

HISTORICAL RECORDS OF POLYCHLORINATED NAPHTHALENES, -BIPHENYLS, -DIBENZO-*P*-DIOXINS, -DIBENZOFURANS IN A DATED SEDIMENT CORE FROM LAKE KITAURA, JAPAN

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Introduction

PCNs were used in a variety of industrial products including capacitor dielectrics, cutting oils, engine oil additives, die casting, ship insulation, wood, paper, and fabric preservatives and wire insulation ¹. Technical formulation of PCNs, PCBs ^{2,3} and other industrial thermal processes (*e.g.* incinerator, chloro-alkali plant) ⁴ are considered as additional sources for environmental contamination by this compound. PCNs are planar, similar to polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), and therefore, some PCN isomers elicit toxic it is similar to PCDD/DFs ⁵. The finger printing method to estimate their sources are getting common for PCBs, PCDDs and PCDFs. However, only few information is available for PCNs to date. In this study, profiles of several characteristic PCN isomers in technical PCNs or thermally formed PCNs were compared and the contribution of thermal sources to environmental contamination was estimated based on a study involving the analysis of a dated sediment core from Lake Kitaura, Japan. Vertical profiles of residues in dated sediment cores have been used as historical records of pollution. Several studies have examined vertical profiles of persistent organic contaminants such as PCBs, PCDDs/DFs and PAHs in sediment cores and found that the temporal trends of these compounds are often preserved in the sediment bed ^{6,7}, but PCNs data is exiguous that these data was deficiency to explain existence of PCNs at the deep section. To our knowledge, this is the first data reconstruct the historical record of PCNs in a long sediment core at length of 3 m.

Materials and Methods

Sampling Location

In December 2000, long sediment core samples (3 m) were taken from the middle of Lake Kitaura (35°59'N, 140°35'E and depth 6 m) by using a piston corer with inner tube (7cm i.d. and 4m long) made of polycarbonate. Samples were transported to laboratory immediately after the collection and sectioned 1-2 cm using a stainless steel slicer. Each section was freeze-dried and stored at -30 °C until analysis. Detailed procedure of sample preparation has been described elsewhere ⁶.

Sedimentation

The estimated sedimentation rate was estimated using ²¹⁰Pb and ¹³⁷Cs profile and volcanic ash stratigraphy based on the correlation of volcanic ash in a sediment core sample from Lake Kitaura. It is a reasonable estimation of the age of core sections. The sedimentation rate was determined to be approximately 0.8 cm yr⁻¹. The sediment core sections at depths of about 50, 60, 100 and 200cm correspond to A.D.1783, A.D.1707, A.D.1108 and A.D.550 ~ 600, respectively.

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Chemical Analysis

Freeze-dried sediments were extracted using a accelerated solvent extractor (ASE-200, DIONEX Co.)⁸. Extraction solvent were using acetone/hexane (1:1, v/v) and toluene. Bottom of extraction cells (33 ml) were packed with 5 g of activated alumina to remove interferences. Extract was applied to multi-layer acidic silica gel column and eluted with 200 mL of *n*-hexane. Eluate was concentrated up to 200 μ l and injected into double column HPLC system. This HPLC system was used for the purpose of separation of PCNs, PCBs, PCDDs/DFs. Hypercarb column (i.d. 4.6 mm x 100 mm) was used to separate di-, mono-*ortho* PCBs and other PCB isomers from PCNs, non-*ortho* PCBs and PCDDs/Fs. The second fractionation was carried out by use of PYE column (i.d. 4.6mm x 250mm, Cosmosil 5-PYE, 5 μ m, Nacalai Co.) to separate each PCN isomers, non-*ortho* PCBs and PCDDs/DFs. A Hewlett-Packard 6890 GC interfaced with a JEOL JMS-700D HRMS was used. PCNs were separated on a DB-17 capillary column coated at 0.25 μ m (30 m x 0.25 mm i.d.). Details of the instrumental conditions for PCN analysis have been described elsewhere^{1,9}. Analytical methods using double column HPLC, preparative GC and HRGC-HRMS enable detection of individual dioxin-like compounds including PCNs with no co-elution.

Results and discussion

The vertical profile of PCN concentrations and congener composition in a sediment core 11 sections were shown in fig.1. The profile was characterized by lesser concentrations in deeper layers, followed by an exponential increase to a subsurface peak and a gradual decrease to the surface. Maximum PCN concentration of 733 pg/g, dry wt, was found in the 14-15 cm section, which corresponded to the early 1980s. Tri- and tetra-CN's accounted for greater than 90 % of the total PCN concentrations at depths below 35 cm and their composition increased gradually with depth. The composition of PCN isomers in environmental samples is characteristic of their sources. The profile of isomers those are typical to Halowax was showed a similarity in which maximum concentration occurred in the 14-15 cm section (fig.2). In surface layers, with the decrease in depth, these isomers decreased gradually. Isomers those didn't exist in technical mixtures, such as 2,3,6-TriCN, 1,3,6,7-, 1,2,6,8-, 2,3,6,7-TeCN, 1,2,3,6,7-PeCN, were detected in sediment samples. Profile of these isomers was very interesting these concentrations increase or do not decrease so remarkably from the 14-15 cm section to the surface. This suggests sources originating from incineration, but there may also exist photodecomposition or biodegradation of HxCN and HpCN isomers resulting in the formation of lower chlorinated isomers and are included in technical PCBs as impurities³.

