

TEMPERATURE DEPENDENCE AND GAS-PARTICLE PARTITIONING OF POLYBROMINATED DIPHENYL ETHERS IN URBAN ATMOSPHERE IN NORTHEAST CHINA

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Abstract

We collected thirty-six pairs of air samples (gas- and particle-phases) in a typical city in northeast of China by using high-volume air sampler from August 2007 to April 2008. Polybrominated diphenyl ethers (PBDEs) were detected in the air samples with a mean concentration of 17.2 pg.m⁻³ and 25.8 pg.m⁻³ in gas and particle phase, respectively. BDE209 was the dominant congener among all PBDEs. The concentration of PBDEs was relatively low and varied with the sampling date. Partial pressure of PBDEs in the gas phase was significantly correlated with the temperature except for BDE66, BDE85 and BDE190, which were detected only in a few samples. A strong temperature dependence of gas-particle partition coefficients (in logK_p) of BDE17, BDE28, BDE47, BDE49, BDE99, and BDE100 was also found for the samples.

Introduction

Polybrominated diphenyl ethers (PBDEs) are one class of brominated flame retardants (BFRs) used in plastics, foams, textiles and other materials for decades. The use of PBDEs has increased over the last 20 years, and a large amount of PBDEs has released to the environment during manufacture and usage. In China, Deca-BDE has been a predominant product, with 3 × 10⁴ tons in 2005. PBDEs have been frequently detected in the air, water, sediment, soil and biota, which had a negative impact to health of humans.

Few studies on the seasonal distribution of PBDEs in atmosphere have been conducted in northeast of China. The City of Harbin, with a population of approximately 3 millions, is the capital of Heilongjiang Province in northeastern China, a major commercial, industrial, and transportation center surrounded by farmland. In this study, we collected air samples in Harbin for 24 hours every week from August 2007 to April 2008 using a high-volume air sampler. Our goal was to understand the temporal trend and seasonality of PBDEs in the northeastern city of China, and the relationship between partial pressure of PBDEs in gas phase and temperature.

Materials and methods

Sampling. Thirty-six air samples were taken at the roof of a building in Harbin using a high-volume air sampler from August 2007 to April 2008. Cleaned polyurethane foam (PUFs) and glass fiber filters (GFFs) were used in the air sampler to collect gaseous and particulate phase samples. After collection, the samples were taken to the laboratory and stored frozen at -20°C before extracted.

Sample Preparation. The polyurethane foam sample were Soxhlet extracted with a mixture of acetone and hexane (1:1,V:V) for 24 h. The extract was cleaned by silica gel column, eluted with 60 mL of hexane:methylene chloride (1:1,V:V), and the final extract volume was reduced to 1.0 mL by evaporation at room temperature under a gentle stream of nitrogen. The glass fiber filter were pretreated the same as glass fiber filter except for the extracted solvent was dichloromethane. The internal surrogate standard employed for quantization of PBDEs was added after the extraction of polyurethane foam and glass fiber filter.

Analysis. Fourteen PBDE congeners, BDE17, 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, 184, 190, and 209 were analyzed with Agilent 6890 gas chromatography /5975B mass spectrometry in electron capture negative ionization mode equipped with a HP5-MS column (30×0.25mm×0.1μm, J&W Scientific), following temperature program: 110°C for 2 min, 25°C/min to 220°C, 5°C/min to 290°C, and held for 15 min. The temperatures were 150, 230, and 250°C for the quadrupole, ion source, and interface, respectively. For BDE209 Analysis, HP5-MS column (15×0.25mm×0.1μm, J&W Scientific) was used, following temperature program: 110°C for 2 min,

10°C/min to 220°C, 20°C/min to 280°C, and held for 22 min. The temperatures were 106, 250, and 250°C for the quadrupole, ion source, and interface, respectively.

QA/QC. Field blanks and lab blanks were performed during the sampling and sample preparation. One lab blank and one spike sample were treated every ten samples. BDE47 were found in blanks with concentrations less than 10% of BDE47 in the samples. Recoveries of fourteen PBDEs congeners (BDE17, 28, 47, 49, 66, 100, 99, 85, 154, 153, 138, 183, 190 and 209) in spike samples ranged from 88.9% to 135.0%.

Results and discussion

Concentration and temporal distribution of PBDEs. The concentrations of total PBDE congeners ranged from 2.03 pg.m⁻³ to 149 pg.m⁻³ with a mean of 43.0 pg.m⁻³. BDE209 was the predominate congener in Harbin atmosphere with a mean of 27.6 pg.m⁻³. The descriptive statistics of data for PBDEs in the Harbin atmosphere are summarized in Table 1.

