

DECABROMODIPHENYL ETHER AND NOVEL HALOGENATED FLAME RETARDANTS IN BARK FROM THE UPPER YELLOW RIVER, CHINA

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Introduction

Polybrominated diphenyl ethers (PBDEs) have been used in a variety of commercial products, the most used of which has been the decabromodiphenyl ether commercial product, which primarily consists of the decabromodiphenyl ether congener, BDE-209¹. The use of the decabromodiphenyl ether commercial product has been banned in the EU and in some states in the USA^{2,3}, so manufacturers have replaced the brominated diphenyl ethers with alternative flame retardants, some of which, e.g., dechlorane plus (DP), hexabromobenzene (HBB), pentabromobenzene (PBBz), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), and tetrabromo-p-xylene (pTBX), have been called novel halogenated flame retardants (NHFRs). Previous studies showed that some of these analytes are currently being produced in China^{4,6}, but there is still very little information on their concentrations, especially on NHFRs concentrations, in China. The upper Yellow River ends in Togtoh County, Inner Mongolia, and, from the source, includes a total of 3472 km of the river, with an altitude dropping from 4500 m to 1000 m. There are several industrial cities along it, as well as some less industrialized counties. The aim of the study was to assess the current levels of BDE-209, DP, HBB, PBBz, PBT, PBEB, and pTBX in the upper Yellow River area, particularly the high altitude area, by determining the analyte concentrations in bark samples, and then to clarify the relationships between these analytes.

Materials and methods

Willow bark samples (n=15) were collected along the upper Yellow River bank in July 2011. The sampling site information is shown in Table 1. Among the samples, three were collected from the densely populated urban areas (B-8, B-11, and B-15). Each bark sample was taken by chiseling around the trunks of three different willow trees at about 1.5 m above ground level. The bark samples were shipped to the laboratory and stored at 5 °C until analysis.

Table 1 Sampling site information

Site No.	Location	Type	Province	Latitude (°N)	Longitude (°E)	Elevation (m)
B-1	Sanhu Estuary	Rural	Inner Mongolia	40.61	108.77	1020
B-2	Dengkou	Rural		40.28	107.02	1056
B-3	Dusitu River	Rural	Ningxia	39.08	106.89	1094
B-4	Yinchuan	Urban		38.48	106.26	1114
B-5	Yingu Highway Bridge	Rural		38.29	106.23	1117
B-6	Qingtongxia	Rural	Gansu	37.95	105.99	1141
B-7	Jinsha Bay	Rural		37.83	105.94	1193
B-8	Zhongning	Urban		37.49	105.67	1191
B-9	Shapotou	Rural	Gansu	37.45	104.98	1238
B-10	Wufo Temple	Rural		37.46	104.99	1246
B-11	Baiyin	Urban		36.55	104.14	1720
B-12	Yuzhong	Rural		36.4	104.2	1438
B-13	Qingcheng Bridge	Rural		36.36	104.22	1448
B-14	Shichuan Bridge	Rural		36.15	103.99	1487
B-15	Lanzhou	Urban	36.05	103.86	1523	

Each sample was spiked with a known amount of internal standards ($^{13}\text{C}_{12}$ -BDE-139, $^{13}\text{C}_{12}$ -BDE-209, and $^{13}\text{C}_{10}$ -syn-DP), Soxhlet extracted for 24 h with 300 mL of a 1:1 acetone hexane mixture, then divided into two equal aliquots. One aliquot was fractionated using a column packed with (from bottom to top) 1 g activated silica, 4 g silica treated with 30% w/w of 1 M $\text{NaOH}_{(\text{aq})}$, 1 g activated silica, 8 g silica treated with 44% w/w of $\text{H}_2\text{SO}_{4(\text{conc})}$, 2 g activated silica, and 4 g granular anhydrous sodium sulfate, eluted with 100 mL hexane:dichloromethane (97:3, v/v). The other aliquot was cleaned using a column packed with (from bottom to top) 2 g anhydrous sodium sulfate, 8 g deactivated silica gel (3% water), 8 g neutral alumina, and 2 g anhydrous sodium sulfate, eluted with 100 mL of hexane:dichloromethane (7:3, v/v). And all the eluates were concentrated to 100 μL by rotary evaporator and gentle nitrogen flow.

