RESEARCH ARTICLE

Brominated and phosphate flame retardants from interior and surface dust of personal computers: insights into sources for human dermal exposure

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Abstract

It remains unclear whether internal or external sources play the more significant role in flame retardant (FR) contamination of surface dust from personal computers (PCs), which may lead to bias on dermal exposure assessment of FRs. In the present study, the occurrence and profiles of several brominated and phosphate FRs were measured in the interior dust, and the upper surface (keyboard) and bottom surface (bottom cover) wipes of PCs. BDE 209 (639 ng/g), decabromodiphenyl ethane (DBDPE, 885 ng/g), and triphenyl phosphate (TPHP, 1880 ng/g) were the most abundant chemicals in interior PC dust, while tris(2-chloroisopropyl) phosphate (TCIPP), TPHP, and DBDPE were dominant on both surfaces of PCs. No significant correlation between interior dust and both PC surfaces was observed for concentrations of most FRs except BDE 183. Different sources of FRs for interior and surface dust of PCs were further revealed by principal component analysis (PCA). FRs from external sources, rather than emission from inner PC components, are likely the main contributor for FR profiles on PC surfaces. Exposure assessment results demonstrated a minor contribution from PC dermal contact, compared with hand-to-mouth uptake, to total exposure. The applicability of surface wipes to assess dermal exposure to FR-treated products needs to be further investigated.

Keywords Personal computer dust · Surface wipe · Flame retardants · Dermal exposure

Introduction

With the increasing usage of plastic-made products, numerous technical additives have been produced and utilized in daily consumer products, and many of these additives were proved to be environmental contaminants (Hahladakis et al. 2018). Flame retardants (FRs) and plasticizers are additives widely applied in foams, plastics, and electronics. Polybrominated

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diphenyl ethers (PBDEs) were once among the most commonly used FRs (de Wit 2002). However, due to their persistence, bioaccumulation, and toxicity, commercial penta-, octa-, and deca-BDE formulations have been successively listed in the Stockholm Convention as persistent organic pollutants (POPs) in 2009 and 2017 (UNEP 2018). This worldwide restriction and phase-out of PBDEs have led to an increase in the production and consumption of emerging FRs, such as dechlorane plus (DP), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), and organophosphate flame retardants (PFRs), as replacements (Covaci et al. 2011; Sverko et al. 2011; Xian et al. 2011). Most of these alternative FRs and plasticizers do not form a chemical bond with polymers, which facilitates their emission into the surrounding environments (van der Veen and de Boer 2012). Moreover, these alternative FRs exhibit toxicity in organisms, which raises concerns for their potential adverse effects on wildlife and humans (Covaci et al. 2011; Wei et al. 2015; WHO 1998).

The occurrence of pollutants in the indoor environment is of vital importance for human health (Abou-Elwafa Abdallah et al. 2008; Stapleton et al. 2009; Yang et al. 2019), because people spend most of their time indoors (Spengler and Sexton 1983; USEPA 1989). Human exposure to FRs generally occurs via dust ingestion (Ali et al. 2013; Xu et al. 2016), food consumption (Ding et al. 2018; Dirtu and Covaci 2010; Zheng et al. 2012), air inhalation (Hazrati and Harrad 2006; Xu et al. 2016), and dermal uptake (Abou-Elwafa Abdallah et al. 2015, 2016). Numerous studies have investigated the emission of FRs from textiles, consumer products, and insulating materials into the air and surface dust (Abou-Elwafa Abdallah and Harrad 2018; Kemmlein et al. 2003; Rauert et al. 2014b). As essential products in daily life, electronic and electrical products are extensively used, which also introduces FRs into the indoor environment. For example, an old personal computer (PC) was found to influence the PBDE contamination in indoor air, as the PBDE concentrations decreased after the old PC produced in 1998 was replaced by a new one which was manufactured in 2003 (Hazrati and Harrad 2006). According to the results from emission chamber experiments, brominated flame retardants (BFRs) were verified to transfer to surface dust from TV casing via both abrasion of product surface and the sorption of dust (Rauert et al. 2014a). PFRs are generally easier released into the air compared to BFRs, due to their relatively high vapor pressure (Kemmlein et al. 2003). PFRs in cell phone wipes were found to be significantly correlated with those in hand wipes and explained the greatest variation in the urinary metabolites (Yang et al. 2019). These findings emphasized the significance of electrical and electronic products as the primary sources of FRs for daily human exposure indoor.

