Environmental Science and Pollution Research (2023) 30:5903–5916
https://doi.org/10.1007/s11356-022-22437-7

RESEARCH ARTICLE

Influence of different kinds of incinerators on PCDD/Fs: a case study of emission and formation pathway

Yuxuan Ying[1] · Liang Xu[2] · Xiaoqing Lin[1] · Hao Zhang[1] · Xiaodong Li[1] · Shengyong Lu[1] · Yang Cao[3] · Jisheng Long[3]

Received: 29 May 2022 / Accepted: 3 August 2022 / Published online: 19 August 2022

Abstract

Few studies focused on the emission of polychlorinated-ρ-dibenzodioxins and dibenzofurans (PCDD/F) from different kinds of waste incinerators. This study was conducted in a full-scale MSW incineration plant to investigate the influence of different incinerator types on PCDD/F. Experimental results indicated that the 2,3,7,8-PCDD/F concentration in the inlet gas of the air pollution control system (APCS) in the studied fluidized bed was higher (2.03 ng I-TEQ/Nm^3) than that of the grate (0.77 ng I-TEQ/Nm^3). But gas in the outlet of APCS from both incinerators had an approximate concentration, lower than the Chinese emission limit of 0.1 ng I-TEQ/Nm^3. Similar distribution patterns were observed for 2,3,7,8-PCDD/Fs, as well as 136 PCDD/F congeners. Specifically, OCDD and 1,2,3,4,6,7,8-HpCDD were major isomer constituents for 2,3,7,8-PCDD/F isomers. In terms of formation pathways, a similar formation mechanism was observed based on fingerprint characteristics of 136 PCDD/F congeners. De novo synthesis was the dominating formation pathway for both incinerators. Meanwhile, DD/DF chlorination was another contributor to PCDD/F formation, which in the fluidized bed was higher. In addition, little correlation ($0.009 < R^2 < 0.533$) between conventional pollutants (HCl, CO, PM) and PCDD/Fs was found, suggesting little high-temperature synthesis observed and verifying the dominance of de novo synthesis.

Keywords MSW incineration · Grate · Fluidized bed · PCDD/Fs · Emission characteristic · Formation pathway

Nomenclature

APCS	Air pollution control system
CBz	Chlorobenzene
CP	Chlorophenol
DD	Dibenzodioxin
DF	Dibenzofuran
EA	Emission amount
EF	Emission factor
FA	Fly ash
FB	Fluidized-bed type incinerator
GBI	Exhaust gas sampled from the inlet of bag filters
GCH	Exhaust gas sampled from the chimney, which is also after the outlet of bag filters
GI	Grate type incinerator
PCDD/Fs	Polychlorinated dibenzo-*p*-dioxins and dibenzofurans
PM	Particulate matter
I-TEF	International toxic equivalency factor
I-TEQ	International toxic equivalency quantity

Introduction

For the past decade, municipal solid waste (MSW) outputs have sustained growth in China, with an annual increase of 3.31% (Cheng et al. 2020). The amount of MSW clean-up reached 235 million tons/year in 2020 (NBS 2021), posing potential threats to the ecological environment. Correspondingly, by the end of 2020, the disposal capacity of MSW incineration leaped to 467.8 thousand tons/day, accounting for 58.93% of overall MSW treatment (NBS 2021). Until 2020, among 1202 installed MSW

Responsible Editor: Constantini Samara

✉ Xiaoqing Lin
linxiaoqing@zju.edu.cn

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

[2] Tianjin Eco-Environmental Monitoring Center, Tianjin Ecology and Environment Bureau, Tianjin 300192, China

[3] Shanghai SUS Environment Co., Ltd., Shanghai 201703, China

incinerators in China, the grate incinerators occupied 84%, with the rest of the incinerators being fluidized beds (NBS and MEEPRC 2021). The scope and quantity of MSW incineration plants are gaining momentum. Nevertheless, this trend requires a particular emphasis on the environmental criteria, especially for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Xia et al. 2022). The complicated MSW components contain higher chlorine, heavy metals, and lower sulfur contents than coal powder, leading to higher pollutant source strength of PCDD/Fs, 17 isomers of which are highly toxic and carcinogenic (Wielgosiński 2011).

PCDD/Fs, generated from incineration facilities primarily, was mainly produced through low-temperature heterogeneous synthesis and high-temperature homogeneous synthesis (Huang and Buekens 1995, 1996; Shaub and Tsang 1983). The factors of PCDD/F formation included raw materials, furnace temperature, key formation catalysts, and combustion modes (Lenoir et al. 1991; Ma et al. 2020; Wang et al. 2007; Zhang et al. 2008). Specifically, the mechanisms as well as effects of chemical inhibition (Ruokojärvi et al. 2004; Ruokojärvi et al. 1998), physical absorption (Atkinson et al. 2015; Hajizadeh et al. 2011) in both lab and full-scale tests, and removal effects of air pollution control systems (APCS) (Lin et al. 2020) have been well investigated. Furthermore, the characteristics of exhaust gas and fly ash from MSW incinerators for a certain type (fluidized bed or moving grate) have been widely explored. The concentration and distribution of PCDD/Fs have been examined extensively in prior literature (Chang et al. 2011; Qiu et al. 2020). However, different incinerator types may affect the formation and amounts of PCDD/Fs (Freire et al. 2015). The influence of varying incinerator types (especially in the same plant) on PCDD/F emission and formation is relatively underexplored.

Previous studies have delved into PCDD/F generation from these two types of MSW incinerators, respectively. For example, Ma et al. studied the PCDD/F emission of MSW grate incinerator under oxygen-enriched conditions, which revealed a highly growing trend (Ma et al. 2019). Meanwhile, concentrations of 2,3,7,8-PCDD/Fs emitted in exhaust gas from several MSW incineration plants were synthetically presented, and finite differences in PCDD/F I-TEQ concentration were observed (Ni et al. 2009; Zhu et al. 2018). Different factors such as MSW composition and operation of facilities also remarkably influence PCDD/F emission levels in MSW incineration plants in regions (Ma et al. 2020).

Affected by disparities in furnace structure and incineration techniques, fluidized bed incinerators combust the MSW completely with continuous higher temperature and fluidization of mixed solid-gas, as grate incinerators usually have a larger capacity and generate less fly ash (Bourtsalas et al. 2020; Leckner and Lind 2020). Different incinerators also lead to different amounts of the conventional pollutants such as HCl and heavy metals, which may be relevant to the PCDD/F formation (Buekens and Huang 1998). Nonetheless, previous studies (Li et al. 2015; Lu et al. 2012; Zhang et al. 2012) mainly discussed the concentration and fingerprint of 2,3,7,8-PCDD/Fs in the gas/solid phase. To date, the formation mechanism of PCDD/F was seldom elaborated. Integrated congener analysis of tetra- through octa-chlorinated dibenzo-p-dioxins and dibenzofuran (136 PCDD/Fs) was little discussed for incinerators of different types. Additionally, few researchers studied the correlation between conventional pollutants and PCDD/Fs emitted from fluidized bed and grate incinerators sharing the same MSW, which could be closely related to the incinerator types' influence on the PCDD/Fs.

This study explored the emission of conventional pollutants in the exhaust gas from two types of incinerators. Also, mass/I-TEQ concentrations, emission amounts/factors, and fingerprints of 2,3,7,8-substituted PCDD/Fs in the gas and fly ash from the two incinerators were estimated and comprehensively analyzed, respectively. Moreover, the homologue distribution of 136 integral PCDD/F congeners was also investigated in different incinerator-type scenarios, which showed finite differences. To a certain extent, these findings verified the incinerator types' influence on PCDD/F distribution and formation. Consequently, the formation pathway of PCDD/Fs was analyzed and demonstrated, firstly revealing that de novo synthesis was dominant in different-typed incinerators with DD/DF chlorination. In addition, the analysis on the correlation of HCl, CO, and particulate matter (PM) with 136 PCDD/F congeners was also conducted. The results suggested that there was little correlation between conventional pollutants and PCDD/Fs in both incinerators.

Materials and methods

Profile of MSW power plant

Two incinerator systems of fluidized bed and mechanical grate in the same MSW incineration plant located in Zhejiang Province in southeastern China were selected to conduct the study. As is shown in Table 1, though equipped with different types of incinerators, two incinerator subsystems differed slightly in the key parameters of operation, sharing the same waste storage house, where MSW was fermented and homogenized for 3–5 days. Likewise, APCS facilities (shown in Fig. 1a and b) after fluidized bed and grate incinerators were

Table 1 Basic parameters of the incineration system

Parameter index	Incinerator #1	Incinerator #2
Type of incinerator	Fluidized bed	Grate
MSW capacity (t/day)	400	500
Actual steam rate (t/h)	40	45
Furnace outlet temperature (°C)	880	1080
O_2 in furnace outlet (%)	9–10	5–6
O_2 in chimney (%)	13–14	9–10
Gas flow of air blower (Nm^3/h)	140,000	110,000
Annual operation time (h)	7680	8160
Exhaust gas cleaning facilities	SNCR + semi-dry deacidification + active carbon + bag filter	SNCR + semi-dry deacidification + active carbon + bag filter

semblable, following "MSW→incinerator→SNCR denitration→semidry deacidification→active carbon→bag filter→chimney", which cleaned up and cooled down the primary flue gas. Moreover, the studied incinerators shared the feeding MSW in the same pool, which was collected in a certain area of the nearby city.

