VNU Journal of Science: Earth and Environmental Sciences, Vol. 32, No. 2 (2016) 79-84

Characteristics of Dioxin and Furan Emissions from Selected Electric Arc Furnaces in Vietnam

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Received 08 January 2016
Revised 22 January 2016; Accepted 28 June 2016

Abstract: Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) released from thermal processes of various industries have urgently concerned. Stack gas samples were collected from selected electric arc furnaces (EAFs) in Vietnam in order to investigation of PCDD/F concentration, congener profile and emission factors. U.S EPA method 23 was used following the requirements for isokinetic sampling of stack gas emission. The quantification of PCDD/Fs was carried out by high resolution gas chromatography, coupled with high resolution mass spectrometry (HRGC/HRMS). The results suggested that mass concentration and TEQ of PCDD/F in stack gas samples from EAFs in Vietnam ranged from 0.077–2.26 ng/Nm^3 and 0.027–0.264 ngTEQ/Nm^3, respectively. Emission factors of PCDD/Fs are determined in the range of 0.89 – 2.03 µgTEQ/ton of product. Emission factor of PCDD/F from the EAF plants in Vietnam were equivalent to those in some countries in Asia, but higher than those of the industrialized countries in European Union.

Keywords: PCDD/Fs, EAFs, Stack gas, Emission Factors.

1. Introduction

Dioxin contamination from Agent Orange in Vietnam has been received much attention for the past decades. Besides that, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) released from thermal processes of various industries have urgently concerned. The industrialized countries such as the UK, the US and Japan, emission of PCDD/Fs from waste incinerators remain as a major source from the industrial activities, responsible for 30-56, 38 and 87%, respectively, of the total emissions (UNEP, 1999) [1]. In the UK [2], the emissions from metal sector including sinter plants, steel and non-ferrous metals, contribute in total dioxin emissions from 15 to 26%. The PCDD/Fs emissions inventory in Taiwan has reported that sinter plants and electric arc furnaces were more important sources than from waste incinerators, contributing 32 and 23% to the total emissions, respectively [3].

In Vietnam, steel industry was growing at a rate of 13.2% per year during 2005-2009

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(UNIDO, 2012) [4]. In the same period, the steel consumption demand increased by about 15.7% per year and reached a total consumption estimated of 15.37 million tonnes in 2009. About 95% of steel plants use electric arc furnaces (EAFs) for the production processes [4]. The EAF process includes stages of feeding, smelting, oxidation, reduction and steel discharge.

This is one of the first studies in Vietnam to investigate PCDD/Fs emissions from EAF plants. The data from this study will provide more understanding about the emissions of PCDD/F in the country and contribute to its development of inventory of PCDD/F.

2. Experiment

2.1. Sample collection

Four typical EAF in Luu Xa, Thai Binh Duong, Dana-Y and Bien Hoa steel plants have been selected for investigation of dioxin and furan release to the air. Basic information regarding the investigated plants is given in Table 1. The stack gas samples (consisting of both particulate and gas phases) in each of the selected EAFs were isokinetically sampled in accordance the method 23 of the United States Environment Protection Agency (U.S EPA, 1998) [5]. 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}CPCDD/F surrogate standards. Particulate phase was collected on a quartz fiber filter (QFF, Pall Corporation, USA). 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.

2.2. Chemical analyses

Chemical analysis of PCDD/F was carried out using following method 23 (U.S EPA, 1998) with High resolution Gas chromatography coupled with High resolution Mass spectrometer (HRGC/HRMS). Seventeen 2,3,7,8-substituted PCDD/F congeners was carried out by isotope dilution method using Micromass Autospec Ultima system (Waters, UK) with Agilent 7890A gas chromatograph (GC) and DB-5MS capillary column (60 m × 250 μm i.d × 0.25 μm film thickness, J&W Scientific Inc., Folsom, CA). The procedure for sample preparation and equipment operation have described in the previous study [6].

The stack gas samples include XAD2 resin and quartz fiber filter were Soxhlet extracted using toluene for 24 hours. The extracts were concentrated and treated by sulfuric acid (98%). Clean-up and fractionation steps were performed using pre-packed silica column, alumina column, and activated carbon column. Quantification of seventeen 2,3,7,8-substituted PCDD/Fs congeners were carried out by HRGC–HRMS. The method detection limits were 1.00 and 2.00 pg/Nm3 for tetra-CDD/Fs and penta- to octa-CDD/Fs congeners, respectively [6].

