Hu *et al. J Environ Expo Assess* 2023;2:4
DOI: 10.20517/jeea.2022.30

Journal of Environmental Exposure Assessment

Research Article

Open Access

Factors affecting the levels and pathways of atmospheric brominated flame retardant uptake by humans in different weather conditions

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How to cite this article: Hu PT, Zhong SM, Liu DH, Wang L, Yu H, Cao ZG, Li YF. Factors affecting the levels and pathways of atmospheric brominated flame retardant uptake by humans in different weather conditions. *J Environ Expo Assess* 2023;2:4. https://dx.doi.org/10.20517/jeea.2022.30

Received: 29 Aug 2022 **First Decision:** 28 Sep 2022 **Revised:** 15 Oct 2022 **Accepted:** 1 Dec 2022 **Published:** 1 Jan 2023

Academic Editor: Stuart Harrad **Copy Editor:** Ying Han **Production Editor:** Ying Han

Abstract

The health risks posed by atmospheric brominated flame retardants (BFRs) have been widely studied, but there remains a lack of clarity about exposure differences between clear days and haze days. We sampled the total suspended particle (TSP) and gaseous BFRs on clear days in summer, clear days in winter, and haze days in winter in Harbin, China, to investigate the variations in the concentrations and intakes (dermal and inhalation) in the different weather conditions. The concentrations of atmospheric BFRs were highest on haze days in winter (185 pg/m^3), followed by clear days in summer (158 pg/m^3), and clear days in winter (79.2 pg/m^3), and these concentrations were significantly correlated with the concentrations of TSP. The human intake in the different weather conditions followed the pattern of the BFR concentrations, and the human intake of atmospheric BFRs was dominated by inhalation. A comparison of the BFR levels showed that the human intake of gaseous and particulate BFRs varied in the three weather conditions and that the inhalation intake, but not the dermal intake, was influenced under high concentrations of gaseous BFRs with low molecular weight.

Keywords: Weather variations, flame retardants, dermal exposure, human health

INTRODUCTION

Brominated flame retardants (BFRs) are widely used as additives for a wide range of products, including textiles, electronics, furniture, appliances, and interior decoration materials, to reduce their flammability[1,2]. BFRs include polybrominated diphenyl ethers (PBDEs), of which several compounds, including penta-bromodiphenyl ether (penta-BDE), octa-bromodiphenyl ether (octa-BDE), and decabromodiphenyl ether (deca-BDE), are specifically listed in the Stockholm Convention and have been banned, because of their high persistence, bioaccumulation ability, and long-range transport potential[3]. As PBDEs have been phased out, novel brominated flame retardants (NBFRs)[2,4], such as decabromodiphenyl ethane (DBDPE), bis (2-ethylhexyl) tetrabromophthalate (BEHTBP) and 1, 2-bis (2,4,6-tribromophenoxy) ethane (BTBPE)[5], are increasingly produced and used as alternatives. However, as the properties of some NBFRs and persistent organic pollutants (POPs) may be similar[6], NBFRs are now attracting concern because of the potential risks they pose to the environment and human health.

Air pollution has emerged as a serious environmental issue in recent decades[7,8], and is the cause of much concern for both scientists and the general public[9-11], because of the risks to human health from exposure to large discharges of particulate matter (containing heavy metals and polyaromatic hydrocarbons), SO_2 and NO_x. Publics have recognised that abundant airborne particles during heavy haze days increased the risks of inhalation exposure. However, recent studies have reported that the risks to health from several semi-volatile organic compounds (SVOCs) were greater during light haze days than during heavy haze days, because of dermal intake[12-14], and we believe that this new finding deserves further research.

Atmospheric BFRs, such as BDE-209, can exist in the gas phase and particle phase at the same time, and the gas/particle partitioning varies with the temperature and the concentration of total suspended matter (TSP). Harner and Bidleman (1998) reported that the distribution of SVOCs in the gas phase and particle phase was determined by a temperature-dependent parameter (octanol-air partition coefficients, K_{OA}), where the compounds with low K_{OA} (with high temperature) trended to the gas phase and compounds with high K_{OA} (with low temperature) trended to the particle phase[15]. However, TSP, as the main control on gas/particle partition, provides adsorption (defined by the specific surface area) or absorbing media (dominated by organic matters) for gaseous SVOCs, such that SVOCs may show a tendency to distribute on the particle phase during haze explosions[16]. These ongoing variations in SVOCs between the gas phase and particle phase[17] present a challenge for defining and understanding how health risks posed by atmospheric SVOCs vary with the weather and air quality.

Inhalation has long been recognized as the main exposure pathway for atmospheric BFRs and other SVOCs[18-22]. In recent years, in-depth studies of dermal exposure to BFRs have shown that a considerable proportion of the total atmospheric BFRs taken up by humans could permeate into the human body via dermal exposure[23-26]. It was recognized that BFRs in the particle and gas phases could enter the human body in different proportions, and that the amounts would vary by chemical, particularly for dermal absorption/permeation[27,28]. Therefore, in the light of these recent findings, it would be useful to determine how human exposure to, and the inhalation and dermal intakes of, atmospheric BFRs are affected by the weather and air quality.

