Polybrominated diphenyl ethers on window surface films in Chinese trains

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of the brominated flame retardants (BFRs), which have been in large-scale production and use to prevent the spread of fire. PBDE are commonly used in plastics, foams, textiles, electronic parts and other materials for decades. In China, 10 000 tons of BFRs were produced in 2000, and the demand for BFRs is increasing every year at the rate of 8% [1]. Deca-BDE has been produced in more than 20 enterprises since 1980s and became the dominant BFRs product, with 30 000 tons used in 2005 [2] and 15 000 tons in 2006 [3]. PBDEs are toxic, and harmful to ecosystem and human health. In May 2009, tetra-, penta-, hexa-, and hepta-BDEs were added as new members of persistent organic pollutants (POPs) in the Stockholm Convention at the fourth Conference of the Parties (COP-4) [4].

Due to widespread usage, PBDEs have spread out in almost every matrix in the world, including air, water, soil, and biota. The accumulations of these two chemicals have also been found on the window surface films. The study of PBDEs on building films in home, office, and working place were carried out for decades [5-10], but PBDEs on surface films in vehicles are lacking. This work is to study PBDEs on the window surface films in rail trains in China.

Materials and methods

Seven rail trains (2 D-type, 3 K-type, 1 T-type, and 1 Z-type) from 7 cities to Shanghai China were chosen in 2012. The information of these 7 train routs is shown in **Figure 1**. The train window film sampling method was modified from a previous study [5]. Briefly, samples were collected by Kimwipes (Kimtech science; 11×21 cm^2). Prior to sampling, Kimwipes were Soxhlet extracted with dichloromethane (DCM) for 24 hours, vacuum dried, wrapped in pre-baked aluminum foils and stored in glass jars. Train window film samples with an area of approximately 0.16 m^2 (0.4 m × 0.4 m) were collected within 10 cm of the window edge to minimize contamination from exterior caulking, paints, etc. Field blank preparation was identical to the sample preparation, and during "sampling process" these blanks did not contact window surfaces but exposed to air in the same time as the real sampling. All samples were immediately put back to aluminum foils and stored in glass jars and sent back to the International Joint Research Center for Persistent Toxic Substances (IJRC-PTS) Laboratory in Shanghai Maritime University for further process.

The details on the sample treatment and analysis are similar to the treatment of the particle matters collected using GFFs in high volume air samplers and the details can be found in our previous study [11-12]. Briefly, after surrogate (CB-155) added, all the film samples were Soxhlet extracted with a mixture of acetone and hexane (1: 1, V: V) for 24 h with 4-6 extraction circles per hour, respectively. Then the extracts were purified by silica gel column, and the final extract volume was concentrated to 1.0 mL by evaporation and a gentle stream of nitrogen. The internal standard (BDE-71) was applied for quantization before analysis to correct matrix effects.

Field blanks and procedure blanks were performed during the sampling and sample treatment to check any background contaminations. The major contaminant observed in blanks was BDE-209 and -47, with concentrations less than 10% of the concentration in real samples. For the surrogate, the average recoveries were 70.5±9.33% for CB-155. All the reported concentrations were not blank corrected. Method detection limits (MDLs) were calculated by conducting a replicate spike study (n = 7), which were in the range of 0.3-2.7 pg for PBDEs (without BDE-209), and 340 pg for BDE 209.

