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RESEARCH ARTICLE

Residue concentrations and profiles of PCDD/Fs in ash samples from multiple thermal industrial processes in Vietnam: Formation, emission levels, and risk assessment

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Abstract

The residue concentrations and congener profiles of polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) were examined in fly ash and bottom ash released from different thermal industrial processes in Vietnam. PCDD/F concentrations and toxic equivalents (TEQs) in the ash samples varied greatly and decreased in the following order: steel making > aluminum recycling > medical waste incinerator > boilers > municipal waste incinerator > tin production > brick production > coal-fired power plant. Both the precursor and de novo synthesis were estimated as possible formation mechanisms of dioxins in the ash, but the latter pathway was more prevalent. The highest emission factors were estimated for the ash released from some steel-making plants, aluminum-recycling facilities, and a medical waste incinerator. The emission factors of PCDD/Fs in ash released from some steel plants of this study were two to six times higher than the UNEP Toolkit default value. The annual emission amount of ash-bound dioxins produced by 15 facilities in our study was estimated to be 26.2 to 28.4 g TEQ year^{-1}, which mainly contributed by 3 steel plants. Health risk related to the dioxin-containing ash was evaluated for workers at the studied facilities, indicating acceptable risk levels for almost all individuals. More comprehensive studies on the occurrence and impacts of dioxins in waste streams from incineration and industrial processes and receiving environments should be conducted, in order to promote effective waste management and health protection scheme for dioxins and related compounds in this rapidly industrializing country.

Keywords PCDD/Fs · Ash · Thermal industrial processes · Metal industry · Electric arc furnace · Risk assessment

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are typical groups of persistent organic pollutants (POPs) unintentionally produced during chemical manufacturing, waste incineration, and other thermal processes (Zook and Rappe 1994; Stringer and Johnston 2001; Kulkarni et al. 2008; Mudhoo et al. 2013). Besides, there are a great number of PCDD/F structural analogues with similar formation pathways, physicochemical properties, environmental fate, and toxic effects, which are referred to a more generic term as dioxin-related compounds (DRCs) or simply dioxins (Zook and Rappe 1994; Stringer and Johnston 2001). Because of the persistent and hydrophobic nature, DRCs are ubiquitous in the environment and have been found in human and animal fatty tissues (Travis et al. 1989; Zook and Rappe 1994; Van den Berg et al. 1998, 2006). Human exposures to DRCs can cause several adverse effects, including cancer, reproductive and developmental impacts, endocrine disruption, immunotoxicity, neurotoxicity, organ toxicity, and

numerous transient acute health effects (Stringer and Johnston 2001; Mandal 2005; Schecter et al. 2006; Srogi 2008). Numerous environmental pollution events and occupational or accidental exposure cases related to DRCs have been reported worldwide since the late 1950s, raising concerns in the public and scientific interest about these toxicants (Travis et al. 1989; Stringer and Johnston 2001; Hites 2011). Among DRCs, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and other 2,3,7,8-substituted PCDD/Fs are the most well-studied congeners due to their high toxic potency (Mandal 2005; Kulkarni et al. 2008; Mudhoo et al. 2013).

Apart from the majority of PCDD/F emissions from organochlorine industry in the past, the considerable amounts of these compounds have been introduced into the environment mainly associated with the waste stream (e.g., flue gas, fly ash, and bottom ash) generated from the incineration and thermal industrial processes (McKay 2002; Dyke 2003; Kulkarni et al. 2008; Weber et al. 2008). Flue gas has been identified as one of the most abundant sources of PCDD/Fs and widely used as an effective indicator media for monitoring, control, and remediation studies on dioxins (Kulkarni et al. 2008; Mudhoo et al. 2013). However, from a mass balance point of view, solid residues play a more important role in the total dioxin output of waste incinerators and industrial facilities (Abad et al. 2002; Zhang et al. 2012). The ash is usually landfilled or treated for reuse and recycling (Zacco et al. 2014). The ash originated from different sources that vary in composition, structure, and properties has been applied as absorbents, agricultural and industrial additives, building and infrastructure materials, and other applications, after suitable treatment (Lam et al. 2011; Zacco et al. 2014; Min et al. 2018). Economically significant levels of precious metals (e.g., gold, silver, platinum, and copper) have been found in the municipal solid waste incineration ash (Hjelmar 1996; Muchova et al. 2009). Nevertheless, potential adverse impacts of the incineration ash contaminated by heavy metals and organic pollutants (including notable amounts of DRCs) on the environmental and human health have been demonstrated elsewhere (Gidarakos et al. 2009; Li et al. 2016; Wu et al. 2016; Petrlik and Bell 2017; Sun et al. 2017; Tsakalou et al. 2018). An effective management, treatment, and utilization approach for the ash residues is required in order to exploit economic value of this material source, and to control and reduce its hazardous effects, especially in developing countries (Kulkarni et al. 2008; Mudhoo et al. 2013; Tang et al. 2013; Petrlik and Bell 2017).

In Vietnam, residue concentrations of POPs (e.g., chlorobenzenes, polychlorinated biphenyls, and polybrominated diphenyl ethers) as well as multiple organic micro-pollutants have been reported for the ash and receiving media (e.g., soil and road dust) in some industrial areas, implying the environmental degradation related to industrialization (Hue et al. 2016, 2019a; Anh et al. 2018, 2019a, b). However, information about the occurrence of PCDD/Fs in the incineration and industrial ash is still limited in Vietnam and other Southeast Asian developing countries, mainly due to inadequate monitoring proficiency and financial resources. Our preliminary investigation has revealed the abundance of PCDD/Fs and other unintentionally produced POPs (U-POPs) in the waste flows (e.g., flue gas and residual ash) generated from some incinerators and secondary metallurgical plants in northern Vietnam (Hue et al. 2019b; Pham et al. 2019). These observations suggest the need for more comprehensive research on the formation, release behavior, and impacts of U-POPs, especially PCDD/Fs, in the thermal industrial ash residues in this rapidly industrializing country.

