VERTICAL PROFILE OF POLYCHLORINATED NAPHTHALENES AND -BIPHENYLS IN A SEDIMENT CORE FROM TOKYO BAY, JAPAN

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Introduction

Polychlorinated naphthalenes (PCNs) are a group of 75 possible compounds consisting of two fused aromatic rings substituted with one to eight chlorine atoms. PCNs are similar to polychlorinated biphenyls (PCBs) with high thermal stability. PCNs were first synthesized in the middle of the 19th century and used as engine oil additives, wood preservatives, dye production, ship insulation and rubber product additives¹. The production of technical PCN formulations in the United States and Europe was ceased in the 1980s, and they were also manufactured by several industries in Japan². PCNs are released into the environment from various sources, such as municipal waste incineration³, commercial PCN formulations⁴ and as by-products of technical PCB mixtures⁵. PCNs exhibit dioxin-like toxicity with potencies similar to some coplanar PCBs. PCNs have been identified as candidate persistent organic pollutants (POPs) by the United Nations Economic Commission for Europe (UN-ECE) POPs protocol⁶.

Tokyo Bay is a eutrophic coastal region with a surface area of 960 km² with a water volume of 14.4×10^9 m³, and an average depth of 15 m⁷. The Bay is surrounded by major cities of Japan and is densely populated and highly contaminated by industrial and urban wastes. Sediment is an important sink and reservoir of anthropogenic pollutants. Vertical profiles of contaminants in dated sediment cores were used to estimate historical depositions of not only POPs^{8,9}, but also short-lived chemicals such as bisphenols (BPs)¹⁰. The effectiveness of regulations and changes in manufacturing practices of chemicals can be reflected in sediment cores and thus, sediment cores have been used to deduce such information.

The objective of this study was to investigate the vertical profiles in concentrations of PCNs and PCBs to characterize the temporal contamination status of these compounds in Tokyo Bay, Japan. Comparison of vertical profiles between PCNs/PCBs and BPs was also described.

Materials and methods

The collection of sediment core sample was performed in Tokyo Bay (35'35'' N and 139'555''E) using an acrylic tube (120 cm length \times 11 cm i.d.) in April, 2012. The depth of water column at the sampling site was 14.4 m. The core was sectioned into 1 cm sections for the initial 4 cm and 1.5 cm sections thereafter to a maximum depth of 35 cm. Each section was freeze-dried and stored at -20°C until analysis. Freeze-dried sediment core samples were initially extracted using 300 mL dichloromethane (DCM) and followed by 300 mL toluene using a Soxhlet apparatus. The internal standard mixtures were spiked with ¹³C-labled PCBs (EC-4937) before Soxhlet extraction. The extracts were pre-cleaned by passage through a multilayer silica gel column (300 mm length \times 20 mm i.d.) with 200 mL of *n*-hexane. The eluate was concentrated to 1 mL. The analyte was further purified and fractionated using an activated alumina column (300 mm length \times 12 mm i.d.). The analyte was eluted with 10 mL of n-hexane (fraction 1), 20 mL of 0.5% DCM in n-hexane (fraction 2) and 100 mL of 50% DCM in *n*-hexane (fraction 3). The eluant was concentrated to 1 mL. The analyte was further subfractionated using an active carbon impregnated silica gel column (300 mm length \times 15 mm id). The analytes of fractions 2 and 3 were loaded. The active carbon column was eluted using 40 mL of 25 % DCM in *n*-hexane (fraction 2-1 and 3-1) and then eluted using 250 mL of toluene (fraction 2-2 and 3-2). All fractions were concentrated to 200 µL for instrumental analysis. Identification and quantification of individual PCN congeners were accomplished with an Agilent Technologies 6890 series GC coupled to a Waters Micromass Auto Spec high resolution mass spectrometer (HRMS). Separation of PCN and PCB congeners was achieved by both DB-

5MS capillary column. Column oven temperature for PCN analysis was programmed from 70 °C (1 min) to 180 °C at a rate of 15 °C/min, and then to 260 °C at 4 °C /min with a final hold time of 1 min. PCBs were determined by GC/MS (Agilent Technologies). Column oven temperature for PCB analysis was programmed from 70°C (1 min) to 180 °C at a rate of 15 °C /min, and then to 260 °C at 2°C /min with a final hold time of 10 min. PCN and PCB congeners were determined by SIM at the two most intensive ions of molecular ion cluster. Quantification was performed using an external standard method and quantitative standards. The recoveries of target chemicals through the procedure were 95 ± 24 %.

