# CONGENER-SPECIFIC DATA OF PBDEs IN PINE NEEDLES

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## Introduction

Polybrominated diphenyl ethers (PBDEs) are from many years used as one of the most popular group of brominated flame retardants which are added to a variety of goods and especially those based on plastic polymer materials. DecaBDE is the primarily formulation used amongst of PBDEs while less are pentaBDE and octaBDE, which both are banned in Europe since 2004[1-3]. PBDEs in general properties and environmental fate well resemble chlorinated and brominated naphthalenes/biphenyls (PCNs, PBNs, PCBs, PBBs) and seems to possess a similar threat due to bioaccumulation and toxicity. Recently several investigations have done to make clear environmental residue of PBDEs and some of brominated dibenzo-*p*-dioxins (PBDDs) and furans (PBDFs). However most of these analysis subjected in environmental matrix is sediment and biota those show relatively high concentration residues. There is no reliable report of PBDEs/PBDDs/PBDFs in ambient air because of un-clarified resident time related to the relatively easy degradation by photo catalysis in air. It is urgent issue to develop a reliable indicator of air pollution by these chemicals.

In this communication we are presented early data of the analytical method developed enabling simultaneous separation of several PBDE and PBDD/DF congeners as well as good applicability on pine needles as passive indicator of source emission related troposphere pollution with PBDEs in Tokyo Bay area in Japan.

## Materials and methods

The pine needle samples were collected during March 1999 around the Tokyo Bay (Fig. 1). Before being lyophilized and spiked with internal standard materials consisting of $^{13}$C-labeled PBDEs and PBDDs/DFs, the needle samples were homogenized using dichloromethane (DCM). The homogenate was transfered to a soxhlet and, at first, extract with DCM for 7h. Then extraction was continued with toluene for another 7 h. Chlorophyll was removed by using a layer of silica gel followed by further clean up by a multi-layer of silica gel column. Then fractionation was performed by an activated basic alumina column chromatography followed by a 2D HPLC system equipped with Hypercarb and PYE columns, respectively. Details of the sampling campaign and analytical methods using 2D HPLC fractionation and final quantification using HRGC/HRMS and GC-ECD are given elsewhere.[4-

[6] PBDEs (#47, 77, 99, 100, 105, 126, 153, 183, 190, 209, EO-5003, -5100) and PBDDs/DFs (EDF-4153, EDF-4154, EDF-5059; CIL) standard solutions were used for quantitative measure.

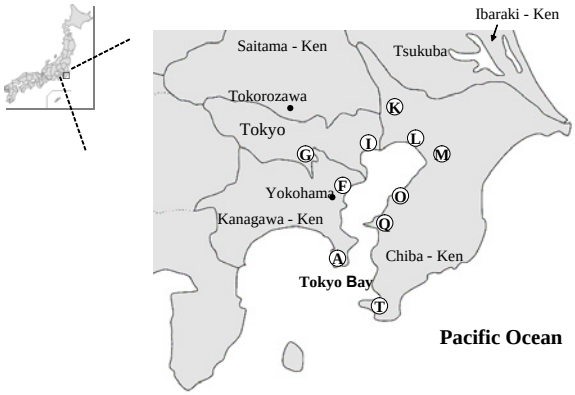


Figure 1. Sampling locations around the Tokyo Bay, Japan.

**Results and Discussion**

PBDEs were found at varying concentration and reflecting impact of potential local emission sources in pine needles from all ten sites around the Tokyo Bay. A relatively higher contamination was recorded at the inner sites (site I), while six times lowest at the control site T, which is located at the top of the Bousou Peninsula (Table 1). Among detected PBDE isomers, #209 constituted more than 90% and it fit the large usage of deca-brominated DE in Japan. Total concentration of PBDE in site I that is relatively contaminated location was 2.4 ng/g and it is four to 1800 times lower than the residue level in sediment in Japan. [7]

A detailed data on composition of tetraBDEs, pentaBDEs, hexaBDEs, heptaBDEs and decaBDE identified in pine needles and fly ash from the MSWI as possible PBDEs source to the ambient atmosphere in the region as well as analytical standard used are presented at Fig. 2 and 3.

Although composition of PBDE in decabrominated preparation used in Japan was known as 3% of hepta-BDE and 97% of deca-BDE, significant amount of terta and penta congeners were detected in pine needle. Such a high percentage of low brominated isomers was not measured in sediment and biological samples in Japan and firstly reported in pine needle. This PBDE composition may suggest pine needle is suitable indicator of air pollution by not only PCB/PCDD but also brominated frame retardants. Further investigation about resident time on pine needle and possible degradation, accumulation, partition among gas phase, particulate and surface of pine needle are necessary to understand the kinetics of PBDEs in environment.

**Acknowledgement**

The authors are grateful to Dr. K Kannan (Wadsworth Center, New York State Department of Health) for gift of PBDE standards and useful technical expertise. This work was supported in part by a Grant-in-aid (Hazardous Chemicals) from the Ministry of Agriculture, Forestry, and Fisheries of Japan (HC-04-2262-04).

