Distributions of Atmospheric Coplanar PCBs, Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans between Vapor Phase and Particle Phase

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Introduction

Recently, it has become apparent that non-ortho coplanar PCBs {3,3',4,4'-tetrachlorinated biphenyl (Co-*tetra*-CB), 3,3',4,4',5-pentachlorinated biphenyl (Co-*penta*-CB), 3,3',4,4',5,5'-hexachlorinated biphenyl (Co-*hexa*-CB)} are formed during the incineration of municipal waste[1], and these Co-PCBs are considered to be an environmental threat along with polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). The atmosphere serves as an important pathway for the transfer of PCDDs, PCDFs and Co-PCBs to land and natural water. The transfer to foods such as fish, shellfish, milk and vegetable is an important problem to be considered because the daily intake of Co-PCBs in toxic equivalent (TEQ) was reported to be much greater than that of PCDDs or PCDFs in Japan[2]. We have already examined the level of the Co-PCBs in the atmosphere[3], and found low toxic contribution from Co-PCBs compared to PCDDs and PCDFs, and significant correlations among these compounds[4]. However, for the above-mentioned reason, more research is needed to investigate the Co-PCBs in the atmosphere in detail. Reliable information on the concentrations in the vapor, and the particle phases in atmosphere is essential for establishing transport models and for estimation of wet and dry deposition rates. We report the concentrations of these compounds in the particle and vapor phases, obtained by a high volume air sampling method.

Experimental

A high volume air sampling method using polyurethane foam plugs (PUFPs) was used to collect atmospheric Co-PCBs, PCDDs and PCDFs, passing through a quartz fiber filter (QFF) for 24 hours in summer and winter. QFF and PUFPs were extracted with toluene and acetone in a Soxhlet extractor for 24 hours. The extracts were fortified with ten kinds of ^{13}C-labeled PCDDs/PCDFs and three kinds of ^{13}C-labeled Co-PCBs as internal quantification standards. The extracts were purified on a silica gel column, alumina column and a charcoal-anhydrous sodium sulfate column. The Co-PCBs, PCDDs and PCDFs were analyzed by HRGC/HRMS technique using a Finnigan MAT-90 mass spectrometer (Finnigan MAT, Germany) directly interfaced with a Varian Model 3400 gas chromatograph. The GC was equipped with a splitless injector and a SP-2331 capillary column for Co-PCBs, PCDDs and PCDFs. For analysis of *hepta*-, *octa*-PCDDs and PCDFs, an OV-17 capillary column was used. During GC/MS data acquisition, perfluorokerosene was bled into the mass spectrometer to obtain high accuracy mass assignments at 8000 to 10000 mass resolution. Two ions of a molecular cluster were recorded.

Results and Discussion

Co-PCBs, PCDDs and PCDFs in air samples were analyzed in PUFPs as the vapor-phase concentration and in QFF as the particle-phase concentration. The average temperature

on each sampling date was 25.5-27.6 °C in summer and 8.3-12.2 °C in winter. Tables 1 and 2 show the distributions of the concentrations and TEQs of these compounds between vapor phase and particle phase. Co-PCBs existed mostly in the vapor phase in summer and partitioning to particle phase increased somewhat in winter. The congener patterns of atmospheric Co-PCBs were similar at all three sampling sites. The order of their concentration was *tetra*-CB>*penta*-CB>*hexa*-CB in vapor phase, and *penta*-CB>*tetra*-CB>*hexa*-CB in particle phase. Co-*penta*-CB was identified as the dominant congener of Co-PCBs, providing a total of about 67 percent of the TEQ loading for the two phases. PCDDs and PCDFs were distributed roughly equally between particle and vapor phases in summer, but in winter the greater part of these compounds was in the particle phase. Therefore, particle-phase PCDDs and PCDFs mainly contributed to the toxicity in atmosphere in winter. Particularly, PCDFs were responsible for most of the toxicity in the atmosphere in both phases. The toxic contribution of Co-PCBs for PCDDs and PCDFs differed extensively in each phase, but was about 11 percent on the average in both phases (Fig.1). Partitioning of these compounds seemed to depend on the temperature during collection, as the logarithm plots of ratio of vapor-phase Co-PCB concentration to particle phase showed a trend of increasing with average temperature on each sampling date (Fig.2). The relationship between the congeners of these compounds in vapor phases and in particle phase was examined. Co-PCBs had a good correlation in the particle phase with each other, but not in the vapor phase. Co-*penta*-CBs showed a significant correlation with *penta*-CDFs in both phases, as Fig.3 shows. These findings suggested that the *penta*-CBs found in the atmosphere were mostly responsible for the toxicity such as that derived from municipal waste incinerators.

