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Higher health risk resulted from dermal exposure to PCBs than HFRs and the influence of haze

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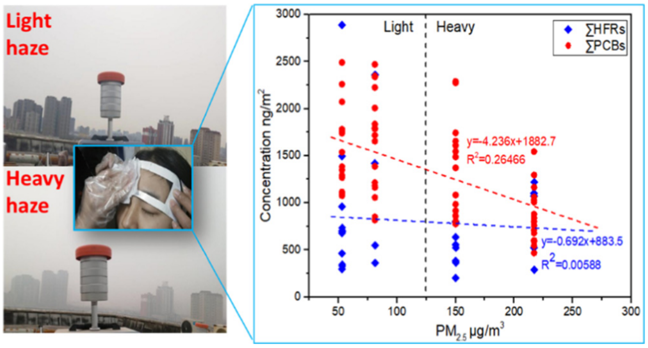
HIGHLIGHTS

- 27 HFRs and 27 PCBs were detected in forehead wipes for the first time.
- BDE-209, DBDPE and PCB-37, PCB-60 were the most abundant compounds in forehead wipes.
- PCBs showed higher residual concentrations on skin than HFRs and leaded to higher health risk.
- Haze decreased dermal exposure to PCBs but had no significant influence on that to HFRs.
- Particle deposition may be significant pathway for dermal exposure to non-volatile compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

To investigate the influence of haze on human dermal exposure to a series of halogenated flame retardants (HFRs) and polychlorinated biphenyls (PCBs), paired forehead wipes were collected from 46 volunteers (23 males, 23 females) using gauze pads soaked in isopropyl alcohol under heavy and light haze pollution levels. The median levels of $\sum_{27}$HFRs and $\sum_{27}$PCBs in all 92 samples were 672 and 1300 ng/m^2, respectively. Decabromodiphenyl ether (BDE-209) (171 ng/m^2) and decabromodiphenylethane (DBDPE) (134 ng/m^2) were the dominant components of HFRs, indicating that dermal exposure may also be the significant pathway for non-volatile compounds. PCB-37 contributed the most to $\sum_{27}$PCBs, with a median concentration of 194 ng/m^2, followed by PCB-60 (141 ng/m^2). Generally, PBDE, PCB and DD (dehalogenated derivatives of DPs) levels on the foreheads of female participants (291, 1340, 0.92 ng/m^2) were higher (p = 0.037, 0.001, and 0.031, respectively) than those of male participants (226, 989, and 0.45 ng/m^2). A significant difference (p = 0.001) in PCBs was found between light (1690 ng/m^2) and heavy (996 ng/m^2) haze pollution conditions. Nevertheless, HFR levels under heavy (median = 595 ng/m^2, ranging from 295 to 1490 ng/m^2) and light haze pollution conditions (ranging from 205 to 1220 ng/m^2 with a median of 689 ng/m^2) did not show significant differences (p = 0.269). The non-carcinogenic health risk resulting from dermal exposure to $\sum_{8}$HFRs and $\sum_{27}$PCBs was 8.72 × 10^{-5} and 1.63 × 10^{-2}, respectively, raising more concern about populations' exposure to PCBs than HFRs.

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1. Introduction

Halogenated flame retardants (HFRs) and polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) which pose a range of health threats (Carolina Ruiz-Fernandez et al., 2014; Cowell et al., 2018; McGrath et al., 2018). HFRs, including polybrominated diphenyl ethers (PBDEs), novel brominated flame retardants (NBFRs) and dechlorane plus (DP), are incorporated into numerous household products to reduce their flammability (Hoffman et al., 2015; Sverko et al., 2011; van der Veen and de Boer, 2012). PBDEs have wide application as flame retardants for carpets, textiles, plastics and electronic casings (Guo et al., 2018; Harrad et al., 2008); however, restrictions on their use have paved the way for the use of NBFRs as replacements for PBDEs (Harrad and Abdallah, 2011). DP has been detected frequently in environmental samples and is of growing environmental concern (Brazeau et al., 2018), and it may sustain the chemical, photochemical or biological degradation leading to dehalogenated derivatives of DP (DDs), a-Cl_{11}-DP and a-Cl_{10}-DP, which have shown to be more toxic than the parent compound (Brazeau et al., 2018). As HFRs incorporated in products are considered unbound to the product (Rauert et al., 2014; Wei et al., 2015), they can be gradually be released into the environment and have been detected in multiple media including indoor dust, water and air (Ge et al., 2014; Sugeng et al., 2017; Venier et al., 2016; Yadav et al., 2017). PCBs have been widely used in industrial and consumer applications, especially in electrical equipment (Breivik et al., 2002). The production and usage of PCBs were prohibited worldwide through the Stockholm Convention on Persistent Organic Pollutants (POPs) passed in 2004 due to their potential mutagenic and carcinogenic effects (Dopico and Gomez, 2015; Robson et al., 2010). However, although no longer produced, PCBs may be released into the environment through improper disposal or leakage from older electrical equipment, the incineration of PCB-containing wastes and vehicular emissions (Carolina Ruiz-Fernandez et al., 2014). Recent publications have emphasized the possible widespread occurrence of PCBs in indoor (Audy et al., 2018; Kraft et al., 2018) and outdoor (Qu et al., 2019; Wong et al., 2018) matrices, revealing the non-negligible exposure risk of humans to PCBs in modern life.

Humans are exposed to HFRs and PCBs from the environment via dust ingestion, dermal absorption and inhalation (Cappelletti et al., 2019; Jacobson et al., 2016; Kim et al., 2014; Mercier et al., 2011). Compared to ingestion and inhalation, information on dermal exposure are rather limited, and the understanding of dermal exposure is very poor to date. However, recent studies have highlighted the importance of dermal absorption as a significant pathway of human exposure to HFRs (Abdallah and Harrad, 2018; Tay et al., 2018) and PCBs (Cappelletti et al., 2019).

China has been suffering from severe haze pollution in recent years, and according to the literatures, mass concentration of airborne particles fluctuates dramatically during normal days and haze days (Feng et al., 2018; Zhou et al., 2016). Notably, both the outdoor and indoor environment have been affected by haze pollution. In particular, the indoor environment is a significant medium for human exposure to semi-volatile organic compounds (SVOCs) (Marek et al., 2017). Evidence has shown that haze has a substantial influence on the occurrence level, gas-particle partition, and particle size distribution of benzene, toluene (Sheng et al., 2018), polychlorinated dibenzo-p-dioxins and dibenzofurans (Zhang et al., 2016), PCBs (Zhu et al., 2018) and BFRs (Cao et al., 2018b; Cao et al., 2018c) in the air. On the other hand, air-to-skin transport has been verified to be a significant dermal exposure pathway for many SVOCs (Cao et al., 2018a; Weschler and Nazaroff, 2012). Thus, there is growing concern that haze will substantially increase human exposure to toxic chemicals.

