HEXABROMOCYCLODODECANE IN TREE BARK FROM BEIJING, CHINA

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Abstract

Five tree bark sample pools taken from Beijing were analyzed for the HBCD contamination level, for the purpose of qualitatively indicating atmospheric contamination levels. The α-、β- and γ-HBCD diastereomers could be consistently identified and quantified in tree bark samples, indicating the presence of HBCD in local environment. ΣHBCD concentrations ranged from 26.4 to 171.9 ng g^{-1} lipid in tree bark samples. It is interesting that γ-HBCD made a greater contribution to ΣHBCD in tree bark (47.1%) than in air, with the opposite trend observed for α-HBCD (36.2%).

Introduction

Hexabromocyclododecane (HBCD) is an additive brominated flame retardants which was used globally for about 20 years. Its primary application is in extruded (XPS) and expanded (EPS) polystyrene foam which is used as thermal insulation in the building industry. Typical HBCD levels in EPS are 0.7% and in XPS are 2.5%. End products include upholstered furniture, interior textiles, automobile interior textiles, as well as in building materials such as house walls, cellars, roofs and parking decks, against frost heaving in roads and railway embankments, packaging material, video cassette recorder housing and electric equipment[1]. HBCD has been identified by the U.K. Chemical Stakeholders Forum as a persistent, bioaccumulative, and toxic chemical and has been included in the OSPAR list of chemicals for priority action[2]. Its contamination has become a serious scientific concern regarding its environmental fate and toxicity.

Tree bark can be used to qualitatively indicate organic pollutant atmospheric contamination levels as long as the mechanism of accumulation is considered. The benefits of using tree bark are that they are easy to obtain, more cost effective than air sample collection and do not need equipment, thus simultaneous monitoring in many spatially distinct locations was practicable. In this study, tree bark has been used to determine regional contamination levels caused by HBCD in Beijing, China.

Materials and Methods

The sampling sites were situated in the campus of Central University for Nationalities, Beijing. Five tree bark sample pools were taken in the winter, 2008. Each pooled bark samples was chiseled from a 10 cm square spot from three individual trees in the same species, 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 pooled bark samples was cut into pieces of <1 cm using pruning shears and

placed into a Soxhlet extraction thimble. The samples were spiked with $^{13}C_{12}$-α-HBCD as internal standards (50μL×0.05μg/ml) and covered with 8~15 g of pre-cleaned 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 content 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 H_2SO_4/silica 44% (w/w), and 2 g of silica topped with 4 g of anhydrous Na_2SO_4. The sample was eluted with 20 ml hexane, followed by 100 ml hexane/DCM (1:1 v/v). The target HBCD was in the second fraction. If necessary, the procedure was repeated but with half amount of the gel in each filler.

Separation of the α-、β-、γ-HBCD diastereomers was achieved using a Waters UPLC system with automatic injector. Reversed phase liquid chromatography separation was performed on a C_{18} column (2.1×50 mm, 1.7 μm) from Waters. Elution solvents were methanol (A), 20% acetonitrile/water (B). Mobile phase composition (A: B, v/v) was 80:20 and flow rate was set at 0.25 mL min^{-1}. Injected volume was 3 μL. Mass spectrometric data were acquired in negative electrospray ionization (ESI$^-$) that performed in multiple reactions monitoring mode (MRM). Capillary voltage was 2.5 and cone voltage was 20 v. Source temperature was 120 ℃ and desolvation temperature was 400 ℃. Desolvation gas flow was 550 L hr^{-1}、cone gas flow was 130 L hr^{-1} and collision gas flow was 0.15 mL min^{-1}. The [M-H]$^-$→ Br$^-$ transition at m/z 640.6→78.9 and 652.4→78.9 was monitored for C_{12}-HBCD and $^{13}C_{12}$-labeled HBCD isomers, respectively. Quantification of α-、β-、γ-HBCD was obtained using MassLynx V4.1 software (Waters).

Results and discussion

The individual HBCD isomer amount was calculated using the calibration curve by the ratio of the peak area of HBCD isomer to that of $^{13}C_{12}$-labeled α-HBCD. All r^2 values for the calibration curves for each diastereomers were＞0.9952. All three diastereomers in procedure blank were not detected.

