



## The Emission of Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans from Steel and Cement-Kiln Plants in Vietnam

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### ABSTRACT

Stack gas and fly ash samples were collected in two steel plants and three cement kiln plants for the determination of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs). A standard sampling method (U.S EPA method 23) was used following the requirements for isokinetic sampling of stack gas emission. The quantification of PCDD/Fs was done by high resolution gas chromatography, coupled with high resolution mass spectrometry (HRGC/HRMS). The results demonstrated that PCDD/F concentrations in steel plants varied from 0.234 to 0.577 ng/Nm<sup>3</sup> on a mass basis, and 0.048 to 0.166 ng/Nm<sup>3</sup> on a TEQ basis. In cement kiln plants, the mass concentration varied from 0.280 to 5.32 ng/Nm<sup>3</sup>, while TEQ concentration varied from 0.033 to 0.837 ng TEQ/Nm<sup>3</sup>. In general, PCDD/F emissions from steel industry in Vietnam were slightly lower than those reported for European Union, and were comparable to those reported for Taiwan and Korea. A similar trend was observed for the emissions of PCDD/Fs from cement kiln industry in Vietnam. PCDD/F emission factors for steel and cement kiln industries were also estimated to compare with the guidelines of the UNEP for persistent organic pollutants (POPs) inventory.

**Keywords:** PCDD/Fs; Emission; Vietnam; Steel industry; Cement kiln; Electric arc furnace.

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### INTRODUCTION

Vietnam ratified the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2004. Accordingly, activities toward reducing and controlling the release of unintentionally produced POPs such as polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) must be implemented in the country. PCDD/Fs are “man-made” toxic pollutants, which have been demonstrated to elicit health effects such as cancer, reproductive problems, developmental abnormalities, immune alterations, disruption of hormones (U.S EPA, 2000).

In Vietnam, environmental issues pertaining to contamination by dioxins and related health consequences have attracted a lot of attention from national and international

communities, since the 1970s. This is due to the fact that during the American War in Vietnam, about 80 million liters of defoliants including Agent Orange (AO), Agent White, Agent Purple, Agent Pink, Agent Green, and Agent Blue were used. The AO accounted for much of the total chemical sprayed over the southern Vietnam, which contain 2,3,7,8-TCDD as the most abundant toxic byproduct (Stellman *et al.*, 2003). As a consequence, about 3.06 million hectare of forests and crops were destroyed, 112 million cubic meters of lumber were lost. 2.1–4.8 million people were exposed to AO/dioxin during the spraying missions (Stellman *et al.*, 2003). The environmental effects and health consequences from AO spraying were observed until the present time. Great efforts from the Vietnamese Government and international communities have been made to overcome the consequences of AO/dioxin in the environment and human health (Minh *et al.*, 2010).

In addition to the issue of AO/dioxin, PCDD/Fs also emit from thermal processes of many industries in Vietnam. There are several different industrial categories, which have the potential to release PCDD/Fs into the environment. The

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emission of PCDD/Fs from waste combustion, metallurgical activities, and cement kiln plants has received great attention. In Vietnam, results from the assessment of the Best Available Technologies/Best Environmental Practices Project (UNIDO, 2012) suggested that those industrial sectors are of concern from the view of PCDD/PCDF emissions. In this study, for the first time, metallurgical industry and cement kiln plants in Vietnam were selected for investigating PCDD/Fs emissions into the environment.

In the recent decades, mechanism and characterization of dioxin formation/emission from combustion processes have been extensively studied. Sakai *et al.* (1999) point out that PCDD/F emissions from metallurgical activities in industrialized countries were higher than those from municipal waste incineration activities. It is also interesting to note that in Taiwan, PCDD/F emissions from waste combustion plants are becoming less important, and the attention is now directed toward other industrial sources, in particular, the metallurgical industry (Chang *et al.*, 2006). In Vietnam, steel industry was growing at a rate of 13.2% per year during 2005–2009 (UNIDO, 2012). In the same period, the steel consumption demand increased by about 15.7% per year and reached a total consumption estimate of 15.37 million tonnes in 2009. About 95% of steel plants use electric arc furnaces (EAFs) for the production processes. The EAF process includes stages of feeding, smelting, oxidation, reduction and steel discharge. So far, in Vietnam there is no official regulation to control PCDD/Fs emission from this industry (UNIDO, 2012). Besides, data on PCDD/Fs emission from this industry in Vietnam are also not available.

Cement kiln plants are another source of PCDD/Fs to the environment (UNIDO, 2012). PCDD/Fs can be detected at different levels in all types of solid samples collected from cement kiln facilities (Karstensen *et al.*, 2006; Karstensen, 2008). Due to the advantages of high temperature and long resident time, cement kilns are also utilized for co-processing of hazardous wastes in many countries (Karstensen, 2008). In 1999, the UNEP assigned an emission factor of 200  $\mu\text{g TEQ/ton}$  for cement kiln, and 2600  $\mu\text{g TEQ/ton}$  for cement kiln with co-processing of hazardous wastes. The UNEP (2005) revised the emission data and suggested three classes of emission factors (0.05, 0.6 and 5  $\mu\text{g TEQ/ton cement}$ ) for cement production facilities based on the differences in kiln types and the temperature of air pollution control devices (APCD). This fact reflects diversity in cement production technologies as well as improvement in this industry. In Vietnam, cement production in 2009 was 45.5 million tonnes and it is estimated that the production will reach 80 million tonnes by 2015. Currently, about 90.4% of cement is produced by dry rotary kiln, a technology with low PCDD/Fs emission factor assigned by the UNEP (2005); High capacity kilns (3000–6000 ton clinker per day) accounted for 68.9% of the production (UNIDO, 2012). Despite the increasing cement production over recent years, there is still very little data on the emission of PCDD/Fs in Vietnam. This is the first study in Vietnam to investigate PCDD/F emissions from such two important industries: steel and cement kiln plants. The data from this study will

provide more understanding on the emissions of PCDD/Fs in the country and contribute to its development of inventory of PCDD/Fs.