Table 1. Descriptive statistics data of PBDEs in the Harbin atmosphere (pg.m⁻³)

congeners	range	mean±SD	congeners	range	mean±SD
BDE17	BDL-4.10	1.11±1.15	BDE100	BDL-2.50	0.42±0.54
BDE28	0.18-11.6	2.40±2.79	BDE138	BDL-14.7	0.75±2.60
BDE47	0.32-20.8	2.90±3.57	BDE153	0.10-2.66	0.95±0.78
BDE49	0.19-4.51	1.31±0.99	BDE154	BDL-1.12	0.31±0.31
BDE66	0.09-4.70	0.66±0.81	BDE183	0.16-8.35	2.35±2.05
BDE85	BDL-13.7	0.69±2.44	BDE190	BDL-2.35	0.22±0.54
BDE99	0.16-3.35	1.30±0.77	BDE209	BDL-129	27.6±32.7

BDL: Below detection limit

Concentration of total PBDE congeners in particle phase were higher than gas phase and associate with the temperature during sampling period (see Fig.1). Due to the weaker volatile ability, BDE209 was the predominate congener in the particle phase other than gas phase. The concentrations in the samples collected from 18/8/2007 to 17/10/2007 were significantly higher than those on other dates. The temperature trend shown in Fig.1 also indicates that temperature is another important aspect to the concentration of PBDE congeners in both gas and particle phase.

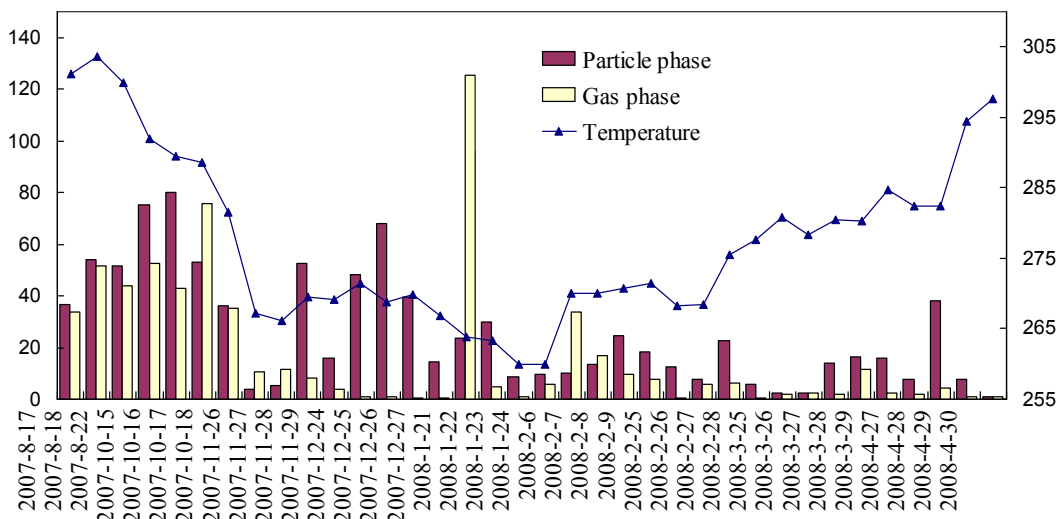


Fig. 1 Trends of BFRs concentrations in gas and particle phase by active sampling

Correlation Between Atmospheric Temperature and Gas-Phase Partial Pressure. The partial pressures of gas-phase organic pollutants are strongly dependent on atmospheric temperature. The functional relationship

is conveniently described by the Clausius-Clapeyron equation:

$$\ln P = -\frac{\Delta H}{RT} + c \quad \ln P = m(1/T) + b \quad (1)$$

where P is partial pressure of the PBDE congeners in gas-phase (in atm), ΔH is the phase transition energy by which a molecule volatilizes from the aquatic or terrestrial environment into the atmosphere (in kJ/mol), R is the gas constant, m is the slope, and b is the intercept. Table 2 shows the detail values derived from a regression using equation 1.

Table 2. Correlation Between Atmospheric Temperature and Gas-Phase Partial Pressure of Seven PBDE Congeners Derived from Regression (P<0.001)

	N	Slope \pm SD	intercept \pm SD	R ²	ΔH_{cal} (kJ/mol)	ΔH_{oa} (kJ/mol)
BDE17	32	-7631 \pm 994	-12.6 \pm 3.6	0.66	63.5 \pm 8.3	72.8
BDE28	33	-9065 \pm 967	-7.4 \pm 3.5	0.74	75.4 \pm 8.0	74.5
BDE47	35	-7661 \pm 1130	-12.9 \pm 4.1	0.58	63.7 \pm 9.4	97
BDE49	34	-4593 \pm 868	-24.1 \pm 3.1	0.47	38.2 \pm 7.2	107
BDE99	34	-3844 \pm 999	-27.0 \pm 3.6	0.32	32.0 \pm 8.3	91.1
BDE153	28	-2750 \pm 805	-31.1 \pm 2.9	0.31	22.9 \pm 6.7	98.2
BDE154	18	-3775 \pm 804	-27.8 \pm 2.9	0.58	31.4 \pm 6.7	94.4

