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Estimation of Exposure to Organic Flame Retardants via Hand Wipe, Surface Wipe, and Dust: Comparability of Different Assessment Strategies

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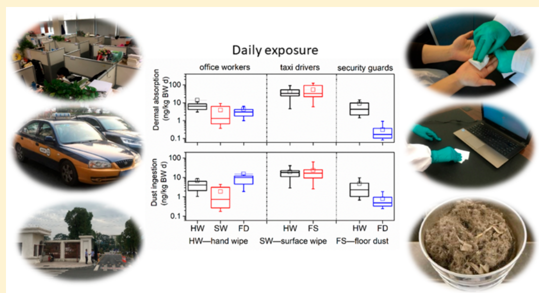
Supporting Information

ABSTRACT: This study aimed to investigate the exposure of three occupational populations (i.e., office worker, taxi drivers, and security guards) to flame retardants by comparing different sampling approaches (i.e., hand wipe, surface wipe, and dust). Hand wipe samples were collected from 68 participants from three populations in Beijing, China. Dust and/or surface wipes were also sampled from their respective occupational workplaces. Ten phosphorus flame retardants (PFRs), two novel brominated flame retardants (NBFRs) and eight polybrominated diphenyl ethers (PBDEs) were analyzed. BDE209, decabromodiphenylethane (DBDPE), tris(chloropropyl) phosphate isomers (∑TCPP), tris(2-chloroethyl) phosphate (TCEP) and triphenyl phosphate (TPHP) were detected in at least 95% of the samples, collectively accounting for over 90% of the total concentrations in each type of samples. Concentrations and composition profiles of flame retardants differed in hand wipes of the three populations with summed level of all target compounds (∑FRs) ranked as taxi drivers > office workers > security guards. Most FRs in hand wipes were significantly correlated with those in surface wipes, whereas the correlations between hand wipes and dust are weak. Estimated exposure to FRs via dust ingestion and dermal absorption for each population varied when using different types of samples for exposure assessment, suggesting the importance of sampling strategy selection. Estimation via hand wipes indicated that taxi drivers were subjected to greater exposure to PFRs among three populations, while office workers were subjected to greater BFR exposure. Our data suggest hand wipes have the potential of being standardized into a noninvasive method for evaluating human exposure to environmental contaminants across different populations.



INTRODUCTION

Organic flame retardants (FRs), such as polybrominated diphenyl ethers (PBDEs) and organophosphorus flame retardants (PFRs), are widely used in various materials, such as plastics, textiles, and polyurethane foam building materials.[1−3] Three major commercial PBDE mixtures, including PentaBDE, OctaBDE, and DecaBDE, have attracted mounting concern because they can enter into the surrounding environment via abrasion or volatilization and exhibit persistent, bioaccumulative, and toxic characteristics.[4−6] Consequently, all three mixtures have been listed in Annex A of the Stockholm Convention as persistent organic pollutants for elimination.[6] To overcome the restrictions placed on the commercial use of PBDEs, a variety of brominated compounds known as novel brominated flame retardants (NBFRs), have been used as alternatives to meet continuous flame retardancy market.[7] These NBFRs include decabromodiphenyl ethane (DBDPE; Deca-BDE replacement) and 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE; Octa-BDE replacement), as well as many others.[7] In addition to NBFRs, several organophosphate flame retardants (PFRs) that have been used as FRs or plasticizers for decades, including tris(2-chloroethyl)-phosphate (TCEP), tris(2,3-dichloropropyl) phosphate (TDCPP) and tris(1-chloro-2-propyl)-phosphate (TCIPP), were also subjected to increasing production in recent years.[8] However, some of these alternative chemicals have also been reported to exhibit various adverse health effects.[9,10]

A number of studies have reported wide occurrences of PBDEs, NBFRs, and PFRs in indoor, outdoor, or vehicle environment.[11−15] Humans may be exposed to FRs via multiple routes, including inadvertent ingestion of dust or

