DEGRADATION OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN SEDIMENTS OF ER-JEN RIVER AND NAN-KAN RIVER BASIN IN TAIWAN

Jui-Hung Yen, Wen-chen Liao and Yei-Shung Wang

Department of Agricultural Chemistry, National Taiwan University, Taipei, Taiwan

Introduction

Polybrominated diphenyl ethers (PBDEs) were widely used as a flame retardant in the industrial products, such as circuit boards in the computer, televisions, and capacitors etc. PBDEs constitute one third of the amount of the brominated fire retardants manufactures and consist predominantly of deca-BDE. After items containing the brominated diphenyl ethers are used, they are discarded and PBDEs are released into the environments. The fate of PBDEs had been concerned as a seriously environmental problem since these chemicals were found to accumulate in the biota, and due to the persistent and highly hydrophobic property, PBDEs may also pollute the sediment and biota in aquatic environments. Recently, industrial use of Penta-BDE and Octa-BDE in Taiwan was strict consideration, not only their environmental pollution problem but also for the export trade to European Union.

Er-Jen River and Nan-Kan River locate at southern and northern part of Taiwan, respectively. They were became seriously contaminated for a long time. This research was focus on the degradation rate of PBDEs by the microorganism in the sediment of both river basins. The effect of PBDEs on the microorganism community in sediment were also studied. Biodegradation might be effective to exclude PBDEs from environments by microorganisms under anaerobic conditions [12].

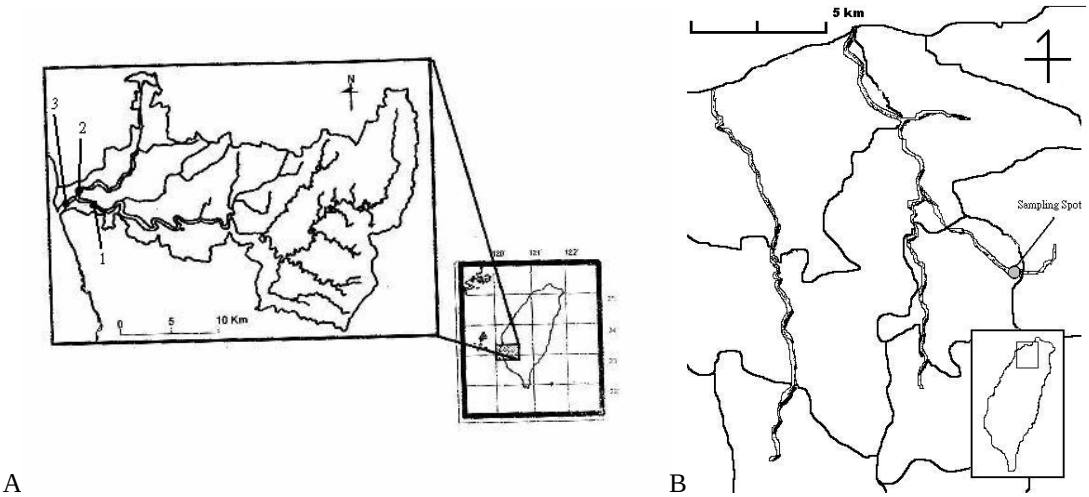
Materials and Methods

Chemicals: 2,2',4,4'-Tetrabromodiphenyl ether (BDE-047), 2,2',4,4',5-Penta- bromodiphenyl ether (BDE-099), and 2,2',4,4',6-pentabromodiphenyl ether (BDE-100) with purities (GC-MS) of 100, 100, and 100%, respectively, were purchased from AccuStandard Inc., CT, USA.

Sediments: Sediment samples were collected from San-yr-kong river entrance locate at upstream of Er-Jen river (site 2 in Figure 1A) and Nan-Kan river basin of northern Taiwan (Figure 1B). A grab sampler was used to collect the sediment in a depth of 0 to 10 cm. The sampling sediment was stored in a jar, kept in 4 ℃ and taken to laboratory for experiment and analysis.

