○ **Environmental Sciences Europe**

Open Access

Seasonal distribution, gas–particle partitioning and inhalation exposure of brominated flame retardants (BFRs) in gas and particle phases

Yuan Meng[1,2], Hongli Zhang[1,3], Yanling Qiu[1,2*] ●, Xinyu Du[2,4], Dong Niu[1,2], Zhibo Lu[1,2], Zhiliang Zhu[1,2], Jianfu Zhao[2,4] and Daqiang Yin[1,2]

Abstract

Background: Atmosphere is one of the sources and sinks to gas- and particle-bound brominated flame retardants (BFRs). Therefore, BFRs can enter human body via inhalation. In the present study, 79 of gas- and particle-phase samples (TSP, PM_{10} and $PM_{2.5}$) were collected during 2015–2016 in urban area of Shanghai, China to investigate the occurrence of 25 polybrominated diphenyl ether (PBDEs) congeners, hexabromobenzene (HBB) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE).

Results: The total concentrations of BFRs ranged from 0.66 to 13.7 pg/m^3, 25.82 to 376.27 pg/m^3, 14.58 to 365.49 pg/m^3 and 15.17 to 304.89 pg/m^3 in gas, TSP, PM_{10} and $PM_{2.5}$, respectively. HBB was the main compound in gas phase; while BDE-209 was the dominant congener in particle phase. Atmospheric BFRs in winter was much lower than in summer, while particle phase showed opposite seasonal tendency.

Conclusions: Clausius–Clapeyron equation suggested that BTBPE, BDE-28, -66, -99, -100, and -154 were more driven by temperature and evaporated from local contamination. Higher-brominated congeners tended to be absorbed in particle phase, while low-brominated compounds partitioned in both gas and particle phases. Gas/particle partitioning results showed that absorption into the aerosol organic matter was the dominant process for BFRs. The inhalation health risk assessment demonstrated that the hazard quotient (HQs) for most PBDEs in winter was higher than in summer.

Keywords: Brominated flame retardants, Seasonal variation, Gas/particle partitioning, Inhalation exposure

Background

Brominated flame retardants (BFRs) are substances added to consumer products to prevent from firing and are widely used in textiles, furniture, electronics, vehicles and other materials [1]. It has been proved that BFRs are ubiquitous in all kinds of environment matrices [1, 2] and can be detected in biology and human [3, 4]. Studies suggested that BFRs could interfere with the reproductive and endocrine system, and cause thyroid disorders, neurobehavioral disorders and other health problems [5, 6].

Polybrominated diphenyl ethers (PBDEs) are the most commonly used compounds among BFRs for decades. Penta-BDE, Octa-BDE, and Deca-BDE are three major technical PBDE products used in the market. Due to the high environmental persistence, bioaccumulation tendency and toxicity [1], they were added to the list of persistent organic pollutants (POPs) and have been phased out gradually [7, 8]. With the extensive restrictions on the use of PBDEs, novel brominated flame retardants (NBFRs) such as hexabromobenzene (HBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) have

*Correspondence: ylqiu@tongji.edu.cn
2 Shanghai Institute of Pollution Control and Ecological Security, 1239 Siping Road, Shanghai 200092, China
Full list of author information is available at the end of the article

Meng *et al. Environ Sci Eur*   (2019) 31:61

Page 2 of 11

been used to meet flammability standards. HBB is used in woods, textiles, electronics and plastics with production volume of 600 t in Qingdao, China annually [9]. BTBPE, currently, is a replacement for the Octa-BDE mixtures and used in polymeric materials, cotton and polyester [9, 10].

As typical semi-volatile organic compounds (SVOCs), atmosphere plays an important role in transportation and transformation of BFRs. The detection of high levels of these compounds in Antarctica and Arctic sites [11, 12] suggests that long-range transport process occurs in atmosphere. It can be accepted that temperature and particle size are important factors influencing the environmental fate of these compounds [13–15]. For example, the partial pressure in gas phase and gas–particle partitioning of most low-molecular-weight PBDEs (except for BDE-85), HBB and BTBPE were significantly correlated with the ambient temperature [16]. Another research found that these compounds tended to be enriched in particles < 50 μm for road dust and hardly detected in particles > 50 μm [13].

Although numerous research have been conducted BFRs in atmosphere worldwide [17–19], only few studies investigated the mechanisms that influence their transport and gas–particle partitioning [20, 21]. Furthermore, there is limited information regarding the seasonal distribution of BFRs and the correlations among BFR levels, particle size and temperature change. In the present study, we examined a total of 24 PBDEs and 2 NBFRs in gas and particle samples from July 2015 to January 2016 in Shanghai, China. The objectives of this project were: (a) to investigate the concentration and composition of BFRs; (b) to assess the seasonal variation and temperature effect of BFRs; (c) to demonstrate the distribution mechanism of gas–particle partitioning for BFRs, and (d) to estimate the human inhalation exposure of BFRs-contaminated air.

Materials and methods
Chemicals and materials
Mixed standards for 9 PBDE congeners (including BDE-28, -47, -66, -85, -99, -100, -153, -154, -183) and for other 15 PBDE congeners (including BDE-194, -195, -196, -197, -198, -199, -200, -201, -202, -203, -204, -205, -206, -207, -209) were both obtained from Wellington Laboratories. These 24 PBDE congeners can be divided into 8 homologues (Additional file 1: Table S1): Tri-BDE, Tetra-BDE, Penta-BDE, Hexa-BDE, Hepta-BDE, Octa-BDE, Nona-BDE and Deca-BDE. Two NBFRs including HBB and BTBPE, the surrogate standards (BDE-77, BDE-138) and internal standard (BDE-118) were purchased from Accu Standard (New Haven, CT, USA). All of the organic solvents were in pesticide residue grade and obtained from

CNW Technologies GmbH. Sulfuric acid was a guaranteed reagent (Sinopharm Chemical Reagent Corporation, Beijing, China). Silica gel (0.063–0.200 mm) was of chromatographic grade (Merck, Darmstadt, Germany) for chromatography.

Sample collection
A total of 79 samples [14 polyurethane foam (PUF), 26 total suspended particulate (TSP), 20 particulate matter with particle size below 10 μm (PM_{10}), 19 particulate matter with particle size below 2.5 μm ($PM_{2.5}$)] were collected from July 2015 to January 2016 in a typical urban region of Shanghai, China. The sampling site is located in the northwest of Shanghai (N31°14′47.35″, E121°21′50.80″), mounted on roof approximately 15 m above the ground. A highway is located in the southeast of sampling site at around 150 m. 1 km to the north was Beijing–Shanghai high-speed railway. Others were residential area around.

Samples were carried out using two high-volume air samplers (ECHO HiVol, Italy) at 24 h per sample. Gas and particle phases were isolated by drawing air through PUF (65 mm × 75 mm, TISCH, USA) and quartz fiber filter (QFF, 102 mm in diameter, Munktell, Sweden) at a flow rate of about 225 L/min. The sampled air volume was approximately 300 m^3. $PM_{2.5}$ and PM_{10} were collected using $PM_{2.5}$ and PM_{10} cyclones, respectively.

Prior to sampling, PUF plugs were Soxhlet extracted for 48 h with acetone/ cyclohexane (1:1, v:v), while QFFs were baked at 400 °C for 5 h and wrapped with aluminum foils to remove any residue organic pollutants. After sampling, the PUFs and QFFs were wrapped in aluminum foils, sealed in polyethylene zip bags separately, and then transported to laboratory and stored at − 20 °C until extraction. Unloaded and loaded QFFs were weighed after 24-h conditioning at constant temperature and humidity chamber to determine the concentrations of TSP, PM_{10} and $PM_{2.5}$.