Toxicity Equivalent Factors (TEFs) scheme by the World Health Organization (WHO, 2005) were used for the calculation of TEQ and comparison in this study. Based on the TEQ concentrations of the investigated EAFs, the emission factors of PCDD/Fs were calculated and compare to UNEP toolkit and other countries [7].

2.3. Emission Factors of PCDD/F

Based on the TEQ concentrations of the investigated emission sources (steel and cement plants), the emission factors of PCDD/F were calculated as follows [7]:

$$EF = \frac{[\text{Concentration (ng TEQ/Nm}^3) \times \text{Flow rate (Nm}^3/\text{h})]}{\text{Product rate (ton/h)} \times 1000}$$

Where:

- Concentration: TEQ concentration in stack flue gas samples (ngTEQ/Nm^3)

- Flow rate: level of emission flow rate per hour (Nm^3/h)

- Product rate: annual capacity of plant (ton)

3. Results and disscution

3.1. PCDD/F emission from selected EAF plants

Table 1 shows basic information about investigated Electric Arc Furnace (EAF) plants. Stack gas samples were collected from four selected EAF plants in Vietnam. The mean concentrations of PCDD/F in stack gas samples are presented in Table 2. The mass concentrations and TEQ of PCDD/Fs in EAF plants ranged from 0.077 to 2.26 ng/Nm^3 and 0.027 to 0.264 $ngTEQ/Nm^3$, respectively. Obtained results showed that EAF3 plant have significant high TEQ concentration compared to those in EAF1, EAF2 and EAF4 plant. 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 $ngTEQ/Nm^3$ and 0.148 – 0.757 $ngTEQ/Nm^3$, respectively [8, 9]. In South Korea, Yu *et al*. (2006) reported slightly lower PCDD/Fs emissions from EAFs, varying from 0.004 – 0.182 $ngTEQ/Nm^3$ [10]. 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 ng I-TEQ/m^3 [11]. These emissions were considerably lower than the results of EAFs in Vietnam.

3.2. Congener profile of PCDD/F

PCDD/Fs congener profiles in stack gas of EAF plants are illustrated in Figure 1. It should be noted that in these profiles, PCDD/F concentrations are presented in mass basis instead of TEQ basis. Each 2,3,7,8-substituted PCDD/F 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 EAF plants, 2,3,4,7,8-PeCDF congener was abundant in stack gas (ranged from 14.6 to 40.2%), followed by 1,2,3,7,8-PeCDD (ranged from 5.5 to 22.0%) and 1,2,3,4,7,8,9-HpCDF (ranged from 0.8-11.9%). Obtained congener profile of EAF1, EAF2 and EAF3 have similar trend while EAF4 was different. As for EAF4 plant, the major congeners in stack gas were 2,3,4,7,8-PeCDF (40.2%), followed by 1,2,3,7,8-PeCDD (22.5%) while hexa CDD and hexa CDF were below Method Detection Limit (MDL, <0.001 ng/Nm^3). 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 [8, 9]. In this study, PeCDFs in stack gas accounted for 14.6% and 40.2% 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* [8]. Nevertheless, 2,3,7,8-substituted PeCDF in stack gas as the major congeners agrees with the results found for sinter plants [3].

Previous study reported by *Thuong et al* (2014) showed the same trends of PCDD/Fs concentration and congener profiles in stack gas and fly ash samples collected from steel plants in Vietnam [6]. In this report, this kind of samples were also collected but will be presented in other report.

3.3. PCDD/F emission factor

The mean emission factors of PCDD/F from the stack gas of EAF plants 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 (ranged from 6480 to 7920 hours, Table 1). As can be seen in Table 2, the emission factor of PCDD/Fs in EAF plants ranged from 0.89 to 2.03 µgTEQ/ton product.

The PCDD/Fs emission factors of four sintering plants in China were 3.95 µgTEQ/ton [12] and for EAFs in Taiwan were from 1.84 to 2.44 µgTEQ/ton [13]. 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) [7]. In this toolkit, emission factors of seventeen 2,3,7,8-substituted PCDD/F to the air from EAF plants using clean scrap were 3 and 0.1 µgTEQ/ton liquid steel, respectively. Overall, the emission factors of EAF plants in this study were lower than the default value of the toolkit (3.0 µgTEQ/ton).

