

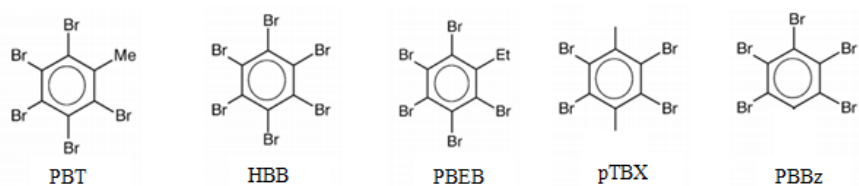
NOVEL HALOGENATED FLAMED RETARDANTS IN BREAST MILK FROM CHINA

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Introduction

Halogenated persistent organic compounds including novel brominated flame retardants (NBFRs) and dechlorane plus (DP) were detected in this study. NBFRs refer to those new to the market or newly observed in the environment, we mainly focus on Pentabromotoluene (PBT), Hexabromobenzene (HBB), Pentabromotoluene (PBEB), tetrabromo-p-xylene (pTBX) and pentabromobenzenes (PBBz). PBT is used mostly in unsaturated polyesters, polyethylene, polypropylene, polystyrene, SBR-latex, textile, rubbers and ABS (acrylonitrile butadiene styrene terpolymer) with a production volume of 600 tons per year at ShouGuang Longfa Chemical Co. Ltd. in Qingdao, Shandong province¹. HBB, which is added into paper, woods, textiles, electronic and plastic goods as flame retardant, is produced 600 tons per year at Shou Guang Longfa Chemical Co. Ltd¹. PBEB was mostly used in thermoset polyester resins and was produced mainly in the 1970s and 1980s in the US. Since 1986, no US production or import volumes have been reported because it was banned due to its persistent, bioaccumulate and toxic characteristic. To date, information on application, production, toxicity of tetrabromo-p-xylene (pTBX) and pentabromobenzenes (PBBz) are not available. DP was first put into production as a substitute for mirex². Commercial DP, including syn-DP and anti-DP isomers, has been used for computer connectors, plastic roofing material, coating electrical wires and cables². The chemical structures of these compounds are listed in Fig. 1.



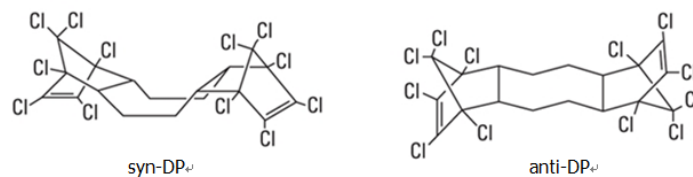


Fig. 1 chemical structures of PBT, HBB, PBEB, pTBX, PBBz, syn-DP and anti-DP

Materials and methods

$^{13}\text{C}_{12}$ -BDE-139 was used as internal standard for PBT, PBEB, pTBX and PBBz, and also $^{13}\text{C}_6$ -HBB for HBB, $^{13}\text{C}_{10}$ -syn-DP for syn-DP and anti-DP.

The samples of breast milk were collected from residents living around the production source region of brominated flame retardants in Laizhou Bay, Shandong province, China in 2007 (n=10) and 2012 (n=18), and stored at -20°C until analysis³. The breast milk and blank samples were spiked with internal standards containing $^{13}\text{C}_{12}$ -BDE-139 (4ng), $^{13}\text{C}_6$ -HBB (4ng) and $^{13}\text{C}_{10}$ -syn-DP (2ng). PBT (100ng), PBEB (40ng), pTBX (40ng) and PBBz (40ng) were only spiked in blank samples.

6M HCL(1mL), isopropanol(6mL) and hexane-methyl tertiary butyl ether(1:1, v/v, 6mL) were added into each sample followed by vortex blending. Then, the organic phases were transferred into the corresponding centrifuge tubes while the rests were extracted twice with hexane-methyl tertiary butyl ether(1:1, v/v, 4mL). After concentrated to about 7mL under nitrogen and added with 1% KCL(4mL), all the samples were extracted again as mentioned above. The samples were evaporated under a gentle nitrogen stream to about 1mL before added with hexane(4mL) and KOH(2mL) and extracted twice with hexane(3mL). The adipose was removed by gel permeation chromatography (26 g SX-3 GPC, 300 mm \times 25 mm) followed by concentrated to 1mL by rotary evaporator. After cleaned up by a multilayer column packing with 0.1g activated silica, 0.5 g silica/ H_2SO_4 (44%, w/w), and topped with 1.5 g Na_2SO_4 , PBT, HBB, PBEB, pTBX, PBBz and DP were eluted by hexane-methylene chloride (1:1, v/v, 12 mL) and the samples were reduced to 100 μL under a gentle nitrogen stream before analyzed by GC-NCI-MS.

