DISTRIBUTIONS OF POLYBROMINATED DIPHENYL ETHERS IN OFFICES

Lee S-J[1], Lee J-M[1], Ale D[1], Choi S-D[2], Chang Y-S[1]
[1]School of Environmental Science & Engineering, POSTECH, San 31, Hyoja-dong, Namgu, Pohang, 790-784, Korea; [2]Department of Physical Environmental Sciences, University of Toronto at Scarborough, 1265 Military Trail, Toronto, Ontario, Canada, M1C 1A4

Abstract
Three offices in a building were investigated for PBDE contamination using a high volume air sampler and XAD-2 resin based passive air sampler (PAS). Two air sampling methods showed consistent results each other, proving this PAS can be a substitute for the conventional active air sampler. Concentrations of indoor PBDEs from our study were found relatively high, which was associated with the items in offices and human activities. Furthermore, volatilization of PBDEs in indoor environment was considered as an important source of human health risk.

Introduction
As flame retardants, polybrominated diphenyl ethers (PBDEs) are used in a variety of electrical component, commercial and household appliances[1]. PBDEs are produced 40×10^6 kg globally, which have a high potential to leach out of the polymers. In recent years, their environmental fate and human exposure to PBDEs have become a serious concern[1]. Many reports show that our contemporaries are living under the highly contaminated environments by PBDEs[2,3]. The indoor air is relatively halted with little or no difference in temperature throughout a year, where people spend their time about 80% of the day. As the modern life styles and important non-dietary exposure of inhalation, the contamination of indoor air may play an important role in human health risk[4]. Therefore, we conducted indoor monitoring of PBDEs in offices with active and passive air samplers (AAS and PAS).

Materials and Methods
A high volume air sampler (HVS) and XAD-2 resin based PAS developed by Wania et al.[5] were used for indoor air sampling. HVS was operated to collect both gaseous and particulate PBDEs by three sampling campaigns, while XAD-2 resin based PAS were deployed during 10 months (Table 1). To compare the distributions of PBDEs indoors, HVS was also operated outdoors. Office A ($66m^2$) was a documentary storeroom. Office B ($24.8m^2$), contained five computers, desks and office machines (two printers, book shelves and a table) for five persons. This office was congested and all machines were switched on everyday. Office C ($98m^2$) was a seminar venue and class room, where many people came in and out often. This seminar room had desks and chairs for 50 people and curtains along the windows.

Glass fibre filters and polyurethane foams collected by HVS and XAD-2 resin of PAS were subjected to gel permeation, silica gel and alumina chromatography after the Soxhlet extraction. Samples were analyzed by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The capillary column used was a DB5-MS (30 m, 0.25 mm i.d., 0.1 μm film thickness) for the separation of mono- to hepta-BDE congeners[6].

Results and Discussion
Variations of PBDEs in indoor and outdoor air using a high volume air sampler
The contents of particulate matter (PM) by HVS were 6.7-fold higher in outdoor air than indoor air (20.03 ± 10.99 μg/m^3), while the concentrations of PBDEs outdoors (10.33 and 43.53 pg/m^3 in background and urban site, respectively) were much lower than indoors (0.095 – 648 ng/m^3). Outdoor air had urban-rural gradient of PBDE levels. PBDE levels derived by PAS were 41.6, 87.0 and 204935 ng/PAS for office A, B and C, respectively. The PBDE levels collected by PAS and AAS correlated well. Office C having the highest levels of PBDEs, was the largest office with many desks and chairs. Office B had the middle levels despite being the smallest room with many PBDE sources. Lastly, Office A, room with the lowest levels, had many books and electrical items not used. Global monitoring of PBDEs estimated by PAS revealed up to 24 pg/m^3 in worldwide background sites[7] and 340 pg/m^3 in China, 5.0-71 pg/m^3 in Japan and 2.0-27 pg/m^3 in South Korea[8]. The concentrations of PBDEs in three offices had some variations although they were in the same building; office C was observed the highest

PBDE levels, up to 2-3 orders higher than others. Shoeib et al.[9] monitored PBDEs in laboratory, house and outdoor using a high volume air sampler. They observed the mean indoor air concentrations for PBDEs to be 1518 pg/m^3 for house and 358-410 pg/m^3 for the laboratories. Homes and workplaces in UK[10] were detected PBDE levels with 1620 and 2300 pg/m^3. This implies that the indoor ventilation of contaminants is an important source of the external air of the building[9].

As shown in Table 1, large differences of PBDEs were found among offices and between sampling campaigns. The PBDE levels during second sampling periods were two, 39 and four times higher than those during first collecting in each office. Harrad et al.[4] also found the rooms in the same building had also large variations of PBDEs; the positive correlations were observed between PBDE levels and the number of electrical appliances and polyurethane foam-containing chairs. Particularly, Hazrati and Harrad[11] observed after the replacement of old computers, a sharp decrease in PBDE levels into around 60%. In our study, office B and C were changed with the new desks, a copier, and new projector system before the second sampling. Comparatively, insignficiant differences were found in PBDE levels in office A where the condition was not changed over the sampling periods.

