IDENTIFICATION OF HEXABROMOCYCLODODECANE ENANTIOMER AND ITS BROMINATED DERIVATIVES IN JAPANESE RIVERINE ENVIRONMENT

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Introduction

Hexabromocyclododecane (HBCD) used in polystyrene foams and textile products as brominated flame retardant (BFR) has recently been added to a list of global elimination compounds under the Stockholm Convention on Persistent Organic Pollutants[1]. Although physicochemical properties, bioaccumulation, and toxicity of HBCD have been explored much, absolutely no consensus has been achieved as to its persistence in the environment. Some studies attempted to identify its brominated derivatives in various environmental compartments[2,3,4]. It is very important to watch the formation of lower brominated derivatives from HBCD with respect to the degradation affected by abiotic oxidation, reductive debromination, substitution reaction, and so on[5].

In this sense, monitoring data on optical activity of HBCD in the environment is necessary not only to comprehend the transformation of individual diastereomers in both biotic and abiotic environment but also to assess the environmental risk of HBCDs. The purpose of this study is to characterize the interconversion and enantiomer fraction (EF) of HBCD stereoisomers and to identify its brominated derivatives in samples from rivers that have possible HBCD emission sources in their basin.

Materials and methods

Sampling. Fig. 1 shows the sampling locations of this study. Surface water and sediment samples for monitoring study were collected at 17 sites from the 3 rivers; Turumi River (T-1~T-4, n=4), Yodo Rover (Y-1~Y-6, n=6) and Kuzuryu River (K-1~K-7, n=7) in 2011. There is no industrial activity related to the use of HBCD near the Tsurumi River, while numerous production and processing industries using HBCD are located in the basins of Yodo River and Kuzuryu River. Water samples were transported to the laboratory and stored at 4 ºC in the dark until pre-treatment. Sediments were sampled at the same sites, simultaneously with the water samples. The sediment samples in brown glass bottles were immediately brought to the laboratory and were stored at -25 ºC prior to analysis. Activated sewage sludge for degradation experiment was obtained from Tsuzuki Wastewater Treatment Plant, Yokohama City.

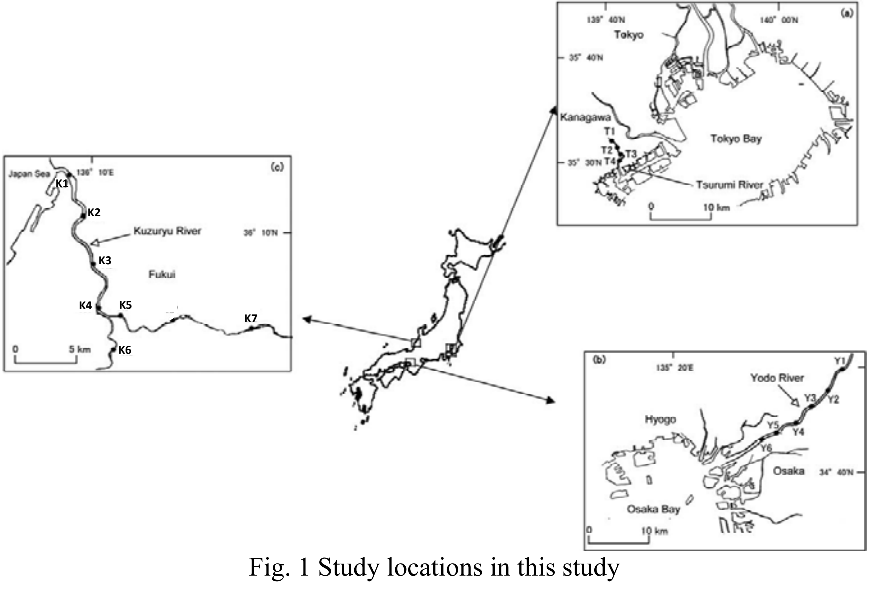

Fig. 1 Study locations in this study

Sample preprocessing. A water sample (1 liter) was spiked with 50 ng each of $^{13}C_{12}$-labeled α-, β-, and γ-HBCD as internal standards. Water sample was passed through a precleaned solid phase extraction disk (Empore Disk Styrenedivinylbenzene (SDB-XD, 47 mm) 3M, USA) at a flow rate of 30 mL/min. After dried in the oven at 45 ºC for 1 hour, the disk was eluted with 4 mL of acetone and 4 ml of dichrolomethane in order. The eluate was evaporated under the flow of nitrogen gas, and then reconstituted in 1 mL of methanol.