Sample pretreatment
Pretreatment procedures followed the previously published method [4] with minor modifications. Briefly, each PUF and QFF sample was spiked with BDE-77 and BDE-138 (2 ng) and then Soxhlet extracted for 48 h with 150 mL acetone/cyclohexane (1:1, v:v) at 65 °C. After evaporated to about 3 mL by a rotary vacuum evaporator (R-210/215, BUCHI Labortechnik), 3 mL concentrated sulfuric acid was added to remove lipids and organic matters. A modified silica column (0.1 g silica + 0.9 g acidic silica + glass fibers at bottom) was used for further clean up. The extract volume was evaporated to 200 μL under a gentle stream of nitrogen and then BDE-118 (2 ng) was added before instrumental analysis.

Meng *et al. Environ Sci Eur* (2019) 31:61

Page 3 of 11

Instrumental analysis

The analysis of BFRs was also carried out based on our previous method [4]. PBDEs and NBFRs were quantified with Agilent 6890 gas chromatograph/5975 mass spectrometer connected with a DB-5MS column (15 m × 0.25 mm × 0.10 μm, J&W Scientific). The negative chemical ionization (NCI) source in selected ion monitoring (SIM) mode was employed. All the target compounds were quantified by scanning bromide ion fragments (m/z 79 and 81). Helium was used as carrier gas to carry the extracts at a set constant flow of 1.4 mL/min, and methane was used as the chemical ionization moderating gas. The ion source, injector, and transfer line temperature was set at 200 °C, 280 °C and 290 °C, respectively. The GC oven temperature program was given as followed: 80 °C for 1 min, 15 °C/min to 300 °C, 2 °C/min to 310 °C and held for 5 min. Each sample was injected in the splitless mode with the injector volume at 1 μL.

Quality assurance/quality control (QA/QC)

Before sample collection, gas-phase breakthrough test was conducted using a second PUF plug in series with the first one. The concentrations of BFRs in the second plug were less than 10% compared to the first plug which showed that PUF breakthrough could be ignored. Procedural blanks were processed for every season while laboratory blanks were taken for every month during the pretreatment procedure to check background contamination. Drift blanks were run after every 10 samples, and the results were acceptable when the relative standard deviation for individual PBDE congener in standards was less than 10%. The limit of detection (LOD) and the limit of quantification (LOQ) were defined as a signal of three times and ten times the noise level, respectively. More details about LOD and LOQ are provided in Additional file 1: Table S1. BFRs concentrations in all samples were blank corrected. Recoveries of BDE-77 and BDE-138 ranged from 60 to 110% and 78 to 115%, respectively. The reported concentrations in this study were not corrected with surrogate recovery.

Statistical analysis

SPSS Version 20 was used for Spearman correlation analysis to investigate correlations between data and other statistical analysis. The normality test suggested non-normal distribution of data, and therefore statistics were expressed as geometric mean (GM), geometric standard deviation (GSD) and median value. Mann–Whitney Test was performed to assess the significance of differences. The level of significance was assigned at 0.05.

Results and discussion

Concentrations and distributions of TSP, PM_{10} and $PM_{2.5}$

Particle concentrations of TSP, PM_{10} and $PM_{2.5}$ were ranged from 57.5 to 274.4 μg/m³, 36.7 to 199 μg/m³ and 30.3 to 183.2 μg/m³ (Additional file 1: Fig. S1a), which were comparable to those reported in China and other Asia countries [22–28], but much higher than developed countries in the UK, Spain and Greece [29] (Additional file 1: Table S2). The median contribution of particles between 0–2.5 μm, 2.5–10 μm and 10–100 μm was 59.7%, 13.4% and 26.9%, respectively (Additional file 1: Fig. S1b), suggesting that finer particles are the dominant fraction in TSP.

Strongly negative correlations were found between temperature (except continued high temperature weather in Jul. and Aug.) and TSP ($P < 0.05$), PM_{10} ($P < 0.01$), $PM_{2.5}$ ($P < 0.01$) (Additional file 1: Fig. S2). Previous studies [30, 31] reported similar temperature pattern in $PM_{2.5}$. This is probably because higher temperature can accelerate air convection, which brings about the dilution and diffusion of the particles [31, 32]. Besides, increased emission by heating and power production in winter can cause enhanced particle concentrations in China.

Concentration of BFRs

The range and geomean concentrations of gas and particle phases are given in Table 1. Low-brominated compounds (Tri-, Tetra-, Penta-, Hexa-, Hepta- BDE and HBB) and BTBPE had higher detected frequency as 85–100% in gas phase. All the BFR compounds were detected in all particle phase (100%) except BDE-28, -47, -66, -99, -100, -183 and -202 with the detection frequency ranged from 25 to 94%. The total concentrations of BFRs (Σ_{25}BFRs) ranged from 0.66 to 13.7 pg/m³, 25.82 to 376.27 pg/m³, 14.58 to 365.49 pg/m³ and 15.17 to 304.89 pg/m³ in gas, TSP, PM_{10} and $PM_{2.5}$ and the GM concentrations were 5.96, 101.70, 49.50 and 44.21 pg/m³, respectively.

HBB and BDE-47 were the most abundant congeners in atmosphere with the GM concentration 1.26 and 1.03 pg/m³, followed by BDE-28 and -66. In particle phase, BDE-209 had the highest GM concentration as 62.56, 29.01 and 21.53 pg/m³ in TSP, PM_{10} and $PM_{2.5}$, respectively. BDE-207 was secondly abundant in particle phase, followed by BDE-206 and -208.

In gas phase, the GM level of Σ_7PBDEs (-28, -47, -99, -100, 153, -154, -183) from this study was 5.8 and 0.9 pg/m³ in summer and winter (Additional file 1: Table S3), which was comparable with those in Yangtze River Delta, China [33], and higher than some European countries like Norway, France [34], but much lower than some other Asian countries like Kuwait [35] and Philippines [34]. Compared with America, the concentration in present

Meng *et al. Environ Sci Eur*   (2019) 31:61

Page 4 of 11

Table 1 Concentrations of BFRs in gas and particle phases (pg/m³)

	Gas $n = 14$		TSP $n = 26$		PM$_{10}$ $n = 20$		PM$_{2.5}$ $n = 19$	
	Range	Geomean	Range	Geomean	Range	Geomean	Range	Geomean
HBB	< LOQ–8.06	1.26	< LOQ–13.3	0.56	< LOQ–6.74	0.16	< LOQ–7.81	0.27
BTBPE	< LOQ–0.21	0.03	0.72–15.67	1.78	< LOQ–8.14	0.69	0.27–7.87	1.06
BDE-28	< LOQ–2.60	0.48	< LOQ–0.60	0.01	< LOQ–0.43	0.01	< LOQ–0.39	0.01
BDE-47	0.26–4.08	1.03	0.01–3.25	0.23	0.01–1.33	0.14	< LOQ–1.40	0.03
BDE-66	0.01–0.88	0.23	< LOQ–2.35	0.04	< LOQ–0.59	0.02	< LOQ–0.79	0.02
BDE-99	< LOQ–1.20	0.19	< LOQ–6.44	0.61	0.12–4.60	0.49	< LOQ–3.51	0.49
BDE-100	0.03–0.87	0.18	0.02–3.71	0.29	< LOQ–2.59	0.13	< LOQ–2.49	0.14
BDE-153	0.02–0.99	0.19	0.08–5.06	0.59	0.07–2.84	0.32	0.04–3.51	0.37
BDE-154	0.02–1.38	0.11	0.11–9.59	0.70	0.09–4.01	0.37	0.05–5.31	0.44
BDE-183	< LOQ–0.70	0.08	0.27–12.48	1.98	0.24–8.13	1.02	0.17–15.07	1.16
BDE-194	nd	–	0.74–12.28	1.81	0.51–5.84	1.07	0.34–7.20	1.02
BDE-196	nd	–	0.69–12.71	2.33	0.65–4.97	1.27	0.49–14.25	1.26
BDE-197/204	nd	–	0.35–6.64	1.04	0.19–4.24	0.56	0.16–4.91	0.61
BDE-198/199/200/203	nd	–	0.19–3.52	0.52	0.15–1.18	0.28	0.10–3.52	0.32
BDE-201	nd	–	0.50–7.59	1.26	0.23–4.60	0.72	0.22–5.86	0.77
BDE-202	nd	–	0.01–6.52	0.76	< LOQ–5.01	0.22	< LOQ–5.58	0.22
BDE-206	nd	–	2.01–18.88	6.24	1.88–13.77	3.58	1.10–12.92	3.38
BDE-207	nd	–	2.49–21.24	6.45	2.19–14.46	3.93	1.43–10.93	3.39
BDE-208	nd	–	0.74–13.56	3.55	0.88–11.12	1.90	0.47–8.74	1.75
BDE-209	nd	–	12.96–311.56	62.56	5.46–283.09	29.01	6.09–268.58	21.23
Σ$_7$PBDEs[a]	0.59–9.06	2.26	0.70–44.82	4.41	0.66–22.93	2.48	0.54–29.04	2.64
PBDEs	0.59–9.39	3.28	25.01–370.96	98.12	14.07–351.20	47.60	14.04–302.08	41.86
BFRs	0.66–13.7	5.96	25.82–376.27	101.70	14.58–365.49	49.50	15.17–304.89	44.21