Sample collection

We sampled exhaust gas and fly ash in the fluidized bed and grate incineration systems in the same period under regular operation, respectively. Before the sampling process, the PCDD/F surrogate standards were added into the XAD-2 resin to check the sampling efficiency. Then effluent exhaust gas samples were parallelly extracted by the exhaust gas sampler in the inlet and outlet of APCS, for 1 h at each sampling time. Under the guidance of U.S.EPA. Method 23 (Table S1-2), the PCDD/F samples for inspection were extracted by an exhaust gas sampler (M5, KNJ Engineering, Japan) and exhaust gas analyzer (DX-4000, Gasmet, Finland). Also, a smoke tester (3012H, Laoying, China) was adopted for the measurement of conventional pollutants.

Specifically, as is shown in Fig. 1, a number of (6+6) PCDD/F gas samples (fluidized bed+grate, same as below) before the bag filter inlets, (8+6) PCDD/F gas samples in the chimney, (4+4) gas samples of conventional pollutants in the chimney, and (3+2) fly ash samples from the bag filters were extracted. In terms of gas samples of PCDD/Fs, liquid of eluents was collected in a brown glass bottle over the same period, while the gas and solid phases of PCDD/Fs were absorbed in the XAD-2 resin and filter, separately. The estimated PCDD/F concentration for each gas sample would be the sum of PCDD/F concentrations in three phases. After the sampling process, all samples were stored in a cooler below 4 °C for further analysis.

Analysis

Pre-treatment and analysis of PCDD/F samples were consistent with our previous studies (Chen et al. 2008), following the U.S. EPA Method 1613B. Each sample was spiked with 1 ng of $^{13}C_{12}$ mass-labeled standards, and then Soxhlet extracted by 250 mL toluene (solid sample for PCDD/Fs of gas and solid phases) or liquid-liquid extracted (liquid sample for PCDD/Fs of liquid phase) for 24 h. Then a

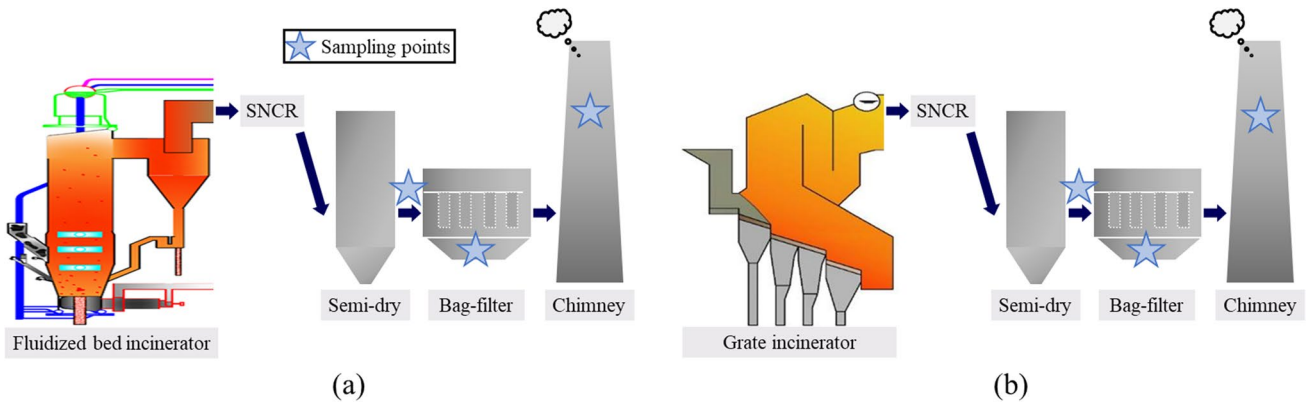

Fig. 1 Schematic diagram of sample points for the fluidized bed and grate incinerators

rotary evaporator concentrated the Soxhlet extract to 1–2 mL. Subsequently, $^{37}Cl_4$-labeled clean-up standard was added into the extract, and then sulfuric acid was used to wash the concentrated extract several times until the solution color turned visible. The washed extract was further cleaned up by means of a multilayer silica gel column and a basic-alumina column. After clean-up procedures, the extract was concentrated to 20 µL with nitrogen and then spiked with 1 ng of $^{13}C_{12}$-labeled internal standards prior to analysis. The index of recovery standards is presented in Table S3 in Supplementary Material. All solvents for pre-treatment were purchased from Mallinckrodt Baker Inc., USA, and were of pesticide residue analysis grade.

After the pre-treatment procedures, the PCDD/Fs in the samples were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (GC/MS, JMS-800D, JEOL, Japan) with a DB-5MS column. Table S4 (Supplementary Material) presented detailed instrumental parameters and procedures of GC/MS. The target compounds were all 136 tetra- to octa-chlorinated dibenzo-p-dioxins and dibenzofuran congeners (136 PCDD/Fs), including the 17 kinds of 2,3,7,8-substituted PCDD/F and as far as separated individually — all congeners from homologue classed TCDD through OCDF. Concentrations of 136 PCDD/Fs were estimated based on the recovery standards, as each chlorinated homologue group has at least one set of standard. The recovery rates of the PCDD/Fs were estimated by $^{13}C_{12}$-PCDD/F surrogates and ranged from 58.4 to 109.7%, satisfying corresponding requirements (EPA 1994; MEP 2008). Following this, NATO/CCMS factors were used for the calculation of international toxic equivalents (I-TEQ). All calculated concentrations of PCDD/Fs and conventional pollutants were normalized to 11% O_2, 273.15 K, and 100 kPa (GB 18485-2014).

MSW characteristics

Studied incinerators of the grate and fluidized bed incinerators shared the same MSW repository, ensuring similar chemical characteristics for the two incinerators to the largest extent. As is shown in Table 2, the industrial and ultimate analysis of MSW was conducted, which was sampled before transporting into the incinerator, under the guidance of corresponding regulations (CJ/T 313-2009). The characteristics of feeding MSW between two incinerators were similar throughout the sampling period. Due to the stacking treatment in the waste repository, the moisture content (36.63%) was lower than raw MSW (usually 40–70%), primarily improving the combustion condition in the furnace with the low heating value of 8114 kJ (Zhou et al. 2014).

Table 2 Composition analysis for MSW (average value) in the incinerator plant

Analysis	Testing index	MSW	Units
Industrial analysis	Moisture	36.63 ± 5.12	%
	Ash	22.03 ± 4.75	%
	Volatile	36.56 ± 7.11	%
	Fixed carbon	4.78 ± 2.36	%
Ultimate analysis	C_{ar}	30.20 ± 4.79	%
	H_{ar}	5.47 ± 1.67	%
	N_{ar}	1.29 ± 0.75	%
	S_{ar}	0.53 ± 0.28	%
	O_{ar}	14.50 ± 3.47	%
	Cl_{ar}	0.97 ± 0.42	%
Low heating value		8114 ± 1677	kJ/kg

*ar—as received basis

Statistical and correlation analyses

The statistical analysis was performed by Dq Editor (JEOL DioK V4.01), and Microsoft Excel (Microsoft). When calculating the general average of data sets, non-detected compounds of PCDD/Fs were treated as the mean value between zero and the detection limit (MEP 2008). To quantitatively illustrate pollutant emission for the fluidized bed and grate incinerator systems, the emission factor (EF) and emission amount (EA) of the conventional pollutants in the emitted exhaust gas were calculated as Eqs. (1) and (2):

$$\text{Emission factor}\left(\text{EF, g/ton}_{\text{MSW}}\right) = [\text{concentration in fluegas}\left(\text{mg/Nm}^3\right) \times \text{fluegasflowrate}\left(\text{Nm}^3\text{/h}\right)]/\left[\textit{capacity level}\left(\text{ton}_{\text{MSW}}\text{/h}\right)\right]/10^3 \quad (1)$$

$$\textit{Emission amounts}(\text{EA, g/year}) = \left[\textit{emission factor}\left(\text{g/ton}_{\text{MSW}}\right)\right] \times \left[\textit{annual MSW treatment amount}\ \left(\text{ton}_{\text{MSW}}\text{/year}\right)\right]/10^6 \quad (2)$$

$$\textit{Flue gas flowrate}\ \text{at standard condition}\left(\text{Nm}^3\text{/h}\right) = \textit{estimated flue gas flowrate}\left(\text{m}^3\text{/h}\right) \times (1 - \textit{moisture}) \frac{0+273.15(\text{K})}{\textit{flue gas temperature (K)}} \frac{(21 - \textit{base oxygen content}\ @\ \text{standard condition})}{(21 - \textit{estimated oxygen content})} \quad (3)$$

Similarly, the EF and EA of the PCDD/Fs in the cleaned exhaust gas from the fluidized bed and grate incinerators were calculated as Eqs. (4) and (5):

$$\text{Emission factor}\left(\text{EF, }\mu\text{g/ton}_{\text{MSW}}\right) = \left[\textit{concentration in flue gas}\left(\text{ng/Nm}^3\right) \times \textit{flue gas flowrate}\left(\text{Nm}^3\text{/h}\right)\right] / \left[\textit{capacity level}\left(\text{ton}_{\text{MSW}}\text{/h}\right)/10^3\right] \quad (4)$$

$$\textit{Emission amounts}(\text{EA, g/year}) = \left[\textit{emission factor}\left(\mu\text{g/ton}_{\text{MSW}}\right)\right] \times \left[\textit{annual MSW treatment amount}\left(\text{ton}_{\text{MSW}}\text{/year}\right)\right]/10^6 \quad (5)$$

