

## SOURCES OF PCBS IN URBAN AIR AND FACTORS AFFECTING THEIR CONCENTRATIONS

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### Introduction

Dioxin-like PCBs are referred to as dioxin-related compounds and are evaluated together with PCDDs/PCDFs in terms of toxicity. In Japan, the contribution of dioxin-like PCBs to the total TEQ of human intake is comparable to that of PCDDs/PCDFs<sup>1</sup>. Understanding the contributions of different PCB sources is important for developing effective countermeasures against dioxin pollution.

The major sources of dioxin-like PCBs in Japan are considered to be those released from industrial PCB products and formed as byproducts during thermal processes<sup>2,3</sup>. Concerning atmospheric PCBs, they are considered to be produced by volatilization from use, storage, or disposal of industrial PCB products, or from contaminated soil, vegetation, or other surfaces and emissions from incinerators.

In this study, in order to estimate the relative contributions of PCBs produced by volatilization and incinerator emissions to atmospheric PCBs, we analyzed the relationships among variations in atmospheric concentrations of congeners, factors affecting atmospheric concentrations, and temperature dependence of atmospheric concentrations.

### Theory

#### *Volatilization of PCBs*

With regard to volatilization of PCBs from their sources, if the concentrations of PCBs in the gas phase above a source ( $C_g$  [pg/m<sup>3</sup>]) and in a sorbing organic materials ( $C_s$  [pg/m<sup>3</sup>]) are in equilibrium (Fig. 1),

$$C_s/C_g \approx \alpha \times K_{OA}, \quad (1)$$

where  $\alpha$  is the factor for conversion from octanol to an organic material, and  $K_{OA}$  [-] is the octanol-air partition coefficient. The plot of  $\log K_{OA}$  vs  $1/T$  ( $T$ : ambient temperature) is almost linear in the range of ambient temperature of interest<sup>4</sup>,

$$\log K_{OA} \approx A / T + B, \quad (2)$$

where  $A$  ( $= \Delta H_{OA}/2.303R$ ,  $H_{OA}$  is the enthalpy of phase change from octanol to air and  $R$  is the ideal gas constant ( $=8.314$  J/mol/K)) and  $B$  are constants.

According to eqs. 1 and 2,

$$\log (C_s/C_g) = A / T + B + \log \alpha. \quad (3)$$

Assuming that volatilized PCBs are transported to ambient air and partly sorbed into suspended particles, the total ambient air concentration in gas and particle phases produced by volatilization ( $C_{vol}$  [pg/m<sup>3</sup>]) under a steady-state condition is

$$C_{vol} = C_g \times F / k, \quad (4)$$

where  $F$  [1/s] is the rate of transport from the source to an ambient environment and  $k$  [1/s] is the first-order rate constant of elimination from air by deposition, degradation, advection, and so forth.

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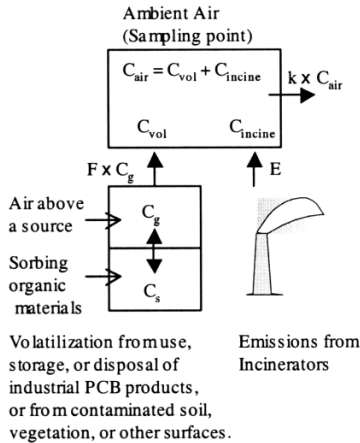


Fig. 1. Atmospheric PCBs produced by volatilization and incinerator emissions.

According to eqs. 3 and 4,

$$\log C_{vol} = -A/T - B - \log \alpha + \log C_s + \log (F/k). \quad (5)$$

Assuming that  $C_s$  is so large that it is not affected by temperature-driven volatilization and that  $F$ ,  $k$ , and  $\alpha$  are independent of temperature, the plots of  $\log C_{vol}$  vs  $1/T$  should exhibit a log-linear relationship with the slope of  $A$  ( $=\Delta H_{OA}/2.303R$ ), and thus

$$\log C_{vol} = -A/T + B' - \log k, \quad (6)$$

where  $B'$  is a constant.

## Emission of PCBs from incinerators

Assuming that there is little difference in elimination rate between atmospheric PCBs produced by volatilization and those by incinerator emissions, the total ambient air concentration in gas and particle phases produced by incinerator emissions ( $C_{incine}$  [pg/m<sup>3</sup>]) under a steady-state condition is

$$C_{incine} = E/k, \quad (7)$$

where  $E$  is the rate of emission of a compound from incinerators [pg/m<sup>3</sup>/s].