The wipe method, an effective procedure for collecting contaminant residual on the skin surface, could be used for dermal exposure assessment by measuring the contamination levels of skin wipes. Dermal exposure occurs throughout the human skin organ, and as a specific skin location exposed to the air directly, forehead wipe has been successfully used as a useful approach to study dermal exposure to contaminants recently (Gong et al., 2014). Comparatively, the presence of HFRs and PCBs on hand wipes could be a consequence of contact with dust or HFR-treated products (Keller et al., 2014; Tay et al., 2018), except for particulate and gaseous HFRs from the air, while the HFRs and PCBs accumulated on the forehead might be primarily from gaseous (Weschler and Nazaroff, 2012) and particulate phase compounds in the air (Lao et al., 2018a). Hence, theoretically, forehead is a more suitable skin location than other parts to reflect the influences of haze on dermal exposure to HFRs and PCBs. However, to the best of our knowledge, very limited data are available on HFR and PCB contamination on the human forehead.

The objectives of this study were (1) to explore the levels and profiles of HFRs and PCBs in forehead wipes; (2) examine factors that may influence HFR and PCB occurrence in forehead wipes, including gender and haze; (3) and assess the exposure doses to HFRs and PCBs via dermal absorption and conduct comparisons between different exposure assessment models.

2. Materials and methods

2.1. Sample collection

Forehead wipe samples were collected from November to December 2016 in Xinxiang, China. A total of 46 volunteers (23 males, 23 females) were recruited from the students and staff in the Henan Normal University for sample collection. All sampling activities were conducted indoors in the evening after daytime exposure under normal condition. Participants were asked not to wash their foreheads for at least 2 h prior to sampling and were also asked to fill out a questionnaire on gender, age, forehead-washing frequency and their use of skincare products on the wipe location. All participants were required to give informed consent prior to sampling, and ethical approval for this investigation was obtained from the Research Ethics Committee of Henan Normal University. Two rounds of sampling were conducted on the same participants under 'light haze pollution' and 'heavy haze pollution' conditions. All participants were asked to stay in the same building and to try to keep similar activity patterns between the two rounds of sampling. 'Light haze pollution' was defined as the state when the air quality index (AQI) values were around 100 ($PM_{2.5}$: 44–88 μg/m^3; PM_{10}: 80–125 μg/m^3), and 'heavy haze pollution' was defined as the state when the AQI values were around 300 ($PM_{2.5}$: 189–217 μg/m^3; PM_{10}: 320–362 μg/m^3). The detailed sampling methods are provided in the Supporting Information.

2.2. Sample analysis

27 HFRs and 27 PCBs (Table SI-1) were measured in this study. Briefly, forehead wipe samples were spiked with known amount of internal standards and then extracted in ultrasonic bath with hexane/acetone (3:1, v/v, 10 mL) for 10 min (repeated for 3 times). The extracts were concentrated to low volume with a rotary evaporator and further concentrated under N_2 stream to nearly dryness. Then 1 mL hexane was added to the extract. Florisil solid phase cartridge (ENVI™-Florisil cartridges, 500 mg bed weight, 3 mL, Supleco, Bellefonte, PA, USA) was used for cleanup, and 6 mL hexane were used for precondition. The extracts were transferred into the Florisil cartridges and eluted with 10 mL of hexane. The eluent was evaporated until 1 mL and loaded onto acidified silica cartridges (44%, pre-washed with 6 mL hexane) for a second clean-up. The extracts were eluted with 10 mL of hexane/dichloromethane (DCM) (1,1, v/v). Afterwards, the eluent was further concentrated to nearly dryness under a gentle stream of N_2, reconstituted with 100 μL isooctane and transferred to injection vials. All samples were stored at −20 °C till analysis. Information about GC–MS analysis is provided in the Supporting Information and Table SI-2.

2.3. Quality assurance and quality control (QA/QC)

The sampling and laboratory glassware was baked at 400 °C for 6 h before use to avoid contamination. The spiked recovery values of forehead wipe sample were obtained by spiking 500 ng, 100 ng, and 10 ng standards of 27 HFRs and 27 PCBs (5 replicates for each) into soaking gauze wipes and were analysed through the same procedure used for the samples. The recovery values of all the compounds were generally acceptable, ranging between 83 and 110% (Table SI-3). Triplicate procedure blanks were analysed for each batch of 12 samples, and only BDE-183 and BDE-209 were detected with amounts all <1% of the mean contents in the samples. A signal of 10 times the noise level was used as the instrument detection limit (IDL). Results were blank subtracted and a value of 1/2 IDL was used if the HFR and PCB levels were less than the IDL during statistical analysis. Statistical analysis was performed using SPSS statistical software package, version 17.0 (SPSS Inc.). Shapiro-Wilk test was used to examine whether the data were normally or log-normally distributed. Results revealed that not all data were log-normally distributed and the relevant data were log transformed. The independent sample *t*-test was used for data comparisons and we used the Pearson correlation coefficient to examine the correlations between forehead washing frequency and HFR and PCB concentrations.

3. Results

3.1. Levels and profiles of HFRs in forehead wipes

Detailed information on HFR and PCB levels are presented in Fig. 1 and Table SI-4. All PBDE congeners were frequently detected in forehead wipes with detection frequencies higher than 90.8%, BDE-209 and BDE-197 were detected in all the samples. For NBFRs, DBDPE (98%) and TBPH (81%) have the highest detection frequencies, while BTBPE had the lowest detection frequency at 67%. The detection frequencies of the DP and DD congeners were all above 90%. PCBs were detected in all forehead wipe samples.

Among the 92 forehead wipe samples, the median concentrations of $\sum_{15}$PBDEs, $\sum_{8}$NBFRs, $\sum_{2}$DPs and $\sum_{2}$DDs, were 258, 280, 6.70 and 0.78 ng/m^2, respectively. The concentration of all $\sum_{15}$PBDEs varied from 0.05 to 3610 ng/m^2. BDE-209 was the predominant PBDE congeners (median = 171 ng/m^2), accounting for about 67% of the contents of $\sum_{15}$PBDEs, followed by BDE-183 (14%). This phenomenon coincided with the fact that the Deca-BDE mixture is one of the most widely used flame retardants around the world, especially in China (Shi et al., 2013; Zhu et al., 2015). However, the less brominated BDEs should also attract attention due to their longer half-lives (years) and ability to be formed through the debromination of higher brominated congeners (Bezares-Cruz et al., 2004). With a median concentration of 134 ng/m^2, DBDPE was the most abundant NBFR congener as an alternative to the Deca-BDE, contributing over 48% to $\sum_{8}$NBFRs. TBPH (97.7 ng/m^2) and HBB (34.9 ng/m^2) represented relatively lower contamination levels, contributing about 35% and 13% to $\sum_{8}$NBFRs, respectively. BTBPE contributed <1% to $\sum_{8}$NBFRs. The abundance of DBDPE was consistent with its high production volume in China (Yu et al., 2016) and the profiles of NBFRs in this study were similar to many former studies on NBFR occurrence in PM$_{2.5}$ in Beijing (Liu et al., 2016), indoor dust in Beijing (Cao et al., 2014) and the air in Southeast Asia (Moeller et al., 2012). Further, as an important substitute for commercial Octa-BDE, the low levels of BTBPE indicated that it was not a widely used HFR in China, which has

