



# Atmospheric deposition and air–soil exchange of polybrominated diphenyl ethers (PBDEs) in a background site in Central China

Lingxi Zhan<sup>1</sup> · Tian Lin<sup>2</sup> · Hairong Cheng<sup>1,3</sup> · Zuwu Wang<sup>1</sup> · Zhineng Cheng<sup>4</sup> · Deng Zhou<sup>5</sup> · Zhengxin Qin<sup>5</sup> · Gan Zhang<sup>4</sup>

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## Abstract

Jinsha (JSH) is one of the regional background sites in Central China. In this study, eight polybrominated diphenyl ethers (PBDEs) were measured in atmospheric deposition samples (dry particle, wet particle, and wet dissolved), air (gaseous and particle) samples, and soil samples that were collected from March 2012 to March 2013. Of all eight PBDEs, BDE-209 was the most abundant congener in both deposition samples and air/soil samples. Average dry particle, wet particle, and wet dissolved deposition fluxes of  $\Sigma_8$ PBDEs were  $270 \pm 310 \text{ pg m}^{-2} \text{ day}^{-1}$ ,  $130 \pm 210 \text{ pg m}^{-2} \text{ day}^{-1}$ , and  $250 \pm 330 \text{ pg m}^{-2} \text{ day}^{-1}$ , respectively, while those of BDE-209 were  $210 \pm 290 \text{ pg m}^{-2} \text{ day}^{-1}$ ,  $80 \pm 120 \text{ pg m}^{-2} \text{ day}^{-1}$ , and  $160 \pm 290 \text{ pg m}^{-2} \text{ day}^{-1}$ , respectively. Dry deposition velocities of individual PBDE ranged from  $0.11 \pm 0.15 \text{ cm s}^{-1}$  (BDE-183) to  $0.24 \pm 0.38 \text{ cm s}^{-1}$  (BDE-209), and total washout ratios ranged from  $5.0 \times 10^3$  (BDE-28) to  $4.2 \times 10^4$  (BDE-209). The calculated net air–soil gas exchange flux of  $\Sigma_8$ PBDEs was  $-16 \pm 13 \text{ pg m}^{-2} \text{ day}^{-1}$ , suggesting the deposition status of PBDEs. The gas exchange flux at the air–soil interface was significantly lower than the deposition flux, which only accounted for 2.5% of the total deposition flux, implying that atmospheric deposition was an important input pathway for PBDEs to soils. Overall, the pollution level of the soil was relatively low, and the soil serves as a sink for PBDEs from adjacent regions.

**Keywords** PBDEs · Wet and dry deposition · Seasonal variation · Air soil gas exchange · Background site

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✉ Hairong Cheng  
chenghr@whu.edu.cn

<sup>1</sup> School of Resource and Environmental Sciences, International Cooperation Base for Sustainable Utilization of Resources and Energy in Hubei Province, Wuhan University, Wuhan 430072, China

<sup>2</sup> State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

<sup>3</sup> Hubei Key Laboratory of Industrial Fume & Dust Pollution Control, Jiangnan University, Wuhan 430056, China

<sup>4</sup> State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

<sup>5</sup> Meteorological Bureau of Xianning, Xianning 437100, China

## Introduction

Flame retardants are chemical additives used in commercial products (e.g., paints, furniture, and electrical equipment) to isolate the source of fire, which mainly contain bromine, chlorine, or phosphorus (Papachlimitzou et al. 2012). Of these, polybrominated diphenyl ethers (PBDEs) are one of brominated flame retardants and were largely produced and used in the 1990s and early 2000s, until the discovery that PBDEs have the potential for bioaccumulation, adverse effects on animals, and long-range atmospheric transport (Stockholm Convention 2014; Moon et al. 2007; Okonski et al. 2014). In an effort to prohibit the production and use of PBDEs, penta- and octa-BDE were listed in the Stockholm Convention as persistent organic pollutants (POPs) in 2009, while deca-BDE is listed in the Annex A of POPs in Stockholm Convention in 2017 but still used on a regular basis (POPs Action in China 2017; Stockholm Convention 2014; Li et al. 2015, 2017; Möller et al. 2012).

The concentration levels of semi-volatile organic compounds (SOCs) in soil and air are greatly affected by air–soil

gas exchange and atmospheric deposition, which may partly influence the regional or global transport/fate of SOCs (Backe et al. 2004; Cetin and Odabasi 2007; Tasdemir et al. 2012). Atmospheric deposition is an important pathway of SOCs to soil surface in remote areas (Birgül and Tasdemir 2011; Fang et al. 2012; Li et al. 2010; Tian et al. 2011). Several authors have evaluated atmospheric depositions of PBDEs at rural areas, urban/suburban areas, factory area, lake regions, and coastal areas (Argiriadis et al. 2014; Moon et al. 2007; Ry et al. 2002; Schure et al. 2004; Venier and Hites 2008), whereas studies on air–soil gas exchange of PBDEs are still scarce. Cetin and Odabasi (2007) have investigated air–soil gas exchange fluxes of  $\Sigma_7$ PBDEs in Izmir, Turkey, while Degrendele et al. (2016) determined air–soil gas exchange fluxes of SOCs [polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and PBDEs] at two background sites in Central Europe.

So far, research on whether the Chinese background soil is a source or a sink is limited. However, based on the continuous use and emission of PBDEs in China during the last decades, it is highly likely that the soil in background areas acts as a sink for PBDEs from atmospheric deposition. When certain amounts of PBDEs reached in the soil, such sites may become PBDE sources and re-emit these substances. This study focused on Jinsha (JSH), one of the regional background Chinese Meteorological Administration Atmosphere Watch Network (CAWNET) sites in Central China, with the following objectives: (1) to investigate the atmospheric deposition fluxes of PBDEs and its seasonal variations, (2) to assess the dry deposition velocities and washout ratios of PBDEs, and (3) the most important, to identify the role of soil as a source or sink at the air–soil interface, based on atmospheric deposition and air–soil gas exchange fluxes.

