INVENTORY STUDY OF PCDD/Fs FOR METAL INDUSTRIES IN SOUTH KOREA

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are some of the most toxic chemicals in the environment. They have never been produced intentionally but are emitted in trace quantities in a variety of industrial and thermal processes[1]. Prior to having installed efficient PCDD/Fs abatement techniques, the incineration of municipal solid waste incinerators (MSWIs) used to be a major source. PCDD/Fs are, however, also emitted from other thermal processes, e.g. cement manufacture, combustion of wood or industrial waste, ferrous and non-ferrous metal plants, etc.[2]

Many countries have recently compiled national inventories of PCDD/Fs emissions to air from regulated, industrial sources in order to gain better understanding of amounts released per annum and to develop strategies to reduce emissions.[3] Based on the presently available data and a reference year around 1995, the central estimation of total annual PCDD/Fs emission is approximately 10,500 g I-TEQ (International Toxic Equivalents). The lower estimate is around 8,300 g I-TEQ/yr and the upper estimate approximately 36,000 g I-TEQ/yr.[1] So far, in Korea, emissions from municipal solid waste incinerators were only evaluated. In this study, we investigated PCDD/Fs in flue gas and fly ash emitted from ferrous metal smelting/refining, ferrous foundries, non-ferrous metals, and cement and lime manufactures for the first time in Korea.

Methods and Materials

Sampling and storage: Stack gas samples were collected for two times following the Korean Standard Method which is a modified US EPA Method 23. The sampling box consisted of a filter (silica glass microfibre, Whatman), resin (amberite XAD-2, Supleco) and 6 impingers (2 waters, 2 empties, 1 diethyleneglycol, 1 silica gel). 2ng of ^{37}Cl-2,3,7,8-TCDD was spiked into the resin to check the sampling efficiency. Fly ash samples were collected for two times from an electrostatic precipitator or bag filter outlet in incinerators.

Extraction and analytical methods: Stack gas and fly ash samples were spiked with 1 ng and 2 ng of a mixture of $^{13}C_{12}$-labeled as PCDD/Fs internal standards (Wellington Laboratories. Ontario, Canada), respectively and extracted for 20h with toluene. Extracted samples were washed with sulphuric acid followed by a multi silica column and an alumina column. The PCDD/Fs congeners were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (Hewlett-Packard Model 6890 / JMS 700D) with a SP-2331 capillary column (60 m × 0.32 mm I.D., film thickness 0.2 μm). The temperature program of capillary column was as follows; (1) 100 initial for 1min, (2) increased at 20 /min to an isothermal hold at 220 , (3) increased at 2 /min to an isothermal hold at 265 for 17.5 min. The sample introduction was achieved by splitless injection. The MS was operated over 10,000 resolution under positive EI conditions (38 eV electron energy), and data were obtained in the selected ion (SIM) mode.

Results and Discussion

Ferrous metal smelting/refining[4]. The production of iron and steel involves several operations including sinter production, coke production, and electric furnaces as potential emission sources of PCDD/Fs. The PCDD/Fs concentrations of stack gas samples ranged between 0.001~1.342 ng I-TEQ/Nm^3 and those of fly ash samples showed a large variation between 0.015~5.664 I-TEQ/kg (Table 1). Congener distribution patterns of stack gas and fly ash samples for ferrous metal smelting/refining are shown in Figure 1.

Table 1. TEQ concentrations of stack gas and fly ash samples

Process		Stack gas (ng I-TEQ/Nm^3)		Fly ash (I-TEQ/kg)	
		Mean	Min. – Max.	Mean	Min. – Max.
Ferrous metal smelting/ refining	Sinter production (n=8)	0.615	0.333 - 1.342	0.288	0.116 - 0.406
	Coke production (n=4)	0.019	0.017 - 0.023	-	-
	Electric furnace (n=32)	0.052	0.001 - 0.558	0.966	0.015 - 5.664
Ferrous foundries (n=20)		0.043	0.004 - 0.182	0.641	0.003 - 2.282
Non-ferrous metals	Copper (n=8,6)	0.139	0.012 - 0.622	2.322	0.003 - 7.270
	Lead (n=6)	0.174	0.001 - 0.410	0.047	0.002 - 0.119
	Zinc (n=6)	0.020	0.001 - 0.063	5.940	0.000 - 18.318
Cement manufacture (n=6)		0.095	0.007 - 0.263	0.177	0.003 - 0.439
Lime manufacture (n=2)		0.050	0.012 - 0.087	0.002	0.001 - 0.003

