

Source apportionment of PCBs in urban ambient air, Japan.

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Introduction

In recent years, source identification and apportionment for PCDDs/DFs and PCBs have come to be studied using statistical methods. For this purpose, it is desired that detailed congener specific concentration data should be used as input data. In this study, all the PCB congeners were measured in ambient air at Yokohama City, Japan and analyzed by principal component analysis (PCA) for source identification. Then the contributions from each source were estimated by multiple regression analysis (MRA).

Methods and Materials

Sample collection and analysis

Ambient air samples were collected at Yokohama National University from March 2002 to February 2003 using high volume air sampler (n=11). Glass fiber filter (GFF) and polyurethane foam (PUF) were added ¹³C-labeled internal standards, and then Soxhlet extracted with distilled toluene over 16 hours. H₂SO₄ silica gel column and activated carbon column were used as cleanup procedure. Finally, ¹³C-labeled recovery standard was spiked for HRGC/HRMS analysis. All the PCB congeners were analyzed by a DB-5 column.

Statistical analysis

PCA was performed using STATISTICA for Windows 5.0J (StatSoft, Inc.). And for MRA, Microsoft Excel program was used. Analytical results for mono- to tri-CB congeners were not included in the statistical analysis because of their low recovery rates. As a result, total of 122 individual and group of congeners were subjected to PCA as input variables.

Results and Discussion

Concentration and TEQ-Concentration in ambient air

PCB homologue concentrations are summarized in Table 1. TEQ concentrations were calculated using WHO-TEFs. The concentration of total PCB and TEQ ranged from 130 to 500 pg/m^3 and from 0.0020 to 0.014 pgTEQ/m^3 , respectively.

Table 1. Sum of gaseous and particulate PCB concentrations. (pg/m^3)

	March	April	May	June	July	August	Sep.	Oct.	Nov.	Dec.	Jan.
Mono-CBs	6.6	3.9	2.8	1.1	0.24	0.51	8.8	15	36	62	36
Di-CBs	27	32	23	26	4.7	11	52	41	64	55	37
Tri-CBs	160	110	90	59	29	56	180	320	160	110	110
Tetra-CBs	53	67	67	67	55	76	150	82	85	71	37
Penta-CBs	17	31	32	32	24	48	69	30	47	10	16
Hexa-CBs	6.5	11	6.6	9.2	10	15	22	10	22	9.9	6.4
Hepta-CBs	2.1	1.8	1.4	1.9	2.5	3.1	4.4	1.8	2.6	2.0	1.8
Octa-CBs	0.31	0.28	0.26	0.40	0.45	0.33	0.87	0.62	0.81	0.66	0.64
Nona-CBs	0.10	0.084	0.094	0.080	0.053	0.037	0.19	0.21	0.29	0.14	0.12
Deca-CBs	0.074	0.058	0.058	0.047	0.03	0.026	0.29	0.20	0.25	0.21	0.17
Co-PCBs	2.7	3.5	4.0	4.3	3.7	6.2	11	4.7	7.5	4.0	2.1
Total Conc.	280	260	220	200	130	210	490	500	420	320	240
TEQ Conc.	0.0055	0.0027	0.0031	0.0034	0.0020	0.0034	0.0097	0.0070	0.014	0.014	0.0081

Among PCB homologues, the ratios of tri-CBs and tetra-CBs to the total PCB concentration were largest, followed by penta-CBs > di-CBs > hexa-CBs. As for dioxin-like PCBs, the levels of mono-*ortho* PCBs were higher than those of the non-*ortho* PCBs. The PCB-118 (IUPAC Nos.) was the most predominant dioxin-like congener, followed by PCB-105 and PCB-77 in terms of concentration, while PCB-126 had the highest TEQ value among all the dioxin-like congeners.

Source identification by PCA

Total of 122 individual and group of congener concentrations in 11 samples were subjected to PCA to study the sources of PCBs in ambient air. The three major principal components (PCs) that had eigenvalue of over 10 were extracted. The loading factor plot of the first and second PC is shown in Figure 1. PC-1 and PC-2 accounted for 43.4% and 23.3% of the total variance, respectively. The congeners highly correlated to PC-2 with factor loadings greater than 0.8 were PCB-198, 205, 189, 126, 81, 194, 169 and 77, etc. The majority of these congeners were known as specific congeners in the flue gas samples (Kim et al., 2004)¹. Therefore, the PC-2 was interpreted as PCBs from combustion sources. Many PCB congeners had strong positive correlation with PC-1. Especially PCB-114, 149/139, 105, 118, 141, 70/76, 89/101/90, 90/95, 182/187, etc. showed factor

loadings higher than 0.8. These congeners were similar to characteristic congeners in Kanechlor (Kim et al., 2004)¹. Thus, PC-1 was interpreted as Kanechlor. PC-3, however, could not be interpreted. These results indicated that Kanechlor and combustion are the two major sources for PCB in air.