## Materials and methods

### Sample collection

Dry particle, wet particle, and wet dissolved deposition samples were collected at JSH (29° 38' N, 114° 12' E, 750 m a.s.l.), a regional background site in Central China (Fig. 1). Detail information about the sampling site was described in our previous study (Zhan et al. 2017). Briefly, it is on an isolated mountain peak and the surrounding area is sparsely populated. During the sampling year, the average temperature was 16.3 °C, the average relative humidity was 78.6%, and both rain and snow were observed. Moreover, the temperature and precipitation were both the highest in summer (Fig. 2).

Sampling was carried out biweekly from March 2012 to March 2013, using a dry–wet deposition sampler (DWDS). The DWDS has a rain sensor, which controls the active cover

to close the dry deposition section when it rains or snows. After a rain or snow event, the active cover moves to the wet deposition section. Both of the receiving areas for wet and dry depositions are 0.071 m<sup>2</sup>. Prior to the sampling, the inner surface of the glass jar was washed with distilled water and wiped with precleaned cotton, which was previously extracted with methanol, acetone, and dichloromethane (DCM). After sampling, the inner surface of the dry deposition glass jar was wiped with precleaned cotton. The cotton and the particles were combined to measure the dry particle deposition fluxes (Li et al. 2010). Wet samples were filtered through glass fiber filters (47 mm diameter, 0.7 μm pore size) to separate particle and dissolved phase. Then, the dissolved phase was filtered with a XAD-2 resin column. These samples were stored at –18 °C until further analysis.

Simultaneously, air and soil samples were collected. Details about air sampling and pretreatment process were described in our previous study (Yang et al. 2018), which is also detailed in Text S2.1. Soil samples were collected approximately once a month around the DWDS (< 10 m) during the sampling year. About 1 kg of soil samples was taken from the top 5 cm of the soil after removal of the large stones and pieces of vegetation. A total of 15 soil samples was collected. After sieving through a 1.0-mm mesh to remove large particles and organic debris, the soil samples were sealed with aluminum foil and stored at 4 °C. About 30 g of soil samples was used to determine the contents of organic carbon, and 30 g was used for PBDE analysis.

### Sample analysis

Prior to extraction, 10 ng of PCB-30, PCB-198, PCB-209, and 2,4,5,6-tetrachloro-*m*-xylene (TCmX) (AccuStandard, New Haven, CT) was added to each sample as a surrogate recovery standard. The wet dissolved deposition samples were eluted from XAD-2 resin column by DCM. Dry particle deposition, wet particle deposition, and soil samples were Soxhlet-extracted separately for 24 h with DCM. The extracts and the wet dissolved deposition samples were separately concentrated to a volume of 1 mL, using a rotary evaporator. An alumina/silica gel column [from the bottom to the top filled with neutral alumina (3 cm, 3% deactivated), neutral silica gel (3 g, 3% deactivated), 50% (on a weight basis) sulfuric acid silica gel (2 cm), and anhydrous sodium sulfate (1 cm)] was used for cleanup and fractionations: the fraction containing PBDEs was eluted with a 15 mL mixture of hexane and DCM (6:4, V/V) and concentrated to 0.2 mL via evaporation with a rotary evaporator and a nitrogen flow. Finally, 10 ng of <sup>13</sup>C-PCB-141 (AccuStandard, New Haven, CT) as an internal standard was added to the samples.

The eight PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209) were analyzed using an Agilent 7890/5975C gas chromatography–