nd means not detected

[a] Σ$_7$PBDE(-28, -47, -99, -100, 153, -154, -183)

study was slightly lower than in St. Lawrence Island and Point Reyes [34]. Besides, it was significantly lower than the research from Guiyu which is a typical e-waste recycling site in China [14] with the Σ$_7$PBDEs 4073.89 and 1916.5 pg/m³ in summer and winter, respectively. The atmospheric GM level of HBB in this study (2.5 pg/m³ in summer) was in accordance with those in Beijing, Xiamen, Tianjin and slightly lower than in Guangzhou [36] in China.

Compared with the PBDEs in TSP from other studies, the GM concentration of Σ$_7$PBDEs in this study (2.20 and 14.37 pg/m³ in summer and winter) was similar to those in Kuwait [35], Italy [37], and significantly lower than those in Guiyu with the average Σ$_7$PBDEs concentration as 2068 and 15,229 pg/m³ in summer and winter [14]. The level of BDE-209 in TSP was 47.79 and 59.36 pg/m³ in summer and winter, which was higher than in Africa [38], France [38], Italy [37], but much lower than in Shanghai [39], Harbin [40] and Guiyu [14] in China. Additionally, the levels of Σ$_7$PBDEs in PM$_{2.5}$ in this study were slightly higher than in East China Sea [41] and

Spain [42]. Overall, the GM levels of gaseous PBDEs in present study were higher than in European countries and comparable to other cities in China, but lower than in America and other Asian countries. In particle phase, the concentration of PBDEs in this study was moderate compared with other cities and countries. However, all the results in this study were significantly lower than in the e-waste city Guiyu in China.

Congener profiles of BFRs

Compositions of BFRs in both gas and particle phases are shown in Additional file 1: Fig. S3. The predominant BFR congeners in gas phase were HBB, Tetra-BDE (BDE-47, BDE-66) and Tri-BDE (BDE-28), accounting for 39%, 25% and 14% among the total BFRs. The relatively high abundance of these lighter BFRs was mainly due to their higher vapor pressure [43]. Similarly, BDE-28, -47 were found to be the major atmospheric congeners in an earlier research [44] in Shanghai rural regions, which accounted for 13.1% and 11.7% in average. Deca-BDE (BDE-209) was the dominant congener

Meng *et al. Environ Sci Eur* (2019) 31:61

Page 5 of 11

in particle phase contributing to more than half of the Σ_{25}BFRs. The excessive of BDE-209 indicated that commercial Deca-BDE may still be in use in the studied area. This result was consistent with another research which reported that BDE-209 contributed 65% and 59% of gaseous plus particle-bound phase at urban and rural sites, respectively, in Lake Chaohu, China [21]. Nona-BDE (BDE-206,-207,-208) was secondly abundant with 17%, 21% and 23% in TSP, PM_{10} and $PM_{2.5}$.

The ratios of BDE-47/99, BDE-99/100 are used to illustrate the source and transformation of PBDEs. In this study, the average ratio of BDE-47/99 in total air concentrations (gas plus particle phase) was 1.04, which was in accordance with other researches in the Arctic (1.1) [45], and slightly lower than those in Lake Chaohu, China (2.6) [21], the USA (1.4–2.4) [46]. This ratio was similar to those in commercial Penta-BDE mixture DE-71 (1.27) and Bromkal 70-5DE (1.05) [47], suggesting the very likely use of these technical products in the sampling site. The ratio of BDE-99/100 in this study (1.92) was comparable to the ratios in Lake Chaohu, China (1.4) [21], northern China (2.4) [48], and lower than other researches reported in the Arctic (5.4) [45], the USA (4.1–5.1) [46], the commercial DE-71 (3.71) and Bromkal 70-5DE (5.73) [49]. For outdoor environment, photolysis under sunlight and photooxidation by ·OH radicals occurs in PBDEs with different degradation rates for each compounds [15, 50]. BDE-47 and -100 show higher degradation rates than BDE-99; thus, ratios of BDE-47/99 and BDE-99/100 are estimated to be lower and higher, respectively [21]. However, higher-brominated PBDE congeners (such as BDE-209) could also degrade into BDE-47, -99 and -100, resulting in the variation of these ratios [38, 44, 51]. Therefore, low ratio of BDE-99/100 in this study was more likely affected by the degradation of high-brominated compounds instead of the different degradation rates.

BTBPE showed significant correlations with most of the BFR homologues and the highest coefficient were found in Hexa-, Hepta- and Octa-BDE (Additional file 1: Tables S4–S7). This was consistent with prior observations as BTBPE is a replacement for commercial Octa-BDE mixtures [52, 53]. Higher correlations were observed among homologues with similar number of bromine, such as Tetra-, Penta- and Hexa-BDE ($r = 0.675$–0.955, $P < 0.01$), or Octa-, Nona-, and Deca-BDE ($r = 0.562$–0.873, $P < 0.01$). Weaker or no significant correlations were found between low-brominated and high-brominated congeners (Octa-, Nona-, Deca-BDE). It was possibly due to complicated environmental fates (e.g., orders magnitude differences of octanol–air partition coefficients) and different usage of commercial BDE mixtures [52].

Seasonal variations and temperature effect of BFRs

The levels of NBFRs and low-brominated congeners in gas phase were ranked as summer > autumn > winter (Additional file 1: Fig. S4). Different tendency was observed in particle phase: the concentration of NBFRs, lower-brominated congeners and Octa-BDE were in the order as winter > autumn > summer; whereas, higher-brominated congeners (Nona- and Deca-BDE) were as autumn > winter > summer.

Low-brominated congeners in gas phase during summer were much higher than in winter with GM concentrations as 8.41 and 1.98 pg/m^3, respectively (Fig. 1). Other researchers also observed elevated atmospheric concentration of BFRs in summer and decreased concentration in winter [36, 44, 54]. This is mainly due to higher volatilization in atmosphere and desorption from particulate phase in higher temperature [36, 55]. Contrarily, particle-bound BFRs were shown to be significantly higher in winter than in summer, which was mainly due to fuel consumption for heating activities.

The temperature dependence of atmospheric organic pollutants can be parameterized by the Clausius–Clapeyron equation (Eq. 1) [56]. It is used to identify whether these gaseous pollutants come from long-range atmospheric transport or local surface release [19].

$$\ln P = -\frac{\Delta H_{\mathrm{vap}}}{RT} + b = \frac{m}{T} + b, \tag{1}$$

where P is the partial pressure of the BFRs in gas phase (atm) calculated by the ideal gas state equation, ΔH_{vap} is the energy of the phase transition by which a molecule volatilizes from the terrestrial or aquatic environment into the atmosphere (kJ/mol), R is the gas constant (8.314 J/(mol K)), T is the ambient temperature (K), while m and b are constants.