Surface wipes from consumer products have been shown to reflect the existence of FRs and have been considered as a promising matrix to assess human exposure via dermal contact with products (Abbasi et al. 2016; Liu et al. 2018). Several recent studies have shown significantly positive correlation between hand wipes and surface wipes from products for BFRs, PFRs (Liu et al. 2018; Yang et al. 2019; Yang et al. 2020a), and some phthalates (Yang et al. 2020b). However, it should be noted that the FRs in surface wipes may not be solely originated from the components of treated products, which act as the primary source of FRs. Air-to-dust partitioning and deposition, product-to-dust contact, and product-to-hand transfer (Rauert and Harrad 2015; Yang et al. 2019; Yang et al. 2020a, 2020b) also account for the FRs on consumer product surfaces. Gallen et al. (2014) compared the levels of BFRs determined by three different strategies, i.e. X-ray fluorescence (XRF) method, surface wipes, and destructive tests. The results showed that the concentrations of octa-BDEs in wipes were predictive for octa-BDE concentrations in products, but the surface wipe results for BDE 209, tetrabromobisphenol A (TBBPA), and hexabromocyclododecane (HBCD) were less reliable to estimate the concentrations of these chemicals in products (Gallen et al. 2014). Thus, the question is as follows: Can surface wipe be the distinguishable indicator for primary source exposure (FR-treated products), or the integrated indicator for the particular exposure pathway, e.g. dermal uptake? In order to answer this question, it is of necessity to look into the concentrations and compositions of FRs from both interior and exterior of commercial products, which will enable better understanding on the origin of FRs in surface wipes.

In the present study, non-destructive tests of FRs in PCs (laptops) were performed by collecting the paired samples of interior dust, and the upper (hand-contacted keyboard) and bottom (desktop-contacted bottom cover) surface wipes of PCs. The aims of the present study were to (i) document the concentrations and profiles of FRs in interior dust from PC; (ii) investigate the relationships between FRs in interior dust and the surface of PCs, in order to assess the suitability or applicability of surface wipe as a matrix for estimating FR exposure via dermal contact; (iii) estimate the dermal exposure to FRs *via* hand contact with PC surfaces.

Materials and methods

Sample collection

A total of 50 PCs (all laptops) belonging to 50 adult residents (> 21 years old) in Guangzhou, a metropolis located in South China, were involved in the present study. As the PC owners, participants were enrolled only if they are non-smokers, and use PCs for work for at least 20 h per week or 4 h per day. A simple questionnaire regarding the personal information of the participants, as well as the brand and production date of their PCs, was filled out. According to the questionnaire results, all

PCs involved were from eight manufacturers and were produced between 2010 and 2015, after phase-out of penta- and octa-BDE commercial formulations (UNEP 2009) but before restriction for deca-BDE in China (MIIT 2016) and worldwide (UNEP 2017a). All the participants were required not to wipe or clean their PCs for at least 14 days before sampling, which was conducted between January and March in 2017. The upper surface of PCs referring to the hand-touched keyboards ($n = 50$) and bottom surface of PCs referring to the desktop-touched bottom covers ($n = 50$) were thoroughly wiped with sterile cotton balls held by solvent-cleaned stainless steel tweezers. The surface areas of both sides of the PCs were calculated according to the dimensions of the keyboard panel or bottom cover. The sampled cotton balls for each PC surface were then wrapped in solvent-cleaned and baked aluminum foil and stored in a labeled zip-lock bag. Prior to use, cotton balls (2 cm in diameter) were ultrasonic-extracted with methanol for 30 min and presoaked with isopropyl alcohol in amber glass vials. Field blanks ($n = 9$) for surface wipes were prepared by exposing cotton balls to the air for approximately 30 s. After surface wipe sampling, interior dust of PCs ($n = 50$) were collected by dismantling the bottom covers and keyboards, then gently gathering the dust samples with rubber aurilave and an ethanol pre-cleaned brush. Interior dust samples for each PC were then transferred into aluminum foil and stored separately in a labeled zip-lock bag. Field blanks ($n = 8$) for interior dust were prepared by parallel exposing combusted and pre-extracted sodium sulfate spread on aluminum foil for the same time when dust sampling. All samples were stored at $-20\ °C$ pending analysis.

Sample preparation and instrumental analysis

All samples were analyzed for 15 PBDE congeners, two DP isomers (*syn*- and *anti*-DP), BTBPE, DBDPE, and 11 PFRs (Table S1). Sample preparation was conducted in accordance with our previous study with some modifications (Zheng et al. 2017a, 2017b). All dust ($n = 50$) and wipe samples ($n = 100$) were spiked with internal standards (BDE 118, BDE 128, ^{13}C-BDE 209, triphenyl phosphate-d_{15} (TPHP-d_{15}), and tri-n-butyl phosphate-d_{27} (TNBP-d_{27})) before ultrasonic extraction, followed by sequential solid-phase extraction using 8 mL hexane (fraction one) and 10 mL ethyl acetate (fraction two) via Supelclean™ ENVI™-Florisil cartridges (500 mg, 3 mL, Supelco; Bellefonte, PA, USA). Fraction one, containing PBDEs, DPs, and DBDPE, was purified by concentrated sulfuric acid and the supernatant was collected for further treatment. Both fraction one and fraction two (containing PFRs) were then concentrated and redissolved in 100 μL of isooctane prior to instrumental analysis. The specific procedures of the pretreatment and cleanup for all samples are given in the Supplementary Material (SI).