In recent years, Harbin, a megacity in Northeast China, has experienced severe and continuous haze conditions in winter, which has had serious impacts on the social economy, ecological environment, and

human health[29,30]. The temperature in Harbin can range from below -30 °C in winter to > 35 °C in summer, so Harbin provides an ideal research area to study how the weather and air quality influence human exposure to atmospheric BFRs. We collected gaseous and particle samples in August 2017, December 2017, and from December 2017 to January 2018 in different weather conditions, namely clear days in summer, clear days in winter, and haze days in winter, and analyzed them for 8 PBDEs and 8 NBFRs. We then (1) investigated the atmospheric levels of BFRs in the different seasons with different air quality conditions; (2) studied the phase distribution of atmospheric BFRs in different seasons and different air quality conditions; and (3) clarified how the temperature and air quality affected human exposure to atmospheric BFRs.

MATERIALS AND METHODS

Sampling information

The sampling site was at an elevation of 15 m above the ground, on the roof of the School of Environment at the Second Campus of Harbin Institute of Technology, Harbin, Heilongjiang Province, China. During the sampling period, the temperatures ranged from -24 to 30 °C. The sampling period was divided into three weather conditions, defined as clear days in summer (August 2017), clear days in winter (December 2017), and haze days in winter (from December 2017 to January 2018). Detailed information about each sample is provided in Supplementary Table 1.

Each sample was collected over a 24 h period using a medium-volume atmosphere sampler (Tisch-1000, Tisch Environmental, Inc. USA) with a flow rate 240 L min^{-1}. The TSP samples were collected using glass fiber filters (GFF, ϕ110 mm) and gaseous samples were collected using polyurethane foam (PUF). Before the samples were collected, all the GFFs were baked in a muffle furnace at 400 °C for 8 h and cooled to room temperature in desiccators. The PUFs were extracted with acetone and *n*-hexane for 24 h, respectively, and then dried in a vacuum drying oven at 80 °C for 2 h and stored in sealed aluminum boxes. After sampling, the TSP samples were stored in a standard filter box that was packed with aluminum foil and then placed in a Ziploc bag. The PUF samples were sealed and kept at -28 °C until analyzed.

Experiments and detection levels

The TSP and PUF samples were prepared for analysis in line with the SVOCs standard pretreatment process of the *International Joint Research Center for Persistent Toxic Pollutants* (IJRC-PTS). The process involves Soxhlet extraction, concentration, purification, and concentration to 0.1 mL, and is described in detail in a previous study[31]. In total, the samples were analyzed for 16 BFRs, 8 PBDEs (BDE-17, BDE-28, BDE-47, BDE-66, BDE-99, BDE-138, BDE-183 and BDE-209), and 8 NBFRs [pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), hexabromobenzene (HBBZ), 2,3-dibromopropyl 2,4,6-tribromophenyl ether (DPTE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB), BTBPE, bis BEHTBP and decabromodiphenylethane (DBDPE)]. The BFRs were determined qualitatively and quantitatively using an Agilent 7890B gas chromatograph coupled with a 5977A mass spectrometer in negative chemical ionization mode. The GC-MS had a DB-5MS (15 m × 0.25 mm × 0.1 μm, Company of J&W Scientific) chromatographic column. The GC was injected with a constant flow of helium (1.7 mL min^{-1}) in splitless mode, with a single injection volume of 2 μL and an injection port temperature of 260 °C. The oven temperature was first maintained at 110 °C for 0.5 min, increased to 220 °C at a rate of 4.5 °C/min, increased to 280 °C at a rate of 15 °C/min, increased to 310 °C at a rate of 5 °C/min, and then held for 3 min. The temperature of the auxiliary thermal controllers between the GC and MS was 270 °C.

Quality assurance and quality control

The instrument detection limits (IDLs) were calculated using a three-times signal-to-noise ratio. Of the eight PBDEs, the IDL was highest for BDE-209 (0.15 ng/mL), and the IDLs of the other seven PBDEs

ranged from 0.01 to 0.03 ng/mL. The IDL of DBDPE was 0.07 ng/mL, and the IDLs of the other seven NBFRs were lower than 0.01 ng/mL. C^{13}BDE-209, BDE-71 and OCN were spiked into each sample as surrogate standards before extraction. Two pairs of field blanks (1 GFF + 1 PUF) and two pairs of experimental blanks were set for each weather type, where no individuals exceeded their corresponding IDL in any of the blanks. The eight PBDE individuals and eight NBFR individuals were all detected in the GFFs samples. In the PUF samples, BDE-138, BEHTBP, and DBDPE were detected at rates of 93%, 87%, and 87%, respectively, and the other BFR individuals had detection rates of 100%.

Gas/particle partitioning

The G/P partitioning quotient (K_P) of SVOCs was defined as[16]:

$$K_P = (C_P / TSP) / C_g \quad (1)$$

where C_p and C_g (both in pg/m^3 of air) were the concentrations of the BFRs in the particle phase and gas phase, respectively, and *TSP* was the concentration of the total suspended particles (μg m^{-3} air) in air.

