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Correlation among Unintentionally-produced Persistent Organic Pollutants Emitted from Stationary Thermal Sources

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A total of 8 stationary emission sources, including incineration plants and sintering and smelting furnaces in ferrous and non-ferrous metal industry were selected to evaluate the levels of unintentionally-produced persistent organic pollutants (UPOPs) emission. Using the same sampling method for polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofuran (PCDDs/PCDFs), gas samples were collected and UPOPs were separated from the gas samples and quantified. UPOPs concentration of gas emitted from sintering furnaces in ferrous metal industry was the highest among the investigated emission sources. PCDDs/PCDFs and co-planar polychlorinated biphenyls (PCBs) as a whole were estimated to be about 9% and 7% of hexachlorobenzene (HCB) concentration, respectively. Good correlations of $R^2 = 0.89$ to 0.93 were observed among PCDDs/PCDFs (ng/Nm^3 and ng-TEQ/Nm^3), co-planar PCBs (ng/Nm^3 and ng World Health Organization-TEQ/Nm^3) and HCB (ng/Nm^3). HCB, which can be more simply measured by a gas chromatograph than PCDDs/PCDFs or co-planar PCBs, could be used as an indicator for the emission level of PCDDs/PCDFs and co-planar PCBs.

Key words: UPOPs, PCDDs/PCDFs, HCB, Stationary sources

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs)/polychlorinated dibenzofuran (PCDFs)s, polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) are known as unintentionally-produced persistent organic pollutants (UPOPs) from a variety of manufacturing and thermal processes[1-3]. The UPOPs are contained in products as impurities or produced as by-products from the manufacturing processes of chlorinated pesticides and solvents, or from the pulp bleaching process. In particular, thermal processes such as incinerator and melting or smelting furnaces produce theses chemicals as products of incomplete combustion (PICs)[4], which resulted from incomplete combustion: usually caused by the insufficient 3Ts (i.e., temperature, time, and turbulence)[5]. In general, UPOPs are difficult not only to estimate the formation and emission concentrations but also to apply any treatment technologies for the control of these chemicals[6,7]. In addition, PCDDs/PCDFs and PCBs have many congeners of 210 and 209 kinds, respectively, and are emitted into atmosphere at trace levels. Thus, the determination of emission concentration for PCDDs/PCDFs and PCBs requires a precise sampling and analytical procedure, which requires considerable time and labor.

Meanwhile, HCB has only one congener, so it can be more simply measured by a gas chromatograph than PCDDs/PCDFs or coplanar PCBs[8]. Owing to these sampling and analysis difficulties for PCDDs/PCDFs and PCBs, a few researchers[9-11], after worked on municipal solid waste (MSW) incinerators, have proposed a simple method to predict emission level of PCDDs/PCDF, in which simply-measurable indicators, such as operating parameters or other low-molecular chemicals in flue gas.

In this study, the levels of UPOPs from major stationary emission sources, such as MSW incinerators,

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and sintering and smelting furnaces in ferrous and non-ferrous metal industry were evaluated. In addition, the feasibility of using HCB as an indicator to predict the emission level of PCDDs/PCDFs and co-planar PCBs was evaluated by making correlation among them.

Methods and Material

Two commercial-scale MSW incinerators, capacities of which were 250 ton/day and 50 ton/day, two sintering furnaces and four smelting furnaces were selected in ferrous and non-ferrous metal foundries (Table 1). Gas samples were collected at stacks by using a sampling device (Fig. 1), which consisted of a probe, a cylindrical filter, two impingers (one was filled with 250 ml of distilled water, and the other was empty), a sorbent (XAD-2) trap, and two impingers (one was filled with 150 ml of ethylene glycol, and the other was empty)[12].

After collected, the samples were soxhlet-extracted and separately pre-treated as shown in Fig. 2. PCDDs/

Table 1. Air pollution control devices in thermal facilities to be studied

Plant	Process (^oC)	Type of furnace (Material/Fuel)
MSW-1	CC (SNCR) → WHB → SDA → (AC) → BF → ID. Fan → Stack	Stoker (250 ton/day, MSW)
MSW-2	CC → WHB → GC → DA → (AC) → BF → ID. Fan → Stack	Stoker (50 ton/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)

