LEVEL OF PCB CONGENERS IN AMBIENT AIR

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Introduction

Polychlorinated biphenyls (PCBs) consist of 209 possible congeners and had been widely used as conductor of heat and transformer oils because of their chemical and thermal stability. Due to the serious impact to the ecosystem, the use and production of PCBs ceased in 1972 and PCBs were withdrawn from their users. The PCBs diffusion into the environment by prior uncontrolled release and their long-term stability has caused serious impact to biological system through bio-magnification with food chains. Recently, understanding of toxic coplanar PCBs' (Co-PCBs) formation by combustion process of waste, congener-specific PCB analysis is required in environmental study.

In this report, we focused on the environmental distribution of PCBs, include Co-PCBs, which were characterized by using high-resolution GC/MS-SIM, and the relations between the PCBs composition and the climate on the sampling date were discussed.

Materials and Methods

Air samples were collected on the roof of the institute in Kobe, 65 samples from September to December in 1996 and 4 samples from November to December in 1997.

Air Sampling

Air samples were collected using high volume air sampler (Kimoto Electric Co., Ltd.) within quart microfiber filter (QMF; Whatman QM-A 8 x 10 inches) for particulate, and 2 pieces of polyurethane foam (PUF, 9cm-diameter x 5cm) for vapor phase. Air samples were collected about 1,000m^3 for 24 hours. PUF plugs were cleaned before sampling by extraction in acetone for 24 hours using Soxhlet extractors.

Sample Extraction

PUF and QMF were several extracted in acetone for 24 hours using Soxhlet extractors, then extracts were reduced to 30mL and re-extraction with n-hexane. Extracts were purified by sulfuric acid, then washed by water. Organic layer was dried on sodium sulfate. Slightly amount of reduced copper added to for reducing sulfur, after concentrated to 1mL(PUF) or 0.3mL(QMF).

GC/MS-SIM Conditions

HRGC/HRMS-SIM analyses of PCB congeners were carried out on a JMS-700 mass spectrometer (JEOL) connected to a HP5890 gas chromatograph (Hewlett Packard). Gas chromatographic separation of samples was carried out on 25m fused silica capillary column of 0.2mmID. coated with a 0.33um film of 5% diphenyl polydimethylsiloxane (HP Ultra-2, Hewlett Packard). Helium was used as carrier gas at a flow late of 1.5ml/min. An aliquot of 2uL of the sample was injected. The injection port temperature was 250°C. The interface temperature was 250°C. The chamber temperature was 250°C. The HRGC was temperature programmed from 70°C(2min)-8°C/min-300°C(8min). The mass spectrometer was operated in electron impact ionization mode with ionization energy of 70eV. The resolution was more than 10,000 (at m/z

219 of perfluorokerosene (PFK)).

Results and Discussion

PCB Concentrations

The concentrations of total PCB in air were an average 600pg/m^3(80~1,700pg/m^3). The PCB concentration of vapor phase and particulate in air ranged widely, 50~1,700pg/m^3 and 2~120pg/m^3 respectively.

Changes of PCB concentrations in air with average temperature(°C), atmospheric pressure(hPa), and precipitation on the sampling date are shown in Figure1. It has seemed that the events of rainfall decreased the concentration of PCB in atmosphere. Relation between distribution of vapor phase and particulate in air with average temperature(°C) and atmospheric pressure(hPa) on the sampling date are shown in Figure2. A slight correlation was observed between the PCB concentration of vapor phase and the temperature, no relation was found to atmospheric pressure. On the contrary, correlation was observed between particulate-PCB and the temperature, the atmospheric pressure. The PCBs in ambient air were released from technical PCB products might adsorb or desorb on the particulate alternately and diffuse in the environment, while polychlorinated naphthalene (PCN) and polychlorinated dioxins (PCDD/PCDF) which were formed during combustion process and tightly bound to the airborne particulate.

Homologue Distributions and Isomeric Pattern

Differences exist on the homologue distributions between vapor phase and particulate. Tri- to penta-chlorinated PCBs were predominant in vapor phase and penta- to hepta- chlorinated PCBs were in particulate. Figure.3 shows the example of homologue distributions of vapor phase and particulate.