In the present study, we conducted a systematic investigation to examine residue concentrations and accumulation profiles of 17 toxic PCDD/F congeners in the fly ash and bottom ash samples collected from several facilities belonging to different thermal industrial processes, such as metallurgical production and metal recycling, waste incineration, brick production, and electricity and heat generation in Vietnam. The results obtained by a synchronous methodology from sampling techniques to analytical methods can produce a comprehensive picture with relevant comparisons about the formation and emission levels of PCDD/Fs from various industrial sectors. The fingerprint profiles of PCDD/Fs were analyzed to understand their potential formation mechanisms and release behaviors. The emission factors and annual emission amounts of PCDD/Fs were estimated in order to provide preliminary inventory data on DRCs in Vietnam. In addition, human health risk related to dioxin-contaminated ash was evaluated for workers in the investigated facilities.

Materials and methods

Sample collection

The field investigation and sampling activities were conducted in 15 thermal industrial facilities located in nine cities and provinces along Vietnam. These facilities belong to nine categories such as steel making (SM-1, -2, -3, -4, -5), tin production (TP), aluminum recycling (AR-1, -2, -3), incinerators for municipal (MU) and medical (ME) wastes, coal-fired power plant (CP), brick making (BR), and industrial (IB) and craft (CB) boilers. The metallurgical facilities investigated in this study belong to secondary-metal industries. Basic information of the investigated facilities is summarized in Table 1. Fly ash (FA) and bottom ash (BA) samples were manually collected according to the method described in our previous studies (Hue et al. 2016, 2019a, b). In brief, the FA samples were obtained from the exhaust systems or the dust-filtering bags, while the BA samples were collected from the bottom or slag-

Table 1 Basic information of the investigated thermal industrial facilities

Category	Facility code	Technology	Capacity (ton h^{-1})	Average operating time (h $year^{-1}$)	Amount of ash produced (kg ton^{-1})	Location in Vietnam
Steel-making plants	SM-1	Electric arc furnace	20	7000	BA 100; FA 20	North-eastern
	SM-2	Electric arc furnace	31.6	7920	BA 100; FA 20	Red River Delta
	SM-3	Electric arc furnace	28.6	7000	FA 20	Red River Delta
	SM-4	Electric arc furnace	0.06	7200	FA 20	South-eastern
	SM-5	Electric arc furnace	18.9	7920	FA 20	South-eastern
Tin production plant	TP	Electric arc furnace	0.06	7000	BA 40	North-eastern
Aluminum-recycling facilities	AR-1	Annular kiln	0.04	2000	BA 150	Red River Delta
	AR-2	Annular kiln	0.05	2000	BA 150	Red River Delta
	AR-3	Annular kiln	0.05	2000	FA 10	Red River Delta
Municipal waste incinerator	MU	Grate incinerator	0.35	7200	BA 100	North Central Coast
Medical waste incinerator	ME	Grate incinerator	0.2	7200	BA 100	Red River Delta
Coal power plant	CP	Coal-fired plant	167	6000	FA 40	North-eastern
Brick-making plant	BR	Tunnel kiln	5	8040	BA 100; FA 5	North-eastern
Industrial boiler	IB	Coal-fired fluidized bed boiler	20	7800	FA 8	Red River Delta
Craft boiler	CB	Coal- and wood-fired boiler	1.2	4000	BA 20	Red River Delta

discharge chambers of the investigated facilities. The average temperature of sampling points for the FA and BA samples were about 50 and 200 °C, respectively. The ash samples were allowed to cool down to ambient temperature, transferred into amber glass jars, and transported to a laboratory. All the collected samples were stored at − 25 °C until chemical analysis.

Chemical analysis

Seven 2,3,7,8-substituted PCDDs and ten 2,3,7,8-substituted PCDFs were analyzed following the Method 8290A of the US Environmental Protection Agency (US EPA 2007). Additional information about the target compounds is provided in Table S1. The detailed analytical procedure of PCDD/Fs in the ash samples was mentioned in our previous study (Hue et al. 2019b). In brief, about 20 g of ash sample was spiked with $^{13}C_{12}$-PCDD/F surrogate standards and Soxhlet extracted with toluene for 24 h. The crude extract was treated with concentrated sulfuric acid and potassium hydroxide solution, and then subjected to a multi-layer silica gel column and a basic alumina column with elution solvents as hexane and dichloromethane in hexane, respectively. The PCDD/F fraction was further cleaned up by using an activated carbon column with elution solvent such as toluene. The clean extract was rotary evaporated, spiked with $^{13}C_{12}$-PCDD internal standards, and blown down to a volume of 0.1 mL under a stream of nitrogen before injecting into a high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC–HRMS) system for quantification.

PCDD/Fs were separated on a 7890A gas chromatograph (Agilent Technologies) using a DB-5MS capillary column (60 m × 0.25 mm I.D. × 0.25 μm film thickness; J&W Scientific Inc.). The quantification was carried out on a Micromass Autospec Ultima system (Waters Corporation) operated in a positive electron impact (EI) ionization mode at a resolution of ≥ 10,000. The mass data was obtained by the selected ion record (SIR) mode. Mass concentrations of PCDD/Fs were derived based on the internal standard method (US EPA 2007). The toxic equivalency factors proposed by the World Health Organization (WHO 2005 TEF; Van den Berg et al. 2006) were used to calculate toxic equivalents (TEQs) in the ash samples (see Table S1). Recoveries of $^{13}C_{12}$-PCDD/F surrogate standards ranged from 75 to 105%. Method detection limits (MDLs) of PCDD/Fs ranged from 0.05 to 0.1 pg g^{-1}.

