

HISTORICAL PROFILE OF POLYCHLORINATED BIPHENYLS IN A DATED SEDIMENT CORE FROM BEPPU BAY, SOUTHWESTERN JAPAN

Takahashi S¹, Aono D¹, Anh HQ^{1,2}, Watanabe I¹, Tomioka K¹, Kuwae M³, Kunisue T³, Sakai S⁴

¹Center of Advanced Technology for the Environment (CATE), Graduate School of Agriculture, Ehime University, Matsuyama, Japan, 790-8566, takahashi.shin.mu@ehime-u.ac.jp; ²Faculty of Chemistry, VNU University of Science, Vietnam National University, Hanoi, Vietnam; ³Center for Marine Environmental Studies (CMES), Ehime University, Matsuyama, Japan, 790-8577; ⁴Environment Preservation Research Center, Kyoto University, Japan, 606-8501.

Introduction:

Polychlorinated biphenyls (PCBs) were commercially synthesized and widely used in numerous industrial applications such as additives in dielectric fluids in transformers and capacitors, heat transfer fluids and hydraulic fluids in partially closed-industrial systems, as well as other open applications like lubricants, casting waxes, surface coatings, adhesives, plasticizers, and inks¹. On the other hand, PCBs can be unintentionally produced during combustion, chlorination bleaching of wood pulp, and different industrial production processes, especially in paint pigment manufacturing^{2,3}. PCBs are extremely persistent in the environment and they have been detected in various environmental media in virtually all parts of the world¹. Marine sediments have been considered as an important sink of PCBs and other organic micro-pollutants; and the vertical distributions of these contaminants in sediment cores can provide relevant information on their historical trends and emission sources⁴⁻⁶.

Before 1950s, PCBs were imported into Japan. In Japan, technical PCB mixtures (Kanechlor) were produced since 1954, and these production activities were stopped in 1972. The total amount of commercial PCBs produced in Japan was estimated to be 59,319 tonnes with a peak production between 1965 and 1969⁷. The issues regarding technical PCBs has received great attention in Japan due to incidental exposures (e.g., the Yusho incidence) to these toxic compounds and their related analogues since the late 1960s^{8,9}. The use and disposal of industrial PCB products (including those kept in depositories for a long time) as well as incineration of industrial and domestic wastes have released considerable amounts of dioxin-like PCBs (dl-PCBs) in Japan¹⁰. A certain level of 3,3'-dichlorobiphenyl (CB-11, an impurity in commercial paints and pigments) was also observed in the air of several urban and industrial areas in Japan, implying the current emission of PCBs³. Several studies on the temporal trends of PCB contamination were performed by using sediment cores collected from different Japanese coastal areas^{6,11-13}; however, these researches focused on a subset of PCB congeners and did not investigate novel substances (e.g., CB-11) In the present study, we analyzed concentrations of all 209 PCBs in a representative sediment core obtained from Beppu Bay, southwestern Japan in order to provide a new and detailed insight into the environmental occurrence and historical profile of this chemical class.

Materials and methods:

The sediment core was collected in 2018 from the depocenter (approximately 70 m water depth) of Beppu Bay (33°16'40.6"N; 131°32'35.2"E) by using a 1.2-m gravity corer. Ages of the sediment layers were determined based on ¹³⁷Cs and excess ²¹⁰Pb radioactivity¹⁴. Total 13 sediment layers (0–25 cm depth, 1 cm each layer) were selected from the core for the analysis of PCBs with the ages ranging from 1954 to 2008. The sedimentation rates in this area are relatively high (>0.2 cm y⁻¹). Dry bulk densities of the selected sediment samples ranged from 0.116 to 0.367 g cm⁻³. Because a barrier made by a 50-m-deep sill at the mouth of the bay causes the accumulation of anoxic bottom water in the depocenter of the bay, structure of the bottom sediment in this area is considered to be kept well chronologically with less bioturbation. Details of stratigraphy in this Beppu Bay sediment were documented in our previous study¹⁴.