Results and discussion

Emission characteristics of conventional pollutants and PCDD/Fs

Conventional pollutants in the exhaust gas

As is indicated in Table 3, the mass concentrations of conventional air pollutants of the two incinerators, including PM, CO, SO_2, NO_x, HCl, Hg, Cd+Ti, As-Ni, were respectively estimated for fluidized bed and grate incinerators, which all satisfied the emission limit of national standard GB18485-2014. Specifically, concentrations of PM, CO, SO_2, and heavy metal for the fluidized bed and grate incinerators were in similar manner, which were 1.58 ± 0.36 and 1.12 ± 0.13 mg/Nm^3 for PM, 12.69 ± 0.85 and 1.00 ± 0.13 mg/Nm^3 for CO, 9.75 ± 1.20 and 4.47 ± 0.86 mg/Nm^3 for SO_2, 139.20 ± 16.87 and 220.00 ± 71.09 for NO_x, 0.0075 ± 0.0011 and 0.044 ± 0.010 μg/Nm^3 for Hg, 0.00131 ± 0.00039 and 0.00713 ± 0.00159 μg/Nm^3 for Cd+Ti, and 0.00376 ± 0.00098 and 0.00166 ± 0.00030 mg/Nm^3 for As-Ni. Nonetheless, the HCl concentration of the grate incinerator was 30.78 ± 7.12 mg/Nm^3, 7 times higher than that of the fluidized bed. Higher furnace temperatures led to thermal NO_x formation and gaseous HCl volatilization, which further generated higher concentrations of NO_x and HCl (Jančauskas and Buinevičius 2020; Matsuda et al. 2005). Moreover, the emission was well-controlled with the implementation of SNCR, semidry desulfurization, and bag filter.

As is shown in Table 4, the emission factors (EF) and emission amounts (EA) were correspondingly calculated based on the key operational parameters in Table 1. The grate incinerator showed a finite difference in EF and EA pattern with the fluidized bed but accumulated higher EF_{GI} and EA_{GI} of HCl, reaching 217.84 ± 50.37 g/ton$_{MSW}$ and 1742.68 ± 402.96 kg/year, respectively. Moreover, it was noteworthy that the EA of NO_x for fluidized bed and grate incinerator reached 6772.79 ± 820.94 kg/year and 12455.82 ± 4025.76 kg/year, a relatively high level than the others, which should arouse the attention during daily operation.

Toxic 2,3,7,8-PCDD/Fs in the exhaust gas and fly ash

The estimated concentrations of 2,3,7,8-PCDD/Fs (Table S5) for fluidized bed and grate incinerators are shown in Tables 5 and 6 and Fig. 2, respectively. As Fig. 2a suggested, 2,3,7,8-PCDD/Fs in the exhaust gas of the grate incinerator before

Table 3 Mean concentrations of conventional pollutants in exhaust gas from FB and GI

	FB	GI	
PM	1.58 ± 0.36	1.12 ± 0.13	mg/Nm^3
SO_2	9.75 ± 1.20	4.47 ± 0.86	mg/Nm^3
NOx	139.20 ± 16.87	220.00 ± 71.09	mg/Nm^3
HCl	4.12 ± 0.22	30.78 ± 7.12	mg/Nm^3
CO	12.69 ± 0.85	1.00 ± 0.13	mg/Nm^3
Hg	(7.5 ± 1.1) × 10^{-6}	(4.4 ± 1.0) × 10^{-6}	mg/Nm^3
Cd + Ti	(1.3 ± 0.04) × 10^{-6}	(7.1 ± 1.6) × 10^{-6}	mg/Nm^3
Sb + As + Pb + Cr +Co+Cu+Mn+Ni	0.0038 ± 0.010	0.0017 ± 0.0003	mg/Nm^3

Table 4 Calculated emission factors and emission amounts of conventional pollutants

	PM	CO	HCl	SO_2	NO_x	Hg	Cd, Ti	As-Ni
EF_{FB} ± stand. dev.(g/ton$_{MSW}$)	10.24 ± 2.37	8.23 ± 0.55	26.73 ± 1.42	63.26 ± 7.79	903.0 ± 109.5	(4.85 ± 0.70) × 10^{-5}	(8.5 ± 2.5) × 10^{-6}	0.02439 ± 0.00633
EF_{GI} ± stand. dev.(g/ton$_{MSW}$)	7.93 ± 0.91	7.08 ± 0.93	217.84 ± 50.37	31.60 ± 6.06	1557.34 ± 502.80	(3.1 ± 0.7) × 10^{-4}	(5.0 ± 1.1) × 10^{-5}	0.01174 ± 0.00209
EA_{FB} ± stand. dev. (kg/year)	76.78 ± 17.75	61.73 ± 4.14	200.46 ± 10.65	474.4 ± 58.4	6772.79 ± 820.94	(3.6 ± 0.5) × 10^{-4}	(6.4 ± 1.9) × 10^{-5}	0.1829 ± 0.0475
EA_{GI} ± stand. dev.(kg/year)	63.47 ± 7.24	56.61 ± 7.48	1742.68 ± 402.96	252.80 ± 48.50	12,455.82 ± 4025.76	0.002491 ± 0.000591	(4.0 ± 0.9) × 10^{-4}	0.0940 ± 0.0167

*As-Ni: As+Sb+Pb+Cr+Co +Cu+Mn+Ni

the bag filter inlet (GBI) were observably higher than that of the fluidized bed. More specifically, the mass concentrations of PCDD/Fs in GBI for fluidized bed and grate incinerators were 14.94 ± 12.99 and 2.31 ± 0.83 ng/Nm^3 (PCDDs), 33.96 ± 22.43 and 7.28 ± 2.75 ng/Nm^3 (PCDFs), and 48.90 ± 35.18 and 9.59 ± 3.58 ng/Nm^3 (PCDD/Fs), respectively. On the I-TEQ level, the concentrations of PCDD/Fs in GBI for fluidized bed and grate incinerators were 2.03 ± 1.09 and 0.77 ± 0.13 ng I-TEQ/Nm^3 (PCDD/Fs), respectively. This phenomenon was possibly due to unburned MSW falling into boiler ash in the grate, while circulating the fluidized bed combusting the waste thoroughly, leading to increment of PCDD/Fs in the boiler outlet (Behnisch et al. 2002; Lu et al. 2012). The source strength of PCDD/Fs in gas from the fluidized bed was 5.1 times higher than the grate incinerator, while the I-TEQ concentration of gas from the grate incinerator was similarly 2.6 times higher. However, 2,3,7,8-PCDD/F homologue analysis was still restricted by 17 kinds of isomers, indicating that comprehensive analysis of more PCDD/F homologues was needed. Moreover, the chlorination degree of PCDD/Fs was calculated (Tables 5 and 6), revealing that 2,3,7,8-PCDD/F in the GBI of the fluidized bed had a chlorination degree of 7.016 compared to 6.452 of the grate, implying a lower proportion of TCDD and PeCDD.

$$Cl_d = \frac{\sum c_j \times n_j}{C} (j = 4, 5, 6, 7, 8)$$

where C_j stands for the concentration of each 2,3,7,8-substituted PCDD/Fs, n_j stands for chlorine atom number of each 2,3,7,8-substituted PCDD/Fs; C stands for the total concentration of PCDD/Fs

Exhaust gas from the chimney (GCH) was cleaned after bag filter, as major organic trace pollutants like 2,3,7,8-PCDD/Fs were adsorbed into agglomeration, forming fly ash in the flue or fabric bag. According to Tables 5 and 6 and Fig. 2, there was limited distinction between the two incinerators in exhaust gas from GCH, which was consistent with previous studies (Chi et al. 2005; Wang et al. 2017). The PCDD/F removal efficiencies of the bag filter for fluidized bed and grate incinerators were 97.86% and 97.50%, respectively, proving the marginal effect of absorption (Giugliano et al. 2002). As the fluidized bed generated more fly ash (40–45 t/day) containing carbon particulate (You 2008), the PCDD/F concentration in the fluidized bed was slightly higher than that of the grate incinerator, reaching 1.668 ± 0.224 ng/g, which was still within the range of 0.034–2.5 ng/g for fly ash from MSW incinerators in China (Chang et al. 2011; Pan et al. 2013). The possible reason was that exhaust gas in FB and GI were both selectively adsorbed by sprayed activated carbon in the bag filter, due to higher vapor pressure of high chlorinated PCDDs. Similarly, the I-TEQ concentrations of 2,3,7,8-PCDD/Fs in GBI and FA from the fluidized bed were higher than in the grate incinerator, which could attribute to the grate incinerator's lower furnace temperature (880–950 °C) and columnar grate structure, leading to less low temperature heterogeneous catalytic synthesis of unburned carbon in the cooling region, as potential precursors of PCDD/F went with unburned bottom ash below grate (Huang and Buekens 1995).

