Correlations of emission concentrations among PCDDs/PCDFs, co-planar PCBs and HCB from major thermal stationary sources

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofuran (PCDFs), polychlorinated biphenyls (PCBs), and hexachlorobenzene (HCB) are known as unintentionally produced chemicals (UPCs) from a variety of manufacturing and thermal processes[1,2,3]. The UPCs are contained in products as impurities or byproducts in the manufacturing processes of chlorinated pesticides and solvents, and in the bleaching process of pulp. In particular, thermal processes such as incinerator and melting or smelting furnaces produce theses chemicals as products of incomplete combustion (PICs)[4], which are resulted from the insufficient 3Ts for complete combustion: temperature, time, and turbulence[5]. These characteristics of UPCs, therefore, lead to difficulty not only in estimating the formation and emission concentrations but also in applying removal technologies for these chemicals. In addition, PCDDs/PCDFs and PCBs have many congeners of 210 and 209 types, respectively, and are emitted into the atmosphere at trace levels. Thus, the analysis of the emission concentration of UPCs requires a precise sampling and analytical procedure, which is time-consuming and high cost-consumable work. Some articles[6,7], which discussed municipal solid waste (MSW) incinerators, have proposed the prediction of the emission level of PCDDs/PCDFs with simply measured indicators, such as operating parameters or other low-molecular-weight chemicals in flue gas. In the present study, major stationary emission sources of UPCs, such as MSW incinerators, sintering furnaces, and smelting furnaces in the ferrous and nonferrous metal industry were selected for an investigation of the emission levels of UPCs. HCB, which has single congener and can be more simply measured by gas-chromatographic separation than PCDDs/PCDFs or co-planar PCBs, was used as an indicator to evaluate the correlation of emission concentrations among UPCs and to predict the emission level of PCDDs/PCDFs and co-planar PCBs.

Methods and Materials

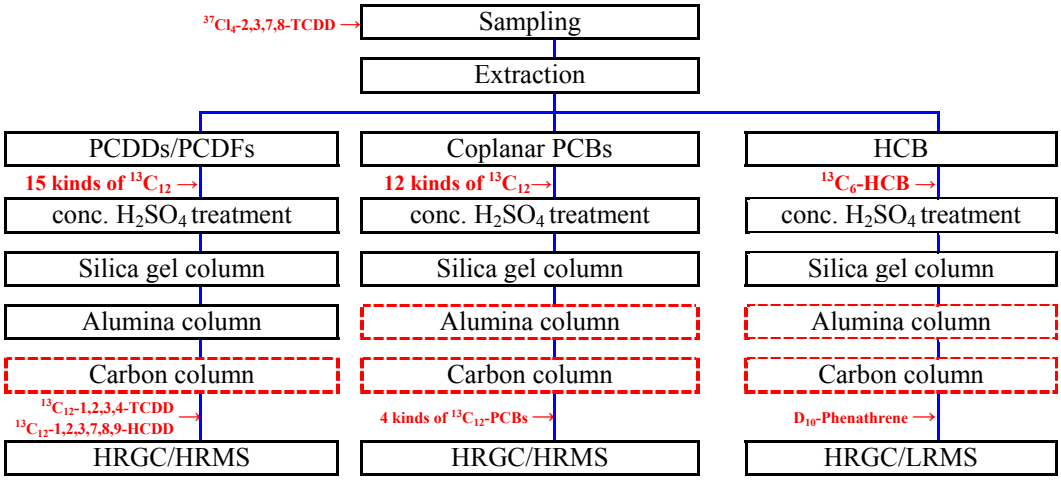
Two commercial-scale MSW incinerators, with incineration capacities of 250 and 50 tons/day, two sintering furnaces, and four smelting furnaces were selected in ferrous and nonferrous metal foundries. Samples were obtained at the stacks by using a sampling train, which consisted, in order, of a probe, a cylindrical filter, two impingers (one of which was filled with 250 ml of

distilled water and the other empty), a sorbent (XAD-2) trap, and two impingers (one of which was filled with 150 ml of ethylene glycol and the other empty)[8]. The samples were soxhlet-extracted and separately pretreated as shown in Figure 1. PCDDs/PCDFs and co-planar PCBs were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (Autospec Ultima, Micromass Co.) above 10,000 resolution with an SP-2331 column of 60 m × 0.32 mm inner diameter × 0.25 μm for PCDDs/PCDFs and a DB-5MS column of 60 m × 0.32 mm inner diameter × 0.25 μm for co-planar PCBs. HCB was analyzed by a GC/mass-selective detector (HP 6890 GC with HP 5973 MSD) with a DB5-MS column of 30 m × 0.32 mm inner diameter × 0.25 μm. Toxic equivalents as 2,3,7,8-TeCDD (TEQs) were calculated by using the international toxicity equivalency factor (I-TEF) for PCDDs/PCDFs and the World Health Organization (WHO-TEF for coplanar PCBs.