BTBPE, BDE-28, -66, -99, -100, and -154 showed significant positive dependence on temperature, accounting for 28–67% (r^2) of the variations (Additional file 1: Table S8). Compared to previous researches, gaseous BFRs were positively correlated with temperature in e-waste sites in southern China (44–78%) [57] and less dependent in Lhasa (3.5–44.1%) [52], lake Chaohu, China (18–44%) [21]. The slope m of these mentioned compounds in this study ($-15,626$ to -7310.9) was much steeper than Lhasa (-8578 to -1649) [52], lake Chaohu, China (-2970 to 4400) [21], northeast China (-7255 to 1667) [16], but shallower than Southern China with the value from $-26,340$ to $-16,120$ [57]. Considering high levels of Penta-BDE in the sampling site, these compounds were more commanded by temperature-driven evaporation from local contamination. As HBB, BDE-47, -153, -183 had no statistic dependence on temperature with much shallower slope m, these congeners tended to

Meng *et al. Environ Sci Eur*   (2019) 31:61

Page 6 of 11
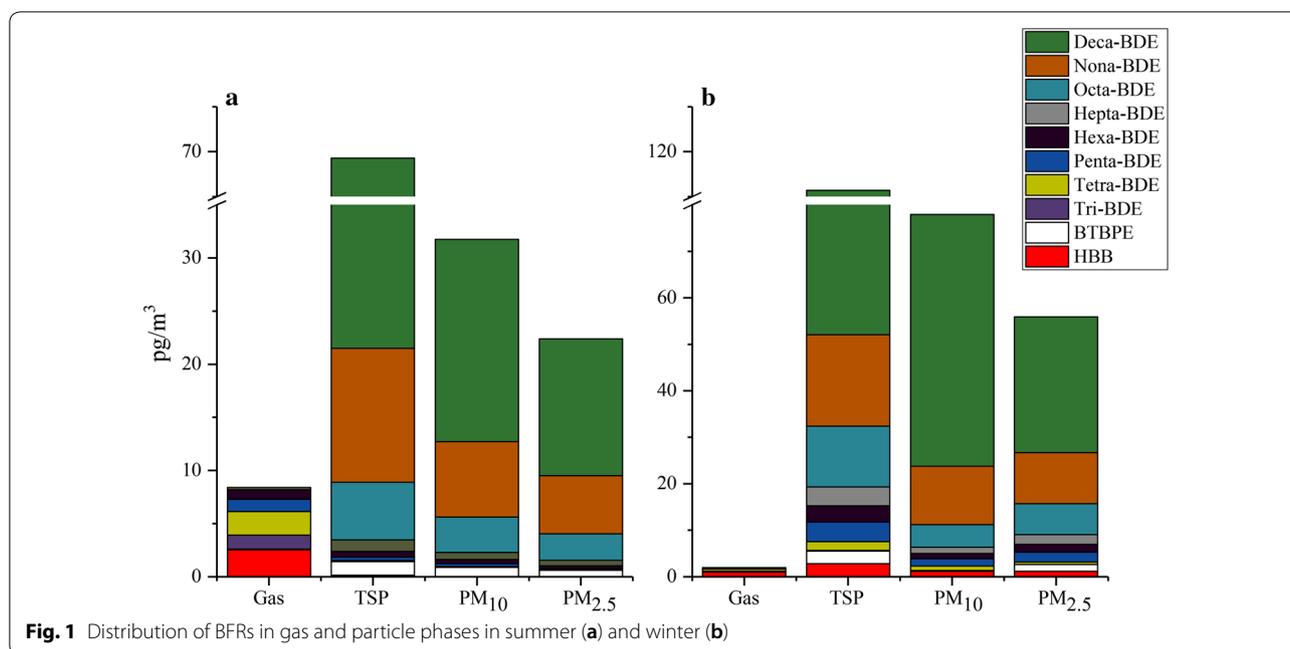
Fig. 1 Distribution of BFRs in gas and particle phases in summer (**a**) and winter (**b**)

be driven by regional or long-range atmospheric transport, consistent with studies in Lhasa [52], lake Chaohu [21], and rural sites in southern China [16].
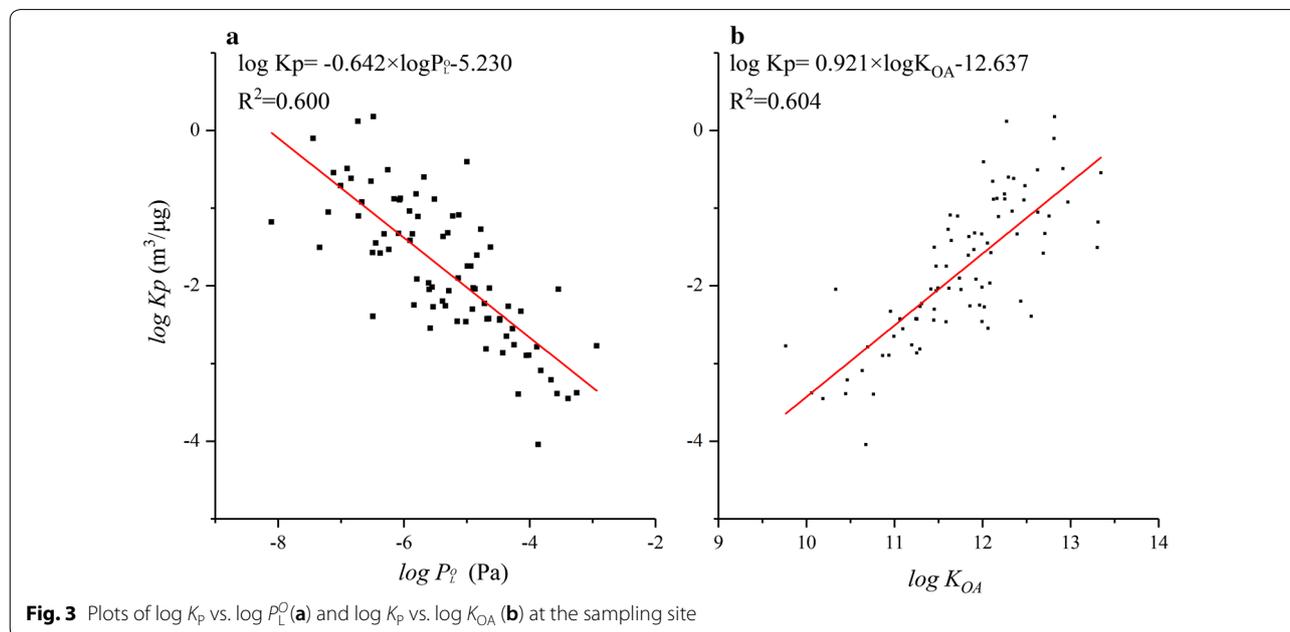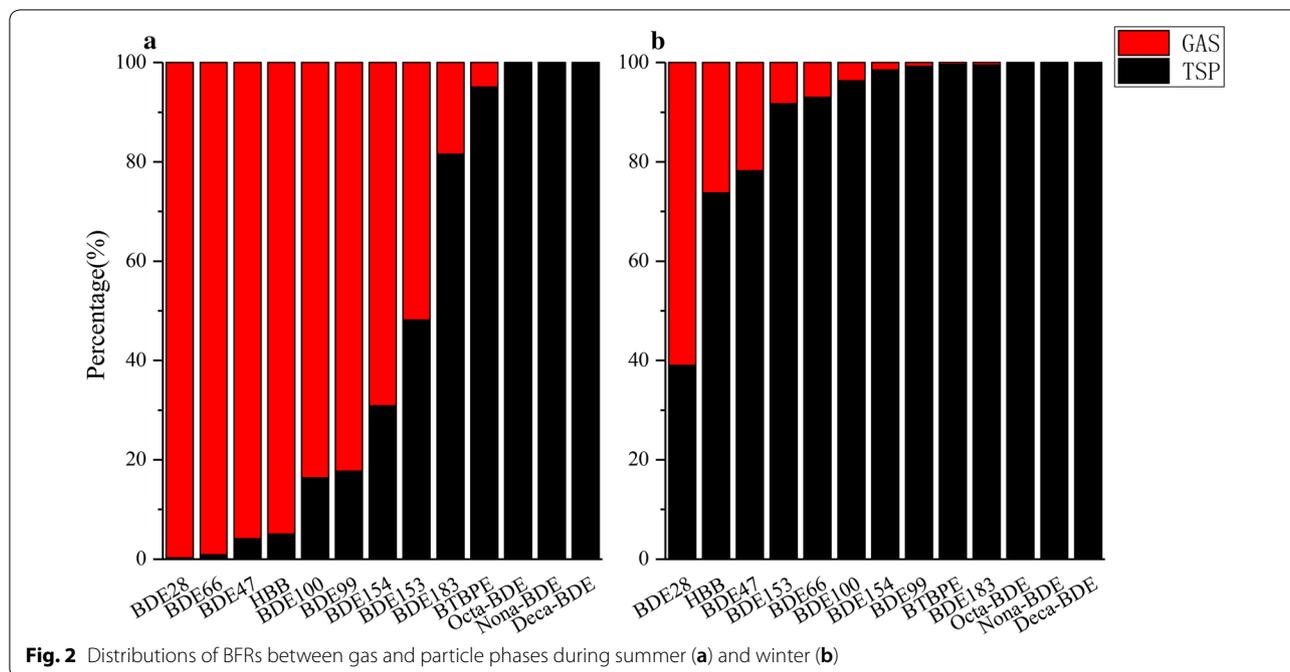
In particle phase, HBB and low-brominated congeners (except Tri-BDE, Hepta-BDE) showed significant negative correlations ($P < 0.01$) with temperature change (Additional file 1: Table S9). Numerous high-brominated compounds also showed negative correlations ($P < 0.05$) with temperature, with much lower correlation coefficient than those in low-brominated ones. These were consistent with previous studies [21, 53, 58] which demonstrated that temperature is an essential factor on the release of BFRs [59]. Generally, low-brominated compounds are more likely to be affected by temperature than high-brominated congeners.