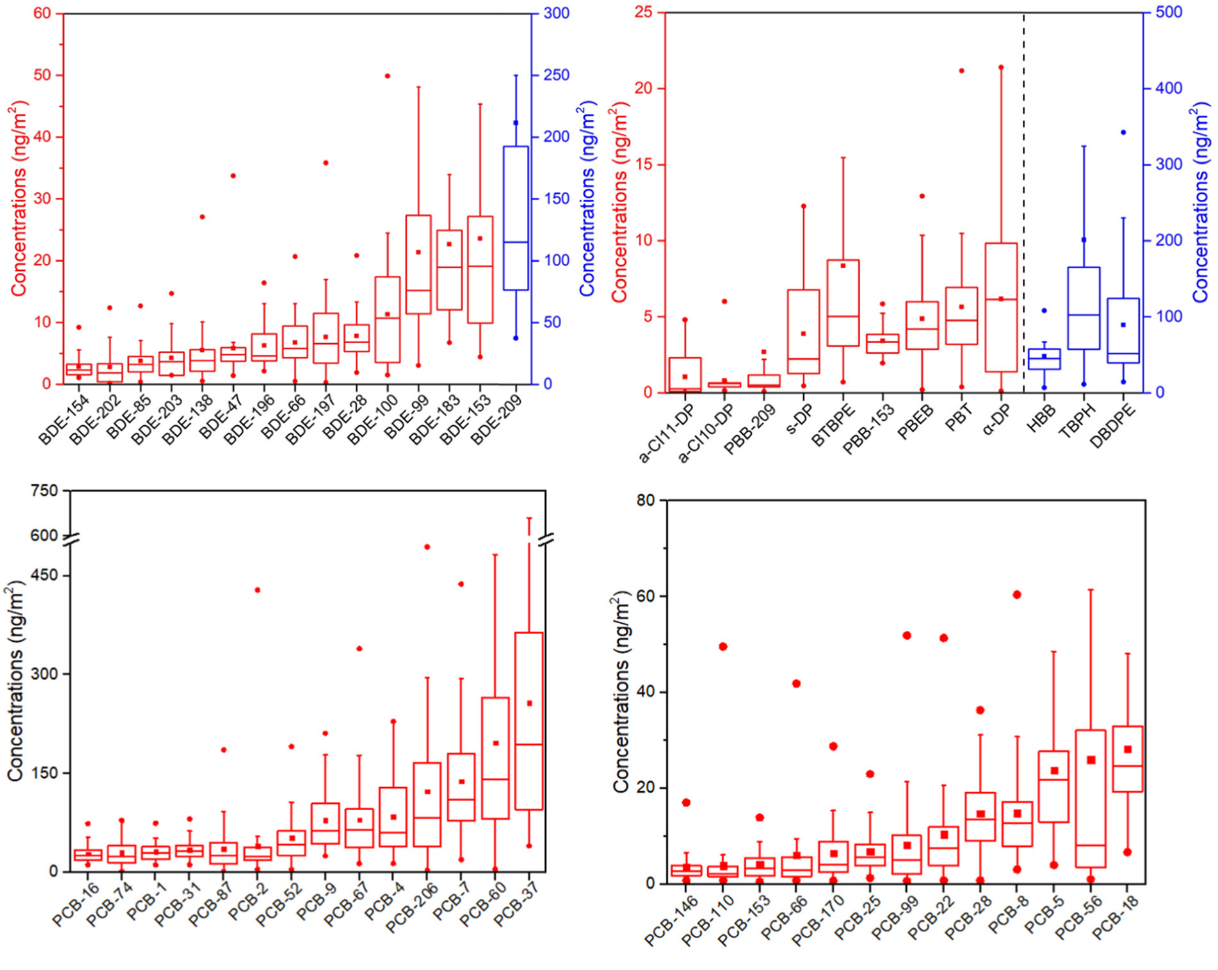

Fig. 1. Concentrations of the measured HFRs and PCBs in forehead wipes.

also been indicated by previous studies (Jiang, 2006; Yu et al., 2016). Data on DP occurrence in skin wipes are rather limited (Liu et al., 2017b). With lower determined levels in forehead wipes, a-DP (4.06 ng/m^2) and s-DP (1.95 ng/m^2) accounted for 61% and 29% of the $\sum_2$DPs, respectively, which was in accordance with the fact that DPs are synthesised as an isometric mixture of anti- and *syn*-DP with an approximate 3:1 anti/syn ratio (Guerra et al., 2011). a-Cl$_{10}$-DP and a-Cl$_{11}$-DP were measured with levels ranging from 0.14 to 6.00 ng/m^2 and 0.05 to 4.80 ng/m^2, with median concentrations of 0.50 and 0.18 ng/m^2, respectively. Though DDs with fewer than 12 chlorines have previously been observed in air (Chen et al., 2011), sediments (Zhou et al., 2017), human serum and hair (Chen et al., 2015), this is the first study, to the best of our knowledge, to detect them in human skin wipes.

To date, there is no data available in the literature on HFR contamination in forehead wipes; hence, a comparison was conducted between our study and other studies which reported HFR occurrence on other skin locations (e.g. hand, forearm) (Table SI-5). Compared with the levels of BDE-28, BDE-47, BDE-183 and DBDPE found in the forearm wipes of adults from Beijing (Liu et al., 2017b), those measured on the forehead wipes in this study were 1.53–18.9 times higher. This may be attributable to the fact that the forearms were covered by clothes, preventing dermal absorption of HFRs to some extent (Wu et al., 2016). Levels of BDE-47, BDE-209 and DBDPE in this study were slightly lower compared with those found in hand wipes of adults from Norway (Tay et al., 2018), which may be explained by the frequent contact of hand with dust or HFR-treated products. However, levels of BDE-47, BDE-99, BDE-209 and DBDPE in children's hand wipes taken from Sweden were comparable to those in the forehead wipes of this study (Kristin Larsson et al., 2018). The level of BDE-209 was much higher in forehead wipes (171 ng/m^2) in this study than in toddlers' back wipes from the Netherlands, with a concentration of around 22 ng/m^2 (1.1 ng/wipe, assuming that the area of the back is 0.05 m^2) (Sugeng et al., 2017).