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food, inhalation of air, or dermal absorption.[15,16] In the assessment of human exposure to FRs, the selection of sampling strategies influences an accurate assessment of exposure routes and risks.[14] Three nonbiological sampling methods, including dust collection, wiping of surfaces (e.g., windows or tables), and wiping of hands, have been utilized to assess indoor/outdoor contamination and exposure risks.[17−20] Collection of floor dust by means of vacuum cleaner or brush has been commonly used in the assessment of dust ingestion or dermal absorption of dust-associated FRs.[12−16] However, the differences in particle sizes of collected dust and actually ingested dust could substantially influence the accuracy of exposure estimation based on this sampling technique.[21,22] Dust from a single environment may not represent the overall exposure scenario for a human being. Surface wipe is useful for collecting surface dust and for the characterization of FR contamination in offices and homes,[17,20] but relatively less used for exposure assessment. For some outdoor occupations (e.g., construction workers), surface wipes may not be collectable or not appropriately represent the main exposure pathways. Hand wipe sampling has been demonstrated as a useful method for evaluating exposure via hand-to-mouth exposure and dermal absorption and hand wipe levels revealed a good correlation with internal exposure (i.e., urine or blood) for certain FR chemicals (e.g., BDE77, BDE99, and TPHP).[23−25] In this study, we further hypothesized that compared with dust and surface wipe, hand wipe is more suitable for being developed as a standardized approach for assessing FR exposure in different populations/occupations.

To evaluate this hypothesis, we investigated FR exposure in three North China populations with quite different occupations (i.e., office workers, taxi drivers, and security guards) via three sampling approaches (i.e., dust, surface wipes, and hand wipes). The security guards studied are referred to those in charge of roadside vehicles and working primarily outside. Thus, the occupational exposure to FRs for these three groups of subjects mainly occur in office, vehicle, and outdoor environments, respectively. Previous human exposure assessments in China have rarely focused on the vehicle or outdoor environments with respect to FR contamination.[26] However, the potential for FR exposure inside vehicles is high, since materials used in vehicles (e.g., textiles and polymers) are required to meet strict fire codes in China. Road dust has also been reported with high levels of PBDEs and alternative BFRs.[12] Therefore, by investigating a variety of FR chemicals in different types of samples, our main study objectives were to (1) compare the levels and profiles of FRs in the working environments of three different groups of populations; (2) assess FR exposure via different sampling methods for each population; and (3) compare the suitability or applicability of different sampling methods for estimating FR exposure in various populations.

■ MATERIALS AND METHODS

Sampling Strategy and Methods. Our study recruited a total of 25 employees who worked in offices with computers, 20 taxi drivers, and 23 outdoor security guards from March to August of 2016. Floor dust and surface wipe samples were collected from offices, whereas only surface wipes were collected from taxi drivers' taxies, as no sufficient floor dust was collectable from taxies. Road dust was collected near each security guard. Hand wipe samples were collected from all three groups of subjects. Prior to participation, verbal consent was obtained from each participant. Participants were also required to fill out a short questionnaire about their gender, age, height, smoking status, the average number of hours they spend in their workplaces, the number of hours between they washed hands and sampling, and whether skincare products were used on their hands before sampling. More details are summarized in Supporting Information (SI) Table S1.

The procedures of hand wipe and surface wipe sampling were described previously.[18] In brief, gauze pads (7.5 × 7.5 cm) were cleaned via ultrasonic extraction in a hexane/acetone mixture (3:1, v/v), which was repeated three times (30 min each), and then immersed into 5 mL of isopropyl alcohol until sampling. The entire surface of a participant's one hand was wiped with a gauze pad from the tips of the fingers to the wrist by an investigator, and another pad was used to wipe the other hand. The area of each hand was measured by using a coordinate paper. After collection, two wipes from the same participant were combined into a 60 mL precleaned (combusted at 450 °C for 6 h) brown glass vial, sealed in a sealing bag, and stored at −20 °C until analysis. Surface wipes were collected from offices and taxies. A fixed area (measured by paper templates and calculation) of ∼575 cm^2 on office tables or ∼500 cm^2 on taxi steering wheels was wiped with gauze pads. These surface wipes were also stored in brown glass vials. Field blanks were prepared by exposing pads to the air for 2−3 s and then placing them into the brown glass vials.