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

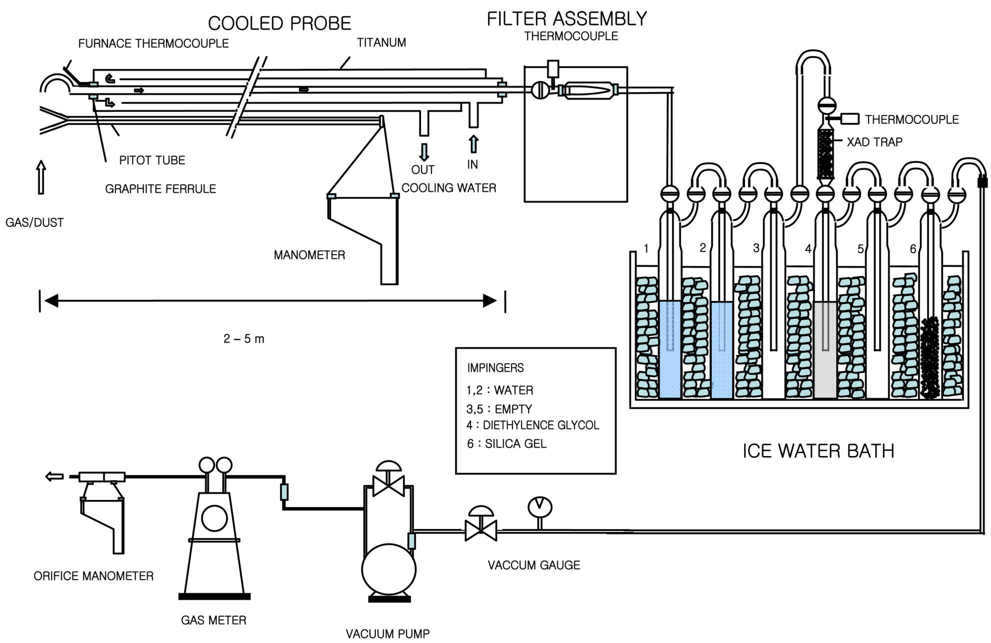
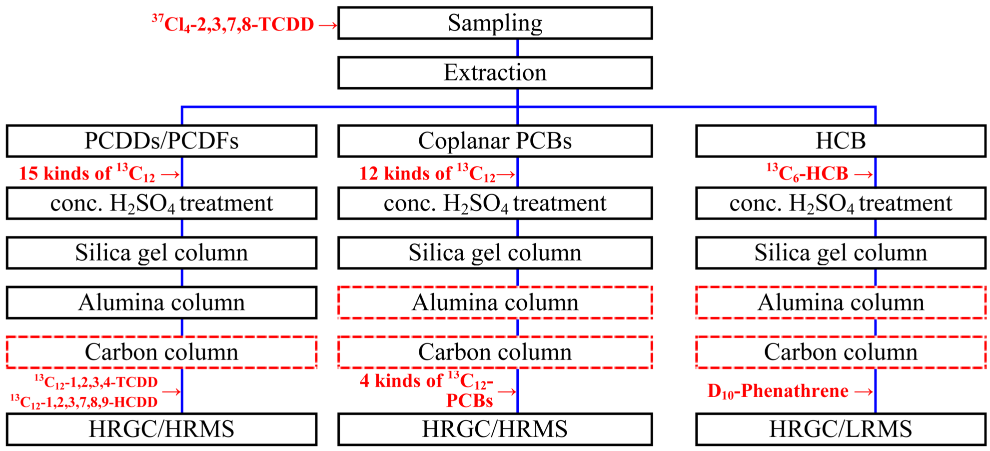


Fig. 1. UPOPs Sampling Train.



IS: Internal Standard. The processes in dotted-line rectangle were performed only when necessary.

Fig. 2. Analytical procedures of PCDDs/PCDFs, co-planar PCBs and HCB.

PCDFs and co-planar PCBs were analyzed with a HRGC/HRMS (high resolution gas chromatograph/high resolution mass spectrometer: Micromass Co., Autospec Ultima) of above 10,000 resolution with SP-2331 column of 60 m × 0.32 mm ID × 0.25 μm for PCDDs/PCDFs and DB-5MS column of 60 m × 0.32 mm ID × 0.25 μm for co-planar PCBs. HCB was analyzed by a GC/Mass Selective Detector (MSD: HP 6890 GC with HP 5973) with DB5-MS column of 30 m × 0.32 mm ID × 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 WHOTEF for co-planar PCBs.