The emission characteristics of MSW incinerators in China were influenced by a variety of factors, including operation, exhaust gas cleaning equipment, MSW characteristics, and EF usually ranged from 0.03 to 10.72 μg I-TEQ/ton$_{MSW}$ (average 1.728 μg I-TEQ/ton$_{MSW}$) (Everaert and Baeyens 2001; Ni et al. 2009). In recent years, research has revealed the emission characteristics of 2,3,7,8-toxic PCDD/Fs for fluidized bed and grate incinerators, which are located in different cities. Due to the variation of MSW in a vast spatial scale, the EF of grate incinerators was 0.03–0.42 μg I-TEQ/ton$_{MSW}$, while the

Table 5 Mean concentrations, emission factors, and emission amounts of 2,3,7,8-PCDD/Fs in the GBI, GCH, and FA of fluidized bad incinerator

	GBI	GCH		FA	
∑PCDDs	14.94	0.591	ng/Nm^3	0.717	ng/g
∑PCDFs	33.96	0.451		0.951	
∑PCDD/Fs	48.90	1.042		1.668	
I-TEQ	2.031	0.051	ng I-TEQ/Nm^3	0.058	ng I-TEQ/g
PCDDs/PCDFs	0.440	1.310		0.753	
Cl-PCDD	7.413	7.383		7.522	Chlorination degree
Cl-PCDF	6.844	6.915		6.531	
Cl-PCDD/F	7.016	7.005		7.192	
EF ± stand. dev. of PCDD/Fs	-	6.761 ± 3.155	μg/ton$_{MSW}$	-	
EA ± stand. dev. of PCDD/Fs	-	0.051 ± 0.024	g/year	-	
EF ± stand. dev. of I-TEQ	-	0.329 ± 0.199	μg I-TEQ/ton$_{MSW}$	-	
EA ± stand. dev. of I-TEQ	-	2.468 ± 1.493	mg I-TEQ/year	-	

*Chlorination degree of PCDD/Fs was calculated as follows:

Table 6 Mean concentrations, emission factors, and emission amounts of 2,3,7,8-PCDD/Fs in the GBI, GCH, and FA of grate incinerator

	GBI	GCH		FA	
∑PCDDs	2.308	1.285	ng/Nm^3	0.320	ng/g
∑PCDFs	7.282	0.628		1.118	
∑PCDD/Fs	9.589	1.914		1.438	
I-TEQ	0.770	0.050	ng I-TEQ/Nm^3	0.048	ng I-TEQ/g
PCDDs/PCDFs	0.317	2.046		0.286	
Cl-PCDD	7.000	7.600		7.573	Chlorination degree
Cl-PCDF	6.277	6.732		7.112	
Cl-PCDD/F	6.452	7.306		7.215	
EF ± stand. dev. of PCDD/Fs	-	13.543 ±5.518	μg/ton$_{MSW}$	-	
EA ± stand. dev. of PCDD/Fs	-	0.108 ±0.044	g/year	-	
EF ± stand. dev. of I-TEQ	-	0.353 ±0.084	μg I-TEQ/ton$_{MSW}$	-	
EA ± stand. dev. of I-TEQ	-	2.826 ±0.672	mg I-TEQ/year	-	

EF of fluidized bed incinerators was 0.12–0.38 μg I-TEQ/ton$_{MSW}$ (Qiu et al. 2020; Zhu et al. 2018). In the studied MSWI plant, emission factors of the two incinerators were consistent with the previous research, reaching 0.329 ± 0.199 μg I-TEQ/ton$_{MSW}$ for the fluidized bed incinerator and 0.353 ± 0.084 μg I-TEQ/ton$_{MSW}$ for the grate incinerator, respectively. As Fig. 2b shows, all the emitted PCDD/F concentrations of the two incinerators met the limitation values of national standards, which were 0.1 ng I-TEQ/Nm^3 (exhaust gas) and 3 ng I-TEQ/Nm^3 (limit value for fly ash into burial ground).

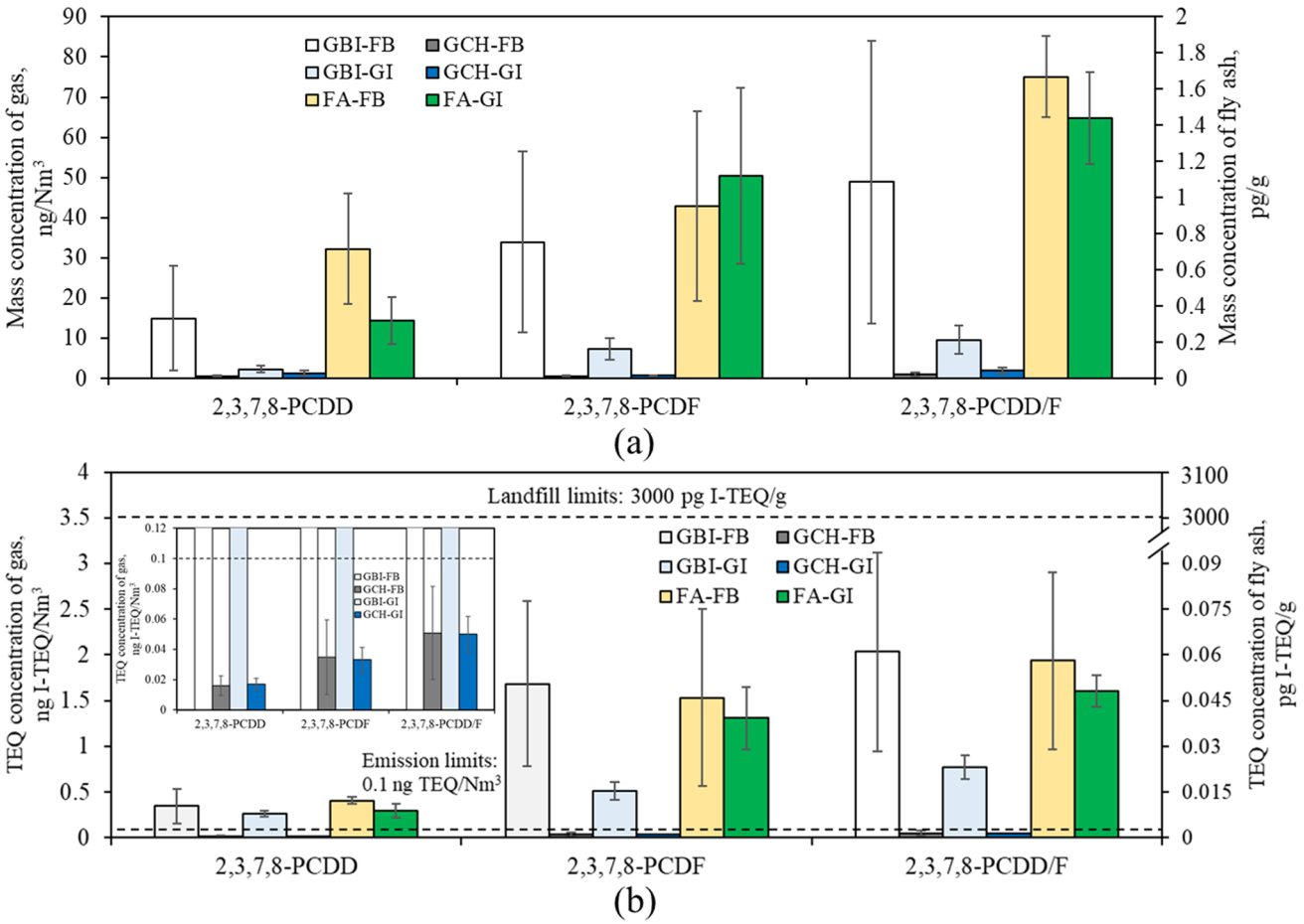

Fig. 2 Mass concentration and I-TEQ concentration of PCDD/Fs in the GBI, GCH, and FA from the fluidized bed and grate incinerator systems

Distribution of PCDD/F homologues

Isomer distribution of 2,3,7,8-PCDD/Fs

The distribution of 2,3,7,8-PCDD/Fs of fluidized bed and grate incinerators is presented in Fig. 3. For toxic PCDD isomers on the mass concentration level, OCDD and 1,2,3,4,6,7,8-HpCDD were dominant, accounting for 18.96% and 8.21% of PCDD/Fs in GBI-FB, 29.05% and 19.30% in GCH-FB, 12.30% and 5.12% in GBI-GI, 47.28% and 15.50% in GCH-GI, 27.55% and 11.76% in FA-FB, and 15.57% and 4.67% in FA-GI, respectively. The results were consistent with prior studies about toxic PCDD/F isomer distribution of MSWI (Chi et al. 2005; Zhang et al. 2018b). The possible reason was the high level of chlorination reaction that occurred in the incinerator, as well as similar representative isomers of PCDD/Fs formed from de novo synthesis of carbon and potential precursor synthesis (Li et al. 2019; Tuppurainen et al. 1998). For toxic PCDF isomers, 1,2,3,4,6,7,8-HpCDF and OCDF of GBI and GCH in the incinerators accounted for the most proportion for 6.94–22.43% on a mass concentration, while the figure for these isomers of FA was 17.03–36.22%, respectively. Compared to the gas phase, 2,3,7,8-PCDD/F in fly ash contained a higher fraction of OCDD and OCDF, indicating that high-chlorinated dioxins were more easily adsorbed by particles and removed by bag filter due to higher saturated vapor pressure (Lin et al. 2008).

Following this, 2,3,7,8-PCDD/Fs concentrations on the I-TEQ level showed different distributions due to varying toxic equivalent factors. 2,3,4,7,8-PeCDF accounted for the highest proportion, reaching 29.04% for GBI-FB, 29.57% for GCH-FB, 25.39% for GBI-GI, 21.47% for GCH-GI, 26.51% for FA-FB, and 21.42% for FA-GI, respectively. Meanwhile, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, and 2,3,4,6,7,8-HxCDF also contributed much to the overall I-TEQ concentrations of PCDD/Fs in the solid and gas phases for both incinerators, ranging from 7.05 to 14.37%. Although the two incinerators were characterized by distinct furnace structures and technical features, the distribution patterns of generated 2,3,7,8-PCDD/Fs in the gas and solid phase were semblable. However, the homologue distributions for 2,3,7,8-PCDD/Fs failed to qualify for deeper analysis.