The Harner-Bidleman model (K_{PE}) is frequently used to predict the G/P partitioning quotients of SVOCs in a state of equilibrium, and is calculated as[15]:

$$\log K_{PE} = \log K_{OA} + \log f_{OM} - 11.91 \quad (2)$$

where f_{OM} is the fraction of organic matter and TSP was assumed as 0.1. K_{OA} was the octanol-air partitioning coefficient, which was a function of the ambient temperature (*T*, unit *K*):

$$\log K_{OA} = A + B / T \quad (3)$$

where *A* and *B* were the Clausius-Clapeyron coefficients and the detailed values of *A* and *B* for eight PBDE and eight NBFR individuals are listed in Supplementary Table 2.

The Li-Ma-Yang steady-state model[32], established by Li *et al.*, considers dry and wet deposition of SVOCs:

$$\log K_{PS} = \log K_{PE} + \log \alpha \quad (4)$$

where the equilibrium term, log K_{PE}, is given by Equation 2, and the non-equilibrium term, log α, is:

$$\log \alpha = -\log (1 + 2.09/C \times 10^{-10} f_{OM} K_{OA}) \quad (5)$$

where *C* was 5 for urban sites.

Calculation of human intakes

Inhalation intake

The daily inhalation intake of gaseous BFRs [DI_g, pg/(kg·day)] in the atmosphere was calculated as follows[33]:

$$DI_g = \frac{C_g \times IR \times f_A}{BW} \quad (6)$$

The daily inhalation intake of particulate BFRs (DI_p) was calculated as[34]:

$$DI_p = \frac{C_p \times IR}{BW} \quad (7)$$

where IR was the human inhalation rate (16 m³/day), BW was the body weight (65 kg), and f_A was the gas alveolar exchange rate (75%).

Dermal exposure intake

The dermal intake of gaseous and particle BFRs were estimated from the transdermal permeability coefficients $k_{p\text{-}g}$ and $k_{p\text{-}d}$, respectively, using the equations derived from the model described by Weschler and Nazaroff[35], as follows:

$$K_{p-cw} = 3600 \times 10^{0.7 \times logK_{ow} - 0.0722 \times MW^{2/3} - 5.252} \quad (8)$$

$$k_{p-g} = 1 \Big/ \left[\frac{2.6 + \left(MW^{0.5} \times K_{p-cw}\right)}{0.026(RT/H) \times K_{p-cw}} + \frac{1}{V_{d(g)}} \right] \quad (9)$$

$$k_{p-d} = 1 \Big/ \left[\frac{2.6 + \left(MW^{0.5} \times K_{p-cw}\right)}{0.026(RT/H) \times K_{p-cw}} + \frac{1}{V_{d(p)}} \right] \quad (10)$$

Here, $K_{p\text{-}cw}$ (cm/h) was the permeability coefficient that describes the transfer of the BFR compound through the stratum corneum with water as the medium that comes into contact with the skin, K_{OW} (unitless) was the octanol-water partition coefficient of the BFR compound, and MW (g/mol) was the molecular weight of the corresponding compound. R (8.314 Pa m³/K/mol) was the ideal gas constant, T (305 K) was the skin temperature, and H [mol/(Pa m³)] was the Henry's law constant. $V_{d(g)}$ and $V_{d(p)}$ (m/h) were the mass-transfer coefficients that describe the BFR compound from the gas and particle phases through the boundary layer adjacent to the skin, and were 6 and 1 m/h, respectively. The detailed parameters for each chemical are shown in Supplementary Table 2.

The daily dermal intake of gaseous [DD_g, pg/(kg·day)] and particulate [DD_p, pg/(kg·day)] BFRs were calculated using Equations 11 and 12.

$$DD_g = \frac{C_g \times k_{p-g} \times SA \times f \times ET}{BW} \quad (11)$$

$$DD_p = \frac{C_p \times k_{p-d} \times SA \times f \times ET}{BW} \quad (12)$$

where SA (m²) is the surface area of human skin, and f is the proportion of human skin exposed to air (only considering the head and hands, $SA \times f = 0.2$ m²)[36]. ET is the daily exposure time (assumed to be 8 h/day in the outdoor environment). $k_{p\text{-}g}$ and $k_{p\text{-}d}$ (m/h) are the permeability coefficients of gaseous BFRs and particle BFRs, respectively, and are calculated with Equations 9 and 10. Data related to the human body were obtained from other studies[33].