## METHODS

### *Sample Collection*

A total of 12 stack gas and 10 fly ash samples were collected in 2012, from two steel plants and three cement kiln plants in Vietnam in order to determine PCDD/Fs concentrations. The stack gas samples (consisting of both particulate and gas phases) in each of the selected plants were isokinetically sampled in accordance with the method 23 of the United States Environment Protection Agency (U.S EPA, 1998). Samples of stack gas were taken using the ESC C5000 sampling train (Environment Supply Company, USA). Before sampling, XAD-2 resin was spiked with  $^{13}\text{C}$ -PCDD/F surrogate standards. Particulate phase was collected on a quartz fiber filter (QFF, Pall Corporation, USA). Semi-volatile organic compounds (SVOCs) including PCDD/Fs in gas phase was pumped through a condenser and trapped in a chamber containing XAD-2 resin. Sampling of stack gas was conducted in the normal operating conditions of plants. Sampling duration for stack gas samples was typical, from three to four hours. The sample volumes were corrected to standard condition at 25°C, 760 mm Hg, dry gas basis and real operating O<sub>2</sub> levels. The isokinetic percent for stack gas sampling conducted in this study ranged from 95 to 103%, which is in an acceptable range of the US EPA method 23 (90–110%). In order to control cross contamination, travel blank and field blank samples were taken during each sampling event.

Representative fly ash samples were collected from hoppers under Air Pollution Control Device (APCD) and simultaneously with the stack gas. The fly ash samples for each APCD hopper were composite, made up of five sub-samples taken during stack gas sampling. The required sample weight of fly ash was approximately 200 g. All samples were kept at 4°C until chemical analysis. Basic information regarding the investigated plants is given in Table 1.

### *Analysis of PCDD/Fs*

Chemical analysis of PCDD/Fs was carried out by following the method 23 (U.S EPA, 1998) with some modifications. In particular, XAD-2 resin and QFF were combined for a representative sample of the corresponding stack gas. The samples were then Soxhlet extracted for 24 hours with 200 mL of toluene. The fly ash samples were air-dried and crushed to less than 1 mm; 10 g of the sample was then Soxhlet extracted by 200 mL of toluene for 24 hours.

The extracts were concentrated to 1 mL and further treated by concentrated sulfuric acid (98%). Clean-up steps were performed by the Fluid Management Systems (FMS, USA) and following the standard procedure recommended by the manufacturer (FMS, 2008) and was validated in our laboratory. Basically, pre-packed silica column (Silica #PCBS-ABN-STD, FMS), alumina column (Alumina #PCBA-BAS-011, FMS) and carbon column (Carbon #PCBC-CCE-034)

**Table 1.** Basic information of the investigated plants.

Parameters	Steel making		Cement kiln		
	EAF1	BOF1	CK1	CK2	CK3
Annual capacity ( $\times 1,000$ tons)	180	160	1,100	1,200	2,000
Operating time per year (hrs)*	7,920	7,920	7,920	7,920	7,920
APCDs in sequence	BHF	WSB	ESP	ESP	ESP
Average temperature of stack gas ( $^{\circ}\text{C}$ )	54	66	152	115	105
Average emission flow rate ( $\text{Nm}^3/\text{h}$ )	687,000	43,000	510,000	363,000	678,000
Oxygen content in stack gas (%)	20.7	8.1	8.3	8.0	9.8

EAF: Electric Arc Furnace; BOF: Blast Oxygen Furnace; CK: Cement Kiln.

ESP: Electrostatic precipitator; BHF: Bag House Filter; WSB: Wet Scrubber,

\* It is assumed that working duration of the steel-making and cement kiln plants are 330 days per year.

were used for cleanup and fractionation of PCDD/Fs. Finally,  $^{13}\text{C}$ -labeled injection standards were added to the concentrated aliquot of the sample and further evaporated under gentle nitrogen stream prior to quantification.

The quantification of seventeen 2,3,7,8-substituted PCDD/Fs congeners was carried out by isotope dilution method using high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC–HRMS) based on the Method 23 (U.S EPA, 1998) and Method 1613B (U.S EPA, 1994). In this study, quantification was conducted using Micromass Autospec Ultima system (Waters, UK) with Agilent 7890A gas chromatograph (GC) and DB-5MS capillary column (60 m  $\times$  250  $\mu\text{m}$  i.d  $\times$  0.25  $\mu\text{m}$  film thickness, J&W Scientific Inc., Folsom, CA). The oven temperature program was as follows: 140 $^{\circ}\text{C}$  to 220 $^{\circ}\text{C}$  at 5  $^{\circ}\text{C}/\text{min}$ , kept at 220 $^{\circ}\text{C}$  for 16 minutes, increased from 220 $^{\circ}\text{C}$  to 235 $^{\circ}\text{C}$  at 5  $^{\circ}\text{C}/\text{min}$ , kept at 235 $^{\circ}\text{C}$  for seven minutes, increased from 235 to 330 $^{\circ}\text{C}$  at 5  $^{\circ}\text{C}/\text{min}$  and kept at 330 $^{\circ}\text{C}$  for four minutes. The injector and interface temperatures were set at 290 $^{\circ}\text{C}$  and 250 $^{\circ}\text{C}$ , respectively. The mass spectrometer was operated with a resolution greater than 10,000 and positive electron impact conditions (EI). Data were obtained in the selected ion record (SIR) mode. The average recovery value of  $^{13}\text{C}$ -PCDD/Fs internal standards for stack gas and fly ash samples were ranged from 70 to 120%. For stack gas samples, the method detection limits were 1.00 and 2.00  $\text{pg}/\text{Nm}^3$  for *tetra*-CDD/Fs and *penta*- to *octa*-CDD/F congeners, respectively. The detection limits of the method for fly ash samples were 0.100, 0.500 and 1.00  $\text{ng}/\text{kg}$  for *tetra*-CDD/Fs, *penta*- to *hepta*-CDD/Fs and *octa*-CDD/Fs congeners, respectively.

