LEVELS OF POLYBROMINATED DIPHENYL ETHERS IN PLANT FROM CHINESE BOHAI BAY

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Abstract
Polybrominated diphenyl ethers (PBDEs) are potentially harmful and persistent environmental pollutants. PBDE concentrations are reported for the main component of penta-BDEs, octa-BDEs, and deca-BDE in plant samples collected from Chinese Bohai Bay. The $\sum_{11}$PBDE concentrations in Bohai Bay plant samples ranged from 69.7 to 5869.3 ng/g. Data show that PBDEs should be considered as an increasing pollution problem in the Bohai Bay region.

Introduction
Polybrominated diphenyl ethers (PBDEs) have been used for more than three decades as flame retardants in a wide variety of manufactured materials such as furniture, vehicles, carpets, building materials, and electronic circuit boards because of their demonstrated fire retarding abilities.Usually, PBDEs are added to the materials as mixtures of penta-BDEs, octa-BDEs, or deca-BDE. Currently, deca-BDE accounts for over 80% of the total PBDE production[1,2]. In China, the domestic production of brominated flame retardants (BFRs) was 10 000 tons in 2000 and deca-BDE was one of the most produced BFRs. The domestic demand of BFRs has increased at a rate of 8% per year in China. In addition, a portion of BFRs currently used in China is expected to be imported from other countries (although the exact amount is unknown), because three of the largest BFR manufacturers in the world (i.e., Great Lakes Chemical, Indianapolis, IN; Albemarle Chemical, Richmond, VA; and Dead Sea Chemical, Beer-Sheva, Israel) all have distributors in China to sell BFRs[3]. 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[4].

In 2005, we began monitoring for PBDEs in water, air, surface sediments, and bivalve samples. The PBDE congeners that were targeted for chemical analysis included BDE-28, -47, -99, -100, -153, -154, -183, -206, -207, -208, and -209, since these congeners are major congeners of the Penta-BDE mixture, Octa-BDE and Deca-BDE mixture. BDE-28, -47, -99, -100, -153, -154,-183 and BDE-209 were selected for two principal reasons, specifically: they have been identified as the most abundant in air and soil and they are the principal congeners monitored in previous comparable studies. BDE-206, -207, -208 were selected because the deca-BDE mixture include 2% various nona-BDEs. They have been detected in variety of environmental medium during our research. The aim of this study was to determine PBDE concentrations in plant from several species of plant including grass, haricot bean and Saline Seepweed to comprehensively examine the status of PBDE contamination in the environment.

Materials and Methods
The four grass samples were taken from BFRs production plant lied at Bohai Bay in 2006, two haricot bean and Saline Seepweed samples were purchased from local market. The samples were wrapped in foil twice and sealed in two plastic bags. The samples were stored in a cool box. Upon arrival in laboratory, the samples were immediately transferred to a freezer where they were stored until analysis.

The 30 g of sample (wet weight) was taken and mixed with Na_2SO_4 to remove water. The sample was then transferred to a pre-extracted glass thimble and spiked with internal standards containing $^{13}C_{12}$-BDE139 and $^{13}C_{12}$-BDE209. The samples were extracted for 16 hours using 300ml acetone/hexane (1:3 v/v), and the extract was evaporated into 2~3ml with rotary distillation. The extract was then further 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 and 100ml hexane/DCM (1:1), the first fraction was discarded, and the following fraction was collected in an amber vial, then reduced in volume to 100μL for analysis. The samples were analyzed for PBDEs by GC-MS.

Just prior to analysis, an aliquot (2 μL×5μg/ml) of recovery standard solution containing $^{13}C_{12}$-PCB138 was added to the auto sampler vial. PBDE congeners were detected by GC/MS on a Agilent 5973 mass spectrometer equipped with a 6890 gas chromatograph. The analytical column was a 30 m×0.25 mm i.d. DB-5 capillary column with a 0.25μm film thickness (J & W Scientific, Folsom, CA) and the temperature program was as follows: oven temperature held at 100℃ for 2 min, increased at 4℃ /min to 300℃, and held for 25 min. Injector and interface temperatures were 280℃ and 320℃, respectively. The carrier gas was Helium at a flow rate of 1.0 ml/min. A 1-μL splitless injection was then analyzed by GC/MS 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=415.6,494.6 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 372,374 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 11 identified tri-BDE through deca-BDE congeners (BDE-28, -47, -99, -100, -153, -154, -183, -206, -207, -208, 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 11 PBDE congers were established. The total PBDE ($\sum_{11}$PBDEs) concentrations were calculated as the sum of these target analytes.

Results and Discussion

The PBDE concentrations in different plants are shown in Table 1, and the PBDE congener profiles in verity of plants(given as the percent of $\sum_{11}$PBDE concentration) are shown in Figure1.The $\sum_{11}$PBDE concentrations in Bohai Bay plant samples ranged from 69.7 to 5869.3 ng/g (Table 1). The highest $\sum_{11}$PBDE levels were found at Grass 1 sample collected from the gate of BFRs production plant. This plant mainly produce deca-BDE mixture. The lower levels of PBDEs at Grass 2,3,4 samples (range 474.7-919.9 ng/g) could be due to their location far away from the production plant, and may be diluted as air is transported. The most abundant PBDE congeners in all plant samples were BDE-209 (Figure 1). BDE-47 and BDE-99, along with BDE-100, BDE-153, and BDE-154, which were also detected in the Grass 1 and Grass 3 samples, are major congeners of the Penta-BDE mixture. BDE-183, the predominant congener from the Octa-BDE mixture, was also detected in Grass 1 and 3 samples.