Results and Discussion

Three out of eight target facilities (two were iron-ore sintering furnaces and the other was lead-melting furnace) were equipped with an electrostatic precipitator (EP) and the rest were equipped with bag filter systems (BF) for dust control (Table 1). The main reason that a sintering plant should be equipped with an EP may be due to the fact that off-gas of about one million or more standard cubic meters per hour is released. In previous domestic research, Kim *et al.*[13] indicated that a sintering furnace not only emits huge amount of off-gas but also a variety of pollutants such as particulate matter, carbon monoxide, and nitrogen oxide, and PCDDs/PCDFs. He also indicated that off-gas released contains about 1.6% of carbon monoxide and this carbon monoxide can't be controlled by EP.

Generally, most of metal sintering or melting processes foreither ferrous or nonferrous metal, are operated under insufficient or starved air supply using the chemical reduction or electric arcing process. Due to the insufficient air supply in furnace or smelter, products of incomplete combustion (PICs) are generated from the sintering or melting processes. Considering that dioxins and dioxin-like PCBs are generated from the incomplete combustion, higher concentration of carbon monoxide together with particulates (organic portion) may lead to higher concentration of PCDDs/PCDFs in off-gas if chlorine donors exit from thermal process. By this reason, the sintering process has been indicated as a remarkable emission source of PCDDs/PCDFs[14~17]. In this study, we also got a similar result to that from Kim's study. Emission levels of PCDDs/PCDFs, co-planar PCBs and HCB from each stack of target thermal plants are summarized in Table 2.

PCDDs/PCDFs

Off-gas from sintering furnaces in ferrous metal industry showed the highest PCDDs/PCDFs concentrations of 11.531~7.225 ng/Nm^3 (0.926~1.492 ng-TEQ/Nm^3), followed by incineration facilities (0.050~

Table 2. Emission concentrations of PCDDs/PCDFs, co-planar PCBs and HCB at stacks

	Name of Plant	PCDDs/PCDFs*2		Co-planar PCBs*4		HCB
		ng/Nm3	ng-TEQ/Nm3	ng/Nm3	ng-TEQ/Nm3	ng/Nm3
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 co-planar PCBs

1.571 ng/Nm^3 (0.000∼0.069 ng-TEQ/Nm^3)), aluminum smelting furnace (0.032 ng/Nm^3 (0.032 ng-TEQ/Nm^3)), 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)). I-TEQ values of them were approximately 12% of total concentration of PCDDs/PCDFs on average, and 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

Similar tendency could be observed in the case of co-planar PCBs. Sintering furnaces emitted the highest PCBs concentrations of 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)), aluminum smelting furnace (0.683 ng/Nm^3 (0.016 ng-TEQ/Nm^3)), 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)). WHO-TEQ values of them were approximately 1.3% of total concentration of co-planar PCBs on average, and major contributing congener to TEQ values of co-planar PCBs was 3,3',4,4',5-PeCB in most cases.

HCB

Off-gas from sintering furnaces showed the highest HCB concentrations of 73.88∼127.28ng/Nm^3, followed by incineration facilities (5.71∼54.86 ng/Nm^3), aluminum smelting furnace (15.56 ng/Nm^3), copper smelting furnace (10.00 ng/Nm^3), and lead smelting furnace (3.27∼3.66 ng/Nm^3). This tendency was similar to the cases of PCDDs/PCDFs and co-planar PCBs.

Correlation

As shown in Fig. 3, good correlations with R^2= 0.89 to 0.93 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.*[9] reported a high correlations between co-planar PCBs and PCDDs/PCDFs ((R = 0.95)), and between PCDDs/PCDFs and HCB (R= 0.98) of the flue gases emitted from industrial waste incinerators. Also, Öberg *et al.*[10] reported the statistically significant correlations between tetra-CDD