Isomer distribution of tetra- through octa-chlorinated dibenzo-p-dioxins and dibenzofuran congeners

It is well known that 75 of PCDDs and 135 of PCDFs are composed of all PCDD/Fs congeners. One hundred thirty-six

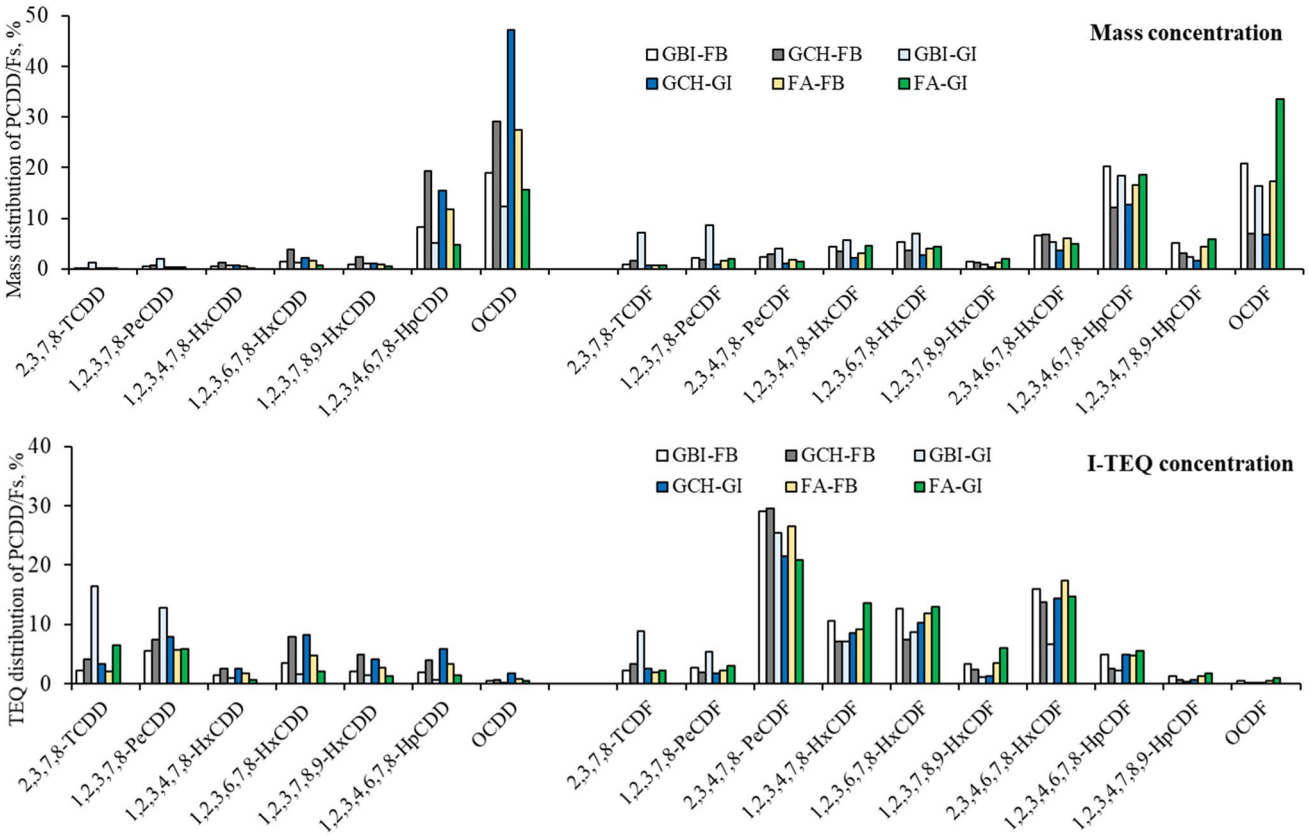

Fig. 3 2,3,7,8-PCDD/F congener distribution (%) in GBI, GCH, and FA for fluidized bed and grate incinerator systems

kinds of tetra- through octa-chlorinated dibenzo-p-dioxins and dibenzofuran congeners (136 PCDD/Fs; Table S6) were representative among all isomers, including 17 kinds of toxic 2,3,7,8-PCDD/F isomers. During the incineration process, Cl in MSW formed toxic and nontoxic PCDD/F isomers simultaneously (Ryu et al. 2004). However, current EU and China's national standards only set emission limits for the toxic equivalent concentration of 2,3,7,8-PCDD/Fs. Meanwhile, researchers were more inclined to investigate the signatures on 2,3,7,8-substituted PCDD/Fs with little focus on the nontoxic ones. Though 2,3,7,8-PCDD/Fs contributed to all of the toxic equivalents, they only occupied a small proportion (Zhang et al. 2018a). Thus, it was necessary to analyze the distribution patterns of PCDD/F homologs to verify the incinerator's influence on the formation pathway of PCDD/Fs.

As is shown in Fig. 4, the fingerprint and distribution characteristics of 136 PCDD/F (P = 4–8) isomers in GBI, GCH, and FA from fluidized bed and grate incinerators were indicated for different clusters, respectively. The isomer distribution represented the ratio of a certain PCDD/F isomer and its corresponding sum homologue. For TCDDs, 1,3,6,8-TCDD and 1,3,7,9-TCDD were the major contributors on the mass concentration level, reaching 16.62–68.39% (1,3,6,8-TCDD) and 10.21–25.30% (1,3,7,9-TCDD) of GBI and GCH, 30.99–47.63% (1,3,6,8-TCDD) and 18.43–21.04% (1,3,7,9-TCDD) of FA, respectively. In terms of the other isomers, 1,2,4,6,8/1,2,4,7,9- and 1,2,3,6,8-PeCDDs, 1,2,3,4,6,8-HxCDD, 1,2,4,6/1,2,4,7/1,3,4,6/1,3,4,7/1,3,4,8-, 1,2,3,7/1,3,6,9-, 2,3,6,7/3,4,6,7-, and 1,2,3,4/1,2,3,6/1,2,3,8/1,4,6,9/1,6,7,8/2,3,6,8-TCDFs, 1,2,4,6,7/1,3,4,6,7/1,3,6,7,8-, 1,2,3,6,8/1,2,4,7,8/1,3,4,7,8-, 1,2,3,4,6- and 1,2,3,6,9/2,3,4,6,7-PeCDFs, 1,2,4,6,7,8/1,3,4,6,7,8- and 1,2,3,6,8,9/2,3,4,6,7,8-HxCDF, and 1,2,3,4,6,7,8-HpCDF occupied most, respectively. In summary, homologue profiles composed of 136 PCDD/F isomers from two different kinds of incinerators were surprisingly similar, indicating proximate potential formation pathways (Zhang et al. 2018b; Zhang et al. 2016). Still, more detailed analysis should be conducted on the discrimination of formation path.

Formation pathway of PCDD/Fs

De novo synthesis or CP route synthesis

The major formation pathway for PCDD/Fs in MSW incineration was generally heterogeneous catalytic synthesis at low temperature (more than 80%), including de novo synthesis and precursor synthesis, and gaseous synthesis at high temperature (Olie et al. 1998). The conditions (Table 1) in the fluidized bed and grate incinerators both satisfied the 3T principle (temperature >850 °C, time >2 s, and turbulence), which reduced the PCDD/F formation in the high-temperature stage to the utmost extent. PCDDs were mostly generated through the condensation or rearrangement of precursors, such as chlorophenol (CP) (Chen et al. 2018). Meanwhile, PCDFs were mainly formed by three pathways: de novo synthesis, chlorination of dibenzofurans (DF), and condensation of a CP and chlorobenzene (CBz) (Luijk et al. 1994; Olie et al. 1998; Zhang et al. 2016).

Previous scholars mostly centered on 2,3,7,8-PCDD/Fs and their fingerprints, which was not representative enough to conduct formation pathway analysis (Zhang et al. 2018a; Zhang et al. 2017). As is shown in Table S7 (Supplementary Material), the integrated mass concentrations of PCDDs, PCDFs, and PCDD/Fs and the ratio of PCDD/PCDF for 136 PCDD/F isomers were presented, respectively. Even though a similar distribution pattern for original PCDD/Fs was obtained in GBI for fluidized bed and grate incinerators, the mass concentrations showed a remarkable gap. The 136 PCDD/F concentrations of GBI-FB and GBI-GI were 135.68 ng/Nm^3 and 46.51 ng/Nm^3, respectively, which suggested the grate incinerator generating more PCDD/Fs in the exhaust gas possibly due to relatively lower furnace temperature, resulting in higher carbon and chlorine contents in the fly ash, and thus activating more potential PCDD/F formation (i.e., low-temperature heterogeneous catalytic synthesis) in the exhaust gas cooling stage (Chen et al. 2020; Zhang et al. 2018c). Also, the PCDD/F concentrations in the exhaust gas after the bag filter were similarly low, which were 5.876 ng/Nm^3 (GCH-FB) and 10.992 ng/Nm^3 (GCH-GI), respectively, which suggested the effective removal of PCDD/F absorption by activated carbon injection coupled with the bag-filter facility. At the same time, the PCDD/F concentration in fly ash from fluidized bed (FA-FB) was slightly higher (4.166 ng/Nm^3) than that in the grate incinerator (2.775 ng/Nm^3), possibly due to more generated fly ash amount in the fluidized bed adsorbing more PCDD/Fs.