Conclusions

1. Co-PCBs in the atmosphere existed mostly in the vapor phase in summer whereas partitioning to particle phase increased somewhat in winter.
2. Co-*penta*-CBs was responsible for most of the toxicity among the congeners of Co-PCBs in both particle and vapor phases.
3. The greater part of PCDDs and PCDFs in winter were in the particle phase.
4. PCDDs and PCDFs in the particle phase in winter contributed greatly to the toxicity .
5. The toxic contribution of Co-PCBs for PCDDs and PCDFs was about 11 percent.
6. Co-penta-CBs showed a significant correlation with *penta*-CDFs in particle phase and in vapor phase.

References

1) Kawakami, I., Matsuzawa, Y.,Tanaka, M., Sakai, S. (1993), Hiraoka, M.Emission level of Co-PCBs from MSW Incinerators.*Short papers Dioxin 93'*, 375-380
2) Takayama, K., Miyata, H., Aozasa, O., Mimura, M., Kashimoto, T (1991). Dietary Intake of Dioxin-Related Compounds through Food in Japan, *J. Food Hyg. Japan*, **32**(6), 525-532
3) Kurokawa, Y., Matsueda, Osaki, Y., T., Nakamura, M., Takada S., Fukamachi K. (1994) Concentrations and Characteristics of Non-ortho Coplanar PCBs in the Atmosphere. *Journal of Environmental Chemistry*, **4**,No.1, 29-38
4) Kurokawa, Y., Matsueda, Osaki, Y., T., Nakamura, M., Takada S. (1993), Fukamachi K. PCDDs, PCDFs and Co-PCBs in the atmosphere. *Abstract of 2rd Symposium on Environmental Chemistry*, **2**, 520-521
5) Safe S (1990). Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans(PCDFs), and related compounds, Environmental and mechanistic considerations which support the development of toxic equivalency factors(TEFs). *Critical Reviews in Toxicology*, 51-88

Table 1. Concentrations of Co-PCBs, PCDDs and PCDFs (pg/m^3)

Site		summer particle phase	summer vapor phase	winter particle phase	winter vapor phase
A	Total PCDDs	1.104	0.482	14.34	0.644
	Total PCDFs	0.970	1.036	7.279	0.741
	3,3',4,4'-TeCB	0.013	0.799	0.077	0.599
	3,3',4,4',5-PeCB	0.002	0.061	0.083	0.067
	3,3',4,4',5,5'-HxCB	0.001	0.003	0.058	0.001
B	Total PCDDs	10.62	4.304	18.19	1.070
	Total PCDFs	4.985	9.017	19.80	1.415
	3,3',4,4'-TeCB	0.005	0.677	0.094	0.320
	3,3',4,4',5-PeCB	0.015	0.319	0.139	0.112
	3,3',4,4',5,5'-HxCB	0.002	0.019	0.070	0.055
C	Total PCDDs	7.927	1.328	18.70	1.183
	Total PCDFs	9.349	4.486	18.92	2.427
	3,3',4,4'-TeCB	0.023	0.785	0.089	0.606
	3,3',4,4',5-PeCB	0.014	0.414	0.126	0.201
	3,3',4,4',5,5'-HxCB	0.015	0.022	0.094	0.017

Table 2. TEQs of Co-PCBs[a], PCDDs and PCDFs[b] (pg(TEQ) /m^3)

Site		summer particle phase	summer vapor phase	winter particle phase	winter vapor phase
A	PCDDs and PCDFs	0.025	0.035	0.291	0.012
	3,3',4,4'-TeCB	<0.001	0.008	0.001	0.006
	3,3',4,4',5-PeCB	<0.001	0.006	0.008	0.007
	3,3',4,4',5,5'-HxCB	<0.001	<0.001	0.003	<0.001
	Total Co-PCBs	<0.001	0.014	0.012	0.013
B	PCDDs and PCDFs	0.184	0.407	0.310	0.046
	3,3',4,4'-TeCB	<0.001	0.007	0.001	0.003
	3,3',4,4',5-PeCB	0.001	0.032	0.014	0.011
	3,3',4,4',5,5'-HxCB	<0.001	0.001	0.004	0.003
	Total Co-PCBs	0.002	0.040	0.018	0.017
C	PCDDs and PCDFs	0.273	0.218	0.614	0.072
	3,3',4,4'-TeCB	<0.001	0.008	0.001	0.006
	3,3',4,4',5-PeCB	0.001	0.041	0.013	0.020
	3,3',4,4',5,5'-HxCB	0.001	0.001	0.005	0.001
	Total Co-PCBs	0.002	0.050	0.018	0.027

a) 2,3,7,8-TCDD toxicity equivalency factor by Safe[5] was used.
b) International toxicity equivalency factor was used.

