

CHARACTERIZATION OF THE PHOTOLYSIS OF DECABROMODIPHENYL ETHER AND THE LEVELS OF PBDES AS ITS PHOTOPRODUCTS IN ATMOSPHERIC AIR OF JAPAN

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Introduction

Polybrominated diphenyl ethers (PBDEs) are produced in large quantities as flame-retardant additives since 1980s in the world. In Japan, large amounts of PBDEs have been also consumed, showing 12,000 tons as maximum consumption in 1990. Since then, PBDEs congener prohibited applying for the industrial materials, and the annual consumption of DeBDE also decreases year after year, and to 2,800 tons in 2000, accompanying the increment of TBBPA consumption¹⁾. Over 95% of PBDEs used as flame-retardant additives is DeBDE, however, we observed that high concentrations of tri- to hexa-BDEs as lower PBDE congeners in the samples of the market fish and human milk in 1999²⁾. As the reason why was detected such lower PBDE congeners in environmental and human samples, it has been considered the rapid photolytic debromination of DeBDE^{3,4)}. In addition, it was also reported the formation of polybrominated dibenzo-p-dioxins (PBDDs) and polybrominated benzofurans (PBDFs) from the photolysis of DeBDE⁵⁾. Therefore, it is important to understand the photo-decomposed pattern of DeBDE in the environment.

In this article, we describe an observation result for the decomposition pattern of DeBDE in organic and water-like solvent under UV-light and sun-light. Further, in order to clear the transportation of the above PBDE congeners after the photolysis of DeBDE, it was surveyed that the PBDE levels in the atmospheric air of Hirakata city, and in the sediments of Muko River of Amagasaki city and Hokokou (Osaka Bay) of Osaka city as urban area in Japan. Finally, we will consider the transportation pathway, which PBDEs pollution in the neighboring waters of Japan preferentially occurs via the atmospheric air or the rivers.

Materials and Methods

1) Samples

100 µg/ml of DeBDE in toluene as organic solvent or a mixture of toluene, ethanol and water (1:3:6) as water-like solvent were prepared as a sample for photolysis. 1ml of this solution were introduced a quartz tube followed by irradiation by UV (254 nm; 120 lx), tungsten-light (10,000 lx) and sun-light (experimental period; 11-17 Nov. 2000, the average illuminance; 4,5000 lx, day/night cycle). After irradiation, the photoproducts present in each sample were analyzed directly by ECD-GC and LRGC-LRMS, as described below. The air samples were collected at the playground of our university in Hirakata city of Osaka prefecture, using the high-volume air sampler. The sediment samples were collected from the Muko River in Amagasaki city of Hyogo prefecture and Hokkou as the coastal area of Osaka Bay in Osaka city of Osaka prefecture.

2) Analytical method

In this study, the isotope dilution methods typically used to quantify dioxins concentrations in

environmental samples was for the analysis of PBDEs. curves for six different $^{13}\text{C}_{12}$ -labelled BDE isomers, 2,4,4'-TriBDE(#28), 2,2',4,4'-TeBDE(#47), 2,2',4,4',5'-PeBDE(#99), 2,2',4,4',5',5'-HxBDE(#153), 2,2',4,4',5',6'-HxBDE(#154) purchased from Wellington Laboratories (Ontario, Canada) and twenty seven unlabelled native standards, 2,2',4'-TriBDE (#17), 2,3',4'-TriBDE (#25), BDE-28, 2,4,6-TriBDE (#30), 2,4,6'-TriBDE (#32), 2,3,4-TriBDE (#33), 3,3',4-TriBDE (#35), 3,4,4'-TriBDE (#37), BDE-47, 2,2',4,5'-TeBDE(#49), 2,3',4,4'-TeBDE(#66), 2,3',4',6'-TeBDE(#71), 2,4,4',6'-TeBDE(#75), 3,3',4,4'-TeBDE(#77), 2,2',3,4,4'-PeBDE(#85), BDE-99, BDE-100, 2,3,3',4,4'-PeBDE(#105), 2,3,4,5,6-PeBDE(#116), 2,3',4,4',6'-PeBDE(#119), 3,3',4,4',5'-PeBDE(#126), 2,2',3,4,4',5'-HxBDE(#138), 2,2',3,4,4',6'-HxBDE(#140), BDE-153, BDE-154, 2,2',4,4',6',6'-HxBDE(#155), 2,3,4,4',5,6-HxBDE(#166) purchased from Wellington Laboratories and Cambridge Isotope Laboratories (MA, USA).

