Environmental Science and Pollution Research (2019) 26:12171–12180
https://doi.org/10.1007/s11356-019-04558-8

RESEARCH ARTICLE

Pine needles as biomonitors of polybrominated diphenyl ethers and emerging flame retardants in the atmosphere of Shanghai, China: occurrence, spatial distributions, and possible sources

Hao-Hao Jia[1,2] · Xue-Tong Wang[1,2] · Hang-Xin Cheng[3,4] · Ying Zhou[1,2] · Rui Fu[1,2]

Received: 27 September 2018 / Accepted: 13 February 2019 / Published online: 4 March 2019

Abstract

In this study, pine needles were used as biomonitors to investigate the levels, spatial distributions, and possible sources of polybrominated diphenyl ethers (PBDEs) and four emerging halogenated flame retardants (HFRs) in the atmosphere of Shanghai, China. The four emerging HFRs were hexabromocyclododecane (HBCD), decabromodiphenylethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), and dechlorane plus (DP), with the first 3 HFRs being non-polybrominated diphenyl ether brominated flame retardants (non-PBDE BFRs). The total concentrations ranged from 3.71 to 4020 ng g^{-1} dry weight (dw) for 52 PBDE congeners (Σ_{52}BDEs), < MDL (method detection limit) to 15.2 ng g^{-1} dw for three non-PBDE BFRs ($\Sigma_3$non-PBDE BFRs), and 0.815 to 1090 pg g^{-1} dw for two DP isomers (ΣDP), respectively. High levels of PBDEs, three non-PBDE BFRs, and DP were found in pine needles from suburbs and Pudong, which was a consequence of industrial activities. The fraction of anti-DP isomer (f_{anti}) in pine needles ranged from 0.515 to 0.939 with a mean value of 0.721, and most of the f_{anti} values were consistent with those of technical DP formulations. Principal component analysis-multiple linear regression (PCA-MLR) model identified four sources of PBDEs in pine needles with the quantified contributions: degradation of technical PBDE formulations (49.5%), technical deca-BDE (6.9%), technical penta-BDE (25.1%), and technical octa-BDE (18.5%). These findings are expected to help understand the pollution level, fate, and possible sources of HFRs in the atmosphere of Shanghai and provide a basis for air pollution control and management in Shanghai.

Keywords PBDEs · Emerging halogenated flame retardants · Atmosphere · Pine needles · PCA-MLR model · Sources

Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of halogenated flame retardants (HFRs) that are widely used in commercial products such as furniture, textiles, plastics, electrical and electronic appliances, building materials, and vehicles (UNEP 2015). PBDEs have been produced and marketed as three technical formulations: penta-, octa-, and deca-BDE. The global production of technical PBDE formulations from 1970 to 2005 were estimated at around 91,000–

Responsible editor: Constantini Samara

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11356-019-04558-8) contains supplementary material, which is available to authorized users.

✉ Xue-Tong Wang
wangxt@shu.edu.cn

✉ Hang-Xin Cheng
hangxin@vip.sina.com

[1] Institute of Environmental Pollution and Health, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China

[2] Key Laboratory of Organic Compound Pollution Control Engineering, Ministry of Education, Shanghai University, Shanghai 200444, China

[3] Key Laboratory of Geochemical Cycling of Carbon and Mercury in the Earth's Critical Zone, Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences, Langfang 065000, China

[4] Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geoscience, Langfang 065000, China

105,000 t for penta-BDE; 102,700–118,500 t for octa-BDE; and 1,100,000–1,250,000 t for deca-BDE, respectively (UNEP 2015). In China, the dominant technical PBDE product is deca-BDE formulation, with a production of 30,000 t in 2005 (Zou et al. 2007; Li et al. 2015). Because of their massive production, extensive use, and tendency to bioaccumulate, the concerns for potential toxicities of PBDEs to ecosystem and human beings have been increased (UNEP 2015, 2017). Animal studies suggested that PBDEs can disrupt endocrine functions and adversely affect nervous and reproductive systems (Linares et al. 2015; Lyche et al. 2015). Due to their persistence, bioaccumulation, potential toxicities, and long-range transport potential, the production and usage of penta-, octa-, and deca-BDE formulations have been banned by the Stockholm Convention (UNEP 2015, 2017).

Since PBDEs were phased out worldwide, several non-polybrominated diphenyl ether brominated flame retardants (non-PBDE BFRs), including hexabromocyclododecanes (HBCD), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), and decabromodiphenyl ethane (DBDPE) have been introduced to the market. The production of HBCD and DBDPE in China in 2006 were about 4500 t and 12,000 t, respectively (Xiao 2006). These non-PBDE BFRs also showed similar characteristics to PBDEs in the aspect of persistence, bioaccumulation, and long-range transport potential (Covaci et al. 2011; Kuramochi et al. 2014). HBCD and DBDPE can induce hepatic damage and alter thyroid hormone homeostasis in mice, posing a potential health risk (Darnerud 2003; Sun et al. 2018). Dechlorane plus (DP) is an emerging chlorinated flame retardant used as substitute to deca-BDE formulation. The annual production of DP was about 300 t in China since 2005 (Wang et al. 2010). DP has a similar structure to the mirex, and its conformation contains two isomers, i.e., syn-DP and anti-DP (Zeng et al. 2014). Toxicological experiments demonstrated that DP can cause hepatotoxicity in mice (Wu et al. 2012a) and neurodevelopmental toxicity in zebrafish (Chen et al. 2017). HBCD, DBDPE, BTBPE, and DP have been found in China in various environmental media, such as air, dust, soil, sediment, plant, biota, and human samples (Covaci et al. 2011; Tian et al. 2012; Wu et al. 2012b; Li et al. 2015; Shi et al. 2016, 2018; Wang et al. 2016a; Wong et al. 2017; Zhu et al. 2017a; Cao et al. 2018). Therefore, it is essential to investigate the occurrence, sources, and environmental risk of these HFR pollutants.

Atmosphere-plant exchange has been considered as an important transfer pathway for semivolatile organic compounds (SVOCs) from atmospheric environment to terrestrial ecosystem. Pine needles were excellent in trapping SVOCs due to their high specific surface area and lipid content. Previous studies successfully used pine needles as biomonitors to investigate atmospheric SVOCs, such as polycyclic aromatic hydrocarbons (Sun et al. 2010; Odabasi et al. 2015, 2016), polychlorinated biphenyls (Tian et al. 2008; Odabasi et al. 2015, 2016), polychlorinated naphthalenes (Odabasi et al. 2015, 2016), perfluorinated alkylated substances (Chropenova et al. 2016a), organochlorine pesticides (Ratola et al. 2014), short- and medium-chain chlorinated paraffins (Wang et al. 2016b), and PBDEs (Ratola et al. 2011). However, the comprehensive researches on atmospheric PBDEs, HBCD, DBDPE, BTBPE, and DP using pine needles are not available yet.