Precursor rearrangement formed most PCDDs (mostly CP route in MSW incineration), together with a very small fraction of de novo synthesis and dibenzodioxin (DD) chlorination (Lomnicki and Dellinger 2003; Nganai et al. 2014). Accordingly, the ratios of PCDD and PCDF were calculated to verify the formation pathway in the incinerators (Luijk et al. 1994; Ryu et al. 2006). Specifically, the PCDD/PCDF ratios of 136 isomers for GBI-FB, GBI-GI, FA-FB, and FA-GI were 0.321, 0.176, 0.300, and 0.252, respectively. This indicated that precursor synthesis (e.g., CP route) was not dominant, yet synthesis accounted for the most proportion in the fluidized bed and grate incinerators sharing the same MSW and operation (Shaub and Tsang 1983; Zhang et al. 2016). Previous researchers (Huang and Buekens 1995; Nganai et al. 2014) already reported that CP was the major source of PCDD in the MSW incineration system, generating 1,3,6,8-, 1,3,7,9-TCDD, 1,2,3,6,8-, 1,2,3,7,9-, 1,2,4,6,8-, 1,2,4,7,9-PeCDD, and 1,2,3,4,6,8-HxCDD of tetra- through octa-PCDDs. Therefore, analysis

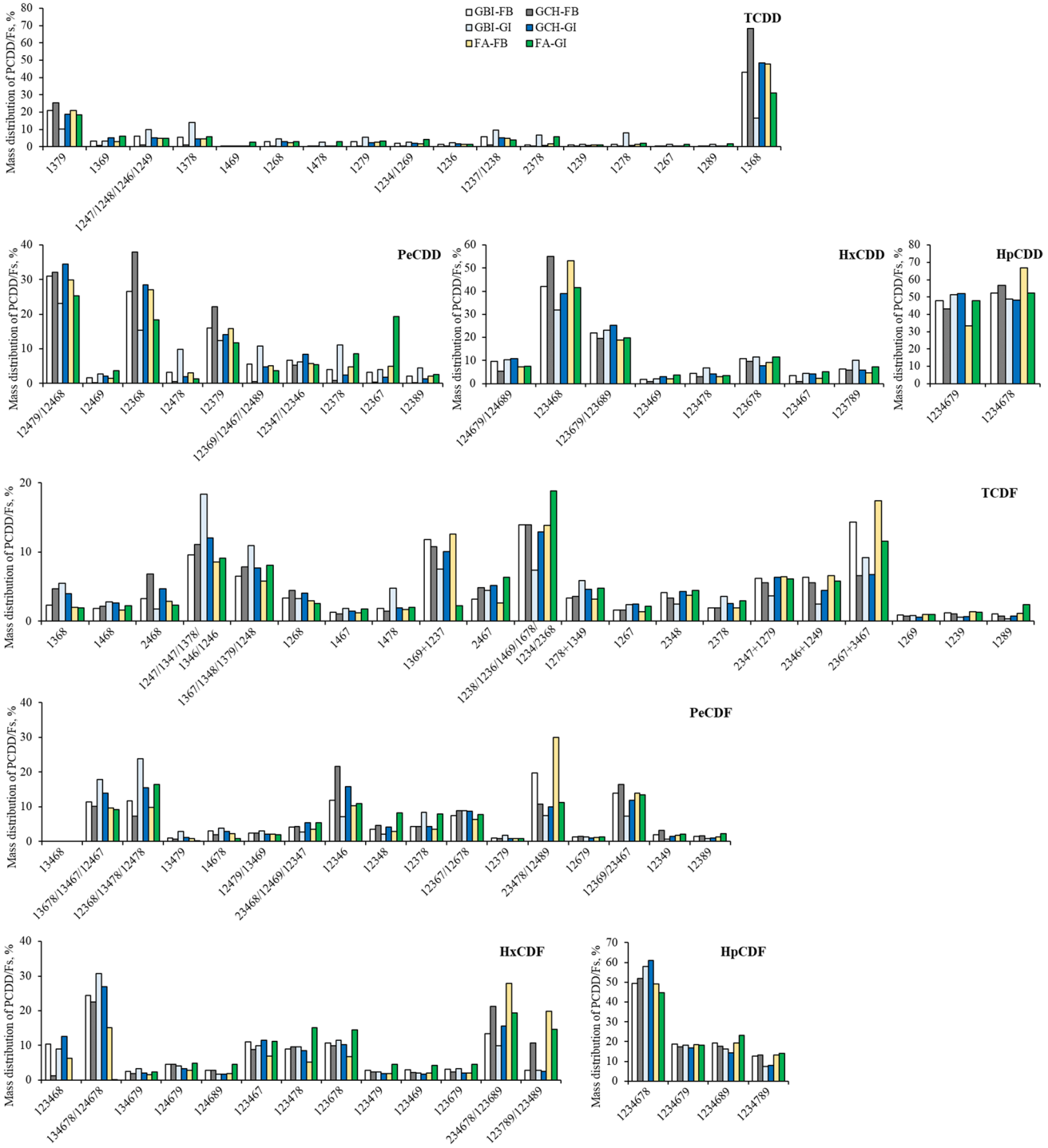

Fig. 4 Congener profiles of the mean percentages of the PCDD/Fs in exhaust gas and fly ash samples from the two incinerators

on the correlation for corresponding PCDD/F isomers was conducted to provide supportive evidence. According to Table S8-9, the mutual R^2 between 1,3,7,9-, 1,3,6,8-TCDD, 1,2,4,7,9-/1,2,4,6,8-PeCDD, and 1,2,3,4,6,8-HxCDD with other PCDDs were mostly ranging from 0.9 to 1 for both fluidized bed and grate incinerator, indicating that the above isomers formed together with other PCDDs, and CP route synthesis was not the dominant precursor. Furthermore, it has been reported that 1,2,3,4/1,2,3,6/1,2,3,8/1,4,6,9/1,6,7,8/2,3,6,8- and 2,4,6,8-TCDF were only identified precursor-synthesis-derived PCDFs, firmly supporting the CP route (Ryu et al. 2006). Therefore, the correlation

was analyzed between the above-specified homologues and other PCDF congeners (Table S10 in Supplementary Material). Specifically, the R^2 for 2,4,6,8-TCDD and 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 in fluidized bed and grate incinerator were 0.9998 and 0.9198, respectively. However, the R^2 of two isomers and remained PCDFs in 136 PCDD/Fs were mostly ranging from 0.7951 to 0.9974 for both incinerators, indicating the common formation pathway of de novo synthesis for most PCDDs, and excluding CP route synthesis for the main position.

Chlorination of dibenzodioxin and dibenzofuran

In terms of the chlorinated level evaluation of dibenzodioxin (DD) and dibenzofuran (DF), Table 7 shows the signal intensity of 2,3,7,8-PCDD/F congeners (i.e., Hagenmaier distribution). Generally, the sequence of 2→8→3→7→1→4→6→9 was followed by DD/DF chlorination, which was competitive with the CP route (Chen et al. 2018). The values of the Hagenmaier distribution indicated the formation tendency of the toxic isomers in their homologs. The Hagenmaier values of PCDD, PCDF, and PCDD/F in fluidized bed (grate incinerator) were 45.346 (33.098) of PCDD, 33.059 (20.665) of PCDF, 36.043 (20.616) of PCDD/F in GBI, 64.596 (57.218) of 2,3,7,8-PCDD, 59.021 (50.447) of PCDF, and 62.493 (51.811) of PCDD/F in FA, respectively, indicating that both DD and DF chlorination existed in fluidized bed and grate incinerator. However, the values of 2,3,7,8-PCDD/F from GBI in fluidized bed increased compared to the grate incinerator, indicating a higher fraction of DD and DF chlorination reaction in overall formation.

Correlation analysis

We carried out an analysis on the correlation to verify the potential interaction between conventional pollutants and tetra- through octa-chlorinated dibenzo-*p*-dioxins and dibenzofuran congeners for different kinds of incinerators. Among the conventional pollutants, CO, HCl, and PM were possibly related to PCDD/F formation. HCl formation and evaporation interacted with the gaseous synthesis of PCDD/F in the particulate surface, and the CO concentration acted as the indicator of incineration status, which could potentially point to the PCDD/F formation (Ying et al. 2021). Therefore, the Pearson correlation coefficient (R) between variables X (x_1, x_2, …, x_n, i.e., 136 PCDD/Fs of GCH) and Y (y_1, y_2, …, y_n, i.e., conventional pollutants of GCH) was calculated as follows:

$$R = \frac{n\left(\sum_{i=1}^{n} X_i y_i\right) - \left(\sum_{i=1}^{n} X_i\right)\left(\sum_{i=1}^{n} y_i\right)}{\sqrt{\left[n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2\right]\left[n\sum_{i=1}^{n} y_i^2 - \left(\sum_{i=1}^{n} y_i\right)^2\right]}} \quad (6)$$

Table 7 Hagenmaier profiles of the 17 toxic PCDD/F isomers for two fluidized bed and grate incinerator systems

