

## BROMINATED FLAME RETARDANTS IN AIR OF CHINA

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### Introduction

Brominated flame retardants (BFRs), including Polybrominated diphenyl ethers (PBDEs) and new non-BDE flame retardant (NBFRs), have been widely used in electronic devices, furniture, construction materials and other products to prevent the spread of fire<sup>[1]</sup>. In China, 10<sup>4</sup> tons of BFRs were produced in the year of 2000, and the demand for BFRs were increasing every year at the rate of 8%<sup>[2]</sup>. It was estimated that nearly 80% of the world's e-waste was exported to Asian countries especially China, which became other current sources of BFRs in China<sup>[3]</sup>.

Two commercial products of PBDEs have been banned by the Stockholm Convention on Persistent Organic Pollutants for global elimination. Deca-BDE, another commercial product of PBDEs, has been produced since the 1980s and became one dominant BFRs product, with a production of 30 000 tons in 2005<sup>[4]</sup> and 15 000 tons in 2006<sup>[5]</sup> in China. Alternative brominated flame retardants were reported as "new" non-BDE flame retardants (NBFRs), among which petabromoethylbenzene (PBEB), pentabromotoluene (PBT), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 1,2,3,4,5-pentabromobenzene (PBBZ), 1,2,5,6,9,10-hexabromocyclododecan (HBCD) and decabromodiphenylethane (DBDPE) was detected in the samples of global atmosphere under the GAPS Network<sup>[6]</sup>. Alternative brominated flame retardants have been produced to replace PBDEs, for example, BTBPE is a replacement for the OctaBDE mixture<sup>[7]</sup>. DBDPE, another high production volume BFRs, has been reported as the replacement of DecaBDE, and reached a production of approximately 11 000 tons in 2006 in China<sup>[8]</sup>.

The polyurethane foam (PUF) disk passive air sampler (PAS) have been described previously<sup>[9]</sup>. It has been used in the monitoring of PCBs in the national scale of China<sup>[10]</sup>, PCBs and PCNs across East Asia<sup>[11]</sup>, and PCBs, PBDEs, and organochlorine pesticides across Asia<sup>[15]</sup> and Europe<sup>[12]</sup>. Passive air samplers (PASs) are a cost-effective medium to collect airborne contaminants, especially in large scale study when the electricity is unavailable.

In this study, twelve PBDEs congeners and six NBFRs were analyzed in the passive air samples collected across China in 2005. The aims of this study are to measure the pollution levels and spatial distribution of BFRs in the air of China, to discuss the difference of BFRs in urban, rural and background sites from which levels of BFRs may be subjected to the human activities, and to evaluate the correlation among BFRs in Chinese air which can reflect the common source of BFRs.

### Materials and methods

The Chinese POPs Soil and Air Monitoring Program phase I (SAMP-I) started in 2005<sup>[13]</sup>. Ninety-seven passive air samples were collected in 4 background sites, 69 rural sites, and 24 urban sites across China in 2005 for 3 months from mid-July to mid-October. The detail information regarding the sample collecting and treatment can be found in our previous study<sup>[10, 14]</sup>. Generally, after Passive air samplers (PASs) comprised of polyurethane foam (PUF) disks were deployed for 3 months, the PUF disks were retrieved, resealed in their original jars at the sampling locations, and returned to the IJRC-PTS laboratories, where they were stored in the refrigerator before extraction.

After the samples were spiked with a recovery standard containing PCB congener 155 (Accustandard, New Haven, CT), samples were Soxhlet extracted for 24 h using acetone and hexane (1:1 v/v). Extracts were cleaned using silica chromatography which consisted of 5 g silica gel. Following a pre-rinse of the column with 25 mL of dichloromethane (DCM), then 25 mL of hexane, the sample was added and eluted with 30 mL of DCM and hexane (1:1 v/v). Eluants were solvent exchanged into isooctane and concentrated to 300  $\mu$ L under gentle stream of UHP (ultra high purity) nitrogen. PBDE congeners 71 and 204 were added as internal standards.

Samples were quantified specifically using Agilent 6890A series gas chromatograph coupled to an Agilent 5975C mass spectrometer (GC/MS) with an electron capture negative ionization (ECNI) ion source. DB-5 MS (15m $\times$ 0.25mm $\times$ 0.1 $\mu$ m, J&W Scientific) column with a constant flow rate of 1.7 mL/min was used for separation

of target chemicals. Injections (2  $\mu$ L) were made in the splitless mode. The oven temperature program was as follows: held at 110  $^{\circ}$ C for 0.5 min; 5  $^{\circ}$ C/min to 220  $^{\circ}$ C; 20  $^{\circ}$ C/min to 310  $^{\circ}$ C, and then held for 9min. Target flame retardants were assessed with the following ions monitored (m/z): 79, 81 and 471.6 for PBBZ; 79, 81 and 485.6 for PBT; 484.3, 486.3 and 488.5 for BDE209; and 79 and 81 for the other brominated compounds.