Office dust was collected via a commercial vacuum cleaner with a nylon sampling sock (precleaned with solvent) placed in the suction nozzle. Each office's floor was vacuumed for 15 min. Road dust was collected from an area of ∼2 m^2 by using precleaned brushes. Between each collection, the nylon sock or brush was cleaned with water and isopropyl alcohol. After collection, dust samples were wrapped with aluminum foil, sealed in polyethylene zip bags, and brought back to the lab. Dust samples were then sieved through <50 μm stainless sieves and stored at −20 °C.

Analytical Method. A total of eight PBDEs (BDE28, 47, 99, 100, 154, 153, 183, and 209), 2 NBFRs (BTBPE and DBDPE), and 10 PFRs (triethyl phosphate (TEP), tri-*n*-propyl phosphate (TPP), tri-iso-butyl phosphate (TIBP), tri-*n*-butyl phosphate (TNBP), tris(2-butoxyethyl) phosphate (TBOEP), TCEP, TDCPP, triphenyl phosphate (TPHP), tricresyl phosphate (TMPP) and tris(monochloropropyl) phosphate (∑TCPP) (mixture of three isomers) were analyzed. The full name and physicochemical parameters of the target compounds are provided in SI Table S2. The analytical method for the determination of FRs in hand wipes, surface wipes, and dust, as well as the information on chemicals, reagents, and instruments, are described in the Supporting Information and our previous papers.[18,19] Briefly, dust or wipe samples were extracted three times using hexane/acetone (3:1; v/v) in an ultrasonic bath. The resulting extract was cleaned through Florisil (Supelco) and separated into two fractions. PBDEs and NBFRs were contained in the first fraction which was further purified by acid silica gel and then determined on a gas chromatography coupled to a mass spectrometer (GC-MS, Shimadzu, Japan) in the electron capture negative ionization mode. The PFRs were included in the second fraction and were determined on GC-MS in the electronic impact ionization mode.

Quality Assurance and Quality Control. The efficiency of removing target FRs from hands by hand wipe sampling was assessed and demonstrated in our previous study.[18] The

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Table 1. Descriptive Statistics of Concentrations of Target FRs in Hand Wipes (ng/m^2) from Three Populations in China[a]

	office workers					taxi drivers					security guards				
compounds	% detected	median	GM	GSD	range	% detected	median	GM	GSD	range	% detected	median	GM	GSD	range
BDE28	75	1.2	0.8	3.1	<0.2−3.3	90	1.8	1.9	3.2	<0.2−28	96	1.4	1.5	2.5	<0.2−6.8
BDE47	89	2.5	2.4	3.4	<0.2−25	100	4.9	4.2	2.4	1.0−52	100	4.2	4.2	2.0	1.6−36
BDE100	0	NA	NA	NA	NA	0	NA	NA	NA	NA	13	NA	NA	NA	<0.2−2.5
BDE99	46	NA	NA	NA	<0.3-21	80	2.9	2.1	3.7	<0.3−25	92	3.0	2.6	3.2	<0.3−49
BDE154	29	NA	NA	NA	<0.2−2.6	25	NA	NA	NA	<0.2−1.1	50	0.3	0.4	2.9	<0.2−11
BDE153	29	NA	NA	NA	<0.4−4.8	35	NA	NA	NA	<0.4−2.9	50	0.8	0.9	3.1	<0.4−21
BDE183	100	5.0	4.3	2.4	1.1−26	85	2.6	1.9	3.1	<0.6−13	96	4.4	4.8	3.2	<0.6−120
BDE209	100	1675	1478	3.3	209−16970	100	911	1.1×10^{03}	3.1	188−17047	100	352	460	2.9	24−13951
DBDPE	100	484	442	2.7	78−4782	100	534	568	4.4	27−16078	96	240	261	4.3	<24.6−18125
BTBPE	100	7.7	8.0	3.1	1.3−138	95	2.9	2.6	2.2	<0.7−12	92	3.7	4.3	3.5	<0.7−234
TNBP						100	259	265	2.1	41−708	5	NA	NA	NA	<12.3−336
TCEP						100	20357	19997	2.4	2815−81593	91	1109	1342	3.1	<114−46954
∑TCPP						100	13825	11057	2.3	979−27813	100	1010	1132	2.6	207−11692
TDCPP						100	4158	4497	2.2	971−20566	41	NA	NA	NA	<87−10669
TPHP						100	1726	1655	2.2	299−9107	100	1039	1223	2.0	360−4446
TBOEP						6	NA	NA	NA	<135−46420	9	NA	NA	NA	<135−1171

