

ISOMER SPECIFIC ANALYSIS OF POLYCHLORINATED NAPHTHALENES FOR ENVIRONMENTAL SAMPLE

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Introduction

In order to analyse the isomer distribution of organochlorine compounds formed from combustion process, we implemented an isomer specific analysis for polychlorinated naphthalenes (PCNs) in the circulating water of solid and liquid waste incinerator¹. New attention has been given to a "new and/or old" PCNs. Because they are chemically and thermally stable, the property and usage were similar to polychlorinated biphenyls (PCBs). Recent measurements^{2,3} of PCN concentrations in ambient air show that their toxicity contribution (TEQ value) were approximately 2 times below compare to the contribution of the coplanar PCBs.

The aim of this study were an identification of isomer and homologue distribution of PCN in environmental samples in Japan including the complete assignment of PCN, a comparison of the TEQ contribution in the total TEQ(PCDD/DF/Co-PCB/PCN), and an index of combustion process in the origin estimation.

Methods and Materials

Standards. All 29 commercially available isomers were obtained as authentic standard for cross-checking the assignment (1-, 2-, 1,2-, 1,4-, 1,5-, 1,8-, 2,3-, 1,2,3-, 1,2,3,4-, 1,2,3,5-, 1,2,5,6-, 1,4,5,8-, 2,3,6,7-, 1,2,3,4,5-, 1,2,3,4,6-, 1,2,3,5,7-, 1,2,3,6,7-, 1,2,3,5,8-, 1,2,3,4,6,7-, 1,2,3,5,6,7-, 1,2,3,5,6,8-, 1,2,3,5,7,8-, 1,2,3,4,5,6-, 1,2,3,6,7,8-, 1,2,4,5,6,8-, 1,2,4,5,7,8-, 1,2,3,4,5,6,7-, 1,2,3,4,5,6,8-, 1,2,3,4,5,6,7,8-). Additionally, some congeners/mixtures of the PCN were donated for the assignment. The chlorine content of commercially available Halowax is as follows: 1000: 26%; 1001:50%; 1013:56%; 1014: 62%; 1031:22%; 1051:70%;1099:52%. The standard mixtures used for the quantification of PCN in the samples were obtained from CIL.

Sampling. Air samples (1000 m³) were collected by high volume air sampler with quartz fiber filter (QMF) for particulate and polyurethane foam plug (PUF) for the vapor phase sampling. Air samples(4 m³) were collected by air sampler with PS-Air cartridge for low chlorinated naphthalenes to confirm the breakthrough by high volume air sampler. The rainwater and dry-deposition were collected using an automatic rainfall, deposition sampler. A sensor was used to detect rainfall and control the opening and closing of the cover.

Cleanup. The PCB fractions from the above samples were further fractionated on silicagel-graphite carbon columns in order to separate the PCNs from the normal PCB. The PCB fraction was eluted with 60mL 30% dichloromethane in n-hexane. The PCN fraction was eluted using 80 mL toluene with reverse direction. The PCN fraction was volume reduced to 100uL using a gentle stream of nitrogen.

GC/MS Analysis. The analysis was carried out using a HP 5890 II gas chromatograph connected

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to a JMS-700 mass spectrometer (JEOL Ltd. Japan) (operating at a resolution >10 000). Temperature program used for isomer specific separation of the PCN on ULTRA-2 column (30m x 0.2mm x 0.33µm): 70°C, 1.7 min. isothermal; 8°C/min. to 300°C.

Results and Discussion

Fig. 1 summarizes the mass contribution of the mono to octa chlorinated PCN homologues. The air samples are dominated by the tri and tetra chlorinated congeners. Potential PCN residue in environment may be significant sources of PCNs to the atmosphere. Combustion process also may

be source of specific congeners¹ similar to coplanar PCB congeners. Harner et al reported that a greater range of air concentrations was observed for PCNs than PCBs^{2,3}. The production amount of PCNs in Japan were less than PCBs. Average level of PCDD/DF/PCB/PCN in ambient air are shown in Fig. 2. PCN congener profile in air, rain, sediment, landfill sludge, and Halowax are shown in Fig. 3. In the atmosphere, congeners such as 1,6,7-TrCN, 1,2,6,7- TeCN and 1,2,3,6,7-PeCN with the beta-position substituted, were different from the isomeric distribution of the technical PCN products (Halowax) and were typical of isomers formed by combustion.