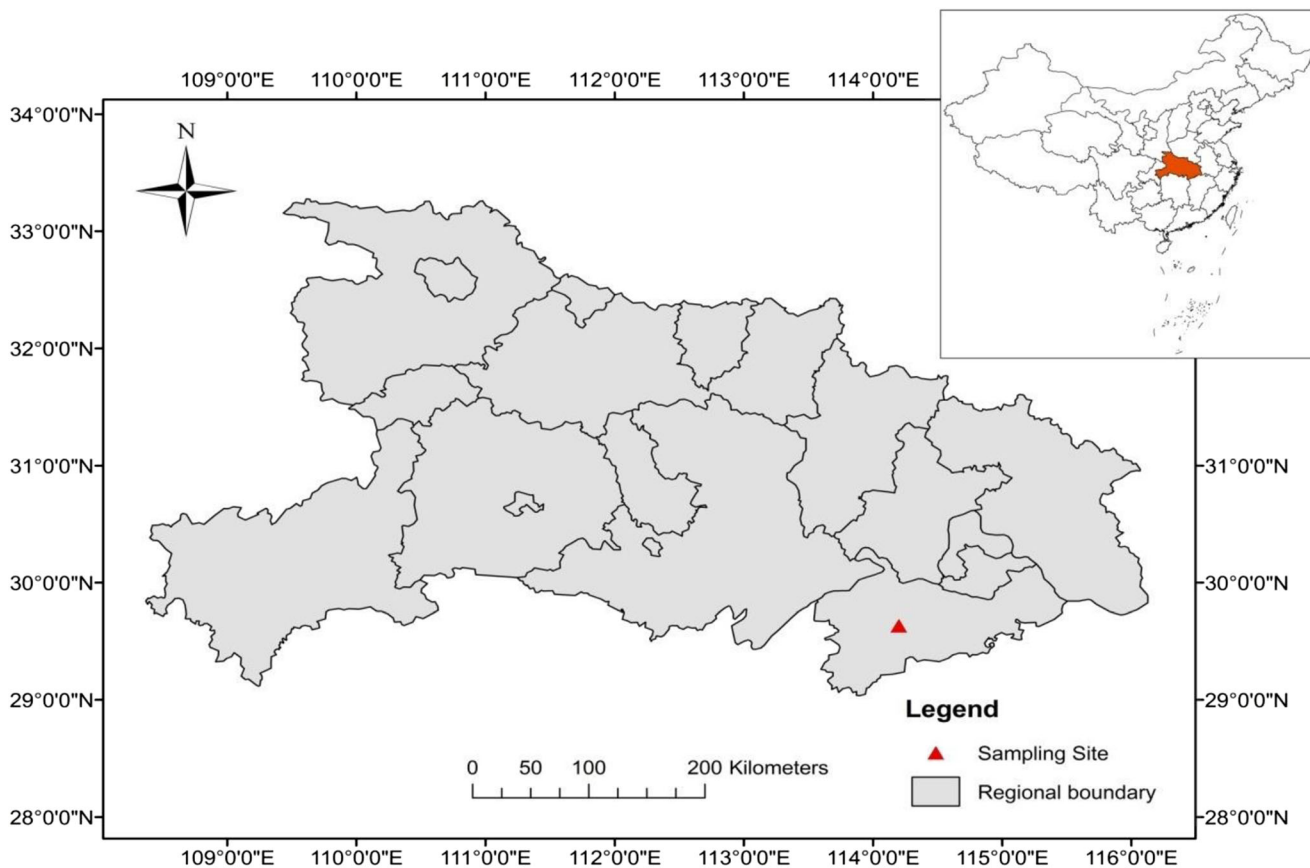


Fig. 1 Sampling location at Jinsha in Central China

mass selective detector (GC-MSD) with a HP-5MS column (15 m × 0.25 mm i.d. × 0.1 μm film thickness) using negative chemical ionization (NCI) under SIM mode. Helium was used as carrier gas, with a column flow rate at 1.2 mL min<sup>-1</sup>. The temperature of the ion source was maintained at 230 °C, while

that of the transfer line was 280 °C. The GC oven temperature program was set at 110 °C for 5 min, followed by 20 °C min<sup>-1</sup> to 200 °C (held for 4.5 min) and, finally, 10 °C min<sup>-1</sup> to 310 °C (held for 12 min). For each analysis, a 1-μL injection of the sample was made in the splitless mode.

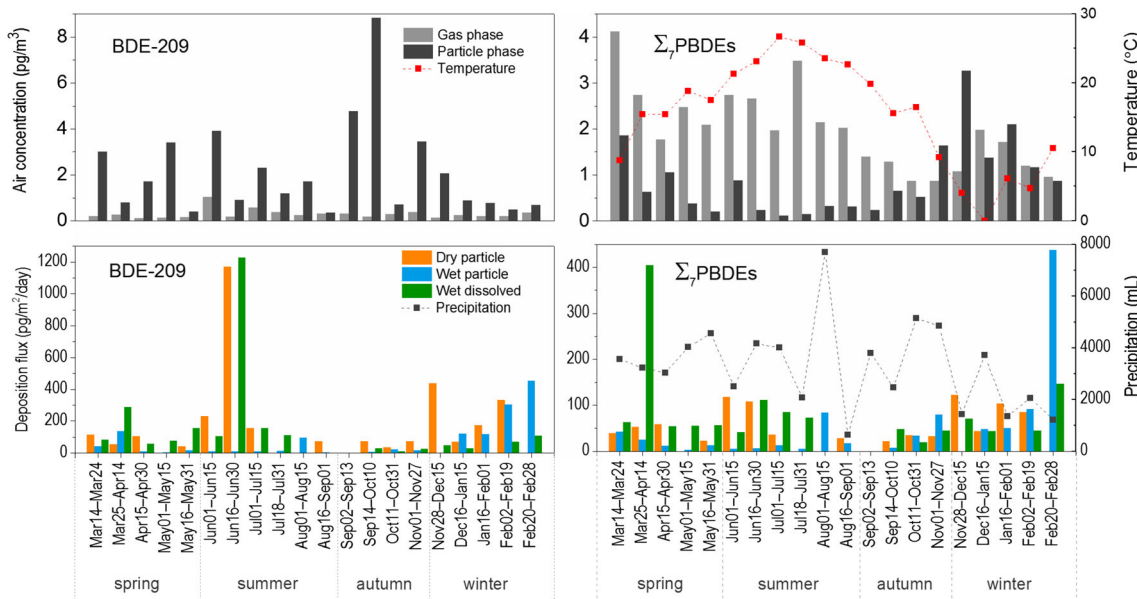


Fig. 2 Seasonal variations of atmospheric concentrations and atmospheric deposition fluxes for PBDEs

### Quality assurance and quality control

Quality assurance (QA) and quality control (QC) were conducted by analyzing laboratory and field blanks, instrument and method detection limits, and standard spiked recoveries. Filters and precleaned cotton were routinely placed in the field as field blanks. Lab blanks were precleaned cotton and filters. In all, five lab blanks and six field blanks were subject to the same analytical procedures as samples. The instrument detection limit (IDL) was defined as a signal of 3 times the noise. The method detection limits (MDLs) were quantified as the mean values of the field blanks plus three times the standard deviation of the field blank values. When compounds could not be detected in the field blanks, the MDLs were calculated as three times the IDLs. In the blank samples, not all compounds could be detected. The IDLs ranged from 0.10 to 0.36 pg, while the MDLs were 0.1–0.6 pg m<sup>-2</sup> day<sup>-1</sup> (the other seven PBDEs) and 2.9 pg m<sup>-2</sup> day<sup>-1</sup> (BDE-209) for deposition samples and ranged from 0.4 to 1 pg g<sup>-1</sup> for soil samples, respectively. The recoveries of PCB-209 were 88.7 ± 13.2% for soil samples, 75.9 ± 10.8% for dry and wet particle deposition samples, and 72.5 ± 8.5% for wet dissolved deposition samples. The recoveries for air samples were reported in our previous study (Yang et al. 2018) and detailed in Text S2.2. All the concentrations and fluxes present in this study were not corrected by the recoveries.

### Calculation of air–soil exchange fluxes

Air–soil exchanges are key input/output processes for SOCs in soil and air. Fugacity is the potential pressure of chemical between different interfaces, and the ratios of fugacities determine the exchange direction between soil and air (Harner et al. 2001). To assess air–soil exchange fluxes of PBDEs during the sampling period, air and soil fugacity as well as air–soil exchange fluxes were calculated.