Fifteen PBDE congeners (detailed in Table S1), DPs, BTBPE, and DBDPE were determined by gas chromatography-electron capture negative ionization mass spectrometry (GC/ECNI-MS) in selected ion monitoring (SIM) mode. A DB-5HT capillary column (15 m × 0.25 mm i.d. × 0.10 μm; Agilent J&W Scientific, CA, USA) was used to separate these targeted analytes. Details of the instrumental conditions were reported elsewhere (Zheng et al. 2012) and quantitation ions for the targets are listed in the Supplementary Material (Table S1). Eleven PFRs (detailed in Table S1) were quantified using a Shimadzu 2010 GC-MS system equipped with an electron impact (EI) ionization source. A DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm; Agilent J&W Scientific, CA, USA) was used for separation, and the MS was operated in SIM mode with two characteristic ions acquired for each compound individual (Table S1). Detailed information about analytical parameters was provided in a previous study (He et al. 2015).

Quality control

Quality control (QC) was performed by the analysis of field, procedural, and matrix spiked blanks (sodium sulfate for interior dust and pre-cleaned cotton balls for surface wipes). No target chemicals were detectable in field blanks. Only traces of target chemicals were detected in procedural blanks ($n = 6$), with mean values of 0.22, 0.13, 0.78, 1.61, 2.69, and 2.17 ng/mL for BDE 153, BDE 209, tri-n-butyl phosphate (TNBP), tri(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), and 2-ethylhexyl diphenyl phosphate (EHDPP), respectively. All dust and wipe samples were blank corrected. A National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) #2585 (house dust) was also analyzed with every batch. The concentrations of FRs in SRM #2585 ($n = 6$) are listed in the Supplementary Material (Table S2), which shows both good repeatability (relative standard deviation (RSD) for individual FRs, between 0.4% and 18.4%) and accuracy (ratio of mean detected SRM value to certified SRM value, between 79 and 114%, except for TCEP with the ratio of 143%) through great consistency with the certified or indicative values. The accuracy of surface wipe analysis was determined as the recoveries of the target compounds in the matrix spiked blanks, which were 67 to 102% for PBDEs, 112% for BTBPE, 77% for DBDPE, 72% and 84% for *syn*-DP and *anti*-DP, and 63 to 116% for PFRs, respectively. All samples were not recovery correction. Instrumental QC was performed by regular injection of solvent blanks and mixture of standard solutions (RSD < 15%).

The limit of quantification (LOQ) was defined as a mean value plus three times the standard deviation of target compound in procedural blanks. LOQs for both interior dust and surface wipes were listed in Table S3. For the undetectable

compounds in blanks, a signal-to-noise ratio of ten was set as corresponding LOQs.

Statistical analysis

Statistical analyses were performed for FRs with detection frequencies (DFs) higher than 50% using the SPSS 22 software for windows (SPSS Inc., Chicago, IL, USA). The values of undetected samples within these sets were treated as LOQs/2 during statistics analyses. The differences of chemical levels on upper and bottom surfaces of PCs were assessed by the Wilcoxon signed-rank test. The correlations between chemical levels in different types of samples were determined by the Spearman rank correlation analysis. The level of significance was set at $p = 0.05$ throughout the study. Principal component analysis (PCA) was conducted using logarithm-transformed FR concentration from interior dust samples and surface wipes to compare the contamination patterns in different types of samples from inner and outer PCs. Data was normalized prior to PCA and the first three factors were considered to account for a significant contribution to the total variance according to the latent root criterion.