Gas–particle partitioning of BFRs

The distribution of BFRs between gas and particle phases varied considerably in summer and winter (Fig. 2). High-brominated compounds were only detected in particle phase which was mainly caused by low subcooled liquid vapor pressure (P_L^O, Pa) and high octanol–air partition coefficient (K_{OA}), making them concentrate on particles easily [55, 60–62]. Low-brominated congeners distributed in both gas and particle phases and the percentage in atmosphere decreased with the increasing of the bromine number. HBB partitioned in gas phase with 95% and 26% in summer and winter, while BTBPE showed just 5% and 0%, respectively. This was in agreement with previous study which suggested that around 60% of HBB

could associated with gas phase [43]. In summer, BDE-28 and BDE-66 mostly distributed in gas phase, and decreased to 61% and 7% in winter. BDE-100, -99 and -154 showed similar distribution with 84%, 82% and 69% in summer in atmosphere, and only 4%, 1%, 1% in winter, respectively. The distribution of gaseous BFRs exhibited a sharp decline in winter due to the low desorption from the particulate phase. Other researches [52, 55] also reported lower levels of BFRs in gas phase during cold period; whereas elevated gas-phase concentrations were observed when ambient temperature was higher.

Adsorption onto the aerosol surface and absorption into the aerosol organic matter have been used to describe the gas/particle partitioning of SVOCs. The linear relationships between the logarithm of gas/particle partition coefficient (K_P) and the logarithm of P_L^O or K_{OA} can describe these two mechanisms. More details of Additional file 1: Eqs. S(2)–S(6) are listed in SI. Slope m between log K_P and log P_L^O is supposed to near -1 for reaching equilibrium partitioning of adsorption and absorption processes; indeed, it often deviated from -1 in previous studies possibly due to thermodynamic factors or non-equilibrium conditions [63, 64]. For example, the fraction of organic matter and inorganic salts (e.g., ammonium sulfate, ammonium nitrate) is likely to affect equilibrium partitioning of BFRs [37, 65, 66]. Moreover, sampling artifacts may also result in this deviation due to the underestimation or overestimation of BFRs concentrations in gas and particle phases. Basically, gaseous BFRs from PUF may be adsorbed

Meng *et al. Environ Sci Eur* (2019) 31:61

Page 7 of 11

Fig. 2 Distributions of BFRs between gas and particle phases during summer (**a**) and winter (**b**)

Fig. 3 Plots of log K_P vs. log P_L^O (**a**) and log K_P vs. log K_{OA} (**b**) at the sampling site

onto the filter; semi-volatile BFRs can also evaporate from the filter and subsequently adsorbed in PUF [57, 67]. Unfortunately, it is difficult to clarify the real bias caused by sampling artifacts since the complicated factors [67]. According to Goss and Schwarzenbach, adsorption process happened with slope m steeper than − 1 and absorption came up with slope shallower than − 0.6 [68]. The slope m of 8 low-brominated compounds was − 0.642 with correlation coefficient R^2 0.6

(Fig. 3), indicating absorption is the dominant process in this study. The m value was consistent with other researches in Greece (− 0.444, − 0.4553 and − 0.5255 for industrial, urban-traffic and urban-background site) [55], south China (− 0.762 and − 0.754 for industrial and urban site) [20], and Italy (− 0.388 to − 0.228 for urban area) [37].

log K_P–log K_{OA} regression line indicates that absorptive partitioning of BFRs between gas and particle phases is

Meng *et al. Environ Sci Eur*   (2019) 31:61

Page 8 of 11

the dominant distribution process [61, 69]. The slope n in the present study (0.921, $R^2 = 0.604$) deviated slightly from 1 suggested the non-equilibrium partitioning [70]. The slope n was much steeper than m value from $\log K_p$ vs. $\log P_L^O$, indicating that absorption process was the dominating sorption mechanism in studied area [71]. Compared with other researches, *n* value in this study was much higher than in Greece (0.5857, 0.5878 and 0.6839 for industrial, urban-traffic and urban-background site) [55] and Italy (0.31–0.51 for urban area) [37]. This was possibly due to different sources, usage pattern and partition mechanisms of those semi-volatile BFRs.

Inhalation exposure and health risk assessment for BFRs

The estimated daily intake of BFRs through inhalation in atmosphere (EDI_{inh}, pg/kg-bw/day) and health risk assessment were calculated for children and adults during different seasons in this study.

$$EDI_{(inh)} = C \times IR \times EF/BW, \tag{2}$$

where *C* is BFRs concentration (pg/m³) in air and $PM_{2.5}$, IR is the inhalation rate (20 m³/day for adults [72] and 12 m³/day for children [73]), EF is exposure fraction and BW is average body weight (31.8 for children, 70 for adults). 100% absorption was assumed for all target BFRs.

The hazard quotient (HQ) was used to estimate the potential non-carcinogenic health risk of PBDEs. Recommended RfD values for daily oral PBDE exposure were obtained from USEPA [74] and Khan et al. [75, 76].

$$HQ = EDI_{(inh)}/RfD \tag{3}$$

It is noted that particle size could affect exposure dose through inhalation. Nevertheless, there were limited data for fine particles and most of the researches mentioned in this study included different sizes of particles. $PM_{2.5}$ and atmospheric BFRs were used to evaluate inhalation health risk in this study. The average inhalation EDI of BFRs was found to be 3.98 pg/kg-bw/day for children, which was higher than adults as 2.15 pg/kg-bw/day (Additional file 1: Table S10, Table 2). Winter had a much higher inhalation *EDI* of BFRs than summer except for HBB, BDE-28, -47, -66 which tended to be absorbed in gas phase in higher temperature.

The HQs for inhalation exposure to 13 kinds of PBDEs in gas and $PM_{2.5}$ in winter were higher than in summer except for BDE-47, -66 and -99 which were mainly detected in gas phase especially in summer (Additional file 1: Table S11). Compared with adults, children had a higher risk inhalation exposure to PBDEs. Among those congeners, BDE-47 had the highest HQ with 8.43E−07 for children and 4.56E−07 for adults, followed by BDE-99, -183 and -209. Overall, the HQs for inhalation exposure were far less than 1 which suggested that health risk for inhalation of atmospheric PBDEs was relatively low.