Polybrominated diphenyl ethers (PBDEs) determination: PBDEs in sediment samples were extracted and determined. Twenty grams of sediment samples (wet weight) were extracted with 20 mL of *n*-hexane under shaken for 3 hrs. After three times of extraction, the extracts were combined and concentrated, the samples were further purified by performance with silica gel column[3], and the effluents were analyzed by GC-MSD.

GC-MSD analysis: A GC-MSD (HP 6890 series GC system, Hewlett Packard Co., USA) equipped with a DB-XLB fused silica capillary column (30 m x 0.25 mm I.D. x 0.1 μm) was used to identify the PBDEs. Helium was used as the carrier gas with a flow rate of 38 cm/sec, splitless. The programmatic column temperature program was set at 100℃ for 1 minute, then increased to 340℃ by 16℃/min and held for 5 minutes. The mass selective detector was HP 5973 MSD. The mass fragments were monitored by selected ion monitoring (SIM). The following ions was used for quantification, m/e 325.8 and 485.6 for group 1 (4 Br) from 6 to 12 minutes, m/e 403.6 and 405.6 for group 2 (5 Br) from 12 to 14 minutes, and m/e 481.5 and 483.5 for group 3 (6 Br) after 14 minutes. The best m/z value for SIM mode to monitor was found out by using the scan mode with 5 μg/mL standard PBDEs.



A B

Figure 1. Sampling sites, located at San-yr-kong river entrance (site 2) in Er-Jen river basin of southern part of Taiwan (A) and Nan-Kan river basin of northern part of Taiwan (B).

Results and Discussion

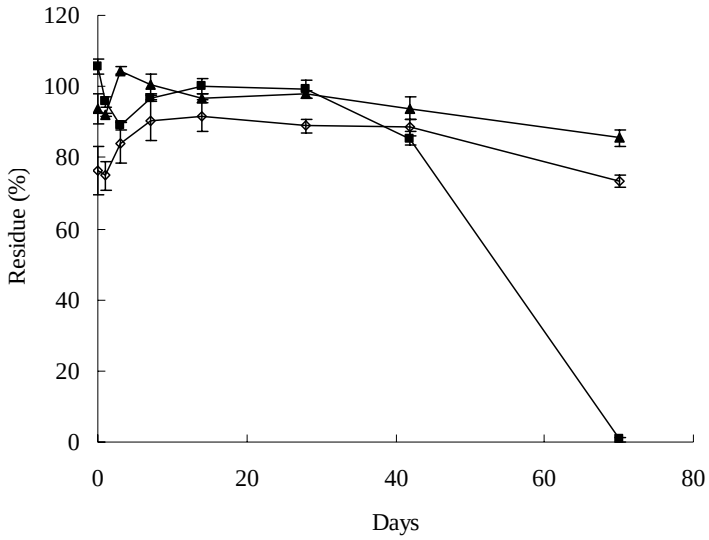
Methods for the chemical analyses of several BDE congeners including BDE 17, 28, 47, 49, 66, 85, 99, 100, 153, 154, 183 and 209 in sewage sludge and wastewater has been developed and validated use by the Department of Environmental Chemistry and Microbiology, National Environmental Research Institute, Denmark[5]. According to the report, the BDEs concentration is in an order BDE 47 = BDE 99 > 209 >100 > 153 and BDE 77 was not detected in all the sampling site[6].

In this study, 0.1μg/mL of BDE 47, 99 and 100 were spiked to the sediments collected from Er-jen and Nan-kan river basins and incubation for 70 days at room temperature under darkness. Sampling at the schedule intervals, the residues of BDE 47, 99 and 100 in the medium were determined by GC-MSD.