Table 1. Air samples collected in indoor and outdoor air by HVS and PAS.

Location	Explanation		Sampling date	Temp. (ºC)	Air volume (m^3)	Particulate matter (μg/m^3)	ΣPBDEs (pg/m^3 for HVS, ng/PAS for PAS)
Outdoor	Background	O1	25-26 Apr. 2006	13.6	1008.0	77.18	10.3
	Urban	O2	25-26 Apr. 2006	13.6	946.1	189.73	43.1
Office A	66 m^2 Department Library	IA1	5-7 Oct. 2005	21.0	1425.0	15.72	95.3
		IA2	14-16 Jul. 2006	28.0	1489.0	7.45	176.4
		IA3	12-14 Dec. 2006	17	1578.5	20.35	266.7
		IAP	Dec. 2004 - Oct. 2005				41.6
Office B	24.5 m^2 Office for 5 persons	IB1	7-9 Oct. 2005	20.0	1782.2	11.61	223.5
		IB2	6-8 Oct. 2006	21.0	1584.0	23.80	8790.9
		IB3	22-23 Dec. 2006	19	884.5	44.09	1651.9
		IBP	Dec. 2004 - Oct. 2005				87.0
Office C	98 m^2 Seminar venue	IC1	7-9 Oct. 2005	23.0	1526.0	18.87	147923.2
		IC2	13-15 Aug. 2006	28.0	1500.0	18.33	648437.5
		ICP	Dec. 2004 - Oct. 2005				204935.0

PBDE profiles in indoor air obtained by HVS and PAS

Atmospheric PBDE profiles derived by PAS and HVS had high correlation (r = 0.983) at 99% of the confident level. PBDEs by PAS correlated well with gaseous PBDEs (r = 0.981). This implies that this passive air sampler is a semi-quantitative sampler of HVS designed to sample gas phase contaminants. Fig. 1 shows the PBDE profiles obtained from this study and commercial PBDE mixtures. BDE-47 was the predominant isomer in both HVS and PAS. BDE-47 and -99 contributed 66% and 19% in PAS and gaseous samples by HVS, respectively. Meanwhile, BDE-47 and -99 attributed about 40% and 36%, respectively in particle phase. Proportions of high chlorinated-BDEs increased in particulate phase, but almost no detectable BDE-183 was observed in others. Possible pathways of release may include volatilization[12] or formation of dusts[13] from the PBDE treated products. When comparing the PBDE profiles between our samples and commercial mixtures, the profiles of penta-BDE

commercial products (70-5DE and DE-71) were similar to those of particulate PBDEs. Volatilization from sources indoors seems to be the main mechanism accounting for the occurrence of PBDEs in indoor air. Wilford et al.[12] also found PBDEs in houses to be directly affected by volatilization.

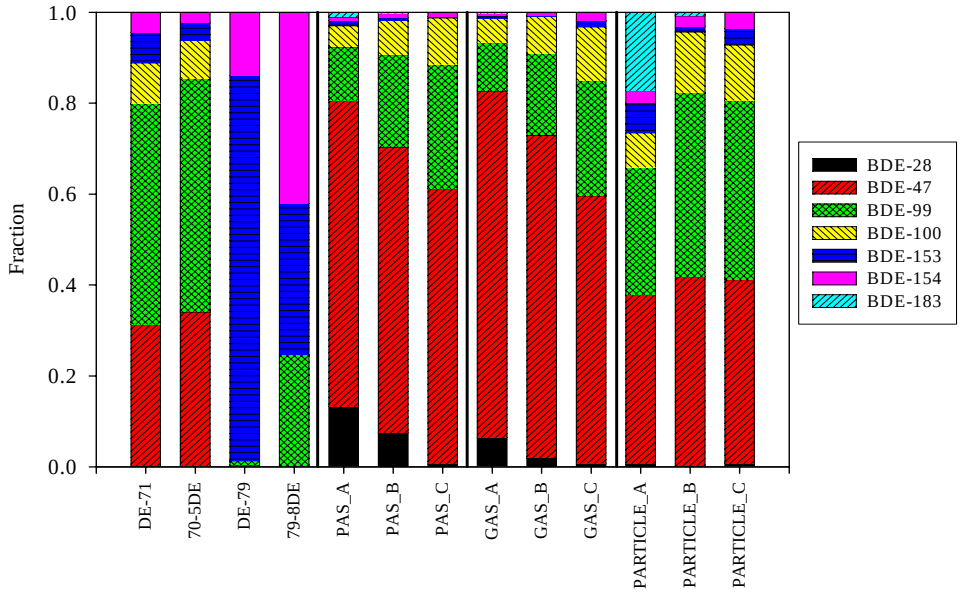

Figure 1. PBDE congener profiles in samples collected and PBDE commercial mixtures.

