PROFILES OF SPECIFIC ISOMERS OF POLYCHLORINATED NAPHTHALENES IN TOKYO BAY SEDIMENT CORE SAMPLE

Takashi Imagawa*, Kurunthachalam Kannan†, Nobuyoshi Yamashita*,
Akira Miyazaki* and John P. Giesy†

*National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba,
Ibaraki 305-8569, Japan
†National Food Safety and Toxicology Center, Institute for Environmental Toxicology,
Michigan State University, East Lansing, MI 48824, USA

Introduction

Polychlorinated naphthalenes (PCNs) were used as capacitor dielectrics, cutting oils, engine oil additives, electroplating stop-off compounds, die casting, ship insulation, wood and paper preservatives and wire insulation. Production of PCNs has been ceased in Japan in the 1970s, although, however, PCNs are still emitted unintentionally from sources such as municipal solid waste incineration1), metallurgical processes2) and chlor-alkali process3). PCNs are also present in technical PCB mixtures as impurities 4). The positions 1-, 4-, 5-, and 8- on naphthalene nuclei has higher reactivity. The composition of PCN isomers in environmental samples is characteristic of their sources. Synthetic PCNs such as Halowaxes tend to contain 1,4- substituted isomers according to the orientation of chlorination reaction. In contrast, PCNs from some of thermal processes contain considerable amount of 2,3- (and/or 6,7-) substituted isomers. In this study, profiles of several characteristic PCN isomers in technical PCNs or thermally formed PCNs are compared and the contribution of thermal sources to environmental contamination is estimated based on a study involving the analysis of sediment core from Tokyo Bay, Japan.

Material and Methods

Sediment core was collected from Tokyo Bay (35'35"N and 139'55"E) in May 1995. The depth of water column at this site was 14 m. Care was taken not to disturb the sediment surface by maintaining approximately 10-20 cm of clear bottom water above the core. The core was sectioned at 2 cm intervals for the initial 20 cm and thereafter at 5 cm intervals to a maximum depth of 93 cm using a clean stainless steel slicer aboard ship immediately after collection.

A portion of freeze-dried sediments was Soxhlet extracted using toluene. The extract was concentrated and cleaned on a acidic silica/silica gel column by eluting with hexane. The hexane extract was concentrated to 1 mL and transferred to a carbon column packed with 1 g of activated carbon-impregnated silica gel. PCNs were eluted with 200 mL of toluene and analyzed by a HRGC-HRMS. A Hewlett-Packard 6890 GC interfaced with a JEOL JMS-700 HRMS was used. Details of the instrumental conditions for PCN analysis have been described elsewhere3),5). Halowaxes 1001, 1014, and 1051, for which congener composition have been determined earlier by GC/AED6), were used as a standard for quantification and ^{13}C-2,3,7,8-T4CDD was used as internal standard.

Results and Discussions

Concentration of PCN homologues (tri- through octa-) in sediment core is shown in Figure 1. In deeper layers, lower chlorinated homologues dominated in composition. Isomer composition of PCNs in sediment core is shown in Figure 2. Higher chlorinated homologues have contributed little in deeper layers, which has resulted in a change in isomer pattern. However, isomer pattern in each homologue is similar for all layers. This characteristic pattern resembles with that of Halowax, except that 1,4,5-T3CN, 1,4,5,8-T4CN, and 1,2,4,5,8-P5CN were lower and 1,3,5,7-T4CN, 1,2,3,5,7-/1,2,4,6,7-P5CN, and 1,2,3,5,6,7-/1,2,3,4,6,7-H6CNs were higher in sediment samples. This phenomenon is likely to be caused by biodegradation. 1-, 4- and 5- (8-) positions seem to be easily dechlorinated.

The isomers typical to Halowax are shown in Figure 3. The profile of 1,2,4-/1,4,6-T3CN, 1,2,5,8, and 1,4,5,8-T4CN showed a similarity in which maximum concentration occurred at a depth 20-25 cm. In surface layers, with the decrease in depth, these isomer decreased gradually. In Figure 4, isomers that are relatively less abundant in Halowaxes are shown. 1,3,5,7-T4CN, which is likely to be accumulated, showed similar profile with that of 1,2,5,8-T4CN or 1,4,5,8-T4CN. This implies that biodegradability does not have great effect on their profile in the same homologue group. 1,2,6,7-T4CN has a maximum concentration at the depth of 14-16cm, which agreed with the depth that contained maximum concentration of sum of tri- through octa- PCNs. Considering that this profile is different from Figure 3, sources other than technical PCNs are contributing for 1,2,6,7-T4CN.