Toxicity Equivalent Factors (TEFs) published by the World Health Organization (WHO) in 2005 were used for the calculation of TEQ in this study. It should be noted that there could be a small difference (less than 10%) between TEQs based on the WHO-TEFs and those based on I-TEFs (Dyke et al., 2002; Tian et al., 2012).

#### Emission Factors of PCDD/Fs

Based on the TEQ concentrations of the investigated emission sources (steel and cement plants), the emission factors of PCDD/Fs were calculated as follows:

$$\text{EF} = \frac{\text{Concentration (ngTEQ}/\text{Nm}^3) \times \text{Flowrate (Nm}^3/\text{h)}}{\text{Productrate (ton/h)} \times 1000} \quad (1)$$

where:

- Concentration: TEQ concentration in stack flue gas samples ( $\text{ng TEQ}/\text{Nm}^3$ )
- Flow rate: level of emission flow rate per hour ( $\text{Nm}^3/\text{h}$ )
- Product rate: annual capacity of plant (ton)

## RESULTS AND DISCUSSION

### PCDD/Fs Emission from Steel Plants

This is the first study in Vietnam to investigate PCDD/Fs emission from steel industries. The mean concentrations of PCDD/Fs in stack gas samples of EAF1 and BOF1 are presented in Table 2. The mass concentrations and TEQ of PCDD/Fs in EAF1 plant were 0.234  $\text{ng}/\text{Nm}^3$  and 0.048  $\text{ng TEQ}/\text{Nm}^3$ , respectively; whereas those in BOF1 plant were 0.577  $\text{ng}/\text{Nm}^3$  and 0.166  $\text{ng TEQ}/\text{Nm}^3$ , respectively.

In Taiwan, Chang et al. (2006) and Wang et al. (2009) reported that PCDD/Fs concentrations from EAF stack gas varied from 0.14–0.35  $\text{ng TEQ}/\text{Nm}^3$  and 0.148–0.757  $\text{ng TEQ}/\text{Nm}^3$ , respectively. In South Korea, Yu et al. (2006) reported slightly lower PCDD/F emissions from EAFs, varying from 0.004–0.182  $\text{ng TEQ}/\text{Nm}^3$ . The results of the present study suggest that PCDD/Fs emissions from EAFs in Vietnam were comparable to those in Taiwan and slightly higher than those observed in South Korea. In developed European Union countries, Quass et al. (2004) reported TEQ concentration in six ferrous foundries ranging from 0.003 to 0.184  $\text{ng I-TEQ}/\text{m}^3$ . These emissions were considerably lower than the results of EAFs in Vietnam (Table 4).

The average concentrations of PCDD/Fs in fly ash collected in EAF1 and BOF1 plants are presented in Table 3. The mean PCDD/Fs mass concentrations in fly ash of EAF1 and BOF1 were 342 and 325  $\text{ng TEQ}/\text{kg}$ , respectively. These concentrations were significantly higher than those of EAF plants in Taiwan (Chang et al. (2006) with approximately 74  $\text{ng TEQ}/\text{kg}$ . Moreover, TEQ concentrations of fly ash in the present study were comparable to those found in a sinter plant in the UK (253  $\text{ng TEQ}/\text{kg}$ ; Wang et al., 2003a). These results suggest that fly ash of the steel plants in Vietnam contained elevated levels of TEQs and thus may be of environmental concern, unless adequate management of this solid waste is followed.