Statistical analysis

Statistical analysis was performed using Microsoft Excel (Microsoft Office 2010) and Minitab 16® Statistical Software (Minitab Inc.). Concentrations of non-detected compounds were treated as zero. The reported concentrations were blankly corrected. The whole data set was analyzed by the Pearson correlation analysis and hierarchical cluster analysis (HCA) to find out possible relationships between the target compounds and between the investigated facilities. The level of statistical significance was set at $p < 0.05$.

Results and discussion

Concentrations of PCDD/Fs in ash samples

In all the investigated samples, PCDD/Fs were detected, but their concentrations varied over several orders of magnitude depending on different categories, facilities, and ash types. The mass concentrations and TEQs of PCDD/Fs in the ash samples of this study are presented in Table 2. In general, PCDD/F concentrations decreased in the following order: steel making > aluminum recycling > medical waste incinerator > boiler > municipal waste incinerator > tin production > brick production > coal-fired power plant ash. PCDD/Fs were preferably concentrated in the FA samples than in the BA samples, except for those observed in a steel plant (SM-1) where bottom ash contained higher dioxin residues than fly ash. The levels of PCDD/Fs in the FA samples from the SM-1 steel plant were quite low compared with other facilities in the same sector, probably reflecting appropriate operating conditions of its air pollution control devices (APCDs) (e.g., bag filters maintained at low temperatures). Meanwhile, the highest dioxin levels were found in the FA samples from the SM-5 steel plant (51,300–52,700 pg g^{-1}; corresponding to 4270–4290 pg TEQ g^{-1}) and a FA sample from the AR-3 aluminum-recycling facility (43,200 pg g^{-1}; corresponding to 2410 pg TEQ g^{-1}). The elevated residue concentrations of PCDD/Fs were also measured in the FA and BA samples from some steel plants, aluminum facilities, and a medical waste incinerator. Minor levels of PCDD/Fs and TEQs were detected in the ash released from the remaining facilities.

TEQ levels in the ash produced from various incineration and thermal industrial processes in Vietnam and other countries are summarized in Table S2. Generally speaking, the residue levels of PCDD/Fs in the Vietnamese ash fall within the low to middle range as compared with those documented in the literature. For example, TEQ levels in the BA samples of our medical waste incinerator (22.9–139 pg TEQ g^{-1}) were comparable with those detected in a similar sample from northern Algeria (146 pg TEQ g^{-1}; Yacine et al. 2018), but significantly lower than levels recorded in Germany (1160–19,710 pg TEQ g^{-1}; Gidarakos et al. 2009). The ash samples from aluminum-recycling facilities of this study were contaminated with dioxins at levels of 23.5 to 2410 pg TEQ g^{-1}, which were within lower-end of the ranges measured in samples from Chinese aluminum smelters (610–27,780 pg TEQ g^{-1}; Li et al. 2019) and secondary aluminum plants (18–10,200 pg TEQ g^{-1}; Ba et al. 2009); and Korean aluminum production plants (3–16,232 pg TEQ g^{-1}; Yu et al. 2006). This point can probably be explained by the fact that the main raw materials for these informal small-scale facilities were obsolete housewares and beverage cans, which may contain less organic impurities than those processed informal plants and smelters (e.g., electric appliances, aluminum foil, end-of-life vehicles, and aluminum sidings). The coal-fired power plant in our study emitted fly ash containing minor dioxin contents (0.0013–0.300 pg TEQ g^{-1}) compared with some coke and power plants elsewhere (Chen et al. 2008; Yive and Tiroumalechetty 2008; Liu et al. 2013). TEQ concentrations in our boiler ash samples (11.7–78.4 pg TEQ g^{-1}) were much smaller than those found in fly ash of woodchip boilers in Taiwan (38,060–98,570 pg TEQ g^{-1}; Bai et al. 2017). However, we detected relatively high dioxin levels in the steel plant fly ash (mean 1500; range 0.174–4290 pg TEQ g^{-1}). Based on these results, we estimated that steel making, informal aluminum recycling, and medical waste incineration were potential sources of PCDD/Fs in the ash of this study.

The extent of dioxin formation and emission during thermal processes generally depends on three main factor categories: (1) the composition of feeding materials; (2) the technology employed during production or treatment processes; and (3) the effectiveness of waste control devices and management systems (Abad et al. 2002; Vehlow 2012). In different industrial sectors, each factor category contains a lot of parameters with various specific technical points that should be considered. However, due to the limited scope of this preliminary investigation, we focused only on some critical issues related to two potential sources of dioxins as described above, including steel-making and informal aluminum-recycling activities. For steel-making plants, the relatively high concentrations of PCDD/Fs in the fly ash were found in some facilities that several orders of magnitude higher than those detected in the other plants, even though they have similar technology as electric arc furnace (EAF). This situation was probably due to the large variation in the content of feedstock (e.g., composition and purity of cast iron and scrap) and the differences in types and operation conditions of APCDs (Chang et al. 2006; Oberg 2007; Thuong et al. 2014). Previous studies indicated that bag filter ash has highest PCDD/F concentrations in steel-making processes in EAFs due to the low-temperature formation of dioxins under catalytic conditions, suggesting that some reduction measures such as inhibition of catalytic activity and maintaining filter bag at lower temperature (e.g., 105 to 115 °C) are necessary (Chang et al. 2006; Oberg 2007; Lin et al. 2008).