Sample preparation for analysis of PBDEs included polyurethane and glass-fiber filter as air sample and 10g of sediment, and 2 ng each of the internal $^{13}\text{C}_{12}$ -labelled BDE standards, followed by the modified method of Ohta et al⁶⁾. Both samples were extracted with 250 ml toluene for 5 hr under reflux. Next, the purification and determination method for PBDEs in the extracts of atmospheric air and sediment were performed, followed by our previous report²⁾. The purified extract was dissolved in 20 μl of n-nonane and analyzed for PBDEs by HRGC-LRMS or HRGC-HRMS in EI-SIM mode. For GC-low resolution MS analysis of the purified sample extracts, a HP 5873 mass spectrometer as quadrupole type (R=1000) connected to HP 6890 GC equipped with an auto-sampler was used. PBDE analyses also were determined using a HP6890 GC-JEOL JMS700 MS (HRGC-HRMS) at high-resolution condition (R=5000), and the analytical data were compared. The sample extract was analyzed on a Supelco SPB-5 (30 m x 0.32 mm, 0.25 m film thickness) with the rate of the heating condition held for 2 min at 120 programmed to 215 °C at 10 °C /min, to 270 °C at 3 °C /min, to 310 °C at 10 °C /min, and finally held for 10 min at 310 °C. Sample introduction was performed by splitless injection of a 2- μl aliquot of the sample extract. On the other hand, the analysis of the photoproducts of DeBDE was also performed to measure the total ion (M/Z=100-900) using LRGC-LRMS in EI-SIM mode. Other GC-MS conditions were the same as describe above.

Results and Discussion

The total ion chromatogram of time alteration of the photolysis of DeBDE in toluene under UV or Sun-light is shown in Fig. 1. Rapid photodecomposition of DeBDE was observed in toluene under the irradiation of UV-light. After 40min, DeBDE was completely decomposed on TI chromatogram. On the other hand, an interesting phenomenon was observed in the sample of DeBDE under Sun-light in outdoor. DeBDE was rapidly decomposed as if its photoproducts temporarily concentrated to the two kinds of HpBDE. We considered that this result was due to the difference of the amounts of ultraviolet between UV-light and Sun-light. Further detailed identification of the two kinds of HpBDE was conducted for the sample under a continuous irradiation of tungsten-light for 120 hr (Fig.2). By comparing with the mass spectra of both peak, one peak of two HpBDEs was identified as 2,2', 3,4,4', 5-HpBDE, another peak was estimated as the extreme similar compound, indicating the only difference of substituent position of bromine atom. Fig. 3 shows the levels of PBDE congeners in the atmospheric air and the sediments of Osaka district in Japan. Total concentration of PBDE congeners in air sample of summer was higher than that of winter, observing the reverse phenomenon of total concentration of dioxin analogues (data not shown). With respect to the PBDEs level in the particle and gas phase of air

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sample, the level in the gas phase was higher than that in the particle phase in the summer, the level was also reversed in the winter. Therefore, the above observation may be derived from the difference of vapor pressure of both compounds. In addition, an interesting phenomenon was found; it could not detect the HxBDE congeners in almost air samples, accompanying with high recoveries of $^{13}\text{C}_{12}$ -labelled BDE isomers. It was suggested that DeBDE may have been photodecomposed to less than PeBDE isomers in the atmospheric air, however the reason is unknown. While, it could detect all congeners from tri- to hexa-BDEs in the sediment samples. From the above results, we considered the main pathway of transportation for PBDEs pollution in the neighboring waters of Japan is through the rivers.