To detect PBT, HBB, PBEB, pTBX, PBBz and DP, the GC used a DB-5MS chromatographic column (30 m \times 0.25 mm i.d., 0.1 μm film thickness, Agilent J&W GC Columns). Helium was used as the carrier gas at a flow rate of 1.0 mL \cdot min⁻¹, and all the samples were injected in splitless mode in 1 μL . The temperature of both MS quadrupole detector and MS source was 150 $^\circ\text{C}$ and methane was used as the chemical ionization gas. The oven

temperature was initiated at 100°C (held for 3min) and increased to 300°C at a rate of 4°C • min⁻¹, and held for 12min.

A method blank sample was analyzed with every batch of samples. The analyte concentrations in the blank samples were satisfactory for all the analytes (<5% of the typical concentration in samples). The method limit of detection (LOD) for NBFrs range from 0.00057-0.013 ng/mL, and the LOD for DP was 0.0067 ng/mL. The recoveries of ¹³C₁₂-BDE-139, ¹³C₆-HBB, ¹³C₁₀-syn-DP in breast milk samples were 112%±13%, 82%±27%, 113%±12%, respectively. The recoveries of PBT, PBEB, pTBX and PBBz in blank samples were 49%±9.8%, 102%±5.8%, 42%±0.85% and 51%±7.6%, respectively.

Results and discussion:

The comparison of concentrations in 2007 and in 2012 is given in Fig. 2. Among the NBFrs, the level of PBBz was the highest, with the median concentration of 0.016 ng/mL in 2007 and 0.014 ng/mL in 2012. The concentrations of NBFrs except pTBX were decreased in 2012 and it's worth noting that pTBX was detected in 2012 while none was detected in 2007. Therefore, we need to pay more attention to the future contamination trends of pTBX.

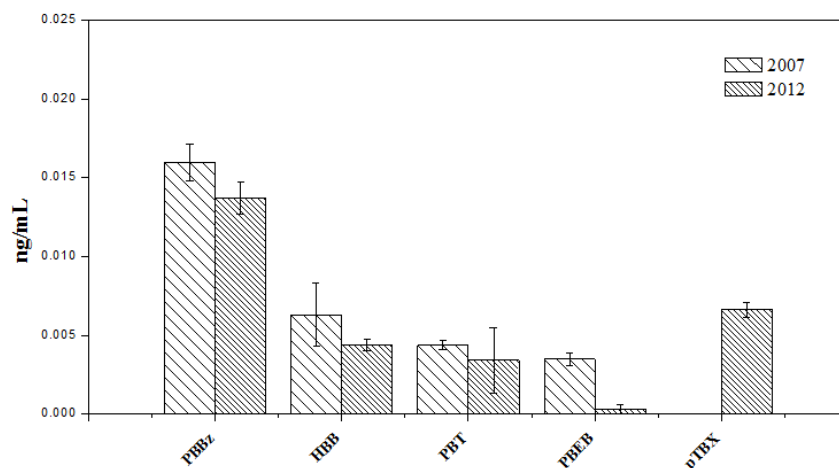


Fig. 2 The concentrations of NBFrs in breast milk in 2007 and 2012

To date, only several researches have reported the NBFrs in human body, and it is the first time to report concentration of PBT, PBEB and pTBX in breast milk⁴. A research on Japanese mothers' breast milk investigated HBB, and the concentration was higher than this study⁵. In the adipose tissue of Japanese, it was found that PBBz was the major metabolites of HBB¹.

DP in breast milk wasn't detectable in any samples in this study. However, DP was detected in 21-40 years old females serum samples from the same area in our previous study, the mean concentration was 3.1 ng/g lipid, indicated that more researches on the transform of DP in human serum and breast milk were necessary⁶.

Acknowledgements:

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