The sediment samples were freeze-dried, grinded with anhydrous sodium sulfate by using mortar and pestle, and Soxhlet extracted with toluene for 8 h. The crude extracts were spiked with ¹³C₁₂-PCB surrogate standards, concentrated, treated with reduced copper powder to remove sulfur, and solvent-exchanged into hexane. The extracts were then purified by using a semi-automated clean-up device equipped with columns containing sulfuric acid-impregnated silica gel, activated silica gel, alumina, and silver nitrate-impregnated alumina (RAPiANA™ column set for 209 PCBs; Miura Co., Ltd.). The eluates from clean-up columns were evaporated under a gentle nitrogen flow and spiked with ¹³C₁₂-PCB internal standards before quantification. Total 209 PCB congeners were determined by a 6890N gas chromatograph (Agilent Technologies) connected to a JMS-800D high resolution mass spectrometer (JEOL). The separation was performed on a HT8-PCB capillary column (60 m × 0.25 mm × 0.25 μm; Kanto Chemical). Detailed information on instrumental analysis was described in our previous study¹⁵. Recoveries of surrogate compounds ranged from 60% to 120%. Method detection limits of PCBs ranged from 3.0 to 30 pg g⁻¹ dry weight.

Results and discussion:

Concentrations of PCBs in the sediment core. Concentrations of total 209 PCBs ($\Sigma 209\text{PCBs}$), 7 indicator congeners ($\Sigma 7\text{in-PCBs}$, including CB-28, -52, -101, -118, -138, -153, and -180), 12 dioxin-like PCBs ($\Sigma 12\text{dl-PCBs}$, including CB-77, -81, -126, -169, -105, -114, -118, -123, -156, -157, -167, and -189), and CB-11 were presented in Fig. 1. Concentrations of $\Sigma 209\text{PCBs}$ (median 16, range 5.6–150 ng g^{-1}), $\Sigma 7\text{in-PCBs}$ (4.3, 1.3–29 ng g^{-1}), and $\Sigma 12\text{dl-PCBs}$ (0.78, 0.22–7.5 ng g^{-1}) showed quite similar temporal trends with major peaks at layers corresponding to the late 1960s. Pattern of dl-PCBs also contained a smaller peak in the early 1980s. Meanwhile, levels of CB-11 ranged from 0.040 to 0.41 (median 0.18) ng g^{-1} and exhibited an unique depth profile with a moderate peak at the mid-1970s, followed by the highest abundance between the mid-1980s to the late 1990s, and then clearly decreased to the early 2000s. However, concentrations of CB-11 showed a slight increase from 2002 onwards. Because of the difference in the congeners investigated, any limitations should be considered to make a relevant comparison of PCB contamination degree between our results and those of previous studies. Nevertheless, concentrations of total PCBs in our samples were comparable to or lower than those recorded in sediment core of Tokyo Bay (3.39–151 ng g^{-1})¹¹ and Osaka Bay (<10–190 ng g^{-1})⁶, Japan; but somewhat higher than levels found in other locations such as Izmit Bay, Turkey (5.4–29 ng g^{-1})¹⁶, Jobos Bay, Puerto Rico (0.42–50 ng g^{-1})¹⁷, and western Adriatic Sea¹⁸ (max 9.0 ng g^{-1}). Concentrations of dl-PCBs in the Beppu Bay sediment core were generally higher than levels detected in samples from other Japanese and Chinese coastal areas^{12,13,19}. Information on the occurrence of CB-11 in marine sediment core is still limited. Giuliani et al. (2017) reported the abundance of this novel congener in sediment core from Izmit Bay, Turkey (0.312–1.72 ng g^{-1})¹⁶, which were about one order of magnitude higher than levels measured in our study.

