

Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins P291

Variation of non-*ortho* coplanar PCBs, polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the atmosphere

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INTRODUCTION

Three non-*ortho* coplanar PCBs, 3,3',4,4'-*tetra*-CB(Co-*tetra*-CB), 3,3',4,4',5-*penta*-CB(Co-*penta*-CB) and 3,3',4,4',5,5'-*hexa*-CB(Co-*hexa*-CB) that are highly toxic compounds¹ similar to polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) structurally, have been detected in environmental samples² and various food samples³. These Co-PCBs have a large impact on the intake of toxic equivalent quantities (TEQ), because the daily intake greatly exceed that of PCDDs or PCDFs in Japan³. These Co-PCBs in the environment were previously thought to originate from commercial PCBs; however, recently it has become clear that Co-PCBs are formed during the incineration of municipal waste⁴, and are now considered to be an environmental threat along with PCDDs and PCDFs. In our previous work⁵, significant correlations were found between Co-*penta*-CB and *penta*-, *hexa*-CDF, and between Co-*hexa*-CB and *penta*-, *hexa*-CDF. We suggested then that most of the Co-*penta*-CB and Co-*hexa*-CB observed in the atmosphere might originate from sources such as municipal waste incinerators. In a recent study, Scholz et al.⁶ showed that large amounts of PCBs were formed on fly ash during thermal experiments, and that PCBs may act as a precursor for PCDF, but not PCDD, especially, Co-*hexa*-CB, which showed a much higher tendency to form a PCDF structure than did a mono-*ortho* PCB. These findings strongly supports our observations. Furthermore, to prove the influences of these Co-PCBs on atmospheric PCBs, we measured the Co-PCBs in the air samples from various sites, including background sites, every two years for six years and investigated in detail the correlations between the Co-PCBs and PCDDs/PCDFs at each site.

EXPERIMENTAL

A high volume air sampling method using polyurethane foam (PUF) plugs was used to collect atmospheric Co-PCBs, PCDDs and PCDFs, passing air through a quartz fiber filter (QFF) for 24 hours at seven sites (A to G) in 1992, 1994 and 1996. Samples were taken for two consecutive days at each site in summer and winter. Site A was a remote site 16 km away from any major incinerators. Sites B and C were located in an urban area with an incinerator 4.3 km south of the site and 5 km south of the site, respectively. Site G was in an industrial area with an incinerator 0.3 km north of the site, whereas site D was in a rural area surrounded by agricultural fields with an incinerator located 8.6 km northeast of the site. Site E was in a suburban residential area of site F with an incinerator 3 km west of the site, and site F was in a urban area with some incinerators within 10 km. QFFs and PUF plugs were extracted with toluene and acetone,

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respectively. 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 washed with concentrated sulfuric acid and purified on a silica gel and alumina column. The Co-PCBs, PCDDs and PCDFs were analyzed by an HRGC/HRMS technique using a Finnigan MAT-90 mass spectrometer (Finnigan MAT, Germany) directly interfaced with a Varian Model 3400 gas chromatograph (GC). The GC was equipped with a splitless injector and an 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.

RESULTS AND DISCUSSION

Three non-*ortho* coplanar PCBs, PCDDs and PCDFs in eighty-four air samples at seven sites were measured in the summer and winter seasons of 1992, 1994 and 1996. Figs. 1, 2 and 3 show the concentrations of atmospheric Co-PCBs; the mean values were used for two consecutive days at each site in summer and winter. Obviously, regional differences were observed in the three Co-PCBs, and each site showed nearly the same tendencies every two years. At remote site A, the concentration of Co-PCBs was lowest, with higher concentrations measured at urban, suburban and industrial site B, C, E, F, G, and even agricultural site D. These levels seemed to indicate that high concentrations of Co-PCBs depend on the presence of the incineration plants near the sites, and this situation did not change significantly during the six years of our testing. Considerable variation of Co-PCB concentrations was seen in these air samples even on two consecutive days at the same site, but this may have been due to the weather conditions such as the wind direction. The order of Co-PCB concentrations was *tetra*-CB > *penta*-CB > *hexa*-CB. Concentrations of Co-PCBs were one digit or two digits lower than those of PCDDs and PCDFs. The concentrations of Co-*tetra*-CBs, Co-*penta*-CBs and Co-*hexa*-CB were 0.059 to 4.3, 0.01 to 0.81 and 0.001 to 0.33 pg/m^3 , respectively. The TEQs of Co-PCBs were calculated using I-TEF and Co-*penta*-CB was the dominant congener of the Co-PCBs, providing a total of about 94% of the TEQ loading. The concentrations of the TEQ levels of Co-PCBs were 0.001-0.083 $\text{pg (TEQ)}/\text{m}^3$. The toxicity contribution of Co-PCBs to dioxin toxicity was low (about 10 %). This percentage was a little higher than that found in the flue gas of municipal solid waste (about 5 %)⁷. The seasonal differences at each sampling site were not obvious in this study, but Co-*tetra*-CBs were slightly higher in the summer than in winter, whereas the Co-*penta*-CB and Co-*hexa*-CB were relatively higher in the winter.

