Emission Characteristics of coplanar PCBs in stationary thermal sources

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Introduction

According to the Stockholm convention in 2001, polychlorinated biphenyl (PCB) is one of persistent organic pollutants (POPs) together with dioxin, furan and hexachlorobenzene, which are known as unintentionally-produced chemicals in thermal processes such as sintering, smelting, incineration etc.¹⁾ Although the industrial use of PCBs has been banned since 1970s, PCBs are still widespread in the environment due to their persistency, bioaccumulation and unintentional formation characteristics²⁾. In order to prevent the increase of pollution caused by PCBs, it might be important to identify the emission characteristics of PCBs, which are released to environment from stationary thermal sources. In this study we would determine the emission characteristics of coplanar PCBs, suggested by WHO, for the major stationary thermal sources, comparing to congener profiles of Aroclor mixtures which were commercially produced by organic synthesis.

Materials and Methods

A total of nine facilities were selected from a sintering furnace in ferrous metal foundries, two smelting furnaces in nonferrous metal foundries, and six incinerators which were three municipal solid waste (MSW) incinerators (6, 7.5, 18 ton/day), two industrial waste (IW) incinerator (13, 60 ton/day) and a specific industrial waste (SIW) incinerator (48 ton/day). Sampling was performed at the stack in accordance with Korean official analytical method for dioxins and furans³⁾. Sampling train was consisted of a probe, a cylindrical filter, two impingers (one of which was filled with 250 ml of distilled water and the other empty), a sorbant (XAD-2) trap and two impingers (one of which was filled with 150 ml of ethylene glycol and the other empty. Collected samples were soxhlet-extracted with toluene for 16 hours, and cleaned up using multi-layered silica gel chromatography. Whole PCBs₁⁻ congeners of 209 kinds, including coplanar PCBs, were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (AutospecUltima, Micromass Co.) above 10,000 resolution with an SPB-Octyl column (30 m _{i ¿} 0.25 mm l.D. _{i ¿} 0.25 µm film thickness) in accordance to the US EPA Method 1668a. Toxic equivalents as 2,3,7,8-TeCDD (TEQs) were calculated by using the World Health Organization (WHO-TEF) for coplanar PCBs.

Results and Discussion

All thermal facilities studied emitted PCBs in the range of $10 \sim 700 \text{ ng/Nm}^3$ as a total concentration, and coplanar PCBs in the range of $1\sim25 \text{ ng/Nm}^3$ which TEQ value were $0.008 \sim 0.324 \text{ ng-TEQ/Nm}^3$. The contribution rates of coplanar PCBs to the total PCBs were in the range of $1\sim21$ %, while that of Aroclor mixture (1242/1248/1254/1260) was about 4 %. In addition, MSW incinerator emitted the highest coplanar PCBs of $0.136 \text{ ng-TEQ/Nm}^3$, followed by SIW incinerator, $0.036 \text{ ng-TEQ/Nm}^3$, IW incinerator, $0.025 \text{ ng-TEQ/Nm}^3$, copper smelting furnace, $0.026 \text{ ng-TEQ/Nm}^3$, aluminum smelting furnace, $0.020 \text{ ng-TEQ/Nm}^3$, and sintering furnace, $0.018 \text{ ng-TEQ/Nm}^3$. TEQ concentration ratios of coplanar PCBs to PCDDs/PCDDFs were in the range $0.3 \sim 5.0$ % as show in Table 1.

Concentration ratio	MSW	IW	SIW	Fe	Cu	Al
Coplanar PCBs (ng-TEQ/Nm ³)	0.136	0.025	0.036	0.018	0.026	0.020
Coplanar PCBs to PCDDs/PCDFs (%) ^{*1}	2.9	1.3	0.3	4.0	5.0	3.2

Table 1. TEQ concentrations ratios of coplanar PCBs to PCDDs/PCDFs

*1: TEQ concentration ratios of coplanar PCBs to PCDDsPCDFs. TEQ concentrations of PCDDs/DFs were calculated by International TEF while those of coplanar PCBs were calculated by WHO-TEF.

