EMISSION OF POLYCHLORINATED DIBENZO-*p*-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM SEVERAL TYPICAL STEEL MAKING AND CEMENT KILN PLANTS IN VIETNAM

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Introduction

Vietnam has joined 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. In Vietnam, results from assessment of the Best Available Technologies/Best Environmental Practices project suggest that those industrial sectors may cause environmental concern due to PCDD/PCDFs emission, especially metallurgical industry and cement kilns[1]. This is the first study in Vietnam to investigate PCDD/Fs emission from two important industries: steel-making and cement kiln plants. The data from this study will provide more understandings on emission of PCDD/Fs in the country and contribute to its future inventory.

Materials and methods

Total of 12 stack gas and 10 fly ash samples were collected in 2012, from two steel-making plants and three cement kiln plants in Vietnam in order to determine PCDD/Fs concentrations. The stack gas samples (both of particulate and gas phases) in each selected plants was isokinetically sampled in accordance with US EPA method 23[2]. The isokinetic percent for stack gas samplings conducted in this study ranged from 95 to 103 %. In order to control cross contaminations, travel blank and field blank samples were taken during each sampling survey. Representative fly ash samples were taken from hoppers under APCD and simultaneously with sampling of stack gas. All samples were kept at 4^0C until chemical analysis. Table 1 gives basic information regarding the investigated plants.

Chemical analysis of PCDD/Fs was carried out following method 23 with some modifications. In particular, XAD2 resin and QFF from each sampling were combined for a representative sample of the corresponding stack gas. The fly ash samples were air-dried and crushed to less than 1mm; 10 g of the fly ash and stack gas sample was then Soxhlet extracted by 200 ml of toluene at 24 hours. Clean-up steps were performed by the Fluid Management Systems (FMS) and following the standard operation procedure recommended by FMS and was validated by our laboratory[3]. Quantification of seventeen 2,3,7,8-substituted PCDD/Fs congeners were carried out by isotope dilution method using high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC–HRMS) based on method 23 and method 1613B[2,4]. The average recovery value of ^{13}C-PCDD/Fs internal standards for samples were ranged from 70 to 120%.

Table 1. Basic information of the investigated plants

	Steel making		Cement kiln		
Parameters	EAF1	BOF1	CK1	CK2	CK3
Annual capacity (x1,000 tons)	180	160	1,200	1,500	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 (^{o}C)	54	66	152	115	105
Average emission flow rate (Nm^3/h)	687,000	43,000	510,000	263,000	678,000
Oxygen content in stack gas (%)	20.7	8.1	8.3	8	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

Results and discussion

PCDD/Fs emission from steel-making plants

Mean concentrations of PCDD/Fs in stack gas samples of EAF1 and BOF1 are presented in Table 2. The mass and TEQ concentrations of PCDD/Fs in EAF1 plant were 0.234 ng/Nm^3 and 0.048 ng TEQ/Nm^3, respectively; while those in BOF1 plant were 0.577 ng/Nm^3 and 0.166 ng TEQ/Nm^3. Results of the present study suggests that PCDD/Fs emission from EAFs in Vietnam is comparable to those in Taiwan and only slightly higher than South Korea[5,6]. Quass *et al*. reported TEQ concentration from six ferrous foundries ranging from 0.003 to 0.184 ng I-TEQ/m^3 in developed nations in European Union[7].

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

	Steel making		Cement kiln		
Compound name	EAF1 (*n=4*)	BOF1 (*n=2*)	CK1 (*n=2*)	CK2 (*n=2*)	CK3 (*n=2*)
PCDDs (ng/Nm^3)	0.089	0.150	0.218	0.394	0.086
PCDFs (ng/Nm^3)	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^3)	0.234	0.577	1.39	5.32	0.280
TEQ (ng TEQ/Nm^3)	0.048	0.166	0.244	0.837	0.033
Emission factor (µg TEQ/ton of product)	1.45	0.353	0.897	1.45	0.093

- 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)

The average concentrations of PCDD/Fs in fly ash collected in EAF1 and BOF1 plants are presented in Table 3. The mean PCDD/Fs concentrations in fly ash of EAF1 and BOF1 were 342 and 325 ng TEQ/kg, respectively. These concentrations were significantly higher than those from EAF plants reported approximately 74 ng TEQ/kg[8]. This fact suggests that fly ash of the steel-making plants in Vietnam contain elevated TEQ levels and thus may be of environmental concern unless adequate management of this solid waste is applied.