Conclusion

The seasonal variation, gas–particle partitioning and health risk assessment of BFRs in gas and particle phases were investigated in Shanghai in this study. The GM concentrations of Σ_{25}BFRs were 5.96, 101.70, 49.50 and 44.21 pg/m³ in gas, TSP, PM_{10} and $PM_{2.5}$, respectively, higher than or comparable to cities in Europe and China, but much lower than the typical e-waste site. HBB and BDE-209 were the most abundant congeners in gas and particle phases, respectively. Gaseous BFRs in summer was much higher than in winter; while the particle phase showed opposite tendency. This is mainly due to higher volatilization or desorption of atmospheric BFRs in summer and emission of BFRs in particle phase through heating and power production in winter. Significant positive correlations were found between temperature and gaseous congeners including BTBPE, BDE-28, -66, -99, -100, -154, suggesting that they were more derived from local contamination evaporation. High-brominated congeners were only absorbed in particle phase; while low-brominated compounds were distributed in both gas and particle phases. The calculation of gas/particle partitioning suggested that absorption into the aerosol organic matter for BFRs was the main mechanism in this study. For most PBDEs, the health risk assessment through inhalation was higher in winter than in summer. Future work should focus on the source apportionment with a longer monitoring time for BFRs.

Table 2 EDI (pg-kg-bw/day) of Σ_{27}BFRs for children and adult in different season

	Phase	Whole		Summer		Winter	
		Children	Adults	Children	Adults	Children	Adults
$EDI_{(inh)}$ (pg/kg-bw/day)	Gas	0.47	0.26	0.69	0.37	0.20	0.11
	$PM_{2.5}$	3.50	1.89	1.84	0.99	5.30	3.01
	Gas + $PM_{2.5}$	3.98	2.15	2.52	1.37	5.50	3.12

Meng *et al. Environ Sci Eur*   (2019) 31:61

Page 9 of 11

Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s12302-019-0257-2.

Additional file 1: Table S1. Description of the target chemicals, the monitoring ion (m/z) and LOD/LOQ. **Table S2**. Concentrations (μg/m^3) of PM$_{10}$ and PM$_{2.5}$ in different countries or cities during summer and winter. **Table S3**. Concentrations (pg/m^3) of BFRs in gas and particle phase between different countries or cities. **Table S4**. Correlation coefficient among BFR homologues in gas phase. **Table S5**. Correlation coefficient among BFR homologues in TSP. **Table S6**. Correlation coefficient among BFR homologues in PM$_{10}$. **Table S7**. Correlation coefficient among BFR homologues in PM$_{2.5}$. **Table S8**. Summary of Clausius-Clapeyron Regression slopes, intercepts, coefficient r^2, P-values, calculated phase transition energy (ΔH_{calvap}) and the phase transition energy (ΔH_{vap}) in the idea gas state (HBB, BTBPE, BDE-28, -47, -66, -99, -100, -153, -154, and BDE-183). **Table S9**. Correlation coefficient between temperature and BFRs in particle phase. **Table S10**. The estimated daily inhalation of BFRs (EDI$_{inh}$) (pg/kg-bw/day) in atmosphere for children and adults. **Table S11**. HQs for PBDEs in children and adults via inhalation (Gas + PM$_{2.5}$). **Figure S1**. Daily mass concentrations of TSP, PM$_{10}$ and PM$_{2.5}$ during entire sampling period. **Figure S2**. Temperature tendency for different size of particles. **Figure S3**. Compositional profiles of BFRs in gas, TSP, PM$_{10}$ and PM$_{2.5}$ cases. **Figure S4**. Seasonal tendency of BFR congeners in gas and particle phase.

Abbreviations

BFRs: brominated flame retardants; EDI: estimated daily intake; GC/MS: gas chromatography/mass spectrometry; GM: geometric mean; GSD: geometric standard deviation; HQ: hazard quotient; K_{OA}: octanol–air partition coefficient; LOD: limit of detection; LOQ: limit of quantification; NBFRs: novel brominated flame retardants; NCI: negative chemical ionization; PBDEs: polybrominated diphenyl ethers; PM$_{10}$: particulate matter with particle size below 10 μm; PM$_{2.5}$: particulate matter with particle size below 2.5 μm; POPs: persistent organic pollutants; PUF: polyurethane foam; P_L^0: subcooled liquid vapor pressure; QFF: quartz fiber filter; RfD: reference dose; SIM: selected ion monitoring; S/N: signal–noise ratio; SRM: standard reference material; SVOCs: semi-volatile organic compounds; TSP: total suspended particulate; BDE-28: 2,4,4′-tribromodiphenyl ether; BDE-47: 2,2′,4,4′-tetrabromodiphenyl ether; BDE-66: 2,3′,4,4′-tetrabromodiphenyl ether; BDE-85: 2,2′,3,4,4′-pentabromodiphenyl ether; BDE-99: 2,2′,4,4′,5-pentabromodiphenyl ether; BDE-100: 2,2′,4,4′,6-pentabromodiphenyl ether; BDE-153: 2,2′,4,4′,5,5′-hexabromodiphenyl ether; BDE-154: 2,2′,4,4′,5,6′-hexabromodiphenyl ether; BDE-183: 2,2′,3,4,4′,5′,6-heptabromodiphenyl ether; BDE-194: 2,3,4,5,2′,3′,4′,5′-octabromodiphenyl ether; BDE-206: 2,2′,3,3′,4,4′,5′,6-nonabromodiphenyl ether; BDE-207: 2,2′,3,3′,4,4′,5,6,6′-nonabromodiphenyl ether; BDE-208: 2,2′,3,3′,4,5,5′,6,6′-nonabromodiphenyl ether; BDE-209: decabromodiphenyl ether; BDE-77: 3,3′,4,4′-tetrabromodiphenyl ether; BDE-118: 2,3′,4,4′,5-pentabromodiphenyl ether; BDE-138: 2,2′,3,4,4′,5′-hexabromodiphenyl ether; BTBPE: 1,2-bis(2,4,6-tribromophenoxy)ethane; HBB: hexabromobenzene.

Authors' contributions

YM performed the chemical and data analysis, and wrote the manuscript. HZ managed part of the chemical and data analysis. YQ made the study design, revised the manuscript and is the PI of the NSFC project. XD and DN involved in study design and the revision of the manuscript. ZL provided the high volume air samplers and instructed on sampling techniques. ZZ, JZ and DY gave suggestions on experimental design. All authors read and approved the final manuscript.

Availability of data and materials

Not applicable.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

Author details

[1] Key Laboratory of Yangtze River Water Environment, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China. [2] Shanghai Institute of Pollution Control and Ecological Security, 1239 Siping Road, Shanghai 200092, China. [3] Building Energy Research Center Fok Ying Tung Research Institute, Guangzhou 511400, China. [4] State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China.

References

1. de Wit CA (2002) An overview of brominated flame retardants in the environment. Chemosphere 46:583–624
2. Yu G, Bu Q, Cao Z, Du X, Xia J, Wu M, Huang J (2016) Brominated flame retardants (BFRs): a review on environmental contamination in China. Chemosphere 150:479–490
3. Hammel SC, Hoffman K, Lorenzo AM, Chen A, Phillips AL, Butt CM, Sosa JA, Webster TF, Stapleton HM (2017) Associations between flame retardant applications in furniture foam, house dust levels, and residents' serum levels. Environ Int 107:181–189
4. Zhou Y, Chen Q, Du X, Yin G, Qiu Y, Ye L, Zhu Z, Zhao J (2016) Occurrence and trophic magnification of polybrominated diphenyl ethers (PBDEs) and their methoxylated derivatives in freshwater fish from Dianshan Lake, Shanghai, China. Environ Pollut 219:932–938
5. Kim YR, Harden FA, Toms LL, Norman RE (2014) Health consequences of exposure to brominated flame retardants: a systematic review. Chemosphere 106:1–19
6. U.S.EPA (2010) An exposure assessment of polybrominated diphenyl ethers (FinalReport). U.S. Environmental Protection Agency, Washington, DC
7. UNEP/POPS (2009) Recommendations of the persistent organic pollutants review committee of the Stockholm convention to amend annexes A, B or C of the convention. Stock. Conv. Persistent Org. Pollut. 1–13, 4 Feb
8. UNEP (2017) The new POPs under the Stockholm Convention. http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511. Accessed 15 Sept 2019
9. 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
10. Takigami H, Suzuki G, Hirai Y, Sakai S (2009) Brominated flame retardants and other polyhalogenated compounds in indoor air and dust from two houses in Japan. Chemosphere 76:270–277
11. Li Y, Geng D, Liu F, Wang T, Wang P, Zhang Q, Jiang G (2012) Study of PCBs and PBDEs in King George Island, Antarctica, using PUF passive air sampling. Atmos Environ 51:140–145
12. Besis A, Samara C (2012) Polybrominated diphenyl ethers (PBDEs) in the indoor and outdoor environments—a review on occurrence and human exposure. Environ Pollut 169:217–229
13. Cao Z, Xu F, Covaci A, Wu M, Wang H, Yu G, Wang B, Deng S, Huang J, Wang X (2014) Distribution patterns of brominated, chlorinated, and phosphorus flame retardants with particle size in indoor and outdoor dust and implications for human exposure. Environ Sci Technol 48:8839–8846