Results and discussion

Concentrations and composition

The concentrations of FRs in PC interior dust are shown in Table 1. Octa- to deca-BDEs (except BDE 208 and BDE 207), DPs, BTBPE, DBDPE, TCEP, EHDPP, triphenyl phosphate (TPHP), and tri-(2-ethylhexyl) phosphate (TEHP) were detected with DFs > 50%. BDE 209 (median: 639 ng/g), DBDPE (median: 885 ng/g), and TPHP (median: 1880 ng/g) were the predominant chemicals, which were also found to be the most abundant FRs in electronic equipment including laptop components (Kajiwara et al. 2011). BDE 209 contributed 66% to the total PBDEs, followed by BDE 183 (18% of PBDEs). This is in agreement with the fact that both deca-BDE and octa-BDE are widely applied in electronics. Additionally, deca-BDE was not mandatorily restricted before it was listed in the Stockholm Convention in 2017 (UNEP 2017b), while the production and consumption of penta-BDE and octa-BDE have been banned since 2009 (UNEP 2009). However, it should be noted that BDE 183 were predominant (58–99% of the total PBDEs) in 8 dust samples (Fig. 1), implying the application of octa-BDE mixture in these devices. Given that these 8 PCs are from three different manufacturers and were produced within the same period, i.e., 2010–2015, as the rest of 42 PCs, it is less likely that octa-BDE was intentionally added to the devices. Another explanation could be the older components containing octa-BDE installed in the devices or thermal degradation of higher

brominated congeners under high temperature during manufacture and/or use (Chen et al. 2010). The detection of BDE 202 (DF = 59%), which does not exist in any commercial PBDE formulations, further indicated the debromination. TPHP contributed 68% to total PFRs, while the proportions of other PFRs were less than 7% for each individual (Fig. 2). TPHP and DBDPE were suggested as the most important FRs as replacements for PBDEs, especially deca-BDE, in PCs (Blum et al. 2019; Covaci et al. 2011; USEPA 2014). The addition of some condensed-type PFRs polymerized from TPHP, such as resorcinol bis(diphenyl phosphate) (PBDPP, or RDP) and bisphenol A bis(diphenyl phosphate) (BPA-DPP, or BDP), might also improve the release of TPHP as an impurity from the PC components (Kajiwara et al. 2011).

As for both upper and bottom surface wipes, BDEs 183, 197, and 209, DPs, DBDPE, and 6 out of 11 PFRs were consistently detected in more than 50% of the samples (Table 1). The median concentrations of PBDEs, DPs, DBDPE, and PFRs were 76.2, 1.97, 213, and 1700 ng/m^2 on upper surface, while they were 56.7, 1.91, 146, and 1560 ng/m^2 on bottom surfaces, respectively (Table 1). The total PBDE levels from PC surface wipes in the present study were comparable with those in a recent study (Yang et al. 2020a), while PFR levels were generally lower than those from the same series study (Yang et al. 2019). BDE 209 dominated the PBDEs, with contribution as 94% and 96% on upper and bottom surfaces of PCs, respectively (Fig. 1). TPHP was the main PFR (upper surface: 41%; bottom surface: 39%), followed by TCIPP (upper surface: 25%; bottom surface: 28%). The predominant chemicals were TPHP, TCIPP, and DBDPE on PC surface (Fig. 2), which were in accordance with the FR composition on PC wipes from our previous study (Zheng et al. 2017b).

FR concentrations have been reported in surface dust from furniture or electronics, but rare data for interior PC dust is available to date. FR concentrations in interior PC dust in the present study were generally lower than those previously observed in surface dust on PC and printer tables in Guangzhou (Zheng et al. 2017a). Extremely high level of BDE 183 (17,100 ng/g) and TPHP (110,000 ng/g) was detected in some specific interior dust samples, which could be attributed to the peeling debris of PC components. As for PC surface wipes, the abundance of BDE 209 in the present study was consistent with that in an Australian study (Gallen et al. 2014) and a recent study from Canada (Yang et al. 2020b), while was inconsistent with another Canadian study where prevalent BDE 47 and 99 was found (Abbasi et al. 2016). It is expectable to find BDE 209-predominant composition due to the extensive usage of deca-BDE formulation in hard plastic including electrical and electronic products (Alaee et al. 2003). The dominance of BDE 47 and 99, however, might be a result of the minor application of penta-BDE in older electronics (Abbasi et al. 2015; UNEP 2017a).

Table 1 Concentrations of FRs (median and range) in PC interior dust (ng/g) and on PC surfaces (ng/m^2)