The net flux ( $N$ , ng m<sup>-2</sup> h<sup>-1</sup>) from the soil to the air was calculated using the following equation (Backe et al. 2004; Tasdemir et al. 2012):

$$N = D_{SA}(f_s - f_a)$$

where  $D_{SA}$  is a transfer coefficient (mol Pa<sup>-1</sup> m<sup>-2</sup> h<sup>-1</sup>), which describes the molar flux between the soil and air compartments, and  $f_s$  and  $f_a$  are the fugacity values of POPs in soil and air, calculated according to the following equations (Harner et al. 2001):

$$f_s = C_s RT / 0.411 \varphi_{om} K_{oa}$$

$$f_a = C_a RT$$

where  $C_s$  is the soil concentration (mol m<sup>-3</sup>),  $C_a$  is the atmospheric gaseous concentration (mol m<sup>-3</sup>),  $R$  is the gas constant (8.314 pa m<sup>-3</sup> mol<sup>-1</sup> K<sup>-1</sup>),  $T$  is the absolute temperature (K),

and  $\varphi_{om}$  is the fraction of organic matter in the soil on a dry soil basis (1.7 times the organic carbon fraction). It was assumed that the fugacity capacity of the soil was entirely attributed to the organic matter fraction and that the soil bulk density was 1.5 × 10<sup>6</sup> g m<sup>-3</sup> (Bidleman and Leone 2004). Here,  $K_{oa}$  is the octanol–air partition coefficient, and the  $K_{oa}$  values of selected PBDEs were obtained and temperature-calculated according to previous studies (Harner and Shoeib 2001; Yadav et al. 2017) and are presented in Table S1. However, not all the SOCs existing in the soils have a tendency to exchange between air and soil; thus, the measured soil fugacities based on soil concentrations may lead to some overestimation (Cabrerizo et al. 2009).

The  $D_{SA}$  was defined by the three-resistance model (Koblizková et al. 2009)

$$D_{SA} = 1 / (1 / D_{SAB} + 1 / (D_{SAA} + D_{SAL}))$$

where  $D_{SAB}$ ,  $D_{SAA}$ , and  $D_{SAL}$  are contributing to the  $D_{SA}$  transfer coefficient and represent the air boundary layer, the soil–air phase diffusion, and the soil–water phase diffusion, respectively

$$D_{SAB} = K_{SA} Z_A$$

$$D_{SAA} = K_{SAP} Z_A$$

$$D_{SAL} = K_{SWP} Z_1$$

$$Z_1 = 1 / (R T K_{AW})$$

where  $K_{SA}$  is the soil–air boundary layer mass transfer coefficient (MTC),  $K_{SAP}$  is the soil–air phase diffusion MTC, and  $K_{SWP}$  is the soil–water phase diffusion MTC, with values of 5 m h<sup>-1</sup>, 0.02 m h<sup>-1</sup>, and 0.00001 m h<sup>-1</sup>, respectively. The fugacity capacity ( $Z$  value, mol m<sup>-3</sup> Pa<sup>-1</sup>) represents the competency of compounds to the environmental media. The  $Z$  value for air ( $Z_A$ ) was equal to 1 /  $RT$ ,  $K_{AW}$  ( $K_{AW} = H / RT$ ) is the dimensionless Henry’s law constant ( $H$ ), and Henry’s law constant values of selected PBDEs were adopted from former reports (Cetin and Odabasi 2005; Tittlemier et al. 2002).

## Results and discussion

### PBDEs in deposition samples

#### Deposition flux

The measured total deposition fluxes (dry particle, wet particle, and wet dissolved deposition) of Σ<sub>8</sub>PBDEs varied from 120 to 2600 pg m<sup>-2</sup> day<sup>-1</sup>, with an average value of 650 ± 590 pg m<sup>-2</sup> day<sup>-1</sup> (Table 1); these values were lower than those of remote mountain regions of Europe (3490–6420 pg m<sup>-2</sup> day<sup>-1</sup>) (Arellano et al. 2014) and a rural site in southern Sweden (25,700–65,200 pg m<sup>-2</sup> day<sup>-1</sup>) (Moon et al. 2007).



**Table 1** Atmospheric deposition fluxes for PBDEs ( $\text{pg m}^{-2} \text{ day}^{-1}$ )

Compounds	Dry particle deposition			Wet particle deposition			Wet dissolved deposition			Total deposition		
	Min	Max	Average	Min	Max	Average	Min	Max	Average	Min	Max	Average
BDE-28	3.9	40	14	1.2	79	10	1.4	70	11	6.4	100	35
BDE-47	0.3	23	8.1	0.1	44	5.6	4.3	69	23	2.9	79	37
BDE-100	0.2	11	2.5	0.1	50	4.3	1.6	37	6.2	0.7	57	13
BDE-99	0.2	23	7.9	0.2	37	5.1	6.3	79	22	7.9	92	35
BDE-154	2.6	13	6.4	0.2	46	5.3	0.4	38	5.1	0.6	55	17
BDE-153	1.1	18	6.0	0.3	41	4.8	0.5	57	7.5	4.1	64	18
BDE-183	4.3	38	15	0.7	160	21	2.5	53	11	7.5	170	47
BDE-209	37	1200	210	2.9	450	80	11	1200	160	70	2400	450
$\Sigma_8$ PBDEs	65	1300	270	8.5	890	130	31	1300	250	120	2600	650

The average dry particle, wet particle, and wet dissolved deposition fluxes of  $\Sigma_8$ PBDEs were  $270 \pm 310 \text{ pg m}^{-2} \text{ day}^{-1}$ ,  $130 \pm 210 \text{ pg m}^{-2} \text{ day}^{-1}$ , and  $250 \pm 330 \text{ pg m}^{-2} \text{ day}^{-1}$ , accounting for 41.7%, 20.2%, and 38.1% of the total deposition flux, respectively (Fig. S1). In this study, wet deposition (wet particle and wet dissolved) flux was higher than dry particle deposition flux, which was in line with the study on a remote site of the Mazzorbetto Island (Gambaro et al. 2009). More specifically, high-brominated PBDEs with a higher octanol–water partition coefficient ( $K_{ow}$ ) (including BDE-153, BDE-154, BDE-183, and BDE-209) were concentrated in particle (dry + wet) deposition samples, whereas some low-brominated PBDEs (such as BDE-47 and BDE-99) were largely distributed in dissolved deposition samples (Fig. S1), which was in agreement with previous studies from Sweden (Schure et al. 2004). However, BDE-28 showed higher levels in particle (wet + dry) deposition samples than wet dissolved samples (Fig. S1), which might be attributed to the revolatilization of dissolved BDE-28 in a wet deposition sampler during the sampling period (about 2 weeks).