[a]NA: not available due to low detection frequencies.

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removal efficiency by wiping table surfaces with gauze pad was examined by three consecutive wipes. The first wipe removed more than 90% of the analytes. Recoveries of the internal standards in dust and wipes ranged from 55% to 133% (SI Table S3). A high level (100 ng each) or a low level (20 ng each) of a standard mixture was spiked into 50 mg of solvent-washed dust and processed in four replicates for each level. The recoveries of spiked standards are summarized in SI Table S4. Recovery efficiencies of spiked FRs during hand wipe analysis were already demonstrated in our previous studies.[18,19] A procedural blank was run with every batch of 12 samples. BDE209 (1.5 ± 1.3 ng), TCEP (7.2 ± 3.4 ng), and TCIPP (6.0 ± 3.3 ng) were detected in field blanks (n = 45) and procedural blanks (n = 18). For these analytes, their concentrations in dust samples were blank-corrected by subtracting the levels in procedural blanks, and the levels in wipe samples were blank-corrected by subtracting the levels detected in field or procedure blanks wherever a higher contamination level was observed. The limit of detection (LOD) or limit of quantification (LOQ) of an analyte, defined as a signal of three or ten times the noise level, is summarized in SI Table S4.

Statistical Analyses. All statistical analyses were performed using SPSS statistical software (version 16.0). For measurements below LOQs for an analyte with detection frequency >80%, a half LOQ was assigned if its geometric standard deviation (GSD) is greater than 3; otherwise, a LOQ/$\sqrt{2}$ was assigned. Data were logarithmically transformed prior to statistical analyses. Given that some data sets were normally distributed after logarithmical transformation whereas others were not, nonparametric tests were conducted in most cases. Spearman correlation coefficients were calculated to examine the associations between different analytes or different sample types. Differences in hand wipe concentrations between any two studied populations were evaluated using two-tailed independent t tests for normally distributed data or Mann–Whitney tests for non-normally distributed data.

■ RESULTS AND DISCUSSION

Concentrations and Profiles of FRs in Different Types of Samples. Concentrations of FRs in hand wipe, dust and surface wipe samples collected from three groups of populations were summarized in Tables 1 and SI Table S7. Fifteen out of 20 target compounds were detected in at least one type of samples. PFR concentrations in samples from offices were previously described in Liu et al.[18]