### Congener Profile of PCDD/Fs Emission from Steel Plants

PCDD/Fs congener profiles in stack gas of EAF1 and

**Table 2.** Concentration of PCDD/Fs in stack gas of steel and cement kiln plants.

Compound name	Steel making		Cement kiln		
	EAF1 (n = 4)	BOF1 (n = 2)	CK1 (n = 2)	CK2 (n = 2)	CK3 (n = 2)
2,3,7,8-TCDD	0.009	0.023	0.032	0.075	0.003
1,2,3,7,8-PeCDD	0.015	0.075	0.057	0.128	0.008
1,2,3,4,7,8-HxCDD	0.007	0.011	0.003	0.004	0.009
1,2,3,6,7,8-HxCDD	0.011	0.013	0.030	0.068	0.009
1,2,3,7,8,9-HxCDD	0.011	0.010	0.025	0.060	0.007
1,2,3,4,6,7,8-HpCDD	0.021	0.008	0.039	0.036	0.021
OCDD	0.014	0.011	0.031	0.022	0.030
2,3,7,8-TCDF	0.006	0.017	0.206	1.215	0.011
1,2,3,7,8-PeCDF	0.022	0.073	0.156	0.852	0.017
2,3,4,7,8-PeCDF	0.046	0.148	0.229	0.978	0.025
1,2,3,4,7,8-HxCDF	0.014	0.067	0.225	0.829	0.034
1,2,3,6,7,8-HxCDF	0.005	0.056	0.126	0.442	0.031
1,2,3,7,8,9-HxCDF	0.012	0.034	0.119	0.342	0.028
2,3,4,6,7,8-HxCDF	0.009	0.009	0.023	0.083	0.006
1,2,3,4,6,7,8-HpCDF	0.016	0.016	0.078	0.168	0.011
1,2,3,4,7,8,9-HpCDF	0.011	0.005	0.003	0.009	0.007
OCDF	0.006	0.004	0.004	0.006	0.024
PCDDs (ng/Nm <sup>3</sup> )	0.089	0.150	0.218	0.394	0.086
PCDFs (ng/Nm <sup>3</sup> )	0.146	0.427	1.169	4.925	0.194
PCDD/PCDF ration	0.560	0.442	0.186	0.080	0.447
Total PCDD/F (ng/Nm <sup>3</sup> )	0.234	0.577	1.39	5.32	0.280
TEQ (ng TEQ/Nm <sup>3</sup> )	0.048	0.166	0.244	0.837	0.033
Emission factor (µg TEQ/ton of product)	1.45	0.353	0.878	1.45	0.089

EAF: Electric Arc Furnace; BOF: Blast Oxygen Furnace; CK: Cement Kiln.

TEQ calculated basing on WHO-TEFs (2005).

Emission factors were calculated basing on formula given by UNEP Toolkit (2005).

**Table 3.** Mean PCDD/F concentration in fly ash of steel and cement kiln plants.

Compound name	Steel making		Cement kiln		
	EAF1 (n = 2)	BOF1 (n = 2)	CK1 (n = 2)	CK2 (n = 2)	CK3 (n = 2)
2,3,7,8-TCDD	56.3	86.2	< 0.100	< 0.100	1.38
1,2,3,7,8-PeCDD	148	213	0.172	0.276	1.45
1,2,3,4,7,8-HxCDD	< 0.500	17.6	< 0.500	< 0.500	1.34
1,2,3,6,7,8-HxCDD	11.3	19.2	< 0.500	0.165	1.78
1,2,3,7,8,9-HxCDD	11.2	19.0	< 0.500	< 0.500	2.23
1,2,3,4,6,7,8-HpCDD	5.91	3.17	7.90	0.897	11.9
OCDD	< 1.00	0.844	68.3	19.9	36.0
2,3,7,8-TCDF	35.7	2.65	3.59	< 0.100	32.4
1,2,3,7,8-PeCDF	21.6	12.8	0.640	0.173	6.1
2,3,4,7,8-PeCDF	347	30.7	2.65	< 0.100	8.4
1,2,3,4,7,8-HxCDF	138	31.6	3.42	0.492	5.5
1,2,3,6,7,8-HxCDF	97.0	27.2	2.01	< 0.500	3.8
1,2,3,7,8,9-HxCDF	30.8	25.9	1.42	< 0.500	3.4
2,3,4,6,7,8-HxCDF	< 0.500	13.9	< 0.500	< 0.500	1.0
1,2,3,4,6,7,8-HpCDF	23.8	3.66	2.41	< 0.500	9.4
1,2,3,4,7,8,9-HpCDF	4.97	4.23	< 0.500	< 0.500	1.2
OCDF	< 1.00	< 1.00	< 1.00	< 1.00	6.2
PCDDs (ng/kg)	233	359	76	21	56
PCDFs (ng/kg)	698	153	16	0.665	77
PCDD/PCDF ration	0.333	2.35	4.73	31.95	0.723
Total PCDD/F (ng/kg)	931	512	92.5	21.9	134
WHO TEQ (ng TEQ/kg)	342	325	2.23	0.373	10.9

EAF: Electric Arc Furnace; BOF: Blast Oxygen Furnace; CK: Cement Kiln.