The samples were analyzed by GC-MS (Agilent 5975N mass spectrometer equipped with a 6890 gas chromatograph). The mass spectrometer ion source and quadrupole temperatures were both 150 °C. HBB, PBBz, PBEB, PBT, and pTBX were analyzed using a DB-5MS column (30 m \times 0.25 mm i.d., 0.1 μm film thickness; J&W Scientific, Agilent Technologies) and an oven temperature program of 100 °C for 2 min, increased by 4 °C /min to 300 °C. The m/z ratios monitored were: 419.6 and 421.5 for pTBX; 471.6 and 473.6 for PBBz; 485.6 and 487.6 for PBT; 499.6 and 501.6 for PBEB; 551.5 and 553.5 for HBB; and 573.6 and 575.6 for $^{13}\text{C}_{12}$ -BDE-139. DP was analyzed using a DB-5MS column (30 m \times 0.25 mm i.d., 0.1 μm film thickness; J&W Scientific, Agilent Technologies). The injector temperature was 250 °C and the oven temperature program was: 100 °C for 5 min, increased to 300 °C at 10 °C /min, then held for 5 min. The m/z ratios monitored were 652 and 654 for syn- and anti-DP and 666 and 668 for $^{13}\text{C}_{10}$ -syn-DP. BDE-209 was analyzed using a shorter DB-5MS column (15 m \times 0.25 mm i.d., 0.1 μm film thickness; J&W Scientific, Agilent Technologies). The injector temperature was 290 °C and the oven temperature program was: 100 °C for 3 min, increased to 300 °C at 4 °C /min, then held for 22 min. The m/z ratios monitored were 407 and 486 for $^{12}\text{C}_{12}$ -BDE-209 and 415 and 494 for $^{13}\text{C}_{12}$ -BDE-209. The carrier gas was helium at a flow rate of 1.0 mL/min. Samples were injected in splitless mode (1 μL). Negative chemical ionization source and selected ion monitoring mode were used for quantitative analysis.

A method blank sample was analyzed with every batch of samples. The analyte concentrations in the blank samples were satisfactory for all of the analytes (<5% of the typical concentration in samples). HBB, PBBz, PBEB, PBT, and pTBX were quantified using $^{13}\text{C}_{12}$ -BDE-139 as the internal standard, syn-DP and anti-DP were quantified using $^{13}\text{C}_{10}$ -syn-DP as the internal standard, and BDE-209 was quantified using $^{13}\text{C}_{12}$ -BDE-209 as the internal standard. The method detection limits (LODs) for BDE-209, DP, and HBB were 100, 0.2, and 0.05 pg/g dw, respectively, and the LODs for PBT, PBBz, PBEB, PBT, and pTBX were all 0.02 pg/g dw. The recoveries of $^{13}\text{C}_{12}$ -BDE-139 and $^{13}\text{C}_{10}$ -syn-DP were higher than 83%, and the BDE-209 recoveries were 53–76%.

Results and discussion

The concentrations of BDE-209, DP, and five novel brominated flame retardants (NBFRs: HBB, PBBz, PBEB, PBT, and pTBX) in the samples are shown in Table 2 and Figure 1. BDE-209 was the dominant analyte in all of the samples, reflecting the fact that it has been the highest usage flame retardant across the world. DP was found at the second highest concentration. The low concentrations of NBFRs compared to BDE-209 and DP agree with their relative current production and usage volumes.

Table 2 Concentrations of the target compounds in bark (pg/g dw)

Compounds	Detection frequency (%)	Mean	Standard error	Minimum	Median	Maximum
BDE-209	100	1.2×10^4	6.3×10^3	4.0×10^3	1.1×10^4	2.5×10^4
DP	100	42	43	3.5	17	1.6×10^2
HBB	93	2.1	1.4	0.72	1.4	5.3
PBBz	100	2.1	1.5	0.67	1.3	5.6
PBT	93	2.1	1.5	0.55	1.5	5.1
pTBX	13	0.5	0.17	0.32	0.5	0.67
PBEB	13	0.39	0.026	0.36	0.39	0.41