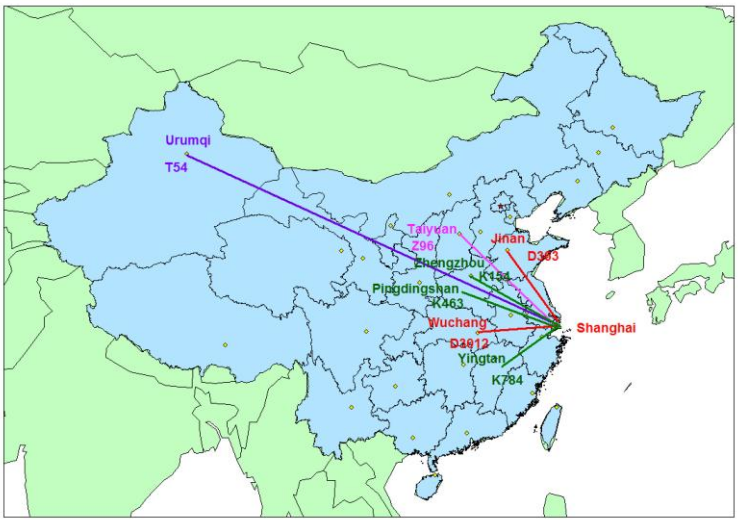

Figure 1. The map of 7 train routs in China.

Results and discussion

Window film samples from the 7 trains were analyzed for 13 PBDEs (BDE 17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183 and 209). The concentrations of the 13 PBDE congeners in the train window films are summarized in **Figure 2**. The train with highest concentration of all 13 PBDEs was Z96 (4200 ng/m^2), followed by D363 (1090 ng/m^2), and K784 (625 ng/m^2). The lowest PBDE concentration (67.4 ng/m^2) was in Train T54. Among 13 PBDEs, BDE 209 was the most abundant congener with a geometric mean (GM) of 352 ng/m^2 (range: 57.2–4200 ng/m^2), followed by BDE-47 with a GM of 3.75 ng/m^2 (0.25–101 ng/m^2), and BDE-28 with a GM of 1.86 ng/m^2 (BDL–89.1 ng/m^2). The values of GM (range) were 365 ng/m^2 (66.7–4200 ng/m^2) for Σ_{13}PBDEs and 13.1 ng/m^2 (BDL–283 ng/m^2) for Σ_{12}PBDEs. Σ_{13}PBDEs refers to the sum of all 13 targeted PBDE congeners, whereas Σ_{12}PBDEs refers to the sum of all targeted PBDE congeners except for BDE-209.

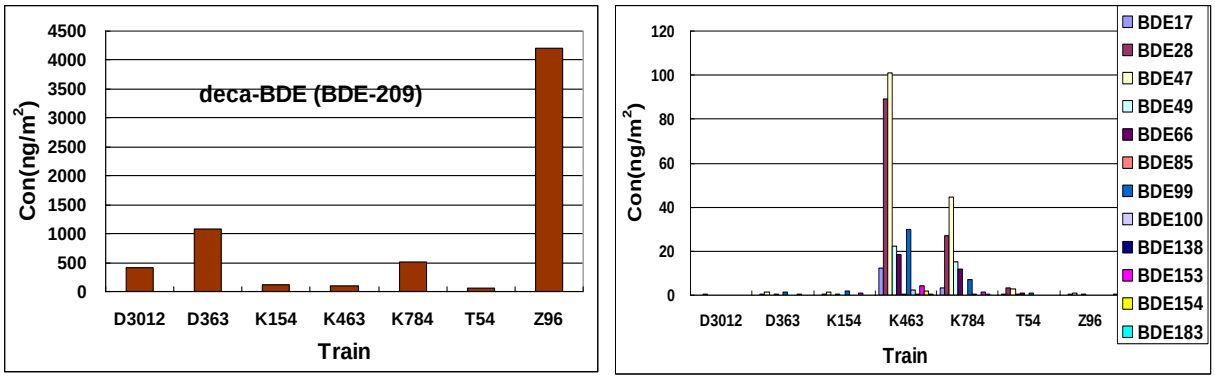

Figure 2. Concentrations of BDE-209 (left panel) and other 12 PBDE congeners (Σ_{12}PBDEs) (right panel) on window films in different Chinese trains.