Analytical procedures were undertaken using strict quality assurances and quality control measures. One method blank and spike blank were treated in every batch of 10 samples. The peaks were integrated only when the signal-to-noise ratio was higher than 3:1. The recovery of the surrogate standards was  $85.2 \pm 11.4\%$ . Low blank values of target compounds in the field blank and method blank samples, thus the result were not blank and recovery corrected.

## Results and discussion

As shown in Table 1, the sum concentrations of the total BFRs ranged from 0.10 to 1500 ng/sample in 2005 samples. The 5th-95th percentile concentrations of total PBDEs typically varied about three orders of magnitude from 0.2 to 81 ng/sample, and the PBDEs congeners also showed a wide range of concentration. The median  $\Sigma_{12}$  BDE concentration was 6.0 ng/sample, with the order of urban (15 ng/sample) > rural (5.9 ng/sample) > background/rural (0.44 ng/sample), showing a typical primary distribution pattern<sup>[18]</sup>. NBFRs also showed the same distribution pattern, with the levels of NBFRs in the urban higher than rural and background sites, which made it clear that urban region was a source of BFRs. However, the concentrations of PBDEs were generally higher than those of NBFRs, with the median concentration of  $\Sigma_{12}$ BDEs 5 times higher than those of  $\Sigma$ NBFRs, indicating a higher usage of PBDEs than NBFRs in 2005.

Table 1. Concentration of BFRs in the passive air samples (ng/sample)

	Background (n=4)		Rural (n=69)		Urban (n=24)	
	Median	5 <sup>th</sup> -95 <sup>th</sup> percentile	Median	5 <sup>th</sup> -95 <sup>th</sup> percentile	Median	5 <sup>th</sup> -95 <sup>th</sup> percentile
BDE17	BDL	BDL-0.04	0.19	BDL-1.0	0.52	BDL-0.91
BDE28	0.05	BDL-0.14	0.29	BDL-3.7	1.5	BDL-5.1
BDE47	0.15	0.09-0.26	0.53	0.09-4.2	1.7	0.11-4.6
BDE66	BDL	BDL-0.04	0.18	BDL-1.4	0.49	BDL-2.0
BDE85	BDL	BDL-BDL	BDL	BDL-0.08	BDL	BDL-0.13
BDE99	0.04	BDL-0.08	0.17	BDL-1.5	0.75	0.04-2.0
BDE100	BDL	BDL-BDL	0.05	BDL-0.23	0.10	BDL-0.46
BDE138	BDL	BDL-BDL	BDL	BDL-0.07	0.02	BDL-0.10
BDE153	BDL	BDL-0.03	0.04	BDL-0.48	0.11	BDL-0.83
BDE154	BDL	BDL-BDL	BDL	BDL-0.16	0.05	BDL-0.23
BDE183	BDL	BDL-0.12	0.08	BDL-0.25	0.13	BDL-0.56
BDE209	BDL	BDL -1.1	4.5	BDL-55	8.1	BDL-270
$\Sigma_{12}$ BDE	0.44	0.11-1.6	5.9	0.21-65	15	0.24-280
PBBZ	0.09	BDL-0.13	0.09	BDL-1.0	0.16	0.06-1.7
PBT	0.07	BDL-0.31	0.21	BDL-2.2	0.21	0.04-2.3
PBEB	BDL	BDL-0.05	0.04	BDL-0.15	0.11	BDL-0.34
HBCD	BDL	BDL-BDL	BDL	BDL-37	4.7	BDL-120
BTBPE	BDL	BDL-0.06	0.04	BDL-0.22	0.08	BDL-0.49
DBDPE	BDL	BDL-BDL	BDL	BDL-26	BDL	BDL-150
$\Sigma$ NBFRs	0.15	0.11-0.41	1.2	0.08-72	15	0.17-340

BDL: Below detection limit.

Lower level of PBDEs was detected in outdoor air at median concentrations of 3.1 ng/sample in Japan, 1.6 ng/sample in South Korea, 3.6 ng/sample in Singapore, with a peak concentration of 4.9 ng/sample in china from September to November, 2004<sup>[15]</sup>, which is higher than the median concentration of 2.3 ng/sample in this study. The median concentration of  $\Sigma$ PBDEs (without BDE209) in this study was lower than those across 22 countries

in Europe in 2002<sup>[12]</sup>. BDE209, which has been used as a substitute of PentaBDE and OctaBDE with high production volume compound, was also detected in North China with a median concentration of 4.0 ng/sample<sup>[16]</sup>, which was comparable with the median level (4.5 ng/sample) in China in 2005. Previous studies on BFRs concentrations in passive air were limited especially for NBFRs. Low concentrations of PBEB, PBBZ, PBT and BTBPE were detected in outdoor air samples in North China from early June to early October 2011<sup>[16,17]</sup>, DBDPE were also measured at relative high concentrations (median: 10 ng/sample) in North China<sup>[17]</sup>.

