

Source Identification of Polychlorinated Biphenyls in Tokyo Bay Sediment on the Basis of Congener Specific Information

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Introduction

To employ improved countermeasures against PCB sources and to reduce the risk to aquatic biota, it is important to identify sources and migration pathways and ascertain their contribution to PCB pollution¹. Thus, a wider range of studies is required to identify potential PCB sources in the environment. The objective of this study is to identify PCB pollution sources affecting Tokyo Bay sediment and estimate source contributions.

Materials and Methods

Study area: Tokyo Bay was selected as a study area because it is one of the most heavily impacted coastal areas by the human activities in Japan. In its basin, the bay has the largest metropolis in Japan, Tokyo, with population of over ten million and lot of industries.

Sampling in Tokyo Bay:

The surface-sediment samples, collected at 0-2 cm below the surface, and some core samples were taken from the entire Tokyo Bay area in February 2004. The sampling points were designated St 1 through St 11 (except St 7) (Figure 1) and the samples were obtained with a Smith McIntyre sediment grab sampler.

The samples were then brought back to our laboratory on the same day and maintained at a temperature of -30°C until a PCB analysis was performed.

PCB analysis: PCB analysis of all congeners was performed according to the procedures established in our laboratory². The procedures are based on the "Sediment survey and analytical manual for dioxins"³ and the U.S. EPA Method 1668 Revision A⁴. PCBs were analyzed with gas chromatography (GC, Agilent HP6890) equipped with a DB-5 column (J&W Scientific). The GC was coupled with a high-resolution mass spectrometer (HRMS, Micromass Autospec Ultima) in SIM mode. The detected peaks were identified by referring to previous reports^{2,5}. The concentrations of individual PCB peaks were determined by the isotope dilution quantification method. For detailed information on the quantitative determination, refer to Kim².

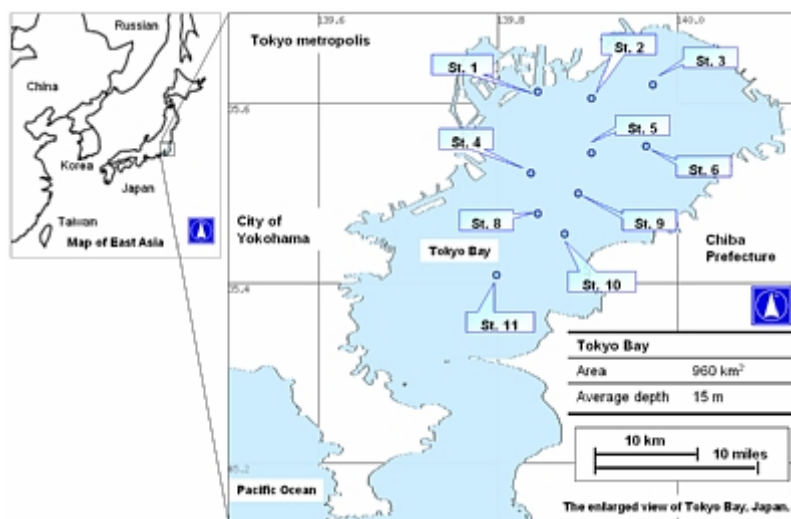


Figure 1 Map of East Asia and the sampling point in the enlarged view of Tokyo Bay, JAPAN

Formation, sources and source inventories

Statistical analysis:

The principal component analysis (PCA) of the data was performed with software packages such as Statistica version 6 (StatSoft, Inc. 2003). The PCB congeners whose concentrations were below the detection limit were eliminated from the PCA. Over 140 individuals and congener groups were used as explicit input variables in the PCA. The eigenvectors obtained were normal varimax rotated for better interpretation of the results.