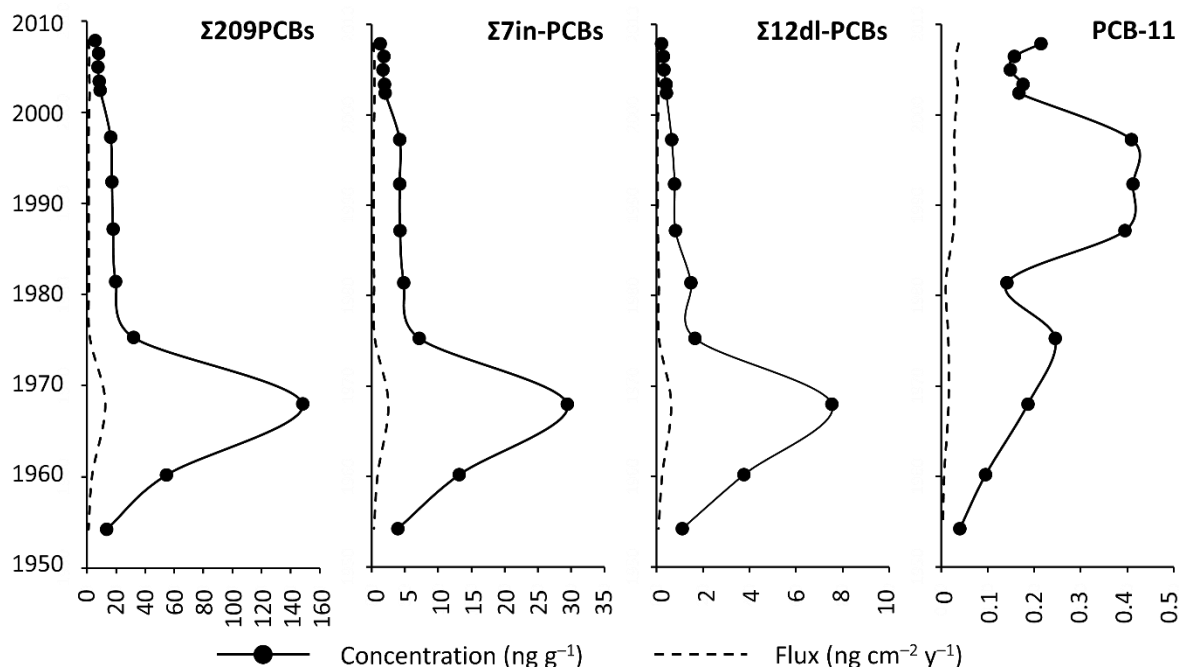


Fig.1. Concentrations and fluxes of PCBs in sediment core from Beppu Bay, southwestern Japan

It is interesting that the temporal variation of total PCBs and indicator PCBs detected in our sediment core was perfectly matched with history of PCB production in Japan, showing major peaks at the late 1960s. Other studies conducted in Osaka Bay⁶ and Tokyo Bay¹¹ revealed time lags between the peaks of PCB production and usage and the depth profile found in the sediment core (peak concentrations observed at the early 1980s or even later). Yamashita et al.¹¹ explained this delay by particulate transport and deposition processes, which are affected by hydraulic residence times and particle settling velocities. On the other hand, Shishime and Watanabe²⁰ estimated chronological changes in the concentrations of PCBs in substances sinking to the bottom of Tokyo Bay by using a non-stationary multimedia model, and suggested such delay in the vertical trend of PCBs observed in the sediment core mainly due to bioturbation. In this study less bioturbation in the bottom sediment derived by a specific anoxic environment in the depocenter of Beppu Bay can therefore be a possible reason to explain simultaneous trends observed between in the historical PCB production and its record in the sediment core.