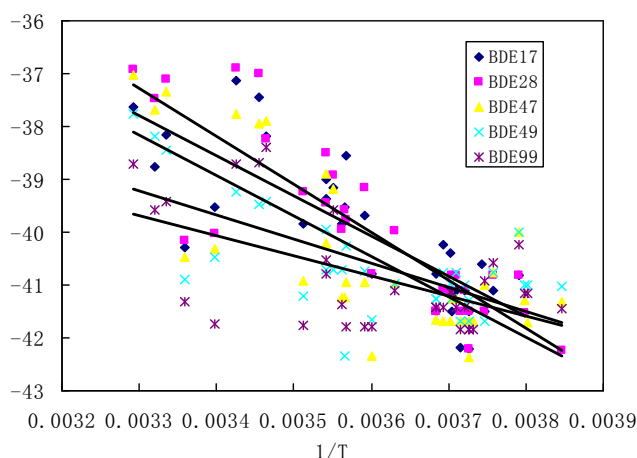


Fig 2. Correlation of Partial Pressures for Five BDE Congeners in Gas-Phase and Temperature.

The phase transition energy measured for different congener were different and lower than the ΔH_{oa} value (1) except for BDE28. This difference suggests that the atmospheric behavior of PBDE congener is different from each other, and may indicate a different source. Lee et al. have reported the values of ΔH_{cal} for BDE-47 as 77 \pm 21 and 115 \pm 18 kJ/mol at two different sites in England during the summer of 2001(2). Gouin et al. reported a ΔH_{cal} value of 41 kJ/mol for BDE47 in southern Ontario during 2002(3). Carlson et al. have point out the ΔH_{cal} values can vary widely depending on the size of the data set, the time of the year, and the range of temperature considered(4).

Gas-Particle Partitioning of PBDEs. PBDEs are semi-volatile organic compounds presented in both gas and particle phase in air. The Gas-particle partitioning in the atmosphere, adsorbing into particle phase or volatilizing into gas phase, is affected by temperature, K_{oa} and vapour pressure. It is important to study the gas-particle partitioning of PBDEs to understanding long-range transportation, half-life, fate and human expose. Studies show that Gas-Particle partitioning are influenced by the properties of the chemical and the atmosphere condition such as temperature. The partition coefficient (K_p) of semi-volatile organic compounds between the particle and gas phases is described as

$$K_p = (F/TSP)/A \quad (2)$$

where F is the concentration of PBDE congeners (pg m^{-3}) in particle phase, A is concentration of PBDE congeners (pg m^{-3}) in gas phase, and TSP is the total suspended particle matter level in air ($\mu\text{g m}^{-3}$). We have

$$\log K_p = A_0 + A_1/T \quad (3)$$

where T is the average atmospheric temperature on the day of sampling, A_1 is the slope, and A_0 is the intercept. The value of A_1 in eq 3 is related to the energy (ΔH) needed to move a molecule from the sorbed state on a particle phase into the vapor phase (5),

$$\Delta H = 2.303RA_1 \quad (4)$$

where R is the gas constant (8.314 J/mol).

The correlation between $\log K_p$ for 5 BDE congeners and $1/T$ based on eq 3 and eq 4 are presented in Table 3. The calculated ΔH values are different from the ΔH_{vap} value, which is with a range of 80-110 kJ/mol (1), indicate that PBDEs in atmosphere haven't reach equilibrium. Many factors include amount and nature of TSP can influence the ΔH values. Eunha Hoh et al. report a ΔH value of 85 ± 11 kJ/mol for BDE28, 93 ± 9 kJ/mol for BDE47, and 80 ± 9 kJ/mol for BDE99 in the atmosphere of the East-Central United States (6).

Table 3. Correlation between $\log K_p$ for 5 BDE congeners and $1/T$ ($P < 0.001$)

	N	slope \pm SD	intercept \pm SD	R^2	ΔH (kJ/mol)
BDE17	27	3080 \pm 605	-13.27 \pm 2.17	0.51	59.0 \pm 11.6
BDE28	29	5207 \pm 452	-21.00 \pm 1.63	0.83	99.7 \pm 8.67
BDE47	35	3701 \pm 440	-15.03 \pm 1.59	0.68	70.9 \pm 8.44
BDE49	33	2792 \pm 514	-11.82 \pm 1.85	0.49	53.5 \pm 9.85
BDE99	34	2051 \pm 369	-9.06 \pm 1.33	0.49	39.3 \pm 7.07

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20977022 and 41101493).

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