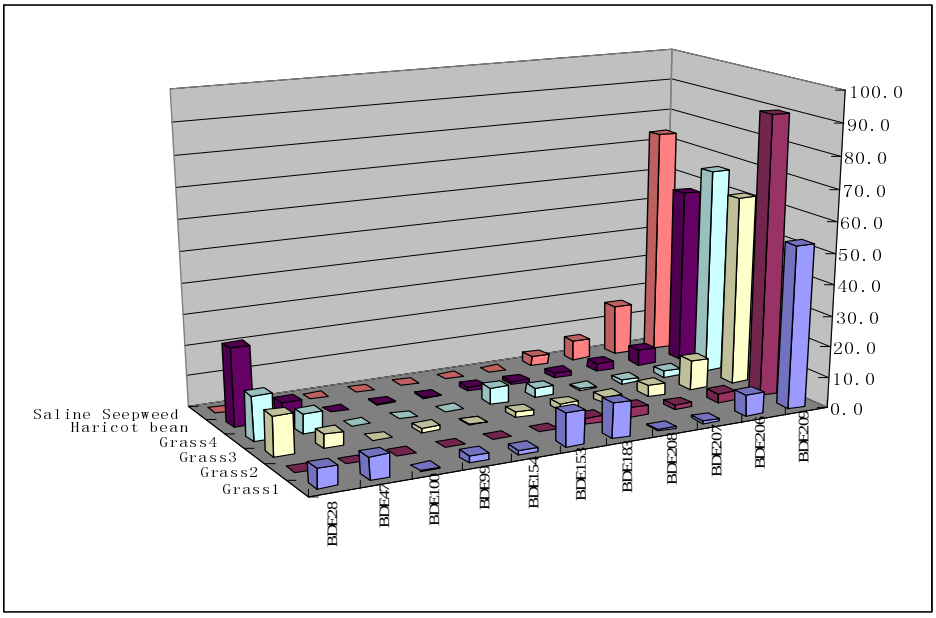
The lowest $\sum_{11}$PBDE levels(range 69.7-157.9 ng/g) were found in haricot bean and Saline Seepweed samples. These samples were purchase from local open market nearby the BFRs production plant. However, congeners profiles of this two samples were very different. Only four PBDE congeners were detected in the Saline Seepweed samples, with BDE-209 (51.5 ng/g) being the most abundant congener followed in decreasing abundance by BDE-206 (11.5 ng/g), BDE-207(4.5 ng/g dry), BDE-208 (2.2 ng/g dry). These congeners are major components of the Deca-BDE mixture. All the target PBDE congeners except BDE-100 were detected in the haricot bean sample. Hence, they were possibly contaminated by different pathway. Further studies on contamination pathway should be studied in detail. PBDEs were detected in all the plant samples collected from Chinese Bohai Bay. Considering these facts, PBDEs should be considered as an increasing pollution problem in the Bohai Bay region, which may be of great concern in the future.

Interestingly, Six plant samples should be contaminated by the same BFRs production plant. However, the congener profiles among them were not similar. Since aerial portions of vegetation receive the bulk of their POPs burden from the atmosphere[5], vegetation can therefore be a very useful indicator of the atmospheric burden of POPs during its lifetime/exposure period. In this study, the BFRs plant produce the deca-BDE mixture. Therefore, the environmental fate and distribution of BDE-209 will affect PBDE distribution on atmospheric particles and further affect the PBDE distribution on the plants.

Table1. The PBDE concentrations in different plants

Congener (ng/g)	Grass1	Grass2	Grass3	Grass4	Haricot bean	Saline Seepweed
BDE28	360.3	0.0	60.4	96.7	39.9	0.0
BDE47	417.6	0.0	21.3	42.9	8.7	0.0
BDE100	12.9	0.0	0.7	0.0	0.0	0.0
BDE99	134.4	0.0	6.7	0.0	0.5	0.0
BDE154	86.5	0.0	1.5	0.0	0.3	0.0
BDE153	627.7	0.1	8.9	35.7	2.1	0.0
BDE183	664.2	19.2	10.2	20.4	1.6	0.0
BDE208	26.4	28.4	10.2	2.9	2.5	2.2
BDE207	46.9	13.7	17.3	8.9	4.1	4.5
BDE206	406.9	27.2	46.2	14.3	8.1	11.5
BDE209	3085.5	831.3	291.3	452.8	90.1	51.5
$\sum_{11}$PBDEs	5869.3	919.9	474.7	674.5	157.9	69.7

Figure 1. PBDE congener profiles in verity of plants(given as the percent of $\sum_{11}$PBDE concentration).



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