Estimation of fluxes of PCBs. Annual PCB fluxes ($\text{ng cm}^{-2} \text{y}^{-1}$) were estimated by using the following equation: $\text{Flux} = C_i \times r \times \rho_i$; where C_i and ρ_i as PCB concentration (ng g^{-1}) and dry bulk density (g cm^{-3}) of sediment layer i , respectively; and r as sediment accumulation rate (cm y^{-1}). Fluxes of total PCBs in the sediment core of this

study ranged from 0.97 to 13 (median 1.6) ng cm⁻² y⁻¹. The maximum fluxes of PCBs were detected in specific layers Sed-1968 (13 ng cm⁻² y⁻¹) and Sed-1960 (3.6 ng cm⁻² y⁻¹), while the remaining layers showed relatively lower and constant fluxes (0.97 to 2.0 ng cm⁻² y⁻¹). Fluxes of Σ7in-PCBs, Σ12dl-PCBs, and major homologs (e.g., tri- to hexa-CBs) exhibited similar trends to those of total PCBs. However, fluxes of mono-CBs and CB-11 displayed declining trends with depth, showing the highest fluxes (0.021 and 0.037 ng cm⁻² y⁻¹ for mono-CBs and CB-11, respectively) in the surface layer (Sed-2008). The fluxes of PCBs estimated in our studies were within the range reported for other locations such as Osaka bay⁶ and Tokyo Bay, Japan¹¹, western Adriatic Sea¹⁸, and Arabian Gulf of Indian Ocean²¹; but higher than those derived for sediment cores from Admiralty Bay, off the Antarctic Peninsula²².

Profiles of PCBs in the sediment core. The predominant PCB homologs detected in our samples were tetra-, tri-, hexa-, and penta-CBs, which accounted for 26% ± 5.0%, 19% ± 5.3%, 19% ± 4.9%, and 18% ± 5.3% of total PCBs, respectively. Particularly, proportion of tetra-CBs in sediment layer with estimated age of 1968 (Sed-1968, 38%) was markedly higher than those found in other layers (14% to 38%); while layer Sed-1954 showed significant predominance of penta- (33%) and hexa-CBs (32%) as compared with the remaining samples where percentages of penta- and hexa-CBs ranged from 14% to 23% and from 10% to 22%, respectively. In contrast, proportions of mono- and di-CBs showed increasing temporal trends with higher percentages in the uppermost layers. Indicator PCBs accounted for 24% ± 2.3% of total PCBs and a strong correlation between Σ209PCBs and Σ7in-PCBs was observed (Pearson's $r = 0.997$, $p < 0.001$). DI-PCBs also significantly associated with indicator PCBs and total PCBs ($r > 0.990$, $p < 0.001$). CB-11 accounted for 22% ± 10% and 1.6% ± 1.1% of di-CBs and total PCBs, respectively. There was no statistically significant relationship among mono-CBs and CB-11 with Σ209PCBs and Σ7in-PCBs ($p > 0.05$).

Estimation of emission sources of PCBs. Homolog and congener-specific profiles of PCBs in the sediment core were compared with those reported by Takasuga et al. (2006) for Kanechlor mixtures (i.e., KC-300, -400, -500, and -600)²³. Percentage-normalized compositions of PCBs in the sediment samples and KC mixtures were analyzed by using hierarchical cluster analysis (HCA) with Ward linkage and correlation coefficient distance, and the results are presented in Fig. 2. Accordingly, most of the sediment samples showed relatively consistent profiles, but were not grouped with any specific KC mixture, reflecting the variation in usage patterns of the commercial PCB formulations and the effects of partition, transportation, and transformation processes of PCBs in the environment. Two exceptional cases were detected for the layer Sed-1968 exhibiting high similarity in both PCB homolog and congener compositions compared with KC-300 and KC-400 mixtures, and the layer Sed-1954 that closely related with KC-500. It was estimated that the production of KC-300 and KC-500 was comparatively higher than other formulations²⁴. KC-400 mixtures were also described as heat transfer fluids in several industrial systems in Japan, which were related to Yusho rice oil poisoning incident in this country in 1968⁹. Few years after the Yusho disease, Japan stopped production of PCBs, leading to declined emissions from technical mixtures.

