

Influence of Different Catalytic Metals on the Formation of PCDD/Fs during Co-combustion of Sewage Sludge and Coal

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ABSTRACT

Co-combustion of sewage sludge (SS) and coal was developed rapidly in China, however, less attention was paid to the formation characteristics of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and the influence factors, such as the catalytic metals (CuCl₂, FeCl₃, ZnCl₂, CuO, Fe₂O₃, and ZnO), sources of carbon and chlorine. During the co-combustion of SS (2.5 wt.%) and coal (97.5 wt.%), the formation content of PCDD/Fs was 0.51 ng g⁻¹ and 0.01 ng I-TEQ g⁻¹. By adding metal chlorides (2.0 wt.% CuCl₂, FeCl₃, and ZnCl₂), the formation contents of PCDD/Fs were increased significantly to 148.99, 67.38, and 53.63 ng g⁻¹ (i.e., 2.10, 1.09, and 1.34 ng I-TEQ g⁻¹), respectively, while the metal oxides (2.0 wt.% CuO, Fe₂O₃, and ZnO) only increased the PCDD/F contents to 1.27, 0.76, and 0.57 ng g⁻¹ (0.03, 0.01, and 0.02 ng I-TEQ g⁻¹), respectively. That is, the promotion effect of different metal additives on PCDD/F formation followed a sequence of CuCl₂ (292×) > FeCl₃ (132×) > ZnCl₂ (105×) >> CuO (2.5×) > Fe₂O₃ (1.5×) > ZnO (1.1×), wherein the metal chlorides showed 2 orders of magnitude higher promotion than that of metal oxides. The proportion of highly chlorinated PCDD/Fs was further increased after adding metal chlorides, while the additional metal oxides decreased it. The de novo synthesis was revealed as the major formation pathway of PCDD/Fs except for adding ZnO. The CuCl₂ and FeCl₃ can also enhance the chlorination routes to generate PCDD/Fs. Only ZnO showed the promotion effect on the CP-route. The chlorine source was an essential limiting factor for generating PCDD/Fs, and the chlorine from metal chlorides was the preference source compared with that contained in SS and coal. The results have important reference value for controlling PCDD/Fs formation in the co-combustion process of SS and coal.

Keywords: PCDD/Fs, Formation characteristics, Formation pathways, Promotion effect, Influence factors

1 INTRODUCTION

In China, the national domestic sewage sludge (SS) has reached 36 Mt and the industrial sewage sludge has reached 37 Mt in 2020 (Intelligence Research Group, 2022). At present, the SS in China is mainly disposed by landfills, which occupies large number of land and the multiple pollutants such as heavy metals, pathogens and organic pollutants would harm to the surrounding soil and groundwater (Zhan *et al.*, 2014). Co-combustion of SS and coal becomes an alternative method, which can either benefit the efficient reduction of SS (Kuo *et al.*, 2021) or help coal-fired power plants achieve a low-carbon transition (Park *et al.*, 2017).

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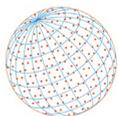
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However, the co-combustion process could increase the emissions of conventional pollutants such as SO₂, NO_x, Hg (Duan *et al.*, 2010; Zhao *et al.*, 2019) and organic pollutants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Chen *et al.*, 2014; Zhang *et al.*, 2019). The formation and emission characteristics of PCDD/Fs in municipal solid waste incinerators (MSWI) and hazardous waste incinerators (HWI) had been well studied (Chen *et al.*, 2020; Qiu *et al.*, 2020), while few studies focused on the co-combustion process of SS and coal. Our previous study reported the formation characteristics of PCDD/Fs under different disposal conditions of SS, including the direct pyrolysis, the direct combustion, and the co-combustion with coal (Rao *et al.*, 2021), wherein the formation content of PCDD/Fs was obviously enhanced by increasing the proportion of SS. However, the formation mechanism of PCDD/Fs in co-combustion process was less revealed, especially the influence factors of catalytic metal compounds, carbon, and chlorine resource.

The generation pathways of PCDD/Fs in combustion systems were mainly ascribed to the homogeneous reaction in high temperature of 500–800°C and the heterogeneous reaction in low temperature of 200–400°C (Stanmore, 2004), and the latter was usually assigned as the major pathway (Altwicker, 1991). Furthermore, the heterogeneous reaction can form PCDD/Fs through de novo synthesis from carbon matrixes or PAHs (McKay, 2002) and precursor synthesis from precursor compounds such as chlorophenols (CPs) and chlorobenzenes (CBz) (Ma *et al.*, 2019). In addition to them, PCDD/Fs can also be generated by the chlorination of dibenzodioxin (DD) or dibenzofuran (DF) (Chen *et al.*, 2018). On the base of the carbon source, the chlorine source and metal catalysts were also essential factors for the heterogeneous formation of PCDD/Fs or their precursors (Zheng *et al.*, 2004). Fujimori and Takaoka found that CuCl₂ and FeCl₃ significantly contributed to the generation of chlorinated aromatic compounds by promoting the formation of organic chlorine (Fujimori and Takaoka, 2009; Fujimori *et al.*, 2010). Moreover, metal oxides, such as CuO, ZnO, MnO₂, TiO₂, and Co₃O₄, also showed positive effects on the PCDD/F formation from precursor PCP (Qian *et al.*, 2005). Fujimori *et al.* (2009) tested eleven metal additives and reported their generative capacity followed by ZnO < PbO < ZnCl₂ < blank < PbCl₂ < Fe₂O₃ < CuO < FeCl₂ · 4H₂O < FeCl₃ · 6H₂O < Cu₂(OH)₃Cl < CuCl₂ · 2H₂O. Zhang *et al.* (2016) reported a promotion sequence as: ZnO < Blank < CdO < NiO < CdCl₂ < Cr₂O₃ < CuO < NiCl₂ < ZnCl₂ < CrCl₃ << CuCl₂. Previous studies were mainly conducted in the waste incineration process. However, the role of key catalytic metals (Cu, Fe, Zn, C, Cl) on the formation of PCDD/Fs and their reaction mechanism during the co-combustion process of SS and coal were insufficient and urgently to be revealed.