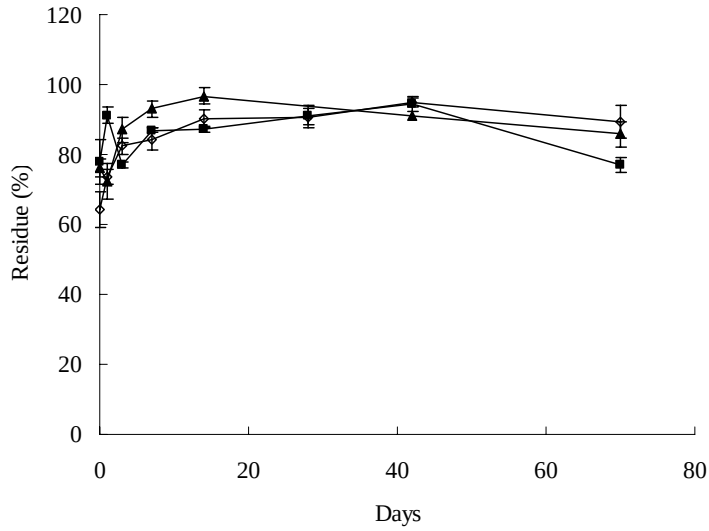
BDE-47 (2,2',4,4'-Tetrabromodiphenyl ether) was not degraded in sterilized sediment, Nan-Ken river sediment and San-yr-kong river in the formal 40 days incubation, but degraded suddenly in sediment of Nan-ken river after 70 days incubation.

BDE-99 (2,2',4,4',5-Penta- bromodiphenyl ether) and BDE-100 was not degraded in three sediments, even after 70 days incubation. More than 80% of BDE-99 and BDE-100 were still remained in all three sediments.

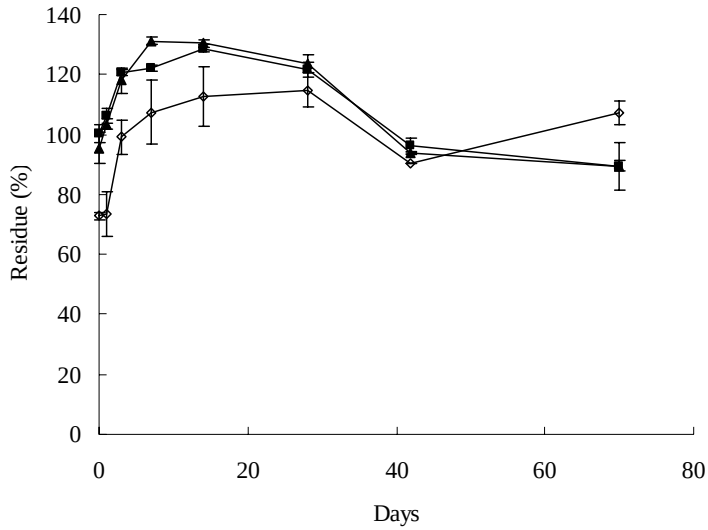
Using DGGE (denaturing gradient gel electrophoresis) method to check the change of bacterial community structure during the incubation period were the further research,. The relationship between the degradation of BDEs and the change of bacterial community in the sediment will be investigated.


120
100
80
60
40
20
0
Residue (%)
0
20
40
60
80
Days

(A)


120
100
80
60
40
20
0
Residue (%)
0
20
40
60
80
Days

(B)



(C)

Figure 2. Degradation rate of BDE-47(A), BDE-99(B), and BDE-100(C) in sterilized sediment(-◇-), Nan-kan river sediment(-■-) and San-yr-kong river sediment(-▲-)

Acknowledgements
The authors thank the National Science Council of the Republic of China for financial support.

References

1. Bünz V, Patricia V.B. and Schmidt S. (1997) *Biotechnol. Adv*. 15: 621-632.
2. Hyötyläinen T. and Hartonen K. (2002) *Trends of analy. Chem.* 21: 13-29.
3. Choi J.-W., Onodera J., Kitamura K., Hashimoto S., Ito H., Suzuki N., Sakai S. and Morita M. (2003) *Chemosphere* 53: 637-643.
4. de Boer J. and Cofino W.P. (2002) *Chemosphere* 46: 625-633.
5. Christensen J.H., Groth B.S., Vikelsoe J. and Vorkamp K. (2003) Polybrominated diphenyl ethers (PBDEs) in sewage sludge and wastewater, method development and validation, NERI Technical Report, No. 481, National Environmental Research Institute, Ministry of the Environment, Denmark.
6. Kokc T.M., MacPherson K.A., Reiner E.J. and Ho T. (2003) 23th Internation Symposium on Halogenated Environmental Organic Pollutants & POPs, Boston, USA; 61: 175-178.