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

	Steel making		Cement kiln		
Compound name	EAF1 (*n=2*)	BOF1 (*n=2*)	CK1 (*n=2*)	CK2 (*n=2*)	CK3 (*n=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

PCDD/Fs congeners profile in stack gas of EAF1 and BOF1 were illustrated in Figure 1. It can be seen that PCDFs were dominant over PCDDs in the stack gas of both the steel-making plants. In EAF1 plant, congener 2,3,4,7,8-PeCDF was the most abundant in stack gas, followed by 1,2,3,7,8-PeCDD, 1,2,3,7,8-PeCDF and 2,3,7,8-TCDF. As for BOF1 plant, the major congeners in stack gas were 2,3,4,7,8-PeCDF, followed by 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDF and 1,2,3,7,8-PeCDF. The contribution of 2,3,7,8-substituded PeCDF in stack gas of both EAF and BOF plants were lower in comparison with those reported[8]. Nevertheless, 2,3,7,8-substituded PeCDF presence in stack gas as the major congeners agrees well with that reported in sinter plants[9,10]. The trends of PCDD/Fs congeners profile in fly ash of EAF1 and BOF1 plant were different. Figure 2 indicates that PCDFs were major congeners to the total PCDD/Fs concentrations for EAF1 plant, while PCDD 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 and 1,2,3,4,7,8-HxCDF. Whereas, 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were dominants in fly ash of BODF1 plant. Higher concentrations of PCDD from BOF1 plant than EAF plant may reflect differences in the feeding materials, operating condition and dust removal efficiency of APCD in the plants [9,10].

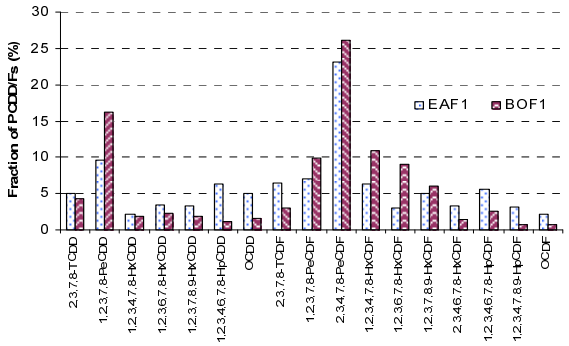

Fig. 1. Congeners profiles of PCDD/Fs in stack gas samples of the steel-making plants

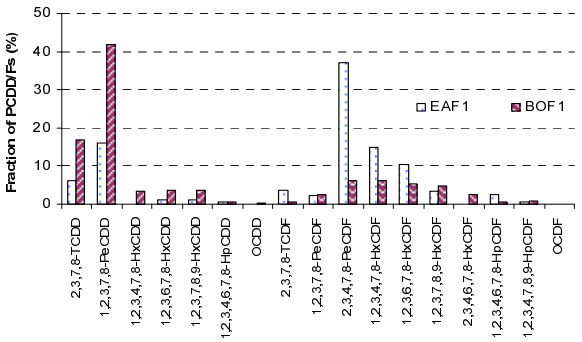

Fig. 2. Congeners profile of PCDD/Fs in fly ash samples of the steel-making plants

The mean emission factor of PCDD/Fs from the stack gas of EAF1 and BOF1 plant were estimated shown in Table 2. The emission factor of PCDD/Fs in EAF1 plant was 1.44 µg TEQ/ton, while those in BOF1 plant was 0.353 µg TEQ/ton. Our results were similar to available data reported in China in 2012[11], but also lower than that in Taiwan[12], which accounted was 1.84-2.44 µg I-TEQ/ton EAF steel. Iron and steel production plants have been identified as the sub-categories in ferrous and non-ferrous categories of UNEP Toolkit[13]. To our knowledge, this is the only available data in Vietnam on PCDD/Fs emission factors which was estimated basing on measurement of air emission of PCDD/Fs from the domestic steel-making industry. Further studies are necessary in order to provide more comprehensive data on the PCDD/Fs concentrations in steel-making process in Vietnam and thereby estimation of the emission factors may reflect better the actual operating conditions.