In this study, a series of experiments were designed to identify the key influence factors and reveal the formation pathways of PCDD/Fs. The promotion effect of different metal compounds (CuCl₂, FeCl₃, ZnCl₂, CuO, Fe₂O₃, and ZnO) and their influence on the formation pathways of PCDD/Fs were revealed. The results can pave the way for further utilization of SS and operation optimization on the co-combustion of SS and coal to control the PCDD/F formation.

2 MATERIALS AND METHODS

2.1 Materials

This study collected the sewage sludge (SS) from a domestic sewage sludge drying plant (150 t d⁻¹) in Guangdong Province, China. The coal was provided by a coal-fired power plant (2 × 700 MW electric generating units) located in Guangdong Province, China, with plan to achieve full co-combustion of the SS (≤ 10%(w/w)) and coal in future. The moisture content of SS and coal was 51.1% and 18.5%, respectively. The contents of basic elements and trace heavy metal elements were detected and listed in Table 1. The contents of “97.5 wt.% Coal + 2.5 wt.% SS” was obtained by mathematical calculation of the contents of Coal and SS. After adding 2.5 wt.% SS, the proportion of carbon was only slightly decreased, while the proportion of chlorine and metal catalysts was increased. The coal was oven-dried at 105°C for 24 h and milled to particles (≤ 200 μm). The SS was directly mixed with coal samples without drying process. To ensure adequate mixing, the SS, coal, and metal additives were mixed by a micro vortex mixer. CuCl₂, FeCl₃, ZnCl₂, CuO, Fe₂O₃, and ZnO were all of analytical grade (Shanghai Macklin Biochemical Company, China).

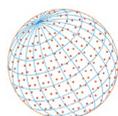


Table 1. Contents of basic elements and heavy metals of SS, coal.

Elements	SS	Coal	97.5 wt.% Coal + 2.5 wt.% SS
Basic elements (%)			
C	13.0	66.7	65.4
Cl	0.60	0.07	0.08
Fe	3.03	0.450	0.510
S	1.01	0.160	0.180
Ca	7.81	0.770	0.950
Trace heavy metal elements (mg kg ⁻¹)			
Hg	17.9	1.11	1.53
Pb	23.0	1.99	2.52
Cd	0.60	0.20	0.21
Cu	150	0.580	4.32
Ni	35.4	7.40	8.10
As	14.4	1.57	1.89
Cr	39.4	10.9	11.6
Zn	193	17.2	21.6

2.2 Experimental Procedures

As shown in Fig. 1, the mixture of coal, SS and the addition were loaded on the quartz boat, then they were thermally treated in the middle of a tube furnace. The experimental conditions were listed in Table 2. To ensure that the samples were fully reacted, the reaction time for each sample was 1 hour.

To avoid the interfere of potential adsorbates, such as PCDD/Fs, other organics, chlorides, and carbon, on the inner surface of the quartz tube, it was heated at 960°C for 15 min under the sweeping of N₂ before each test. Subsequently, the quartz boat loaded with 2.5 g sample was pushed into the center of the quartz tube for 1 h thermal treatment with the reaction atmosphere of air (flow rate of 550 mL min⁻¹). After each test, the XAD-II polymeric resin, toluene absorbent, connecting tubes, and fly ash were collected together as one sample of PCDD/Fs, which would be stored in a cooler below 4°C until further analysis.

2.3 Analytical Methods

The collected samples were treated according to the Environmental Protection Agency method 1613 (U.S. EPA, 1994). Each sample was spiked with 1 ng of ¹³C₁₂-labelled internal standards and then was Soxhlet extracted by 250 mL toluene for 24 h. The following step was using a rotary evaporator to concentrate the Soxhlet extract into 1-2 mL. Then the extract was rinsed by sulfuric acid several times until the color of the solution was visible. After that, the solution was further

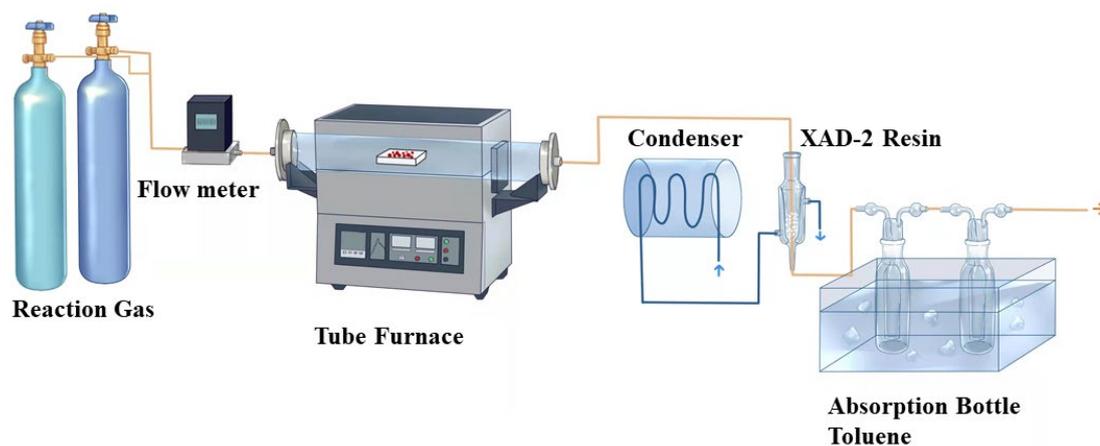
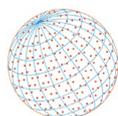


Fig. 1. Schematic diagram of the experiment device.