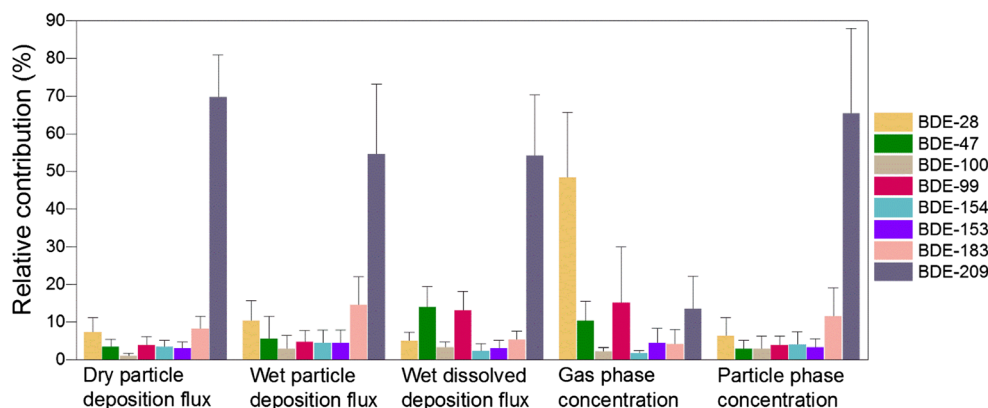
BDE-209 was the most abundant congener in dry particle, wet particle, and wet dissolved deposition, accounting for 69.7%, 54.6%, and 54.2% of  $\Sigma_8$ PBDEs, respectively. This is in line with the ongoing use of deca-BDE in some areas (Li et al. 2017). The deca-PBDE formulation made up 83.3% of the 2001 PBDE global market demand (La Guardia et al. 2006), and this proportion is relatively higher than those in dry and wet depositions at JSH. It may be due to that some BDE-209 underwent debromination or that lighter PBDEs were more prone to volatilization compared with BDE-209. The total deposition flux of BDE-209 at JSH was 70–2400 ( $450 \pm 520$ )  $\text{pg m}^{-2} \text{ day}^{-1}$  (Table 1), which was lower than those of a rural site in Korea (25,400–60,700  $\text{pg m}^{-2} \text{ day}^{-1}$ ) (Moon et al. 2007), a rural site in southern Sweden (4300  $\text{pg m}^{-2} \text{ day}^{-1}$ ) (Schure et al. 2004), and remote mountain regions of Europe (2370–5400  $\text{pg m}^{-2} \text{ day}^{-1}$ ) (Arellano et al. 2014). The average dry particle deposition flux of BDE-209 was 210

$\pm 290$  (6.9–1200)  $\text{pg m}^{-2} \text{ day}^{-1}$ , which was lower than those of a suburban site in Turkey ( $49,400 \pm 89,000 \text{ pg m}^{-2} \text{ day}^{-1}$ ) (Cetin and Odabasi 2007) and an urban site in southern Sweden (10,900  $\text{pg m}^{-2} \text{ day}^{-1}$ ) (Schure et al. 2004). Similarly, the average wet deposition flux (wet particle + wet dissolved) of BDE-209 was  $240 \pm 120 \text{ pg m}^{-2} \text{ day}^{-1}$ , which was also lower than those of semirural sites in the Pearl River Delta (39,000–48,000  $\text{pg m}^{-2} \text{ day}^{-1}$ ) (Zhang et al. 2009) and urban sites in Guangzhou (110,000  $\pm 137,000 \text{ pg m}^{-2} \text{ day}^{-1}$ ) (Guo et al. 2014).

### Seasonal variations and impacting factors

Seasonal variations of atmospheric concentrations and deposition fluxes of BDE-209 and  $\Sigma_7$ PBDEs at JSH are exhibited in Fig. 2. Relatively high dry particle deposition fluxes of BDE-209 were observed in summer and winter. Due to some missing samples that were not well transported or failed in pretreatment process, the average level of dry particle deposition fluxes of BDE-209 may be enhanced in summer. Similar congener profiles were observed between dry particle deposition and atmospheric particle concentration (Fig. 3). However, no obvious correlation was found between atmospheric particle concentrations and dry particle deposition fluxes for BDE-209 ( $R = -0.152$ ,  $p > 0.05$ , Pearson correlation), suggesting that atmospheric particle concentration was only partly influenced dry particle deposition fluxes of BDE-209. In summer, the proportions of BDE-209 in dry particle deposition (84.9%) was similar to that in atmospheric particle concentration (82.2%), while in winter (71.2%), it was about twice higher than that in atmospheric particle concentration (33.6%) (Table S2), possibly because that BDE-209 existed more in the particulate phase in winter (Yang et al. 2018), implying the influence of temperature. In addition, the increased bromine number is accompanied by the decreased saturated vapor pressure and volatility (Tittlemier et al. 2002), so that BDE-209 was more inclined to deposit as a particle compared with other

**Fig. 3** Composition profiles of PBDEs in atmospheric gaseous-phase concentration, particle phase concentration, dry particle deposition flux, wet particle deposition flux, and wet dissolved deposition flux



PBDEs (proportions of BDE-209 in dry particle deposition were both higher than those in atmospheric particle concentration in summer and winter). For the other PBDEs, dry particle deposition fluxes were higher in winter, and significant correlations were found between dry particle deposition fluxes and atmospheric particle concentrations of  $\Sigma_7$ PBDEs ( $R = 0.535, p < 0.05$ ), BDE-154 ( $R = 0.524, p < 0.05$ ), and BDE-183 ( $R = 0.691, p < 0.01$ ), suggesting a high influence by atmospheric particle concentrations.