Under field conditions, Simonich and Hites have shown that the differences in the pollutant concentration in needles, leaves, seeds, and tree bark collected from the same site can be minimized by normalizing it to the lipid concentration[3]. The concentrations of α-、β-、γ- and ΣHBCD in bark samples are shown in Table 1.

Table 1 Concentrations of α-、β-、γ- and ΣHBCD in tree bark samples (ng g^{-1} lipid)

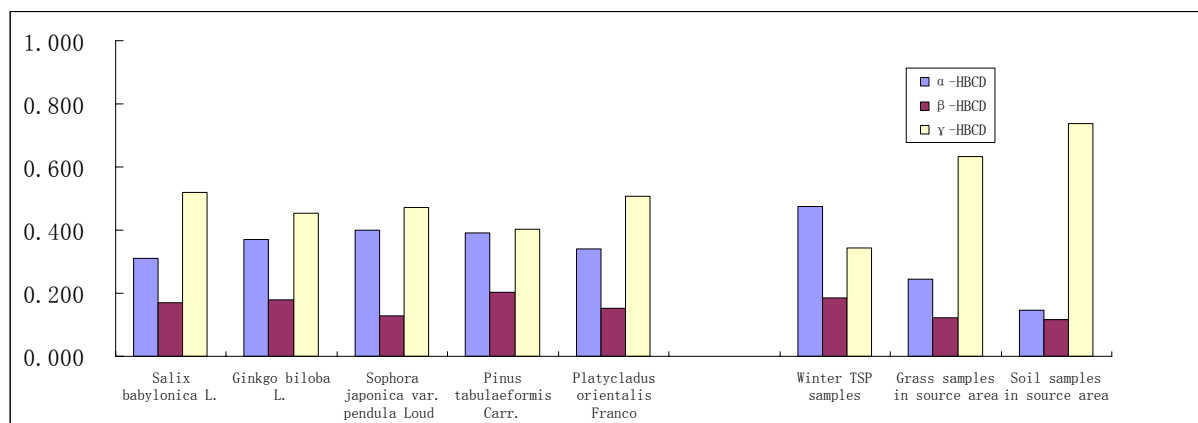| Tree species	α-HBCD	β-HBCD	γ-HBCD	ΣHBCD
Salix babylonica L.	53.3	29.3	89.3	171.9
Ginkgo biloba L.	17.4	8.4	21.3	47.1
Sophora japonica var. pendula Loud	10.5	3.4	12.5	26.4
Pinus tabulaeformis Carr.	15.0	7.8	15.5	38.3
Platycladus orientalis Franco	19.6	8.8	29.2	57.6

Fig.1 The comparison of diastereomer profiles in tree bark samples with winter TSP samples (Beijing) and reported in grass samples[4] and soil samples[5] (near a HBCD manufactory)

The analysis on diastereomer profiles indicated that γ-HBCD was the dominant isomer and β-HBCD was a minor isomer in all tree bark samples (Fig. 1). Since α-HBCD (average, 47.3%) was the dominated diastereomer in particle-phase of Beijing air samples collected in winter in our previous study, while γ-HBCD account for about 34.2% of ΣHBCD, it seems that the diastereomer profile in tree bark was different from that in air. It is apparently that γ-HBCD made a greater contribution to ΣHBCD in tree bark (47.1%) than in air, with the opposite trend observed for α-HBCD (36.2%). This phenomenon could be explained as follows. First, the Octanol/water partition coefficient for α-、 β- and γ-HBCD were 5.07, 5.12 and 5.47, respectively[6]. It seems γ-HBCD may be slightly easier concentrated in the lipid of tree bark than other two isomers, which may directly cause the relatively increase/decrease in the contribution of γ-HBCD/α-HBCD. Second, it was reported that γ-HBCD was the dominant isomer (63.4%) in grass stems and leaves[4], thus HBCD isomers in tree bark may be simultaneously contributed by inner-transmission and tree bark accumulation from ambient air.

Since simultaneous PAH concentration measurements in air allowed for direct comparison to the PAH concentrations and profiles measured in the vegetation[3], and two studies[7,8] have showed that tree bark could be used to indicate pollutant contamination levels, tree bark seems to be robust as atmospheric contamination indicator. The purpose of this study was to use HBCD concentrations in tree bark to qualitatively indicate atmospheric contamination levels. The future work will focus on the spatial distribution of HBCD and the investigation of possible contamination sources in Beijing.

References

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