Results and discussion

Vertical distribution of PCNs and PCBs

Concentrations of total PCNs and total PCBs in a sediment core sample collected from Tokyo Bay in Japan in 2012 are shown in Figure 1. The concentrations of PCNs and PCBs ranged from 0.03 to 0.60 ng/g dry weight (dw) and 1.26 to 10.1 ng/g dw, respectively. Among the 9 sediment core layers, the highest concentration of PCNs was found in the layer 20.5-22 cm, with a corresponding sedimentation year of 1998. Sediment sections above 20.5 cm showed a gradual decrease in total PCN concentrations. The vertical profile of PCBs showed a pattern similar to PCNs. The highest concentration of PCBs was found in the layer 23.5-25 cm, with a corresponding sedimentation period of 1996, and a gradual decrease was observed afterwards. The total production of technical PCNs in Japan from 1940 to 1976 was 4005 tons, and technical PCNs were banned after 1979 in Japan¹¹. PCBs were produced in Japan since the early 1950s, and the production increased until the early 1970s. After the ban on the production of PCNs and PCBs in Japan, the vertical distributions of PCNs and PCBs in the sediment core were still high until the 1990s, and gradually decreased thereafter. This may suggest a time lag between production/usage and deposition of POPs in the marine environment.

The concentrations of PCNs in the sediment core from Tokyo Bay were compared with those reported in previous studies (Table 1). The concentrations of PCNs in our study (0.03-0.60 ng/g dw) were relatively higher than those reported for Yellow Sea, China (0.004-0.006 and 0.01-0.03 ng/g dw)¹² and lower than the ranges reported from Lake Esthwaite, England (0.49-12 ng/g dw)¹³, Lake Kitakura, Japan (0.002-1.3 ng/g dw)¹⁴ and for Tokyo Bay, in 2000 (na-4.4 ng/g dw)¹⁵. It seems that PCN concentrations highly depend on year of sampling.



Figure 1. Vertical concentrations of PCNs and PCBs in a sediment core from Tokyo Bay, Japan.

Table 1. Com	parison of PC	N concentrations	(ng/g dry	weight) ir	n sediment	cores
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Country	Estimated year	Ν	Mean	Range	Reference
China (Yellow sea)	1944-1993	12	0.03	0.004-0.006	Pan et al. $(2012)^{12}$
China (Yellow sea)	1971-1992	5	0.02	0.01-0.03	Pan et al. $(2012)^{12}$
England (Lake Esthwaite)	1870-1995	10	0.60	0.49-12	Gevao et al. $(2000)^{13}$
Japan (Lake Kitaura)	<500-2000	17	0.23	0.002-1.3	Horii et al. (2004) ¹⁴
Japan (Tokyo Bay)	1907-1992	8	2.15	na ^a -4.4	Yamashita et al. $(2000)^{15}$
Japan (Tokyo Bay)	1996-2012	10	0.22	0.03-0.60	This study
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ana = not available.

Relative profiles of PCN and PCB homologues

The relative compositions of PCN and PCB homologues (expressed as percentage of the total) in total concentrations were calculated for the sediment core from Tokyo Bay (Figure 2). The profiles of PCN homologues in the sediment core varied depending on the depth. For the PCN homologues in the sediment core, lower chlorinated homologues (TrCNs to PeCNs) were dominant in the upper layers above 17.5-19 cm. These profiles of PCN homologues seem to resemble the data reported in the publication related to Tokyo Bay sediment core^{3,15}. In deeper layers, the compositions of lower chlorinated homologues decreased with depth, only the compositions of PeCBs were dominants. The relative composition of PCB homologues in the sediment core was almost stable in each layer. TeCBs and PeCBs were the predominant homologues in most of the sediment core layers.

The relative contribution of PCN congeners in sediment core from Tokyo Bay in Japan are summarized in Figure 3. The pattern of PCN congeners was divided to two different profiles. Sediment section of 1-2 cm, represented the surface layers, the relative contribution of PCN congener was comparable in the most of congeners. The nos.21/24/14 and 33/34/37 were predominant congeners accounting for 18% and 10% of the total concentration respectively. Imagawa et al.³ provide similar pattern of PCN congeners in sediment core from Tokyo Bay. The no.52/60 and 61 were the predominant congener in the layer 20.5-22cm represented the deeper layer, accounting for 26% of the total concentration. Except PeCN congeners, most of relative contribution of PCN congeners in the layer 20.5-22 cm was lower than surface layer. The nos.52/60 have been reported to be formed during incineration of municipal solid waste¹⁶. Incineration processes represented here by the sediment core pattern have to be considered as possible PCN sources in industrial areas.



Figure 2. Relative composition (%) of PCN and PCB homologues in a sediment core from Tokyo Bay, Japan.



Figure 3. Relative composition (%) of PCN congeners in sediment core from Tokyo Bay, Japan.

Comparison profiles of PCNs/ PCBs and BPs

Figure 4 shows vertical profiles in concentrations of selected BP analogues, PCNs, and PCBs in the sediment core from Tokyo Bay, Japan. According to the published data¹⁰, the total concentration of BPs ranged from 1.88 to 28.2 ng/g dw. The total concentration in BPs was higher than that in PCNs/PCBs. Moreover, the sediment layer that showed the highest concentration was obviously different between BPs and PCNs/PCBs. These results suggest the differences between current and historical releases of BPs and PCNs/PCBs. PCNs/PCBs, are conventional environmental pollutants used heavily in the past whereas BPs, are emerging contaminants.



Figure 4. Vertical concentrations of PCNs, PCBs, and BPs in a sediment core from Tokyo Bay, Japan.

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