Wet particle deposition fluxes of both BDE-209 and  $\Sigma_7$ PBDEs were high in winter (Fig. 2). Similar congener profiles were also observed for wet particle deposition and atmospheric particle concentration (Fig. 3). Whereas no obvious correlation was found for wet particle deposition fluxes (both BDE-209 and  $\Sigma_7$ PBDEs) and atmospheric particle concentration, implying partly the effect of atmospheric particle concentration on wet particle deposition fluxes. In winter, the proportion of BDE-209 in wet particle deposition was higher than that in atmospheric particle concentration (Table S2), which can also be explained with that BDE-209 existed more in the particulate phase in winter and tended to be deposited. In addition, a negative correlation between wet particle deposition fluxes of BDE-209 and temperature was found ( $R = -0.493, p < 0.05$ ), suggesting the influence of temperature on wet particle deposition fluxes, whereas it reversed in summer that the proportion of BDE-209 in wet particle deposition was lower than that in atmospheric particle concentration, which might be attributed to the precipitation type and intensity and enhanced proportions of the other seven PBDEs, especially low-brominated PBDEs. Certain amounts of particulate low-brominated PBDEs (such as BDE-28 and BDE-47) remained in the atmosphere and did not reach critical deposition levels; once it rained, they would be deposited (precipitation was highest in summer), suggesting that precipitation had a strong scavenging effect on atmospheric particulate low-brominated PBDEs.

Wet dissolved deposition fluxes of PBDEs were high in summer and spring (Fig. 2). Wet dissolved deposition fluxes of PBDEs were uncorrelated with atmospheric concentrations

or temperature, and the congener profile of wet dissolved deposition was considerably different from the atmospheric gaseous concentration, but comparable to the atmospheric particle concentration (Fig. 3). These findings indicate the combined influence of precipitation and atmospheric concentration. In other words, contaminants in the atmosphere were effectively washed out by rain at the initial period, a period that wet dissolved deposition flux was positively related to atmospheric concentration. Once precipitation decreases or the contaminants in the atmosphere are all washed out, the flushing efficiency decreases (Koester and Hites 1992). In addition, PBDEs that volatilized from soil (by air–soil exchange) enhanced the atmospheric gaseous concentration, which might also have influences on wet dissolved deposition.

### Dry deposition velocities and washout ratios

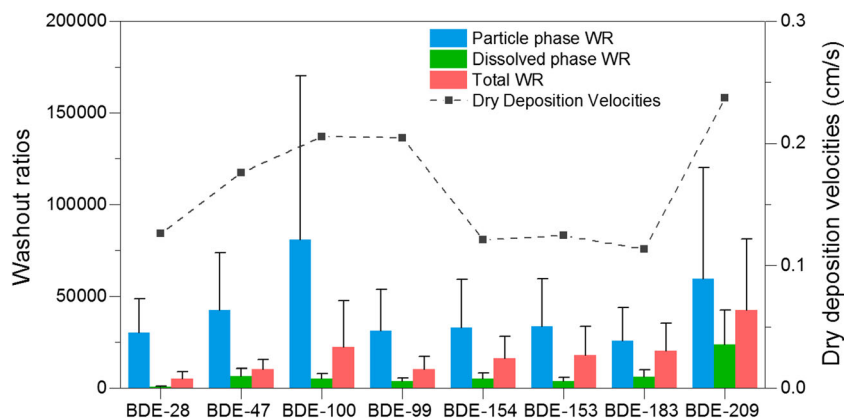
#### Dry deposition velocities

In the absence of precipitation, compounds in the atmosphere reach the ground through dry deposition (Cetin and Odabasi 2007). Dry deposition velocities ( $V_D$ ), which strongly depend on atmospheric concentrations, particle size distributions, wind speed, and deposition surface, are calculated based on dry particle deposition flux ( $F_D$ ) and particulate concentrations in the atmosphere ( $C_{p,air}$ ) (Li et al. 2010; Schure et al. 2004)

$$V_D = F_D / C_{p,air}$$

The  $V_D$  values of PBDEs ranged from  $0.11 \pm 0.15 \text{ cm s}^{-1}$  (BDE-183) to  $0.24 \pm 0.38 \text{ cm s}^{-1}$  (BDE-209) (Fig. 4), comparable to values reported from Hong Kong ( $0.24\text{--}0.32 \text{ cm s}^{-1}$ ) (Li et al. 2010) and urban Guangzhou ( $0.11\text{--}0.28 \text{ cm s}^{-1}$ ) (Zhang et al. 2012) but significantly lower than those measured at an urban site in Sweden ( $1.2\text{--}49 \text{ cm s}^{-1}$ ) (Schure et al. 2004) and a suburban site in Turkey ( $3.9\text{--}11.5 \text{ cm s}^{-1}$ ) (Cetin and Odabasi 2007). The difference may be ascribed to that the higher sampling height might reduce the velocities of dry

**Fig. 4** Average washout ratios and dry deposition velocities for PBDEs (with 95% confidence intervals)



deposition, and  $V_D$  was expected to be higher at urban sites than at background area (Shannigrahi et al. 2005; Su et al. 2007).

Significant correlations between  $V_D$  and dry particle deposition fluxes were found for BDE-47 ( $R = 0.618$ ,  $p < 0.05$ ), BDE-99 ( $R = 0.770$ ,  $p < 0.01$ ), and BDE-209 ( $R = 0.937$ ,  $p < 0.01$ ), while no correlations between  $V_D$  and wind speed or humidity were found. In addition,  $V_D$  did not significantly differ between each individual PBDE, indicating that all PBDEs have similar particle size distribution. Moreover, the highest  $V_D$  values of PBDEs all occurred in summer, implying higher mechanical and thermal turbulences at high temperatures (Zhang et al. 2012).