**Table 2.** Experimental conditions.

Catalytic compounds	Adding amount (g)	2.5% SS + 97.5% Coal (g)	Temperature (°C)	Ambient gas (mL min ⁻¹)
None	0	2.50	960	Air, 550
CuCl ₂	0.05	2.45	960	Air, 550
FeCl ₃	0.05	2.45	960	Air, 550
ZnCl ₂	0.05	2.45	960	Air, 550
CuO	0.05	2.45	960	Air, 550
Fe ₂ O ₃	0.05	2.45	960	Air, 550
ZnO	0.05	2.45	960	Air, 550

cleaned up by a multilayer silica gel column and a basic alumina column. Then the extract was concentrated to 20 µL by nitrogen-blowing and spiked with 1 ng of ¹³C₁₂-labelled recovery standards. Finally, the samples were detected by a high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) (JMS-800D, JEOL, Japan). The recoveries of PCDD/F standards ranged from 26.4% to 113.9%, under the requirements of U.S. EPA 1613 method. The pretreatment process and the analysis methods of the PCDD/Fs samples had been detailed reported in our previous study (Chen *et al.*, 2008).

The elemental compositions of SS and coal were analyzed by X-ray fluorescence spectrometer (XRF, ARL ADVANT'X IntelliPower™ 4200, ThermoFisher Scientific, USA). And the metal content was determined by inductively coupled plasma and mass spectrometry (ICP-MS, Agilent 7700, USA).

2.4 Statistical Analysis

The theoretical numbers of PCDD and PCDF congeners was 136. In this study, only 38 PCDD and 53 PCDF congeners were detected and analyzed, because the peak times of some PCDD/F congeners were quite close and cannot be separated with each other.

The average chlorination degree of PCDD/Fs (d_c) explained the average number of chlorine substituents, which was calculated as follows:

$$d_c = \frac{\sum c_j \times n_j}{c} \quad (j = 4, 5, 6, 7, 8) \quad (1)$$

where C_j mean the content of the different PCDD/Fs homologues, n_j referred to the number of the substituted chlorine in the different PCDD/Fs, and C represented the total content of PCDD/Fs.

The toxic content of PCDD/Fs were calculated based on the international toxic equivalents (I-TEQ) and toxic equivalency factors (I-TEF) (Bhavsar *et al.*, 2008).

$$I-TEQ_{PCDD/F} = \sum_{i=1}^{17} (C_i \times I-TEF_i) \quad (i = 1, 2, \dots, 16, 17) \quad (2)$$

where C_i referred to the content of the 2,3,7,8-substituted congeners, $I-TEF_i$ represented the corresponding toxic equivalence factor.

3 RESULTS AND DISCUSSION

3.1 Promotion on PCDD/F Formation

Fig. 2 illustrated the PCDD/F contents in each experiment. During the co-combustion of SS (2.5 wt.%) and coal (97.5 wt.%), the generated content of PCDD/Fs was 0.51 ng g⁻¹ (0.01 ng I-TEQ g⁻¹), dominated by PCDFs (0.42 ng g⁻¹). The addition of metal chlorides significantly increased both the mass contents of PCDD/Fs and toxic content. In which the CuCl₂ enhanced most on the formation

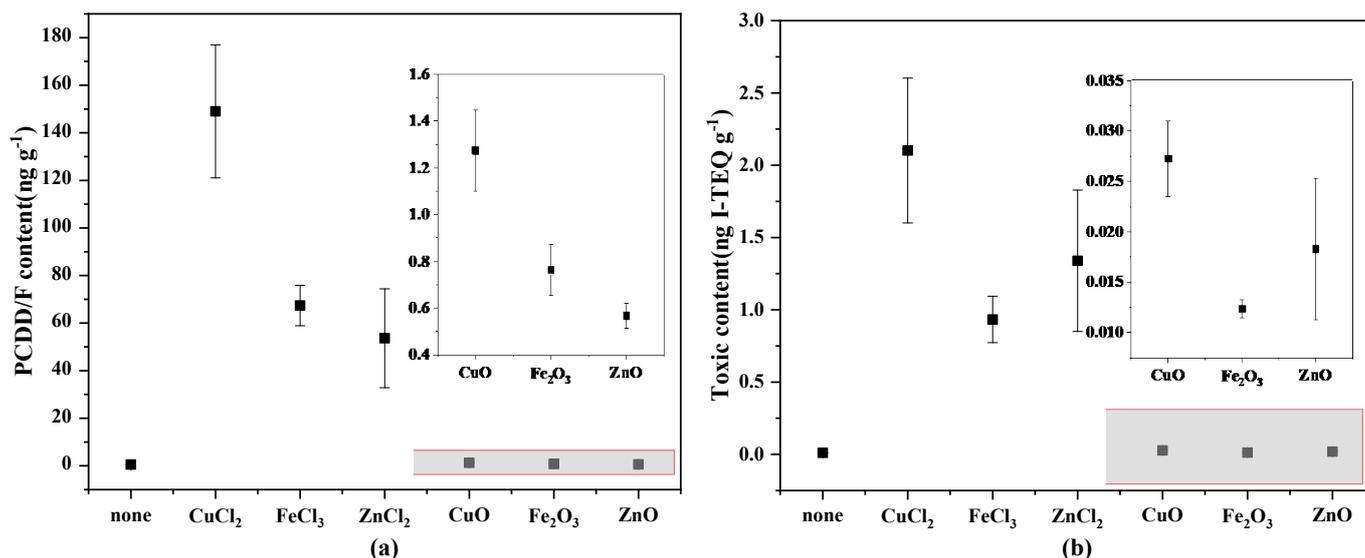
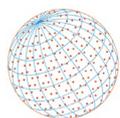


Fig. 2. The promotion effect on the PCDD/F formation by different metal compounds: (a) mass content (ng g⁻¹); (b) toxic content (ng I-TEQ g⁻¹).