Table 2 Concentrations of PCDD/Fs in the bottom ash (BA) and fly ash (FA) samples from different thermal processes in Vietnam

Category	Facility	Samples	Mass concentration (pg g^{-1})			TEQs (pg TEQ g^{-1})		
			PCDDs	PCDFs	PCDD/Fs	PCDD-TEQs	PCDF-TEQs	PCDD/F-TEQs
Steel-making plants	SM-1	BA ($n = 1$)	85.5	40.4	126	3.36	4.45	7.81
		FA ($n = 2$)	5.99 (4.04–7.94)	3.76 (2.21–5.31)	9.75 (9.35–10.2)	0.016 (0.002–0.030)	0.391 (0.172–0.609)	0.407 (0.174–0.639)
	SM-2	BA ($n = 1$)	10.6	10.0	20.6	0.178	1.00	1.18
		FA ($n = 1$)	12,400	8240	20,600	670	873	1540
	SM-3	FA ($n = 2$)	4560 (3360–5760)	13,700 (12,400–14,900)	18,200 (15,800–20,700)	494 (334–654)	1140 (1040–1250)	1640 (1370–1900)
	SM-4	FA ($n = 2$)	218 (2.09–434)	857 (1.60–1700)	1080 (3.69–2150)	17.9 (0.273–35.5)	71.0 (0.061–142)	88.9 (0.334–178)
	SM-5	FA ($n = 2$)	12,300 (12,200–12,400)	39,700 (39,100–40,300)	52,000 (51,300–52,700)	1350 (1340–1360)	2930 (2920–2940)	4280 (4270–4290)
Tin production plant	TP	BA ($n = 1$)	12.0	44.6	56.6	0.797	4.16	4.96
Aluminum-recycling facilities	AR-1	BA ($n = 1$)	587	2770	3360	258	278	536
	AR-2	BA ($n = 1$)	29.4	203	232	5.24	18.3	23.5
	AR-3	FA ($n = 1$)	9420	33,800	43,200	667	1740	2410
Municipal waste incinerator	MU	BA ($n = 2$)	11.8 (9.28–14.3)	62.0 (60.7–63.3)	73.8 (70.0–77.6)	1.72 (1.56–1.88)	6.39 (6.37–6.41)	8.11 (7.93–8.29)
Medical waste incinerator	ME	BA ($n = 3$)	574 (100–1040)	813 (212–1610)	1390 (312–2650)	24.0 (7.13–40.2)	55.1 (15.8–99.1)	79.1 (22.9–139)
Coal power plant	CP	FA ($n = 4$)	1.57 (0.610–4.01)	0.460 (0.120–1.10)	2.03 (0.730–4.47)	0.038 (0.0002–0.152)	0.043 (0.0001–0.143)	0.081 (0.0013–0.300)
Brick-making plant	BR	BA ($n = 1$)	0.510	0.100	0.610	0.110	0.010	0.120
		FA ($n = 1$)	24.0	5.52	29.5	0.353	0.184	0.537
Industrial boiler	IB	FA ($n = 1$)	334	439	773	32.1	46.3	78.4
Craft boiler	CB	BA ($n = 1$)	6.58	158	164	0.0020	11.7	11.7

Dioxin abatement is more difficult in the case of informal aluminum-recycling activities. In these facilities, aluminum scrap (mainly beverage cans) is melted at about 800 °C in coal-fired annular furnaces without any appropriate pollution control device. Wu et al. (2018) have indicated that fly ash from secondary aluminum smelting can greatly supplement PCDD/F formation over a temperature range of 250 to 450 °C. In fact, the temperature of the atmosphere above these furnaces is not controlled and may meet the requirements for dioxin formation. Furthermore, high proportions of dirty aluminum scrap may enhance the dioxin emission levels and influence their pattern by increasing the ratios of PCDDs to PCDFs (Li et al. 2019). To reduce dioxin releases from the well-controlled modern plants, several improvements, such as scrap treatment, application of APCDs with fabric filters and lime injection, and high-temperature treatment of fly ash, have been suggested (Ba et al. 2009; Wu et al. 2018; Li et al. 2019). However, except for the first suggestion (i.e., effective pretreatment of raw materials to remove organic impurities), the remaining methods seem impossible to apply in these primitive workshops.

Profiles and formation mechanisms of PCDD/Fs in ash samples

Congener profiles of 17 PCDD/F congeners in the ash samples were analyzed in order to understand the formation pathway and release behavior of dioxins in the investigated facilities. The mass ratios of PCDFs to PCDDs ($R_{F/D}$) have been used to estimate the formation of dioxins by a de novo synthesis ($R_{F/D}$ larger than one) or by precursor mechanism ($R_{F/D}$ much lower than one) (Luijk et al. 1994; Huang and Buekens 1995; Tuppurainen et al. 1998; Everaert and Baeyens 2002). In almost the ash samples examined, the $R_{F/D}$ ratios were greater than one (range 0.77–24; mean 4.55), suggesting the de novo synthesis as the predominant mechanism. However, in the samples collected from the facilities such as SM-1, SM-2, CP, and BR, these ratios ranged from 0.11 to 1.31 (mean 0.52), indicating a possible different mechanism of dioxin formation and distribution. The detailed mass profiles of PCDD/Fs in the ash are shown in Fig. 1, and the dendrogram of cluster analysis based on these profiles is presented in Fig. S1. According to these results, the PCDD/F profiles can be classified into three main groups: (1) PCDDs are more abundant than PCDFs with OCDD and 1,2,3,4,6,7,8-HpCDD as predominant congeners (e.g., SM-1, SM-2, CP, and BR); (2) PCDFs are more abundant than PCDDs with tetra- and pentachlorinated furans as major congeners (e.g., AR-1, AR-2, TP, MU, and CB); and (3) PCDFs are more abundant with high proportions of octa- and heptachlorinated congeners (e.g., SM-3, SM-4, SM-5, AR-3, IB, and ME).