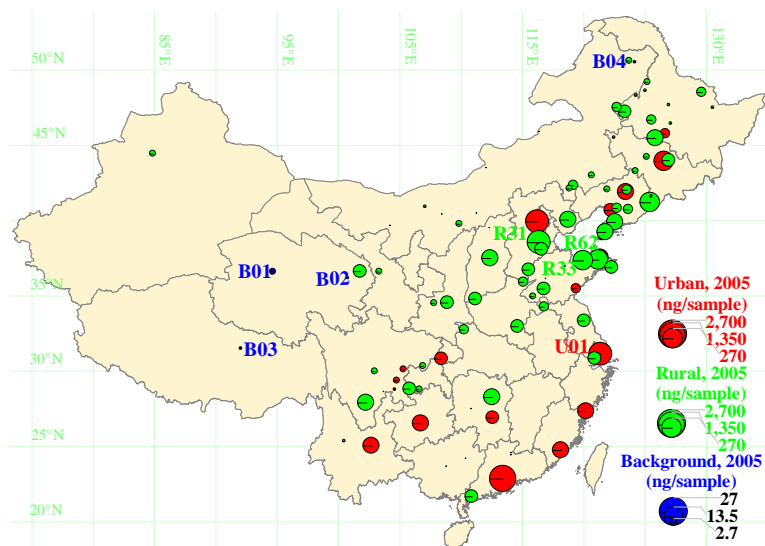


Fig 1. Spatial distribution of total BFRs in the passive air samples of China.

The composition showed a different pattern. The percentage of low molecular weight chemicals increased from the urban to rural and background sites. Low mass (LM) chemicals such as PentaBDE and LM-NBFRs (sum of PBEB, PBBZ and PBT), which were more volatile and mobile in air, thus could travel more far than high mass (HM) chemicals such as HM-NBFRs (sum of BTBPE, HBCD and DBDPE), whose molecular weight is higher than LM-NBFRs. This phenomenon was referred to as primary fractionation in a previous study<sup>[18]</sup>.

As shown in Fig 2, significant and positive correlation were found among BFRs in the 97 sampling sites. The most significant correlation in 2005 samples is between Penta- and Octa-BDE ( $r=0.80$ ). PBDEs and NBFRs show less correlation except for low mass NBFRs and PentaBDE. For individual chemicals, the correlation among PBDEs congeners showed the most significant correlation, while for NBFRs, an exception is HBCD which show less correlation with other chemicals, suggesting a different application of HBCD from other BFRs. In fact, HBCD has been used mainly in the production of expanded and extruded polystyrene for thermal insulation in buildings and in upholstery textiles<sup>[19]</sup>. The correlation between groups showed that the

The spatial distribution of  $\Sigma$ BFRs were shown in Fig 1. Generally, an higher concentration could be found in those figures, which were those metropolis such as Beijing(BJ), Guangzhou(GZ) and Shanghai(SH). The concentration of BFRs in background sites were generally low. However in the rural sites of north China, high concentration of BFRs were detected around the Laizhou Bay, Shandong Province, such as R31, R33 and R62, which has been reported as manufacture area for BFRs<sup>[17]</sup>. A significant correlation between total BFRs concentration and GDP were found in the samples ( $p<0.001$ ).

The concentration in the urban site was generally the highest for most of the target chemicals, while the

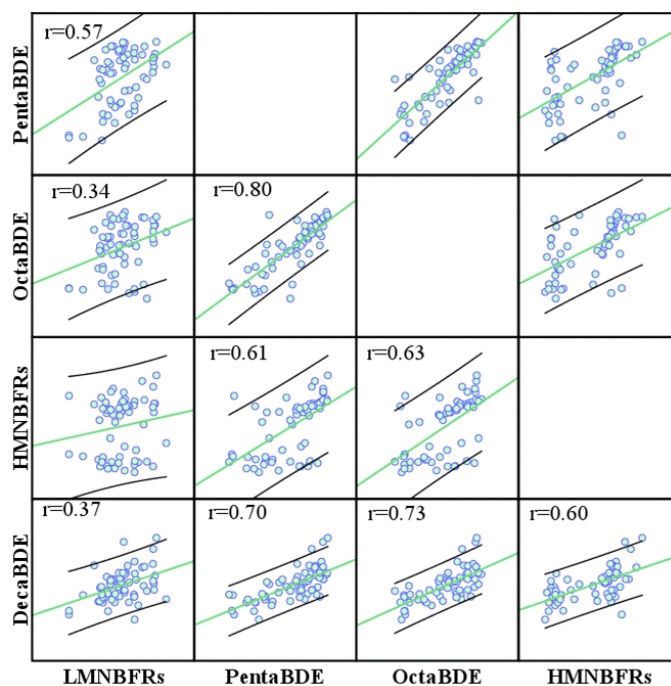


Fig 2. Correlation matrix of natural logarithm concentration of BFRs groups in 97 sites of China.

correlation among low mass BFRs was more significant, indicating a possible common source of BFRs and a similar atmospheric transmission.

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