Isomers that were non-existent in technical mixtures, such as 1,3,6,7-, 2,3,6,7-T4CN or 1,2,3,6,7-P5CN, were also detected in sediment samples. To investigate the source of these isomers, isomer profiles of selected isomers in technical PCN are shown in Figure 5. Some of these isomers were detected in technical PCBs as impurities$^{7)}$. The profile of 1,3,6,7-T4CN and 1,2,3,6,7-P5CN was very interesting when compared with other isomers. These isomers do not decrease so remarkably from the depth 14-16cm to the surface. This suggests sources originating from incineration, but there may also exist photodecomposition or biodegradation of H6CN and H7CN isomers resulting in the formation of lower chlorinated isomers. Some H6CN isomers also showed a similar profile to that of 1,3,6,7-T4CN and 1,2,3,6,7-P5CN (Figure 6). The reason for this trend in H6CN isomers profiles should be investigated further.

Acknowledgement

We wish to thank Dr. Shinya Hashimoto (Tokyo University of Fisheries) for supporting the sampling of sediment core.

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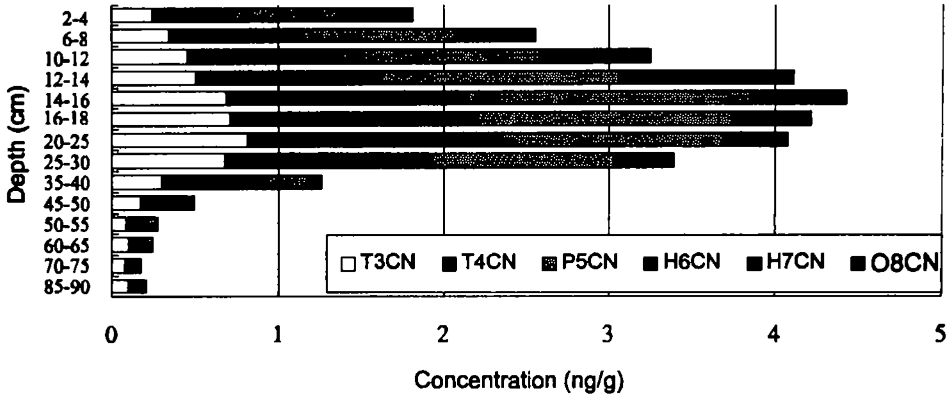

Fig. 1. PCN homolog profiles in a sediment core from Tokyo bay, Japan.