of PCDD/Fs. The FeCl₃ and ZnCl₂ seem to have their own selectivity, i.e., FeCl₃ facilitated the increase of mass content, and the ZnCl₂ contributed more to increasing toxic content, which was influenced by the different distribution of homologues and their corresponding I-TEF values. The presence of CuCl₂ increased the PCDD/F content by 292 times and reached 148.99 ng g⁻¹ (2.10 ng I-TEQ g⁻¹). The additional FeCl₃ and ZnCl₂ increased the PCDD/F contents by 132 times (i.e., 67.38 ng g⁻¹, 1.09 ng I-TEQ g⁻¹) and 105 times (i.e., 53.63 ng g⁻¹, 1.34 ng I-TEQ g⁻¹), respectively. To reveal the influence of chlorine in metal catalysts, the catalytic effect of the metal oxides (CuO, Fe₂O₃, and ZnO) was also investigated in this study. Overall, their promotion effect on generating PCDD/Fs was approximately 100-fold lower than their corresponding chlorides. By adding CuO, Fe₂O₃ and ZnO, the formation contents of PCDD/Fs increased to 1.27, 0.76, and 0.57 ng g⁻¹ (0.03, 0.01, and 0.02 ng I-TEQ g⁻¹), respectively. Note that the CuCl₂ was the strongest promoter on generating PCDD/Fs, and FeCl₃ and ZnCl₂ showed the so-called selectivity. Therefore, the promotion effect on increasing the mass content of PCDD/F by six catalytic compounds follow a sequence:

CuCl₂ > FeCl₃ > ZnCl₂ >> CuO > Fe₂O₃ > ZnO.

At the same time, the promotion effect on the I-TEQ content follow a sequence:

CuCl₂ > ZnCl₂ > FeCl₃ >> CuO > ZnO > Fe₂O₃.

Among the six metal additives, CuCl₂ was the most active one, which could be attributed to its catalytic gasification of carbon source and important role on the oxychlorination cycle (Takaoka *et al.*, 2005; Wang *et al.*, 2022). Similarly, FeCl₃ acted the same role but with lower activities, and its major promotion worked on the carbon chlorination by oxychlorination and surface oxygen complexes (Fujimori *et al.*, 2010). ZnCl₂ mainly promotes the formation of PCDD/F precursors (e.g., chlorinated aromatic compounds) (Fujimori *et al.*, 2011). The lower promotion effect of metal oxides on PCDD/F formation could be ascribed to the lack of chlorine source and the lower activity level of oxygen atoms than that of chlorine atoms (Chin *et al.*, 2011). In three metal oxides, CuO showed higher catalytic ability due to the promotion effect on chlorination of aliphatic intermediates and ring formations (Lomnicki and Dellinger, 2003; Qian *et al.*, 2005). Besides, the added CuO would enhance the PCDD/F formation by the synergistic effect of the Fe₂O₃ in SS and/or coal (Liu *et al.*, 2019; Potter *et al.*, 2018). Fe₂O₃ promoted PCDD/F generation by catalyzing the dimerization on the surface of the carbon matrix like CuO (Nganai *et al.*, 2009). Some studies showed that ZnO had suppressive effect on the PCDD/F formation due to the block effect of ZnO on the formation of chlorinated aromatic compounds (Fujimori *et al.*, 2009, 2011; Zhang *et al.*, 2016). However, ZnO showed weak promotion in this study. This may be due to the weak of chlorine source which amplified the promotion of ZnO to generate PCDD/Fs from chlorophenol pathway and diminished the block effect of ZnO.

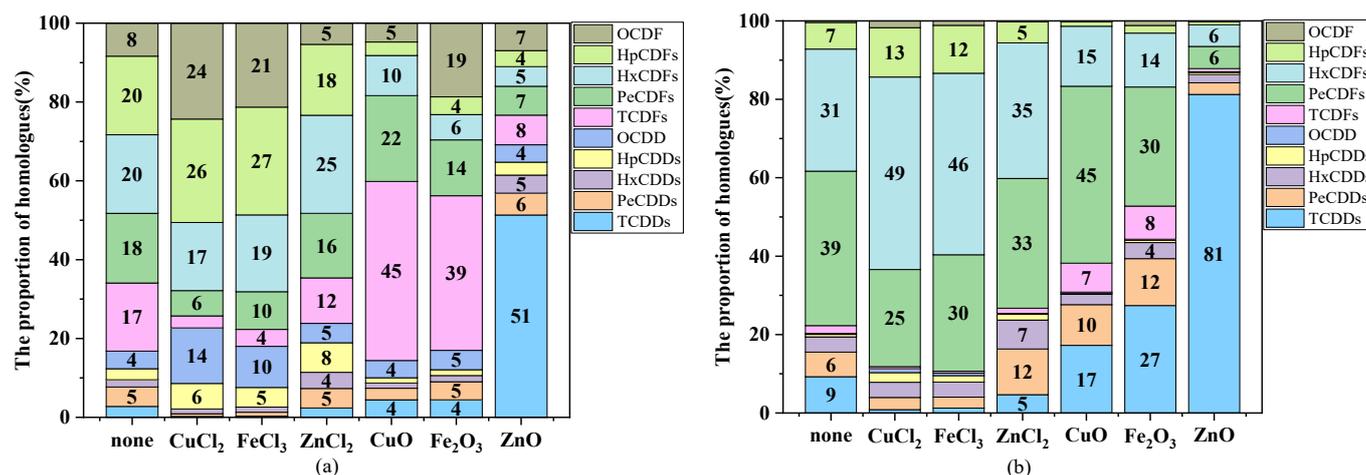
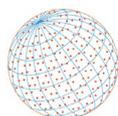


Fig. 3. The proportion distribution of PCDD/F homologues based on (a) mass content and (b) toxic content.