	PC Dust (n = 50)			Upper surface (n = 50)			Bottom surface (n = 50)		
	DF%	Median	Range	DF%	Median	Range	DF%	Median	Range
BDE 47	2	nd	nd–8.42	18	nd	nd–11.1	10	nd	nd–2.32
BDE 100	25	nd	nd–98.7	4	nd	nd–2.65	6	nd	nd–0.37
BDE 99	8	nd	nd–27.6	4	nd	nd–14.5	0	nd	nd
BDE 154	27	nd	nd–32.5	2	nd	nd–0.19	0	nd	nd
BDE 153	18	nd	nd–22.8	0	nd	nd	0	nd	nd
BDE 183	84	20.4	nd–17,100	69	1.20	nd–59.0	54	0.65	nd–45.3
BDE 202	59	1.89	nd–257	16	nd	nd–10.2	4	nd	nd–4.92
BDE 197	61	3.50	nd–161	92	0.60	nd–2.19	83	0.50	nd–3.97
BDE 203	63	4.78	nd–644	22	nd	nd–2.85	60	0.64	nd–4.68
BDE 196	65	5.84	nd–728	20	nd	nd–1.64	71	0.30	nd–4.11
BDE 208	47	nd	nd–184	8	nd	nd–5.95	4	nd	nd–8.23
BDE 207	49	nd	nd–316	10	nd	nd–10.2	6	nd	nd–13.1
BDE 206	67	25.9	nd–389	33	nd	nd–24.2	21	nd	nd–19.8
BDE 209	88	639	nd–18,300	98	68.5	nd–1780	96	54.6	nd–1160
BTBPE	65	3.12	nd–505	45	nd	nd–9.82	81	0.55	nd–5.11
DBDPE	94	885	nd–26,700	98	213	nd–1360	96	146	nd–1390
syn-DP	76	5.60	nd–56.5	80	0.62	nd–11.4	88	0.48	nd–9.89
anti-DP	86	19.2	nd–448	80	1.35	nd–43.3	71	1.28	nd–17.3
TNBP	14	nd	nd–3940	8	nd	nd–39.1	10	nd	nd–33.0
TCEP	59	78.3	nd–2430	100	125	nd–708	96	107	nd–1840
TCIPP	45	nd	nd–25,400	100	245	nd–7650	96	287	nd–4400
TDCIPP	43	nd	nd–5010	67	27.6	nd–1120	61	12.9	nd–334
TPHP	96	1880	nd–110,000	100	584	nd–64,900	96	522	nd–5770
EHDPP	63	74.6	nd–1940	100	82.9	nd–6390	96	123	nd–1870
TEHP	57	94.6	nd–5670	98	88.4	nd–1840	90	69.4	nd–1280
∑PBDEs	98	1080	nd–19,500	98	76.2	nd–1820	94	56.7	nd–1190
∑DPs	88	27.2	nd–504	84	1.97	nd–54.8	86	1.91	nd–23.8
∑PFRs	98	3190	nd–110,000	100	1700	nd–67,700	96	1560	nd–8900

nd, not detectable or lower than the detection limit
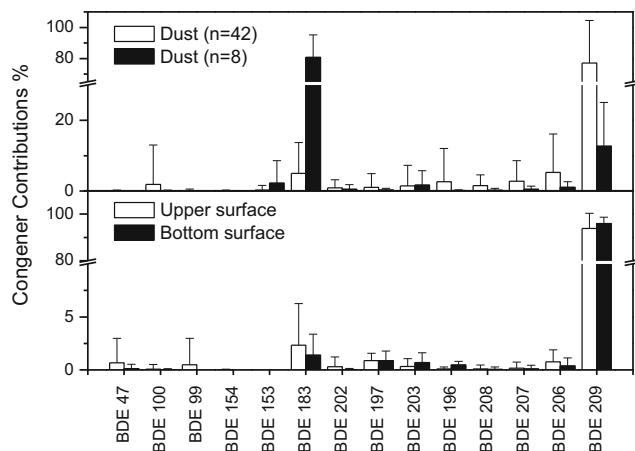
Fig. 1 Compositions of PBDEs in PC dust and on PC surfaces
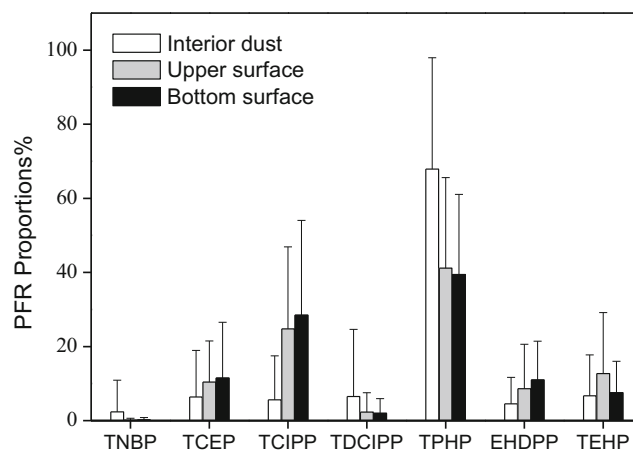
Fig. 2 Compositions of PFRs in PC dust and on PC surfaces

The upper surface had more contact with hands, whereas the bottom surface had more contact with tables, which might lead to different patterns of FRs on the two sides of PCs. However, no significant differences ($p > 0.05$) were revealed between the concentrations of all FRs, with exception for BDE 197 and TEHP. The composition patterns of PBDEs and PFRs were also consistent between upper and bottom surfaces (Figs. 1 and 2), indicating FRs on both surfaces were derived from similar sources. Significant correlations between upper and bottom surfaces were found for most of the FRs with DF > 50% ($p < 0.05$, Table S4), which further validated their common sources.