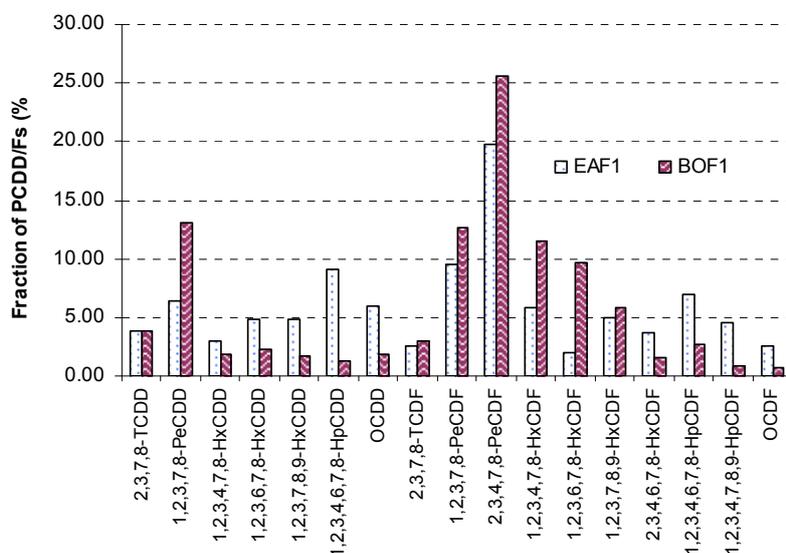
BOF1 are illustrated in Fig. 1. It should be noted that in these profiles, PCDD/Fs concentrations are presented in mass basis instead of TEQ basis. Each 2,3,7,8-substituted PCDD/Fs congener was normalized to the sum concentration of 17 PCDD/Fs. It can be seen that PCDFs were dominant over PCDDs in the stack gas of both the steel plants. In EAF1 plant, 2,3,4,7,8-PeCDF congener was abundant in stack gas (accounted for 23.2%), followed by 1,2,3,7,8-PeCDD (9.6%), 1,2,3,7,8-PeCDF (7.0%) and 2,3,7,8-TCDF (6.4%). As for BOF1 plant, the major congeners in stack gas were 2,3,4,7,8-PeCDF (26.2%), followed by 1,2,3,7,8-PeCDD (16.2%), 1,2,3,4,7,8-HxCDF (11.0%), and 1,2,3,7,8-PeCDF (10.0%). It was reported in previous studies that 2,3,4,7,8-substituted PeCDFs were the typical congeners in stack gas of sintering and EAF plants (Aries et al., 2006; Chang et al., 2006). In this study, PeCDFs in stack gas accounted for 30.2% and 36.1% of total PCDD/F concentrations in EAF1 and BOF1, respectively. The contribution of 2,3,7,8-substituted PeCDF in stack gas of both EAF1 and BOF1 plants were lower in comparison with those reported by Chang et al. (2006). Nevertheless, 2,3,7,8-substituted PeCDF in stack gas as the major congeners agrees with the results found for sintering plants (Wang et al., 2003b; Wang et al., 2009). The trends of PCDD/F congener profiles in fly ash of EAF1 and BOF1 plants were different. Fig. 2 indicates that PCDFs were the major congeners to total PCDD/F concentrations for EAF1 plant, while PCDDs were the major congeners for BOF1 plant. For EAF1 plant, 2,3,4,7,8-PeCDF was the highest, followed by 1,2,3,7,8-PeCDD (16.0%) and 1,2,3,4,7,8-HxCDF (14.9%). Whereas, 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were the dominant congeners in fly ash of BOF1 plant, which accounted 17.0% and 41.9% respectively. Previous studies reported that high chlorinated congeners dominate the distribution in fly ash of sinter plant and EAF plant (Aries et al., 2006; Chang et al., 2006). The PCDD/F congener profiles in fly ash of EAF1 and BOF1 in this case study were totally different trend compared to those studies. Higher concentrations of

PCDDs from BOF1 plant than in EAF plant may be due to the fact that the feedstock in BOF1 contained up to 50% of cast iron and scraps while those in EAF1, it was only about 5–10%. The contents of cast iron and scraps are diverse and very variable which may contain precursors for specific PCDD/F congeners. It might be explained that presence of low chlorinated aromatic compounds in feedstock may lead to formation of low chlorinated PCDD/F through precursors, which is considered to be characteristic of precursors formation (Buser et al., 1978; Gullett et al., 1992). Besides, it was recognized that BOF1 plant underwent some maintenance activities before the sampling survey and it is unclear if it reached a stable manufacturing conditions. Differences in operating conditions of the plants could be reasons for elevated PCDDs found in BOF1. Therefore, further investigations need conduct fly ash samples from more EAF and BOF plants in Vietnam as well as identify feedstock containing precursors in order to understanding typical PCDD/F congener profiles in fly ash of steel plants.

**PCDD/Fs Emission Factor of the Steel Plants**

The mean emission factors of PCDD/Fs from the stack gas of EAF1 and BOF1 were estimated and presented in Table 2. The emission factors were calculated based on the average flow rates of stack gas and the operating time per year of each plant (about 7920 hours, Table 1). As can be seen in Table 2, the emission factor of PCDD/Fs in EAF1 plant was 1.44 µg TEQ/ton of product while that in BOF1 plant was 0.353 µg TEQ/ton.

The PCDD/Fs emission factor for four sintering plants in China was 3.95 µg TEQ/ton (Tian et al., 2012) and for EAFs in Taiwan was from 1.84 to 2.44 µg TEQ/ton (Chiu et al. (2011)). The emission factors in Vietnam were comparable to those reported in Taiwan and slightly lower than those in China. Iron and steel production plants have been identified under the sub-categories of ferrous and non-ferrous categories of the UNEP Toolkit (UNEP, 2005). In this toolkit, emission factors of seventeen 2,3,7,8-substituted



**Fig. 1.** Congeners profiles of PCDD/Fs in stack gas samples of the steel plants.

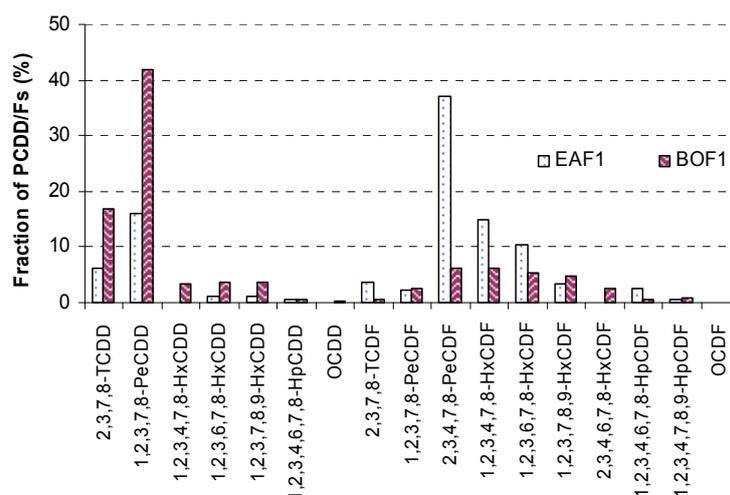


Fig. 2. Congeners profile of PCDD/Fs in fly ash samples of the steel plants.