For the first group, it is difficult to affirm the dioxin formation from precursors in these facilities due to the lack of input material data. The abundance of PCDDs compared with PCDFs was recorded in several fly ash samples collected from a bagasse-fired power plant in Mauritius, and then the both de novo and precursor mechanisms were suggested (Yive and Tiroumalechetty 2008). Zhang et al. (2017) have indicated that the presence of metal catalysts (e.g., Cu and $CuCl_2.2H_2O$) and low carbon contents (e.g., 2%) can support the formation of PCDDs superiorly to that of PCDFs on the fly ash. The second group was mainly related to the bottom ash released from aluminum-recycling, tin production, municipal waste incineration, and craft boiler activities, with major furan congeners as TCDF; 1,2,3,7,8-PeCDF; 2,3,4,7,8-PeCDF; and 1,2,3,4,6,7,8-HpCDF; and major dioxin congeners as OCDD and 1,2,3,4,6,7,8-HpCDD. Previous studies have revealed that PCDDs (mainly octa- and heptaCDDs) dominated PCDD/F patterns in the bottom ash because of their low vapor pressure and volatility, resulting in high adsorption affinity onto ash particles (Abad et al. 2002; Chen et al. 2006; Zhang et al. 2012, 2018). The reason for the abundance of tetra- and pentaCDFs in these samples was unclear because such profiles were more frequently observed in the stack gas and fly ash rather than in the bottom ash (Ni et al. 2009; Nie et al. 2011; Pan et al. 2013). The remaining samples (e.g., fly ash from SM-3, SM-4, SM-5, and AR-3; and bottom ash from ME) were grouped together, exhibiting the dominance of high-molecular-weight compounds with similar chlorine substitution positions such as OCDD/F and 1,2,3,4,6,7,8-HpCDD/F. These profiles were in agreement with those previously detected in the ash from multiple thermal industrial sources (Chen et al. 2006; Lin et al. 2008; Liu et al. 2013, 2015; Li et al. 2019), reflecting the important role of heterogeneous thermochemical and stereo-selective chlorination reactions in the de novo synthesis of dioxins (Tondeur et al. 2015; Zhang et al. 2018; Li et al. 2019).

The TEQ proportions of 17 PCDD/Fs in the ash samples of this study are presented in Fig. 2. In general, the average percentages (± standard deviation) of PCDD/Fs in TEQ levels decreased in the following order: 2,3,4,7,8-PeCDF (27 ± 12%) > TCDD (16 ± 25%) > TCDF (12 ± 8%) ≈ 1,2,3,7,8-PeCDD (11 ± 10%) > 1,2,3,4,7,8-HxCDF (8 ± 5%) ≈ 1,2,3,6,7,8-HxCDF (6 ± 3%) ≈ 2,3,4,6,7,8-HxCDF (6 ± 3%). The contributions of the remaining congeners were insignificant. The proportions of TCDD, the most toxic congener of this chemical group, differed greatly between the samples with the highest percentages of 46 to 92% detected in the ash from the coal-fired power and brick plants. It is obvious that the major TEQ contributors described above have high TEF values from 0.1 to 1. Although some highly chlorinated compounds such as 1,2,3,4,6,7,8-HpCDD/F and OCDD/F were measured at elevated mass concentrations in many samples, their TEQ percentages were quite minor due to their low TEFs of 0.01 and 0.00003, respectively. Our TEQ patterns were similar to those observed in several solid waste incinerators