## Normalization

Since the atmospheric concentration of a compound is variable with the change of  $k$ , the atmospheric concentration of the compound of interest is normalized by dividing it by the atmospheric concentration of a reference compound ( $C_{ref}$ ) produced by incinerator emissions. It is assumed that the elimination rate of the reference compound is equal to that of the compound of interest, that the emission rate of the reference compound from incinerators ( $E_{ref}$  [pg/m<sup>3</sup>/s]) and  $E$  are independent of temperature, and that  $E/E_{ref}$  is constant, and thus

$$\log (C_{vol}/C_{ref}) = -A/T + B' - \log E_{ref} \quad (8)$$

$$\log (C_{incine}/C_{ref}) = \log (E/E_{ref}). \quad (9)$$

If the compound of interest is mostly produced by volatilization, the  $\log (C_{air}/C_{ref})$  should be related to  $1/T$  in eq. 8 ( $C_{air}$  is the atmospheric concentration of the compound of interest). On the other hand, if the compound of interest is mostly produced by incinerator emissions,  $\log (C_{air}/C_{ref})$  should be constant against temperature change as in eq. 9. From this, the contributions of volatilization and incinerator emissions to atmospheric PCBs can be determined.

## Materials and Methods

### *Sample collection and analysis*

Air samples were collected in Yokohama during the period from Oct. 1998 to Mar. 2000 using a high-volume air sampler ( $n=22$ ). The details of sample collection and analysis were reported in our previous study<sup>5</sup>. For results and discussion, the total concentrations in gas and particle phases were used.

### *Statistical analysis*

Principal component analysis (PCA) and multiple regression analysis (MRA) were performed using Statistica for Windows 5.0J (StatSoft, Inc.).

For PCA, 82 peaks of PCDDs/PCDFs and 43 peaks of PCBs ( $n=15-22$ ) were subjected. Variances of the logarithm of atmospheric concentrations of PCDDs/PCDFs and PCBs were normalized to unity using the correlation matrix to determine their relative variation. The eigenvectors were normal-varimax-rotated for better interpretation of the results.

For MRA, reciprocal temperature (the average during each sampling time), logarithm of wind speed (the average during each sampling time), and sampling date were used as independent variables, and logarithms of atmospheric concentrations of PCDDs/PCDFs and PCBs were used as dependent variables.

## Results and Discussion

### *Relationships among variations in atmospheric concentrations of congeners*

To detect similarities, differences, and relationships of the variations in atmospheric concentration among congeners, PCA of the data was conducted. The result showed that the first two principal components, PC-1 and PC-2, accounted for 66 and 23% of the total variance, respectively. The plot of loadings on PC-1 and PC-2 is shown in Fig. 2. The congeners related to PC-1 that had high loading are PCDDs/PCDFs and PCB-126, 169, 189, and 198 (IUPAC Nos.), and these congeners are located close to each other, indicating that they are highly correlated to one another and hence may have come from an identical emission source category and may behave identically in the atmospheric environment. The majority of PCB congeners are related to PC-2, which may be different from the congeners related to PC-1 in terms of emission sources or behavior in the atmospheric environment. PCB-81, 156, 157, 170, 172, 173, 190, and 191, which were located near the radius of the region between PC-1 and PC-2 in the plot of loadings, were considered to be influenced by both PCs.

### *Factors affecting atmospheric concentrations of congeners*

From the results of MRA, the contributions of temperature to the variations of atmospheric concentrations of the congeners related to PC-2 were higher than those of wind speed and sampling date, whereas the contributions of temperature to the variations of atmospheric concentrations of the congeners related to PC-1 were not significant. A possible explanation for this could be that the congeners related to PC-1 are produced by incinerator emissions, whereas the congeners related to PC-2 are produced by volatilization. This result is consistent with that of our previous study<sup>6</sup>, which shows that the isomer distributions of atmospheric PCDDs/PCDFs in the Kanto region (including Yokohama) corresponded well with those of incinerator emissions.

### *Source contributions estimated by temperature dependence of atmospheric PCB concentrations*

In order to estimate source contributions, the relationships between  $\log(C_{\text{air}}/C_{\text{ref}})$  and  $1/T$  are examined. 2,3,4,7,8-penta-CDF was used as the reference compound in eqs. 8 and 9 (little difference in the result was obtained when other PCDD/PCDF congeners were used instead of 2,3,4,7,8-penta-CDF because atmospheric concentrations of PCDD/PCDF congeners were highly correlated to each other, as shown in Fig. 2). The  $\log(C_{\text{air}}/C_{\text{ref}})$  of the majority of PCBs were strongly dependent on ambient temperature, and the slopes of the plots were almost equal to the predicted slopes ( $=-A = -\Delta H_{\text{OA}}/2.303R$ ), which ranged from -3300 to -4700<sup>4,7-8</sup> (Fig. 3 and Table 1). Such congeners include PCB-105, 114, 118, 123, and 180. This result suggests that these congeners are produced by volatilization rather than by incinerator emissions. On the other hand, the slopes of plots of  $\log(C_{\text{air}}/C_{\text{ref}})$  vs  $1/T$  for several congeners, such as PCB-81, 126, 157, 169, 170, and 189, were moderate. In particular, the plot of PCB-169 showed an almost constant slope in the range of the overall ambient temperature, suggesting that