RESULTS AND DISCUSSION

Variations in the residual levels of atmospheric BFRs in different weather conditions

We investigated the concentrations of 16 BFRs, including 8 PBDEs and 8 NBFRs, in the atmosphere over Harbin during clear days in summer, clear days in winter, and haze days in winter. The weather and atmospheric conditions varied considerably in the three sampling periods. On clear days in summer, the temperature ranged from 15 to 30 °C and the AQI ranged from 46 to 61. On clear days in winter, the temperature ranged from -24 to -11 °C and the AQI ranged from 48 to 89. In the haze days in winter, the temperature ranged from -24 to -10 °C and the AQI ranged from 70 to 312 (for the detailed concentrations see Supplementary Table 3). The concentrations of the Σ_{16}BFRs also varied between the different sampling periods and were lowest on clear days in winter and highest on haze days in winter. In addition, the concentrations varied between the particle phase and the gas phase for the different sampling periods, but without an obvious pattern. On clear days in winter, the geomeans (GM) (ranges) of the particle phase and the gas phase were 56.6 pg/m^3 (43.5-73.9 pg/m^3) and 21.7 pg/m^3 (16.8-26.5 pg/m^3), respectively. On clear days in summer, the GM (ranges) of the particle phase and the gas phase were 58.3 pg/m^3 (41.3 to 109 pg/m^3) and 91.1 pg/m^3 (57.5 to 166 pg/m^3), respectively. On haze days in winter, the GM (ranges) of the particle phase and the gas phase were 165 pg/m^3 (95.2 to 220 pg/m^3) and 201 pg/m^3 (16.0 to 30.0 pg/m^3), respectively.

The levels of Σ_{16}BFRs (gas phase + particle phase) were higher on clear days in summer than on clear days in winter, which may indicate volatile BFRs sourced from their added substances (see Figure 1). Furthermore, the high levels of BFRs in the atmosphere during haze days reflect the higher amounts of airborne particles.

The GM concentrations and ranges of the Σ_8PBDEs in the atmosphere in Harbin for the three weather types followed the same pattern as those of the Σ_{16}BFRs, and were 32.5 pg/m^3 (14.3-49.1 pg/m^3) on clear days in winter, 47.9 pg/m^3 (34.7-101 pg/m^3) on clear days in summer, and 138.2 pg/m^3 (77.3-182 pg/m^3) on haze days in winter. For the three weather types, BDE-209 was the dominant congener and accounted for 86%, 83%, and 93% of the Σ_8PBDEs, respectively. The percentage of BDE-209 was lower on clear days in summer than on clear days in winter, and may reflect the relative abundance of highly volatile individuals (such as BDE-17 and BDE-47) in summer. The Σ_8NBFR distribution differed from the Σ_{16}BFR and Σ_8PBDE distributions, and the Σ_8NBFR means (ranges) were highest on clear days in summer [104 pg/m^3 (65.7-174 pg/m^3)], followed by haze days in winter [46.5 pg/m^3 (35.1-67.54 pg/m^3)], and were lowest on clear days in winter [44.6 pg/m^3 (38.8 to 51.3 pg/m^3)]. The difference in the seasonal distributions between Σ_8NBFRs and Σ_8PBDEs reflects the difference in use, as NBFRs are still used and commercial PBDEs are listed in the restricted list of the *Stockholm Convention*. NBFRs were dominated by PBT in summer (77.3%), reflecting the high temperature and frequent exchange of indoor/outdoor air in summer. On clear and haze days in winter, DBDPE dominated atmospheric NBFRs and accounted for 65.1% of Σ_8NBFRs.

Variations in BFRs with TSP in the different weather conditions

The GM concentrations of TSP in Harbin were 68.8 μg/m^3 (61.9-80.4 μg/m^3) on clear days in summer, 94.9 μg/m^3 (62.8-131 μg/m^3) on clear days in winter, and 175 μg/m^3 (107-277 μg/m^3) on haze days in winter. The TSP concentrations, and Σ_{16}BFRs, were highest on haze days in winter and were lowest on clear days in summer. The residual levels of BFRs in the atmosphere in Harbin may have been influenced by the volatilization of BFRs from the indoor environment in summer and the TSP concentrations.

The relationships between the concentrations of BFRs and the concentrations of TSP were determined using Spearman correlation analysis. As shown in Supplementary Table 4 , the concentrations of Σ_{16}BFRs