2,3,7,8-PCDD/Fs	GBI-FB	GCH-FB	GBI-GI	GCH-GI	FA-FB	FA-GI
2,3,7,8-TCDD	1.200	0.126	6.625	0.685	1.647	5.969
1,2,3,7,8-PeCDD	3.981	0.772	11.105	2.503	4.807	8.592
1,2,3,4,7,8-HxCDD	4.291	3.091	6.787	0.185	2.882	3.466
1,2,3,6,7,8-HxCDD	10.779	9.515	11.602	0.587	9.123	11.584
1,2,3,7,8,9-HxCDD	6.275	5.879	10.076	0.293	4.561	7.300
1,2,3,4,6,7,8-HpCDD	52.272	56.765	48.747	48.143	66.670	52.267
OCDD	28.139	8.195	16.918	10.009	47.827	40.040
Average of PCDD	45.346	16.002	33.098	14.218	64.596	57.218
2,3,7,8-TCDF	1.949	1.942	3.562	2.532	1.917	2.958
1,2,3,7,8-PeCDF	4.251	2.994	8.385	4.253	3.444	7.954
2,3,4,7,8- PeCDF	4.655	4.741	3.932	5.084	4.047	5.630
1,2,3,4,7,8-HxCDF	8.931	9.540	9.502	8.441	5.176	15.166
1,2,3,6,7,8-HxCDF	10.619	9.964	11.522	10.133	6.674	14.479
1,2,3,7,8,9-HxCDF	2.802	3.261	1.408	1.255	1.969	6.763
2,3,4,6,7,8-HxCDF	13.414	18.670	8.812	14.093	9.801	16.328
1,2,3,4,6,7,8-HpCDF	49.294	51.915	57.982	61.013	48.978	44.730
1,2,3,4,7,8,9-HpCDF	12.558	13.090	7.441	7.906	13.196	14.057
OCDF	9.910	3.315	3.958	6.629	9.040	21.728
Average of PCDF	33.059	20.665	18.415	32.183	59.021	50.447
Average of PCDD/F	36.043	17.734	20.616	17.409	62.493	51.811

$$*Hagenmaier\ values = \frac{2,3,7,8\text{–}substituted\ PCDD/F\ (e.g.2,3,7,8\text{–}TCDD)}{\sum Corresponding\ PCDD/F\ isomer\ (e.g.\sum TCDDs)} \times 100\%$$

As is shown in Table S11, mutual R^2 between HCl, CO, PM, and 136 PCDD/F isomer concentrations from GCH in two incinerators ranged from 0.001 to 0.625, some of which were even below 0.300. Only 1,4,6,9-, and 1,2,8,9-TCDD may be relevant to the HCl in the fluidized bed, with the R^2 of 0.844 and 0.850. Likewise, 1,4,7,8-TCDD and 1,2,6,7,9-PeCDF may be relevant to CO in the grate incinerator, with R^2 of 0.880 and 0.816, respectively. Meanwhile, the p values between HCl (CO, PM) and PCDD, PCDF, and PCDD/Fs were 0.0322 (0.0278, 0.0512), 0.0218 (0.0444, 0.0161), and 0.0445 (0.0491, 0.0521), respectively, indicating remarkable differences between the data sets, which verified the effectiveness of data.

Following this, the R^2 between HCl (CO, PM) and PCDDs, PCDFs, and PCDD/Fs were 0.419 (0.269, 0.226) with PCDDs, 0.427 (0.268, 0.235) with PCDFs, 0.425 (0.268, 0.533) with PCDD/Fs in the fluidized bed, 0.186 (0.196, 0.055) with PCDDs, 0.113 (0.009, 0.009) with PCDFs, and 0.165 (0.101, 0.035) with PCDD/Fs in the grate incinerator, suggesting little correlation between conventional pollutants and PCDD/F formation. The possible reason was that de novo synthesis was the dominant formation pathway for both incinerators, which usually occurred on fly ash surfaces in the temperature range of 200–400 °C (Stieglitz et al. 1989). PCDD/Fs were mostly polymerized by C, H, O, and Cl elements through Cu, Fe, and other metal elements as catalysts in fly ash (Altwicker 1996). Thus, the PCDD/F formation with little high-temperature synthesis was not significantly influenced by HCl of low source intensity.

Conclusion

This study comprehensively analyzed pollutants, especially PCDD/Fs, for the fluidized bed and grate incinerator with the same MSW. Specifically, the emission evaluation of conventional pollutants, emission characteristic, and formation pathway of PCDD/Fs from both incinerators was determined. Moreover, the relation analysis between PCDD/F and conventional pollutants was conducted. The conclusions were as follows:

(1) The emission concentrations, emission factors, and amounts of conventional pollutants (PM, SO_2, NO_x, Hg, Cd+Ti, As+Sb+Pb+Cr+Co+Cu+Mn+Ni) from emitted exhaust gas in the fluidized bed and grate incinerator were similar and both satisfied the national standard. Still, the HCl concentration of the grate incinerator was 30.78 ± 7.12 mg/Nm^3, which was about 7 times higher than that of the fluidized bed.

(2) The source strength of 2,3,7,8-PCDD/Fs in GBI-FB was 5.09 times higher (48.90 ng/Nm^3), while the I-TEQ concentration was 2.6 times higher (2.03 ng I-TEQ/Nm^3). 2,3,7,8-PCDD/F concentrations in fly ash of the two incinerators were similar, 1.668 ng/g (0.058 ng I-TEQ/g) and 1.438 ng/g (0.048 ng I-TEQ/g) for the fluidized bed and grate incinerator, respectively. All emitted pollutants satisfied national emission limits.

(3) Isomer distribution and fingerprint of 2,3,7,8-PCDD/F and 136 PCDD/F isomers were conducted. For 2,3,7,8-PCDD isomers, OCDD and 1,2,3,4,6,7,8-HpCDD (mass concentration) and 2,3,4,7,8-PeCDF (I-TEQ concentration) accounted for the highest proportion, respectively. Moreover, a similar distribution pattern for 136 PCDD/F isomers was obtained, indicating similar potential formation pathways.

(4) The 136 kinds of PCDD/F concentration of gas before APCS in the fluidized bed were 2.9 times higher (135.68 ng/Nm^3) than in the grate incinerator (46.51 ng/Nm^3). Results indicated that CP route synthesis could be excluded for both incinerators. De novo synthesis dominated the formation for both incinerators, and DD/DF chlorination also contributed. However, DD/DF chlorination in the fluidized bed was stronger. In addition, the analysis on the correlation indicated little correlation between conventional pollutants and PCDD/F formation ($0.009 < R^2 < 0.535$) for fluidized bed and grate incinerators.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-022-22437-7.

Author contribution Yuxuan Ying: writing, methodology, software, formal analysis, investigation, visualization; Liang Xu: review and editing, formal analysis; Hao Zhang: methodology, data investigation; Xiaodong Li: project administration, funding acquisition; Shengyong Lu: funding acquisition; Yang Cao: data investigation; Xiaoqing Lin, Jisheng Long: methodology, validation, resources, writing — review and editing, project administration, supervision.

Funding This study was funded by the National Key Research and Development Program of China (2020YFC1910100).

Data availability All data generated or analyzed during this study were included in this published article.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

References

Altwicker ER (1996) Formation of PCDDF in municipal solid waste incinerators: laboratory and modeling studies. J Hazard Mater 47:137–161

Atkinson J, Hung P, Zhang Z, Chang M, Yan Z, Rood M (2015) Adsorption and destruction of PCDD/Fs using surface-functionalized activated carbons. Chemosphere 118:136–142

Behnisch PA, Hosoe K, Shiozaki K, Kiryu T, Komatsu K, Schramm K-W, Sakai S-I (2002) Melting and incineration plants of municipal waste. Environ Sci Pollut Res 9:337–344

Bourtsalas A, Huang Q, Zhang H, Themelis N (2020) Energy recovery in China from solid wastes by the moving grate and circulating fluidized bed technologies. Waste Disposal Sustain Energy 2:27–36

Buekens A, Huang H (1998) Comparative evaluation of techniques for controlling the formation and emission of chlorinated dioxins/furans in municipal waste incineration. J Hazard Mater 62:1–33

Chang Y-M, Fan W-P, Dai W-C, Hsi H-C, Wu C-H, Chen C-H (2011) Characteristics of PCDD/F content in fly ash discharged from municipal solid waste incinerators. J Hazard Mater 192:521–529

Chen T, Gu Y-l, Yan J-h, Li X-d, Lu S-Y, Dai H-F, Cen K-f (2008) Polychlorinated dibenzo-p-dioxins and dibenzofurans in flue gas emissions from municipal solid waste incinerators in China. J Zhejiang Univ-Sci A 9:1296–1303

Chen Z, Lin X, Lu S, Li X, Qiu Q, Wu A, Ding J, Yan J (2018) Formation pathways of PCDD/Fs during the Co-combustion of municipal solid waste and coal. Chemosphere 208:862–870

Chen T, Sun C, Wang T, Lomnicki S, Zhan M, Li X, Lu S, Yan J (2020) Formation of DF, PCDD/Fs and EPFRs from 1, 2, 3-trichlorobenzene over metal oxide/silica surface. Waste Manag 118:27–35

Cheng J, Shi F, Yi J, Fu H (2020) Analysis of the factors that affect the production of municipal solid waste in China. J Clean Prod 259:120808

Chi KH, Chang MB, Chang-Chien GP, Lin C (2005) Characteristics of PCDD/F congener distributions in gas/particulate phases and emissions from two municipal solid waste incinerators in Taiwan. Sci Total Environ 347:148–162

EPA (U.S. Environmental Protection Agency) (1994) Method 1613 tetra-through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS. U.S. Environmental Protection Agency

Everaert K, Baeyens J (2001) Correlation of PCDD/F emissions with operating parameters of municipal solid waste incinerators. J Air Waste Manag Assoc 51:718–724

Freire M, Lopes H, Tarelho LA (2015) Critical aspects of biomass ashes utilization in soils: Composition, leachability, PAH and PCDD/F. Waste Manag 46:304–315

Giugliano M, Cernuschi S, Grosso M, Miglio R, Aloigi E (2002) PCDD/F mass balance in the flue gas cleaning units of a MSW incineration plant. Chemosphere 46:1321–1328