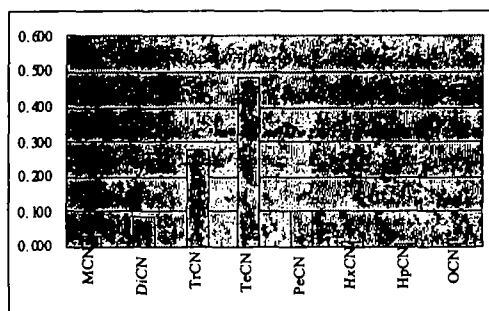


Fig. 1 PCN homologue distribution in ambient air.

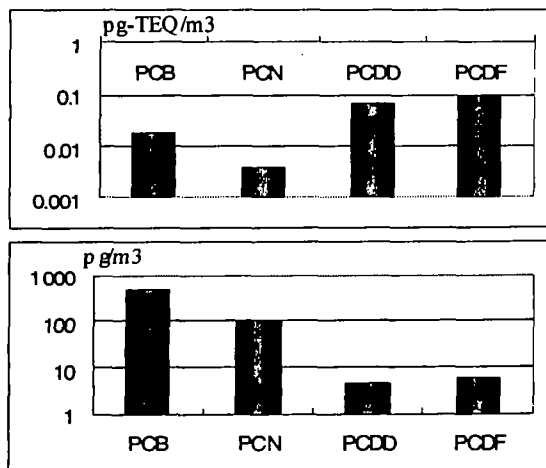


Fig. 2 Average level of PCDD/DF/PCB/PCN in ambient air.

In the white-tail sea eagles, Falandysz⁴ et al detected isomers resulting from combustion process that were not contained in the technical PCN mixtures (Halowax). The existence of such as 1,2,3,6,7-PeCN demonstrates that these isomers are diffused through the atmosphere from the combustion process and enter the Baltic Sea coastal ecosystem. Among the residual PCNs in the ecosystem, most of the HxCN consisted of 1,2,3,4,6,7- and 1,2,3,5,6,7 HxCN, and the isomers in the atmosphere had a similar distribution.

The multi beta-position substituted congeners in the atmosphere such as 1,6,7-TrCN, 1,2,6,7-TeCN and 1,2,3,6,7-PeCN, unlike the isomer distribution of the Halowax, are formed by incineration. In the case of PCB, the pattern of isomers in the air is similar to that of technical PCB products KC300, 400, 500 and 600. However, in the case of PCN, the pattern of PCN isomers in the air was different from that of technical PCN products. The combustion process, mainly the incineration of municipal waste, is thought to be the principal source of PCDD/DF in the atmosphere. The analysis of the

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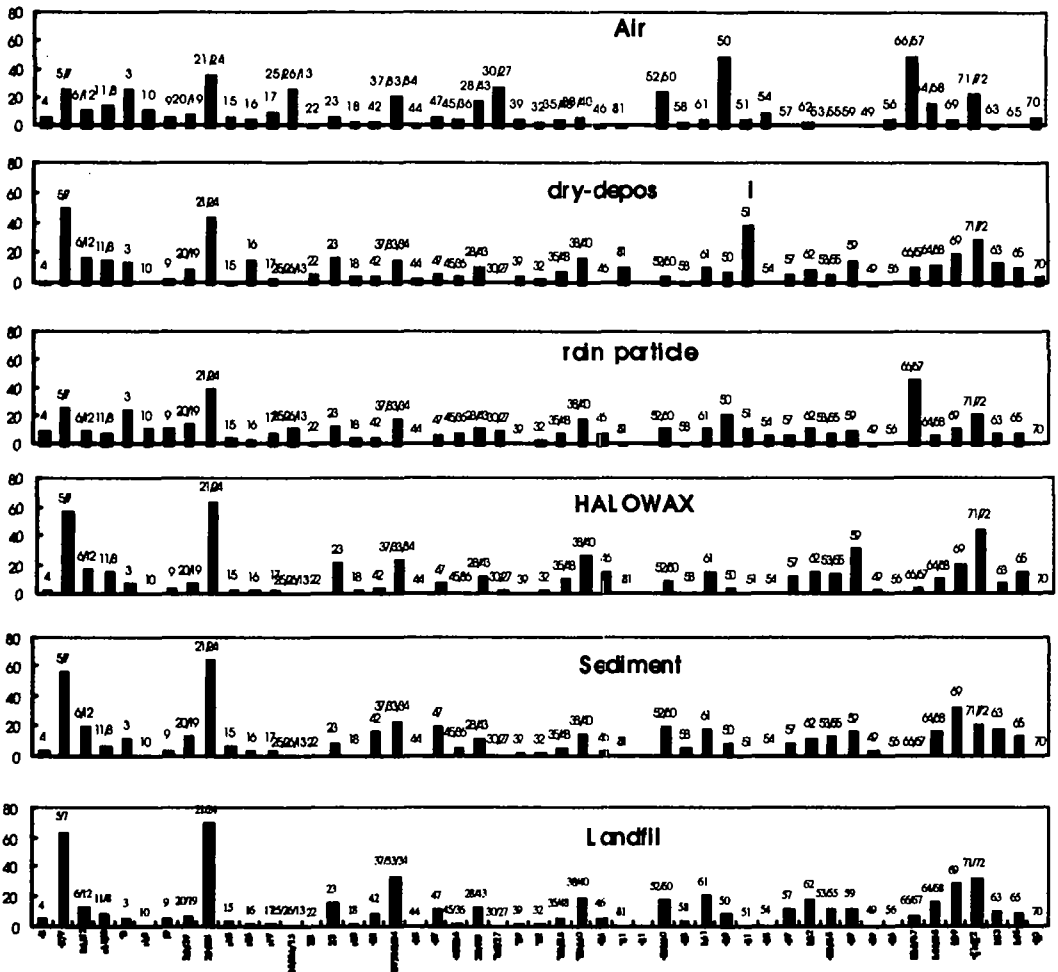