Relationships between Co-PCBs and PCDFs were investigated at each site. Co-*penta*-CBs and Co-*hexa*-CBs correlated with each other but not with Co-*tetra*-CBs. Good correlations were found between Co-*penta*-CB and *penta*-, *hexa*-CDF, and between Co-*hexa*-CB and *penta*-, *hexa*-CDF at all sites, except sites A and D as shown in Figs. 4, 5 and 6. The lack of a correlation in area A may have been due to the degradation of Co-PCBs and PCDDs/DFs during the long-range transport that occurred in the remote area, but another reason must be assumed in agricultural site D. We also found significant correlation between Co-*penta*-CBs and 2,3,4,6,7-*penta*-CDF ($r=0.96$ for 28 data at 1992) and less correlation between Co-*penta*-CBs and 2,3,4,7,8-*penta*-CDF ($r=0.70$ for 28 data at 1992). Weak steric hindrance might have influenced this. These relationships between Co-PCBs and PCDFs lead us to the assumption that part of the PCBs were converted to PCDFs in proportion to the amount of the PCBs close to PCDFs structurally when PCBs were formed on fly ash.

Considering other coplanar PCBs, including toxic mono-*ortho*- and di-*ortho*-PCBs, more research is needed to reveal the real influences from sources such as incinerators.

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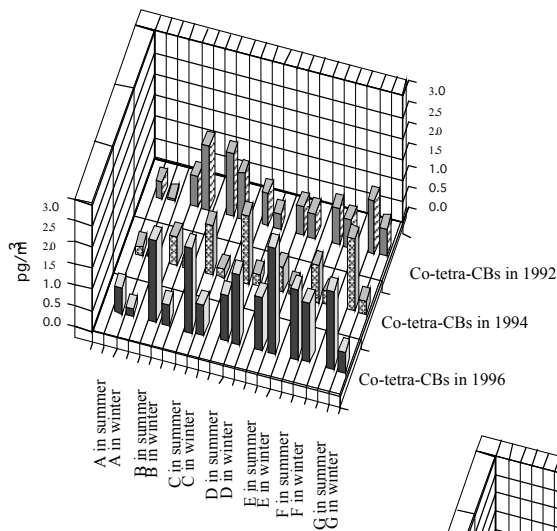


Fig.1 Variation of Co-tetra-CBs in the atmosphere at seven sites (A to G)

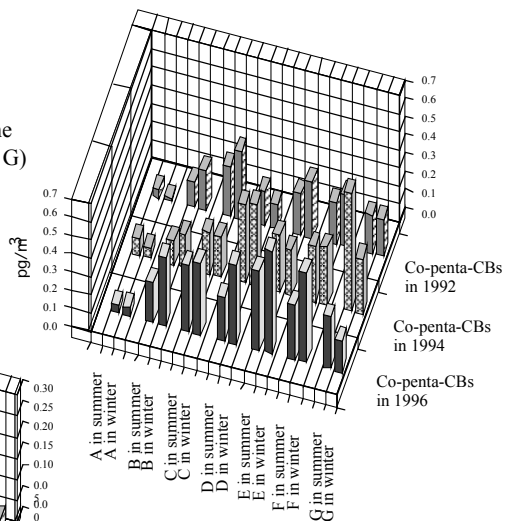


Fig.2 Variation of Co-penta-CBs in the atmosphere at seven sites (A to G)