To our knowledge, there has not been any data published regarding the PBDEs on the window film in rail train to which we can compare our data. It will be useful, however, to compare our data to those on window films in buildings, including residences and offices. **Table 1** presents a comparison of total PBDE film concentrations of our data with those obtained from interior windows in buildings published. Total PBDE concentrations on train window films from our study are more than 10 times higher than those reported for interior residential and office windows in Canada [6] and Turkey [10], comparable to the data on interior urban building window films in Hong Kong, China [9], half of the data obtained at the electronics recycling facility in

Toronto, Canada [6], and less than those on interior urban building window films in Guangzhou, China by ~3.5 times [9].

Table 1. Geometric mean of total PBDEs and the composition of BDE-209 in window films in Different Environments.

Matrix	Sampling Places	PBDE congeners targeted	ΣPBDE (ng/m^2)	BDE-209 (%)	Source
Train window	China	BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, 209	365	96.4	The present study
Building window	Guangzhou, China	BDE-28, -47, -99, -100, -153, -154, -183, -209	1300	97.0	[9]
Building window	Hongkong, China	BDE-28, -47, -99, -100, -153, -154, -183, -209	426	98.94	[9]
Building window	Urban, Canada	41 PBDE congeners	34.4	53	[6]
Building window	Rural, Canada	41 PBDE congeners	10.3	53	[6]
Building window	electronics recycling facility, Canada	41 PBDE congeners	755	53	[6]
Building window	Urban, Turkey	BDE-28, -47, -99, -100, -153, -154, -209	40	31.84	[10]
Car windshield	USA	BDE-28, -47, -66, -77, -85, -99, -100, -138, -153, -154, -209	365	1.6	[7]

The composition profiles of PBDE homologues on window films in different Chinese trains are given in **Figure 3**. It is worthwhile to notice that the concentration of BDE-209 was lower while other PBDE homologues were higher in K- and T-type trains than other D- and Z-type trains. This could possibly be explained by the fact that the K- and T-type trains are older style, using older furniture than other types of train. In China, commercial Penta-BDE was used before 1990s, after which, commercial Deca-BDE was used.

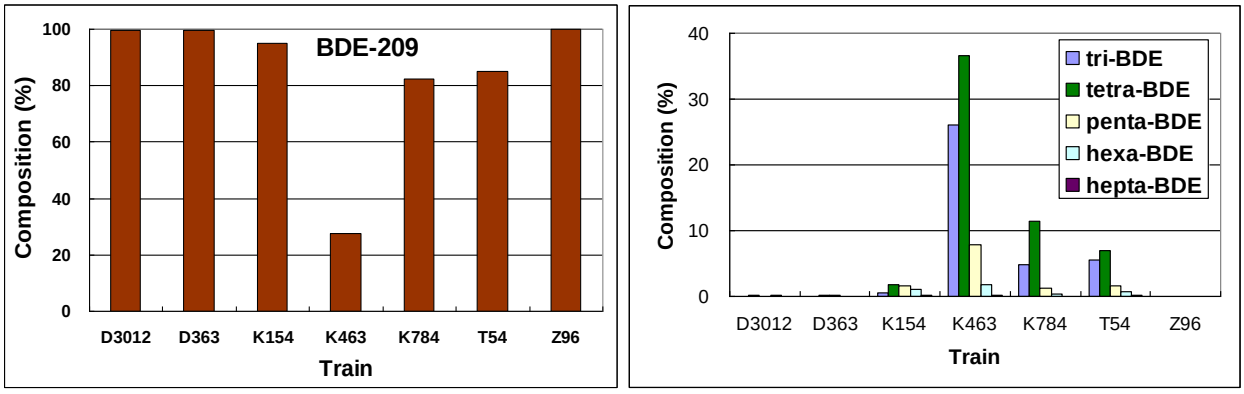

Figure 3. The composition profiles of PBDE homologues on window films in different Chinese trains. The left panel is for deca-BDE (BDE-209), and the right panel for other homologues.

Acknowledgements

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