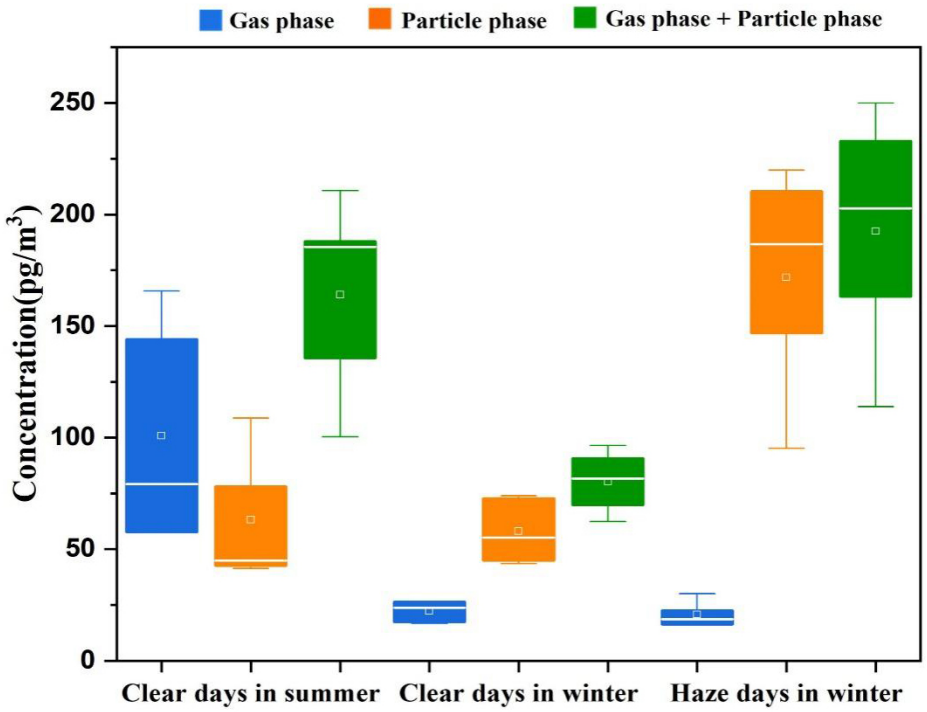

Figure 1. The concentrations of the $\sum_{16}$BFRs in the three weather types.

(gas phase + particle phase) in the atmosphere were positively correlated with the concentrations of TSP ($P < 0.05$). In particular, the particle phase concentration of each individual BFR (except PBT and DPTE) was positively correlated with the concentration of TSP ($P < 0.01$), and the absence of relationships for PBT and DPTE may reflect their high use in Harbin and high volatilization of their added products in summer. However, the gas phase concentration of each monomer (except BDE-209) was not significantly correlated with the TSP concentration. Therefore, the variation in the TSP in the three weather types had a strong influence on the BFRs in the atmosphere.

Gas/particle partitioning of BFRs in the three weather conditions

The distributions of the 16 BFRs between the particle phase and the gas phase in the three weather types are plotted in Figure 2. The PBDE and NBFR individuals were mostly dominated by the particle phase in all the weather types, with the exception of NBFRs on clear days in summer. The particle phase was highest on haze days in winter (PBDEs = 97.8%, NBFRs = 58.5%), followed by clear days in winter (PBDEs = 92.8%, NBFRs = 56.2%), and was lowest for clear days in summer (PBDEs = 86.7%, NBFRs = 15.9%). On the haze days in winter, the particulates accounted for more than 50% of all the PBDE and NBFR individuals. All the high molecular weight individuals (BDE-209, DBDPE, BBDE-183 and BEHTBP) were dominated by particulates for the three weather types. The low molecular weight individuals, such as PBT, PBEB, HBBZ, BDE-17, and BDE-28, were dominated by gas on clear days in summer and winter, especially PBT on clear days in summer, when 99.4% of the total PBT concentration was gaseous.

We investigated the gas/particle partitioning of BFRs in the three weather types, and compared them with the predictions of the equilibrium state model (Harner-Bidleman model) and the steady state model (Li-Ma-Yang model). The Li-Ma-Yang model divided the gas/particle partition into three log K_{OA} regions, namely the equilibrium domain (log $K_{OA} < 11.4$), non-equilibrium domain ($11.4 \leq \log K_{OA} \leq 12.5$), and the maximum partition domain (log $K_{OA} > 12.5$). The accuracy of the model predictions was evaluated with