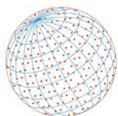
3.2 Influence on PCDD/F Characteristics

The proportion distribution of the PCDD/F homologues profiles was illustrated in Fig. 3. During co-combustion of SS (2.5 wt.%) and coal (97.5 wt.%), the mass content of PCDD/Fs were dominated by PCDFs (83%), especially the TCDFs (17%), PeCDFs (18%), HxCDFs (20%), and HpCDFs (20%) (Fig. 3(a)). The toxic content was also dominated by PCDFs (79%), and the major homologues were PeCDFs (39%) and HxCDFs (31%), resulted from the different I-TEF value of each PCDD/F congener (Fig. 3(b)). The addition of CuCl₂ increased the proportions of higher chlorinated homologues of PCDD/Fs ($d_c \geq 7$), i.e., HpCDFs (26%), OCDF (24%), HpCDDs (6%), and OCDD (14%) based on mass content, as well as the HxCDFs (49%) and HpCDFs (13%) based on toxic content. All of which reflected the obvious chlorination effect of CuCl₂. FeCl₃ showed similar influence on the distribution of PCDD/F homologues. However, its promoting impact on the chlorination of PCDD/F homologues was lower than CuCl₂ according to the chlorination degree of PCDD/Fs in Table 3, i.e., CuCl₂ increased the d_c values from 5.86 to 6.96, while FeCl₃ increased that to 6.76. The addition of ZnCl₂ could have changed the promotion model, which contributes more on the formation of highly chlorinated homologues of PCDDs ($d_c \geq 6$) and the HxCDFs (Fig. 3(a)). And the d_c was as low as 5.97, compared with those of CuCl₂ and FeCl₃ (Table 3), which revealed the weak chlorination effect of ZnCl₂. Based on the I-TEQ content, ZnCl₂ increased a lot on PeCDFs and HxCDD/Fs, resulting in the higher increase of toxic content than FeCl₃ (Fig. 3(b)).

As the comparison, the addition of CuO and Fe₂O₃ significantly increased the generation of TCDFs (from 17% to 45% and 39%, respectively), and the higher chlorinated homologues were less enhanced (Fig. 3(a)), i.e., their d_c even decreased to 4.99 and 5.47, respectively (Table 3). On the one hand, these indicated their weaker chlorination ability compared with their corresponded chlorides; on the other hand, it also proved the essential effect of the chlorine in metal chlorides to the chlorination reaction of PCDD/F homologues. Moreover, the CuO and Fe₂O₃ contributed a lot to I-TEQ contents by increasing the content of PCDD homologues (Fig. 3(b)). For the ZnO, its promotion pathway on PCDD/F formation was different to CuO and Fe₂O₃, and the chlorination effect is even ignorable compared with CuO and Fe₂O₃. It distinctly increased the TCDD proportion from 3% to 51% (Fig. 3(a)), resulting in decreasing its d_c to 5.00 (Table 3). Meanwhile, the proportion of TCDDs achieved as high as 81%, which explain the higher I-TEQ content of PCDD/Fs enhanced by ZnO than Fe₂O₃.

Table 3. PCDD/PCDF ratio and chlorination degrees of PCDDs, PCDFs, and PCDD/Fs.

Addition	None	CuCl ₂	FeCl ₃	ZnCl ₂	CuO	Fe ₂ O ₃	ZnO
PCDD/PCDF	0.20	0.29	0.22	0.31	0.17	0.20	2.38
d_c -PCDDs	6.08	7.48	7.35	6.32	5.88	5.87	4.61
d_c -PCDFs	5.81	6.81	6.63	5.86	4.84	5.39	5.86
d_c -PCDFs	5.86	6.96	6.76	5.97	4.99	5.47	5.00



Overall, the Cu and Fe additives and the Zn additive showed a so-called selectivity on promoting the PCDD/F formation, i.e., the presence of CuCl₂, FeCl₃, CuO, and Fe₂O₃ mainly promoted the formation of PCDFs, while the ZnCl₂ and ZnO mainly contribute to generating PCDDs. In addition, the chlorine source from the metal chlorides (CuCl₂, FeCl₃, and ZnCl₂) were quite essential for the formation of PCDD/Fs, especially the chlorination procedure of PCDD/F homologues.

3.3 The Formation Pathways of PCDD/Fs

3.3.1 *De novo* synthesis

Based on the above analysis, the metal chlorides (CuCl₂ > FeCl₃ > ZnCl₂) distinctly promoted the PCDD/F formation compared with metal oxides. However, it is hard to distinguish the formation and promotion pathways. Usually, the PCDD/PCDF ratio was applied to identify the major formation pathway of PCDD/Fs (Black *et al.*, 2012). As showed in Table 3, the ratios of PCDD to PCDF in original condition is 0.2, which was far lower than 1, i.e., the major formation pathway could be ascribed to the *de novo* synthesis (Ooi and Lu, 2011; Tuppurainen *et al.*, 1998). With the addition of CuCl₂, FeCl₃, ZnCl₂, CuO, and Fe₂O₃, the ratios of PCDD to PCDF fluctuated at 0.20 due to their different promotion effect (Table 3). However, all of which changed nothing on the major formation pathway of *de novo* synthesis. Contrarily, the PCDD/PCDF ratio was increased oppositely to 2.38 after the addition of ZnO, which revealed the major formation pathway could have changed from *de novo* synthesis to precursors pathway.

In the original condition, the *d_c-PCDDs*, *d_c-PCDFs*, and *d_c-PCDD/Fs* were 6.08, 5.81, and 5.86, respectively. After adding the CuCl₂, FeCl₃, and ZnCl₂, the chlorination degrees increased obviously and the higher promotion effect of CuCl₂ and the weaker activities of ZnCl₂ were observed. As the comparison, the *d_c-PCDDs*, *d_c-PCDFs*, and *d_c-PCDD/Fs* decreased after adding CuO and Fe₂O₃, and larger decrease happened on the *d_c-PCDFs* after CuO addition due to its bigger contribution on the TCDFs (Fig. 3(a)). The ZnO distinctly decreased the *d_c-PCDDs* to 4.61 due to the huge increase of TCDD (Fig. 3(a)) and slightly increased the *d_c-PCDFs* to 5.86. ZnO could inhibit the aromatic-Cl formation when Zn dominated other metal elements (Fujimori *et al.*, 2011), which reduced the formation of highly chlorinated PCDD/Fs. ZnO may be able to inhibit *de novo* synthesis or promote precursor synthesis under limited chlorine content. Herein, on the one side, the deferent promotion effect between metal chlorides and metal oxides further confirmed the essential effect of chlorine in metal chlorides; on the other side, the different selectivity between Zn additives and the Cu and Fe additives could be ascribed to the chlorine source as well as the metal characteristics.

