235^{*} E_H - 0.689$	0.575	0.003
E2-Q1	51	$y = 2.662 f_3 + 2.557^{***} n_a + 0.785^{**} dE - 9.391$	0.334	<0.001	17	$y = -1.167 f_1 + 1.676 n_a - 0.770^{*} E_H - 4.288$	0.553	0.003
E2-Q2	51	$y = -0.817^{***} f_1 + 0.416 f_3 + 0.287^{***} dE + 0.075$	0.589	<0.001	17	$y = -0.945^{***} f_1 - 0.294^{**} E_H + 0.463$	0.601	<0.001
***y* denotes vapor-phase concentrations of isomer**								
E1-Q1	51	$y = 0.053\, nd + 0.043^{***} dE - 0.156$	0.206	0.001	17	$y = 0.252 f_3 - 0.053^{*} E_H + 0.137 E_L - 0.334$	0.283	0.064
E1-Q2	51	$y = -0.013 f_1 + 0.074^{**} f_3 + 0.015^{**} dE - 0.089$	0.152	0.013	17	$y = -0.040^{***} f_1 - 0.032^{**} n_a - 0.012^{**} E_H + 0.076^{*}$	0.630	0.001
E2-Q1	51	$y = 0.020^{*} f_1 + 0.145^{***} f_3 + 0.026^{***} dE - 0.226^{***}$	0.469	<0.001	17	$y = -0.022^{**} E_H - 0.043^{**} E_L - 0.083$	0.637	<0.001
E2-Q2	51	$y = -0.237^{***} f_1 + 0.505^{***} f_3 + 0.139^{***} dE - 0.459$	0.426	<0.001	17	$y = -0.402^{**} f_1 - 0.172 n_a - 0.119^{**} E_H + 0.540$	0.557	0.003
***y* denotes vapor/solid distribution coefficient of isomer**								
E1-Q1	51	$y = 4.131^{***} f_1 + 2.881^{*} f_3 + 1.316 n_a - 8.521^{*}$	0.538	<0.001	17	$y = 2.695^{***} f_1 - 2.676^{*}$	0.645	<0.001
E1-Q2	51	$y = 1.621^{***} f_1 - 1.553$	0.201	<0.001	17	$y = 0.734^{***} f_1 - 0.800^{*}$	0.577	<0.001
E2-Q1	51	$y = 2.731^{***} f_1 - 3.017^{*}$	0.330	<0.001	17	$y = 1.160^{***} f_1 - 1.386^{*}$	0.558	<0.001
E2-Q2	51	$y = 4.063^{***} f_1 - 2.745$	0.371	<0.001	17	$y = 3.334^{***} f_1 + 1.110 n_a - 1.171 E_L - 4.006$	0.831	<0.001

Vapor/solid distribution coefficient is vapor-phase concentration of isomer versus that of solid-phase.
Notes: The symbol * denotes the significance of parameter.

stable combustion and prevention of PCDD/Fs formation in the furnace.

(iii) The prediction precision for vapor-phase isomers was not associated with vapor-phase concentrations of isomers. Vapor-phase concentrations in E1-Q1 situation and E2-Q2 situation were higher than those in the other situations, but the R^2 values of the regression models taking vapor-phase concentrations as the dependent variable were smaller, suggesting that the disturbance from the economizer and the change of the operating condition weakened the regularity.

(iv) Three classes of molecular descriptors had different contributions in the QSAR modeling. Firstly, only a few key descriptors were selected as the independent variables due to the multicollinearity. For example, both f_1 and f_2 referred to the chlorine substitution number, and both f_3 and f_4 differentiated between PCDDs and PCDFs. Secondly, basic descriptors were actually contributing factors in PCDD/Fs formation. The descriptor f_1 negatively correlated with the vapor-phase concentration, due to the lower saturated vapor pressure of highly chlorinated homologues. Thirdly, structural amendment factors were only minor contributing factors in PCDD/Fs formation, due to the lack of specificity in the 2,3,7,8-substituted homologues. The multicollinearity indeed existed between structural amendment factors and basic descriptors. Lastly, orbital energy factors such as dE and E_H were dominating factors in PCDD/Fs formation because they can be used to distinguish different isomerides from all the 2,3,7,8-substituted homologues.

3.3. QSAR modeling for PCDD/Fs removal

Although particle matters adsorbing PCDD/Fs could be effectively intercepted to be<3.5 mg/Nm^3 by the bag filter, the removal rates of PCDD/Fs by the APCDs were limited in this study. The removal rates of solid-phase PCDD/Fs were 93% and 95% under E1 and E2 conditions, and the removal rates of vapor-phase PCDD/Fs were 74% and 79%, respectively. Since there were more vapor-phase PCDD/Fs under E2 condition, the removal rate of PCDD/Fs under E2 condition was only 87.4%, less than that under E1 condition (91.5%). The phenomenon that vapor-phase congeners were more difficult to remove is in accordance with the literature (Chi et al., 2006a). As one possible reason, the limited removal rates of lowly chlorinated congeners restricted the removal rate of vapor-phase PCDD/Fs. Altering daily operating conditions (e.g. the switch from E1 to E2) increased the concentration of vapor-phase PCDD/Fs, which would trigger a substandard result of PCDD/Fs emission (0.153 ng I-TEQ/Nm^3). Thus, stable operation may help to better control dioxin emission.

