

## ASSESSMENT OF THE SPATIAL DISTRIBUTION OF POLYBROMINATED DIPHENYL ETHERS IN AN INDUSTRIAL REGION USING PASSIVE AIR SAMPLERS

Baek S-Y<sup>1</sup>, Choi S-D<sup>2</sup>, Ale D<sup>1</sup>, Chang Y-S<sup>1</sup>

<sup>1</sup>School of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), San 31, Hyoja-dong, Nam-gu, Pohang, 790-784, Republic of Korea; <sup>2</sup>Department of Physical and Environmental Sciences, University of Toronto at Scarborough, 1265 Military Trail, Toronto, Ontario, Canada, M1C 1A4

### Abstract

Passive air sampling for polybrominated diphenyl ethers (PBDEs) was conducted in a heavily industrialized region in South Korea for six months (January 2006–July 2006). The levels and spatial distribution of selected PBDEs were investigated to identify a potential source in the study area using polyurethane (PUF) disk passive air samplers. They were deployed in the steel complex, residential area near the steel complex, rural area, and petrochemical complex. The level of PBDEs was found to be the highest in the steel complex, followed by the petrochemical complex. Although there has been no report that these industries are the major source of PBDEs, our results suggest that they are likely to be an important source of PBDEs in the study area.

### Introduction

Polybrominated diphenyl ethers (PBDEs) have been used as flame retardants in various products such as furniture, textiles, and electronic equipments. At present, PBDEs are a candidate for persistent organic pollutants (POPs) under the Stockholm convention, because they are persistent in the environment, undergo long-range transport (LRAT), and exist in the multimedia environments. Although PBDEs are ubiquitous chemicals, it is rather difficult to investigate the source/receptor relationship using traditional monitoring methods. Recently, passive air samplers (PAS) have been developed in order to assess the level and distribution of POPs in the atmosphere.<sup>1</sup> The PAS are a simple and useful tool to elucidate concentrations of POPs in various sites from local to global scale.

In this study, we conducted a passive air sampling study in a highly industrialized region of South Korea. In order to assess the distribution of PBDEs and to identify a source of PBDEs, PAS were deployed at 16 sites for 6 months.

### Materials and Methods

#### *Sampling*

The sampling area is located in the south coast of South Korea and a heavily industrialized region with the steel and petrochemical complexes. Polyurethane foam (PUF) disk PAS were deployed at 16 sites twice for three months: Period 1: January–April 2006 (winter-spring), Period 2: April–July 2006 (spring-summer). The sampling sites are divided into 4 groups (steel complex, residential area near the steel complex, rural area, and petrochemical complex). More details on the PUF disk PAS can be found in the previous publications.<sup>1,2</sup>

#### *Extraction and Cleanup*

PUF disks were pre-cleaned by Soxhlet-extraction for 24 h once with acetone and twice with dichloromethane (DCM). After sample collection, the PUF disks were stored in solvent-rinsed 500 mL amber bottles having Teflon-lined lids and at -4°C condition. The PUF disks were Soxhlet-extracted for 24 h with 250 mL of DCM. Cleanup was performed with concentrated sulfuric acid treatment and multi-layer silica column (from top to bottom: Sodium sulfate, silica-sulfuric acid, silica, silica-sodium hydroxide, silica, sodium sulfate) to separate PBDEs. The column was conditioned with Hexane and DCM (1:1 v/v). Samples were eluted with 70 mL of Hexane and DCM (1:1 v/v) and evaporated with a rotary evaporator (R124-A, Buchi) to 0.5 mL and transferred to a GC vial. Finally, the samples were totally evaporated by N<sub>2</sub> purging. <sup>13</sup>C-BDE-28, -47, -99, -100, -153, -154, -183 were used as internal standard and <sup>13</sup>C-BDE-77, -138 were used as recovery standards.

*Instrumental Analysis*

PBDEs were determined using a Hewlett-Packard 6890 gas chromatograph (GC) equipped with a Jeol 700T high resolution mass spectrometer (HRMS). A DB-5HT column (J&W Scientific, 30 m, 0.25 mm, 0.1  $\mu\text{m}$  thickness) was used. The GC oven program was as follows: 110°C initial for 3 min, and then increased at 40°C min<sup>-1</sup> to an isothermal hold at 200°C for 5 min, and then increased at 10°C min<sup>-1</sup> to an isothermal hold at 330°C for 5 min. 1  $\mu\text{L}$  was injected at a temperature of 280°C, and the MS was operated under positive EI conditions (38 eV). Data were obtained in the selected ion monitoring (SIM) mode.

**Results and Discussion**

The total amounts of PBDEs varied from 9.49 to 98.2  $\text{pg day}^{-1} \text{PAS}^{-1}$  with an average of 25.41  $\text{pg day}^{-1} \text{PAS}^{-1}$  during the period 1 and from 13.52 to 61.83  $\text{pg day}^{-1} \text{PAS}^{-1}$  with an average of 28.30  $\text{pg day}^{-1} \text{PAS}^{-1}$  during the period 2 (Table 1). The highest concentrations were found in the steel complex, but there were considerable differences of PBDE amounts between the sampling sites in the steel complex. It might be dependent with distance from a PBDE source and the major wind direction. This result suggests that the selection of sampling site is important.