Hand Wipe. A summary of the concentrations determined in hand wipe samples is provided in Table 1. BDE28, BDE47, BDE183, BDE209, and DBDPE were detected in more than 70% of the hand wipe samples collected from three populations. Among the individual BFRs, BDE209 was the most abundant in all three populations. DBDPE, a replacement for BDE209, was the second most abundant BFR found in hand wipes. BDE209 levels in hand wipes in our study exceeded those from general populations in the U.S. (SI Table S5), whereas other BDEs were much lower than those reported in the U.S. studies.[17,27,28] In particular, BDE47 (median: 73 ng) and BDE99 levels (median: 72 ng) in hand wipes collected from the U.S. population were 2 orders of magnitude higher than those found in our study. This is likely because PentaBDE was subjected to greater applications in the U.S. than in China.[29] Compared with PBDEs and NBFRs, PFRs were more abundant in hand wipe samples from all three populations (SI Figure S1). TCEP, ∑TCPP, TPHP were frequently detected and exhibited the highest concentrations among the suite of PFRs. The levels of these three PFRs in hand wipes from our study were much higher than those reported in the U.S.[25,27,30] and Norway,[14] which suggested that these three PFRs were more widely used in China (SI Table S6).

Hand wipes from three populations differed in both FR composition profiles and concentrations. PFRs in taxi drivers' hand wipes were not only 1 order of magnitude greater in concentrations than those found in hand wipes from the other two populations, but also contributed most to the overall FR burdens among three populations. Hand wipes from security guards exhibited the statistically lowest concentrations of PFRs ($p < 0.05$). In particular, chlorinated PFRs, including TCEP, TDCPP, and ∑TCPP, had a greater contribution to the overall PFR concentrations in drivers' hand wipes (average: 91%) compared with the compositional profiles for the other two populations (average: 64% and 63%, respectively) (Figure 1). The differences suggest a more extensive application of

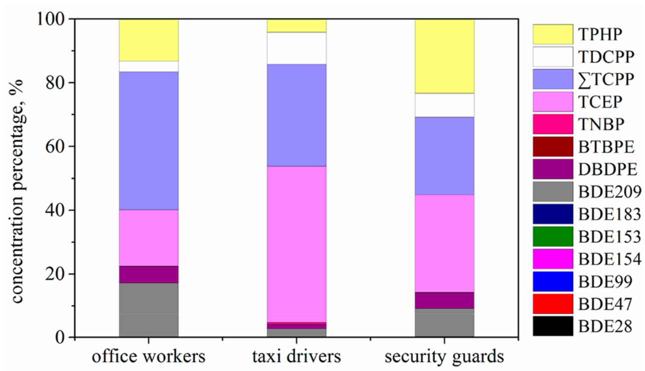

Figure 1. Concentration profiles of detected FRs in hand wipes of office workers, taxi drivers, and security guards.

PFRs, particularly chlorinated PFRs, in the materials inside the vehicles. In 2014, a standard (GB/T 30512–2014) for prohibited chemicals was established in China, which requires the mass fraction of PBDEs to be lower than 0.1% in the materials applied in vehicles.[31] This standard may lead to the intensive usage of PBDE replacements, such as PFRs, in recently manufactured vehicles. By contrast, the levels of BDE209 and DBDPE were more abundant in office workers' and drivers' hand wipes than those from security guards (p < 0.05), whereas the levels did not differ between office works and taxi drivers. These results clearly suggest differences in FR sources between various working environments.

In addition to occupation-related exposure sources, behavioral and environmental factors may also contribute to the variations in FR compositions and levels on hands from different populations. Taxi drivers were recorded with a much longer time of not washing hands prior to sampling (4.6 h in average) than security guards (3.7 h in average) and office workers (2.8 h in average). Our previous study demonstrated that hand washing with water could remove substantial amounts of TCEP, TCIPP, and TPHP from hands.[18] In addition, the percentage of smokers in taxi drivers (75% current smokers) was greater than that in outdoor security guards (50% current smokers) or in office workers (14% current smokers). Although the smoking influence on the FR level is not well studied, smoking has been reported to be

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associated with elevated urine levels of TPHP metabolite.[32] Future studies will incorporate these additional factors for a better elucidation of human exposure via hand wipe sampling.