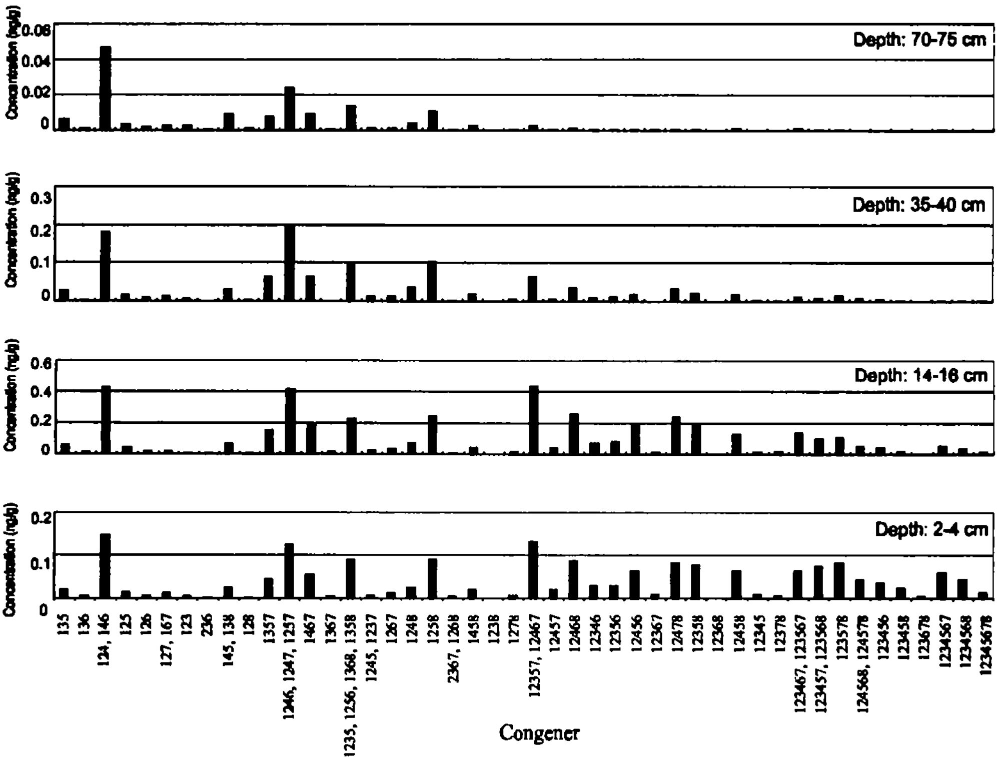

Fig. 2. Profile of PCN isomers in selected depths of a sediment core from Tokyo Bay, japan.

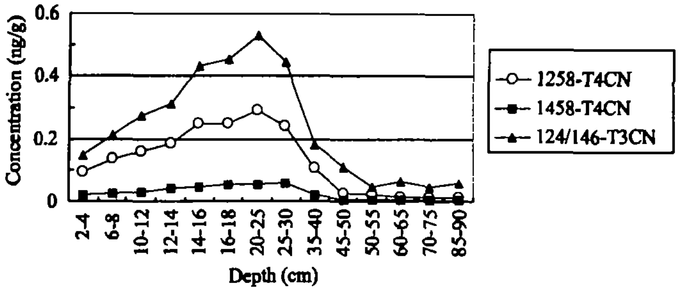

Fig. 3. Sediment core profiles of PCN isomers that are abundant in technical PCN mixtures.

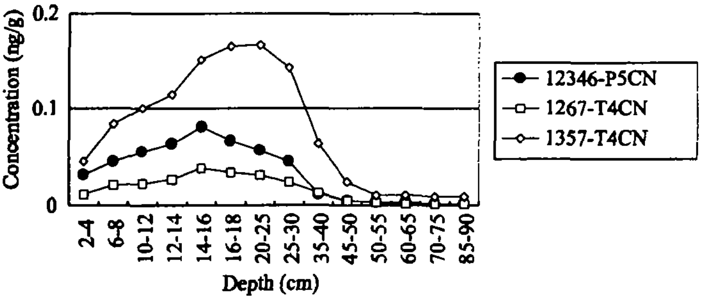

Fig. 4. Sediment core profiles of PCN isomers that are present in technical PCN mixtures and incination related sources.

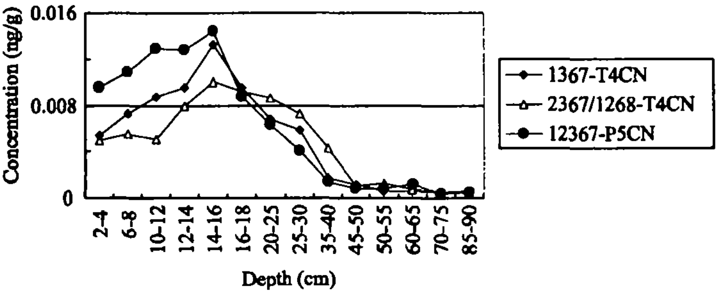

Fig. 5. Sediment core profiles of PCN isomers that are non-existent in technical mixtures, but present in incineration related sources.

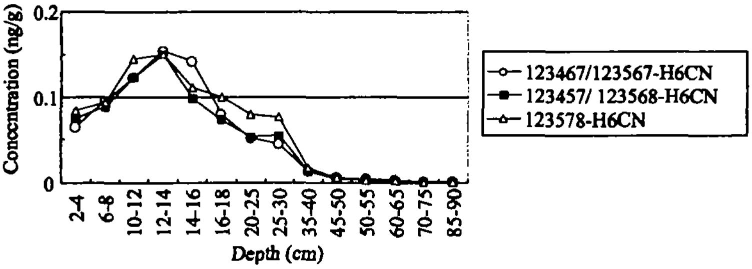

Fig. 6. Sediment core profiles of several H6CN isomers.