Congener patterns of coplanar PCBs from metallurgical industry

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Introduction

Polychlorinated biphenyls (PCBs) are widespread contaminants in environment because of not only worldwide use of commercial PCB products in the past, but also air emission from thermal sources such as sintering, smelting and incinerating processes in the present. PCB congeners, having four or more chlorine atoms with no or a few chlorine substitutions in the 2,2',6,6'-ortho positions, have a coplanar conformation, thus are called as coplanar PCBs. These coplanar PCBs congeners are known to more strongly react with aryl hydrocarbon receptor than other PCB congeners. This reaction, which is mostly known in dioxin and furan congeners[1], is believed to initiate adverse health effects. Of the twelve coplanar PCBs congeners, non-ortho-PCB, such as #77, #81, #126 and #169, and mono-ortho-PCB, such as #105, #114, #118, #123, #156, #157, #167 and #189, have been identified as producing dioxin-like toxicity. Thus, they are sometimes referred to as the "dioxin-like PCBs", and have been assigned toxic equivalency factors (TEF) by the World Health Organization (WHO).[2,3]

The metallurgical industry such as sintering plant and secondary nonferrous smelting plant is known as one of major emission sources of unintentionally produced chemicals.

In comparison with polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), emission data for coplanar PCBs from thermal sources are little available. Therefore, this study was performed in order to investigate emission status and congener profile on 12 kinds of coplanar PCBs from the ferrous and nonferrous industries in Korea.

Material and Methods

A total of 99 flue gas samples were collected from the ferrous and nonferrous metal industries, such as iron-ore sintering furnaces, coke ovens and converters in ferrous metal, and copper, zinc, and aluminum smelting furnaces in nonferrous metal in the year of 2001 to 2003. Sampling was performed at the stack 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). Collected samples were soxhlet-extracted, and separately cleaned up for coplanar PCBs and PCDDs/PCDFs using multi-layer silica gel column (Na_2SO_4 6g, 10% $AgNO_3$ silica gel 3g, silica gel 0.9g, 22% H_2SO_4 silica gel 3g, silica gel 0.9g, 44% H_2SO_4 silica gel 3g, silica gel 0.9g, 2% KOH silica gel 3g, silica gel 0.9g), alumina column and activated carbon column. Also, finalized samples, after cleaned up and concentrated, were separately analyzed by high-resolution gas chromatography/ high-resolution mass spectrometry (Autospec Ultima, Micromass Co.) above 10,000 resolution with a DB-5MS column of 60 m × 0.32 mm inner diameter × 0.25 µm for co-planar PCBs, and an SP-2331 column of 60 m × 0.32 mm inner diameter × 0.25 µm for PCDDs/PCDFs. Toxic equivalents as 2,3,7,8-TeCDD (TEQs) were calculated by using the WHO-TEF for both coplanar PCBs and PCDDs/PCDFs.

Results and Discussion

As a total concentration of coplanar PCBs, aluminum smelting furnaces emitted the highest concentrations of 0.0375~105.7931 ng/Nm^3 (n=38, average 13.3071), followed by sintering furnaces, 1.7574~9.1509 ng/Nm^3 (n=12, average 5.4834), converters, 0.0365~24.0693 ng/Nm^3 (n=25, average 4.3510). But, as a TEQ concentration of them, sintering furnaces emitted the highest concentrations of 0.0192~0.1203 ng WHO-TEQ /Nm^3 (n=12, average 0.0663), followed by copper smelting furnaces, 0.0000~0.7886 ng WHO-TEQ/Nm^3 (n=11, average 0.0234), aluminum smelting furnaces, 0.0002~0.0921 ng WHO-TEQ/Nm^3 (n=38, average 0.0224). The contribution rates of coplanar PCBs to total WHO-TEQs ranged from 5.8% to 13.4%, showing that metallurgical facilities were major contaminating sources of coplanar PCBs, and PCB #126 occupied most portion of total TEQ values of coplanar PCBs (90~97%).

Table1. Emission concentration of coplanar PCBs and PCDDs/PCDFs in ferrous metal and nonferrous metal industries

Name of Plant		Coplanar PCBs[*1]			PCDDs/PCDFs[*2]
		ng WHO-TEQ /Nm^3	ng/Nm^3	Contribution to total WHO-TEQ[*3](%)	ng WHO - TEQ/Nm^3
Ferrous metal	Sintering Furnace (n=12)	0.0192~0.1203 (0.0663)	1.7574~9.1509 (5.4834)	6.4	0.2294~2.0595 (0.9768)
	Coke Oven (n=2)	0.0012~0.0041 (0.0026)	0.0690~1.6112 (0.8401)	9.7	0.0229~0.0256 (0.0243)
	Converter (n=25)	0.0001~0.0357 (0.0081)	0.0365~24.0693 (4.3510)	5.8	0.0034~0.2409 (0.1307)
Nonferrous metal	Copper (n=11)	0.000~0.7886 (0.0234)	0.0458~4.7619 (1.5370)	10.3	0.0054~0.5661 (0.2030)
	Zinc (n=11)	0.0002~0.0379 (0.0118)	0.0331~4.0712 (1.1762)	13.4	0.0000~0.2514 (0.0764)
	Aluminum (n=38)	0.0002~0.0921 (0.0224)	0.0375~105.7931 (13.3071)	8.7	0.0017~0.9550 (0.2361)

*1 : Summation of 12 kinds of coplanar PCBs. *2 : Summation of 17 kinds of 2,3,7,8-PCDDs/PCDFs. *3 : total WHO-TEQs = PCDDs/PCDFs (ng WHO- TEQ/Nm^3) + Coplanar PCB(ng WHO- TEQ/Nm^3) *4: The figure in parentheses is average value.