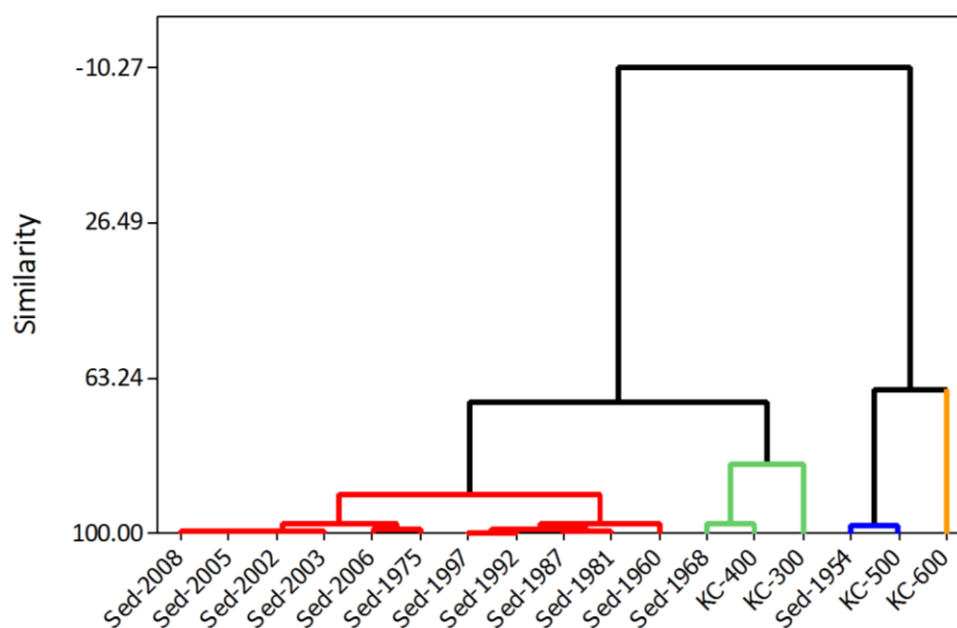


Fig. 2. Hierarchical cluster analysis of compositions of PCB homologs (% to total PCBs) in a sediment core from Beppu Bay, Japan (Sed-1954 to 2008) and in Japanese PCB technical mixtures (KC-300 to 600)

In contrast, mono-CBs and CB-11 showed increasing temporal trends, indicating their on-going emissions from specific sources other than legacy PCB-containing products. Emission of mono-CBs and other lower chlorinated PCBs from unintentional sources such as cement combustion and iron-making furnaces was estimated to contribute to the total PCB inventory in Japan at significant proportions²⁵. A dichlorinated congener, CB-11, were detected in several commercial paint pigments on Japanese markets³. CB-11 was found as major congeners in the ambient air of an urban area in Sapporo (mean 11, range 2.4–37 pg m⁻³, accounting for 3.0% on average of total PCBs) and an industrial area in Muroran, northern Japan (mean 8.0, range 1.9–27 pg m⁻³, accounting for 10% on average of total PCBs)³. Information on the occurrence of CB-11 in Japanese marine sediments is relatively scarce. Our preliminary result revealed that this compound can contribute upto 4.0% of total PCBs in the surface sediment layer, accompanied with an increasing trend. It is unclear whether the presence of this special congener in the sediment core of Beppu Bay has been derived by atmospheric deposition through an air-water partitioning and/or by riverine discharge to the sea, as well as their relative contributions. Further comprehensive studies on the distribution of PCBs including all 209 congeners in the Japanese marine environments are needed.