3.2. Levels and profiles of PCBs in forehead wipes

Comparatively, PCBs (1030 ng/m^2) showed higher levels than HFRs (545 ng/m^2) in the forehead wipes of this study. TriCB (median = 303 ng/m^2), TetraCB (median = 282 ng/m^2) and DiCB (median = 268 ng/m^2) were the dominant PCBs in the forehead wipes, accounting for approximately 83% of $\sum_{27}$PCBs. PentaCB (3%), HexaCB (0.6%) and HeptaCB (0.4%) represent a minor contribution. Among the individual substances of PCBs, with PCB-37 (median = 194 ng/m^2) and PCB-60 (median = 141 ng/m^2) being the most abundant congeners in the forehead wipes, PCB-52 (42.5 ng/m^2), PCB-28 (13.5 ng/m^2) and PCB-153 (3.4 ng/m^2) exhibited lower levels in the wipes and PCB-110 (2.2 ng/m^2) showed the lowest level. To the best of our knowledge, this is the first report on the detection of PCBs in human skin wipes. Hence, PCB levels and profiles in air, atmosphere particles, indoor dust and soil samples were summarised and compared with data in this study. For PCBs in indoor air, the dominant congeners were PCB-52 and PCB-28, which contributed around 40.3% and 39.8%, respectively, to $\sum_{37}$PCBs in Canada (Audy et al., 2018). DiCB and TriCB represented approximately one-third of the $\sum_{39}$PCBs in the indoor air of North Rhine-Westphalia, Germany (Kraft et al., 2018). The PCBs in atmospheric particles were dominated by highly chlorinated PCBs and concentrations of HexaCB and HeptaCB accounted for 64.7% and 59.8 of the $\sum_{28}$PCBs, respectively, from an isolated island in Fujian, China (Lao et al., 2018b). With regard to PCBs in dust samples, only highly chlorinated congeners of PCB-138 (12.1 ng/g) and PCB-180 (12.8 ng/g) were detected in the Czech Republic (Audy et al., 2018), and the contribution of HexaCB (40%) was the highest in dust samples collected from Taizhou, China (Xing et al., 2011). Highly chlorinated congeners were abundant in soil samples in Italy (Qu et al., 2019), mostly dominated by HexaCB, HeptaCB and PentaCB at 35%, 29% and 14%, respectively. Overall, the PCB profile in the forehead wipes (dominated by TriCB, TetraCB and DiCB) aligned with that measured in indoor air samples, which is consistent with the fact that the lower-chlorinated congeners are more volatile (Breivik et al., 2002). This suggests that PCBs on foreheads were more likely accumulated from the air, indicating that air-to-skin transport might be the dominant pathway of human dermal exposure to PCBs. Generally, according to the literature, PCB concentrations in indoor air generally ranged from 0.1 to 479 ng/m^3 (Kraft et al., 2018; Xing et al., 2011), and PBDE concentrations in the air generally ranged from 1.12 to 170 pg/m^3 (Cequier et al., 2014; Wong et al., 2018), indicating that PCB contamination is still a serious issue in China and human exposure to PCBs should be given more attention in the future.

4. Discussions

4.1. Influence of gender

As Fig. 2 shows, the median concentrations of $\sum_{15}$PBDEs was higher in female forehead wipes (290 ng/m^2) than in male forehead wipes (225 ng/m^2), and statistical differences were found between females and males for most PBDE congeners (Table SI-6). BDE-183 levels were higher for females (22.0 ng/m^2) than males (16.5 ng/m^2), with p values of 0.039. BDE-28, BDE-47, BDE-66 and BDE-99 showed higher values of 6.50, 5.33, 7.79 and 10.6 ng/m^2, respectively, for females than the values for males (2.85, 2.32, 4.79 and 3.02 ng/m^2), representing p values all lower than 0.01. However, no statistically significant difference was found for BDE-209 ($p = 0.45$). $\sum_8$NBFR levels were higher in males (376 ng/m^2) than females (242 ng/m^2) ($p = 0.069$). The median concentrations of HBB, PBT, PBEB PBB-153 were higher in female forehead wipes (49.7, 5.20, 4.77, 3.47 ng/m^2, respectively) than in male forehead wipes (31.4, 3.52, 3.24, 2.50 ng/m^2, respectively), with p values all lower than 0.05, suggesting a potential gender difference. However, as the dominant congener, no significant statistical difference ($p = 0.253$) was found for DBDPE between females and males. For DPs, with median levels of 2.31 ng/m^2 in forehead wipes for females and 1.07 ng/m^2 for males, only the p value for s-DP was lower than 0.05. DDs had a median concentration of 0.92 and 0.45 ng/m^2 for females and males, respectively, displaying a gender difference with p value of 0.031. With regard to PCBs, $\sum_{27}$PCBs levels for females (1610 ng/m^2) were remarkably higher than for males (1090 ng/m^2) ($p = 0.001$). Significant differences were found between females and males for MonoCB ($p = 0.014$), DiCB ($p = 0.011$), TetraCB ($p < 0.001$), HeptaCB ($p = 0.001$) and NonaCB ($p = 0.001$), which all represented higher values for females (65.7, 365, 434, 7.74 and 134 ng/m^2, respectively) than males (45.1, 252, 249, 3.09 and 54.9 ng/m^2, respectively). TriCB showed higher levels for males (339 ng/m^2) than females (293 ng/m^2), though no significant statistical difference was observed ($p = 0.666$). Of the PCB congeners

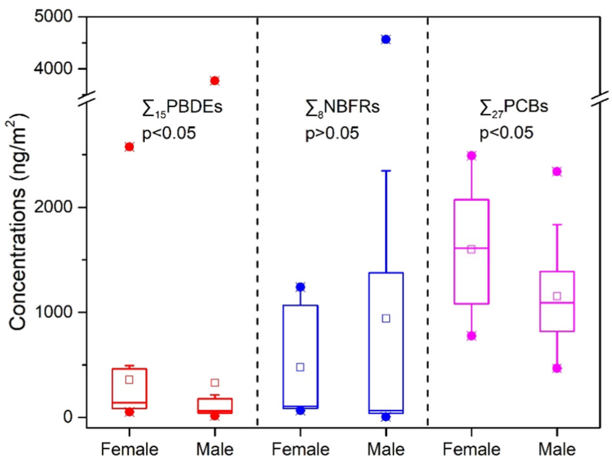

Fig. 2. Concentrations of $\sum_{15}$PBDE, $\sum_8$NBFR and $\sum_{27}$PCB levels for females and males.

measured, median concentrations of PCB-206, PCB-67 and PCB-74 in female and male forehead wipes were 134, 85.9 and 39.0 ng/m^2, and 54.9, 40.3 and 15.5 ng/m^2, respectively, and statistically significant differences were observed (with p values of 0.001).