PCDD/Fs emission from cement kiln plants

Six stack gas samples were collected from three cement kilns (name as CK1, CK2 and CK3). Mean concentration of PCDD/Fs and TEQ are summarized in Table 2. Mean mass PCDD/Fs concentration varied from 0.28 to 5.32 ng/Nm^3, while TEQ varied from 0.033 to 0.837 ng TEQ/Nm^3. The highest TEQ concentration was found in CK2 with 0.837 ng TEQ/Nm^3 which is exceeding the regulation guideline issued by the Vietnam Government for co-processing of hazardous waste in cement kiln (0.6 ng TEQ/Nm^3; QCVN 41:2011/BTNVMT)[14]. Other samples exhibited much lower TEQ concentration compared to the Vietnamese guideline. In fact, the European Union (EU) and UNEP proposed guidelines for PCDD/Fs emission from cement kilns of 0.1 ng TEQ/Nm which is 6-fold lower than those in Vietnam[13]. If compared to the EU and UNEP guidelines, two kilns in the present study had higher concentration (0.244 and 0.837 ng TEQ/Nm^3 for CK1 and CK2, respectively). Among the tree investigated kilns, CK3 was installed with the modest combustion technology and APCD. As the result stack gas from CK3 had lowest TEQ level which was below both the guideline (0.033 ng TEQ/ Nm^3). Table 3 shows total TEQ concentration in fly ash samples collected in three cement kiln plants. The TEQ levels were between 0.373 – 10.9 pg TEQ/g dry wt. In Vietnam, there is no regulation regarding to maximum level of TEQ in fly ash in cement kiln. However, in compared to available data, the results from this study are relatively comparable. For example, low TEQ concentrations in dust sample of cement kilns were reported in several studies in UK (0.001-30.0 pg TEQ/g dry wt.)[15] and Germany (1.0-40.0 pg TEQ/g dry wt)[16].

Figure 3 showed PCDD/Fs congener profiles in stack gas samples collected in the cement kilns. PCDF contribution was higher than that of PCDD. All seventeen PCDD/Fs were found in the stack gas samples, and the presence of PCDD decreased when increasing of chlorine atom in the molecular from TCDD, PeCDD to OCDD. The same trend was observed for PCDF congener. The results also comport with those reported by Karstensen[17]. PCDD/Fs congeners profile in dust samples collected in the three cement kiln plants were illustrated in Figure 4. Generally, all of seventeen PCDD/Fs congeners were found in the dust samples with different range of concentration. However, the contribution of HpCDD, OCDD and TCDF has dominated total

PCDD/F concentration. PCDD/Fs congener profiles in this study were in well agreement with those presented prevously[15,17].

Similarly, the PCDD/Fs emission factors of the cement kiln plants were estimated same as the emission factor of the iron and steel making plants. The calculated results were presented in Table 2, the emission factor of PCDD/Fs for three cement kiln plants ranged between 0.093 to 1.450 µg TEQ/ton of product. These results were similar to available data reported previously[18,19]. UNEP prepared in 1999, a national and regional inventory of PCDD/Fs emissions showing that the emission factor of PCDD/Fs from the cement industry in Germany in 1995 was 0.0448 µg TEQ/ton cement[20].

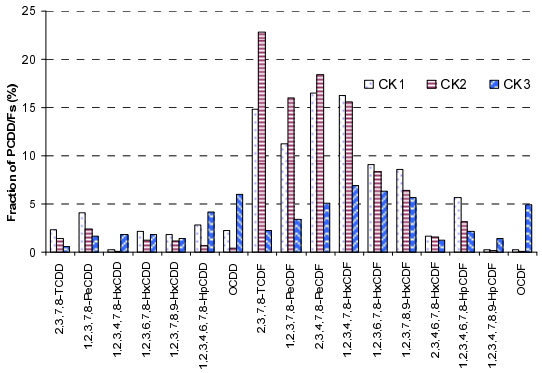

Fig. 3. Congener profile of PCDD/Fs in stack gas samples of the cement kiln plants

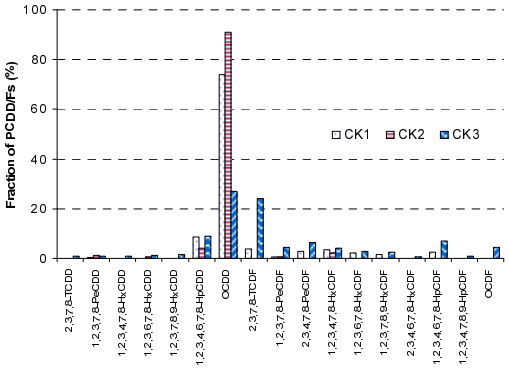

Fig. 4. Congener profile of PCDD/Fs in fly ash samples of the cement kiln plants

Comparison of our results with other reported data, the emission factors at three cement kiln plants in Vietnam are slightly higher than that in industrialized countries. This is the first and preliminary research presenting results about the PCDD/Fs pollution status and estimated the emission factor for cement kiln industry in Vietnam. In order to have more comprehensive information the emission of PCDD/Fs further studies may be needed in future.

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