LEVELS OF POLYBROMINATED DIPHENYL ETHERS IN TREE BARK FROM BEIJING, CHINA

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Abstract

Polybrominated diphenyl ethers (PBDEs) were measured in tree bark samples from 5 tree species in Beijing. The concentrations of total PBDEs ranged from 99 to 728 ng/g lipid weight. The congener profiles of PBDEs wree similar for all the tree bark samples and the most abundant congener was BDE-209. The results suggested that the deca-BDE product gave predominant contribution to PBDEs pollution in the air of Beijing.

Introduction

Polybrominated diphenyl ethers (PBDEs) flame retardants are persistent organic pollutants that have been found globally in the environment. They can enter the environment during their production and migrate from the treated products over their entire lifetimes[1]. Worldwide, PBDEs production is dominated by the deca-BDE technical mixture, with an estimated 56100 t global demand in 2001. The domestic demand for brominated flame retardants (including PBDEs) in China has increased at an annual rate of 8%, and the predominant product is the deca-BDE technical mixture, amounting to 30000 t in 2005. Because of their ubiquitous use, lipophilicity and inert characteristics, PBDEs have been detected in a variety of environmental media, including soil, sediment and aquatic systems, air, and biological samples[2].

Tree bark has been used as a passive sampler to monitor PBDEs[3,4], since it is easy and inexpensive to sample. As a result of bark's high lipid content and large surface area, bark is a good passive sampler for the persistent organic compounds with high K_{ow} values even when present at low atmospheric concentrations[5]. Furthermore, tree bark usually stays on the tree for 3~5 years; thus, bark acts as an integrating sampler over this time period.

The objective of this study is to know levels of PBDEs in air of Beijing by measuring the concentrations of 9 PBDEs congeners in tree bark samples.

Materials and Methods

The bark samples were taken respectively from 5 tree species in the campus of Central University for Nationalities in winter of Beijing 2008, they were *Salix babylonica L.* (SB); *sophora japonica var. pendula Loud* (SJ); *Ginkgo biloba L.* (GB); *Pinus tabulaeformis Carr.* (PT) and *Platycladus orientalis Franco* (PO). Each bark sample was chiseled from a 10 cm square spot from three different trees, at a height of 1.5 m above ground level. The samples were wrapped in aluminum foil and sealed in plastic bags, then kept at -20℃ until extraction.

Approximately 8~20 g of each bark sample was cut into pieces of <1 cm using pruning shears and placed into a

Soxhlet extraction thimble. The samples were spiked with internal standards containing $^{13}C_{12}$-BDE139 and $^{13}C_{12}$-BDE209 and cover with 8~15 g of precleaned anhydrous Na_2SO_4. The samples were Soxhlet extracted for 36 h with 300ml acetone/hexane (1:3 v/v). Throughout the extraction and analysis procedure, the analytes were protected from light by wrapping the containers with aluminum foil.

The lipid concentration was determined gravimetrically. The extract was evaporated into 2~3ml with rotary distillation. Then cleaned with one multilayer silica columns (15mm i.d.) filled from the bottom with 1 g of activated silica, 4 g of silica/NaOH (1M), 1 g of activated silica, 8 g of silica/H_2SO_4 44% (w/w), and 2 g of silica topped with 4 g of Na_2SO_4. The sample was eluted with 20ml hexane, followed by 100ml hexane/DCM (1:1 v/v), the PBDEs were in the second fraction. If necessary, a second column (the amount of each filler cut half) was used to further remove residual lipids and other impurities. The samples were analyzed by gas chromatographic mass spectrometry.

Just prior to analysis, an aliquot (2µl×5µg/ml) of recovery standard solution containing $^{13}C_{12}$-PCB138 was added to the auto sampler vial. The samples were analyzed on an Agilent 6890 series gas chromatograph coupled to an Agilent 5975 mass spectrometer. The analytical column was a 30 m×0.25 mm i.d. DB-5 capillary column with a 0.1 µm film thickness (J&W Scientific, Folsom, CA) and the temperature program was as follows: isothermal at 100℃ for 3 min, 4℃/min to 300℃, and held at 300℃ for 25 min. Injector and interface temperatures were held at 320℃ and 300℃, respectively. The carrier gas was Helium at a flow rate of 1.0 ml/min. A 1 µl splitless injection was then analyzed by gas chromatographic mass spectrometry operated with negative chemical ionization source in selected ion monitoring mode. Methane was used as the chemical ionization gas. Two masses (m/z: 79,81) from the molecular ion cluster were used to monitor each of the target analytes except BDE209. Two masses (m/z: 407.6 and 486.6) were used to monitor BDE209, m/z 415.6 and 494.6 were monitored for $^{13}C_{12}$-BDE209 and m/z 574.6 and 576.6 were selected for monitoring $^{13}C_{12}$-BDE139. In addition, m/z 372.0 and 374.0 were used to monitor $^{13}C_{12}$-PCB138.