Meng *et al. Environ Sci Eur*   (2019) 31:61

Page 10 of 11

14. Chen D, Bi X, Liu M, Huang B, Sheng G, Fu J (2011) Phase partitioning, concentration variation and risk assessment of polybrominated diphenyl ethers (PBDEs) in the atmosphere of an e-waste recycling site. Chemosphere 82:1246–1252

15. Pan Y, Tsang DCW, Wang Y, Li Y, Yang X (2016) The photodegradation of polybrominated diphenyl ethers (PBDEs) in various environmental matrices: kinetics and mechanisms. Chem Eng J 297:74–96

16. Qi H, Li W, Liu L, Song W, Ma W, Li Y (2014) Brominated flame retardants in the urban atmosphere of Northeast China: concentrations, temperature dependence and gas-particle partitioning. Sci Total Environ 491–492:60–66

17. Chakraborty P, Zhang G, Cheng H, Balasubramanian P, Li J, Jones KC (2017) Passive air sampling of polybrominated diphenyl ethers in New Delhi, Kolkata, Mumbai and Chennai: levels, homologous profiling and source apportionment. Environ Pollut 231:1181–1187

18. Zhang X, Barnes J, Lei YD, Wania F (2017) Semivolatile organic contaminants in the Hawaiian atmosphere. Environ Sci Technol 51:11634–11642

19. Yang M, Qi H, Jia H, Ren N, Ding Y, Ma W, Liu L, Hung H, Sverko E, Li Y (2013) Polybrominated diphenyl ethers in air across China: levels, compositions, and gas-particle partitioning. Environ Sci Technol 47:8978–8984

20. Chen L, Mai B, Bi X, Chen S, Wang X, Ran Y, Luo X, Sheng G, Fu J, Zeng EY (2006) Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China. Environ Sci Technol 40:1190–1196

21. He W, Qin N, He Q, Kong X, Liu W, Wang Q, Yang C, Jiang Y, Yang B, Bai Z, Wu W, Xu F (2014) Atmospheric PBDEs at rural and urban sites in central China from 2010 to 2013: residual levels, potential sources and human exposure. Environ Pollut 192:232–243

22. Hu R, Liu G, Zhang H, Xue H, Wang X, Wang R (2018) Particle-associated polycyclic aromatic hydrocarbons (PAHs) in the atmosphere of Hefei, China: levels, characterizations and health risks. Arch Environ Contam Toxicol 74:442–451

23. Liu Y, Zhang T, Liu Q, Zhang R, Sun Z, Zhang M (2014) Seasonal variation of physical and chemical properties in TSP, PM_{10} and $PM_{2.5}$ at a roadside site in Beijing and their influence on atmospheric visibility. Aersol Air Qual Res 14:954–969

24. Fang G, Chang S (2010) Atmospheric particulate (PM_{10} and $PM_{2.5}$) mass concentration and seasonal variation study in the Taiwan area during 2000–2008. Atmos Res 98:368–377

25. Tian Y, Shi G, Huang-Fu Y, Song D, Liu J, Zhou L, Feng Y (2016) Seasonal and regional variations of source contributions for PM_{10} and $PM_{2.5}$ in urban environment. Sci Total Environ 557–558:697–704

26. Wang Q, Jiang N, Yin S, Li X, Yu F, Guo Y, Zhang R (2017) Carbonaceous species in $PM_{2.5}$ and PM_{10} in urban area of Zhengzhou in China: seasonal variations and source apportionment. Atmos Res 191:1–11

27. Arif M, Kumar R, Kumar R, Eric Z, Gourav P (2018) Ambient black carbon, $PM_{2.5}$ and PM_{10} at Patna: influence of anthropogenic emissions and brick kilns. Sci Total Environ 624:1387–1400

28. Hussein T, Alghamdi A, Khoder M, AbdelMaksoud S, Al-Jeelani H, Goknil K, Shabbaj I, Almehmadi M, Hyvärinen A, Lihavainen H, Hämeri K (2014) Particulate matter and number concentrations of particles larger than 0.25 μm in the urban atmosphere of Jeddah, Saudi Arabia. Aersol Air Qual Res 14:1383–1391

29. Kassomenos P, Vardoulakis S, Chaloulakou A, Grivas G, Borge R, Lumbreras J (2012) Levels, sources and seasonality of coarse particles (PM_{10}-$PM_{2.5}$) in three European capitals—implications for particulate pollution control. Atmos Environ 54:337–347

30. Tran HNQ, Mölders N (2011) Investigations on meteorological conditions for elevated $PM_{2.5}$ in Fairbanks, Alaska. Atmos Res 99:39–49

31. Yang Q, Yuan Q, Li T, Shen H, Zhang L (2017) The relationships between $PM_{2.5}$ and meteorological factors in china: seasonal and regional variations. Int J Environ Res Public Health 14:1510

32. Luo J, Du P, Samat A, Xia J, Che M, Xue Z (2017) Spatiotemporal pattern of $PM_{2.5}$ concentrations in mainland China and analysis of its influencing factors using geographically weighted regression. Sci Rep 7:40607

33. Zhang L, Dong L, Huang Y, Shi S, Yang W, Zhou L (2016) Seasonality in polybrominated diphenyl ether concentrations in the atmosphere of the Yangtze River Delta, China. Chemosphere 150:438–444

34. Rauert C, Schuster JK, Eng A, Harner T (2018) Global atmospheric concentrations of brominated and chlorinated flame retardants and organophosphate esters. Environ Sci Technol 52(5):2777–2789

35. Gevao B, Ghadban AN, Porcelli M, Ali L, Rashdan A, Al-Bahloul M, Matrouk K, Zafar J (2013) Seasonal variations in the atmospheric concentrations of polybrominated diphenyl ethers in Kuwait. Sci Total Environ 454–455:534–541

36. Li Q, Yang K, Li K, Liu X, Chen D, Li J, Zhang G (2017) New halogenated flame retardants in the atmosphere of nine urban areas in China: pollution characteristics, source analysis and variation trends. Environ Pollut 224:679–688

37. Cincinelli A, Pieri F, Martellini T, Passaponti M, Bubba D, Vento D, Katsoyiannis A (2014) Atmospheric occurrence and gas-particle partitioning of PBDEs in an industrialised and urban area of Florence, Italy. Aersol Air Qual Res 14:1121–1130

38. Castro-Jiménez J, Barhoumi B, Paluselli A, Tedetti M, Jiménez B, Muñoz-Arnanz J, Wortham H, Ridha Driss M, Sempéré R (2017) Occurrence, loading, and exposure of atmospheric particle-bound POPs at the African and European edges of the western Mediterranean sea. Environ Sci Technol 51:13180–13189

39. Yu Z, Liao RE, Li H, Mo L, Zeng X, Sheng G, Fu J (2011) Particle-bound Dechlorane Plus and polybrominated diphenyl ethers in ambient air around Shanghai, China. Environ Pollut 159:2982–2988