On the other hand, the congener patterns of coplanar PCBs in flue gases showed that the abundances of relatively toxic non-ortho-PCBs, such as #126 and #169, were in the range of 7.7~20.1% to total coplanar PCB's concentrations in most facilities, with the exception of aluminum smelting furnaces, 1.9%. In addition, contribution rate of these congeners in Aroclor mixture(1242:1248:1254:1260) is less than 0.1% of total coplanar PCB's concentrations on average.[4] However, mono-ortho-PCBs such as #105 and #118 in most of facilities amounted to 21.0~46.9% of total coplanar PCB's concentrations on average, with the exception of aluminum smelting furnaces, 78.8%, while contribution rate of these congeners in Aroclor mixture is more than 85% of total coplanar PCB's concentration on average.

Our results were consistent with the previous investigation showing the substitution tendency towards meta- and para-position in the thermal processes, in comparison with ortho- and para-substitution tendency in commercial PCB products.[5] From these results, it might be concluded that formation mechanism of PCBs in thermal sources is different from those in non-thermal sources.

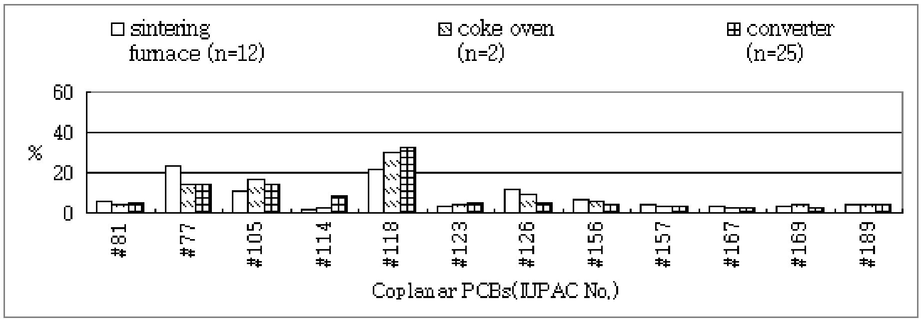

Figure 1.Congener profilesof coplanar PCBs in flue gases of ferrous metal facilities.

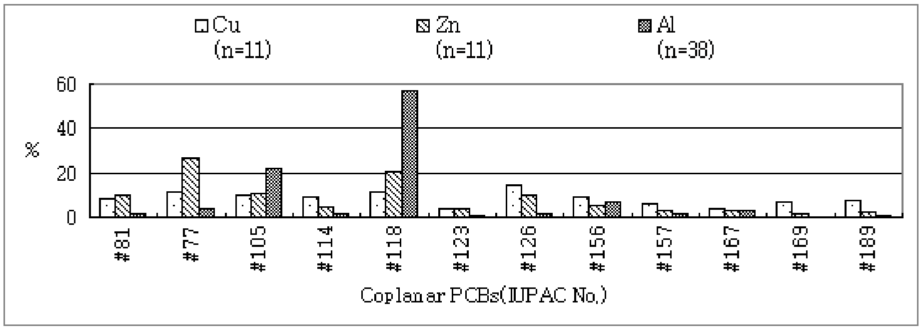

Figure 2.Congener profilesof coplanar PCBs in flue gases of nonferrous metal facilities.

Meanwhile, good correlations were observed between coplanar PCBs (ng WHO-TEQ /Nm^3) and PCDDs/PCDFs (ng WHO-TEQ/Nm^3) in flue gases from ferrous and nonferrous metal facilities as follows:

- Ferrous metal: $Y = 15.320X – 0.0557$ (R^2=0.950, n = 39)

- Nonferrous metal: $Y = 9.264X + 0.0058$ (R^2 = 0.780, n = 60)

If postulated main formation of PCDDs/PCDFs into two pathways in thermal processes, i.e., *de novo* synthesis from unburned carbon or hydrocarbon and precursor formation from chlorinated aromatic compounds, probably the formation mechanisms which can apply to PCDDs/PCDFs would also apply to PCBs, especially coplanar PCBs.[6] Accordingly, good correlation might be from similar formation mechanism between coplanar PCBs and PCDDS/PCDFs.

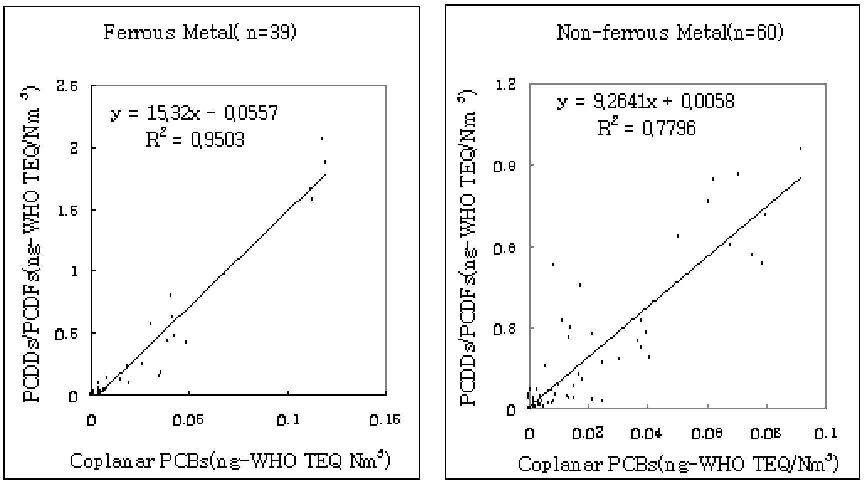

Figure 3.Correlations of PCDDs/PCDFs vs. Coplanar PCBs.

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