PCDD/Fs to the air of EAF and BOF using clean scrap were 3 and 0.1  $\mu\text{g TEQ/ton}$  liquid steel, respectively. Overall, the emission factor of EAF1 plant (1.44  $\mu\text{g TEQ/ton}$ ) was lower than the default value of the toolkit (3.0  $\mu\text{g TEQ/ton}$ ), while that for BOF1 plant was higher than the default value (0.353 versus 0.1  $\mu\text{g TEQ/ton}$ ).

To our knowledge, this is the only available data in Vietnam on the PCDD/Fs emission factors, which were estimated based on the real measurements of air emission of PCDD/Fs from the domestic steel industry. The results of the present study may suggest that the PCDD/Fs emission factor to the air in Vietnam could be around 1.40  $\mu\text{g TEQ/ton}$  for EAFs and around 0.3  $\mu\text{g TEQ/ton}$  for BOFs. Further studies are necessary in order to provide more comprehensive data on the PCDD/F emission from steel-making processes in Vietnam.

#### PCDD/Fs Emission from Cement Kiln Plants

Six stack gas samples were collected from three cement kilns (denoted as CK1, CK2 and CK3). The CK1 and CK2 cement kiln plants are in the north of Vietnam, while CK3 cement kiln plant is in the south. These cement kiln plants are equipped with a five-stage pre-heater and a pre-calciner system. The stack gas samples were collected twice at each cement kiln. Mean PCDD/F mass concentration and TEQ are summarized in Table 2. PCDD/F mass concentration varied from 0.28 to 5.32  $\text{ng/Nm}^3$  while TEQ varied from 0.033 to 0.837  $\text{ng TEQ/Nm}^3$ . The highest TEQ concentration was found in CK2 with 0.837  $\text{ng TEQ/Nm}^3$ , which is exceeding the regulatory guideline issued by the Vietnamese Government for co-processing of hazardous waste in cement kiln (0.6  $\text{ng TEQ/Nm}^3$ ; QCVN 41:2011/BTNVMT). Other samples exhibited much lower TEQ concentrations compared to the Vietnamese guideline. In comparison, the European Union (EU) issued the guideline for PCDD/Fs emission from cement kilns of 0.1  $\text{ng TEQ/Nm}^3$ , which is six-fold lower than those in Vietnam. It is also seen that two kilns in the present study had concentrations higher than the EU guideline (the kiln CK1 and CK2 with TEQ of 0.244 and 0.837  $\text{ng TEQ/Nm}^3$ , respectively). Among the three

investigated kilns, CK3 was installed with the most modern technologies for combustion and APCD. As the result, stack gas from CK3 had the lowest TEQ level, which was below both the guideline (0.033  $\text{ng TEQ/Nm}^3$ ). In an earlier test burn for insecticides carried out in the cement kiln namely Holcim (Vietnam), Karstensen (2006) showed that air concentrations of all 17 PCDD/F congeners were below the detection limit and thus calculation using half the detection limit value gave 0.095 and 0.014  $\text{ng TEQ/m}^3$  for baseline and the test burn, respectively.

Table 4 shows geographical comparison of PCDD/Fs emission among various countries. It can be seen that stack gas PCDD/Fs concentrations from cement kilns in Vietnam were relatively higher than those reported in the industrialized countries (EU countries: 0.016  $\text{ng TEQ/Nm}^3$ , Japan: < 0.094  $\text{ng TEQ/Nm}^3$ , Australia: 0.001–0.007  $\text{ng TEQ/Nm}^3$ ) as well as in some developing countries (Thailand: 0.105  $\text{ng TEQ/Nm}^3$ , Sri Lanka: 0.018  $\text{ng TEQ/Nm}^3$  and Philippines: 0.00038–0.013  $\text{ng TEQ/Nm}^3$ ).

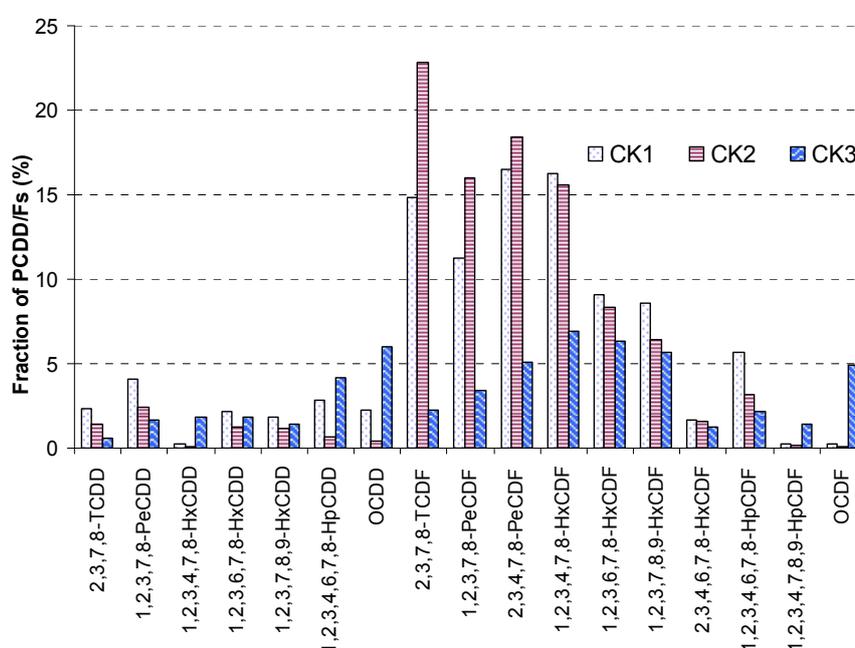
Table 3 shows the total TEQ concentrations in fly ash samples collected in three cement kiln plants. The TEQ levels were between 0.373–10.9  $\text{pg TEQ/g dry wt}$ . In Vietnam, there is no regulation regarding to the maximum level of TEQ in fly ash from cement kilns. However, compared with the available data in the world, the results of this study are within the typical range of values reported elsewhere. For example, low TEQ concentrations in dust samples of cement kilns were reported in several studies in the UK (0.001–30.0  $\text{pg TEQ/g dry wt}$ , Ames *et al.*, 2012) and Germany (1.0–40.0  $\text{pg TEQ/g dry wt}$ , Zemba *et al.*, 2011).