Table 1. Basic information about investigated EAF plants

Parameters	EAF1	EAF2	EAF3	EAF4
Annual capacity (1000 tons)	160	250	250	180
Operating time per year (h)*	7920	6840	6840	7920
APCDs in sequence	BHF	BHF	BHF	BHF
Average temperature of stack gas (^oC)	54.0	49.7	50.5	56.0
Average flow rate of stack gas (Nm^3/h)	604,800	1,249,200	164,000	687,000
Total Suspended Particles (mg/Nm^3)	4.50	1.70	43.4	4.70
Oxygen content in stack gas (%)	20.5	20.8	20.5	20.7

EAF: Electric Arc Furnace; BHF: Bag House Filter

*It is assumed that working duration of the EAF plants are 330 days per year

Table 2. Concentration of PCDD/F in stack gas samples of EAF plants

Compounds	EAF1 (n=4)	EAF2 (n=4)	EAF3 (n=3)	EAF3 (n=3)
∑PCDDs (ng/Nm^3)	0.110	0.045	0.393	0.050
∑PCDFs (ng/Nm^3)	0.181	0.127	0.744	0.091
Total PCDD/Fs (ng/Nm^3)	0.291	0.171	1.137	0.141
Ration of PCDD/F	0.610	0.453	0.509	0.513
WHO-TEQ (ng TEQ/Nm^3)	0.066	0.051	0.198	0.067
Emission Factor (ug TEQ/ton of product)	1.98	1.74	0.89	2.03

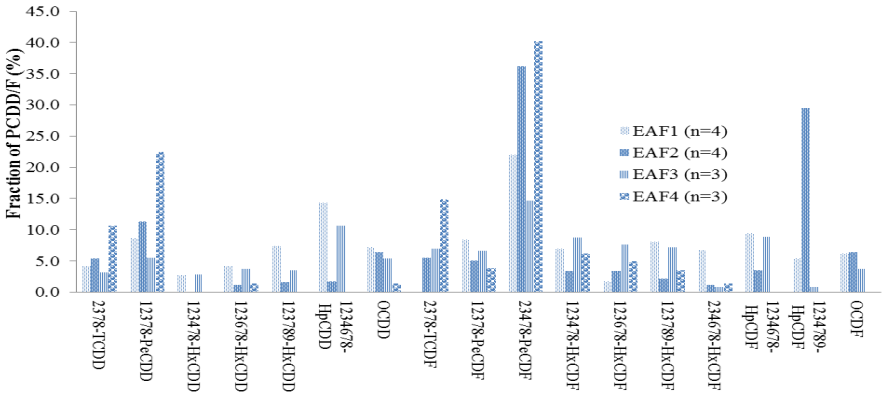

Fig 1. Homolog profile PCDD/Fs in selected EAF plants in Vietnam. Vertical bars represent the percentage of each homolog to total PCDD/Fs concentrations

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 of EAF plants in Vietnam could be around 1.66 µgTEQ/ton of product when using average emission factor in this study. Further studies are necessary in order to provide more comprehensive data on the PCDD/Fs emission not only from EAF plants but also steel-making processes in Vietnam.

4. Conclusion

Emission of PCDD/Fs from EAF plants was investigated in Vietnam. 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 0.89 and 2.03 µgTEQ per ton product. This study provides important data to implement more accurate PCDD/Fs 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.

Acknowledgments

This study was implemented under the research grant **KHCN-33.01/11-15** from the Vietnam National Science and Technology Research Program KHCN-33/11-15 (Research and overcoming long-term consequences of Agent Orange/Dioxin on the environment and the human health in Vietnam). The authors would like to express sincerest thanks to companies where participated in this study and make advantageous condition for sampling.

References

[1] UNEP. (1999). Dioxin and furan inventory: National and Regional emission of PCDD/Fs. United Nations Environment Program. UNEP Chemical, Geneva, Switzerland.

[2] Aries, E., Anderson, David.R., Fisher, R., Fray, A.T.A, Hemfrey, D. (2006). PCDD/F and "Dioxin-like" PCB emissions from iron ore sintering plants in the UK. Chemosphere 65: 1470–1480.