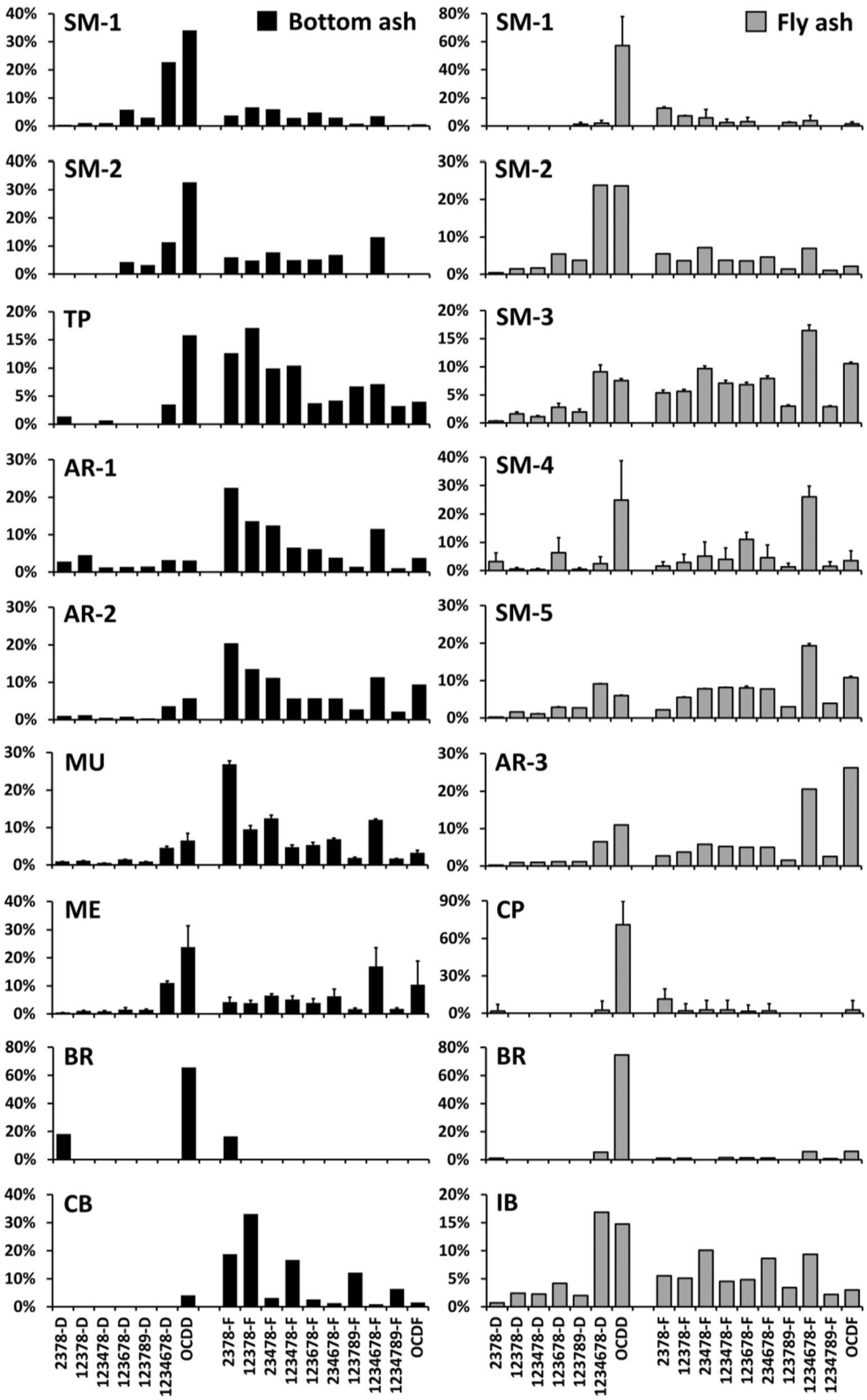

Fig. 1 Profiles of PCDD/Fs in ash samples from thermal industrial facilities in Vietnam. Bar and error bar indicate the mean and range of the mass concentration percentage of the total PCDD/Fs

(Abad et al. 2002; Zhang et al. 2012; Wu et al. 2016; Sun et al. 2017) and metallurgical plants (Ba et al. 2009; Lv et al. 2011) from other countries.

We applied the Pearson correlation analysis on the mass and TEQ concentrations of 17 PCDD/Fs and the WHO-TEQs and international toxic equivalents (I-TEQs) derived

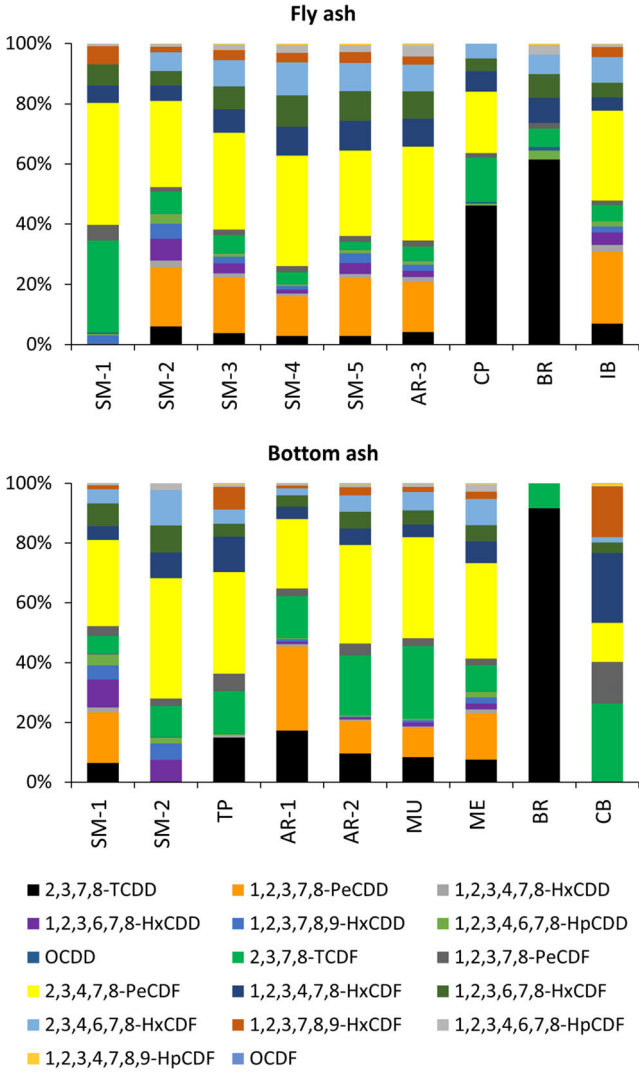

Fig. 2 Proportions of PCDD/Fs in TEQs of ash samples from thermal industrial facilities in Vietnam

by the international equivalency factors (I-TEFs; Kutz et al. 1990). Significant positive associations between concentrations of individual congeners and TEQs were observed (Pearson's $r > 0.70$; $p < 0.001$), indicating the similarities in their formation, distribution, and fate. Among these congeners, 1,2,3,7,8-PeCDD, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, and 2,3,4,6,7,8-HxCDF showed the highest correlation coefficients with WHO-TEQs and I-TEQs (Pearson's $r > 0.99$; $p < 0.001$). The relationships of these compounds with TEQ levels were further confirmed by regression analysis in order to find out potential indicator congeners for the TEQs in ash, and the results are summarized in Table 3. The congener 2,3,4,7,8-PeCDF has been widely used as an indicator of I-TEQs in stack emissions and ash residues from different thermal sources (Fiedler et al. 2000; Chen et al. 2008; Sun et al. 2017; Yacine et al. 2018). In the present study, this compound exhibited a good relationship with both WHO-TEQs and I-TEQs, suggesting possibilities of a screening method to predict total TEQ levels by determining a single congener (Fiedler et al. 2000). Besides, we also found some other compounds such as 1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDF, and 2,3,4,6,7,8-HxCDF that can be used as potential markers of TEQs in the ash released from multiple thermal industrial processes.