#### Congener Profile of PCDD/Fs Emission from Cement Kiln Plants

Fig. 3 shows PCDD/Fs congener profiles in stack gas samples collected in the cement kilns. It can be seen that in PCDD/F congener profiles from the cement kilns of this study, PCDFs contributed higher mass percentage than that of PCDDs. All seventeen PCDD/Fs were found in the stack gas samples, and the mass distribution of PCDFs is dominant over PCDDs in all stack gas samples. For stack gas samples,

**Table 4.** Comparison of PCDD/F emission in some countries in the world.

Country	Year of reference	Sample kind	Conc. Range (ng I-TEQ/Nm <sup>3</sup> )	References
<i>Steel industry</i>				
Taiwan	2009–2010	Stack gas	0.148–0.757	Wang et al., 2009; Wang et al., 2010
Korea	2006	Stack gas	0.004–0.128	Yu et al., 2006
Germany	2001	Stack gas	0.010–0.260	Quass et al., 2004
Canada	2003	Stack gas	0.044–0.254	Canadian Council, 2004
<i>Cement kiln industry</i>				
Australia	2002	Stack gas	0.001–0.007	Karstensen, 2008
European Union	2004	Stack gas	0.016	Karstensen, 2008
Japan	2000	Stack gas	0.094	Karstensen, 2008
Thailand	2001	Stack gas	0.0105	Karstensen, 2008
Sri Lanka	2001	Stack gas	0.018	Karstensen et al., 2010
Philippines	2004	Stack gas	0.0059–0.013	Lang Th., 2004
Philippines	2005	Stack gas	0.00038–0.0013	Schimpf, 2005
Vietnam	2006	Stack gas	0.014	Karstensen, 2006



**Fig. 3.** Congener profile of PCDD/Fs in stack gas samples of the cement kiln plants.

the fractions of PCDFs in total PCDD/Fs were 69.1%; 84.3% and 92.6% for CK3, CK1 and CK2, respectively. Besides, congeners 2,3,4,7,8-PeCDF and 1,2,3,4,7,8-HxCDF were the most abundant among PCDFs.

PCDD/F congener profiles in dust samples of the three cement kiln plants were illustrated in Fig. 4. Generally, all 17 PCDD/F congeners were found in the dust samples with different concentration ranges. However, major contributions were from HpCDDs, OCDD and TCDF. The congener profiles in cement kilns were in agreement with those reported by Karstensen (2008) and Ames et al. (2012).

Fig. 4 demonstrates that the contribution of OCDD congener in fly ash samples ranged from 27% to 91% for CK3 and CK2, respectively. It is interesting to note that while the contribution of OCDD congener in fly ash of the CK3 (27%) was in a typical range of reported value (Ames

et al., 2012), those of CK2 (91%) was relatively elevated. A reason for this phenomenon is still unclear. However, in our observation, there could be a number of factors that lead to the elevated levels of OCDD in the fly ash of CK2. Firstly, the average emission flow rate at CK2 plant was relative low in comparison with CK1 and CK3 (Table 1). This low flow rate might influence the distribution of OCDD between gas phase and particulate phase and preferential adsorption of OCDD in particulates (due to its lower vapour pressure). Ames et al. (2012) also observed similar phenomenon with relatively high OCDD in emission samples from two cement kilns.

**PCDD/Fs Emission Factor of the Cement Kiln Plants**

The PCDD/Fs emission factors of the cement kilns were estimated similar with those of the steel plants, as

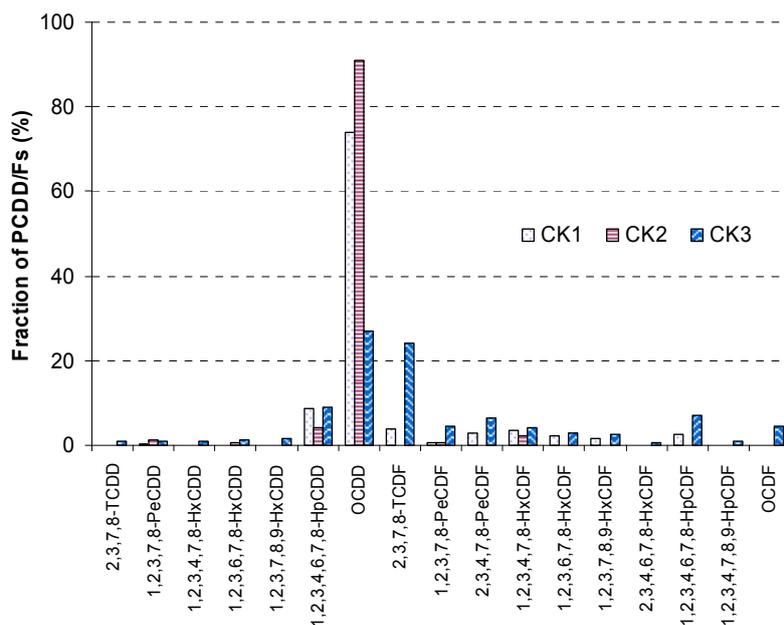


Fig. 4. Congener profile of PCDD/Fs in fly ash samples of the cement kiln plants.