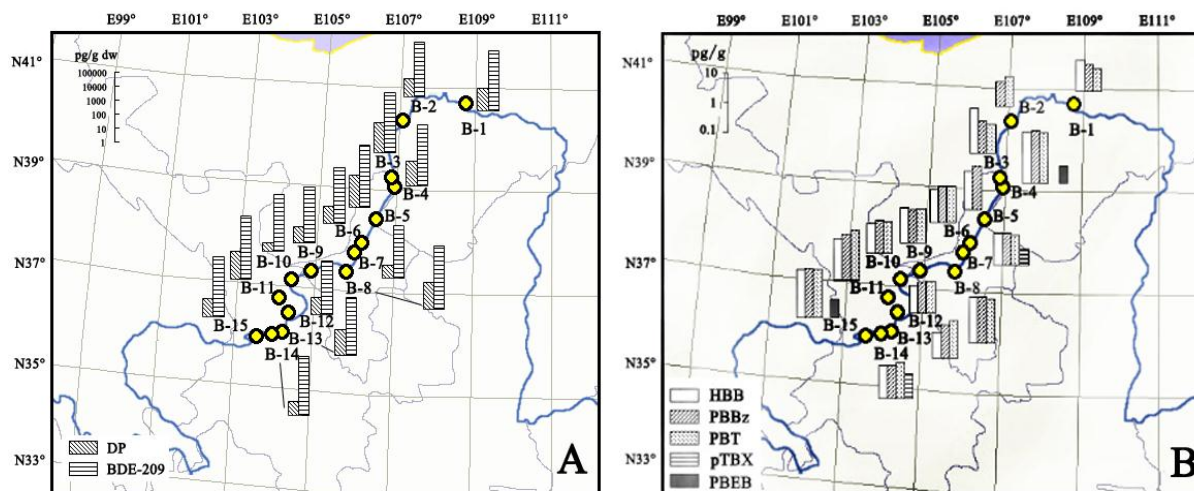


Fig.1 BDE-209 and DP distributions (A) and NBFRs distributions (B) in the bark

BDE-209 was detected in all of the samples, at concentrations of 4.0–25 ng/g dw (median 11 ng/g dw). The highest concentration was found in sample B-11 (25 ng/g dw). The relatively high concentrations and detection frequencies indicated that BDE-209 is a ubiquitous contaminant in the environment of the upper Yellow River.

DP was also found in all of the bark samples, at concentrations of 3.5–160 pg/g dw (median 17 pg/g dw). The highest concentration was found at site B-5. The DP concentrations were higher in samples from urban areas (51 ± 23 pg/g dw) than in samples from rural areas (38 ± 47 pg/g dw), indicating a relationship between DP concentrations and human activities, which has also been found in other areas of China^{7,8}. DP has syn- and anti-stereoisomers, which have different physical and chemical properties, leading to differences in their persistence and fate in the environment. The ratio of the syn-DP concentration to the sum of the syn-DP and anti-DP concentrations (f_{syn}) was 0.23 ± 0.05 in our study, which is close to ratios that have been reported for commercial DP mixtures (0.20–0.25)³.

HBB was detected in 14 of all the 15 bark samples, at concentrations between 0.72 pg/g dw and 5.3 pg/g dw. The highest HBB concentration was found at site B-4, near which are a large number of chemical plants. High concentrations of other NBFRs were also found at site B-4. The HBB concentrations in the rural bark samples (median 1.2 pg/g dw) were lower than the concentrations in urban samples (median 3.9 pg/g dw).

PBBz was detected in all of the bark samples, at concentrations of 0.67–5.6 pg/g dw (median 1.3 pg/g dw). The highest PBBz concentration was found in bark samples from site B-4 (5.6 pg/g dw). The concentrations in the rural bark samples (median 1.3 pg/g dw) were lower than the concentrations in the urban samples (median 4.0 pg/g dw). PBBz was detected in all of the samples analyzed and we suggest that it could be a potential threat to the environment

PBT was also detected in all of the samples, at concentrations of 0.55–5.1 pg/g dw (median 1.5 pg/g dw). The highest concentration was found in samples from site B-4. We found mean PBT concentrations of 1.1 ± 0.5 pg/g dw in rural and 4.2 ± 0.8 pg/g dw in urban samples. There have been very few reports of PBT in environmental samples. PBT has a $\log K_{\text{OW}}$ of 5.87 ± 0.62^5 and was found to be widespread in the upper Yellow River area, so we believe that it should also be considered to be a potential POP.

PBEB and pTBX were detected in bark samples from two sampling sites, at mean concentrations of 0.39 pg/g dw (PBEB at sites B-4 and B-15) and 0.50 pg/g dw (pTBX at sites B-7 and B-14). pTBX concentrations were relatively high in samples from site B-14. Site B-14 was in the suburbs of Lanzhou City, which is dominated by the chemical industry, and this industry may be a local source of pTBX. In this study, the PBEB concentrations found in bark samples were quite low and PBEB and pTBX were not found to be ubiquitous in the environment.

The flame retardants that were analyzed have some structural similarities, so correlations between their concentrations can provide useful insights into their environmental behaviors⁴. We assessed the correlations between all seven of the flame retardants analyzed in the bark samples using the bivariate Spearman correlation tests, and found that HBB, PBBz, and PBT significantly correlated with each other (HBB and PBBz, $r=0.881$, $p<0.001$; HBB and PBT, $r=0.721$, $p=0.002$; PBBz and PBT, $r=0.835$, $p<0.001$), suggesting that these compounds may have come from the same sources. PBBz is a less brominated homolog of HBB and they have been shown

to have common sources^{4,9}, so it is not surprising that there was a strong correlation between the concentrations of these chemicals in our samples. Positive correlations were found between BDE-209 and HBB ($r=0.563$, $p=0.029$) and between BDE-209 and PBBz ($r=0.600$, $p=0.018$) in the bark samples, and this relationship could be caused by the thermal degradation of BDE-209 being a source of HBB and PBBz to the environment, as has been suggested in a previous study⁹. BDE-209 also correlated significantly with DP ($r=0.600$, $p=0.018$). It has been reported that DP has been used as a replacement for BDE-209¹⁰, so they may have had the same (although not necessarily concurrent) sources in the upper Yellow River.

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