BDE-209 contributed 63% to $\sum_{15}$PBDEs in female forehead wipes (Fig. SI-1), while the proportion in male wipes was 75% and no significant gender difference was observed ($p = 0.866$). DBDPE (47% for females and 45% for males) ($p = 0.755$) and HBB (20% for females and 8% for males) ($p = 0.166$) showed larger contributions to $\sum_8$NBFRs for females, while TBPH contributed a larger proportion to $\sum_8$NBFRs for males (44%) than females (25%) ($p = 0.673$). s-DP ($p = 0.032$) represented a relatively higher contribution to $\sum_2$DPs for females (60%) than males (15%) and a-Cl$_{10}$-DP ($p = 0.765$) accounted for 79% of $\sum_2$DDs for males, which was higher than the 67% contribution for females. In short, gender had a higher influence on the DP profile compared to other HFRs. TetraCB and NonaCB accounted for 32% and 10% of $\sum_{27}$PCBs in females, which were higher proportions than for males (25% and 6%; $p = 0.002$, $p = 0.006$). TriCB represented a higher contribution to $\sum_{27}$PCBs for males (34%) than females (21.8%) ($p = 0.06$).

Though the gender difference can, to some extent, be explained by different skin properties, behaviour patterns and living habits between females and males, statistical differences ($p < 0.05$) were also found for the BDE-47, BDE-66, BDE-85, BDE-99, BDE-100, BDE-196, BDE-202, PBT, PBB-153, HBB, DiCB, TetraCB, NonaCB, DP and DD values of participants according to their cosmetic use habits (Table SI-6). This indicates that different exposure patterns to HFRs and PCBs between genders may also be associated with the use of cosmetics. In this study, 22 female and 0 male participants were cosmetic users and it was determined that cosmetics might play a promoting role in dermal exposure to HFRs and PCBs. Similar to our results, previous studies had demonstrated that cosmetics may contain certain ingredients, such as surfactants, which can increase the partitioning of chemicals to the skin surface by altering the skin's lipid domain (Lane, 2013).

According to the literature, levels of monoethyl phthalate (MEP) and monobenzyl phthalate (MBzP) in urine samples (around two times, $p < 0.05$, $p < 0.01$) (Silva et al., 2004), DP and DD in human hair samples (around ten times, $p < 0.01$) (Chen et al., 2015), DP in serum samples (around two times, $p < 0.05$) (Yan et al., 2012), DPHP (phenopyrazone) in urine samples (almost two times, $p < 0.01$) (Hoffman et al., 2015) and BFRs in the forearm and hand wipes ($p < 0.05$) (Liu et al., 2017a) all showed higher levels for females than males, similar to the results of this study. This may be due to the differences in behaviour patterns, personal product application and living habits between genders, and females are possibly suffering higher exposure risk to flame retardants and relative contaminants. The consistency between the literature and our study illustrates that there may be positive correlations between dermal exposure and internal exposure to some extent, implying that dermal exposure might be an important pathway for human exposure to a series of indoor contaminants.

As shown in Table SI-7, though $\sum_{27}$HFR and $\sum_{27}$PCB levels did not represent apparent correlation with the duration from the last forehead washing to sampling (forehead washing frequency) ($R^2 = 0.01$, $p = 0.67$; $R^2 = 0.001$, $p = 0.74$), significantly positive correlations were found for BDE-202 ($R^2 = 0.15$, $p = 0.004$), BDE-183 ($R^2 = 0.21$, $p = 0.01$), a-Cl$_{11}$-DP ($R^2 = 0.17$, $p = 0.03$) and PCB-99 ($R^2 = 0.10$, $p = 0.01$). Thus, HFRs and PCBs may not only gradually accumulate on human skin from the air but can also be affected by human activities, including occasional hand-forehead contact. Furthermore, it is also possible that the partition of some HFRs and PCBs between the air and the skin lipid on forehead can reach equilibrium within a short time period (Weschler and Nazaroff, 2012).

4.2. Influence of haze

In China, haze pollution has become the most significant environmental problem in recent years and considerable effort has been invested in exploring its impact on human health. Because HFRs and PCBs on the skin surface (especially the forehead, which rarely comes in contact with indoor surfaces) can originate in substantial amounts from the air, and haze has been shown to influence the concentration and distribution of SVOCs in the air (Cao et al., 2018c; Zhu et al., 2018), we hypothesized that haze would indirectly affect human dermal exposure to HFRs and PCBs.

Fig. SI-2 shows the concentration ratio of HFRs and PCBs under light and heavy haze pollution conditions. The median ratio for the 27 HFR compounds ranged from 0.22 to 1.77 and the ratio for the 27 PCBs ranged from 0.28 to 1.85. Fig. 3 shows the concentration variations of typical HFRs and PCBs with PM$_{2.5}$, PM$_{10}$ and AQI. Negative correlations were found between the concentrations of most PCBs and PM$_{2.5}$, PM$_{10}$, AQI, and no obvious correlations were found between HFRs and PM$_{2.5}$, PM$_{10}$ and AQI. Overall, haze did not significantly influence HFR occurrence, indicating that for most HFRs in forehead wipes, human exposure sources, routes and doses do not change under the two haze pollution conditions. However, a statistical difference was found for PCB occurrence between light and heavy haze pollution conditions, indicating haze had a higher influence on PCBs than HFRs.

The median concentration of $\sum_{27}$HFRs was 594 ng/m^2 in light haze pollution condition, which is higher than the 485 ng/m^2 observed in the heavy haze pollution condition ($p = 0.269$). Specifically, the median concentrations of $\sum_{15}$PBDEs, $\sum_8$NBFRs and $\sum_2$DPs in the light haze pollution condition (277, 276 and 7.64 ng/m^2) were all higher than that in the heavy haze pollution condition (240, 241 and 3.19 ng/m^2), with p values of 0.087, 0.069 and 0.003, respectively. Comparable levels of $\sum_2$DDs were found in both haze levels (0.86 ng/m^2 and 0.59 ng/m^2 in the light and heavy haze pollution condition, respectively). The median concentrations of BDE-28, BDE-47, BDE-66 and BDE-209 in the light haze pollution condition were 4.93, 4.38, 5.34 and 193 ng/m^2, respectively, which was slightly higher than those of the heavy haze pollution condition (4.40, 3.81, 7.23 and 147 ng/m^2, respectively) ($p = 0.845$, 0.475, 0.395 and 0.564, respectively). Nevertheless, BDE-100, BDE-183 and BDE-196 exhibited slightly higher levels in the heavy haze pollution condition with median levels of 11.6, 21.2 and 5.31 ng/m^2 compared to 10.7, 18.6 and 4.18 ng/m^2 in the light haze pollution condition ($p = 0.432$, 0.855 and 0.334), respectively. DBDPE showed a higher level of 154 ng/m^2 in the light haze pollution condition compared to 83.1 ng/m^2 in the heavy haze pollution condition ($p = 0.059$). Levels of HBB and TBPH were 44.3 and 100 ng/m^2 in the heavy haze pollution condition, higher than the 34.4 ($p = 0.197$) and 75.5 ng/m^2 ($p = 0.449$) observed in the light haze pollution condition, respectively. A statistical difference was observed in $\sum_{27}$PCBs ($p = 0.001$), with a higher concentration (1686 ng/m^2) in light haze pollution than in heavy haze pollution condition (996 ng/m^2). DiCB ($p = 0.011$), TetraCB ($p = 0.001$) and NonaCB ($p = 0.001$) all showed higher levels in the light haze pollution condition (398, 376 and 108 ng/m^2, respectively) compared to the heavy haze pollution condition (244, 289 and 51.8 ng/m^2, respectively). Among the individual PCBs, PCB-60, PCB-206, PCB-4 and PCB-9 all had higher concentrations in the light haze pollution condition (163, 109, 107 and 92.0 ng/m^2, respectively) than in the heavy haze pollution condition (123, 52.0, 43.6 and 54.7 ng/m^2, respectively) ($p = 0.045$, 0.009, 0.001 and 0.03, respectively). PCB-5 (23.7 ng/m^2) and PCB-16 (28.0 ng/m^2) showed higher levels in the heavy haze pollution condition than the light haze pollution condition (17.3 and 20.3 ng/m^2, respectively), but no significant difference was found ($p = 0.066$ and 0.116).