Surface Wipes. Surface wipes were collected from offices (n = 16) and taxies (n = 16) (SI Table S7). Greater levels of PFRs were observed in all surface wipe samples than those of BFRs, consistent with the results from hand wipes. BDE209 and DBDPE were the dominate BFRs in both office and taxi surface wipes, while ∑TCPP exhibited the highest levels among all PFRs, followed by TCEP. Significant correlations were observed between individual chemicals with detection frequencies above 70% within the group of PFRs or BFRs, but the intergroup correlations between individual BFRs and individual PFRs were weak (SI Table S8). This suggested BFRs and PFRs in surface wipes had different sources or their relative potency in remaining in surface dust particles were not consistent. Concentrations of all individual PFRs as well as DBDPE in taxi surface wipes were significantly higher than those in office surface wipes ($p < 0.05$), whereas no statistical difference was observed for BDE209, BDE99, and BDE183. This is similar to the results observed in hand wipes from taxi drivers and office workers, reflecting overall greater contamination inside vehicles than regular offices.

Dust. Dust was collected from offices (n = 17) and roads (n = 15) (SI Table S7). Similar to the results in surface wipes, PFRs dominated in both office dust and road dust, accounting for 93% and 80% of the total FRs, respectively (SI Figure S1). In both office and road dust, TCEP, TPHP, and ∑TCPP were predominant PFRs with high detection frequencies (>95%), while BDE209 was the most abundant BFR, followed by DBDPE. Except for BTBPE, concentrations of all individual FRs in road dust were significantly lower than those in office dust ($p < 0.05$). We would like to point out that concentrations of ∑PBDEs in road dust samples of this study were almost 2 orders of magnitude lower than the levels reported in road dust collected in Beijing in 2012.[12] A possible explanation could be that in the 2012 study road dust was sampled from main roads with heavy traffic, while this study collected dust from bypasses. Cao et al. also reported the decrease of road dust-associated BFR concentrations along with the decreasing traffic densities.[33] However, the median concentration of ∑PFRs found in 2012 road dust samples (315 ng/g) was lower than the median concentration found in this study (1805 ng/g), which likely suggests a contemporary increase in PFR usage in China.

Correlations between Hand Wipes, Surface Wipes, and Dust. The Spearman's rank correlation coefficient (r_s) was used to investigate the relationships between paired hand wipe and surface wipe or dust samples for individual FRs (SI Table S9). It should be noted that the correlations were examined without separating the data for each population due to the limitation of sample size. The relationships between dust and surface wipes were not investigated also due to the limitation by a small sample size (n = 13).

Concentrations of DBDPE in dust were moderately correlated with those in hand wipes (r_s = 0.40, p = 0.03). Moderate correlations were also found between dust and hand wipes for the two isomers of ∑TCPP (r_s = 0.42 and 0.45, respectively; $p < 0.05$ in both cases), whereas no correlation was observed for BDE209, TCEP, or TPHP. By contrast, significant correlations were observed between hand wipes and surface wipes for almost all FRs (except BTBPE and BDE47), particularly for TCEP (r_s = 0.83, $p < 0.0001$), TCIPP (r_s = 0.81, $p < 0.0001$), and TDCPP (r_s = 0.81, $p < 0.0001$).

In general, most target FRs exhibited better correlations between hand wipes and surface wipes than those between hand wipes and dust. Flame retardants attached with hands may be a consequence of various processes including the contact with dust particles. In addition to dust, air may also contribute semivolatile compounds, such as many PFRs, to the levels on hand skin. Stubbings et al. reported a bell shape of the relationship between log K_{oa} (octanol-air partition coefficient) and the dust/air partition of PFRs in indoor environment.[34] The physicochemical properties of individual FRs affect its distribution and fate in indoor environment, thus influencing the exposure pathways and levels to humans. In addition, whereas dust well reflects the contamination status in the environment where dust is collected, hand wipes may reflect an integrated outcome of exposure under different environments. Therefore, the correlation between dust and hand wipes may be weakened by additional sources and factors and appears to be chemical specific due to variations in chemicals' physicochemical properties. Dust may not well represent the real exposure scenarios, particularly those resulting from hand-to-mouth transfer and dermal absorption. Surface wipes are better than dust in reflecting hand-associated FRs, but surface wipes are not valid for the evaluation of certain populations working outside, such as security guards assessed in the present study.