40. Li W, Huo C, Liu L, Song W, Zhang Z, Ma W, Qiao L, Li Y (2016) Multi-year air monitoring of legacy and current-use brominated flame retardants in an urban center in northeastern China. Sci Total Environ 571:633–642

41. Li Y, Lin T, Wang F, Ji T, Guo Z (2015) Seasonal variation of polybrominated diphenyl ethers in $PM_{2.5}$ aerosols over the East China Sea. Chemosphere 119:675–681

42. Beser MI, Beltrán J, Yusà V (2014) Design of experiment approach for the optimization of polybrominated diphenyl ethers determination in fine airborne particulate matter by microwave-assisted extraction and gas chromatography coupled to tandem mass spectrometry. J Chromatogr A 1323:1–10

43. Qiu X, Zhu T, Hu J (2010) Polybrominated diphenyl ethers (PBDEs) and other flame retardants in the atmosphere and water from Taihu Lake, East China. Chemosphere 80:1207–1212

44. Zhu Y, Sun D, Yang N, Ding Y, Feng W, Hong W, Zhu S, Li Y (2017) Temporal and spatial distributions of PBDEs in atmosphere at Shanghai rural regions, China. Environ Sci Pollut Res 24:10885–10892

45. Su Y, Hung H, Sverko E, Fellin P, Li H (2007) Multi-year measurements of polybrominated diphenyl ethers (PBDEs) in the Arctic atmosphere. Atmos Environ 41:8725–8735

46. Hoh E, Hites RA (2005) Brominated flame retardants in the atmosphere of the east-central United States. Environ Sci Technol 39:7794–7802

47. Anh HQ, Tomioka K, Tue NM, Tri TM, Minh TB, Takahashi S (2018) PBDEs and novel brominated flame retardants in road dust from northern Vietnam: levels, congener profiles, emission sources and implications for human exposure. Chemosphere 197:389–398

48. Wang C, Li W, Chen J, Wang H, Li T, Shen G, Shen H, Huang Y, Wang R, Wang B, Zhang Y, Tang J, Liu W, Wang X, Tao S (2012) Summer atmospheric polybrominated diphenyl ethers in urban and rural areas of northern China. Environ Pollut 171:234–240

49. 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

50. Raff JD, Hites RA (2007) Deposition versus photochemical removal of PBDEs from lake superior air. Environ Sci Technol 41:6725–6731

51. Fang L, Huang J, Yu G, Wang L (2008) Photochemical degradation of six polybrominated diphenyl ether congeners under ultraviolet irradiation in hexane. Chemosphere 71:258–267

52. Ma W, Li W, Zhang Z, Liu L, Song W, Huo C, Yuan Y, Li Y (2017) Occurrence and source apportionment of atmospheric halogenated flame retardants in Lhasa City in the Tibetan Plateau, China. Sci Total Environ 607–608:1109–1116

53. Kurt-Karakus PB, Alegria H, Jantunen L, Birgul A, Topcu A, Jones KC, Turgut C (2017) Polybrominated diphenyl ethers (PBDEs) and alternative flame retardants (NFRs) in indoor and outdoor air and indoor dust from Istanbul-Turkey: levels and an assessment of human exposure. Atmos Pollut Res 8:801–815

54. Li W, Qi H, Ma W, Liu L, Zhang Z, Mohammed MOA, Song W, Zhang Z, Li Y (2015) Brominated flame retardants in Chinese air before and

Meng *et al. Environ Sci Eur*   (2019) 31:61

Page 11 of 11

after the phase out of polybrominated diphenyl ethers. Atmos Environ 117:156–161

55. Besis A, Voutsa D, Samara C (2016) Atmospheric occurrence and gas-particle partitioning of PBDEs at industrial, urban and suburban sites of Thessaloniki, northern Greece: implications for human health. Environ Pollut 215:113–124

56. Hoff RM, Brice KA, Halsall CJ (1998) Nonlinearity in the slopes of Clausius–Clapeyron plots for SVOCs. Environ Sci Technol 32:1793–1798

57. Tian M, Chen S, Wang J, Zheng X, Luo X, Mai B (2011) Brominated flame retardants in the atmosphere of E-waste and rural sites in southern China: seasonal variation, temperature dependence, and gas-particle partitioning. Environ Sci Technol 45:8819–8825

58. Moon H-B, Kannan K, Lee S-J, Choi M (2007) Atmospheric deposition of polybrominated diphenyl ethers (PBDEs) in coastal areas in Korea. Chemosphere 66:585–593

59. Zhang X, Diamond ML, Ibarra C, Harrad S (2009) Multimedia modeling of polybrominated diphenyl ether emissions and fate indoors. Environ Sci Technol 43:2845–2850

60. Tittlemier SA, Halldorson T, Stern GA, Tomy GT (2002) Vapor pressures, aqueous solubilities, and henrys law constants of some brominated flame retardants. Environ Toxicol Chem 21:1804

61. Harner T, Shoeib M (2002) Measurements of octanol–air partition coefficients (KOA) for polybrominated diphenyl ethers (PBDEs): predicting partitioning in the environment. J Chem Eng Data 47:228–232

62. Yang M, Li Y, Qiao L, Zhang X (2018) Estimating subcooled liquid vapor pressures and octanol–air partition coefficients of polybrominated diphenyl ethers and their temperature dependence. Sci Total Environ 628–629:329–337

63. Cetin B, Odabasi M (2008) Atmospheric concentrations and phase partitioning of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey. Chemosphere 71:1067–1078

64. Bidleman TF, Harner T (2000) Sorption to aerosols. In: Boethling RS et al (eds) Handbook of property estimation methods for chemicals: environmental and health sciences. CRC Press LLC, Boca Raton

65. Fang X, Bi X, Xu H, Wu J, Zhang Y, Feng Y (2017) Source apportionment of ambient PM_{10} and $PM_{2.5}$ in Haikou, China. Atmos Res 190:1–9

66. Shahid I, Kistler M, Mukhtar A, Ghauri BM, Ramirez-Santa Cruz C, Bauer H, Puxbaum H (2016) Chemical characterization and mass closure of PM_{10} and $PM_{2.5}$ at an urban site in Karachi–Pakistan. Atmos Environ 128:114–123

67. Kavouras IG, Lawrence J, Koutrakis P, Stephanou EG, Oyola P (1999) Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: source reconciliation and evaluation of sampling artifacts. Atmos Environ 33:4977–4986

68. Goss KU, Schwarzenbach RP (1998) Gas/solid and gas/liquid partitioning of organic compounds: critical evaluation of the interpretation of equilibrium constants. Environ Sci Technol 32:2025–2032

69. de la Torre A, Barbas B, Sanz P, Navarro I, Artíñano B, Martínez MA (2018) Traditional and novel halogenated flame retardants in urban ambient air: gas-particle partitioning, size distribution and health implications. Sci Total Environ 630:154–163

70. Barbas B, de la Torre A, Sanz P, Navarro I, Artíñano B, Martínez MA (2018) Gas/particle partitioning and particle size distribution of PCDD/Fs and PCBs in urban ambient air. Sci Total Environ 624:170–179

71. Su P, Tomy GT, Hou C, Yin F, Feng D, Ding Y, Li Y (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

72. U.S.EPA (2012) Integrated risk information system. http://www.epa.gov/iris. Accessed 15 Sept 2019

73. U.S.EPA (2010) An exposure assessment of polybrominated diphenyl ethers. National Center for Environmental Assessment, Washington, DC

74. U.S.EPA (2008) Integrated risk information system. https://cfpub.epa.gov/ncea/iris. Accessed 15 Sept 2019

75. Khan MU, Li J, Zhang G, Malik RN (2016) First insight into the levels and distribution of flame retardants in potable water in Pakistan: an underestimated problem with an associated health risk diagnosis. Sci Total Environ 565:346–359

76. Khan MU, Li J, Zhang G, Malik RN (2016) New insight into the levels, distribution and health risk diagnosis of indoor and outdoor dust-bound FRs in colder, rural and industrial zones of Pakistan. Environ Pollut 216:662–674

Publisher's Note