Generally, the influence of haze on HFR and PCB in the forehead wipes was compound-specific, possibly resulting from their different exposure pathways. There are mainly two pathways for the accumulation of HFRs and PCBs on the human forehead: namely direct air-to-skin transport (gas phase) (Weschler and Nazaroff, 2012) and particle deposition (Lao et al., 2018a). The contribution of these two pathways to total dermal exposure might vary between compounds due to their different physico-chemical properties. Air-to-skin transport might be

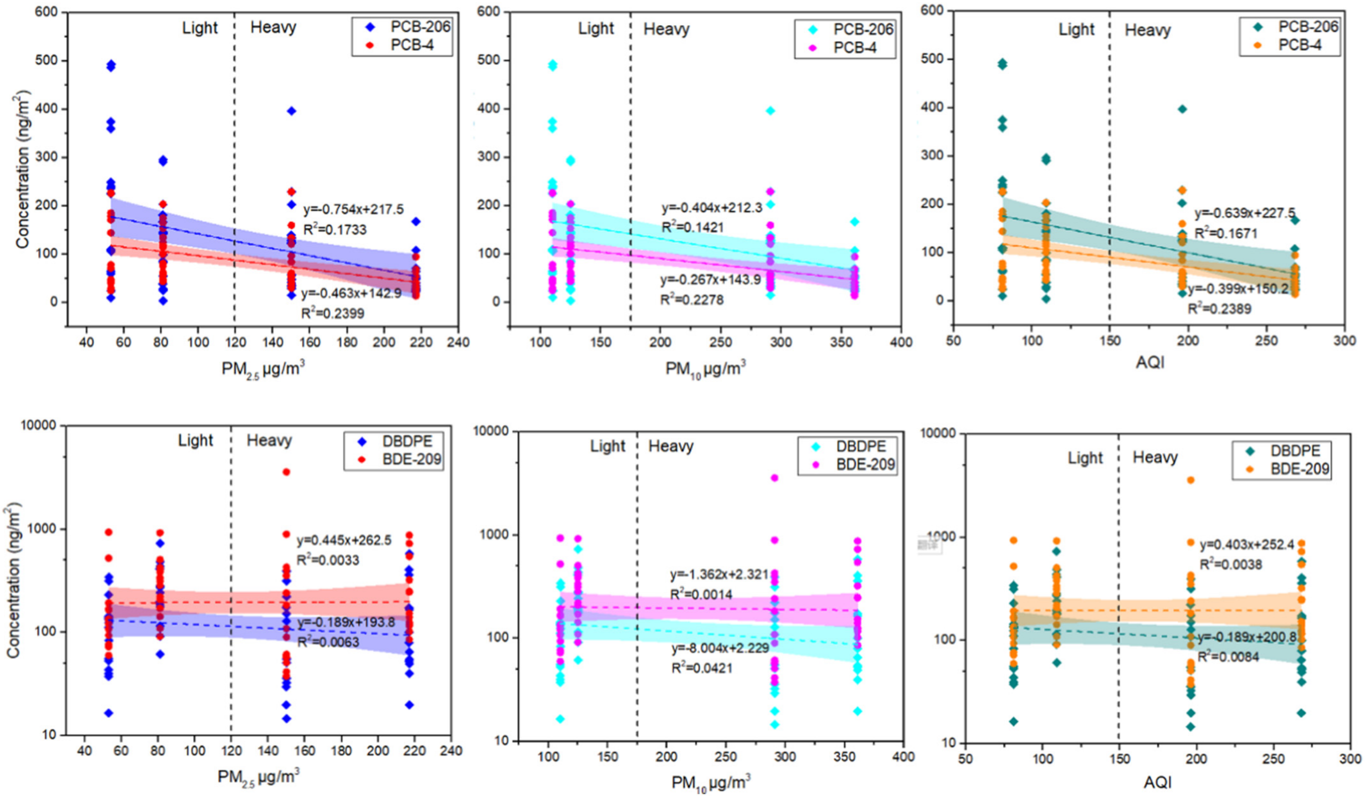

Fig. 3. Variation in the concentration of HFRs and PCBs with the atmospheric levels of $PM_{2.5}$, PM_{10} and AQI.

the dominant pathway for some compounds, while others may be governed by particle deposition. Additionally, haze substantially shapes the gas-particle partition and size distribution of SVOCs in the air (Sheng et al., 2018; Zhu et al., 2018). Haze may decrease the gas phase concentrations of SVOCs in the air (Cao et al., 2018b), and if air-to-skin transport is the dominant pathway for all compounds, dermal exposure to HFRs and PCBs should be all lower under heavy haze pollution condition than light haze pollution condition theoretically. However, contrary phenomenon were found between HFRs and PCBs in this study. Overall, volatility seems to have an apparent influence on dermal exposure to HFRs and PCBs (Fig. SI-4). For some more volatile compounds (e.g. PCBs), it is presumed that under the heavy haze pollution condition, PCBs can be massively partitioned onto atmospheric particles and their gas-phase concentration decreased compared to that in the light pollution condition (Zhu et al., 2018). This results in higher levels of PCBs in forehead wipes under the light haze pollution condition when air-to-skin transport is the dominant accumulation mechanism of PCBs on the human forehead (Shi and Zhao, 2014). For some less volatile compounds, heavier haze may possibly increase their volume concentration in the air but reduce their gas phase concentration and mass concentration in the particulate phase (Cao et al., 2018b). Only in case that particle sedimentation is the dominant dermal exposure pathway, haze can possibly increase (e.g. BDE-183 and BDE-196) or maintain (e.g. BDE-203 and BTBPE) the dermal exposure levels to non-volatile compounds. Conclusively, all these factors make the influence of haze on the occurrence of HFR and PCB on the forehead complex and it can increase, maintain, or even reduce human exposure to HFRs and PCBs through dermal uptake subject to their physico-chemical properties.