**References**

1. R.C. Hale, M.J. La Guardia, E. Harvey, T.M. Mainor, *Chemosphere*, **46**, 729-735 (2002)
2. J. de Boer, P.G. Wester, A. van der Horst, P.E.G. Leonards, Environmental Pollution, **122**, 63-74 (2003)
3. C.A. de Wit, *Chemosphere*, **46**, 583-624 (2002)
4. N. Hanari, Y. Horii, S. Taniyasu, N. Yamashita, J. Falandysz, I. Bochentin, A. Orlikowska, T. Puzyn, *Pol. J. Environ. Stud*., **13**, 139-151 (2004)
5. N. Hanari, Y. Horii, S. Taniyasu, N. Yamashita, J. Falandysz, I. Bochentin, A. Orlikowska, T. Puzyn, *J. Environ. Monit*., **6**, 305-312 (2004)
6. Y. Horii, J. Falandysz, N. Hanari, P. Rostkowski, T. Puzyn, M. Okada, K. Amano, T. Naya, S. Taniyasu, N. Yamashita, *J. Environ. Sci. Health*, **39A**, 583-605 (2004)
7. CHEMICALS IN THE ENVIRONMENT, Ministry of the Environment, Japan (2003)

Table 1. Concentration (pg/g, wet wt.) of PBDE isomers in pine needle.

| IUPAC no. of PBDE isomers | Site I | Site T |
|---|---|---|
| #47 | 91 | 12 |
| #77 | 2.1 | 0.4 |
| #100 | 7.5 | 1.3 |
| #99 | 42 | 6.5 |
| #126 | <0.33 | <0.33 |
| #105 | 0.7 | <0.33 |
| #153 | 2.0 | 1.3 |
| #183 | 17 | <1.2 |
| #190 | <1.2 | <1.2 |
| #209 | 2265 | 367 |
| Total concentration | 2427 | 388 |