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most of the atmospheric PCB-169 are produced by incinerator emissions. The plot of PCB-126 showed an almost constant slope in the range of low ambient temperature but increased as ambient temperature increased (as  $1/T$  decreased in Fig. 3), suggesting that most of the atmospheric PCB-126 are produced by incinerator emissions in winter and by volatilization of PCBs in summer. Since PCB-126 and 169 together account for nearly all of the TEQ of atmospheric PCBs, incinerator emissions are considered to give a significant contribution to TEQ of atmospheric PCBs although the majority of PCBs is considered to be produced by volatilization rather than by incinerator emissions. The trend of the contributions of potential sources to atmospheric PCBs obtained from this study is consistent with that to accumulations of PCBs in sediments determined using a chemical mass balance approach <sup>9</sup>.

## References

1. Ministry of Health and Welfare of Japan (1999) Total diet study 1998.
2. Sakai, S., Hirakawa, K., Takatsuki, H. and Kawakami, I. (2001) Environ. Sci. Technol. 35, 3601-3607.
3. Masunaga, S. (2000) in: Proc. of the 3rd International Workshop on Risk Evaluation and Management of Chemicals (Yokohama), 80-93.
4. Harner, T. and Mackay, D. (1995) Environ. Sci. Technol. 29, 1599-1606.
5. Ogura, I., Masunaga, S. and Nakanishi, J. (2001) Organohalogen Compounds 52, 483-486.
6. Ogura, I., Masunaga, S. and Nakanishi, J. (2001) Chemosphere 45, 173-183.
7. Harner, T., Green, J. L., and Jones, K.C. (2000) Environ. Sci. Technol. 34, 3109-3114.
8. Kömp, P. and McLachlan, M.S. (1997) Environ. Toxicol. Chem. 16, 2433-2437.
9. Ogura, I., Masunaga, S., Yoshida, K. and Nakanishi, J. (2002) submitted to Dioxin 2002.

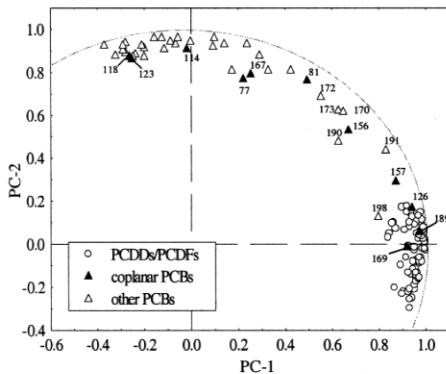


Fig. 2. Plot of loadings on PC-1 and PC-2 for the logarithm of atmospheric concentrations of PCDDs/PCDFs and PCBs. Numbers represent IUPAC Nos. of PCBs.

Table 1. Slopes of the plots of  $\log(C_{air}/C_{ref})$  vs  $1/T$  for dioxin-like PCBs.

IUPAC No.	Slope	IUPAC No.	Slope
118	-5001	167	-3324
123	-4981	81	-2868
114	-4414	170	-2722
105	-4240	157	-2609
180	-4046	126	-1379
156	-3462	189	-870
77	-3456	169	-471

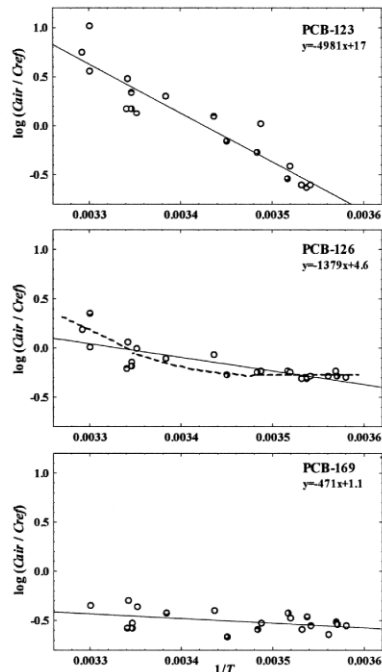


Fig. 3. Plots of  $\log(C_{air}/C_{ref})$  vs  $1/T$ .