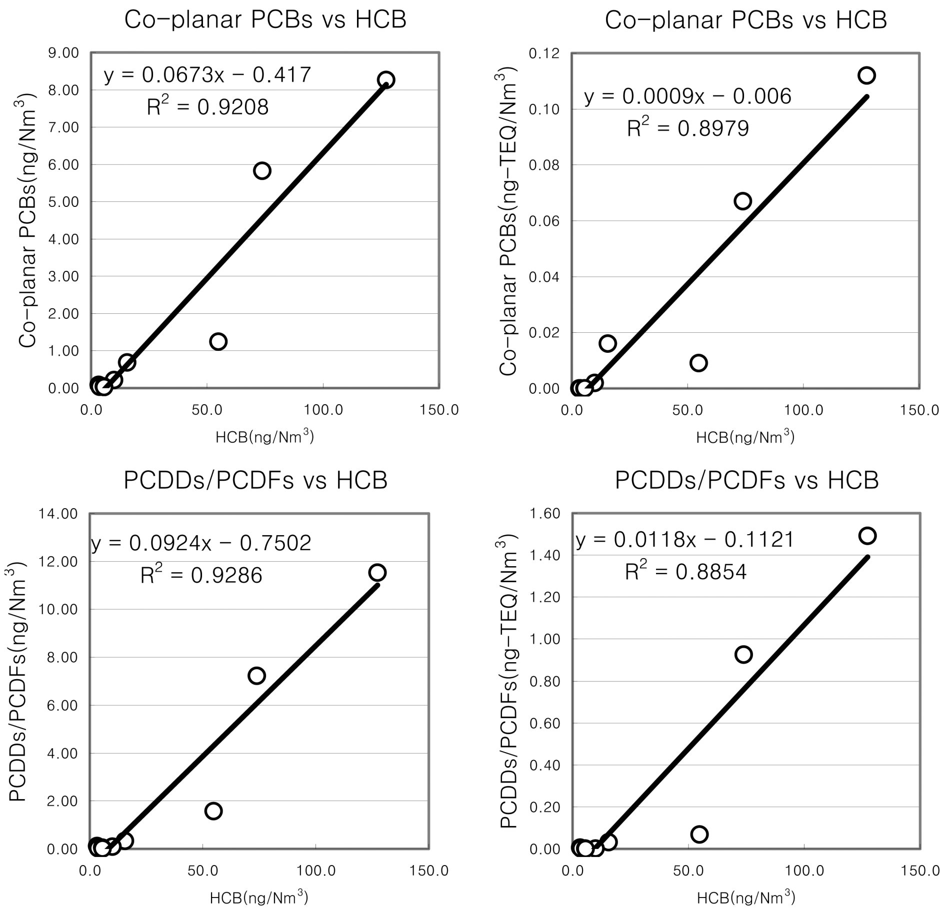


Fig. 3. Correlations of emission concentrations among PCDDs/PCDFs, Co-planar PCBs and HCB.

and HCB (R= 0.57, n=31), between penta-CDD and HCB (R= 0.58, n=23) and between penta-CDF and HCB (R= 0.55, n= 25) in their study on the off-gas from Scandinavian combustion plants. As a domestic research, Chung et al.[18] reported that there was a good correlation (R= 0.87, n=8) between HCB (ng/Nm^3) and PCDDs/PCDFs (ng-TEQ/Nm^3) in off-gas emitted from municipal solid waste incineration facilities. From these results, there seem to be positive correlations among different UPOPs from incineration plants.

We also got good correlations between HCB and PCDDs/PCDF or co-planar PCBs not only from an MSW incinerators but also from metallurgic sources such as ferrous and nonferrous furnaces. Emissions concentrations of PCDDs/PCDFs and co-planar PCBs as a total value were estimated about 9% and 7% of HCB concentration, respectively. Consequently, HCB, which is thought as one of precursors of the formation of dioxins and dioxin-like PCBs, could be used as an index for predicting the emission concentrations of these chemicals.

Conclusions

To evaluate the emission characteristics of UPOPs, a total of 8 stationary emission sources were selected including an MSW incineration plant and sintering and smelting furnaces in ferrous and non-ferrous metal industry. The result is summarized as follows:

1. Sintering furnaces in ferrous metal industry emitted flue gas with the highest concentrations of UPOPs among the stationary emission sources.
2. I-TEQ value of PCDDs/PCDFs was approximately 12% of total concentration of PCDDs/PCDFs on

average, and major contributing congener to TEQ values of 2,3,7,8-PCDDs/PCDFs was 2,3,4,7,8-PeCDF in most cases.

3. WHO-TEQ value of co-planar PCBs was approximately 1.3% of total concentration of co-planar PCBs on average, and major contributing congener to TEQ values of co-planar PCBs was 3,3',4,4',5-PeCB in most cases.
4. Levels of PCDDs/PCDFs and co-planar PCBs as a total were estimated about 9% and 7% of HCB, respectively.
5. Good correlations with $R^2 = 0.89$ to 0.93 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).
6. HCB, which has a single congener and can be more simply measured by a gas chromatograph than PCDDs/PCDFs or coplanar PCBs, can be used as an indicator to predict the emission levels of PCDDs/PCDFs and co-planar PCBs.

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