Emission factors and annual emission amounts

The emission factors (EFs) and annual emission amounts (EAs) of PCDD/Fs in the ash generated from the studied facilities were estimated by Eqs. 1 and 2, respectively:

$$\mathrm{EF}\left(\mu\mathrm{g\ TEQ\ ton^{-1}}\right) = \mathrm{Concentration\ in\ ash}\left(\mathrm{pg\ TEQ\ g^{-1}}\right) \times \mathrm{Amount\ of\ ash\ produced}\left(\mathrm{kg\ ton^{-1}}\right) \times 10^{-3} \quad (1)$$

$$\mathrm{EA}\left(\mathrm{g\ TEQ\ year^{-1}}\right) = \mathrm{EF}\left(\mu\mathrm{g\ TEQ\ ton^{-1}}\right) \times \mathrm{Capacity}\left(\mathrm{ton\ h^{-1}}\right) \times \mathrm{Average\ operating\ time}\left(\mathrm{h\ year^{-1}}\right) \times 10^{-6} \quad (2)$$

The parameters such as the amount of ash produced, capacity, and average operating time are summarized in Table 1, while TEQ concentrations in the ash are tabulated in Table 2. The EF and EA values of PCDD/Fs in fly ash and bottom ash estimated for the facilities of our study varied over a wide range (Table 4). The highest EF values were estimated for the bottom ash released from two aluminum-recycling facilities (AR-1 and AR-2; 3.53–80.5 μg TEQ ton^{-1}) and from one medical waste incinerator (ME; 2.29–13.9 μg TEQ ton^{-1}), and the fly ash from some steel-making plants (SM-2, SM-3, and SM-5; 27.4–85.8 μg TEQ ton^{-1}) and from an aluminum-recycling facility (AR-3; 24.1 μg TEQ ton^{-1}). Meanwhile, the ash emission factors of dioxins calculated for the remaining facilities were relatively low, for example, the coal-fired power plant (CP; 0.00005–0.012 μg TEQ ton^{-1}) and the brick-making plant (BR; 0.003–0.012 μg TEQ ton^{-1}). When capacity factors and production scale were considered, three steel plants (i.e., SM-2, SM-3, and SM-5) have emitted significant amounts of ash-bound dioxins compared with other facilities of this work. The total emission amount of dioxins in the ash produced by 15 facilities investigated in our study was estimated to be 26.2 to 28.4 g TEQ per year.

A comparison of emission factors and annual emissions of PCDD/Fs in the ash from various studies is given in Table S2. Although the emission factors of dioxins in the bottom ash from the waste incinerators in this study are of the same order of magnitude as those estimated for some municipal waste incinerators in Taiwan (Lin et al. 2008) and southern China (Zhang et al. 2012), our annual emission amounts (0.0019–0.020 g TEQ $year^{-1}$) are significantly lower than the values reported elsewhere (Abad et al. 2002; Zhang et al. 2012). Limited information about EF and EA of dioxins in the ash produced from other industrial processes leads to difficulty in

Table 3 Relationships between mass concentrations of selected PCDD/Fs and TEQ levels in the ash samples expressed by linear regression equation $y = a \times x + b$ with a coefficient of determination R^2

Response (y)	Predictor (x)	Slope (a)	y-intercept (b)	R^2	References
WHO-TEQ	1,2,3,7,8-PeCDD	5.20	9.70	0.9916	This study
		4.5978	–	0.9639	Pan et al. 2013
		10.15	37	0.93	Liu et al. 2015
	1,2,3,7,8-PeCDF	1.52	5.37	0.9933	This study
		1.67	1024	0.89	Liu et al. 2015
	2,3,4,7,8-PeCDF	1.03	− 12.04	0.9962	This study
		1.3797	–	0.9028	Pan et al. 2013
		1.12	722	0.96	Liu et al. 2015
	2,3,4,6,7,8-HxCDF	1.07	47.25	0.9883	This study
		0.78	1016	0.60	Liu et al. 2015
I-TEQ	1,2,3,7,8-PeCDD	5.78	15.35	0.9882	This study
	1,2,3,7,8-PeCDF	1.69	9.20	0.9933	This study
	2,3,4,7,8-PeCDF	1.15	− 10.89	0.9980	This study
		1.4	–	0.99	Fiedler et al. 2000
		1.06	–	0.9990	Chen et al. 2008
		1.086	0.01	0.9945	Sun et al. 2017
		1.04	9.34	0.90	Yacine et al. 2018
	2,3,4,6,7,8-HxCDF	1.20	55.49	0.9892	This study

making comparisons. The EF values estimated in our study were generally lower than the default values in the Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs proposed by the United Nations Environment Programme (UNEP 2013). However, the emission factors of PCDD/Fs in fly ash from some steel plants (SM-2, SM-3, and SM-5; 27.4 to 85.8 μg TEQ ton^{-1}) were two to six times higher than the highest EF value of the UNEP Toolkit of 15 μg TEQ ton^{-1} proposed for iron- and steel-making plants with dirty scrap and limited controls. This gap suggests the need for a more comprehensive/detailed evaluation to update the Toolkit's database, especially for facilities having low-technology production processes and inadequate pollution control systems. Our previous studies have indicated that stack gas and ash residues from some Vietnamese metallurgical plants of steel and zinc production contained elevated levels of dioxins (Thuong et al. 2014; Hue et al. 2019b; Pham et al. 2019). In the present study, the important contribution of steel-making activities in the total dioxin emissions was confirmed. In addition, we provided preliminary inventory data of PCDD/Fs in the ash from several sectors such as informal aluminum recycling, brick making, and boilers, which have not been reported earlier. Among these sectors, the EFs of dioxins in both fly ash and bottom ash from three representative aluminum-recycling facilities were relatively high, but the AEs were insignificant due to their low production scale. However, in fact, there are several hundred workshops in this recycling area and almost all of them have primitive technology without an effective waste treatment and management system, probably releasing a considerable amount of dioxins in ash.