Located in the eastern China, Shanghai, is an international metropolis and also a large production center for textiles, rubbers, plastics, electrical and electronic appliances, and chemical industries (SMSB and SONBS 2016). With the rapid increase of human and industrial activities in the past decades, Shanghai is facing various environmental pollution problems. Previous studies on atmospheric pollution of HFRs in Shanghai were mainly focused on PBDEs in outdoor air (Yu et al. 2011; Li et al. 2012; Han et al. 2016; Liu et al. 2016; Lyu et al. 2016; Zhu et al. 2017b; Su et al. 2018). Only a few studies about emerging HFRs including HBCD, DBDPE, BTBPE, and DP in outdoor air were reported in Shanghai (Yu et al. 2011; Li et al. 2012; Liu et al. 2016). Moreover, detailed data about the pollution of PBDEs, HBCD, DBDPE, BTBPE, and DP in plant from Shanghai are not available to date. Pine needles were employed in Shanghai to investigate these atmospheric HFRs for the first time. The objectives in this study were to investigate the levels and spatial distributions of PBDEs, three non-PBDE BFRs including HBCD, DBDPE, and BTBPE, and DP in pine needles from Shanghai, to determine the compositional patterns of PBDEs and isomer ratios of DP, and to identify and quantitatively assess source contributions to the PBDE burden in pine needles.

Materials and methods

Sampling site and sample collection

The sampling sites, collection, and pretreatment of pine needles from Shanghai were described elsewhere (Wang et al. 2016b). In brief, the whole sampling region was divided into four units: Puxi (old industrial urban area), Pudong (new industrial urban area), suburbs (new industrial and agricultural mixed area), and Chongming Island (ecological protection area). The locations of sampling sites are shown in Fig. S1. One hundred thirty-one pine needle samples were taken from Puxi (1–36), Pudong (37–46), suburbs (47–106), and Chongming Island (107–131) in April 2015. For each sampling site, pine needles were collected from three to five trees at an equivalent height of ~ 1.6 m above ground, pooled together to form one composite sample, and subsequently wrapped in aluminum foil, sealed into zipper bags. Prior to chemical

analysis, pine needles were rinsed sequentially with tap water and distilled water, air-dried in an individual room, and ground into powder using a high-speed pulverizer, then kept at − 20 °C until extraction.

Chemicals and materials

PBDEs calibration standards including BDE-AAP-A-15X (containing 39 PBDE congeners: BDE1–3, 7, 8, 10–13, 15, 17, 25, 28, 30, 32, 33, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153–155, 166, 181, 183, and 190) and BDE-OND (containing BDE 194–209) were obtained from AccuStandard Inc. (New Haven, CT, USA) and Wellington Laboratories Inc. (Guelph, Ontario, Canada), respectively. Standard solutions of HBCD, BTBPE, and DBDPE were purchased from AccuStandard Inc. (New Haven, CT, USA). Individual solutions of anti- and syn-DP were supplied by Wellington Laboratories Inc. (Guelph, Ontario, Canada). $^{13}C_{12}$-BDE139 and $^{13}C_{12}$-BDE209 (surrogate standards) and $^{13}C_{12}$-PCB138 (injection internal standard) were all obtained from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). Silica gel (100–200 mesh) (Qingdao Haiyang Chemical Co., Shandong, China), neutral alumina (100–200 mesh) (Sinopharm Chemical Reagent Co., Shanghai, China) were activated at 130 °C for 16 h, then neutral alumina was deactivated by Milli-Q water (6%, *w*/*w*), and acid silica gel (30%, *w*/*w*) was prepared by mixing 100 g of silica gel with 44 g of concentrated sulfuric acid, and kept in a desiccator for later use. Granular anhydrous sodium sulfate (Sinopharm Chemical Reagent Co., Shanghai, China) was baked at 450 °C for 5 h before use. All organic solvents were of analytical grade and redistilled using a glass system prior to use.

Extraction, cleanup, and instrumental analysis

The procedures employed in extraction, cleanup, and analysis of PBDEs, HBCD, BTBPE, DBDPE, and DP in pine needles were described previously (Wang et al. 2015). Briefly, about 5 g of pulverized pine needles were mixed with 20 g of anhydrous Na_2SO_4, spiked with 6 ng of $^{13}C_{12}$-BDE139 and 15 ng of $^{13}C_{12}$-BDE209, and then Soxhlet extracted with 120 mL of 1:1 (*v*/*v*) mixed solvent of *n*-hexane and acetone for 24 h. Ten percent of the extract was used to determine the lipid content of pine needles. The remaining extract (90%) was further purified in a deactivated neutral alumina/acid silica gel column, then concentrated by a K-D concentrator, and reduced to almost dryness under a gentle N_2 stream, and finally redissolved in 50 μL of isooctane containing 6 ng of $^{13}C_{12}$-PCB138 prior to GC/MS analysis.

Analysis of PBDEs, HBCD, BTBPE, DBDPE, and DP were performed on an Agilent 6890 N gas chromatograph-5975 mass selective detector system in the electron capture negative ionization mode (GC-ECNI/MS). The target compounds were separated using two fused-silica capillary columns (J&W Scientific, Folsom, USA): DB-5 (30 m × 0.25 mm i.d., 0.25-μm film thickness) for di- to hepta-BDEs, HBCD, BTBPE and DP, and DB-5HT (15 m × 0.25 mm i.d., 0.25-μm film thickness) for octa- to deca-BDEs and DBDPE. The compounds were monitored at *m/z* 79 and 81 for di- through hepta-BDE, HBCD, DBDPE, and BTBPE; *m/z* of 79, 81, 407, 409, 486, and 488 for octa-BDE; *m/z* of 79, 81, 486, and 488 for nona- and deca-BDE; and *m/z* 654 and 652 for DP isomers. PBDEs, HBCD, BTBPE, DBDPE, and DP were quantified using 5-point calibration curves ($r^2 > 0.99$). BDE1–3 were not analyzed in this work due to their low sensitivity in GC-ECNI/MS.

Quality assurance and quality control

Strict quality assurance and control measures were performed to ensure the identification and quantification of the target analytes. Glassware were heated at 450 °C for 12 h to minimize the risk of contamination before use. One procedural blank, one solvent blank, one spike blank, and duplicate samples were processed within every batch of 12 samples to monitor background levels and possible carryover between samples. The spike blanks were prepared using anhydrous Na_2SO_4 spiked with known concentrations of target analytes to monitor the precision and accuracy of the analytical method. Target compounds in procedural blanks were below the method detection limits (MDLs). The variation coefficients of target compounds in duplicate samples were less than 15%. Method recoveries were determined by analyzing clean pine needles (uncontaminated pine needles collected from a site away from anthropogenic activities) spiked with standard solutions of PBDEs, HBCD, BTBPE, DBDPE, and anti- and syn-DP. The recoveries of target compounds spiked in pine needles ranged from 81.5% to 104%, and the relative standard deviations ($n = 7$) were less than 15%. The recoveries of $^{13}C_{12}$-BDE139 and $^{13}C_{12}$-BDE209 spiked in pine needles varied from 86.6% to 98.5%. The MDLs of target compounds were defined as the mean blank values plus three times the standard deviations. The MDLs of di- to nona-BDEs, BDE209, HBCD, DBDPE, BTBPE, and anti- and syn-DP were 0.01–0.02 ng g^{-1} dw, 0.06 ng g^{-1} dw, 0.02 ng g^{-1} dw, 0.06 ng g^{-1} dw, 0.02 ng g^{-1} dw, 0.2 pg g^{-1} dw, and 0.2 pg g^{-1} dw, respectively. Lipid contents of pine needles were determined by the gravimetric method. All concentrations of target compounds in pine needles were expressed on a dry weight basis without recovery correction.