The vertical profile of TEQs contributed by PCNs, PCDDs/DFs and PCBs was shown in fig.3. There were calculated by using TEF⁵. Maximum PCN-TEQ concentration of approximately 0.1 pg/g, dry wt, was found in the 14-15 cm section, which corresponded to peak of maximum PCN concentration, but PCN-TEQ concentrations in surface layers not much decreased as PCN concentrations, and maximum PCDF-TEQ concentration was detected in the 4-6 cm section above the depths of maximum PCDD and PCB-TEQ concentration. This data suggests PCN-TEQ profile in surface layers was reflected the incineration origin which contains many isomers with dioxin-like toxicity. Maximum concentration of total TEQ contributed by PCNs, PCDDs/DFs and PCBs was detected at 16.5 pg/g, dry wt in the 4-6 cm section, which corresponded to peak of maximum PCDF-TEQ concentrations (fig.4). PCDDs accounted for greater than 95% of the total TEQ at depths below 35 cm. PCDD-TEQ composition increased gradually from the latter 1960s to the early 1990s. Vertical profile of the total TEQ was not reflected by PCN-TEQ concentration, accounted for a few percent.

As the result, PCNs was detected in deeper layer than their industrial synthesis. Possible explanations include the following, such as incorrect dating core, physical mixing by bioturbation, sample contamination during preparation and analysis, selective downward migration of compounds in

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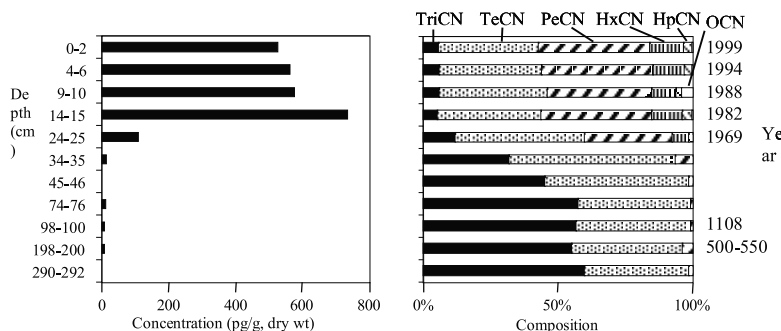


Figure 1. Vertical profile of PCN concentrations and homologue composition in a sediment core from Lake Kitaura.

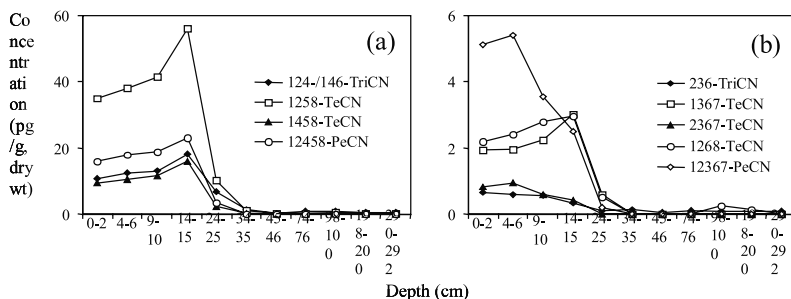


Figure 2. Vertical profile of selected PCN isomers that are abundant in technical PCN mixtures (a) and are non-existent in technical mixtures, but present in incineration related source (b).

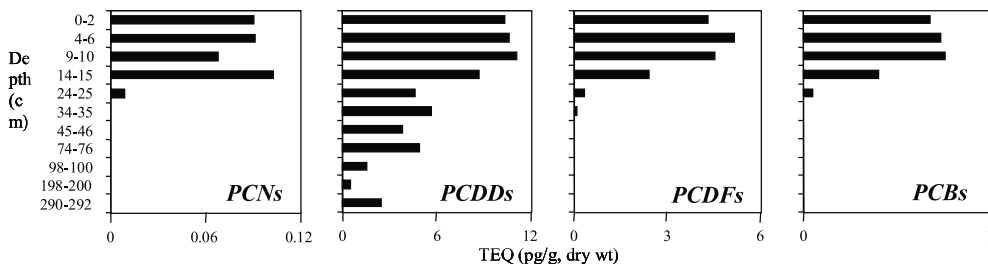


Figure 3. Vertical profile of 2,3,7,8-TCDD equivalents (TEQs) contributed by PCNs, PCDDs, PCDFs and PCBs in a sediment core from Lake Kitaura.

the sediment column, production from natural and/or anthropogenic combustion sources ⁷. It was suggest that low chlorinated compounds might move to the deep sections by moving a pore water, because PCN isomer composition at depths below 75 cm was different from surface sections, was detected only a low chlorinated compounds with comparatively high water solubility and their concentrations decreased gradually with depth.

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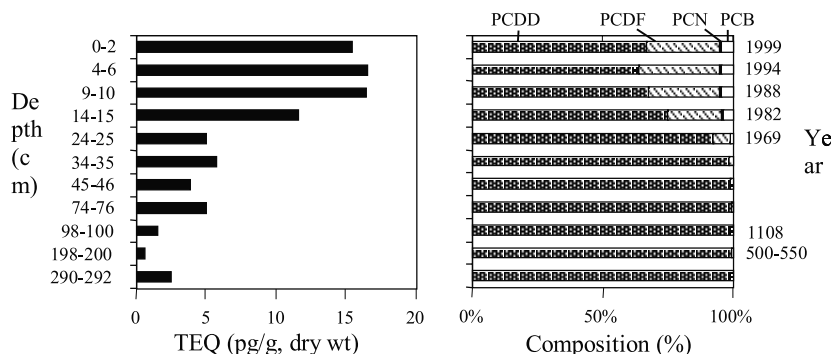


Figure 5. Vertical Profile of total 2,3,7,8-TCDD equivalents (TEQs) and composition contributed by PCNs, PCDDs, PCDFs and PCBs in a sediment core from Lake Kitaura.

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