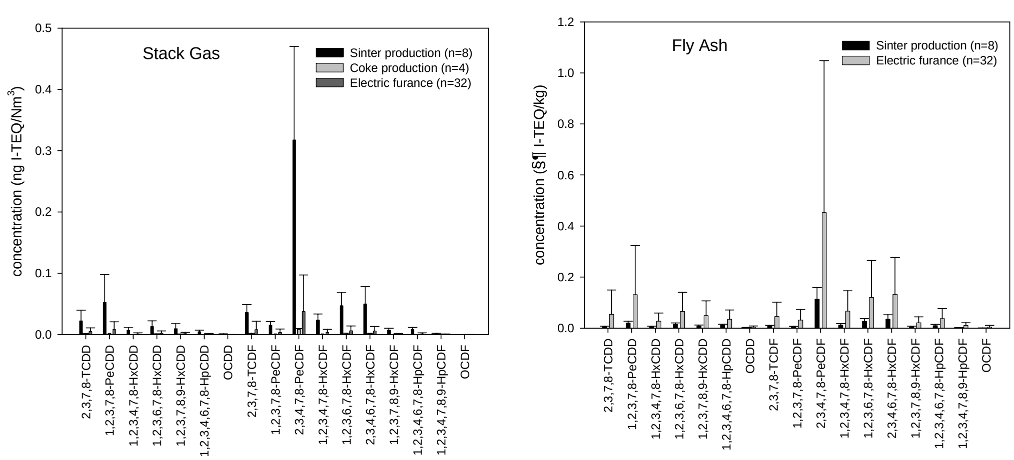

Figure 1. Congener distribution patterns of stack gas and fly ash samples of ferrous metal smelting/refining

The emission factor for ferrous metal smelting/refining is 985 ng I-TEQ/ton. The total annual emissions from this source were estimated to be 35.47 g I-TEQ based on this study.

Ferrous foundries. The PCDD/Fs concentrations of stack gas samples ranged between 0.004 and 0.182 ng I-TEQ/Nm^3 and those of fly ash samples showed a large variation between 0.003 and 2.282 I-TEQ/kg (Table 1). Congener distribution patterns of stack gas and fly ash samples for ferrous foundries are shown in Figure 2. The most abundant congener is 2,3,4,7,8-PeCDF which constitutes around 43% of the total concentration of the 17 target compounds. The emission factor for steel industries was determined as 185 ng I-TEQ/ton by taking the average of ten plants. The total annual emissions from this source were estimated to be 0.16 g I-TEQ based on this study.

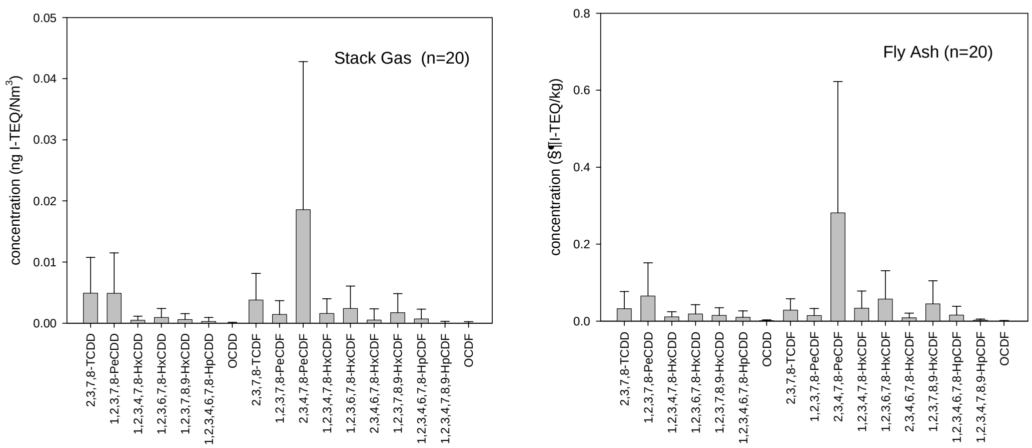

Figure 2. Congener distribution patterns of stack gas and fly ash samples of ferrous foundries.

Non-ferrous metals. Processing of non-ferrous metals is heterogeneous and dispersed, especially when compared to that of the steel industry[5]. The PCDD/Fs concentrations of stack gas samples were in the range from 0.012 to 0.622 ng I-TEQ/Nm^3, and those of fly ash samples showed a large variation between 0.000 and 18.318 I-TEQ/kg (Table 1). Congener distribution patterns of stack gas and fly ash samples for non-ferrous metals are shown in Figure 3.