### Washout ratios

At rain events, pollutants in the atmosphere are washed out, and the washout ratio can be used to measure the removal efficiency of pollutants in the atmosphere (Cindoruk and Ozturk 2016). The total washout ratios ( $WR_T$ ), which depend on the conditions, the characteristics of SOCs, the atmospheric contents, and other factors (Bidleman 1988), were empirically calculated by dissolved washout ratios ( $WR_D$ ), particulate washout ratios ( $WR_P$ ), and particulate concentration fraction ( $\varphi$ ). In addition,  $WR_D$  and  $WR_P$  are calculated by gaseous/dissolved and particulate concentrations in air and rain samples, respectively (Ry et al. 2002; Schure et al. 2004)

$$WR_D = C_{d,rain}/C_{g,air}$$

$$WR_P = C_{p,rain}/C_{p,air}$$

$$WR_T = (1-\varphi)WR_D + \varphi WR_P$$

The calculated average  $WR_T$  of PBDEs ranged from  $5.0 \times 10^3$  (BDE-28) to  $4.2 \times 10^4$  (BDE-209) (Fig. 4), which were comparable with that measured in the Pearl River Delta (average of  $\Sigma_{15}PBDE$  was  $4.1 \times 10^4$ ) (Zhang et al. 2009) but lower than those reported in Sweden ( $3.3 \times 10^5$ – $1.1 \times 10^6$ ) and Hong Kong and Guangzhou ( $7.7 \times 10^3$ – $3.5 \times 10^8$ ). Continuous and intense rain events might enhance the

volume but reduce the concentration of the deposition sample (Zhang et al. 2009).  $WR_T$  of BDE-209 was the highest among all PBDEs at JSH, which was comparable to that in the Pearl River Delta ( $6 \times 10^4$ ), suggesting that BDE-209 was the most easily to be scavenged by rain (Schure et al. 2004; Zhang et al. 2009). Negative correlations between  $WR_T$  and temperature were found for BDE-28 ( $R = -0.587$ ,  $p < 0.01$ ) and BDE-47 ( $R = -0.535$ ,  $p < 0.05$ ), indicating that temperature was an important influencing factor on wet deposition of them.

The calculated  $WR_P$  of PBDEs ranged from  $2.6 \times 10^4$  (BDE-183) to  $8.1 \times 10^4$  (BDE-100), which were comparable to those of an urban site in Paris ( $4 \times 10^4$ – $5 \times 10^5$ ) (Tlili et al. 2012). Moreover,  $WR_P$  of PBDEs was several times higher than  $WR_D$ , which was consistent with the finding in Sweden that particle scavenging rather than gas scavenging is the main removal mechanism for PBDEs (Schure et al. 2004), implying that wet particle deposition was more efficient than wet dissolved deposition. Significant correlations were found between  $WR_P$  and wet particle deposition fluxes for BDE-183 ( $R = 0.805$ ,  $p < 0.01$ ) and BDE-209 ( $R = 0.872$ ,  $p < 0.01$ ), implying that the removal efficiency of particle-bound high-brominated PBDEs was high.

The calculated  $WR_D$  of PBDEs ranged from  $5.4 \times 10^2$  (BDE-28) to  $2.3 \times 10^4$  (BDE-209), and  $WR_D$  of BDE-209 is significantly higher than those of other PBDEs (Fig. 4). It is attributed that gaseous-phase concentrations of BDE-209 were lower than those of  $\Sigma_7PBDEs$ , whereas dissolved deposition fluxes of BDE-209 were higher than those of  $\Sigma_7PBDEs$ . Moreover, relatively lower dissolved deposition fluxes of  $\Sigma_7PBDEs$  might due to their re-volatilization in a wet deposition sampler during the sampling period (about 2 weeks), which may not correspond to the original levels. In this study,  $WR_D$  was not correlated separately with meteorological parameters, deposition fluxes, or atmospheric concentrations, suggesting that it might be affected by air–soil exchange or the combined influence of these factors.

### Soil concentrations and air–soil gas exchange

Soil samples were collected throughout the sampling year, and soil concentrations of PBDEs are presented in Table S3. The concentrations of  $\Sigma_8$ PBDEs ranged from 29 to 240  $\text{pg g}^{-1}$  and were significantly lower than those of European background soils (65–12,000  $\text{pg g}^{-1}$  DW) (Hassanin et al. 2004). Here, BDE-209 was also dominant in  $\Sigma_8$ PBDEs, with an average concentration of  $75 \pm 52 \text{ pg g}^{-1}$ , and accounted for 67% of the  $\Sigma_8$ PBDEs. The concentrations of the other seven PBDEs were all below 20  $\text{pg g}^{-1}$ , which was in accordance with the characteristics of the background area.

To further understand the exchange at the air–soil interface, air–soil gas exchange fluxes of PBDEs were calculated (Table S4). The average air–soil gas exchange fluxes for the eight individual PBDEs ranged from  $-0.33$  to  $-6.00 \text{ pg m}^{-2} \text{ day}^{-1}$ , indicating net gas deposition status. The average net air–soil gas exchange flux of  $\Sigma_8$ PBDEs was  $-16.1 \pm 12.7 \text{ pg m}^{-2} \text{ day}^{-1}$ , which was significantly lower than that of a suburban site in Turkey, with a gas deposition flux of  $13,000 \text{ pg m}^{-2} \text{ day}^{-1}$  for  $\Sigma_7$ PBDEs (without BDE-183) based on a 1-year observation (Cetin and Odabasi 2007).

Seasonal variations of air–soil gas deposition fluxes of eight PBDEs are shown in Fig. 5. The net air–soil gas deposition fluxes of BDE-209 were high, especially in autumn, which might be attributed to the high atmospheric concentrations. Significant seasonal variations of net air–soil gas exchange fluxes for BDE-100, BDE-99, BDE-154, BDE-153, and BDE-183 were observed, which were scavenged largely in winter and early spring and reached an equilibrium in summer. Moreover, for these PBDEs, good correlations between the air–soil gas exchange fluxes and temperature were found (Table S5), indicating the influence of temperature on air–soil gas exchanges. For BDE-28 and BDE-47, they were scavenged largely in spring and summer and kept at deposition/

equilibrium status in autumn. Correlations for air–soil gas exchange fluxes of BDE-28 and BDE-47 with temperature (Table S5) and soil/air concentrations ( $C_s/C_a$ ) (Table S6) indicated that the status of BDE-28 and BDE-47 was more related to  $C_s/C_a$  rather than to temperature.