Hajizadeh Y, Onwudili JA, Williams PT (2011) Removal potential of toxic 2378-substituted PCDD/F from incinerator flue gases by waste-derived activated carbons. Waste Manag 31:1194–1201

Huang H, Buekens A (1995) On the mechanisms of dioxin formation in combustion processes. Chemosphere 31:4099–4117

Huang H, Buekens A (1996) De novo synthesis of polychlorinated dibenzo-p-dioxins and dibenzofurans Proposal of a mechanistic scheme. Sci Total Environ 193:121–141

Jančauskas A, Buinevičius K (2020) The grate-firing boilers grate movement impact onto NOx, SO2 emissions. Mechanika 26:503–510

Leckner B, Lind F (2020) Combustion of municipal solid waste in fluidized bed or on grate–a comparison. Waste Manag 109:94–108

Lenoir D, Kaune A, Hutzinger O, Mützenich G, Horch K (1991) Influence of operating parameters and fuel type on PCDD/F emissions from a fluidized bed incinerator. Chemosphere 23:1491–1500

Li Y, Wang H, Jiang L, Zhang W, Li R, Chi Y (2015) HCl and PCDD/Fs emission characteristics from incineration of source-classified combustible solid waste in fluidized bed. RSC Adv 5:67866–67873

Li X, Ma Y, Zhang M, Zhan M, Wang P, Lin X, Chen T, Lu S, Yan JJWD, Energy S (2019) Study on the relationship between waste classification, combustion condition and dioxin emission from waste incineration. Waste Disposal Sustain Energy 1:91–98

Lin Y-S, Chen K-S, Lin Y-C, Hung C-H, Chang-Chien G-P (2008) Polychlorinated dibenzo-p-dioxins/dibenzofurans distributions in ash from different units in a municipal solid waste incinerator. J Hazard Mater 154:954–962

Lin X, Ma Y, Chen Z, Li X, Lu S, Yan J (2020) Effect of different air pollution control devices on the gas/solid-phase distribution of PCDD/F in a full-scale municipal solid waste incinerator. Environ Pollut 265:114888

Lomnicki S, Dellinger B (2003) A detailed mechanism of the surface-mediated formation of PCDD/F from the oxidation of 2-chlorophenol on a CuO/silica surface. J Phys Chem A 107:4387–4395

Lu S-Y, Du Y, Yan J-H, Li X-D, Ni M-J, Cen K-F (2012) Dioxins and their fingerprint in size-classified fly ash fractions from municipal solid waste incinerators in China—mechanical grate and fluidized bed units. J Air Waste Manag Assoc 62:717–724

Luijk R, Akkerman DM, Slot P, Olie K, Kapteijn F (1994) Mechanism of formation of polychlorinated dibenzo-p-dioxins and dibenzofurans in the catalyzed combustion of carbon. Environ Sci Technol 28:312–321

Ma C, Li B, Chen D, Wenga T, Ma W, Lin F, Chen G (2019) An investigation of an oxygen-enriched combustion of municipal solid waste on flue gas emission and combustion performance at a 8 MWth waste-to-energy plant. Waste Manag 96:47–56

Ma Y, Lin X, Chen Z, Li X, Lu S, Yan J (2020) Influence factors and mass balance of memory effect on PCDD/F emissions from the full-scale municipal solid waste incineration in China. Chemosphere 239:124614

Matsuda H, Ozawa S, Naruse K, Ito K, Kojima Y, Yanase T (2005) Kinetics of HCl emission from inorganic chlorides in simulated municipal wastes incineration conditions. Chem Eng Sci 60:545–552

MEP (Ministry of Environmental Protection of the People's Republic of China) (2008) HJ 77.2-2008 Ambient air and flue gas – determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) isotope dilution HRGC-HRMS. Ministry of Environmental Protection of the People's Republic of China

NBS (National Bureau of Statistics) (2021) China Statistics Yearbook-2021, China statistics Press (Beijing)

NBS (National Bureau of Statistics), MEEPRC (Ministry of Ecology and Environment of the People's Republic of China) (2021) China Environmental Statistics Yearbook-2020, China Environmental Statistics Press (Beijing)

Nganai S, Dellinger B, Lomnicki S (2014) PCDD/PCDF ratio in the precursor formation model over CuO surface. Environ Sci Technol 48:13864–13870

Ni Y, Zhang H, Fan S, Zhang X, Zhang Q, Chen J (2009) Emissions of PCDD/Fs from municipal solid waste incinerators in China. Chemosphere 75:1153–1158

Olie K, Addink R, Schoonenboom M (1998) Metals as catalysts during the formation and decomposition of chlorinated dioxins and furans in incineration processes. J Air Waste Manag Assoc 48:101–105

Pan Y, Yang L, Zhou J, Liu J, Qian G, Ohtsuka N, Motegi M, Oh K, Hosono S (2013) Characteristics of dioxins content in fly ash from municipal solid waste incinerators in China. Chemosphere 92:765–771

Qiu J, Tang M, Peng Y, Lu S, Li X, Yan J (2020) Characteristics of PCDD/Fs in flue gas from MSWIs and HWIs: emission levels, profiles and environmental influence. Aerosol Air Qual Res 20:2085–2097

Ruokojärvi PH, Halonen IA, Tuppurainen KA, Tarhanen J, Ruuskanen J (1998) Effect of gaseous inhibitors on PCDD/F formation. Environ Sci Technol 32:3099–3103

Ruokojärvi PH, Asikainen AH, Tuppurainen KA, Ruuskanen J (2004) Chemical inhibition of PCDD/F formation in incineration processes. Sci Total Environ 325:83–94

Ryu J-Y, Mulholland JA, Dunn JE, Iino F, Gullett BK (2004) Potential role of chlorination pathways in PCDD/F formation in a municipal waste incinerator. Environ Sci Technol 38:5112–5119

Ryu J-Y, Choi K-C, Mulholland JA (2006) Polychlorinated dibenzo-p-dioxin (PCDD) and dibenzofurna (PCDF) isomer patterns from municipal waste combustion: Formation mechanism fingerprints. Chemosphere 65:1526–1536

Shaub WM, Tsang W (1983) Dioxin formation in incinerators. Environ Sci Technol 17:721–730

Stieglitz L, Zwick G, Beck J, Roth W, Vogg H (1989) On the de-novo synthesis of PCDD/PCDF on fly ash of municipal waste incinerators. Chemosphere 18:1219–1226

Tuppurainen K, Halonen I, Ruokojärvi P, Tarhanen J, Ruuskanen J (1998) Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: a review. Chemosphere 36:1493–1511

Wang L-C, Hsi H-C, Chang J-E, Yang X-Y, Chang-Chien G-P, Lee W-S (2007) Influence of start-up on PCDD/F emission of incinerators. Chemosphere 67:1346–1353

Wang T, Chen T, Lin X, Zhan M, Li X (2017) Emission and distribution of PCDD/Fs, chlorobenzenes, chlorophenols, and PAHs from stack gas of a fluidized bed and a stoker waste incinerator in China. Environ Sci Pollut Res 24:5607–5618

Wielgosiński G (2011) The reduction of dioxin emissions from the processes of heat and power generation. J Air Waste Manag Assoc 61:511–526

Xia H, Tang J, Aljerf L (2022) Dioxin emission prediction based on improved deep forest regression for municipal solid waste incineration process. Chemosphere 294:133716

Ying Y, Ma Y, Li X, Lin X (2021) Emission and migration of PCDD/Fs and major air pollutants from co-processing of sewage sludge in brick kiln. Chemosphere 265:129120

You X (2008) Polycyclic aromatic hydrocarbon (PAH) emission from co-firing municipal solid waste (MSW) and coal in a fluidized bed incinerator. Waste Manag 28:1543–1551

Zhang H-J, Ni Y-W, Chen J-P, Zhang Q (2008) Influence of variation in the operating conditions on PCDD/F distribution in a full-scale MSW incinerator. Chemosphere 70:721–730

Zhang G, Hai J, Cheng J (2012) Characterization and mass balance of dioxin from a large-scale municipal solid waste incinerator in China. Waste Manag 32:1156–1162

Zhang M, Yang J, Buekens A, Olie K, Li X (2016) PCDD/F catalysis by metal chlorides and oxides. Chemosphere 159:536–544

Zhang M, Buekens A, Olie K, Li X (2017) PCDD/F-isomers signature-effect of metal chlorides and oxides. Chemosphere 184:559–568

Zhang M, Buekens A, Li X (2018a) Statistical analysis as a tool for discriminating dioxin formation pathways. J Mater Cycl Waste Manag 20:1516–1529

Zhang M, Buekens A, Li X (2018b) Characterising boiler ash from a circulating fluidised bed municipal solid waste incinerator and distribution of PCDD/F and PCB. Environ Sci Pollut Res 25:22775–22789

Zhang R-z, Luo Y-h, Yin R-h (2018c) Experimental study on dioxin formation in an MSW gasification-combustion process: an attempt for the simultaneous control of dioxins and nitrogen oxides. Waste Manag 82:292–301

Zhou H, Meng A, Long Y, Li Q, Zhang Y (2014) An overview of characteristics of municipal solid waste fuel in China: physical, chemical composition and heating value. Renew Sustain Energy Rev 36:107–122

Zhu F, Li X, Lu J-W, Hai J, Zhang J, Xie B, Hong C (2018) Emission characteristics of PCDD/Fs in stack gas from municipal solid waste incineration plants in Northern China. Chemosphere 200:23–29