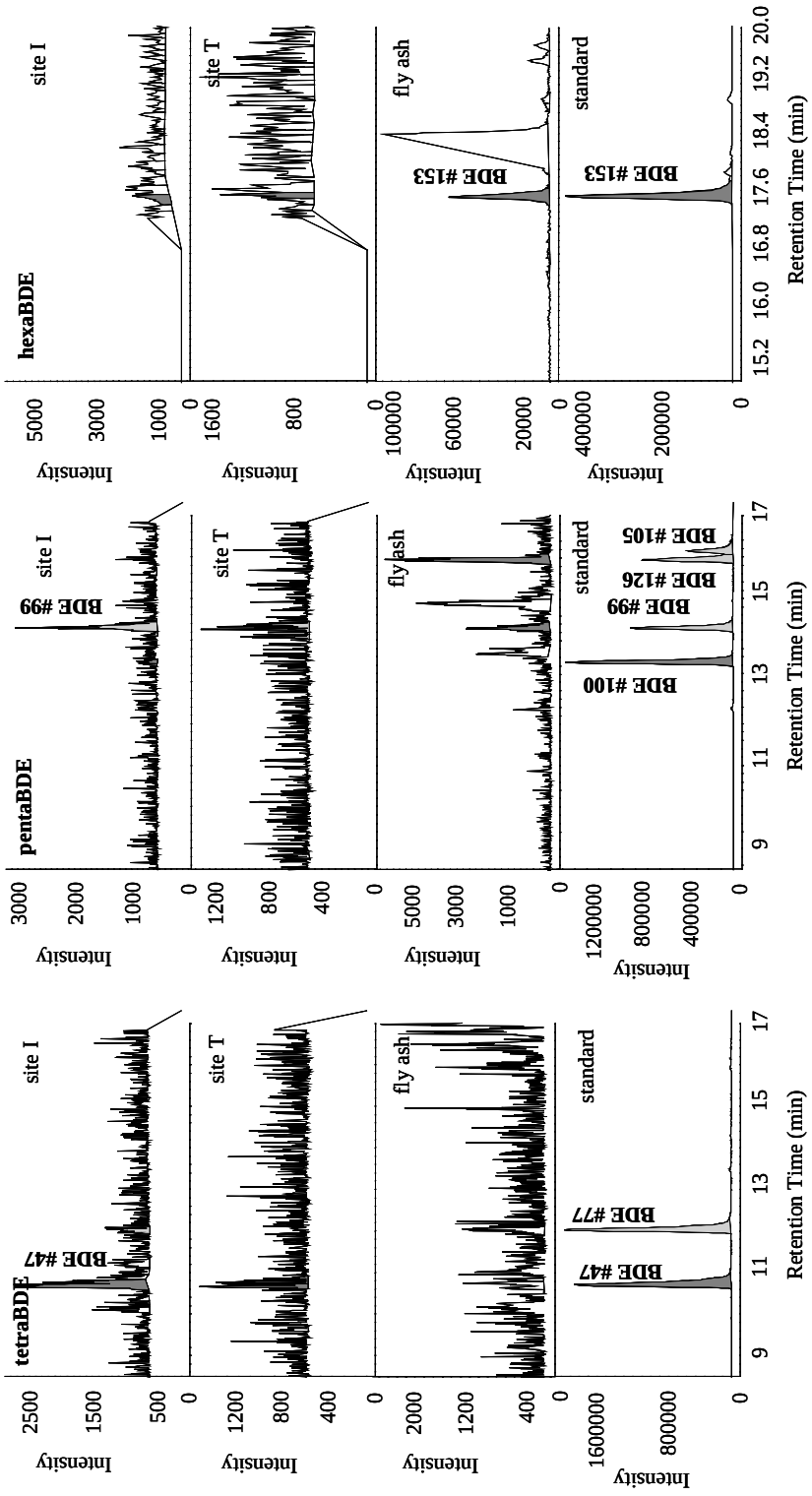


Fig. 2. HRGC/HRMS chromatograms of tetra- to hexa-BDEs in matrices examined (DB-5).

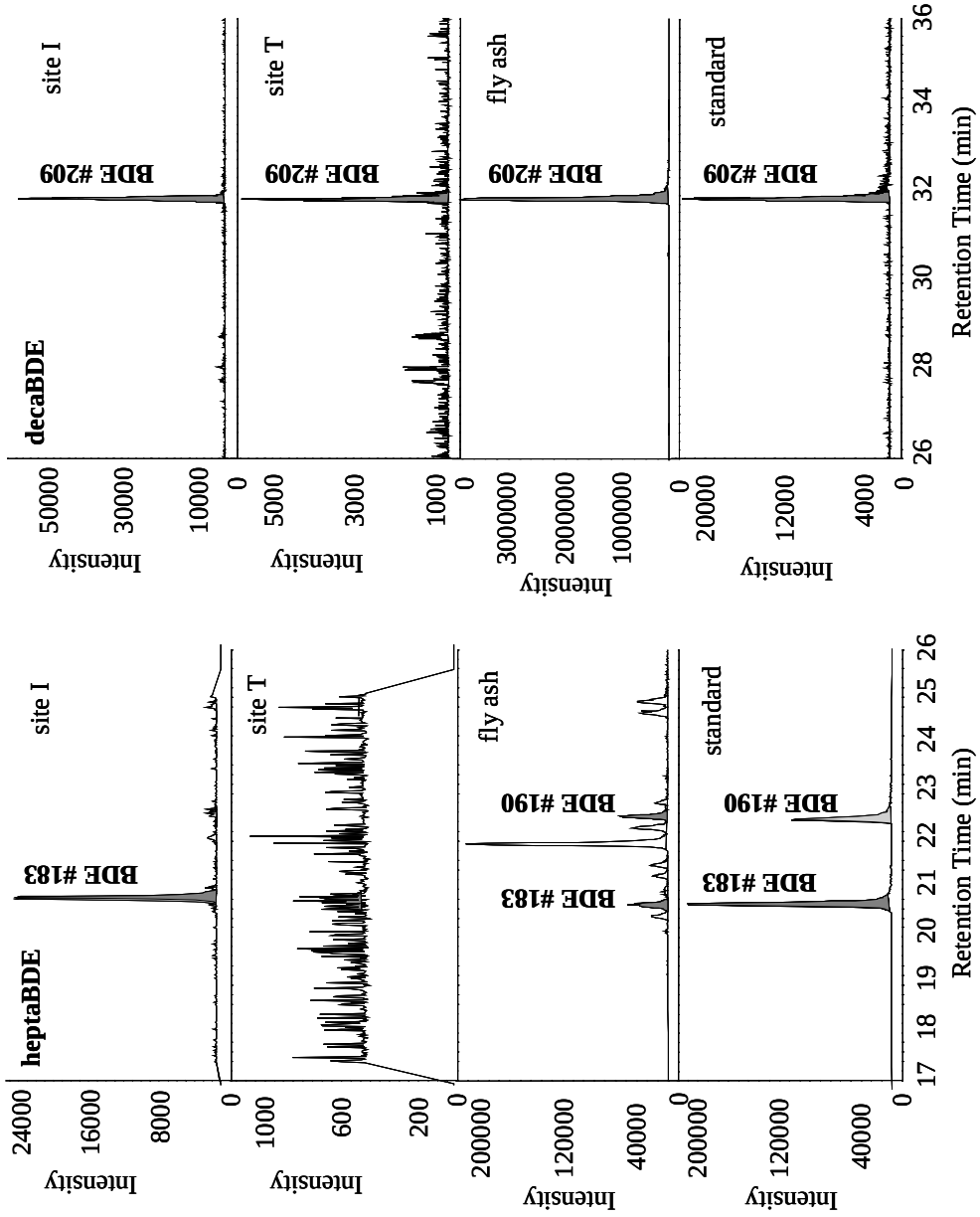


Fig. 3. HRGC/HRMS chromatograms of hepta- and deca-BDEs in matrices examined (DB-5).