It should be pointed out that our correlative analyses are limited by including three populations due to small sample sizes. This prevented us from scrutinizing the influences of occupation-related factors and other environmental factors on the exposure pathways and the validity of different sampling strategy for different populations. Our future study will expand sample sizes and investigate the influence of occupational and environmental factors on the exposure risks by utilizing statistical methods beyond correlative analyses.

Exposure Assessment and Implication for Method Selection. We used measured levels in hand wipes, surface wipes, and dust to estimate the daily exposure to ∑FRs via dust ingestion and dermal absorption, respectively (Table 2). Details of equations and parameters are given in SI Table S10. It should be noted that the hand wipe or surface wipe evaluation approach assumes a fixed proportion of dust particles attached with hands or table/steering wheel surfaces are transferred to mouth through hand-to-mouth contact. The dermal absorption factors of most FRs were obtained from in vitro studies.[35−37] and the exposed location for dermal absorption was limited to hands. Daily exposure frequency (times/d) was assumed as 4 times per day for taxi drivers, 6 times per day for security guards, and 8 time per day for office workers according to their respective hand-washing frequencies.

Our results showed the estimated human exposure could differ greatly when using data from different sampling strategies (Table 2). For office workers, the estimated dust ingestion exposure to ∑FRs via floor dust was significantly higher than the estimation via hand wipes; the latter estimation was greater than that assessed via surface wipes. However, for security guards, the estimated dust ingestion exposure was significantly lower when assessed via dust than via hand wipes ($p < 0.05$). Even greater differences are observed for the estimated dermal exposure. The median exposure estimation for security guards via hand wipes (4.3 ng/kg BW d) is

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Table 2. Estimated Daily Exposure to ∑FRs by Different Methods for Three Populations (ng/kg BW d)

	median	mean	5th	95th
office workers				
dust ingestion estimation via floor dust	10.0	14.9	4.5	11.9
dust ingestion estimation via surface wipes	0.7	1.9	0.3	3.2
dust ingestion estimation via hand wipes	4.1	6.9	2.1	6.4
dermal absorption estimation via floor dust	2.0	2.9	0.9	3.0
dermal absorption estimation via surface wipes	1.0	2.9	0.4	4.8
Dermal absorption estimation via hand wipes	4.8	10.4	3.1	6.5
taxi drivers				
dust ingestion estimation via surface wipes	16.5	23.5	9.3	29.1
dust ingestion estimation via hand wipes	17.9	19.2	10.3	23.3
dermal absorption estimation via surface wipes	16.5	26.8	10.9	47.7
dermal absorption estimation via hand wipes	18.3	22.6	12.2	28.6
security guards				
dust ingestion estimation via floor dust	0.5	0.3	0.3	1.0
dust ingestion estimation via hand wipes	2.3	9.0	1.0	5.4
dermal absorption estimation via floor dust	0.2	0.8	0.1	0.4
dermal absorption estimation via hand wipes	4.3	4.7	2.0	10.2

approximately 20 times higher than that via dust (0.2 ng/kg BW d). Estimated dermal exposure via floor dust for office workers was also significantly lower than those via hand wipes ($p < 0.05$). For taxi drivers, no significant differences in exposure estimation for both pathways (i.e., dust ingestion and dermal absorption) were obseved when assessed via surface wipes versus hand wipes for both pathways. These data indicate that different sampling approaches resulted in quite different estimation outcome for a specific population and the pattern (i.e, the exposure estimation via one approach relative to that via another approach) also varied largely across different populations.