Statistical analysis

Statistical analyses, including descriptive statistics, Shapiro-Wilk test, Spearman correlation analysis, hierarchical cluster analysis (HCA), and principal component analysis (PCA) were performed using IBM SPSS statistics software version 19 (SPSS Inc., USA). PCA was conducted using the standardized PBDE concentration dataset by factor extraction after varimax rotation. Values of HFR concentrations below MDLs were considered as zero for statistical analysis. Extreme and outlier values of PBDEs, three non-PBDE BFRs and DP concentrations were checked with box-and-whisker plot procedure. Spatial distributions of these HFRs in pine needles were depicted using Surfer 8.0 (Golden Software, Inc., USA).

Results and discussion

Levels of HFRs in pine needles

Descriptive statistics for the concentrations of individual PBDE congeners, sum of 51 PBDE congeners without BDE209 (Σ_{51}BDEs), sum of 52 PBDE congeners (Σ_{52}BDEs), individual non-PBDE BFRs, sum of 3 non-PBDE BFRs ($\Sigma_3$non-PBDE BFRs), individual DP isomers, and sum of 2 DP isomers (ΣDP) in pine needles from Shanghai are given in Table 1. PBDEs, three non-PBDE BFRs, and DP were detected in pine needles at most sampling sites, indicating that these HFRs are widespread contaminants in the atmospheric environment of Shanghai. Obviously, PBDEs were the main HFRs in pine needles from Shanghai.

Table 1 Concentrations of PBDEs, three non-PBDE BFRs (ng g^{-1} dw), and DP (pg g^{-1} dw) in pine needles from Shanghai

	Min	Max	Mean	Median	SD	DF%
BDE7	<MDL	114	16.7	5.16	24.4	76.3
BDE15	<MDL	3360	119	28.9	322	83.2
BDE30	<MDL	351	16.6	<MDL	51.9	42.0
BDE75	<MDL	273	21.9	1.74	41.4	63.4
BDE49/71	<MDL	213	19.6	5.43	30.8	78.6
BDE47	<MDL	109	9.87	0.758	21.0	61.1
BDE66	<MDL	414	20.9	2.46	58.6	77.9
BDE100	<MDL	55.5	6.26	0.396	10.7	63.4
BDE99	<MDL	408	23.2	0.661	47.6	69.5
BDE154	<MDL	32.6	0.933	<MDL	3.34	39.7
BDE153	<MDL	29.6	2.31	0.032	4.52	53.4
BDE138/166	<MDL	427	17.7	0.099	52.0	64.9
BDE183	<MDL	3.55	0.413	0.100	0.718	64.9
BDE201	<MDL	12.4	0.272	<MDL	1.14	40.5
BDE204/197	<MDL	5.02	0.297	0.119	0.609	77.1
BDE208	<MDL	6.10	0.649	0.141	1.12	51.9
BDE207	<MDL	6.51	0.856	0.447	1.23	76.3
BDE206	<MDL	11.6	1.15	0.343	1.91	62.6
BDE-209	<MDL	324	13.9	1.69	38.2	71.0
Σ_{51}BDEs	3.20	3990	363	235	495	100
Σ_{52}BDEs	3.71	4020	377	237	38.2	100
HBCD	<MDL	11.4	0.957	0.040	2.12	51.9
BTBPE	<MDL	12.5	0.145	<MDL	0.366	48.9
DBDPE	<MDL	2.81	0.862	0.074	2.24	55.7
$\Sigma_3$non-PBDE BFRs	<MDL	15.2	1.96	0.714	3.50	92.4
anti-DP	0.647	856	103	64.4	131	100
syn-DP	0.154	237	33.8	22.3	38.8	100
ΣDP	0.815	1090	137	86.3	169	100
f_{anti}	0.515	0.939	0.721	0.733	0.088	
Lipid (%)	3.21	11.4	6.54	6.35	1.35	

SD standard deviation; *DF* detection frequencies; *CV* coefficient of variation; *<MDL* below the method detection limit; *$\Sigma_3$non-PBDE BFRs* the sum of HBCD, BTBPE, DBDPE analyzed in sample; *f_{anti}* anti-DP/(anti- + syn-DP)

Most of the PBDE congeners were frequently detected in pine needle samples, with the detection frequencies of 39.7%–83.2% for 52 PBDE congeners. The concentrations varied from 3.71 to 4020 ng g^{-1} dry weight (dw) with a mean value of 377 ng g^{-1} dw for Σ_{52}BDEs, of which Σ_{51}BDEs concentrations ranged from 3.20 to 3990 ng g^{-1} dw and BDE209 concentrations varied from <MDL (method detection limit) to 324 ng g^{-1} dw, with mean values of 363 and 13.9 ng g^{-1} dw, respectively. The compositional profiles of PBDE homologues in pine needles from Shanghai are shown in Table S1. Di-, tri-, tetra-, and penta-BDE had the higher relative contributions to Σ_{52}BDEs in pine needles, with median values of 40.6%, 14.0%, 22.1%, and 9.96%, respectively. As presented in Table 2, some pairs of the lower brominated PBDE homologues exhibited significant correlation ($p < 0.01$), which implied that they might share common sources and behave similarly in the environment. Moreover, neither the concentrations of individual PBDE homologues nor Σ_{52}BDEs were significantly correlated with the lipid content of pine needles ($p > 0.05$), indicating that lipid contents had little influence on accumulation of PBDEs in pine needles in the studied area. Similar results were also observed in pine needles from Aliaga and Iskenderun, Turkey (Odabasi et al. 2015, 2016).