Predominant congeners of di-chlorinated isomers in air samples were #5(2,3-)/#8(2,4'-), #11(3,3'-), #12(3,4-)/#13(3,4'-), and #15(4,4'-). Figure.4 shows the example of component ratios of the PCB isomers in each homologue groups. As compared to KC (equivalent mixture of Kanechlor 300, 400, 500 and 600), in case of tri-chlorinated isomers, congeners of #22(2,3,4'-), #35(3,3',4-), and #37(3,4,4'-) increased. In case of tetra-chlorinated isomers, congeners of #70(2,3',4',5-), #66(2,3',4,4'-), #56(2,3,3',4'-), and #77(3,3',4,4'-) increased comparable to KC. Predominant congeners of penta-chlorinated isomers were #118(2,3',4,4',5-) and #105(2,3,3',4,4'-). And, congeners of #82(2,2',3,3',4-), #123(2,3',4,4',5'-), #107(2,3,3',4',5-), and #126(3,3',4,4',5-) increased comparable to KC. Especially, in particulate, congener of #126(3,3',4,4',5-) increased comparable to KC. In case of hexa-chlorinated isomers, congeners of #155(2,2',4,4',6,6'-) that was involved at least in KC, was detected in air samples. Congeners of #156(2,3,3',4,4',5-), #157(2,3,3',4,4',5'-) and #169(3,3',4,4',5,5'-) increased comparable to KC.

References

1. Takasuga T., Inoue T., Ohi E., Ireland P., Suzuki T. and Takeda N. (1994) Organohalogen Compounds, **19,**173-176

2. Garcia A.L., Boer A.C.D. and De Jong A.P.J.M. (1996) Environ.Sci.Technol.**30**, 1032-1037

3. Kurokawa Y., Matsueda T., Osaki Y., Nakamura M., Takata S. and Fukamachi K. (1994) Journal of Environmental Chemistry, **4**(1), 29-38

4. Nakano T., Tsuji M. and Okuno T. (1990) Atmospheric Environment, **24A**(6), 1361-1368

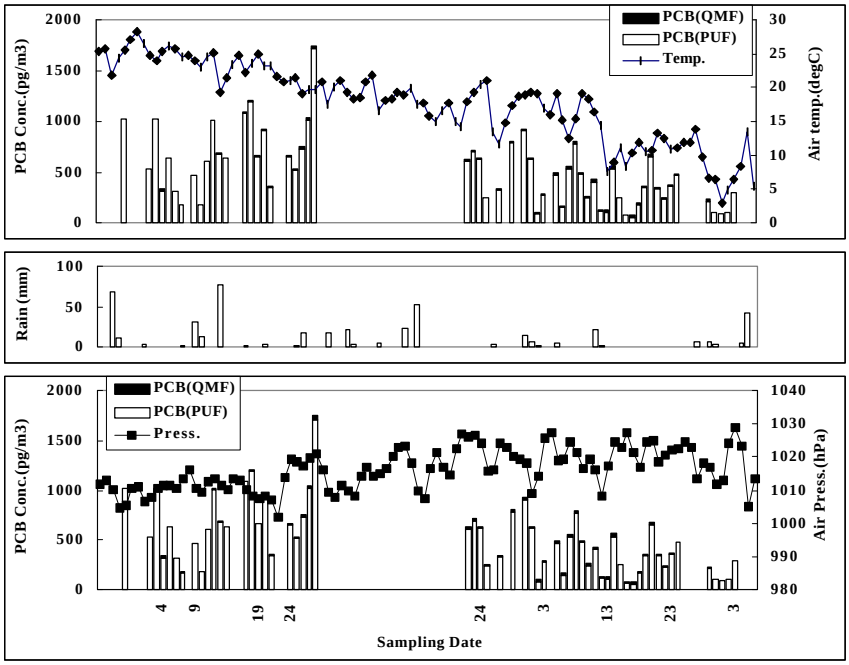

Figure 1. Changes of PCB concentrations in air with average temperature (°C), atmospheric pressure (hPa), and precipitation (mm) on the sampling date.

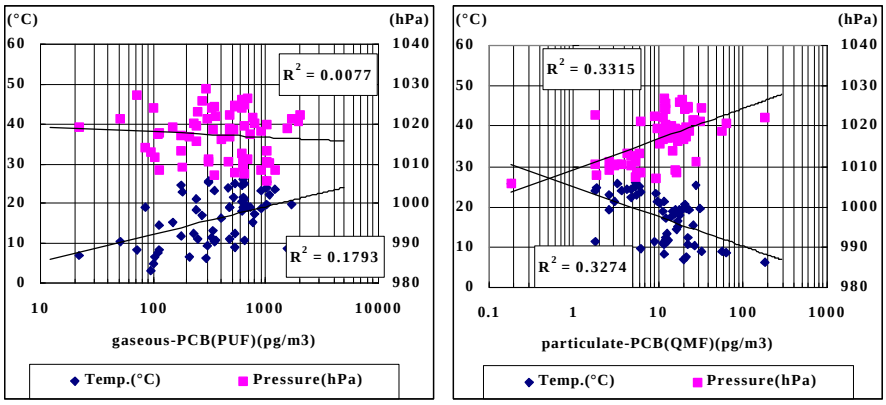

Figure 2. Relation between distribution of gaseous-PCB and particulate-PCB with temperature (°C) and atmospheric pressure (hPa).