Results and Discussion

Spatial and vertical concentration of PCBs and Dioxin-like PCB:

The concentration of total PCBs in the Tokyo Bay surface sediment ranged from 4.00 to 126 ng/g-dry sediment (average concentration; 55.5 ng/g). For dioxin-like PCBs, the TEQ concentrations were calculated with WHO-TEFs, and they ranged from 0.18 to 4.22 pg-TEQ/g-dry sediment (average concentration; 2.29 pg-TEQ/g). Total PCB and TEQ concentrations tend to be higher in the closed-off section of the bay. The sampling point with the highest total PCB and TEQ concentration was St 1 and it was located in the estuary of the Ara River.

In the core sediment, where in all samples the PCBs concentration ranged from 71.3 to 810 ng/g. The PCBs concentration peaked at 1962 which was estimated from the sedimentation rate determined using radiometric ²¹⁰Pb and ³⁷Cs dating, and then declined progressively. The TEQ concentrations ranged from 2.24 to 17.0 pg-TEQ/g.

PCB homologue composition:

In surface sediment samples, the group total including 4CBs (chlorinated biphenyl) to 7CBs accounted for more than 76% of the total PCB concentration. The homologue compositions were almost identical among the samples from the closed-off section of the bay; however, the ratios of 3CBs to 5CBs were relatively higher than those in the samples taken from the bay entrance. These results showed that these compositions were analogous to those of Kanechlor, and thus qualitatively suggested that Kanechlor could be a dominating PCB source.

Principal Component Analysis (PCA) of PCB all congeners in surface sediment:

PCA was applied to determine the PCB sources in surface sediments. Over 140 individuals and a group of PCB congeners in ten samples were subjected to PCA. The factor loading plot of PCA is shown in Figure 2. As a result, two principal components (PCs) and two minor ones were extracted with eigenvalue greater than 1. PC1 and PC2 accounted for 52.5% and 33.7% of the total variance, respectively. PCB congeners related to PC1 with factor loading greater than 0.7 were IUPAC #77, #101, #118/106, etc., which were classified as 3CBs, 4CBs, and 5CBs. A majority of these congeners are characteristically present in Kanechlor². The congeners related to PC2 were mainly 7CBs and 8CBs including IUPAC #169, #175, #189, #195, etc., which were reported to occur in flue-gas samples². Therefore, the presence of PC2 could be attributed to incinerator sources. The congeners related to PC3 with loadings more than 0.7 were IUPAC #54, #208, and #206, and those related to PC4 were IUPAC #202; however, the presence of PC3 and PC4 could not be explained. Two PCs could be attributed to PCBs from Kanechlor (PC1) and incinerator sources (PC2) and accounted for about 86% of the cumulative contribution (Table 1).

Table 1 Results of principal component analysis with normalized varimax rotation

PCs	PC1	PC2	PC3	PC4
Proportion (%)	52.5	33.7	4.58	2.85
Cumulative proportion (%)	52.5	86.2	90.78	93.63
Characteristic congeners (factor loading >0.7) **	Most congeners, #77, #101, #118/106, etc	#169, #189, higher chlorinated congeners	#54, #208, #206	#202

*Principal component with eigenvalue > 1 were extracted.

**IUPAC # for PCBs congeners

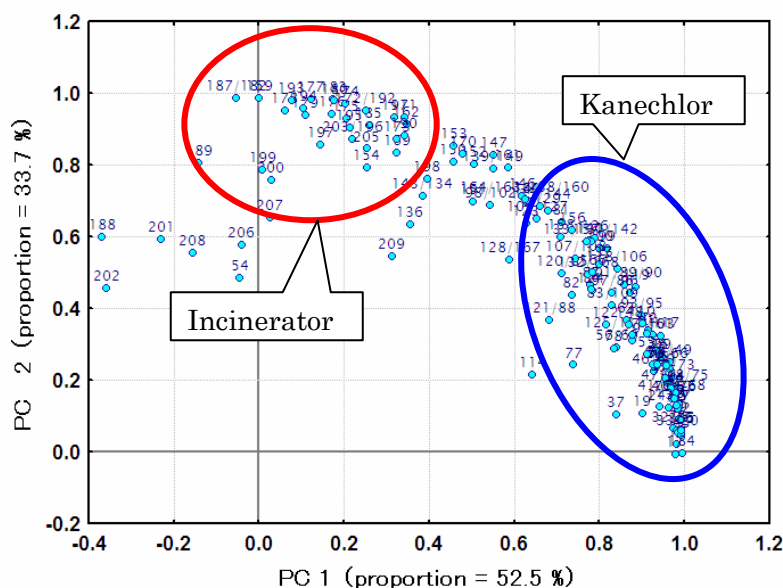


Figure 2 Factor loading plot of PCA results with congener in 3CB to 10CB homologues