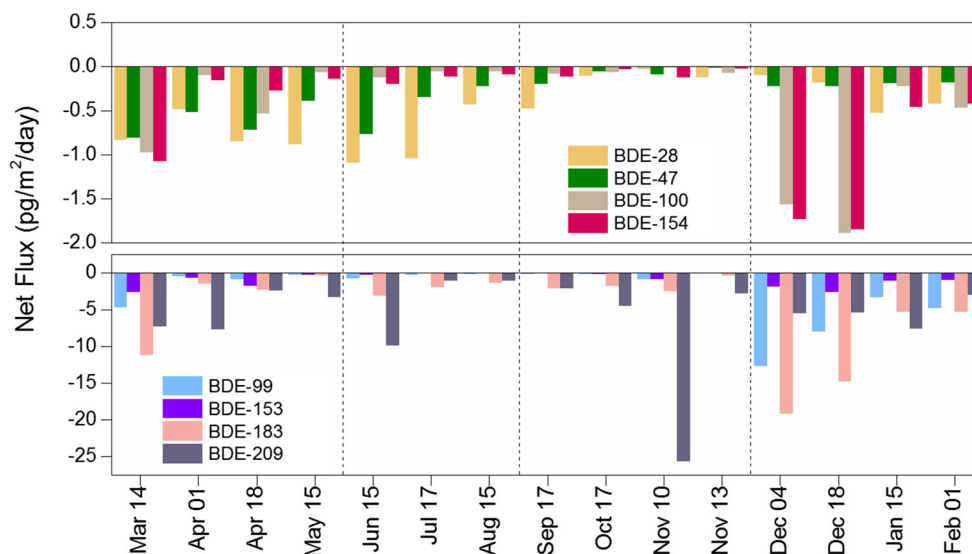
### Is the soil the source or the sink?

This study investigated the four processes: dry particle deposition, wet particle deposition, wet dissolved deposition, and air–soil gas exchange at the air–soil interface. The first two processes were related to particulate contaminants whereas the latter two were related to gaseous/dissolved contaminants. The annual fluxes of the four processes for PBDEs are summarized in Fig. 6, and the leading process was different for individual PBDEs.

As for BDE-209, dry particle deposition was the most important process at the air–soil interface, followed by wet dissolved deposition and wet particle deposition. Moreover, atmospheric deposition flux was significantly higher than net air–soil gas exchange flux (Fig. 6), indicating that atmospheric deposition was more important compared with air–soil gas exchange. Wet dissolved deposition fluxes of BDE-47 and BDE-99 were not only higher than dry and wet particle deposition fluxes but also much higher than net air–soil gas exchange fluxes, suggesting the dominance of wet dissolved deposition over the input to the soil. As for BDE-28, BDE-100, BDE-154, BDE-153, and BDE-183, dry particle, wet particle, and wet dissolved deposition fluxes were almost similar and higher than net air–soil gas exchange fluxes, implying the collective input of dry particle, wet particle, and wet dissolved deposition. Overall, atmospheric deposition was an important input of PBDEs to soils at JSH.

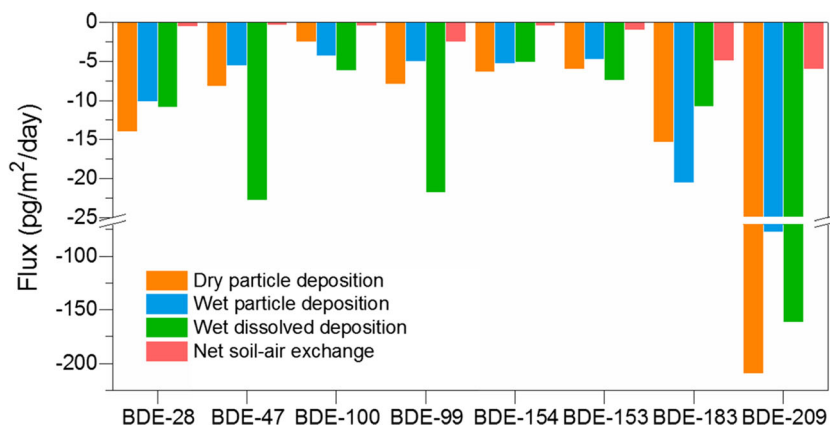
In this study, the net air–soil gas exchange flux of  $\Sigma_8$ PBDEs accounted for 2.5% of the total deposition flux

**Fig. 5** Seasonal variation of net air–soil gas exchange fluxes for PBDEs





**Fig. 6** Comparison of net air–soil gas exchange fluxes and deposition fluxes for PBDEs



and 6.0% of dry particle deposition, which was largely lower than that of a suburban site in Turkey (19.1% of dry particle deposition) (Cetin and Odabasi 2007). This suggested that air–soil gas exchange was not the principal process at the air–soil interface, and the levels of PBDEs in the soil were extremely low so that the re-volatilization of PBDEs from the soil was not significant. Therefore, the current PBDE pollution at JSH is relatively low, indicating that the overall PBDE pollution is lower in Central China compared to Southeastern China. In the long term, the soil at JSH will still be an important sink for contaminants and will not be converted into a source.

## Conclusion

The measured atmospheric deposition and air–soil exchange fluxes of PBDEs at JSH were comparable to or lower than those of other background/rural sites. BDE-209 was the most prominent congener in deposition fluxes. Dry and wet particle deposition fluxes were primarily influenced by atmospheric particle concentrations and temperature, while wet dissolved depositions were controlled by precipitation and total atmospheric concentrations. Dry particle deposition velocities and washout ratios of PBDEs at JSH were lower than or comparable to those of other studies. The highest  $V_D$  and  $WR_T$  values were found for BDE-209, suggesting that BDE-209 was the most easily removed by wet and dry deposition. However, relatively lower  $WR_D$  of the other seven PBDEs may suggest their re-volatilization in the wet deposition sampler. It should be noted that due to several missing deposition data and sampling artefacts, limitations of these results might exist. Air–soil gas exchange fluxes of PBDEs were mainly influenced by temperature and air/soil concentrations. The result of atmospheric depositions and air–soil gas exchange fluxes indicated that the soil was an important sink for PBDEs, and atmospheric deposition played a more important role compared with air–soil gas exchange, especially particle deposition for high-brominated PBDEs and wet dissolved deposition for low-

brominated PBDEs. Air–soil gas exchange fluxes were largely lower than deposition fluxes, indicating that the re-volatilization of PBDEs from the soil was not significant.

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