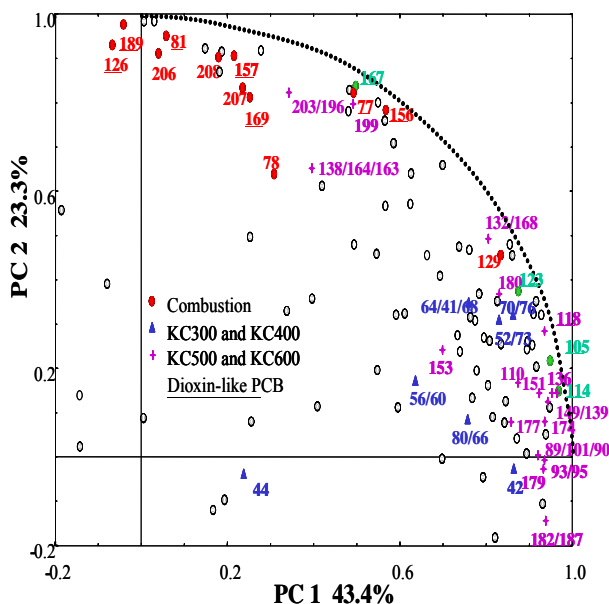


Figure 1. Loading factor plot for PC-1 and PC-2 after normal-varimax rotation. The square, triangle and cross mark represent congeners relate to combustion, KC300-400 and KC500-600, respectively (Kim et al., 2004)¹.

Source apportioning by chemical mass balance (CMB) model

The contributions (a_j) of sources j to ambient air were estimated by minimizing square of residual error χ^2 , as shown by the equation below.

$$\chi^2 = \sum_i^n \left(C_i - \sum_j^p a_j X_{ij} \right)^2$$

Where X_{ij} is the mass fraction of congener i for source j , n is the number of congeners, and p is the number of sources. The detail of this method was described by Ogura et al.²

Under the assumption that incinerator emission gas and Kanechlor were the only sources of PCBs in ambient air in Japan, contributions of sources to ambient air were estimated. The calculation was performed for isomers in each homologue and

then they were summed up. The congener profiles for incinerator emission gas and Kanechlor were taken from the data of Kim et al¹.

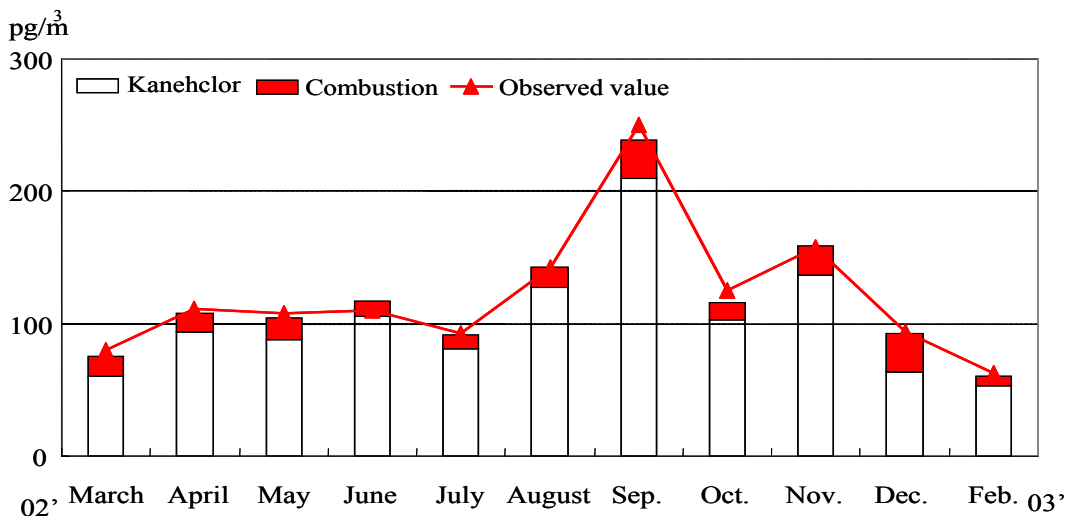


Figure 2. Contribution of each source to ambient air.

Difference between observed and predicted PCB values might be explained by unknown PCB sources and/or error of this estimation. In this study, the contribution of Kanechlor accounted for 70% to 90% of PCBs in ambient air. This indicated that Kanechlor products still are the major contributor of PCB in Japanese ambient air, although production and new use of PCB was stopped over 30 years ago.

Acknowledgements

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References

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2. Ogura I., Masunaga S., Yoshida K. and Nakanishi J. (2002) *Organohalogen Compounds*, 56, 473-476.