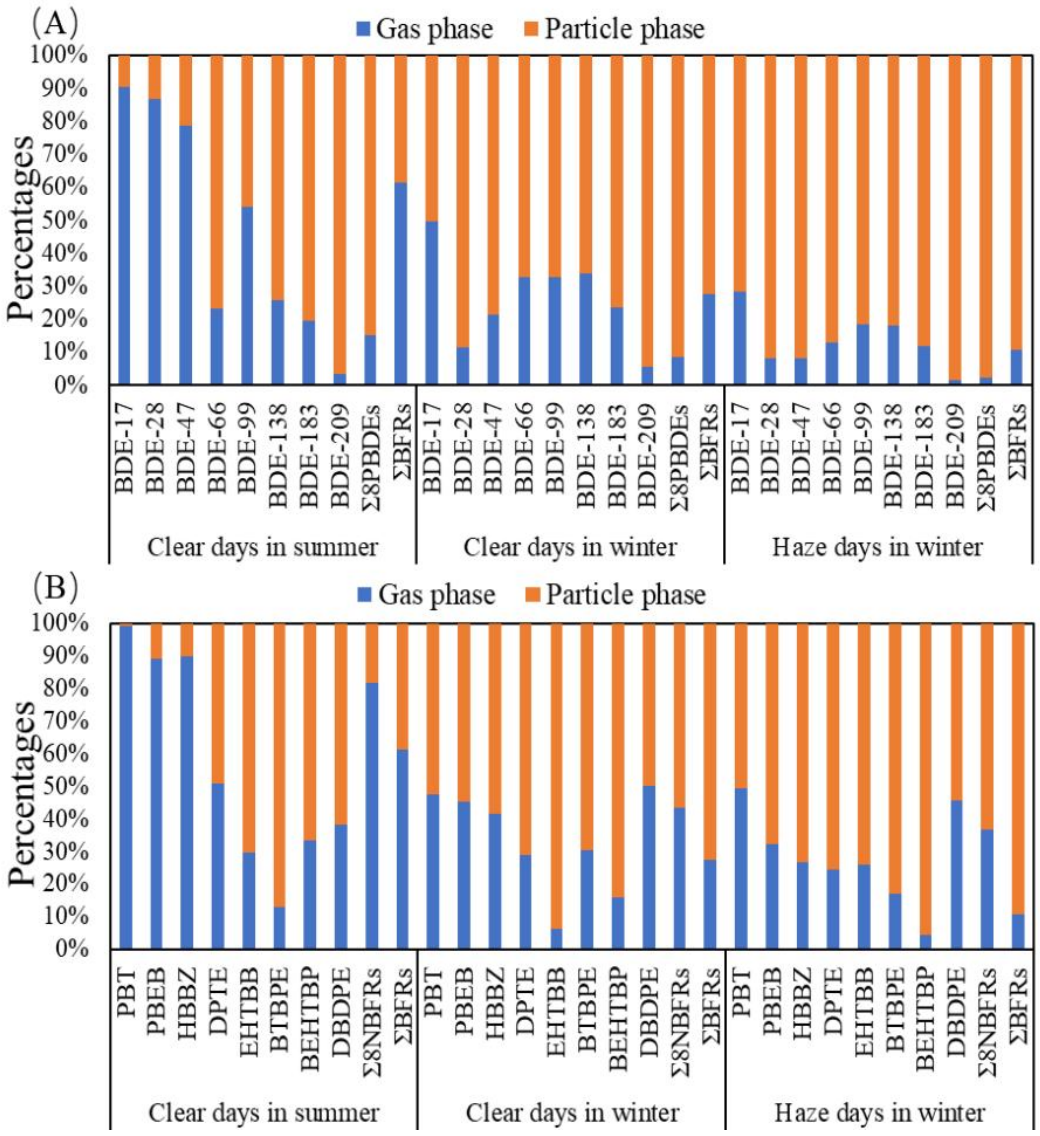

Figure 2. The distribution of the (A) 8 polybrominated diphenyl ethers (PBDEs) and (B) 8 novel brominated flame retardants (NBFRs) between the particle phase and the gas phase.

reference to an acceptable deviation range (ADR), which was defined as ± 1 order of magnitude of the predicting model (for detailed percentages, see Supplementary Table 5).

On clear days in summer, the Harner-Bidleman model and the Li-Ma-Yang model predicted 66.2% and 76.6% of the monitoring data, respectively, and the gas/particle partitioning was mostly in the equilibrium domain (see Figure 3). On clear days and haze days in winter, the gas/particle partitioning of BFRs was similar, and was mostly in the maximum domain and remained at around -1.53. On these days, the Harner-Bidleman model predicted 25.0% and 35.4% of monitoring data, underestimated the non-monitoring data, and overestimated 75% and 64.6% of the monitoring data for clear and haze days, respectively. In contrast, the Li-Ma-Yang model agreed well with the monitoring data on clear (96.3%) and haze days (92.4%) in winter. It should be noted that the similar gas/particle partitioning patterns on clear and haze days in winter do not indicate similar gas and particle phase distributions. The high TSP concentrations on haze days

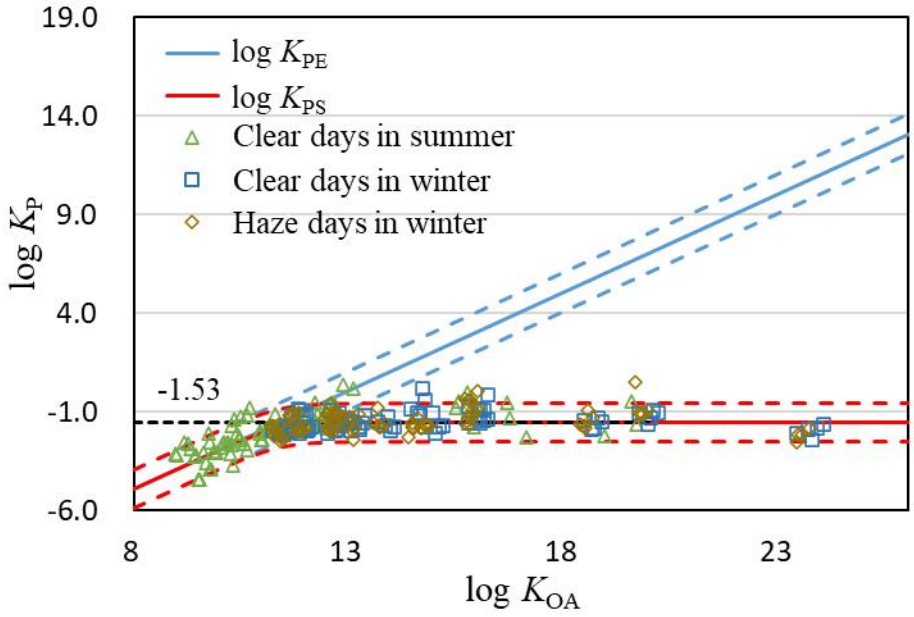

Figure 3. The differences in the gas/particle partitioning of brominated flame retardants (BFRs) in the three weather types and the predictions from the equilibrium state model and the steady state model.

provided abundant ab/adsorptive materials for BFRs, but did not change the ab/adsorptive abilities of TSP.