The identification of specific PBDEs was performed by comparing peak retention times with a standard solution containing 9 identified tri-BDE through deca-BDE congeners (BDE-28, -47, -99, -100, -153, -154, -183, -206 and -209, Cambridge Isotope Laboratories Inc). Quantification of the suite of PBDEs except BDE-209 in the samples was determined by the internal standard method. Quantification of BDE-209 was detemined by isotope dilution method. Five point calibration curves for the 9 congers were established. The total PBDEs (ΣPBDEs) concentrations were calculated as the sum of these target analytes.

Results and Discussion

The concentrations of the PBDEs in the tree bark samples are given in Table 1. The ΣPBDEs concentrations ranged from 99 to 728 ng/g lipid weight (Table 1), and 9 target analytes were detected in all of the tree bark samples investigated, suggesting that PBDEs exist in the Beijing environment. Given that PBDEs are not directly applied to trees, it seems likely that the PBDEs detected in these tree bark samples came from the accumulation of these compounds by way of atmospheric deposition. Zhu and Hites measured Brominated flame

retardants in 87 tree bark samples from 29 locations in North America, the concentration of total PBDEs (BDE-47, -49, -66, -85, -99, -100, -153, -154, -183, -206, -207, -208 and -209) from 17 locations ranged from 63.38 to 800 ng/g lipid weight (average, 219 ng/g) [3]. These concentrations are similar to this study.

Table1. The PBDEs concentrations in different tree barks (ng/g lipid)

Congener	SB	SJ	GB	PT	PO
BDE28	3.7	0.5	1.0	0.3	0.5
BDE47	6.1	0.9	1.6	0.6	0.8
BDE100	1.7	0.2	1.0	0.2	0.3
BDE99	3.4	0.5	1.6	0.4	0.6
BDE154	2.7	0.3	1.4	0.3	0.4
BDE153	3.4	0.7	1.9	0.4	0.5
BDE183	3.7	2.6	2.0	0.5	0.7
BDE206	7.2	0.8	5.1	1.4	2.2
BDE209	696	100	456	95	252
ΣPBDEs	728	107	472	99	258

The PBDEs congener profiles in verity of tree bark samples (given as the percent of ΣPBDEs concentration) are shown in Figure 1. The congener profiles were similar for all tree bark samples and the most abundant PBDEs congener was BDE-209 (Figure 1). In other studies, the higher BDE-47 and BDE-99 profiles were reported[3,6]. However, there were no more main congeners except BDE-209 in this study. The reason may be the different historical PBDEs product usage. At the same time, it suggested that the deca-BDE product gave predominant contribution to PBDEs pollution in the air of Beijing.

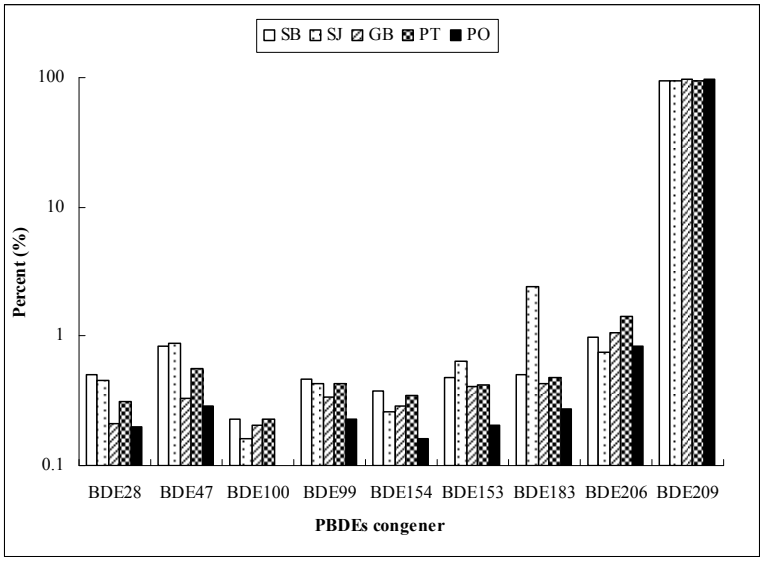

Figure 1. PBDE congener profiles in verity of tree bark samples (given as the percent of ΣPBDEs concentration).

Acknowledgements

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