[3] Wang, L.C., Lee, W.J., Tsai, P.J., Lee, W.S and Chang-Chien, G.P. (2003). Emissions of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from Stack flue Gases of Sinter Plants. Chemosphere 50: 1123–112.

[4] UNIDO. (2012). Report of the Introduction for BAT/BEP to Control Formation and Releases of PCDD/F in Selected Industries of Vietnam, Project GF/VIE/08/005. United Nation Industrial Development Organization.

[5] U.S EPA. (1994). Method 23: Determination of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from stationary sources. Washington DC, USA.

[6] Thuong NV, Nam VD, Hue NTM, Son LK, Thuy NV, Tung HD, Tuan NA, Minh TB, Huy DQ, Minh NH. (2014). The emission of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from Steel and Cement kiln in Vietnam. Aerosol and Air Quality Research 14: 1189–1198.

[7] UNEP. (2005). Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases, Second Edition, United Nations Environment Program, Geneva, Switzerland.

[8] Chang, M.B., Huang, H.C., Tsai, S.S., Chi, K.H. and Chang-Chien, G.P. (2006). Evaluation of the Emission Characteristics of PCDD/Fs from Electric Arc Furnaces. Chemosphere 62: 1761–1773.

[9] Wang, J.B., Hung, C.H., Hung, C.H. and Chang-Chien, G.P. (2009). Polychlorinated Dibenzo-p-dioxin and Dibenzofuran Emissions from an Industrial Park Clustered with Metallurgical Industries. J. Hazard. Mater. 161: 800–807.

[10] Yu, B.W., Jin, G.Z., Moon, Y.H., Kim, M.K., Kyoung, J.D. and Chang, Y.S. (2006). Emission of PCDD/Fs and Dioxin-like PCBs from Metallurgy Industries in S. Korea. Chemosphere 62: 494–501.

[11] Quass, U., Fermann, M. and Bröker, G. (2004). The European Dioxin Air Emission Inventory Project-Final Results. Chemosphere 54: 1319–1327.

[12] Tian, B., Huang, J., Wang, B., Deng, S. and Yu, G. (2012). Emission Characterization of Unintentionally Produced Persistent Organic Pollutants from Iron ore Sintering Process in China. Chemosphere 89: 409–415.

[13] Chiu, J.C., Shen Y.H., Li H.W., Lin L.F., Wang L.C. and Chang-Chien G.P. (2011). Emissions of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from an Electric Arc Furnace, Secondary Aluminum Smelter, Crematory and Joss Paper Incinerators. Aerosol Air Qual. Res. 11: 13–20.

Đặc điểm phát thải Dioxin và Furan từ một số lò luyện thép hồ quang điện ở Việt Nam

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Tóm tắt: Polychlorinated dibenzo-p-dioxin và polychlorinated dibenzofurans (PCDD/Fs) phát sinh từ gia nhiệt trong quá trình sản xuất của các ngành công nghiệp khác nhau đã được quan tâm đặc biệt. Các mẫu khí trong ống khói được lấy từ một số lò hồ quang điện (EAFs) ở Việt Nam để xác định nồng độ, đặc trưng đồng loại và hệ số phát thải của PCDD/Fs. Phương pháp U.S EPA 23 được sử dụng để lấy mẫu khí thải trong ống khói theo nguyên tăc lấy mẫu đẳng động lực. Các chất PCDD/Fs được định lượng bằng thiết bị sắc ký khí khối phổ phân giải cao (HRGC/HRMS). Kết quả nghiên cứu chỉ ra rằng, nồng độ khối lượng và nồng độ TEQ của PCDD/Fs tương ứng trong các mẫu khí ống khói của các lò EAFs ở Việt Nam nằm trong khoảng từ 0,077 – 2,26 ng/Nm3 và 0,027 – 0,264 ngTEQ/Nm3. Và hệ số phát thải PCDD/Fs được tính toán nằm trong khoảng 0,89 – 2,03 µgTEQ/tấn sản phẩm. Hệ số phát thải PCDD/Fs từ các lò EAF ở Việt Nam tương đương với một số nhà máy ở Châu Á, nhưng cao hơn so với các quốc gia công nghiệp phát triển ở Châu Âu.

Từ khóa: PCDD/Fs, EAFs, Khí trong ống khói, Hệ số phát thải.