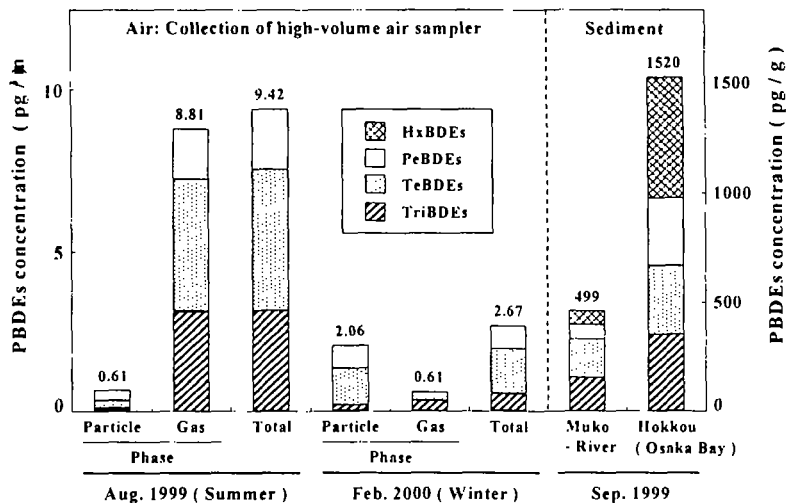


Fig. 3; Levels of PBDE congeners in the atmospheric air and the sediments of Osaka district in Japan

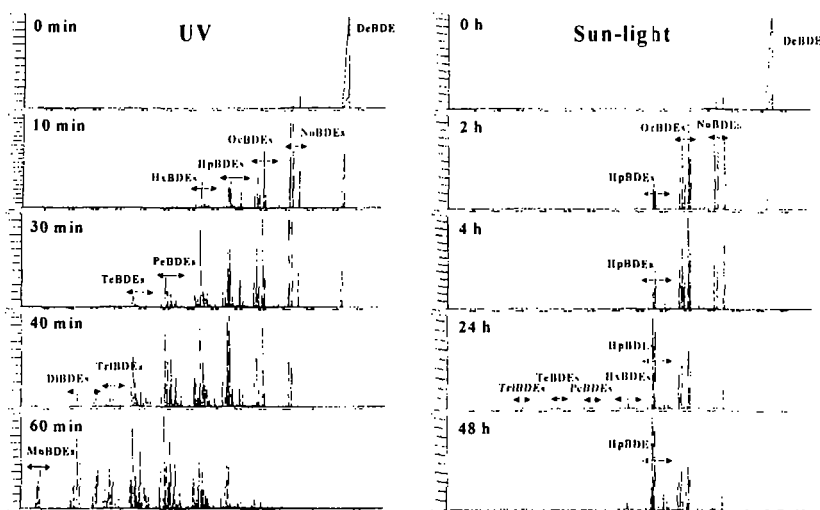


Fig. 1; Total ion chromatograms of time alteration of the photolysis of DeBDE in the toluene under UV or Sun-light

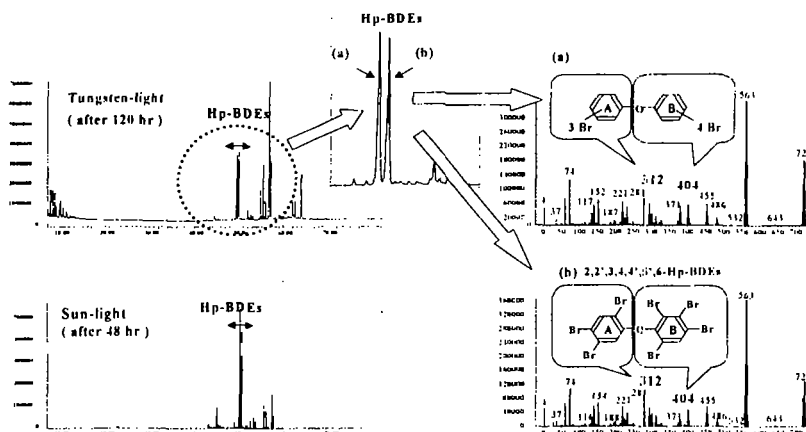


Fig. 2; Mass spectra of two kinds of HpBDE shown in TI chromatogram

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References

1. The Statistical Data of "Kagaku Kogyo Nippo" as Newspaper during period of 1987-2000 in Japan.
2. Ohta S., Ishizuka D., Nishimura H., Nakao T., Aozasa O., Miyata H. (2000) *Organohal Comp.* 47, 218.
3. Eriksson J., Jakobsson E., Marsh G., Bergman A. (2001) *Abstracts of BFR 2001*, 203.
4. Tysklind M., Sellstrom U., Soderstrom G., de Wit C. (2001) *Abstracts of BFR 2001*, 51
5. Watanabe I., Tatsukawa R. (1987) *Bull. Environ. Contam. Toxicol.*, 39, 955.
6. Ohta S., Kuriyama S., Aozasa O., Nakao T., Miyata H. (2000) *Bull. Environ. Contam. Toxicol.*, 64, 630.