Association between FRs in PC interior dust and PC surface wipes

In general, more BFRs (i.e., PBDEs, BTBPE, and DBDPE) were frequently detected (DFs > 50%) in PC interior dust than in surface wipes, while opposite result was observed for PFRs (Table 1). The high DFs for PFRs on PC surfaces may partly attribute to the higher volatility of PFRs than BFRs (Rauert et al. 2014b). We also found the median ratios of PFRs/BFRs increased from 1.20 in PC interior dust, to 5.42 and 7.90 on upper and bottom surfaces of PCs, respectively. However, in view of individual PFRs, the proportion of TPHP and TDCIPP with lower log K_{OA} (Table S10) decreased, whereas the proportion of EHDPP and TEHP increased from interior dust to surface wipes (Fig. 2), suggesting that log K_{OA} or vapor pressure was not the sole factor for the partitioning of FRs between PC interior and the surface (Abbasi et al. 2016; Rauert et al. 2014a). Dust deposition and/or transfer between other PFR-containing surface dust, such as furniture surface dust, via direct contact (Rauert and Harrad 2015) or hand-mediated contact (Yang et al. 2020a) should also be considered. This could be supported by the fact that TCIPP as the most abundant PFR on PC surfaces, which was also the main PFR in dust from bedrooms and offices in Guangzhou (Zheng et al. 2017a). Additionally, concentrations of all the individual PFR were statistically uncorrelated between interior dust of PCs and surface wipes of PCs (Table S4), indicating their different sources.

As for BFRs, significant correlation of concentration was only found for BDE 183 between interior dust and both surface wipes of PCs (Table S4). Gallen et al. (2014) also demonstrated significant correlation of BDE 183 level between PC surface wipes and destructive detection of PC sub-samples. Compared with PBDE patterns in interior dust, the proportion of BDE 183 decreased, while the proportion of BDE 209 increased on PC surface (Fig. 1). Particularly for those 8 PCs, in which BDE 183 was the most abundant PBDE congener in interior dust, the BDE 183 levels were conversely at least 5-time lower than those of BDE 209 on the surface. The extremely low volatile FRs, such as BDE 209, were proposed

to preferentially migrate to the surface of the FR-containing products via directly physical transfer to dust particles or contact with the settled dust rather than volatilization (Webster et al. 2009; Rauert et al. 2014b; Rauert and Harrad 2015), in which the influence of vapor pressure is minimized. However, the abundance of BDE 209 on all PC surfaces, as well as its lack of correlation between PC surface and interior dust (Table S4), suggested that the PC components might not be the main contributor of PBDEs on surfaces. Other migration pathways, such as dust deposition, abrasion from deca-containing items, and/or contact with other surface dust, are also likely to attribute to the condensed BDE 209 on PC surface.

PCA was performed to gain further insight into the sources of FRs in PCs (Fig. 3). The first three factors accounted for 64.3% of the total variances. Table S5 summarizes the factor loadings of the 15 variables in PCA. The first factor was heavily weighted by BDE congeners (Fig. 3). It also showed moderate loadings on DPs and BTBPE, which exhibit the comparable log K_{OA} as deca-BDE (Table S10). Factor 2 represented highly association with most PFRs, while factor 3 was mainly composed of DBDPE and TPHP (Fig. 3,
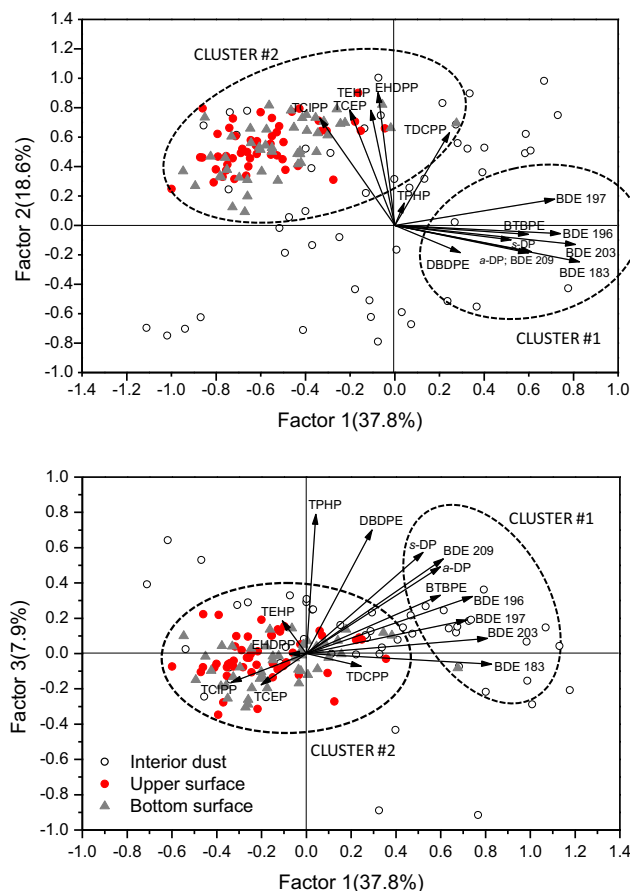
Fig. 3 Principal component analysis biplot of log-transformed FR concentrations in PC interior dust and surface wipes (The arrows referred to factor loadings, while the plots referred to factor scores of each sample)