From hand wipes alone, we may compare the exposure risks among the studied three populations (SI Table S11). Office workers had greater exposure to BFRs (particularly BDE209 and DBDPE) than taxi drivers and security guards. The estimated median exposure to ∑PBDEs via dust ingestion for office workers, taxi drivers and security guards were determined to be 1.9, 0.4, and 0.2 ng/kg BW d, respectively. By contrast, taxi drivers were subjected to greater exposure to ∑PFRs than the other two populations (i.e., median estimated daily exposure via dust ingestion: 16.8 versus 3.4 and 2.0 ng/kg BW d; median estimated daily exposure via dermal absorption: 18.2 versus 5.2 and 4.3 ng/gkg BW d). However, it is noted that the use of hand wipes for the estimation of dermal absorption exposure may underestimate the actual exposure risks, as it limits exposure via hand skin only.

Our study suggests hand wipes may be a better matrix than the other two matrixes for assessing human exposure to FRs, especially for comparing exposure between different populations. Estimated exposure based on dust, surface wipes and hand wipes could differ in about 2 orders of magnitude for the same population, indicating the comparability of exposure between different sampling strategies is weak in some cases. As a noninvasive sampling approach, hand wipes are easy to collect and develop as a standardized approach for different populations. Hand wipes were suggested to be able to reflect the integrated exposure from multiple environments and the influences of personal behaviors (e.g., touching and hand-washing frequency). Dust or surface wipe from a single location (e.g., home, office, or outdoor environment) may not reflect the overall exposure scenario, while collecting dust/surface wipe from multiple locations are time-consuming and not practicable in most cases. Hand wipe collection may be easier to standardize than the collection of dust, since dust collection between studies may vary in the dust type (floor dust vs elevated dust), collection method (vacuum cleaners vs brush vs wipe), sampling areas, and how dust is sieved. Results from surface wipe may also vary greatly in the collection method (i.e., wiping site within indoor/vehicle environment, wiping area, etc.). Thus, by standardizing the hand wipe collection method, hand wipes are particularly suitable for comparing exposure in various populations with different occupations and life styles, even from different studies.

The suitability of using hand wipes for the estimation of human exposure to FRs is supported by recent studies revealing a good relationship between hand wipes and internal exposure. For example, Hoffman et al. reported TDCIPP and TPHP in hand wipes were correlated with their respect metabolites in urine, while no correlations were observed between dust and urine.[25] Although surface wipe gives a prediction on human exposure close to that via hand wipe for taxi drivers, little has been done to demonstrate the correlation between surface wipe and internal exposure for different populations. Although human biological samples (i.e., urine or blood) give a better elucidation of internal exposure than nonbiological samples, human samples are not possible to collect for some populations or studies, limiting the comparability of exposure risks across populations/studies.

It should also be noted that the information from hand wipe collection might be limited by multiple factors, such as sampling time and hand-washing activities. Previous studies suggest that hand washing frequency greatly influenced hand-associated FRs,[18,23] Therefore, a better standardization of hand wipe collection is critical to the feasibility of using it as a standard, noninvasive, approach for evaluating human exposure to not just FRs, but also other chemicals that may enter human bolides via hand-to-mouth contact and dermal absorption. .

There are several limitations of the present study. First, the sample sizes of each population and each sample types were relatively small. Second, the lack of internal exposure samples (urine, serum, etc.) limits a better elucidation of the validity of the methods for external exposure assessment. Third, additional human exposure scenarios, such as inhalation and hand-to-mouth contact, are not discussed in our work, limiting a more comprehensive evaluation of humane exposure scenarios.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b02723.

Details about the (1) information about participants and target compounds, (2) sample preparation and analysis, (3) QA/QC, and (4) human exposure assessment (PDF)

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Notes

The authors declare no competing financial interest.

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