Risk assessment

The chronic daily intake (CDI), hazard index for non-cancer risk (HI), and cancer risk (CR) of PCDD/Fs in the ash were estimated for workers in the investigated facilities. An integrated approach considering multiple exposure pathways such as ingestion, inhalation, and dermal contact with ash was applied (see details in Table S3). The risk assessment method used in this study was similar to those mentioned in previous studies (Li et al. 2016; Wu et al. 2016; Sun et al. 2017) with default exposure factors mainly adopted from the US EPA guidelines (US EPA 2014). The estimated CDI, HI, and CR values are shown in Table S4. The overall CDI values ranged from 1.3×10^{-16} to 4.2×10^{-10} mg TEQ kg^{-1} d^{-1}. These daily intake doses were lower than the oral reference dose (RfD) of 7×10^{-10} mg kg^{-1} d^{-1} derived by the US EPA for reproductive effects of TCDD (US EPA 2012) and the tolerable daily intake (TDI) of 1 to 4 pg TEQ kg^{-1} d^{-1} established by the WHO (Van Leeuwen et al. 2010). As a result, all the HI values were lower than the critical value of 1 (1.8×10^{-7} to 6.0×10^{-1}), implying unserious non-cancer risk. The total CR values varied between 1.7×10^{-11} and 5.5×10^{-5}. These values were lower than or within the range of 10^{-6} to 10^{-4} and were generally considered acceptable (US EPA 2005). But from another point of view, a CR value greater than 10^{-5} may imply a potential cancer risk (WHO 2008). In the latter case, workers at some metallurgical

Table 4 Emission factors (EF) and annual emission amounts (EA) of PCDD/Fs in bottom ash (BA) and fly ash (FA) estimated for different thermal industrial facilities in Vietnam

Category	Facility	Ash type	EF (μg TEQ ton^{-1})	EA (g TEQ year^{-1})
Steel-making plants	SM-1	BA	0.781	0.109
		FA	0.008 (0.003–0.013)	0.001 (0.0005–0.002)
	SM-2	BA	0.118	0.030
		FA	30.8	7.71
	SM-3	FA	32.8 (27.4–38.0)	6.57 (5.49–7.61)
	SM-4	FA	1.78 (0.007–3.56)	0.001 (0.000003–0.002)
	SM-5	FA	85.6 (85.4–85.8)	12.8 (12.7–12.9)
Tin production plant	TP	BA	0.198	0.00008
Aluminum-recycling facilities	AR-1	BA	80.5	0.006
	AR-2	BA	3.53	0.0004
	AR-3	FA	24.1	0.002
Municipal waste incinerator	MU	BA	0.811 (0.793–0.829)	0.0020 (0.0019–0.0021)
Medical waste incinerator	ME	BA	7.91 (2.29–13.9)	0.011 (0.003–0.020)
Coal power plant	CP	FA	0.003 (0.00005–0.012)	0.003 (0.00005–0.012)
Brick-making plant	BR	BA	0.012	0.0005
		FA	0.003	0.0001
Industrial boiler	IB	FA	0.627	0.098
Craft boiler	CB	BA	0.234	0.001

facilities with steel-making and aluminum-recycling activities (e.g., SM-2, SM-3, SM-5, and AR-3) were estimated to be threatened by higher cancer risk than those from the other facilities in this study (see Table S4). In terms of the exposure pathway contribution, the ingestion and dermal contact routes played a more important role in the daily intakes and potential health risks of ash-bound PCDD/Fs, as compared with those of ash-emitted inhalation. It should be noted that these estimations focused only on the workplace ash, whereas food and other media such as indoor and outdoor air, soil, and house dust are considerable sources of human exposure to dioxins (Srogi 2008; Demond et al. 2012; Tue et al. 2013; Li et al. 2016). Therefore, a more comprehensive risk assessment of PCDD/Fs and other DRCs is needed, especially for the high-risk occupational groups.

Summary

In summary, this study comprehensively reports the residue concentrations, distribution profiles, potential formation mechanisms, emission inventory, and occupational health risk of PCDD/Fs in the ash produced from various Vietnamese thermal industrial facilities. Some steel-making plants and informal aluminum-recycling facilities have emitted the ash contaminated with elevated amounts of PCDD/Fs, whereas ash samples from the remaining enterprises exhibited relatively low dioxin contents as compared with those previously detected elsewhere. Besides the major contribution of steel-making sector in total annual emission of dioxins in ash, preliminary inventory data has been reported for several "novel" sectors such as aluminum recycling, brick making, and craft boiler. The emission factors of PCDD/Fs in ash released from the investigated facilities of this study were generally lower than the UNEP Toolkit default values, except for some EAF steel plants with relatively high EFs. A certain level of human health risk related to dioxin-containing ash was detected, suggesting the need to improve labor protection conditions and to enhance people's awareness about the toxic effects of dioxins. Our results may provide updated data to close the information gap about current emission sources and adverse impacts of PCDD/Fs in Vietnam as well as the Southeast Asian region, and to fulfill the obligations of a Party under the Stockholm Convention on POPs. However, this study probably exhibited some disadvantages such as limited numbers of analyzed samples and focusing only on 2,3,7,8-substituted PCDD/F congeners. These limitations suggest that more intensive investigations on a wider scope of industrial sectors with a larger sample size and detailed profiles of PCDD/Fs should be conducted in the future to provide relevant insights into their emission levels and formation mechanisms.

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