Table S5). The factor-loading biplot of PCA clearly displays two clusters: Cluster #1 contained most BFRs and cluster #2 contained most PFRs (Fig. 3), suggesting their different sources from each other. The separation of DBDPE from BFRs, and TPHP from PFRs was possibly attributed to their different sources and/or environmental behaviors from other contaminants. DBDPE is a high-molecular-weight compound with extremely high log K_{OA} (18.2), leading to its different product-to-dust transfer process (Rauert and Harrad 2015). TPHP is documented as substitute for deca-BDE formulation which is extensively applied in electronic and electrical equipment (USEPA 2014), whereas the other PFRs in this study are commonly used in consumer products and construction materials except for TCIPP (van der Veen and de Boer 2012; Blum et al. 2019). Another possible source for TPHP was its inevitable presence as by-product in RDP and BDP technical formulation (up to 5%), which are both alternatives for deca-BDE (Lowell Center for Sustainable Production 2005). As illustrated in Fig. 3 and Table S5, BDE 209 shared a moderate loading in factor 3, suggesting similar source with DBDPE and TPHP. This could be further supported by the consistently significant pairwise correlation among TPHP, DBDPE, and BDE 209 ($p < 0.05$) apart from other FRs in all samples (Table S6-S8).

Almost all surface wipe samples, both upper and bottom, fell into cluster #2, in which most PFRs were associated (Fig. 3). This result indicated that contamination of the surface wipes was largely affected by the release of PFRs. The interior dust in PCs, by contrast, were scattered on the factor-loading plot, suggesting their complex composition patterns differed from surface samples. More specifically, interior dust exhibited significantly higher scores in both factors 1 and 3 but lower scores in factor 2 (one-way ANOVA, LSD test, $p <$ 0.05) (Fig. S1), implying its stronger association with BFRs (factor 1) compared to PFRs except TPHP (factor 2). Interior dust could be considered as the direct reservoir of chemicals released from inner PC components, whereas surface wipes may encounter multiple sources of contaminants from the surrounding environment. The PCA results revealed that external sources, rather than internal sources (the FRs-containing products themselves), contributed more to the FRs in PC surface wipes. Among the FRs concerned, special attention needs to be attracted on PFRs due to their close association with surface dust.

Dermal exposure to FRs on upper surface of PCs

Although recent studies have highlighted the significance of dermal uptake as a pathway of human exposure to FRs (Abou-Elwafa Abdallah et al.,2016, 2018; Tay et al. 2018), data are still limited to date. The continuous contact with upper surface (keyboards, front panels, etc.) of PCs could lead to FR exposure. We assessed dermal exposure to FRs via contact with PC surfaces, using the median concentration of FRs measured in upper surface wipes of PCs. Information for assessment method and exposure factors were detailed in the Supplementary Material (Table S9 and S10).

As shown in Table 2, dermal exposure estimates revealed significantly higher uptake of PFRs compared to BFRs via contact with PCs. This may attribute to the major contribution of PFRs to total FRs on PC surface (Table 1, Fig. S2), as well as the higher bioavailability of PFRs than BFRs. A study that assessed dermal exposure for both BFRs and PFRs also found significantly elevated exposure to PFRs than to BFRs in all the three investigated populations (i.e., office worker, taxi drivers, and security guards) from their corresponding occupational workplaces in Beijing, China (Liu et al. 2018). The results again demonstrated the critically potential risk of daily exposure to PFRs compared to BFRs in indoor environment (Blum et al. 2019).