Meanwhile, in order to identify the emission from where, it will be useful to know the emission profile of PCB congeners, including coplanar PCBs, which can discriminate the emission sources. For this purpose, we compared PCBs₁⁻ emission patterns to that of Aroclor which was intentionally produced for industrial use several decades ago.

As a result, all thermal treatment facilities studied emitted the whole coplanar PCBs_i⁻ congeners in a unique emission pattern, including $3,3_i^-,4,4_i^-,5$ -PeCB (#126) and $3,3_i^-,4,4_i^-,5,5_i^-$ (#169) which were not contained in Aroclor mixture.

In particular, $3,3_i^-,4,4_i^-$ -TeCB (#77) was dominating congener as a total concentration in SIW incinerator, ferrous sintering furnace, and aluminum smelting furnace, while $2,3_i^-,4,4_i^-,5$ -PeCB (#118) was the most abundant congener in Aroclor mixture. Thus, $3,3_i^-,4,4_i^-,5$ -PeCB (#126) and $3,3_i^{(0)},4,4_i^-,5,5_i^{(0)}$ -HxCB (#169), whose WHO-TEF values are 0.1 and 0.01 respectively, are the main contributors to the overall TEQ concentration of coplanar PCBs. This result was similar to the previous reports which were investigated for incinerators and other thermal sources^{4,5)}.

On the other hand, we analyzed and examined whole PCB congeners of 209 kinds for the thermal facilities, and a portion of results, i.e., compositional ratios for penta-CBs₁⁻ congeners, were presented in Figure 1. The most abundant congener of Aroclor mixture was $2,3,3_i^-,4_i^-,6$ -PeCB (#110) followed by $2,3_i^-,4,4_i^-,5$ -PeCB (#118) and $2,2_i^-,3,5_i^-,6$ -PeCB (#95), but in thermal sources $2,3,3_i^-,4,4_i^-$ -PeCB (#105), $2,3_i^-,4,4_i^-,5$ -PeCB (#118) or $3,3_i^{(B)},4,4_i^-,5$ -PeCB (#126) was founded as a predominating peak while $2,3,3_i^-,4_i^-,6$ -PeCB (#110) was determined as a relatively weak peak. As mentioned above, coplanar PCB $3,3_i^{(B)},4,4_i^-,5$ -PeCB (#126) was all determined in thermal sources to be studied, and noticeably it was the most abundant congener in SIW incinerator and copper melting furnace.

Recently, Hirota et al. ⁶⁾ investigated the reaction path on coplanar PCBs formation using abinitio molecular orbital calculation, and suggested the minimum energy path on coplanar PCBs formation based on $3,3_i^-,4,4_i^-,5,5_i^-$ -HxCB (#169). It could be one of the explanations for coplanar PCBs emission from the thermal processes such as incineration, sintering, smelting etc.

In this study, we reviewed the emission characteristics of coplanar PCBs from a few thermal sources, comparing the emission patterns of PCBs_j⁻ whole congeners, but it is needed to study further thermal sources including unregulated sources.

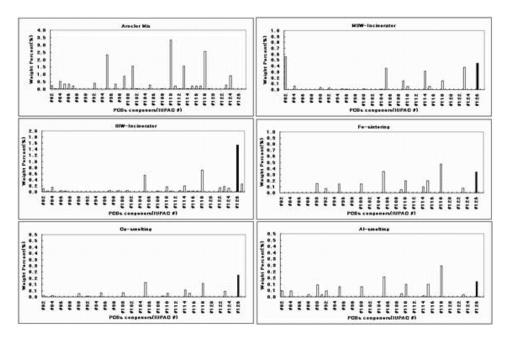


Figure 1. Congener profiles of penta-CBs from thermal sources.

References

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