As for the three non-PBDE BFRs, the detection frequencies were 51.9% for HBCD, 48.9% for BTBPE, and 55.7% for DBDPE, respectively. The total concentrations of the three non-PBDE BFRs in pine needles ranged from <MDL to 15.2 ng g^{-1} dw, with a mean value of 1.96 ng g^{-1} dw. For individual non-PBDE BFRs, the concentrations ranged from <MDL to 11.4 ng g^{-1} dw for HBCD (mean = 0.957 ng g^{-1} dw), from <MDL to 2.81 ng g^{-1} dw for DBDPE (mean = 0.862 ng g^{-1} dw), and from <MDL to 12.5 ng g^{-1} dw for BTBPE (mean = 0.145 ng g^{-1} dw), respectively. HBCD and DBDPE were the major components of the three non-PBDE BFRs, accounting for, on average, 38.9% and 37.8% of $\Sigma_3$non-PBDE BFRs, respectively (Table S2). Compared with the lower detection frequencies of three non-PBDE BFRs, both anti- and syn-DP isomers had the higher detection frequencies of 100%. The concentrations varied from 0.815 to 1090 pg g^{-1} dw with a mean value of 137 pg g^{-1} dw for ΣDP, of which anti-DP concentrations ranged from 0.647 to 856 pg g^{-1} dw and syn-DP concentrations varied from 0.154 to 237 pg g^{-1} dw, with mean values of 103 and 33.8 pg g^{-1} dw, respectively. Anti-DP was the predominant isomer for DP. The concentrations of $\Sigma_3$non-PBDE BFRs and ΣDP were also not significantly correlated with lipid contents of pine needles ($p > 0.05$) (Table S3), suggesting that the effect of lipid contents on accumulation of these non-PBDE BFRs and DP in pine needles was similar to that of PBDEs mentioned above.

Spatial distributions of HFRs in pine needles

The spatial distributions of Σ_{52}BDEs, $\Sigma_3$non-PBDE BFRs, and ΣDP in pine needles from Shanghai are depicted in Figs. 1 and 2, respectively. For the four sampling areas, the mean concentrations of Σ_{52}BDEs, $\Sigma_3$non-PBDE BFRs, and ΣDP in pine needles were 228 ng g^{-1} dw, 0.816 ng g^{-1} dw, and 92.2 pg g^{-1} dw in Puxi; 509 ng g^{-1} dw, 1.12 ng g^{-1} dw, and 251 pg g^{-1} dw in Pudong; 540 ng g^{-1} dw, 3.43 ng g^{-1} dw, and 183 pg g^{-1} dw in suburbs; and 148 ng g^{-1} dw, 0.445 ng g^{-1} dw, and 43.9 pg g^{-1} dw in Chongming, respectively (Fig. 3). The pollution levels for Σ_{52}BDEs, $\Sigma_3$non-PBDE BFRs, and ΣDP in pine needles in suburbs and Pudong were higher than those in Puxi and Chongming, which may be due to the fact that various industrial parks were mainly located in suburbs and Pudong. Spearman correlation analysis results showed that the concentrations of $\Sigma_3$non-PBDE BFRs and ΣDP were significantly correlated with those of Σ_{52}BDEs ($p < 0.01$) (Table S3), indicating that Σ_{52}BDEs, $\Sigma_3$non-PBDE BFRs, and ΣDP in pine needles

Table 2 Spearman's rank correlation coefficients among PBDE homologue concentrations in pine needles from Shanghai

	Lipid%	Di-BDE	Tri-BDE	Tetra-BDE	Penta-BDE	Hexa-BDE	Hepta-BDE	Octa-BDE	Nona-BDE	Deca-BDE
Di-BDE	0.056									
Tri-BDE	0.045	0.618**								
Tetra-BDE	0.093	0.730**	0.586**							
Penta-BDE	0.080	0.763**	0.658**	0.777**						
Hexa-BDE	0.082	0.479**	0.480**	0.491**	0.642**					
Hepta-BDE	−0.012	0.514**	0.491**	0.477**	0.505**	0.385**				
Octa-BDE	0.115	0.330**	0.263**	0.414**	0.439**	0.302**	0.332**			
Nona-BDE	0.147	0.642**	0.568**	0.615**	0.689**	0.456**	0.425**	0.530**		
Deca-BDE	0.107	0.446**	0.362**	0.402**	0.584**	0.427**	0.400**	0.308**	0.566**	
Σ52BDEs	0.121	0.893**	0.745**	0.846**	0.899**	0.631**	0.568**	0.432**	0.744**	0.558**

*$p < 0.05$; **$p < 0.01$

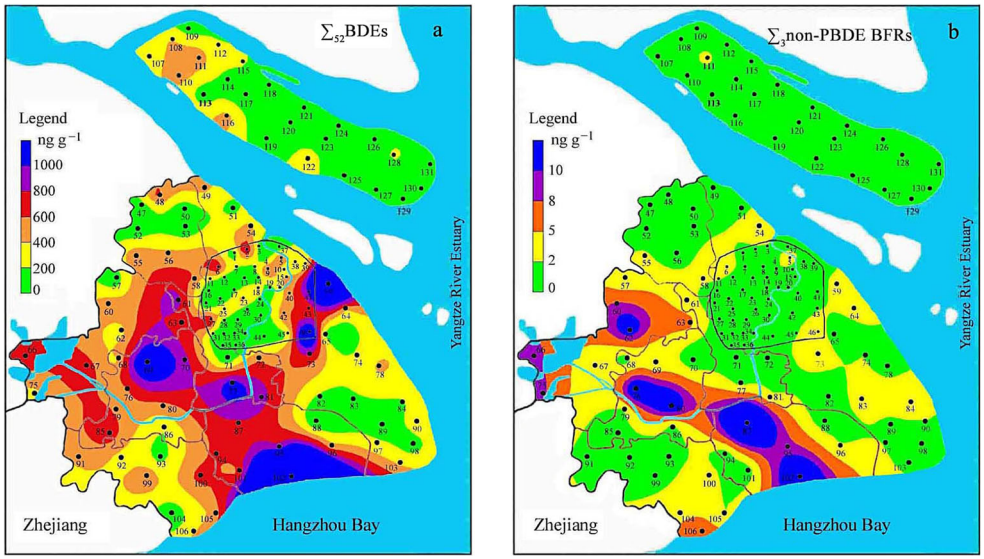

Fig. 1 Spatial distributions of Σ_{52}BDEs (**a**) and $\Sigma_3$non-PBDE BFRs (**b**) in pine needles from Shanghai

from Shanghai might share similar sources. Shapiro-Wilk test results indicated that none of the concentrations of Σ_{52}BDEs, $\Sigma_3$non-PBDE BFRs, and ΣDP in pine needles was normally distributed ($p < 0.05$). The frequency distribution histograms for the concentrations of Σ_{52}BDEs, $\Sigma_3$non-PBDE BFRs, and ΣDP in pine needles from Shanghai are shown in Fig. S2. The data displayed a positively skewed distribution, suggesting that the concentrations of Σ_{52}BDEs, $\Sigma_3$non-PBDE BFRs, and ΣDP were at lower levels in most pine needle samples.