Previous theoretical analysis has generally stated that only for more volatile compounds can dermal uptake be significant for human exposure to SVOCs (Pelletier et al., 2017; Weschler and Nazaroff, 2012). However, some recent studies and our results indicate that non-volatile compounds were dominant on the human skin (Liu et al., 2017b; Tay et al., 2018), which implies that, other than air-to-skin transport, particle sedimentation might also be a significant pathway for dermal exposure to HFRs and PCBs, especially for non-volatile components.

4.3. Exposure doses and non-carcinogenic risk assessment

In recent years, dermal exposure, expressed in daily average dose (DAD) in this study, has attracted widespread attention. There are several dermal exposure assessment models available (Abdallah et al., 2016; Cao et al., 2017a; Tay et al., 2018) which can be classified into two categories. Firstly, the relative absorption (RA) model proposed by USEPA has been widely applied (Eq. (1)) (Cao et al., 2017a; Cao et al., 2017b). The permeability coefficient (PC) method was developed in recent years and has also been commonly applied by several studies (Eqs. (2), (3)) (Gong et al., 2014; Tay et al., 2018). All the corresponding parameter values are shown in Table SI-8.

The RA model (Eq. (1)), PC model with $K_{p\text{-}l}$ (Eq. (2)) and PC model with $K_{p\text{-}cl}$ (Eq. (3)) for the calculation of DAD (ng/kg/d) are delivered as follows. Equations and detailed information on the derivation of the PC models are described in the Supporting Information. $K_{P\text{-}l}$ (cm/h) and $K_{P\text{-}cl}$ (cm/h) are the permeability coefficient of HFRs from lipids to dermal capillaries and to tissue layers, respectively. Because $K_{P\text{-}l}$ and $K_{P\text{-}cl}$ values were only available for a limited number of HFR compounds (Abdallah et al., 2015; Frederiksen et al., 2016) and no studies have examined the percutaneous penetration coefficient of PCBs, we only calculated the DAD_{PC} from the skin lipids to tissue layers (Eq. (2)) for 7 PBDEs (BDE-28, BDE-47, BDE-99, BDE-154, BDE-153, BDE-183 and BDE-209) and 2 NBFRs (BTBPE and DBDPE) in this study. We also calculated DAD_{PC} from the skin lipids to dermal capillaries (Eq. (3)) for 5 PBDEs (BDE-28, BDE-47, BDE-99, BDE-154 and BDE-153) and 2 NBFRs (BTBPE and DBDPE). We hypothesized that the wipes only sampled the skin surface lipids and the thickness of the skin lipid was assumed to be 1.3 μm for adults (Nazzaro-Porro et al., 1979).

$$DAD_{RA} = \frac{C_s \times SA \times N \times ED \times EF \times ABS}{BW \times AT} \qquad (1)$$

$$DAD_{PC} = \left[\frac{\frac{C_s}{I_m} \times K_{p\text{-}l}] \times SA \times N \times EF \times ED}{BW \times AT} \right. \qquad (2)$$

$$DAD_{PC} = \left[\frac{\frac{C_s}{I_m} \times K_{p-cl}] \times SA \times N \times EF \times ED}{BW \times AT} \right. \qquad (3)$$

The DAD_{RA} of $\sum_9$HFRs and $\sum_{27}$PCBs calculated with the RA model (Eq. (1)) were 1.66×10^{-1} and 3.26×10^{-1} ng/kg/d; BDE-209 (5.49×10^{-2} ng/kg/d) and PCB-37 (6.10×10^{-2} ng/kg/d) represented the largest contribution to $\sum_9$HFRs and $\sum_{27}$PCBs, respectively (Table 1 and Table 2). The DAD_{PC} of $\sum_7$PBDEs and $\sum_2$NBFRs penetrating the tissue layers (Eq. (2)) were 2.59 and 0.69 ng/kg/d, while the DAD_{PC} of $\sum_5$PBDEs and $\sum_2$NBFRs penetrating the dermal capillaries (Eq. (3)) were 0.28 and 0.07 ng/kg/d, respectively. Accordingly, the values of DAD_{PC} penetrating the tissue layers were approximately 10 times higher than that penetrating the dermal capillaries, and 2 orders of magnitude higher than DAD_{RA}. For the DAD_{PC} (Eq. (3)), it is notable that although BDE-209 (1.46 ng/kg/d) has lower dermal bioavailability and lower $K_{P\text{-}cl}$ value compared to other less brominated compounds (Abdallah et al., 2015; Frederiksen et al., 2016), it contributed >56.4% to the total DAD_{PC} of $\sum_7$PBDEs and the contribution of DBDPE (0.68 ng/kg/d) to that of $\sum_2$NBFRs was about 98.6%.

Results from the three models varied greatly, indicating that the assessment models may have high evaluation uncertainty. Because dermal exposure assessment methodology is generally not unified across different studies, the need to verify which model is more accurate for assessing human exposure is urgent. Efforts should be made to improve the comparability of different models and the accuracy of relevant parameters in the future, including the bioaccessibility of HFRs and PCBs in skin wipes (Cao et al., 2017a; Gong et al., 2014; Liu et al., 2017a).

The whole body dermal exposure to HFRs and PCBs (DAD_W) and the corresponding health risk assessment were conducted based on Eq. S6. Our systemic dermal exposure estimates highlight the importance of dermal exposure as a significant pathway of human exposure to HFRs and PCBs (Fig. SI-5). The estimated exposure doses of $\sum_{15}$PBDEs, $\sum_8$NBFRs, $\sum_2$DDs, $\sum_2$DPs and $\sum_{27}$PCBs throughout the skin of the entire body were 3.28, 4.46, 1.03×10^{-2}, 7.34×10^{-2} and 14.2 ng/kg/d, respectively, which were 1–2 orders of magnitude higher than on the forehead, with values for $\sum_{15}$PBDEs, $\sum_8$NBFRs, $\sum_2$DDs, $\sum_2$DPs and $\sum_{27}$PCBs of 8.68×10^{-2}, 1.01×10^{-1}, 2.52×10^{-4}, 1.69×10^{-3} and 3.26×10^{-1} ng/kg/d, respectively. Compared to the estimated exposure dose from dust ingestion and inhalation (Besis and Samara, 2012; Tay et al., 2018), it is possible that dermal exposure is the dominant pathway for human exposure to HFRs and PCBs.