3.3.2 Chlorophenol routes

Chlorophenols (CPs), such as 2,4,6-, 2,3,4,6- and 2,3,4,5,6-CPs, were important precursors that could synthesize PCDD/Fs through condensation. There were some characteristic congeners for PCDD/Fs generated by CP-routes, including 1,3,6,8- and 1,3,7,9-TCDD, 1,2,4,6,8-, 1,2,4,7,9-, 1,2,3,6,8- and 1,2,3,7,9-PeCDD, 1,2,3,4,6,8-HxCDD, 1,2,3,8/1,2,3,6/1,4,6,9/1,6,7,8/1,2,3,4/2,3,6,8-TCDF and 2,4,6,8-TCDF (Ryu *et al.*, 2005).

Table 4 summarized the contribution of PCDD/Fs generated by CP-routes within their own homologue groups. The average signal intensity of PCDD/Fs under original condition was 21.3%, 7.25% and 17.7%, respectively for PCDDs, PCDFs, and PCDD/Fs. After adding metal chlorides, the average signal intensity of PCDDs was distinctly impaired (8.46%–8.95%), and that of PCDFs was slightly influenced (6.26%–7.44%). By adding CuO, Fe₂O₃, and ZnO, the CP-route on generating PCDDs gradually came back (12.8% and 22.1%, respectively for CuO and Fe₂O₃) and even became stronger (26.2% for ZnO), but the CP-route on generating PCDFs was still weak or inhibited. Generally, the average signal intensity of PCDD/F decreased with the addition of metal additives except ZnO. The enhancement of chlorophenol pathway by adding ZnO was consistent with literature (Gullett *et al.*, 1992; Qian *et al.*, 2005). To directly compare the contribution of different isomers, the contribution of the above-mentioned PCDD/Fs were standardized (Table 5). In the original co-combustion condition, the isomers that contributed more to the CP-route were 1,3,6,8-, 1,3,7,9-TCDD and 1,2,4,6,8-, 1,2,4,7,9-PeCDD. After adding three metal chlorines, the two highest contributing isomers were 1,2,3,8/1,2,3,6/1,4,6,9/1,6,7,8/1,2,3,4/2,3,6,8-TCDF and 2,4,6,8-TCDF. These results indicated that the CuCl₂, FeCl₃, ZnCl₂, CuO, and Fe₂O₃ promoted the formation of PCDD/Fs by other pathways rather than CP-route, while the ZnO could enhance the

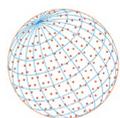


Table 4. The relative importance of CP-route congeners (%).

Congeners	none	CuCl ₂	FeCl ₃	ZnCl ₂	CuO	Fe ₂ O ₃	ZnO
1,3,6,8-TCDD	22.5	5.85	6.42	4.40	12.5	17.4	5.40
1,3,7,9-TCDD	14.1	5.69	5.33	4.81	8.86	13.7	4.77
Sum, % of TCDD	36.6	11.5	11.8	9.21	21.4	31.1	10.2
1,2,4,7,9/1,2,4,6,8-PeCDD	65.2	16.5	17.9	17.3	2.86	33.1	18.3
1,2,3,6,8-PeCDD	5.68	8.00	6.85	7.59	10.8	7.10	14.7
1,2,3,7,9-PeCDD	5.21	9.04	7.85	9.07	24.1	35.4	45.3
Sum, % of PeCDD	76.1	33.6	32.6	34.0	37.7	75.6	78.3
1,2,3,4,6,8-HxCDD	14.6	8.62	8.33	7.57	17.9	25.8	68.5
Average, % of PCDD	21.2	8.95	8.78	8.46	12.8	22.1	26.2
2,4,6,8-TCDF	1.74	3.01	1.82	2.80	1.43	1.44	2.41
1,2,3,8/1,2,3,6/1,4,6,9/1,6,7,8/1,2,3,4/2,3,6,8-TCDF	12.8	11.9	11.6	9.72	8.53	7.22	10.5
Sum, % of TCDF	14.5	14.9	13.5	12.5	9.96	8.66	12.9
Average, % of PCDF	7.25	7.44	6.72	6.26	4.98	4.33	6.46
Average, % of PCDD/F	17.7	8.58	8.26	7.91	10.9	17.7	21.2

Table 5. The relative importance of CP-route congeners after standardization (%).

(%)	none	CuCl ₂	FeCl ₃	ZnCl ₂	CuO	Fe ₂ O ₃	ZnO
1368-TCDD	211	54.9	60.3	41.3	117	164	50.7
1379-TCDD	172	69.6	65.2	58.9	108	167	58.4
12479/12468-PeCDD	267	67.6	73.1	70.8	11.7	135	74.7
12368-PeCDD	65.5	92.3	79.1	87.6	124	81.9	170
12379-PeCDD	26.8	46.5	40.4	46.7	124	182	233
123468-HxCDD	67.7	39.9	38.5	35.0	82.8	119	317
2468-TCDF	83.1	144	86.9	134	68.5	68.7	115
1238/1236/1469/1678/1234/2368-TCDF	124	115	113	94.2	82.6	70.0	102

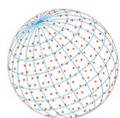
CP-Route by promoting the formation of higher chlorinated congeners (1,2,3,7,9-PeCDD and 1,2,3,4,6,8-HxCDD) rather than the 1,3,6,8-TCDD and 1,3,7,9-TCDD.