discussed earlier. The calculation of emission factors for the cement kilns was based on the average flow rates of stack gas and the operating time per year of each plant (Table 1), and results are presented in Table 2. The emission factors of PCDD/Fs for three cement kilns in this study ranged 0.089–1.450  $\mu\text{g TEQ/ton}$  of product. Similar measurements were made in Australia during 1991–2001 and showed that PCDD/Fs emission in cement kilns ranged 0.0032–0.216  $\mu\text{g TEQ/ton}$  cement (Environment Australia, 2002; Pacific Air and Environment, 2002). In Spain, the average emission factors per ton of clinker and cement in 2000–2003 were 36.53 and 28.82  $\text{ng TEQ/ton}$  product, respectively (Fabrellas *et al.*, 2004). A report of UNEP (UNEP, 1999) showed that the emission factor of PCDD/Fs from the cement industry in Germany in 1995 was 0.0448  $\mu\text{g TEQ/ton}$  cement. In comparison with the above results, the emission factors at three cement kiln plants in Vietnam are higher than those reported in the industrialized countries. Perhaps, differences in characteristics and operation of difference technologies for APCD may cause the higher emission in cement kilns in Vietnam. It is important to note that PCDD/Fs concentration in the stack gas (and thus the emission factor) is influenced by temperature of the EPS (UNEP, 2005). Consequently, a default emission factor of 5  $\mu\text{g TEQ/ton}$  of cement is assigned to vertical shaft kilns and wet kilns with duct collectors over 300°C; the factor of 0.6  $\mu\text{g TEQ/ton}$  of cement is for wet kilns where the dust collector temperature between 200°C–300°C; and the factor of 0.05  $\mu\text{g TEQ/ton}$  of cement is for all dry and wet kilns where dust collector temperature below 200°C.

In this study, the emission factor of CK3 is 0.089  $\mu\text{g TEQ/ton}$  of product, which is lower compared to those of CK1 and CK2 (Table 2). As above discussion, the higher emission factor of CK1 and CK2 compared to CK3 was perhaps due to different temperature in dust collection area of such cement kilns. In fact, CK3 is a modern plant, its

operating parameters are monitored at the controlling center and the dust collector temperature was maintained at about 145°C. On the other hand, the dust collector's temperature in the CK1 and CK2 varied between 230°C–250°C. It is also interesting to observe a large drop of temperature from the dust collector of CK2 to its sampling point (115°C, Table 1). This phenomenon may be due to lower flow rate of exhausted gas in CK2 (7.46 m/s) compared to those of CK1 and CK3 (20.0 m/s and 17.5 m/s, respectively). Besides, it was also seen in the sampling survey that CK2 had longer piping from APCD to the stack compared to the other kilns.

Another factor contributes to the lower emission factor of CK3 is that as being mentioned elsewhere in previous parts, CK3 is equipped with the advanced APCD using ESP which results in higher efficiency for dust removal, leading to lower PCDD/Fs concentration in the emission samples of CK3. In fact, the measured data on TSP (Total Suspended Particulates) in emission gas of three cement kilns showed that CK3 kiln had the lowest TSP concentration (33.0  $\text{mg/Nm}^3$ ) compared to CK1 (57.9  $\text{mg/Nm}^3$ ) and CK2 (91.3  $\text{mg/Nm}^3$ ).

On the other hand, according to the *de novo* synthesis, PCDD/Fs are formed on the surface of particulates and tend to be absorbed in their surface, especially for fine particulates. Therefore, accumulation of the particulates in APCD of CK3 (due to the higher dust removal efficiency) could be a reason for higher PCDD/Fs level found in fly ash of CK3 compared to the other kilns.

This is the first study designed to investigate PCDD/Fs emission representing for cement kiln industry in Vietnam. We believe that more comprehensive picture on PCDD/Fs emission from the cement industry can be obtained when more samples are collected from larger number of plants with diverse production and APCD technologies. Therefore, future studies toward these directions may be needed for better understandings and accurate PCDD/Fs emission inventory.

## CONCLUSIONS

Emission of PCDD/Fs from steel and cement kiln plants was investigated in Vietnam for the first time. The results suggested that PCDD/F emissions from the steel industry were comparable to those in some countries in Asia, but higher than those of the industrialized countries in European Union. On the other hand, PCDD/Fs emission from the cement kiln industry was slightly higher than in most of the referenced countries. Basing on the actual measurements, the emission factors of PCDD/Fs in steel industry were estimated to be between 0.353 and 1.45  $\mu\text{g}$  TEQ per ton of product, while those for cement kilns were from 0.089 to 1.45  $\mu\text{g}$  TEQ per ton of product. This study provides important data to implement more accurate PCDD/F emission inventory from the industries in Vietnam. Moreover, with the rapid development of industries in recent years, there should be continuous investigations with larger number of plants.

In order to reduce PCDD/Fs emissions from industries in Vietnam, selection and application of BAT/BEP (Best Available Technologies/Best Environmental Practices) are practical solutions since investment in new technologies will cost relatively large budgets. In particular, for steel plants, solutions may include screening for raw materials, optimization of temperatures and reinforcement of gas treatment devices. For cement kilns, good control of APCD such as maintaining temperature of dust collector around 150°C, improving dust removal efficiency and using active carbon for further adsorption of PCDD/Fs is very important to minimize the PCDD/Fs emission.

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