Variation in the human intake of BFRs in different weather conditions

We evaluated the human intake of atmospheric BFRs in the different weather conditions from the dermal intakes (*DD*) and the inhalation intakes (*DI*) of BFRs on clear days in summer, clear days in winter, and haze days in winter. The human intakes (*DD* + *DI*) were highest on haze days in winter [49.6 pg/(day·kg)], followed by clear days in summer [32.8 pg/(day·kg)], and clear days in winter [21.2 pg/(day·kg)] (see Supplementary Tables 6 and 7). The pattern in the intakes was similar to the distribution of their concentrations for the three weather types. As shown in Figure 4, the inhalation intake was the main exposure pathway in the three weather types, and was 43.3 pg/(day·kg), 30.1 pg/(day·kg), and 17.1 pg/(day·kg), and accounted for 91.6%, 87.2%, and 80.6% of the total intakes of BFRs, on haze days in winter, clear days in summer, and clear days in winter, respectively. However, the dermal intakes of BFRs were lowest on clear days in summer [2.74 pg/(day·kg)], even though the atmospheric concentrations of PBT were abnormally high in this weather type. There was dermal intake of BFRs in the three weather types, with DBDPE and BDE-209 as the main contributors, and there was inhalation intake on clear and haze days in winter. PBT had the highest concentration and accounted for most (44.1%) of the inhalation intake of the 16 BFRs on clear days in summer 13.3 pg/(day·kg), but only accounted for a small proportion (9.69%) and amount [0.27 pg/(day·kg)] of the dermal intakes of the 16 BFRs. This reflects the low $k_{p\text{-}g}$ and $k_{p\text{-}d}$ values for PBT. Elsewhere, these values were high for high molecular weight individuals (such as BDE-209 and DBDPE).

To gain insights into how the different weather types influenced the human intakes of BFRs, we analyzed the contributions of gaseous and particulate BFRs to both the dermal intakes and inhalation intakes of the 16 BFRs (see Figure 5). Gaseous BFRs accounted for most of the dermal intake on clear days in winter (69.5%), followed by clear days in summer (52.0%), and haze days in winter (38.8%). Further, the contributions of gaseous and particulate BFRs to the inhalation intake were consistent with their phase

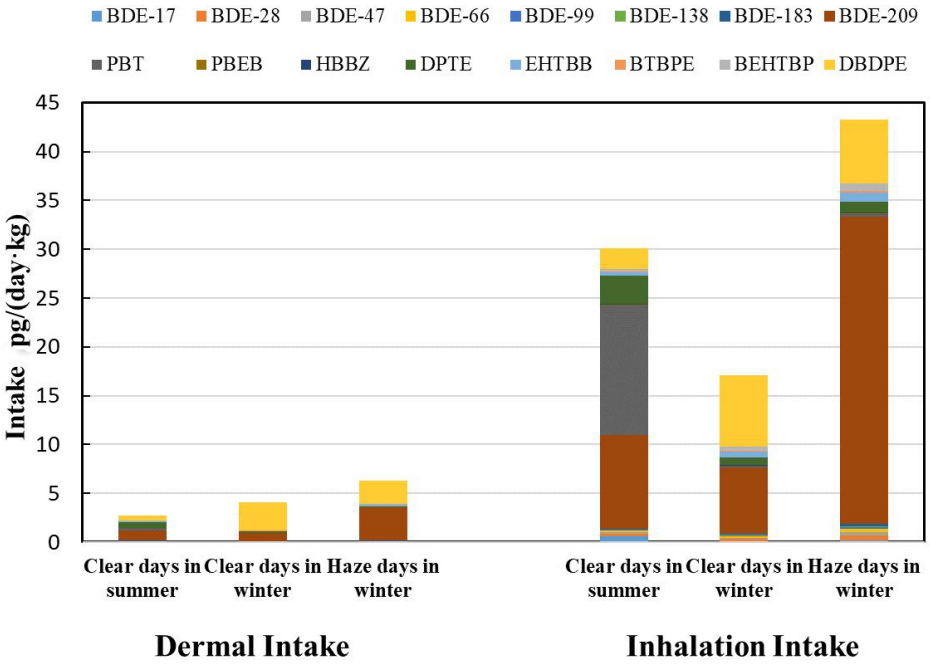

Figure 4. The human intakes of atmospheric brominated flame retardants (BFRs) in the three weather types.