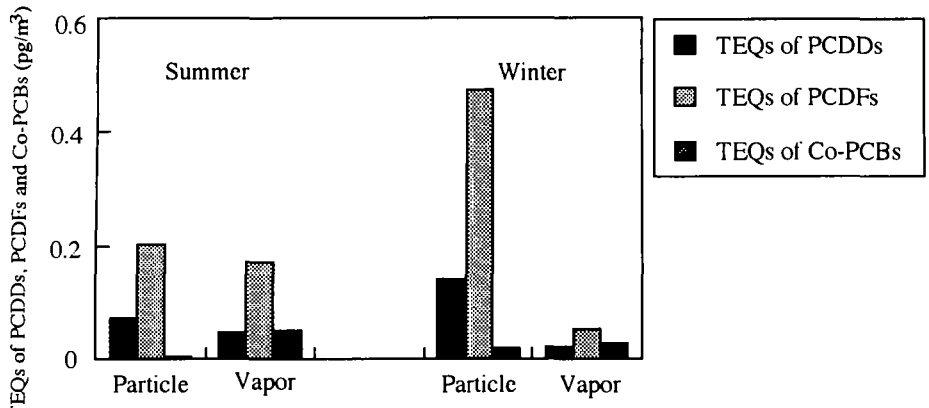

Fig.1 TEQs of PCDDs, PCDFs and Co-PCBs in particle and vapor phases in summer and winter at C site

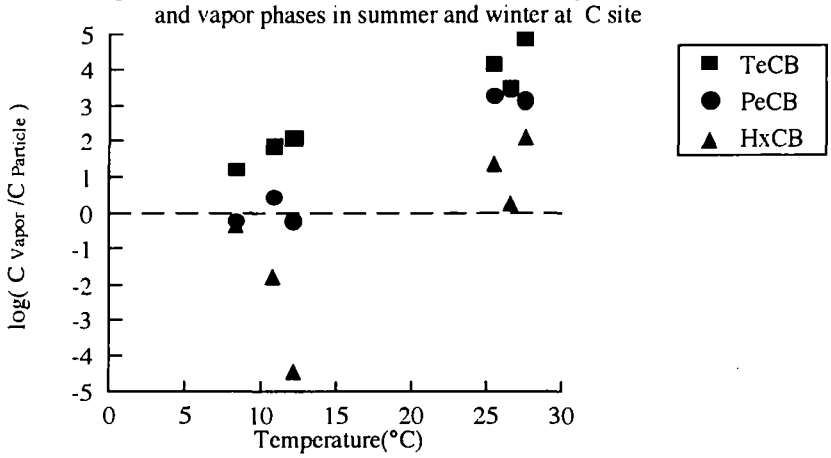

Fig.2 Plots of log(Cvapor phase/Cparticle phase) versus average temperature at sampling date

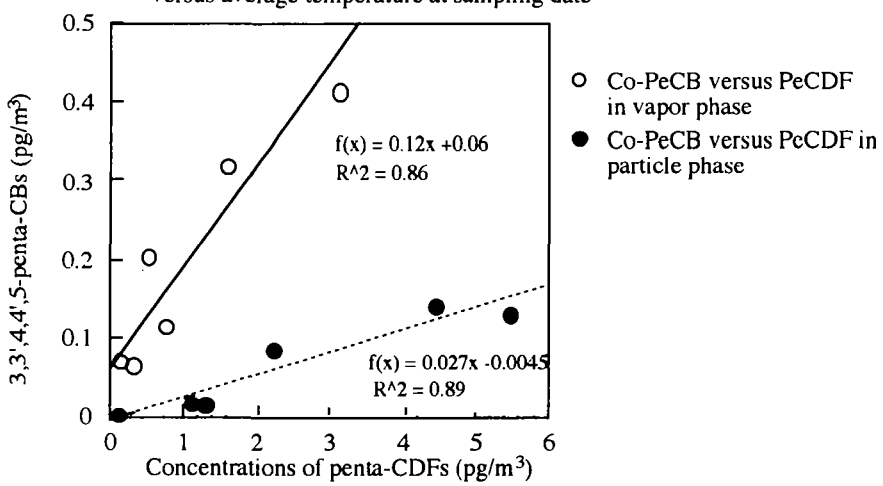

Fig.3 Concentrations of Co-penta-CBs versus penta-CDFs in particle phase(●) and in vapor phase(○)