Source apportionment of PCBs by a chemical mass balance (CMB) model:

In the CMB model, the input data for Kanechlor and incinerator sources were obtained from a previous research (Kim et al., 2004), which were employed as independent variables. The regression coefficients for the two sources were obtained and source apportionment was carried out with these coefficients. The results obtained were summed, and the contribution of the two sources in terms of the total PCB concentration was calculated for each surface and core sediment samples. The equation for this procedure is below.

$$\chi^2 = \sum_i^n \left(C_i - \sum_j^p a_j X_{ij} \right)^2$$

C_i is the concentration of congener i in the sample; a_j is the contribution of source j ; and X_{ij} , the concentration of congener i in source j . In the CMB model, the least-squares solutions of a set of linear equations express the concentration of the chemicals in the environment as the linear sum of the products of the source profiles and the contribution. In ordinary least-squares methods, the contribution of source j was calculated by minimizing the value of χ^2 .

The result shows that Kanechlor was the major contributor to the PCB pollution concentrations in the Tokyo Bay surface sediment, accounting for about 60% or more, and the contribution of incinerator sources was about 40% or less in all the samples (Figure 3). The ratios of the contribution of Kanechlor to that of the incinerator sources were almost identical in all samples. The predicted and observed total PCB concentrations were in good agreement.

In core sediment samples (St 5), the result showed that Kanechlor had been the greatest contributor to core sediment pollution in lead and cesium isotopic age of all. Its contribution peaked in 1974 (about 80%) and declined progressively. The contribution from incinerator peaked in 1969 (about 30% or more) and once it had decreased rapidly in 1974, then it had been increased up to the present date (Figure 4).

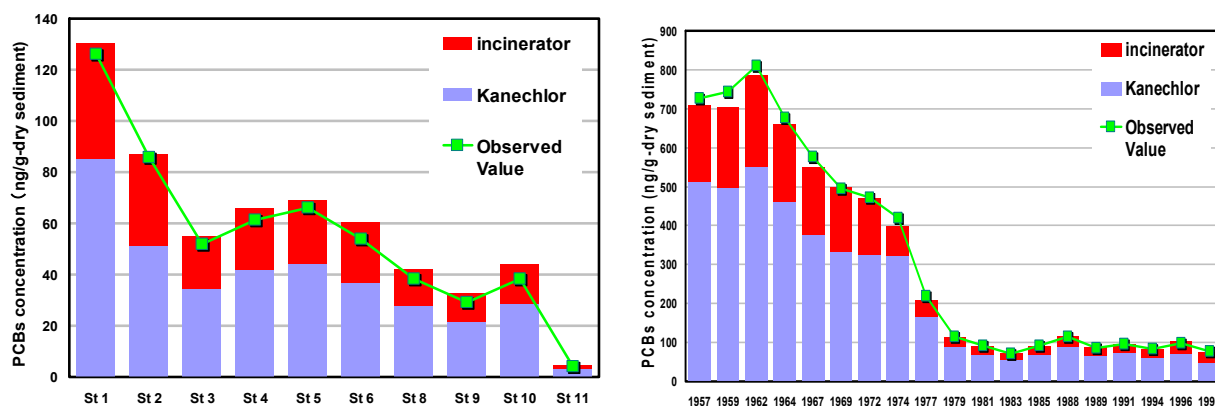


Figure 4 Observed total PCB values and estimated source contributions from the two sources in Tokyo Bay surface sediments, and Figure 5 in core sediment

Acknowledgements

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