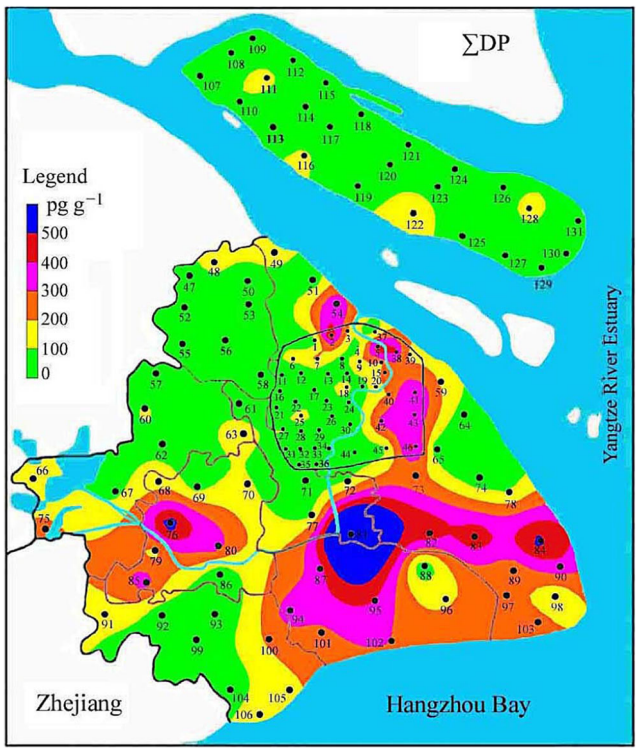

Fig. 2 Spatial distributions of ΣDP in pine needles from Shanghai

The higher concentrations of Σ_{52}BDEs were observed at sites 46, 69 (outliers), 102, and 59 (extremes) (Fig. 1a), which might be due to the reason that these sites were located closely to textile plants and plastics plants. The higher concentrations of $\Sigma_3$non-PBDE BFRs were observed at sites 63, 54 (outliers), 87, 102, 76, 80, 62, 66, 95, 75, 60, and 106 (extremes) (Fig. 1b). The non-PBDE BFRs at sites 63, 87, 102, 66, 75, 60, and 106 might be influenced by plastics plants, and non-PBDE BFRs at sites 76, 80, 62, and 95 may be related to electric wire and cable plants. Iron and steel plant might be the main source of non-PBDE BFRs at site 54. The higher concentrations of ΣDP were observed at sites 76, 84, 5, 2, 83, 82 (outliers), and 81 (extreme) (Fig. 2). DP at sites 76, 84, 83, 82, and 81 might be ascribed to electric wire and cable plants and plastics plants. Site 2 was located to a metal processing plant and site 5 was near an aquatic product processing plant, implying that metal processing plant and aquatic product processing plant might be the potential source of DP. Therefore, these findings indicated that industrial activities have a significant influence on the spatial distributions of these HFRs in pine needles from Shanghai.

Comparison with other studies

In order to assess the pollution levels of these HFRs in pine needles from Shanghai, the concentrations of HFRs in pine needles reported around the world are given in Table S4. The concentrations of ΣPBDEs in pine needles from Shanghai were comparable to those in mainland China (Zhu et al. 2018) and were higher than those in Ottawa, Canada (St-Amand et al. 2008); Spain inland (Ratola et al. 2011); Foia, Benlhevai, and Porto, Portugal (Silva et al. 2015); Aliaga and Iskenderun, Turkey (Odabasi et al. 2015, 2016); Little Fatra, Great Fatra, and Tatra mountains, Slovakia (Chropenova et al. 2016b); and an e-waste site and its neighboring rural

agricultural region in south China (Tian et al. 2012, 2013). The concentrations of BDE209 in pine needles from Shanghai were similar to those in mainland China (Zhu et al. 2018) and were higher than those measured in Ottawa, Canada (St-Amand et al. 2008), and Spain inland (Ratola et al. 2011), but lower than those reported in an e-waste site and its neighboring rural agricultural area in south China (Tian et al. 2012, 2013).

There were limited data to compare with the three non-PBDE BFRs and DP concentrations in pine needles in this study. The concentrations of HBCD in pine needles from Shanghai were much lower than those in the inner leaf of pine needles sampled in the vicinity of an expanded polystyrene material manufacturing plant in Tianjin, China, and pine needles from mainland China (Zhu et al. 2017a, 2018). The concentrations of DBDPE and BTBPE in pine needles from Shanghai were all lower than those in an e-waste site and its neighboring rural agricultural region in south China (Tian et al. 2012, 2013) and mainland China (Zhu et al. 2018), and the concentration of ΣDP in pine needles in Shanghai was much lower than that in an e-waste recycling site of Qingyuan, China (Chen et al. 2011). These results suggested that the concentrations were at higher level for PBDEs and lower level for the other HFRs in pine needles from Shanghai when compared with those in other regions around the world.

Compositional patterns of PBDEs and isomer ratios of DP

To better understand the compositional patterns of PBDEs in pine needles from Shanghai, hierarchical cluster analysis (HCA) was performed to group the similar pine needle samples based on the analysis for mass fractions of the nine PBDE homologues (di- to deca-BDE). Four major groups were obtained and visualized by dendrogram in Fig. S3, which distinguished 131 pine needle samples and 6 technical PBDE formulations (La Guardia et al. 2006) (Table S5). The relative abundances of the PBDE homologues in pine needles of each group are plotted in Fig. 4.

Group 1 included 48 pine needle samples, which was featured with di-, tri-, and tetra-BDE, accounting for 41.2%–86.8%, <MDL–23.6%, and 0.445%–30.6%, respectively. This group was not associated with any technical PBDE formulations. These lower brominated PBDEs might be the debromination products of higher brominated PBDEs under the effects of microbes or sunlight (Lee and He 2010; Wei et al. 2013; Stiborova et al. 2015). Group 2 was composed of three pine needle samples and was characterized by nona- and deca-BDE, accounting for 0.893%–12.1% and 35.6%–63.6%, respectively. This group was correlated with Saytex 102E, Bromkal 82-0DE and Bromkal 79-8DE. Therefore, the pine needle samples in this group might be influenced by technical octa- and deca-BDE formulations. Group 3 was comprised of 30 pine needle samples, which was predominated by di-, tri-, and octa-BDE, accounting for 5.99%–51.5%, 6.60%–64.7%, and 0.106%–33.6%, respectively. This group was linked with DE-79 formulation. Thus, the PBDEs in pine needle samples of this group might be ascribed to technical octa-BDE formulation. Group 4 consisted of 50 pine needle samples, which was dominated by di-, tetra-, and penta-BDE, accounting for <MDL–46.1%, 1.68%–59.6%, and 0.460%–51.4%, respectively. This group was related to technical DE-71 and Bromkal 70-5DE. Consequently, the PBDEs in pine needle samples of group 4 might be attributed to technical Penta-BDE formulations.