Gas/particle partitioning of PBDEs

To check the distribution of atmospheric PBDEs between gas and particle phases, gas/particle partitioning of HVS samples were investigated. Sub-cooled liquid pressure (P_L^0) were calculated based on melting points of PBDE congeners[14] and equations[15]. The slopes of plots between P_L^0 and partitioning coefficient (K_P) reach to -1 when gas/particle partitioning goes to equilibrium conditions[16,17]. The slopes of indoor samples ranged -0.61 and -0.14, implying PBDEs were entering into the air continuously from the sources. Fig. 2 represents the comparison of particle-bound PBDEs measured against predicted ones by Junge- Panknow adsorption model[16,17]. Similarly with the data of regression, we could observe the relatively low particle fractions of PBDEs in offices. Meanwhile, outdoor samples were closer to Junge-Pankow model than indoor samples. As explained above, gaseous PBDEs released from many products indoors play an important role in the pollution of indoor air.

Monitoring of indoor contamination by PBDEs is arising as a significant issue for human risk assessment by the contaminated air. We could confirm that the indoor air can act as a source emitting PBDEs to the outside environment. As modern life style with diverse electric devices and polymers, daily intake by inhalation of indoor air should not be neglect to understand the magnitude of exposure to PBDEs. Furthermore, using PAS long-term monitoring was possible to get reliable data. In view of our observations, comprehensive indoor monitoring will give us valuable information to elucidate to assess health risk of the moderns.

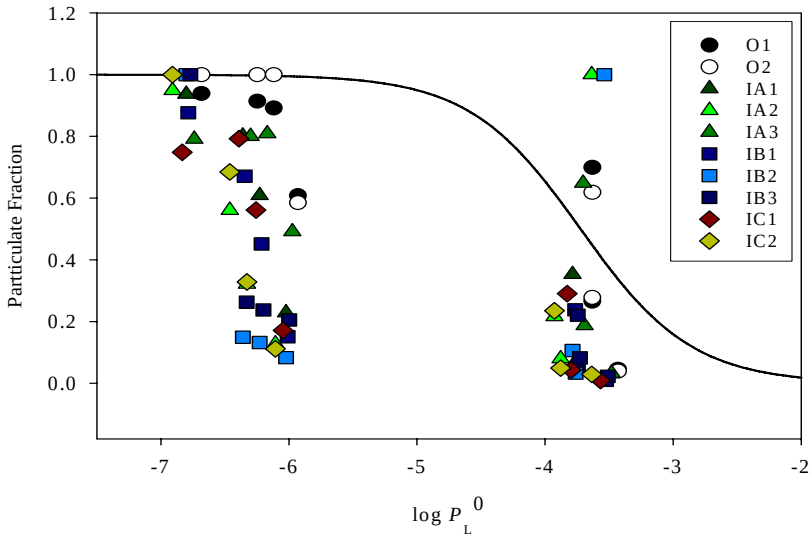

Figure 2. Comparison of the measured particulate fractions of PBDEs with theoretical predictions by the Junge-Pankow model.

Acknowledgements
This study was financially supported by the Brain Korea 21 project and by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-213- C00030).

References

1. Alaee M; Arias P; Sjödin A; Bergman Å. *Environ Int* 2003; 29:683.
2. Meironyté D; Norén K; Bergman Å. *J Toxicol Environ Health Perspect* 1999; 58:329.
3. Lee S-J; Ikonomou MG; Park H; Baek S-Y; Chang Y-S. *Chemosphere* 2007; 67:489.
4. Harrad S, Wijesekera R; Hunter S; Halliwell C; Baker R. *Environ Sci Technol* 2004; 38:2345.
5. Wania F; Shen L; Lei YD, Teixeira C, Muir DCG. *Environ Sci Technol* 2003; 37:1352.
6. Ikonomou MG; Fraser TL; Crewe NF; Fischer MB; Rogers IH; He T; Sather PJ; Lamb RF. *Can Data Rep Fish Aquat Sci* 2001; 2389:1.
7. Pozo K; Harner T; Wania F; Muir DCG; Jones KC; Barrie LA. *Environ Sci Technol* 2006; 40:4867.
8. Jaward FM; Zhang G; Nam JJ; Sweetman AJ; Obbard JP; Kobara Y; Jones KC. *Environ Sci Technol* 2005; 39:8638.
9. Shoeib M; Harner T; Ikonomou M; Kannan K. *Environ Sci Technol* 2004; 38:1313.
10. Wijesekera R; Halliwell C; Hunter S; Harrad S. *Organohalogen Compd* 2002; 55:239.
11. Hazrati S; Harrad S. *Environ Sci Technol* 2006; 40:7584.
12. Wilford BH; Harner T; Zhu J; Shoeib M; Jones KC. *Environ Sci Technol* 2004; 38:5312.
13. Hale RC; La Guardia MJ; Harvey E; Mainor TM. *Chemosphere* 2002; 46:729.
14. Tittlemier S; Halldorson T; Stern G.; Tomy, G.T. *Environ Toxicol Chem* 2002; 21:1804.
15. Oh J-E; Choi J-S; Chang Y-S. *Atmos Environ* 2001; 35:4125.
16. Junge CE. In: *Fate of pollutants in the air and water environment*. Wiley-Interscience, New York, 1977.
17. Pankow JF. *Atmos Environ* 1987; 22:2275.