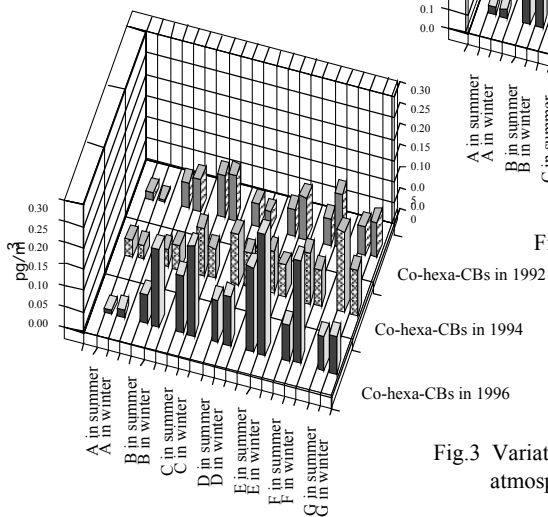


Fig.3 Variation of Co-hexa-CBs in the atmosphere at seven sites (A to G)

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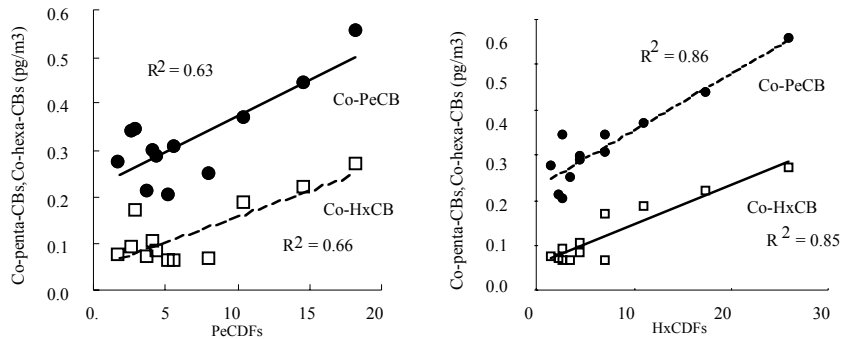


Fig. 4 Concentrations of the Co-penta-CBs and Co-hexa-CBs versus PeCDF (left) and HxCDF (right) at site F (suburban area) ● Co-PeCB □ Co-HxCB

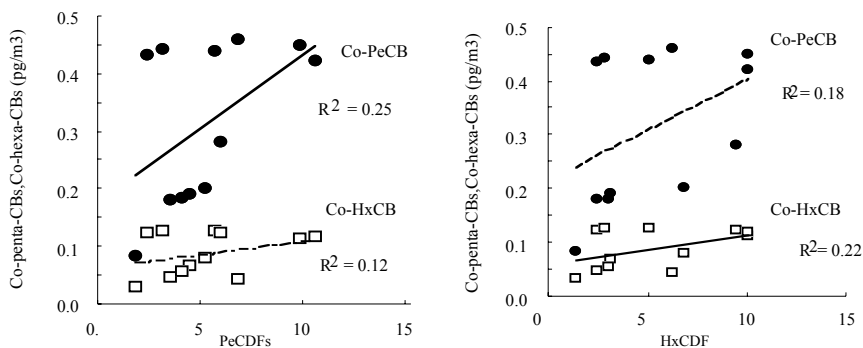


Fig. 5 Concentrations of the Co-penta-CBs and Co-hexa-CBs versus PeCDF (left) and HxCDF (right) at site D (agricultural area)

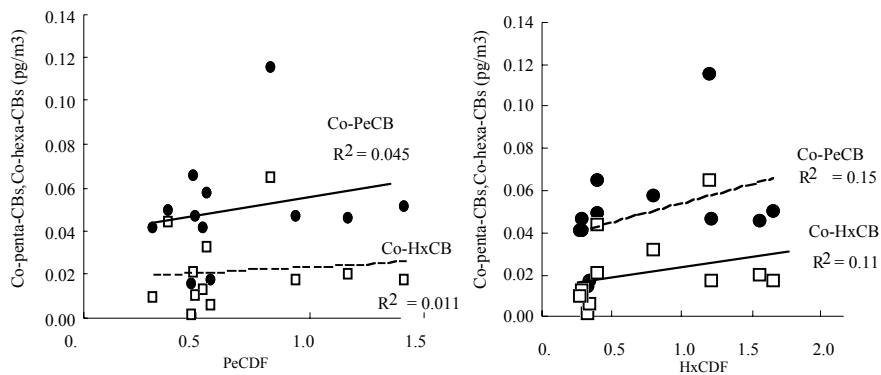


Fig. 6 Concentrations of the Co-penta-CBs and Co-hexa-CBs versus PeCDF (left) and HxCDF (right) at site A (remote area)

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