The fractions of anti-DP (f_{anti}: the ratio of anti-DP concentration to ΣDP concentration) in pine needle samples ranged from 0.515 to 0.939, with a mean value of 0.721. The frequency distribution of f_{anti} values showed that most of the f_{anti}

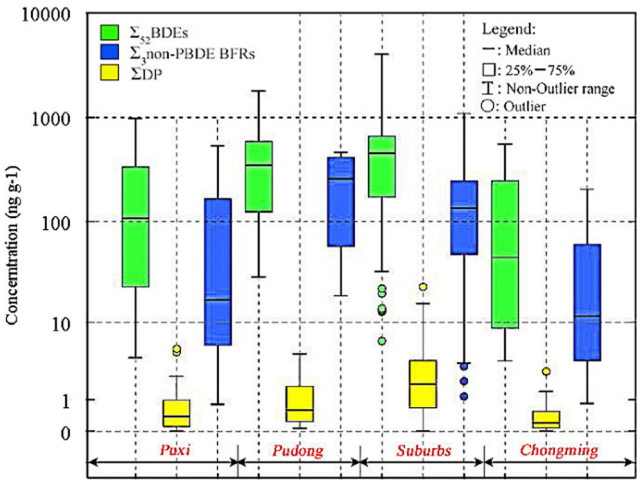

Fig. 3 Box-and-whisker plots of Σ_{52}BDEs, $\Sigma_3$non-PBDE BFRs and ΣDP concentrations in pine needles from different sampling areas in Shanghai (ΣDP concentration unit = pg g^{-1} dw)

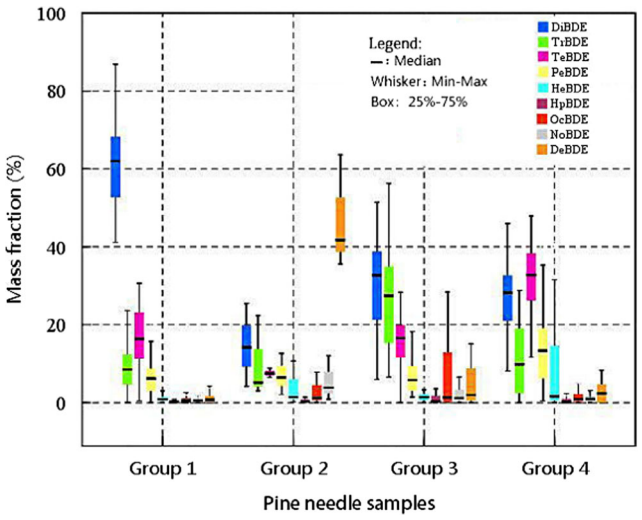

Fig. 4 Box-and-whisker plot of relative abundance of PBDE homologs in pine needles calculated for groups 1, 2, 3, and 4

values were consistent with those in technical DP formulations (0.65–0.80) (Hoh et al. 2006; Tomy et al. 2007; Ben et al. 2013) (Fig. S4). The f_{anti} values of DP in pine needles were also comparable to those in the ambient air of Shanghai (Yu et al. 2011), indicating that there was no obviously isomer-specific uptake of DP from the air by pine needles. The mean f_{anti} value of DP in pine needles in the studied area was higher than that in an e-waste recycling site in Qingyuan, South China (Chen et al. 2011), which might be ascribed to the vulnerability of anti-DP to photolytic or thermal degradation (Zheng et al. 2010; Wang et al. 2011).

Source identification and apportionment of PBDEs

Principal component analysis (PCA) was employed to further identify possible sources of PBDEs in pine needles from Shanghai, and identified four principal components (PCs) which aggregately explained 60% of the total variances of the original database. The fractions of variance explained by the four PCs were as follows: 28%, 12%, 11%, and 9%, respectively (Table 3). PC1 had the high loadings of the lower brominated PBDEs and might represent the degradation of technical PBDE formulations. PC2 was strongly linked with nona-BDE and BDE209, thus it was considered as the contribution of technical Deca-BDE. PC3 showed the high loadings of BDE47, 49/71, 99, and 138/166 and might reflect the contribution of technical penta-BDE. PC4 was highly correlated with BDE195, 196, and 197/204, indicating the contribution of technical octa-BDE.

Table 3 Principal component analysis on different PBDE homologues

	Components			
	PC1 (28%)	PC2 (12%)	PC3 (11%)	PC4 (9%)
BDE7	0.732	0.285	0.067	− 0.005
BDE15	0.529	− 0.149	0.108	0.227
BDE32	0.590	0.138	− 0.012	0.020
BDE17/25	0.653	0.144	0.140	− 0.122
BDE35	0.822	0.215	0.152	0.057
BDE37	0.832	0.173	0.084	− 0.066
BDE49/71	0.238	0.116	0.768	− 0.112
BDE47	− 0.070	0.145	0.763	− 0.061
BDE100	0.639	0.025	− 0.134	0.437
BDE99	0.297	− 0.068	0.772	0.318
BDE138/166	0.079	− 0.077	0.552	0.465
BDE183	0.393	0.141	0.255	0.116
BDE197/204	0.077	0.213	0.199	0.826
BDE195	0.084	0.180	− 0.276	0.699
BDE196	− 0.047	0.100	0.158	0.705
BDE208	0.107	0.735	0.166	0.046
BDE207	0.327	0.742	− 0.044	0.255
BDE206	0.134	0.875	0.150	0.009
BDE209	0.202	0.700	− 0.099	0.245

The principal component analysis with multiple linear regression (PCA-MLR) model was used to quantitatively assess the source contributions of PBDEs in pine needles. The detailed analysis procedure of PCA-MLR was described elsewhere (Larsen and Baker 2003). Briefly, the factor scores were regressed against the standard deviates of the total PBDEs. The resulting equation was expressed as:

$$Y = 0.709FS_1 + 0.099FS_2 + 0.359FS_3 + 0.265FS_4$$

where Y are the standard deviates of the total PBDEs, and FS_i are factor scores ($i = 1, 2, 3, 4$). The fitting plot showed that PCA-MLR model provided good correlations between the measured and predicted total PBDEs values ($R^2 = 0.711$, $p < 0.001$) (Fig. S5). Overall, the relative contributions of the four factors were 49.5% for F1 (degradation of technical PBDE formulations), 6.9% for F2 (technical Deca-BDE), 25.1% for F3 (technical Penta-BDE), and 18.5% for F4 (technical Octa-BDE). In addition, it should be noted that Deca-BDE formulation was the predominant technical PBDE product used in China (Zou et al. 2007) and deca-BDE has a lower propensity for volatilization than the lower brominated PBDEs (Environment Canada 2006). Therefore, the contributions of technical Deca-BDE formulation in pine needles might be lower than those in soil (Jiang et al. 2010) and sediment (Wang et al. 2015) reported in Shanghai.

Conclusions

PBDEs, three non-PBDE BFRs including HBCD, DBDPE and BTBPE, and DP in pine needles from Shanghai were investigated in the present work. These HFRs were widespread pollutants and PBDEs were predominant HFRs in pine needles. The concentrations were at higher level for PBDEs and lower level for the other HFRs in pine needles from Shanghai when compared with other studies in the world. Di-, tri-, tetra-, and penta-BDE were the dominant PBDE homologues in pine needles, which might be related to the degradation of higher brominated PBDEs. Most of the fractions of anti-DP in pine needles were close to those of DP formulations. Four sources of the PBDEs in pine needles were identified by PCA-MLR model, and the primary source was the degradation of technical PBDE formulations. These results obtained in this study can help to understand the pollution level, fate, and possible sources of atmospheric PBDEs, HBCD, DBDPE, BTBPE, and DP in Shanghai. The areas of pine needles with high level of PBDEs should be paid more attention and further research is needed to assess the potential risk of these HFRs to the ecosystem near pine trees.