3.3.2 Chlorination routes

The PCDD/F chlorination was reported to follow an order of 2 → 8 → 3 → 7 → 1 → 4 → 6 → 9 (Luijk *et al.*, 1992; Wehrmeier *et al.*, 1998). The 2,3,7,8-substituted congeners based on the Hagenmaier profile were summarized in Table 6. The average signal intensity of 2,3,7,8-substituted PCDD/Fs increased significantly when CuCl₂ or FeCl₃ was added. It indicated that the addition of CuCl₂ and FeCl₃ could promote the chlorination pathway of PCDD/Fs, and the CuCl₂ showed higher chlorination effect, which corresponded to above findings. However, the average signal intensity of ZnCl₂ was extremely close to that of original condition, indicating that ZnCl₂ promoted the formation of PCDD/Fs by other pathway (i.e., *de novo* synthesis) and its low activity on the chlorination pathway could be ascribed to the weak oxychlorination cycle. The CuO and Fe₂O₃ slightly increased the contribution of chlorination pathway to PCDD, while the ZnO showed ignorable activity or even inhibition effect on the PCDD/F chlorination. Hence, the chlorination pathway of DD/F was not the major promotion route of ZnCl₂, CuO, Fe₂O₃, and ZnO, while CuCl₂ and FeCl₃ showed the obvious contribution on this chlorination pathway.

3.3.3 Correlation analysis

To better reveal the emission and influence factors of PCDD/Fs in the co-combustion process, this study analyzed the relationship among the total content, homologues signal intensity, chlorination degree of PCDD/Fs, contents of catalytic metals, carbon, and chlorine of seven samples (Fig. 4(a)). The variance explained by Factor 1 was 60.60%. The carbon was away from other factors, which indicated the carbon source was adequate for generating PCDD/Fs in the study, highly corresponded to the fuel properties of SS and coal. Chlorine source and isomers of PCDD/Fs (especially TCDD

**Table 6.** Hagenmaier profile of 17 2,3,7,8-PCDD/Fs isomers (%).

Congeners	none	CuCl ₂	FeCl ₃	ZnCl ₂	CuO	Fe ₂ O ₃	ZnO
2,3,7,8-TCDD	7.10	5.22	6.46	4.93	8.30	9.99	5.00
1,2,3,7,8-PeCDD	5.39	12.9	8.87	11.7	15.2	8.45	3.42
1,2,3,4,7,8-HxCDD	14.7	12.7	14.1	12.3	13.2	12.1	2.81
1,2,3,6,7,8-HxCDD	15.7	16.8	16.4	15.7	14.8	14.5	4.88
1,2,3,7,8,9-HxCDD	14.6	15.7	16.3	17.3	14.2	15.4	6.75
1,2,3,4,6,7,8-HpCDD	50.7	53.7	52.9	49.7	56.4	60.1	54.1
OCDD	26.6	62.1	58.0	20.6	30.4	29.0	6.38
PCDD average	19.3	25.6	24.7	18.9	21.8	21.4	11.9
2,3,7,8-TCDF	2.48	2.37	1.69	2.87	3.48	3.48	3.43
1,2,3,7,8-PeCDF	4.32	2.69	2.74	5.51	8.17	9.65	6.48
2,3,4,7,8-PeCDF	9.03	10.7	9.58	9.54	8.06	5.99	4.22
1,2,3,4,7,8-HxCDF	6.98	5.94	7.15	9.98	11.1	12.5	11.1
1,2,3,6,7,8-HxCDF	8.25	8.66	8.84	11.2	12.2	12.4	9.53
2,3,4,6,7,8-HxCDF	13.9	21.0	4.42	11.3	7.62	7.66	10.4
1,2,3,7,8,9-HxCDF	3.98	4.53	17.3	2.17	1.23	2.07	4.10
1,2,3,4,6,7,8-HpCDF	66.7	59.9	64.1	68.3	61.8	58.9	50.6
1,2,3,4,7,8,9-HpCDF	5.62	7.92	6.63	6.42	8.55	11.6	10.4
OCDF	10.1	31.5	22.0	7.06	5.58	22.5	21.6
PCDF average	13.1	15.5	14.4	13.4	12.8	14.7	13.2
PCDD/F average	15.7	19.7	18.7	15.7	16.5	17.4	12.7

and PeCDD) gathered in one cluster, which confirmed the chlorine source as an important factor for promoting PCDD/Fs synthesis. The poor correlation between TCDD, PeCDD and chlorine could attribute to the contribution of CP-route on their synthesis. Fig. 4(b) illustrated the influence of metal oxides. Zn bordered on TCDD, and Fe was close to OCDF. Cu had a stronger correlation with many isomers of PCDD/Fs than Fe, Zn, which was consistent with the promotion effect of CuO, Fe₂O₃, and ZnO on PCDD/F formation (Fig. 2). Note that the C and Cl were overlapped with each other due to their same source of SS and coal. Fig. 4(c) illustrated the impact of metal chlorides. Cu still had a close relationship with chlorination degree and many congeners, corresponding to the excellent promotion effect of CuCl₂. Fe also distributed to the same cluster with Cu. However, Zn was in the left higher cluster and was close to HxCDD and HxCDF but in different cluster with PCDD/F content. Note that the C and Cl were no longer overlapped and were far away with each other, indicating the chlorine source was different with metal oxides addition and the PCDD/F formation preferred the chlorine from metal chlorides.

Overall, the de novo synthesis should be the major formation pathway of PCDD/Fs in the co-combustion process. Only ZnO showed the promotion effect on the CP-route. The CuCl₂ and FeCl₃ also enhanced the chlorination routes to generate PCDD/Fs. The chlorine source was an essential limiting factor for generating PCDD/Fs, and the Cl from metal chlorides was the preference source compared with that contained in SS and coal.

4 CONCLUSIONS

In this study, series of experiments were conducted to reveal the formation pathways of PCDD/Fs during the co-combustion of SS and coal, as well as identify the key influence factors, such as the catalytic metals (CuCl₂, FeCl₃, ZnCl₂, CuO, Fe₂O₃, and ZnO), sources of carbon and chlorine.