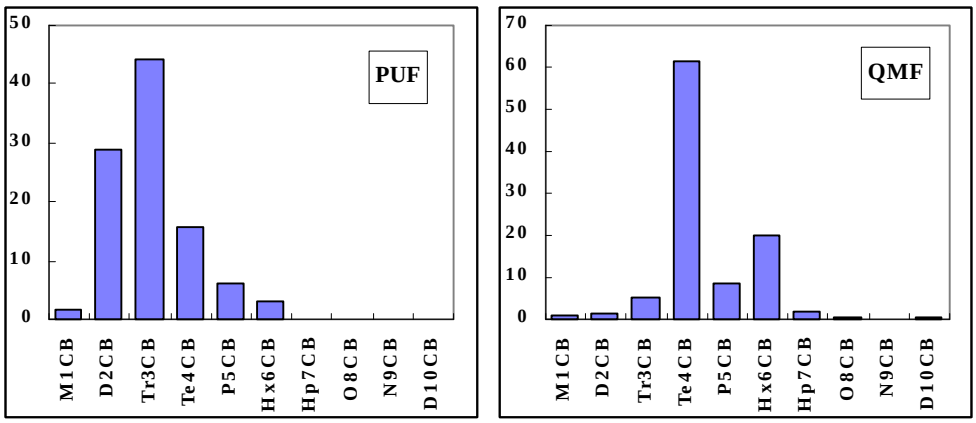

Figure 3. Homologue distributions of gas phase and particle.

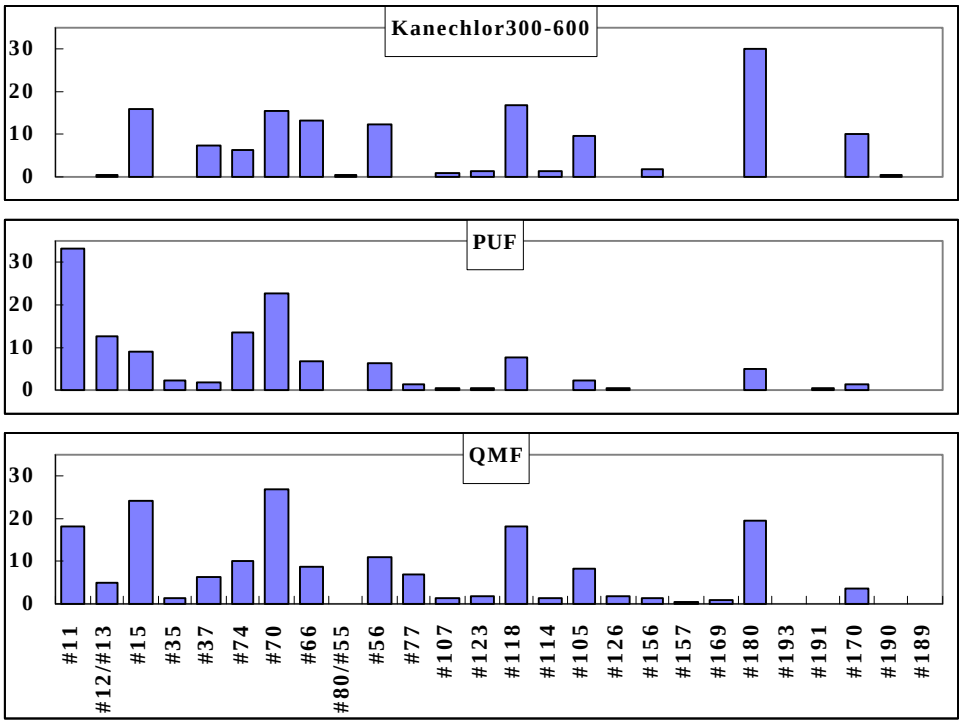

Figure 4. Component ratios of the PCB isomers in each homologue groups.