Acknowledgments This work was financially supported by Program for Innovative Research Team in University (No. IRT13078).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

References

Ben YJ, Li XH, Yang YL, Li L, Di JP, Wang WY, Zhou RF, Xiao K, Zheng MY, Tian Y, Xu XB (2013) Dechlorane plus and its dechlorinated analogs from an e-waste recycling center in maternal serum and breast milk of women in Wenling, China. Environ Pollut 173:176–181

Cao XH, Lu YL, Zhang YQ, Khan K, Wang CC, Baninla Y (2018) An overview of hexabromocyclododecane (HBCDs) in environmental media with focus on their potential risk and management in China. Environ Pollut 236:283–295

Chen SJ, Tian M, Wang J, Shi T, Luo Y, Luo XJ, Mai BX (2011) Dechlorane plus (DP) in air and plants at an electronic waste (e-waste) site in South China. Environ Pollut 159:1290–1296

Chen XP, Dong QX, Chen YH, Zhang ZX, Huang CJ, Zhu YX, Zhang Y (2017) Effects of dechlorane plus exposure on axonal growth, musculature and motor behavior in embryo-larval zebrafish. Environ Pollut 224:7–15

Chropenova M, Karaskova P, Kallenborn R, Greguskova KE, Cupr P (2016a) Pine needles for screening of perfluorinated alkylated substances (PFASs) along ski tracks. Environ Sci Technol 50:9487–9496

Chropenova M, Greguskova EK, Karaskova P, Pribylova P, Kukucka P, Barakova D, Cupr P (2016b) Pine needles and pollen grains of Pinus mugo turra—a biomonitoring tool in high mountain habitats identifying environmental contamination. Ecol Indic 66:132–142

Covaci A, Harrad S, Abdallah MAE, Ali N, Law RJ, Herzke D, de Wit CA (2011) Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. Environ Int 37:532–556

Darnerud PO (2003) Toxic effects of brominated flame retardants in man and in wildlife. Environ Int 29:841–853

Environment Canada (2006) Canadian environmental Proctection act, 1999. Ecological screening assessment report on polybrominated diphenyl ethers (PBDEs). https://www.canada.ca/content/dam/eccc/migration/main/lcpe-cepa/documents/substances/pbde/sar_pbde-eng.pdf

Han WL, Fan T, Xu BH, Feng JL, Zhang G, Wu MH, Yu YX, Fu JM (2016) Passive sampling of polybrominated diphenyl ethers in indoor and outdoor air in Shanghai, China: seasonal variations, sources, and inhalation exposure. Environ Sci Pollut Res 23:5771–5781

Hoh E, Zhu LY, Hites RA (2006) Dechlorane plus, a chlorinated flame retardant, in the Great Lakes. Environ Sci Technol 40:1184–1189

Jiang YF, Wang XT, Zhu K, Wu MH, Sheng GY, Fu JM (2010) Occurrence, compositional profiles and possible sources of polybrominated diphenyl ethers in urban soils of Shanghai, China. Chemosphere 80:131–136

Kuramochi H, Takigami H, Scheringer M, Sakai SI (2014) Estimation of physicochemical properties of 52 non-PBDE brominated flame retardants and evaluation of their overall persistence and long-range transport potential. Sci Total Environ 491–492:108–117

La Guardia MJ, Hale RC, Harvey E (2006) Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ Sci Technol 40:6247–6254

Larsen RK, Baker JE (2003) Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. Environ Sci Technol 37:1873–1881

Lee LK, He JZ (2010) Reductive debromination of polybrominated diphenyl ethers by anaerobic bacteria from soils and sediments. Appl Environ Microbiol 76:794–802

Li HR, Mo LG, Yu ZQ, Sheng GY, Fu JM (2012) Levels, isomer profiles and chiral signatures of particle-bound hexabromocyclododecanes in ambient air around Shanghai, China. Environ Pollut 165:140–146

Li WL, Qi H, Ma WL, Liu LY, Zhang Z, Mohammed MOA, Song WW, Zhang ZF, Li YF (2015) Brominated flame retardants in Chinese air before and after the phase out of polybrominated diphenyl ethers. Atmos Environ 117:156–161

Linares V, Belles M, Domingo JL (2015) Human exposure to PBDE and critical evaluation of health hazards. Arch Toxicol 89:335–356

Liu D, Lin T, Shen KJ, Li J, Yu ZQ, Zhang G (2016) Occurrence and concentrations of halogenated flame retardants in the atmospheric fine particles in Chinese cities. Environ Sci Technol 50:9846–9854

Lyche JL, Rosseland C, Berge G, Polder A (2015) Human health risk associated with brominated flame-retardants (BFRs). Environ Int 74:170–180

Lyu Y, Xu TT, Li X, Cheng TT, Yang X, Sun XM, Chen JM (2016) Size distribution of particle-associated polybrominated diphenyl ethers (PBDEs) and their implications for health. Atmos Meas Tech 9:1025–1037

Odabasi M, Falay EO, Tuna G, Altiok H, Kara M, Dumanoglu Y, Bayram A, Tolunay D, Elbir T (2015) Biomonitoring the spatial and historical variations of persistent organic pollutants (POPs) in an industrial region. Environ Sci Technol 49:2105–2114

Odabasi M, Dumanoglu Y, Falay EO, Tuna G, Altiok H, Kara M, Bayram A, Tolunay D, Elbir T (2016) Investigation of spatial distributions and sources of persistent organic pollutants (POPs) in a heavily polluted industrial region using tree components. Chemosphere 160:114–125

Ratola N, Alves A, Santos L, Lacorte S (2011) Pine needles as passive bio-samplers to determine polybrominated diphenyl ethers. Chemosphere 85:247–252

Ratola N, Homem V, Silva JA, Araujo R, Amigo JM, Santos L, Alves A (2014) Biomonitoring of pesticides by pine needles-chemical scoring, risk of exposure, levels and trends. Sci Total Environ 476–477:114–124

Shi ZX, Zhang L, Li JG, Zhao YF, Sun ZW, Zhou XQ, Wu YN (2016) Novel brominated flame retardants in food composites and human milk from the Chinese total diet study in 2011: concentrations and a dietary exposure assessment. Environ Int 96:82–90

Shi ZX, Zhang L, Li JG, Wu YN (2018) Legacy and emerging brominated flame retardants in China: a review on food and human milk contamination, human dietary exposure and risk assessment. Chemosphere 198:522–536

Silva JA, Ratola N, Ramos S, Homem V, Santos L, Alves A (2015) An analytical multi-residue approach for the determination of semi-volatile organic pollutants in pine needles. Anal Chim Acta 858:24–31

SMSB and SONBS (Shanghai Municipal Statistics Bureau and the Survey Office of the National Bureau of Statistics in Shanghai) (2016) Shanghai statistical yearbook 2016. China Statistics Press, Beijing (in Chinese)

St-Amand AD, Mayer PM, Blais JM (2008) Seasonal trends in vegetation and atmospheric concentrations of PAHs and PBDEs near a sanitary landfill. Atmos Environ 42:2948–2958