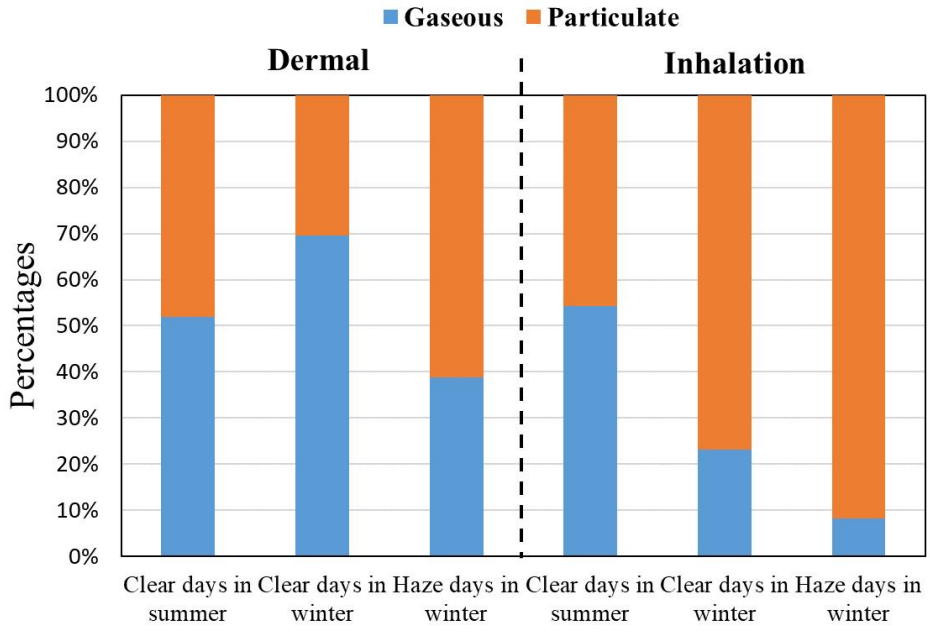

Figure 5. Contributions of gaseous and particulate brominated flame retardants (BFRs) to dermal intake and inhalation intake of the 16 BFRs.

distribution among the three weather types, and gaseous BFRs were highest on clear days in summer and lowest on haze days in winter, while particulate BFRs were lowest on clear days in summer and highest on haze days in winter.

Discussion

The differences in the human intakes of atmospheric BFRs in the three weather conditions may be attributed to, among other factors, the different intake pathways (dermal and inhalation) and the degree of exposure. The dermal intake and inhalation intake of atmospheric BFRs result from different exposure mechanisms. BFRs taken in by inhalation may enter the human respiratory system directly when an individual breathes, such that the intake doses of both gaseous and particulate BFRs vary with their atmospheric concentrations. Dermal exposure involves two main processes, where (1) particulate and gaseous chemicals are ad/absorbed by surface skin; and (2) BFRs on the surface skin permeate into the human body through the dermal. The ad/absorption fluxes of particulate and gaseous BFRs were different, and the fluxes for gaseous BFRs were much greater than the fluxes of particulate BFRs, depending on the particle size. However, the permeation process varied by chemical, and tended to increase with the molecular weight. These differences between dermal exposure and inhalation exposure meant that individual BFRs with high molecular weights, especially gaseous individuals, entered the human body more easily than those with low molecular weights. As such, the high residual levels of PBT experienced on clear days in summer would only contribute noticeably to the inhalation intake but not the dermal intake.

Behavior habits also affect human exposure to atmospheric BFRs. The inhalation intake of atmospheric BFRs was noticeably higher than the dermal intake in the three weather conditions; thus, residents who wear face masks effectively reduce the exposure risk to atmospheric BFRs via inhalation. The dermal intakes of BFRs were calculated from the dermal areas of the hand and head only. However, people might expose their arms and legs to the air in summer, thereby increasing the exposure area, or wear hats, gloves, and masks in winter, which decreases the exposure area, meaning that people with different habits will have different BFR intakes.

CONCLUSIONS

The differences in the residual levels and human intakes of atmospheric BFRs in clear days in summer, clear days in winter, and haze days in winter were investigated in this study. When the concentrations of TSP are high, e.g., on haze days, there is the potential for high ad/adsorption of gaseous BFRs that may escape from indoor environments. The levels of PBT will be high on clear days in summer when there is an obvious local source of PBT, meaning that the BFR concentrations could be higher on clear days in summer than on clear days in winter. The human intake of BFRs tended to follow the same pattern as their atmospheric concentrations, and was mostly dominated by the inhalation exposure pathway. The dermal intake was not, but the inhalation intake was, affected by the concentrations of low-molecular weight gaseous BFRs.

DECLARATIONS

Authors' contributions

Writing - original draft, writing - review & editing, data curation, visualization, supervision: Hu R
Writing - original draft, writing - review & editing, data curation, visualization: Zhong S
Writing - review & editing: Liu D
Data curation: Wang L
Methodology: Yu H
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All authors read and approved the final manuscript.

Availability of data and materials

The authors do not have permission to share data.

Financial support and sponsorship

This work was supported by the State Key Laboratory of Urban Water Resource and Environment (Harbin Institute of Technology) (No. 2019DX04), National Natural Science Foundation of China (No. 42077341), the Postdoctoral Research Foundation of Henan Normal University (5101219470246), the Scientific Research Starting Foundation of Henan Normal University (5101219170829), the National Natural Science Foundation of China (42122057, 41977308) and the University Science and Technology Innovation Talent Support Program of Henan Province (20HASTIT011).

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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