Table 1. Schematic flow of air-pollution devices in thermal facilities to be studied

Plant	Process	Type of furnace (material/fuel)
MSW-1	CC (SNCR) → WHB → SDA → (AC) → BF → ID. Fan → Stack	Stoker (250 tons/day, MSW)
MSW-2	CC → WHB → GC → DA → (AC) → BF → ID. Fan → Stack	Stoker (50 tons/day, MSW)
Fe-1	SF → GC → EP → ID Fan → Stack	Dwight-Lioyd (Iron ore/coke, coal)
Fe-2	SF → GC → EP → ID Fan → Stack	
Pb-1	MF → Cyclone → BF → WS → Stack	Cupola (waste battery/coke)
Pb-2	MF → WHB → WS → EP → DT → Stack	(Lead ores/no use)
Cu-1	MF → HE → BF → ID Fan → Stack	(Crude copper/electricity)
Al-1	MF → HE → BF → ID Fan → Stack	(Al ingot/ Bunker C oil)

AC: activated carbon, BF: bag filter, CC: combustion chamber, DA: dry absorber, DT: drying tower, EP: electrostatic precipitator, GC: gas cooler, HE: heat exchanger, MF: melting furnace, SDA: spray dryer absorber, SF: sintering furnace, SNCR: selective noncatalytic reduction, WHB: waste heat boiler, WS: wet scrubber.



IS: Internal Standard. The processes in dotted-line rectangle were performed only when necessary.
Figure 1. Flow diagrams of analytical procedures for PCDDs/PCDFs, co-planar PCBs and HCB.

Results and Discussion

PCDDs/PCDFs: Sintering furnaces in the ferrous metal industry showed the highest concentrations, 11.531~7.225 ng/Nm^3 (0.926~1.492 ng-TEQ/Nm^3), followed by incineration facilities, 0.050~1.571 ng/Nm^3 (0.000~0.069 ng-TEQ/Nm^3), the aluminum smelting furnace, 0.032 ng/Nm^3 (0.032 ng-TEQ/Nm^3), the copper smelting furnace, 0.095 ng/Nm^3 (0.002 ng-TEQ/Nm^3), and lead smelting furnaces, 0.023~0.119 ng/Nm^3 (0.002~0.006 ng-TEQ/Nm^3). The I-TEQ value was approximately 12% of the total concentration of PCDDs/PCDFs, on average, and the major contributing congener to TEQ values of 2,3,7,8-PCDDs/PCDFs was 2,3,4,7,8-PeCDF in most cases.

Co-planar PCBs: A similar tendency was observed in co-planar PCBs: sintering furnaces emitted the highest concentrations, 5.824~8.259 ng/Nm^3 (0.067~0.112 ng-TEQ/Nm^3), followed by incineration facilities, 0.027~1.244 ng/Nm^3 (0.000~0.009 ng-TEQ/Nm^3), the aluminum smelting furnace, 0.683 ng/Nm^3 (0.016 ng-TEQ/Nm^3), the copper smelting furnace, 0.217 ng/Nm^3 (0.002 ng-TEQ/Nm^3), and lead smelting furnaces 0.033~0.082 ng/Nm^3 (0.000 ng-TEQ/Nm^3). The WHO-TEQ value was approximately 1.3% of total concentration of co-planar PCBs on average, and the major contributing congener to TEQ values of coplanar PCBs was 3,3',4,4',5-PeCB in most cases.

HCB: Sintering furnaces emitted the highest concentrations, 73.88~127.28ng/Nm^3 in HCB, followed by incineration facilities, 5.71~54.86 ng/Nm^3, the aluminum smelting furnace, 15.56 ng/Nm^3, the copper smelting furnace, 10.00 ng/Nm^3, and the lead smelting furnace, 3.27~3.66ng/Nm^3. This tendency was similar to the results for PCDDs/PCDFs and co-planar PCBs

Correlation: Good correlations were observed among PCDDs/PCDFs (ng/Nm^3 and ng-TEQ/Nm^3), co-planar PCBs (ng/Nm^3 and ng WHO-TEQ/Nm^3), and HCB (ng/Nm^3), as follows:

PCDDs/PCDFs (ng/Nm^3) vs. HCB (ng/Nm^3): $y = 0.0924x - 0.7502$ ($R^2 = 0.9286$)
PCDDs/PCDFs (ng I-TEQ/Nm^3) vs. HCB (ng/Nm^3): $y = 0.0118x - 0.1121$ ($R^2 = 0.8854$)
co-planar PCBs (ng/Nm^3) vs. HCB (ng/Nm^3): $y = 0.0673x + 0.417$ ($R^2 = 0.9208$)
co-planar PCBs (ng WHO-TEQ/Nm^3) vs. HCB (ng/Nm^3): $y = 0.0009x - 0.006$ ($R^2 = 0.8979$)

Meanwhile, Kenichi et al. (2002)[6] reported a high correlation (R = 0.95) between co-planar concentrations of PCBs and PCDDs/PCDFs and a significant correlation (R = 0.98) between concentrations of PCDDs/PCDFs and HCB in the flue gases of industrial waste incinerators. Öberg et al. (1985)[7] has also reported the statistically significant correlations between tetra-CDD to HCB (R = 0.57, n = 31), penta-CDD to HCB (R = 0.58, n = 23), and penta-CDF to HCB (R = 0.55, n = 25) from studies on Scandinavian combustion plants.

In the present study, emissions concentrations of PCDDs/PCDFs and co-planar PCBs as total values were estimated as about 9% and 7% of HCB concentrations, respectively, with good correlations. As a consequence, HCB might be used for predicting the emission concentrations of PCDDs/PCDDFs and coplanar PCBs, because it is simpler to monitor this item than PCDDs/PCDFs or co-planar PCBs.

Table 2. Emission concentrations of PCDDs/PCDFs, coplanar PCBs, and HCB at the stacks

	Name of Plant	PCDDs/PCDFs*2		Coplanar PCBs*4		HCB
		ng/Nm^3	ng-TEQ/Nm^3	ng/Nm^3	ng-TEQ/Nm^3	ng/Nm^3
MSW incinerator	MSW-1	0.050*3	0.001*3	0.046	0.000	5.58
		0.009*3	0.000*3	0.027	0.000	5.71
	MSW-2	1.571*3	0.069*3	1.244	0.009	54.86
Ferrous metal	Fe-1*1	11.531	1.492	8.259	0.112	127.28
	Fe-2*1	7.225	0.926	5.824	0.067	73.88
Non ferrous metal	Pb-1	0.119	0.006	0.082	0.000	3.27
	Pb-2	0.023	0.002	0.033	0.000	3.66
	Cu-1	0.095	0.002	0.217	0.002	10.00
	Al-1	0.332	0.032	0.683	0.016	15.56
Mean		2.328	0.281	1.824	0.023	33.31

*1: From sintering furnace, *2: Summation of 17 kinds of 2,3,7,8-PCDDs/PCDFs, *3: Corrected by 12% O_2, *4: Summation of 12 kinds of coplanar PCBs

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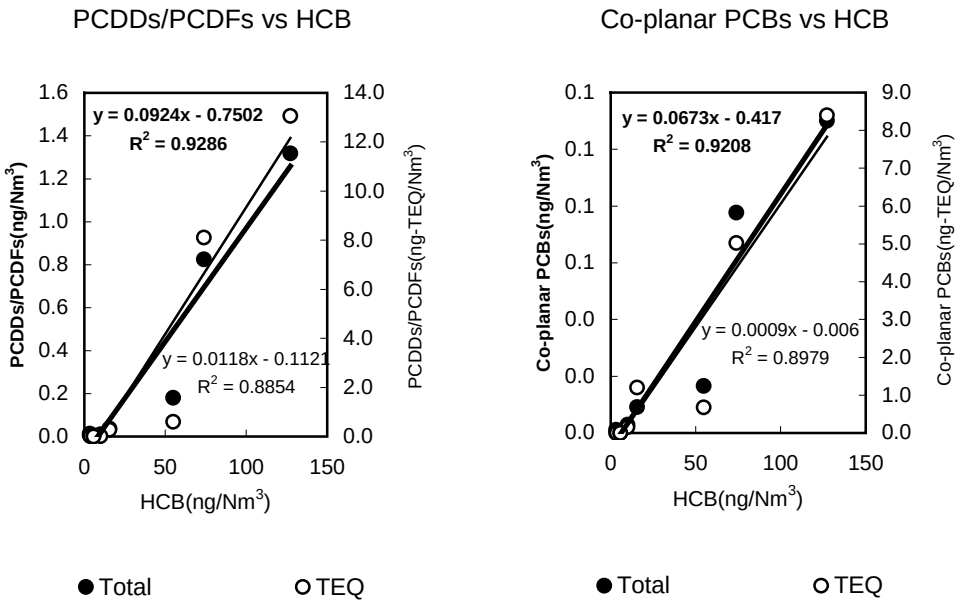

Figure 2. Correlations of emission concentrations among PCDDs/PCDFs, co-planar PCBs, and HCB.