All the sediment samples were homogenized, freeze-dried, and sieved by a 2 mm sieve prior to analysis. Each sample was spiked with 50 ng each of $^{13}C_{12}$-labeled α-, β-, and γ-HBCD as internal standards. Extraction was carried out using Accelerated Solvent Extraction instrument (ASE 200, Dionex) with dichloromethane (DCM) and hexane (80:20 v/v) at 100 ºC and 1500 psi. Cleanup procedure was performed using chromatography column packed with 8 g of 44% sulfuric coated silica gel. The eluate was evaporated to dryness under N_2, and redissolved in 1 mL of methanol prior to LC-MS/MS analysis.

LC-MS/MS analysis. Liquid chromatograph (Waters 2695; Milford, MA, USA) and triple-quadrupole mass spectrometer (Micromass Quattro Ultima triple-quadrupole MS; Micromass, Milford, MA, USA) were used for the determination of HBCDs and its derivatives. While A ZORBAX Eclipse XDB-C18 column (150 mm, 2.1 mm, 3.5 μm) was used to separeate HBCD diastereomers and its derivatives, enantiomer separation of α-, β-, γ-HBCDs was achived by Chiral NUCLEODEX beta-PM column (4.0 × 200 mm, 5 μm, Macherey-Nagel GmbH and Co., Germany) with Nucleodex beta-PM guard cartridge. The tandem MS analysis was performed using negative electrospray ionization (ESI) with multiple reactions monitoring (MRM) mode. In this study, EF values corrected by $^{13}C_{12}$-labeled HBCDs were used for all the samples to offset the matrix effects, such as mobile phase and column bleed in the LC-ESI-MS analysis[6].

Results and discussion

Trends of HBCD concentration in the three rivers. HBCDs were detected in all the water/sediment samples as summarized in Fig. 1. It would be interesting to see if there were disparities of resutls between this study and the previous study[7] which collected samples from almost the same locations. Higher total HBCD concentrations (mean value of 12 ng g^{-1} dw, this study) were obserbed in this study than the previous study (mean value of 2.7 ng g^{-1} dw) for Tsurumi River. For Yodo and Kuzuryu Rivers, lower cencentrations were observed in this study (mean values of 49 and 550 ng g^{-1} dw, respectively) than the previsou study (mean values of 57 and 730 ng g^{-1} dw for only K-1 ~ K-5, respectively). To our knowledge, there were no industrial activity that used HBCD in the Tsurumi River basin. Even though there was no specific emission sources of HBCD, house dust from curtains/insulating boards and cleaing wastewater of curtains might have been significant sources of HBCD to the Tsurumi River through the domestic wastewater. On the other hand, the Japanese Textiles and Furniture Association and Japan EPS/XPS industry Association have been making voluntary efforts to reduce environmental emissions of HBCD by replacing HBCD with alternative flame retardants since Feb. 2008[8]. These activities must have contributed to reduction of concentration levels in the near-source areas such as Yodo and Kusuryu Rivers.

HBCD diastereomeric patterns: Relative diastereomeric patterns of HBCDs in water and sediment samples were calculated. In this study, γ-HBCD was the predominant diastereomer in all the water (30–82%) and sediment samples (56–89%), indicating diastereomeric compositions of HBCD in all the samples were influenced by technical mixture of HBCD (75–89% γ-HBCD, 10–13% α-HBCD, and <0.5–12% β-HBCD[9]).

Enantiomer fractions: Enantiomer fraction (EF) of α-, β-, and γ-HBCD in water and sediment samples were determined (Fig. 2) to understand the aquatic environmental behavior of HBCD in this study area. The mean enantiomer fraction for γ-HBCD in sediments of the three rivers ranged from 0.357 (standard deviation: 0.023) to 0.472 (0.014), suggesting that biotic transformation to γ-HBCD possibly occured in the study location.