Stiborova H, Vrkoslavova J, Lovecka P, Pulkrabova J, Hradkova P, Hajslova J, Demnerova K (2015) Aerobic biodegradation of selected polybrominated diphenyl ethers (PBDEs) in wastewater sewage sludge. Chemosphere 118:315–321

Su PH, Tomy GT, Hou CY, Yin F, Feng DL, Ding YS, Li YF (2018) Gas/particle partitioning, particle-size distribution of atmospheric polybrominated diphenyl ethers in Southeast Shanghai rural area and size-resolved predicting model. Chemosphere 197:251–261

Sun FF, Wen DZ, Kuang YW, Li J, Li JL, Zuo WD (2010) Concentrations of heavy metals and polycyclic aromatic hydrocarbons in needles of Masson pine (Pinus massoniana L.) growing nearby different industrial sources. J Environ Sci 22:1006–1013

Sun RB, Shang S, Zhang W, Lin BC, Wang Q, Shi Y, Xi ZG (2018) Endocrine disruption activity of 30-day dietary exposure to decabromodiphenyl ethane in Balb/C mouse. Biomed Environ Sci 31:12–22

Tian FL, Chen JW, Qiao XL, Cai XY, Yang P, Wang Z, Wang DG (2008) Source identification of PCDD/fs and PCBs in pine (cedrus deodara) needles: a case study in Dalian, China. Atmos Environ 42:4769–4777

Tian M, Chen SJ, Wang J, Luo Y, Luo XJ, Mai BX (2012) Plant uptake of atmospheric brominated flame retardants at an e-waste site in southern China. Environ Sci Technol 46:2708–2714

Tian M, Chen SJ, Luo Y, Wang J, Zhu ZC, Luo XJ, Mai BX (2013) Air-plant exchange of brominated flame retardants at a rural site: influencing factor, interspecies difference, and forest scavenging. Environ Toxicol Chem 32:1248–1253

Tomy GT, Pleskach K, Ismail N, Whittle DM, Helm PA, Sverko E, Zaruk D, Marvin CH (2007) Isomers of dechlorane plus in Lake Winnipeg and Lake Ontario food webs. Environ Sci Technol 41:2249–2254

UNEP (United Nations Environment Programme) (2015) Guidance for the inventory of polybrominated diphenyl ethers (PBDEs) listed under the Stockholm convention on persistent organic pollutants. http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-COP.7-INF-27.English.pdf

UNEP (United Nations Environment Programme) (2017) The 16 new POPs under the Stockholm Convention. http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-PUB-Brochure-16NewPOPs-201706.English.pdf

Wang B, Iino F, Huang J, Lu Y, Yu G, Morita M (2010) Dechlorane plus pollution and inventory in soil of Huai'an city, China. Chemosphere 80:1285–1290

Wang J, Tian M, Chen SJ, Zheng J, Luo XJ, An TC, Mai BX (2011) Dechlorane plus in house dust from e-waste recycling and urban areas in South China: sources, degradation, and human exposure. Environ Toxicol Chem 30:1965–1972

Wang XT, Chen L, Wang XK, Zhang Y, Zhou J, Xu SY, Sun YF, Wu MH (2015) Occurrence, profiles, and ecological risks of polybrominated diphenyl ethers (PBDEs) in river sediments of Shanghai, China. Chemosphere 133:22–30

Wang P, Zhang QH, Zhang HD, Wang T, Sun HZ, Zheng SC, Li YM, Liang Y, Jiang GB (2016a) Sources and environmental behaviors of dechlorane plus and related compounds—a review. Environ Int 88:206–220

Wang XT, Zhou J, Lei BL, Zhou JM, Xu SY, Hu BP, Wang DQ, Zhang DP, Wu MH (2016b) Atmospheric occurrence, homologue patterns and source apportionment of short- and medium-chain chlorinated paraffins in Shanghai, China: biomonitoring with Masson pine (Pinus massoniana L.) needles. Sci Total Environ 560–561:92–100

Wei H, Zou YH, Li A, Christensen ER, Rockne KJ (2013) Photolytic debromination pathway of polybrominated diphenyl ethers in hexane by sunlight. Environ Pollut 174:194–200

Wong F, Suzuki G, Michinaka C, Yuan B, Takigami H, de Wit CA (2017) Dioxin-like activities, halogenated flame retardants, organophosphate esters and chlorinated paraffins in dust from Australia, the United Kingdom, Canada, Sweden and China. Chemosphere 168:1248–1256

Wu B, Liu S, Guo XC, Zhang Y, Zhang XX, Li M, Cheng SP (2012a) Responses of mouse liver to dechlorane plus exposure by integrative transcriptomic and metabonomic studies. Environ Sci Technol 46:10758–10764

Wu JP, Zhang Y, Luo XJ, She YZ, Yu LH, Chen SJ, Mai BX (2012b) A review of polybrominated diphenyl ethers and alternative brominated flame retardants in wildlife from China: levels, trends, and bioaccumulation characteristics. J Environ Sci 24:183–194

Xiao J (2006) A perspective on the development of brominated flame retardants in China. http://www.polymer.cn/Html/IndustryNews/2006-12/15/_2007529102655763.htm (in Chinese)

Yu ZQ, Liao RE, Li HR, Mo LG, Zeng XY, Sheng GY, Fu JM (2011) Particle-bound dechlorane plus and polybrominated diphenyl ethers in ambient air around Shanghai, China. Environ Pollut 159:2982–2988

Zeng LX, Yang RQ, Zhang QH, Zhang HD, Xiao K, Zhang HY, Wang YW, Lam PKS (2014) Current levels and composition profiles of emerging halogenated flame retardants and dehalogenated products in sewage sludge from municipal wastewater treatment plants in China. Environ Sci Technol 48:12586–12594

Zheng J, Wang J, Luo XJ, Tian M, He LY, Yuan JG, Mai BX, Yang ZY (2010) Dechlorane plus in human hair from an e-waste recycling area in South China: comparison with dust. Environ Sci Technol 44:9298–9303

Zhu HK, Zhang K, Sun HW, Wang F, Yao YM (2017a) Spatial and temporal distributions of hexabromocyclododecanes in the vicinity of an expanded polystyrene material manufacturing plant in Tianjin, China. Environ Pollut 222:338–347

Zhu YJ, Sun D, Yang NE, Ding YS, Feng WB, Hong WJ, Zhu SM, Li YF (2017b) Temporal and spatial distributions of PBDEs in atmosphere at Shanghai rural regions, China. Environ Sci Pollut Res 24:10885–10892

Zhu HK, Sun HW, Yao YM, Gan ZW, Wang Y, Kannan K (2018) Legacy and alternative brominated flame retardants in outdoor dust and pine needles in mainland China: spatial trends, dust-plant partitioning and human exposure. Environ Pollut 243:758–765

Zou MY, Ran Y, Gong J, Mai BX, Zeng EY (2007) Polybrominated diphenyl ethers in watershed soils of the Pearl River Delta, China: occurrence, inventory, and fate. Environ Sci Technol 41:8262–8267