Hazard quotients (HQs) were used to characterise non-carcinogenic risks of HFRs and PCBs, and the HQ of each specific congener was calculated based on Eq. (4) (U.S.EPA, 2011). RfD is the reference dose of individual HFRs and PCBs (mg/kg/day). The hazard index (HI) approach was used to assess the total non-carcinogenic risk posed by more than one congener by summing the HQs. The HIs of the HFRs and PCBs were calculated using Eq. (5). HI values <1 indicate that there was a negligible risk of adverse health effects for the exposed population, while HI values >1 indicate that the exposed population might suffer from potential non-carcinogenic effects (Man et al., 2010). Due to the lack of RfD values, we calculated the HQ and HI of 8 HFRs (BDE-47, BDE-99, BDE-153, BDE-154, BDE-183, BDE-209, BTBPE and DBDPE) and 27 PCBs. DAD_W values calculated by the RA model were adopted for HQ estimation, and the RfD values of 8 HFRs and 27 PCBs are provided in Table SI-9.

$$HQ = \frac{DAD}{RfD} \qquad (4)$$

$$HI = \Sigma HQ_i \qquad (5)$$

Notably, $\sum_{27}$PCBs (1.63×10^{-2}) exhibited apparently higher HI values than $\sum_8$HFRs (8.72×10^{-5}). Specifically, PCB-37 (3.05×10^{-3}) showed the highest HQ value for PCBs and PCB-110 exhibited the lowest HQ value (3.35×10^{-5}). Among HFRs, BDE-183 (3.15×10^{-5}) showed the highest HQ value for HFRs, followed by BDE-99 (2.20×10^{-5}), BDE-153 (1.24×10^{-5}) and BDE-209 (1.66×10^{-7}). PCB congeners all showed higher HQ values than HFRs, implying that PCBs posed a more considerable health threat than HFRs to the investigated populations in this study.

5. Conclusions

27 HFRs and 27 PCBs were all pervasively detected in human forehead wipes for the first time. Gender differences were found for most HFRs and PCBs, which may be associated with the use of cosmetics. Haze had a more significant influence on PCB occurrence in the forehead wipes than HFRs, possibly due to their different volatility. With higher volatility, PCBs can be massively partitioned onto atmospheric particles, resulting in a reduction of dermal exposure to PCBs under the heavy haze pollution condition when air-to-skin transport is the dominant accumulation mechanism of PCBs on the human forehead. Two different dermal exposure assessment models were employed to estimate the daily intake dose of HFRs through dermal absorption, and the estimated DAD values from the PC method were about 1–2 orders of magnitude

Table 1
Daily dermal absorption dose (ng/kg/d) of HFRs.

Compound	$K_{p\text{-}l}$ (cm/h)	$K_{p\text{-}cl}$ (cm/h)	DAD[a] (ng/kg/d)	DAD[b] (ng/kg/d)	DAD[c] (ng/kg/d)	HQ[a]
BDE-28	1.76×10^{-3}	1.14×10^{-2}	2.07×10^{-3}	0.02	0.13	–
BDE-47	1.26×10^{-3}	1.38×10^{-2}	1.50×10^{-3}	0.02	0.13	1.23×10^{-5}
BDE-99	8×10^{-3}	1.42×10^{-2}	5.00×10^{-3}	0.14	0.24	2.20×10^{-5}
BDE-154	4×10^{-3}	1.56×10^{-2}	7.83×10^{-4}	0.02	0.07	2.72×10^{-6}
BDE-153	4×10^{-3}	1.56×10^{-2}	5.93×10^{-3}	0.08	0.30	1.24×10^{-5}
BDE-183		5.33×10^{-3}	6.31×10^{-3}	NA	0.26	3.15×10^{-5}
BDE-209		3.49×10^{-3}	3.80×10^{-2}	NA	1.46	1.66×10^{-7}
BTBPE	2.4×10^{-4}	3.43×10^{-3}	1.47×10^{-3}	0.001	0.01	2.35×10^{-8}
DBDPE	2.2×10^{-4}	2.2×10^{-3}	2.21×10^{-2}	0.07	0.68	6.00×10^{-6}

NA: not available due to lack of data on reference dose.

[a] Daily dermal absorption dose of HFRs calculated depended on relative absorption methods.

[b] Represents the transdermal flux and daily dermal absorption dose of HFRs from skin lipid to dermal capillaries based on permeability coefficient method.

[c] Represents the transdermal flux and daily dermal absorption dose of HFRs from skin lipids to tissue layers based on permeability coefficient method.

Table 2
Daily dermal absorption dose (ng/kg/d) of PCBs.

Compound	DAD[a] (ng/kg/d)	HQ[a]	Compound	DAD[a] (ng/kg/d)	HQ[a]	Compound	DAD[a] (ng/kg/d)	HQ[a]
PCB1	9.54×10^{-3}	4.77×10^{-4}	PCB22	2.32×10^{-3}	1.16×10^{-4}	PCB67	1.87×10^{-2}	9.35×10^{-4}
PCB2	7.35×10^{-3}	3.68×10^{-4}	PCB25	1.78×10^{-3}	8.90×10^{-5}	PCB74	8.10×10^{-3}	4.05×10^{-4}
PCB4	1.76×10^{-2}	8.79×10^{-4}	PCB28	4.63×10^{-3}	2.32×10^{-4}	PCB87	7.34×10^{-3}	3.67×10^{-4}
PCB5	6.26×10^{-3}	3.13×10^{-4}	PCB31	1.07×10^{-2}	5.33×10^{-4}	PCB99	1.46×10^{-3}	7.29×10^{-5}
PCB7	3.88×10^{-2}	1.94×10^{-3}	PCB37	6.10×10^{-2}	3.05×10^{-3}	PCB110	6.69×10^{-3}	3.35×10^{-5}
PCB8	3.71×10^{-3}	1.85×10^{-4}	PCB52	1.43×10^{-2}	7.15×10^{-4}	PCB146	8.76×10^{-4}	4.38×10^{-5}
PCB9	2.00×10^{-2}	1.00×10^{-3}	PCB56	2.38×10^{-3}	1.19×10^{-4}	PCB153	1.04×10^{-3}	5.20×10^{-5}
PCB16	8.43×10^{-3}	4.22×10^{-4}	PCB60	4.65×10^{-2}	2.33×10^{-3}	PCB170	1.30×10^{-3}	6.49×10^{-5}
PCB18	8.02×10^{-3}	4.01×10^{-4}	PCB66	9.87×10^{-4}	4.93×10^{-5}	PCB206	2.24×10^{-2}	1.12×10^{-3}

[a] Daily dermal absorption dose of PCBs calculated depended on relative absorption methods.

higher than those derived from the RA model. The HI values of HFRs and PCBs were all lower than 1, indicating that there were no apparent non-carcinogenic effects, while the HI of PCBs were higher than HFRs, suggesting that dermal exposure to PCBs should cause more concern in the future.

Declaration of Competing Interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

More detailed information of chemicals, materials, instrumental analysis, some additional tables and figures as noted in the text can be found online at https://doi.org/10.1016/j.scitotenv.2019.06.429.

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