The metal chlorides (2.0% CuCl₂, FeCl₃, and ZnCl₂) significantly increased the formation content of PCDD/Fs from 0.51 ng g⁻¹ (0.01 ng I-TEQ g⁻¹) to 148.99, 67.38, and 53.63 ng g⁻¹ (i.e., 2.10, 1.09, and 1.34 ng I-TEQ g⁻¹), respectively, while the metal oxides (2.0% CuO, Fe₂O₃, ZnO) only slightly increased the PCDD/F contents to 1.27, 0.76, and 0.57 ng g⁻¹ (0.03, 0.01, and 0.02 ng I-TEQ g⁻¹), respectively.

The sequence of different metal additives on increasing the mass content of PCDD/Fs followed:

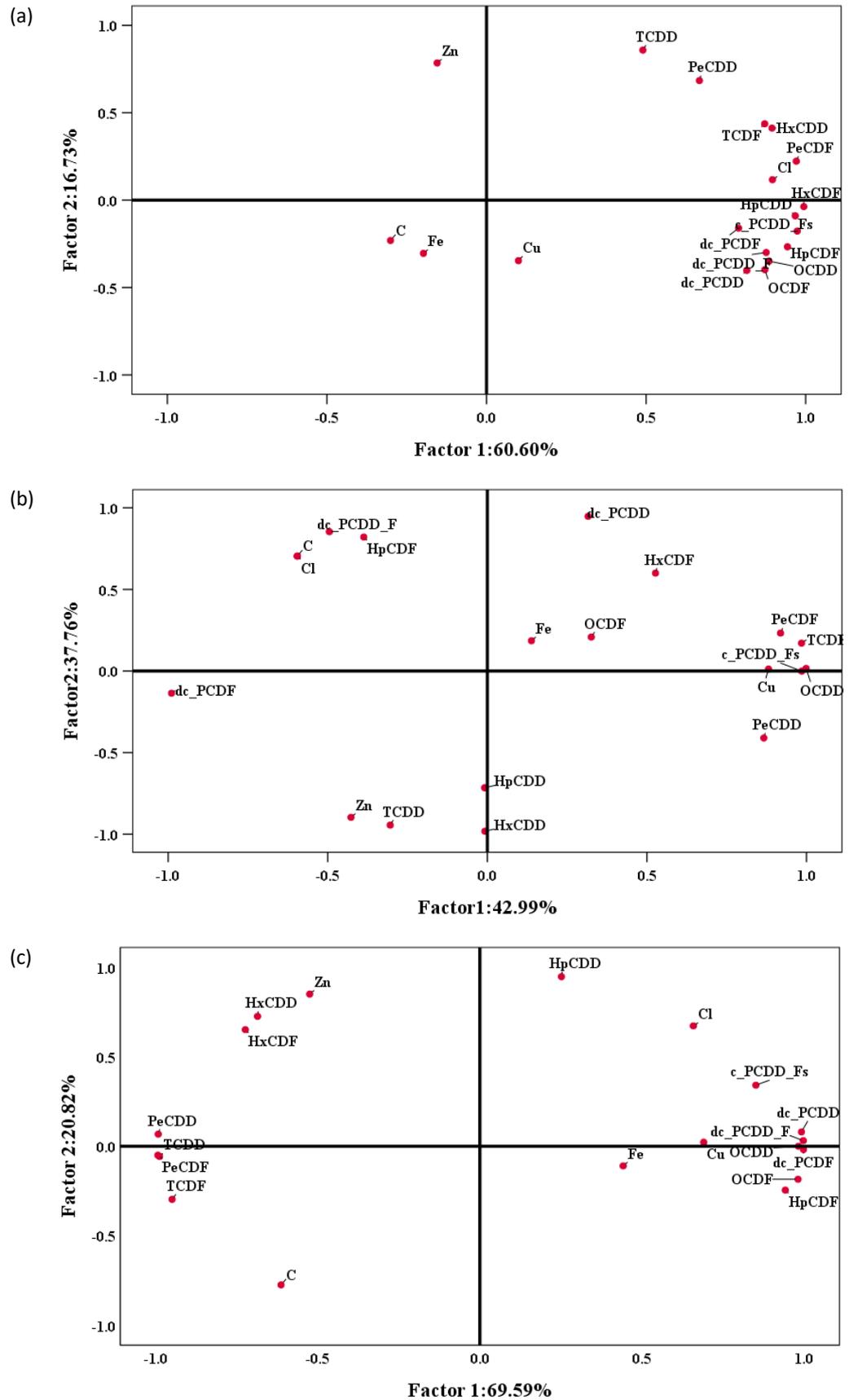
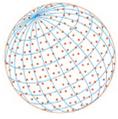
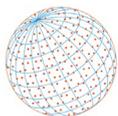


Fig. 4. Principal component analysis results of PCDD/F characteristics and key elements: (a) metal oxides and chlorides; (b) metal oxides; (c) metal chlorides.



CuCl_2 (292 \times) > FeCl_3 (132 \times) > ZnCl_2 (105 \times) \gg CuO (2.5 \times) > Fe_2O_3 (1.5 \times) > ZnO (1.1 \times), wherein the metal chlorides showed 2 orders of magnitude higher promotion than that of metal oxides.

The de novo synthesis should be the major formation pathway of PCDD/Fs except for adding ZnO. Only ZnO showed the promotion effect on the CP-route. The CuCl_2 and FeCl_3 can also enhance the chlorination routes to generate PCDD/Fs.

The chlorine source was an essential limiting factor for generating PCDD/Fs, and the chlorine from metal chlorides was the preference source compared with that contained in SS and coal.

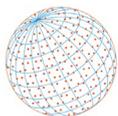
The results are helpful to further optimize co-combustion of SS and coal through controlling the PCDD/F emission from co-combustion process.

ACKNOWLEDGEMENT

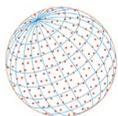
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