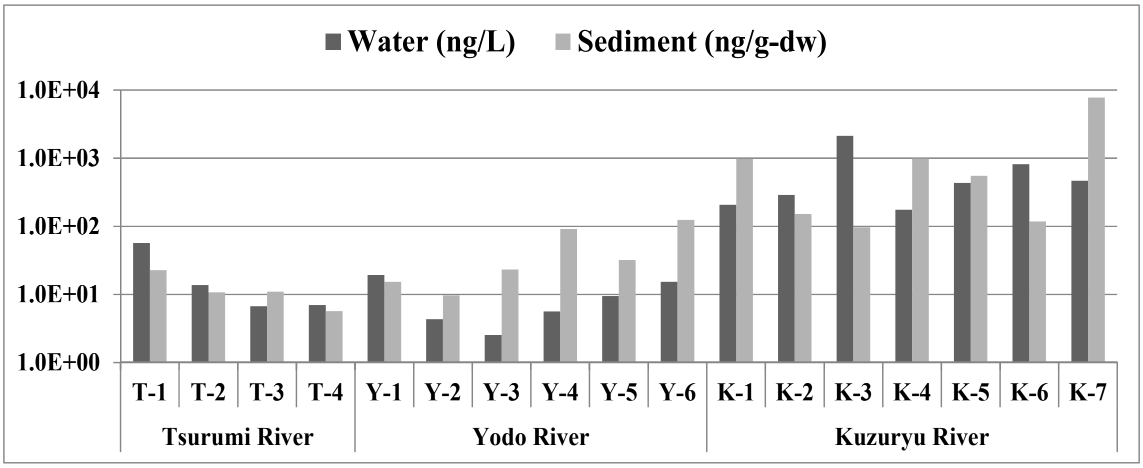

Fig. 1 Total HBCD concentrations (sum of α-, β-, and γ-HBCD) at riverine samples

Occurence of HBCD derivatives: In the present study, lower brominated derivatives of HBCD (pentabromocyclododecenes: PBCDs), which could be regarded as degradation products via loss of HBr from HBCD[2] were determined by MRM transition of m/z 560.8→79, using the same analytical condition for HBCD diastereomers. PBCDs were detected in some water samples from Kuzuryu River (ranged from 2.2 to 14 ng L^{-1}) and in some sediment samples from Yodo River and Kuzury River (ranged from 0.45 to 19 ng g^{-1} dw). We confirmed the occurrence of 4 kinds of PBCD isomers in the samples. One of those four isomers was identified to have the same retention time as a PBCD standard (Wellinton Laboratories Inc, Canada). Due to the limitation of available PBCD standards, however, quantification of all the detected PBCD isomers was not possible.

In this study, we concluded that the distribution of HBCD in the study locations was heavily influenced by the near-sources (i.e. domestic sewage, industries using HBCD). The concentrations of HBCDs in the indstrially impacted rivers decreased by some degrees probably due to the volantary efforts of the indsutries to reduce the use of HBCD. Moreover, different diastereomer/enantiomer compositions and identification of lower brominated derivatives indicated that some transformation processes of HBCD stereoisomers occured in the three rivers.

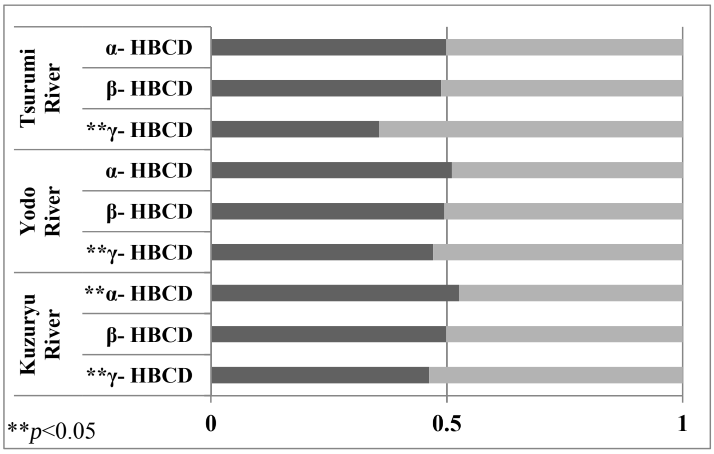

Fig. 2 Enantiomer Fraction of HBCDs in some Japanese rivers

Acknowledgements

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References

1. "Global Ban for Flame Retardant," *E&CN*, 13 May 2013: 19
2. Harrad S., Abdallah M. A. E., Rose N. L., Turner S. D., Thomas A. (2009) *Environ Sci Technol.* 43(24): 9077-9083
3. Abdallah M. A., Harrad S. (2009) *Environ Int.* 35:870-876
4. Davis J.W., Gonsior S.J., Markham D., Friederich U., Hunziker R., Ariano J. (2006) *Environ Sci Technol.* 40: 5395-5401
5. Eljarrat E., Feo M. L., Barcelo D. (2011) *Hdb Env Chem* 16: 187-202
6. Marvin C.H., MacInnis G., Alaee M., Arsenault G., Tomy G.T. (2007) *Rapid Communications in Mass Spectrometry* 21, 1925–1930
7. Managaki S., Enomoto I., Masunaga S. (2012) *J. Environ. Monit.* 14(3): 901-907
8. BSER fact sheep (2009) http://www.bsef.com/uploads/Documents/documents/HBCD_factsheet.pdf (2013. 5. 30 access)
9. Becher G. (2005) *Chemosphere* 58(7): 989-991