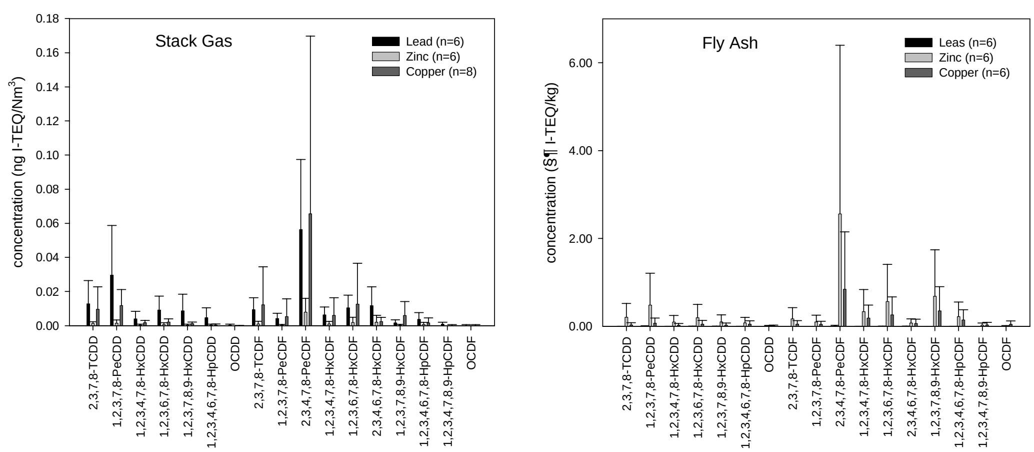

Figure 3. Congener distribution patterns of stack gas and fly ash samples of non-ferrous metals.

The most abundant congener is 2,3,4,7,8-PeCDF in stack gas and fly ash samples. The emission factor for non-ferrous metals was determined as 1,369.35 ng I-TEQ/ton and total amounts of production were 5.51× 10^6 tons based on this study, resulting in the total PCDD/Fs emission of 7.54 g I-TEQ.

*Cement, lime manufactures***.** Production of mineral materials such as cement, lime, glass, and brick is generally performed at very high temperatures. The mean concentrations of stack gas (n=8) and fly ash (n=8) samples for this process are 0.083ng I-TEQ/Nm^3 and 0.134 μ I-TEQ/kg (Table 1). Congener distribution patterns of stack gas and fly ash samples for cement and lime manufactures are shown in Figure 4. 2,3,4,7,8-PeCDF is the most abundant congener both in stack gas and fly ash samples. The emission factor for this source is 98 ng I-TEQ/ton. The total annual emissions from these manufactures were estimated to be 1.55 g I-TEQ based on this study.

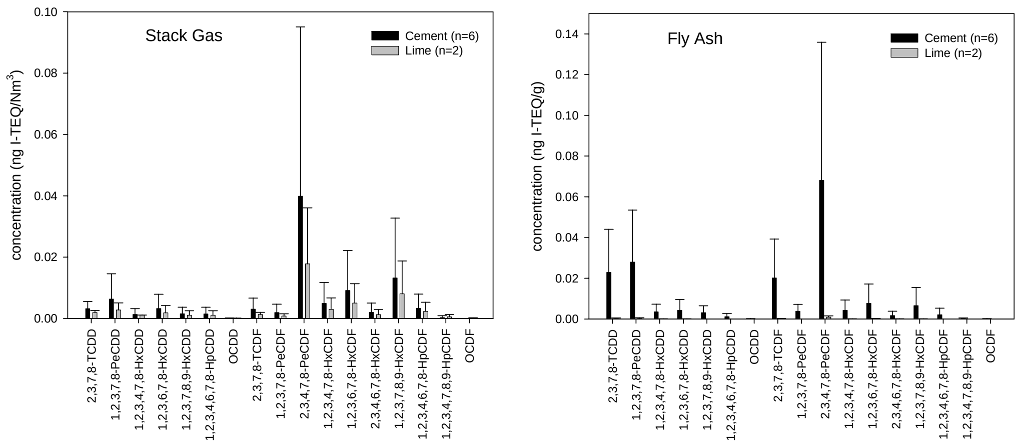

Figure 4. Congener distribution patterns of stack gas and fly ash samples of cement and lime manufactures.

Acknowledgements

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