Table 1. Amounts ( $\text{pg day}^{-1} \text{PAS}^{-1}$ ) of PBDEs for the steel complex, residential, rural area, and petrochemical complex for the sampling period

Compound	Steel complex (n=8)	Residential (n=3)	Rural (n=3)	Petrochemical (n=2)
First sampling ( January 12, 2006 – April 14, 2006)				
BDE 28	1.48–2.83	1.45–1.82	1.26–1.76	2.73–6.62
BDE 47	5.23–23.71	4.80–7.98	4.18–5.67	8.36–8.79
BDE 66	<dl–1.67	0.45–0.65	0.44–0.48	1.32–1.41
BDE 85	<dl–1.55	<dl–0.29	<dl	<dl
BDE 99	3.60–38.37	2.50–6.09	1.61–2.24	3.57–4.92
BDE 100	1.16–7.02	0.64–1.34	0.60–0.97	1.11–1.53
BDE 153	0.22–6.57	0.25–0.64	0.15–0.24	0.45–0.49
BDE 154	0.39–3.79	0.32–0.53	0.26–0.53	0.71–0.80
BDE 183	0.50–13.16	0.78–1.29	0.58–1.25	8.80–8.84
$\Sigma_9$ PBDE	13.01–98.20	12.41–20.26	9.49–12.42	27.51–32.94
Second sampling (April 14, 2006 – July 21, 2006)				
BDE 28	0.81–3.59	1.54–2.50	0.66–1.29	1.49–15.34
BDE 47	8.29–30.32	11.21–19.32	7.16–9.89	11.63–26.38
BDE 66	0.51–2.10	0.89–1.01	<dl–1.03	0.94–1.90
BDE 85	<dl–0.64	<dl–0.05	<dl–0.40	<dl–0.26
BDE 99	3.41–16.38	3.62–12.46	3.69–6.22	5.38–9.51
BDE 100	1.12–4.32	1.04–3.62	1.20–1.46	1.48–3.20
BDE 153	0.19–1.78	0.22–1.16	0.16–0.95	0.64–1.00
BDE 154	0.41–1.13	0.37–1.05	0.37–0.72	0.52–1.05
BDE 183	0.21–2.05	<dl–0.71	<dl–1.59	1.35–1.89
$\Sigma_9$ PBDE	15.95–61.83	19.69–41.51	13.52–23.54	23.42–60.53

Amounts of PBDEs increased 1.4–1.9 times almost sites except for the steel complex. BDE-47 was the most dominant congener, followed by BDE-99. Percentage of BDE-47 increased from 34% to 49% with changing periods. However, total amounts of PBDEs were the relatively same between the periods, and there was no statistically significant difference in concentrations between the periods ( $p > 0.05$ ).

Figure 1(a) shows a gradient of PBDEs between the sites. The amounts of PBDEs decreased in the following order: steel complex > petrochemical complex > residential area > rural area (1st sampling), petrochemical complex > residential area  $\approx$  steel complex > rural area (2nd sampling). Although many previous studies suggest that urban areas act as a source of PBDEs,<sup>3</sup> there are few studies related to steel and chemical industries. Our study suggests that the steel and chemical industries are likely to be an important source of PBDEs, but a more thorough investigation is required to support this observation.

The residential area near the steel complex has the medium level of PBDEs. While the level of PBDEs decreased in the steel complex during the second period, the level of PBDEs increased in the residential area. It means that the residential area itself can also act as a source of PBDEs. The rural area having limited sources has the low level of PBDEs, suggesting that the region was not strongly affected by the industrial complex.

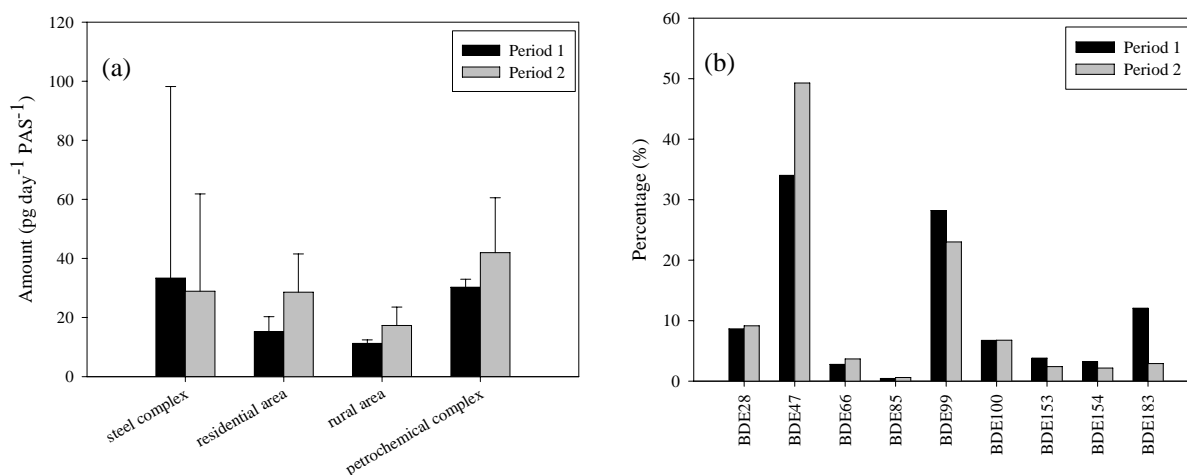


Figure 1. (a) Average amounts of PBDEs at the east of steel complex (n=8), residential (n=3), rural area (n=3), and petrochemical complex (n=2), (b) Average compositions of PBDE congeners for the entire sampling period.

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