Conclusions:

This study provides an interesting picture on the occurrence, detailed congener-specific profiles, and temporal variation of 209 PCBs in a dated sediment core from Beppu Bay, Japan. Concentrations and fluxes of total PCBs, indicator PCBs, and dl-PCBs have peaks in the late 1960s, reflecting historical production and usage of technical PCB mixtures in Japan. Meanwhile, mono-CBs and CB-11 showed an increasing trend with higher proportions detected in the shallowest depths, implying their specific emission sources related to manufacturing and utilizing of paints and pigments and/or other industrial processes such as cement combustion and iron-making furnaces.

Acknowledgements:

This study was supported by the Environment Research and Technology Development Fund (SII-3-2) of the Environmental Restoration and Conservation Agency of Japan (ERCA). The authors would like to thank Ms. Kana Kadota and students of CATE and CMES, Ehime University in sampling activities and sample analysis.

References:

1. UNEP (1999) <http://www.pops.int/Implementation/IndustrialPOPs/PCBs/Guidance>
2. Erickson MD (1997) *Analytical Chemistry of PCBs* (second ed.) CRC Press, Boca Raton.
3. Anezaki K, Nakano T (2014) *Environ. Sci. Pollut. Res.* 21: 998-1009.
4. Bigus P, Tobiszewski M, Namiesnik J (2014) *Mar. Pollut. Bull.* 78: 26-42.
5. Korosi JB, Cheng W, Blais JM (2015) http://doi.org/10.1007/978-94-017-9541-8_8.
6. Sakai S, Deguchi S, Takatsuki H (2002) *J. Environ. Sci. Soc.* 15: 361-376 (in Japanese).
7. de Voogt P, Brinkman UAT (1989) <http://doi.org/10.1016/b978-0-444-81029-8.50005-9>.
8. Watanabe I, Yakushiji T, Kuwabara K, et al. (1977) *Japan. J. Public Health* 24: 749-756 (in Japanese).
9. Masuda Y (1994) https://doi.org/10.1007/978-1-4899-1462-0_19.
10. Sakai S, Hayakawa K, Takatsuki H, et al. (2001) *Environ. Sci. Technol.* 35: 3601-3607.
11. Yamashita N, Kannan K, Imagawa T, et al. (2000) *Environ. Sci. Technol.* 34: 3560-3567.
12. Okumura Y, Yamashita Y, Kohno Y, et al. (2004) *Water Res.* 38: 3511-3522.
13. Kim YS, Eun H, Katase T (2008) *Arch. Environ. Contam. Toxicol.* 54: 395-405.
14. Kuwae M, Yamamoto M, Ikehara K, et al. (2013) *J. Asian Earth Sci.* 69: 133-148.
15. Anh HQ, Watanabe I, Tomioka K, et al. (2019) *Sci. Total Environ.* 652: 345-355.
16. Giuliani S, Bellucci LG, Cağatay MN, et al. (2017) *Sci. Total Environ.* 590-591: 799-808.
17. Alegria H, Martinez-Colon M, Birgul A, et al. (2016) *Sci. Total Environ.* 573: 1003-1009.
18. Combi T, Misericocchi S, Langone L, et al. (2016) *Sci. Total Environ.* 562: 580-587.
19. Pan J, Yang Y, Taniyasu S, et al. (2012) *Bull. Environ. Contam. Toxicol.* 89: 1240-1246.
20. Shishime T, Wanatabe M (2004) *Kaigan-kougaku ronbunshu* 51: 971-975 (in Japanese).
21. Gevao B, Aba AA, Al-Ghadban AN, et al. (2012) *Arch. Environ. Contam. Toxicol.* 62: 549-556.
22. Combi T, Martins CC, Taniguchi S, et al. (2017) *Mar. Pollut. Bull.* 118: 447-451.
23. Takasuga T, Senthilkumar K, Matsumura T, et al. (2006) *Chemosphere* 62: 469-484.
24. Takasuga T, Kumar KS, Noma Y, et al. (2005) *Arch. Environ. Contam. Toxicol.* 49: 385-395.
25. Hirai Y, Sakai S (2017) *Material Cycle Waste Manag. Res.* 28: 143-148 (in Japanese).