As the saturated vapor pressure is one of the main factors that influence the removal of PCDD/Fs congeners, the saturated vapor pressure (denoted by P_L^O) and the proportion of isomers (denoted by *Pro*) were taken as independent variables in QSAR modeling for PCDD/Fs removal. The P_L^O of each PCDD/F isomer can be calculated on the basis of their retention index from the experimental determination (Donnelly et al., 1987; Wang and Wong, 2002, 2003; Chu and Hong, 2004). As a result, a multiple linear regression equation, Eq. (1), can be used to predict the removal rate of each isomer (denote by *RE*). The R^2 values of Eq. (1) was about 0.70.

$$RE = -0.51P_L^0 + 0.0024Pro + 1.9 \quad (1)$$

For each isomer, the proportion and P_L^O jointly determined its removal rate. As shown in Fig. 4, the removal efficiency of PCDD/F congeners increased with increasing number of chlorination (especially for PCDDs) under two operating conditions. Same as what noted in the literatures (Hung et al., 2011; Zhou et al., 2015a), lowly chlorinated congeners with larger P_L^O had higher tendencies to exist in the vapor phase, while highly chlorinated con-

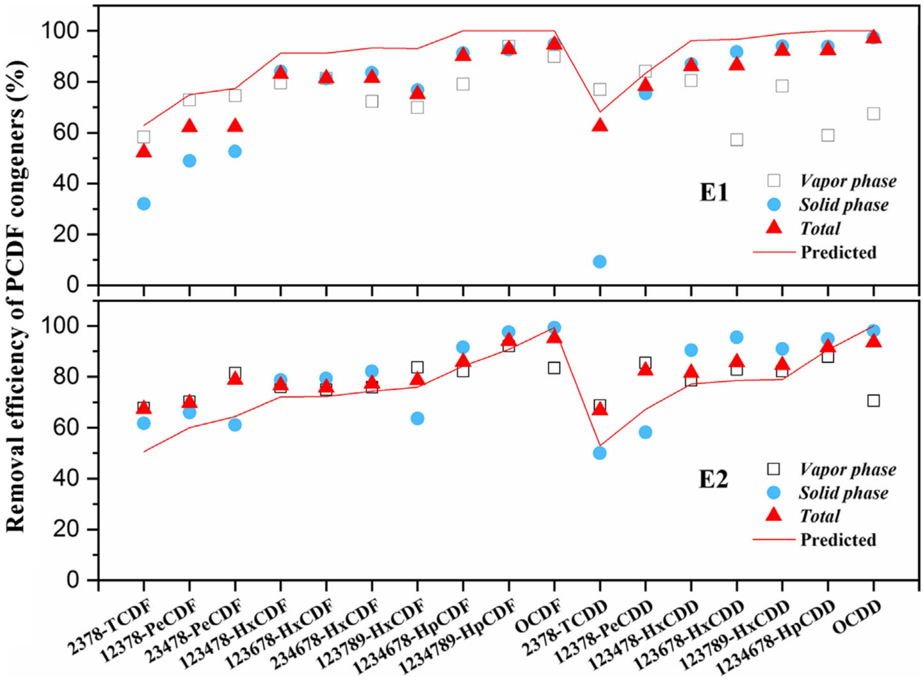

Fig. 4. Removal efficiency of PCDD/F congeners. The predicted line indicates the removal rate of PCDD/F congeners both in solid phase and vapor phase.

geners were easier to be captured by activated carbon and more effectively removed by APCDs. In addition, the predicted removal rates were lightly higher than the observed values under E1 condition, in contrast to the result under E2 condition. The reason was that the vapor-phase partitions increased when the operating condition changed from E1 to E2.

Since the proportion of isomer as an independent variable was added in Eq. (1), the predicted lines fitted with the observed data very well, especially when it came to highly chlorinated congeners. The deviations between observed and predicted values were mostly <10%. The existing studies such as the vapor/solid partition model proposed by Chi and Chang (2005) could explain why lowly chlorinated congeners with larger P_L^O were mostly distributed in the vapor phase and why solid-phase PCDD/Fs were easier to be removed by the APCDs, but the model didn't fitted well with highly chlorinated congeners. In comparison, the proposed model for PCDD/Fs removal in this study outperformed the model proposed by Chi and Chang (2005).

4. Conclusions

The process tracing of PCDD/Fs during solid waste incineration confirmed that physicochemical processes in the boiler influenced by the alternation of operating conditions considerably affected the discharge of dioxins. After increasing air supply by 2.3%, the generation and emission of PCDD/Fs increased by at least 42.4%, and a series of disturbances in PCDD/Fs vapor/solid partition occurred as well. This change could ultimately cause PCDD/F emissions to exceed the national standard. Thus, stable operation might help to better control dioxin emission.

Besides, PCDD/Fs concentrations decreased by half in the economizer, and such phenomenon has never been discovered in previous studies. QSAR modeling was also performed to provide insights into which aspect of the molecular structure influenced the re-formation of PCDD/Fs for the first time. According to the modeling, three classes of molecular descriptors had different contributions in the re-formation and transformation of PCDD/Fs, with orbital energy factors d_E and E_H as dominating ones. Moreover, PCDD/F isomers with more chlorine atoms in 2, 3, 6, and 8 positions occupied larger proportions in the congener profile, which was probably derived from the homogeneous gas-phase formation in the high temperature zone downstream of the incinerator

Finally, the removal rate of PCDD/F congeners could be effectively predicted by saturated vapor pressure and proportions of isomer. The gap between the predicted lines and the observed data was small (<10%), especially when it came to highly cholorinated congeners, and therefore the proposed model is superior compared to other ones in previous studies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary Material.docx: Process tracing of PCDD/Fs from economizer to APCDs during solid waste incineration: Re-formation and transformation mechanisms. Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2020.11.007.

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