Comparison between studies should be conducted with caution because study populations and regional contamination backgrounds can vary. We compared these results to our previous work which was conducted in the same geographical region, Guangzhou, China (Zheng et al. 2017a). Referring to the previous results, median dermal uptakes via PC surface contact were much lower than the respective exposure via table surface dust (Table 2). Compared to other dermal exposure estimates based on different sampling strategies, including skin/hand wipes and settled dust collection, the exposure level in this study was generally far lower than those of other studies (Table 2). Hand or skin wipes were suggested to reflect the integrated dermal exposure from multiple microenvironments, while surface dust was considered as time-integrated exposure indicators for specific items or scenario (Liu et al. 2018; Yang et al. 2019). Another possible transfer route for surface dust to human could be hand-to-mouth ingestion (Liu et al. 2018; Stapleton et al. 2008; Yang et al. 2020b). Daily exposures to FRs from PC surface via hand-to-mouth transfer were also estimated, which were respectively order(s) of magnitude higher than that of dermal absorption, with the only exception for TCEP (Table S11). This is attributed to the relatively high efficiency of hand-to-mouth transfer (non-contaminant dependent) compared to dermal absorption (contaminant dependent), especially for the chemicals with higher log K_{OW}. Our results, therefore, demonstrated the contribution of PC dermal contact to total human exposure for the investigated FRs would be lower than that *via* hand-to-mouth uptake.

Limitations of the present study

There are several limitations in the interpretation of the data in our study. First, it is only a preliminary study designed to identify the origin of FRs via PC contact, through investigating the association between FRs in interior dust (internal source) and surface dust (possible

Table 2 Comparison of estimated dermal exposure (pg/kg bw/day)[a] to FRs for adults based on surface wipes, skin wipes, and settled dust

	Surface wipe	Skin wipe				Settled dust		
BDE183	0.005	0.059						
BDE209	0.003	2.2			3			
DBDPE	0.009	0.83			2			
syn-DP	< 0.001							
anti-DP	< 0.001							
TCEP	2.9		87	600	1200	10 (< 10)	87	100
TCIPP	5.0		507	1000	2400	10 (10)	3618	380
TDCIPP	0.29		587			< 10 (< 10)	1541	200
TPHP	6.1 [g]		-	300	600	40 (10)	1609	
EHDPP	0.87 [g]		135			< 10 (< 10)	162	
TEHP	0.93 [g]		205			< 10 (< 10)	757	
Region	Guangzhou, China	Norway	Norway	Beijing, China	Beijing, China	Guangzhou, China	Norway	UK
Ref.	This study	Tay et al. (2018)[b]	Xu et al. (2016)[b,h]	Liu et al. (2017)[c]	Liu et al. (2018)[b]	Zheng et al. (2017a)[d]	Xu et al. (2016)[e,h]	Abou-Elwafa Abdallah et al. (2016)[f]

[a] Median values unless specified

[b] Estimation based on hand wipes

[c] Estimation based on skin wipes, including palms, backs-of-hands and forearms

[d] Estimation based on surface dust from printer table (or PC table), maximum concentrations were used

[e] Estimation based on surface dust from furniture and decoration items

[f] Estimation based on floor dust from living room and office.

[g] The same absorption fraction as TDCIPP was used.

[h] Mean values were used for assessment.

external source). No data was available from the surrounding microenvironment or desktop surface where the PCs were placed, resulting in the lack of direct and strong evidence to support our discussion on the migration process of FRs on PC surface. Second, in order to simulate the real exposure scenarios in daily life (few people are prone to clean their PCs frequently while using), we did not remove the surface dust before wiping. Further studies are needed to synchronously investigate the FRs in "pre-wipe" dust and "post-cleaning" wipe, to discriminate dust contamination from direct emission from products. Third, we only enrolled laptop computers in the present study, which limited the extension of the results to electronic and electrical products. More frequently daily used electronic and electrical products should be involved to obtain a more comprehensive exposure assessment associated with such products, as well as the significance of this exposure route to the total exposure burden. Although the results of the present study contained several uncertainties, FR emission from internal source is likely not the main contributor to the FRs on PC surface. Our results revealed that surface wipe from consumer products might not be suitable to be an indicator used to assess dermal exposure to FR-containing products.

Conclusions

The present study investigated the FRs in interior PC dust, and on upper and bottom PC surfaces. Different FR compositions were observed in interior dust and on PC surfaces. The decrease of PFRs with higher volatility but increase of those with lower volatility from interior dust to surface of PCs suggested impact from external sources of PFRs on PC surface. The lack of correlations between interior dust and surface wipes for BDE 209 and all PFRs revealed the different input of these contaminants, rather than originating from PCs. Results from PCA analysis further confirmed the variation of sources for most PFRs and BFRs. FR profiles on PC surfaces were highly dependent on the emission of PFRs, while FR profiles in interior dust were more relevant to BFRs. Based on the exposure assessment results, dermal absorption via PC surface contact accounted for less contribution to daily exposure to the investigated FRs than that via hand-to-mouth transfer. Compared to BFRs, PFRs show greater significance in dermal exposure assessment.

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