Fig. 3. PCN congener distribution in air, dry-deposition, rain particle, Halowax, sediment and landfill sludge. (IUPAC No.)

congener distribution of PCNs formed through combustion will be a crucial aid in identifying the formation mechanism of dioxin-related compounds.

Distribution of PCN congeners in Environmental Samples

The isomer patterns of PCN in the environmental samples were analyzed. In the Halowax, the 1,4,5- and 1,4,5,8- isomers with the alpha (peri-)position of the naphthalene substituted with chlorine were predominant component, while there were no congeners such as 1,2,6,7-, 1,2,3,6,7- with the beta-position selectively substituted¹. The source of the PCN in the atmosphere could be accounted for by either of two processes: evaporation of the PCN residue into the atmosphere, or de novo formation from combustion process. The source of PCN in air may be account for as an intermediate position between PCB and PCDD/DF in contribution of technical product and combustion process. Fig. 3 shows the different pattern of PCN congener profile between environmental samples. This confirms that the isomeric pattern of PCN in the air and water is a distinctive trend, dependent on the routes of diffusion and transport and the physico-chemical properties of congeners.

Average level of PCDD/DF/PCB/PCN in ambient air

Toxic equivalent factors (TEFs) have been determined for PCBs (WHO 1998), and several 7 PCN congeners. Average levels for the 6 air samples were PCN = 100pg m⁻³, PCB = 480pg m⁻³, PCDD/DF= 10pg m⁻³, and TEQ values were PCN = 4fg-TEQ m⁻³, PCB = 20fg-TEQ m⁻³, PCDD/DF= 170fg-TEQ m⁻³. The ratio of TEQ contribution was approximately 2: 10: 85 for PCN, PCB, PCDD/DF.

Acknowledgment

We are grateful to Dr. Imagawa, National Institute of Resource Environment (NIRE) for donating some standards to assign PCN chromatogram.

References

- 1 Nakano, T., Umeda, H. and Okuno T. (1994) *Organohalogen Compound*, 20,315.
- 2 Harner, T., Kylin, H., Bidleman, T.F., Halsall, C., Strachan, W.M.J., Barrie, A. and Fellin, P. (1998) *Environ. Sci. Technol.*, 32, 3257.
- 3 Harner, T., Lee, R.G.M, Gevao, B. , Ockenden, W., Thomas, G. , Northcott, G. and Jones, K. C. (1999) *Organohalogen Compound*, 43, 97.
- 4 Falandysz, J., Strandberg, L., Kulp, S. E., Strandberg, B., Bergqvist, P. and Rappe C. (1996) *Chemosphere*, 33(1), 51.
- 5 Lee, R.G.M., Jones, K. C. (1999) *Environ. Sci. Technol.*, 33, 705.