

Identifying Dermal Uptake as a Significant Pathway for Human Exposure to Typical Semivolatile Organic Compounds in an E-Waste Dismantling Site: The Relationship of Contaminant Levels in Handwipes and Urine Metabolites

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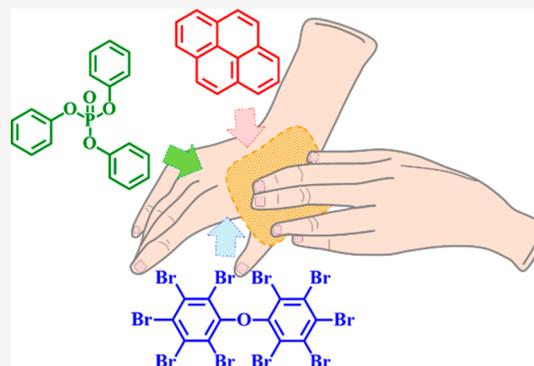
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ABSTRACT: Dermal exposure to semivolatile organic compounds (SVOCs) has recently attracted widespread attention; understanding these exposures is particularly important for people whose skin is frequently exposed to different pollution surfaces. In this study, handwipes were collected from exposed occupational workers and local residents near a typical electronic waste (e-waste) dismantling area; urine samples were also sampled. The wipes were analyzed for three typical SVOCs: polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), and organophosphate flame retardants (OPFRs). The median levels of PAHs, OPFRs, and PBDEs in handwipes from e-waste dismantlers were 96.0, 183, and 238 ng, respectively. The analytes were higher in the handwipes collected from workers than those from residents, indicating that they were subjected to greater dermal exposure during primitive e-waste dismantling activities. Among the three SVOCs, the strongest correlation was found between triphenyl phosphate (TPhP) in handwipes and diphenyl phosphate (DPhP) in paired urine; the next strongest correlations were between PAHs and PBDEs and their corresponding urinary metabolites. The results showed that TPhP contributed the highest exposure to e-waste dismantlers via dermal exposure. Our research highlights the importance of dermal exposure to TPhP, which should be considered in future exposure risk assessments.

KEYWORDS: PAHs, OPFRs, PBDEs, handwipes, urinary metabolites, dermal exposure



1. INTRODUCTION

Semivolatile organic compounds (SVOCs) are ubiquitous organic contaminants released into the environment by different sources and as a result of widespread applications.^{1,2} For example, polycyclic aromatic hydrocarbons (PAHs) are mainly derived from vehicle emissions, biomass coal, and petroleum combustion.³ Organophosphate flame retardants (OPFRs) and polybrominated diphenyl ethers (PBDEs) are flame retardants (FRs) that are frequently used in various commercial products, including electronics, furniture, and plastics to prevent the spread of flames.^{4,5} Due to their chemical properties and low vapor pressures, SVOCs emitted from sources can be distributed across surfaces, and in dust and the air, raising concerns about human exposure.² Previous epidemiological and toxicological research has reported various adverse effects associated with human exposure to SVOCs, such as carcinogenicity, thyroid hormone disorders, and sphingolipid balance effects.^{6–8}

People can be exposed to SVOCs via ingestion of indoor dusts, inhalation of ambient air, dermal contact, and dietary intake.^{9–11} Recently, concerns about direct dermal contact

have increased, because a few works have indicated that human exposure of some SVOCs via dermal contact is comparable to, or may even exceed, exposures via inhalation.^{12,13} Dermal exposure to SVOCs can occur by directly touching the products and dust on surfaces or direct transdermal uptake from air.^{2,14–16} Handwipe sampling has been demonstrated to be a useful method for evaluating dermal exposure to different contaminants in a population due to low capital cost and ease of use.^{17–19} Handwipes also provide a good prediction of the levels of some SVOCs, such as pentabromodiphenyl ether, in the serum of office workers.²⁰ Levels in handwipes showed a good correlation with internal exposure (i.e., blood or urine) of PBDEs and OPFRs in a general population of adults and children.^{21–24} In addition, SVOCs in handwipes collected from

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different populations have been used to distinguish the main exposed pollutants. Estimating FRs using handwipes from three occupational groups found that taxi drivers were subjected to higher exposure to OPFRs than office workers and security guards, while office workers were subjected to higher brominated flame retardant exposure.¹⁵ In addition, PAHs were also detected on skin wipes of roofing workers and firefighters who were highly exposed to PAHs.^{2,5,26}

These studies demonstrate that handwipes can reflect external exposures of organics and establish a connection with internal exposures. Therefore, assessing the dermal exposure of SVOCs using handwipes with different occupationally exposed groups is an important tool for assessing exposure routes. However, few studies have matched and analyzed handwipes and human biological samples, and comprehensively assessed and compared dermal exposure to different types of SVOCs to explore the relationship between internal and external exposures to multiple SVOCs in exposed populations.

Electronic waste (e-waste) dismantling areas are typical zones where people are exposed to multiple pollutants simultaneously. Several studies have reported that e-waste recycling activities are a major source of typical SVOCs, such as PAHs, OPFRs, and PBDEs.^{3,27–29} These SVOCs have been found in different environmental matrices such as air, dusts, soils, sediments, and organisms in e-waste dismantling areas.^{3,27,30–33} However, these typical SVOCs significantly differ with respect to their physical and chemical properties, their gas-particle distribution characteristics, and their half-lives (PAHs, within 12 h;³⁴ OPFRs, hours to days;³⁵ PBDEs, weeks or even months³⁶) in the human body. These differences impact the main exposure routes into the human body. A study found that dermal uptake from airborne SVOCs was a major route of exposure for people living locally subjected to combustion fumes from e-waste dismantling activities.³⁷ Recent evidence collected using handwipes found that the occupational dermal exposure to e-waste dismantlers was a crucial exposure route to SVOCs.^{38–40} This highlights the need to investigate the dermal exposure to SVOCs of populations in e-waste dismantling sites. Few studies have systematically assessed dermal exposure to typical SVOCs with different half-lives using handwipe samples collected from workers in an e-waste dismantling area to investigate the differences in dermal exposure caused by compounds with different physical and chemical properties. There is also a lack of comparisons of the dermal exposure of different exposed populations in the e-waste dismantling area to judge the importance of dermal exposure of occupationally exposed populations.

In this study, paired handwipes and urine were sampled simultaneously from e-waste dismantling workers and residents near a typical e-waste dismantling area to analyze exposure levels of three classes of SVOCs with different half-lives. They are PAHs and OPFRs with short half-lives; PBDEs with long half-lives in handwipes; and their corresponding urinary metabolites, including hydroxyl PAHs (OH-PAHs), metabolites of OPFRs (mOPFRs) and brominated phenols (BRPs) were studied to more systematically compare the correlation between dermal exposure and internal exposure of SVOCs with different half-lives. Although most studies assess the human body load of PBDEs by analyzing OH-PBDE in serum,^{41,42} the concentrations of BRPs in urine may also serve as an alternative indicator for assessing the body burden of

PBDEs.^{43,44} The study aims to (1) determine levels and composition profiles of PAHs, OPFRs, and PBDEs in handwipes collected from different groups of populations, including workers at an e-waste dismantling industrial park and surrounding residents (including juvenile residents and adult residents); (2) assess whether there are correlations between these three SVOCs in handwipes and the corresponding urinary metabolites; and (3) compare the SVOC exposure assessments through different exposure pathways based on the concentrations found in handwipe samples.

2. MATERIALS AND METHODS

2.1. Reagents and Materials. The chemicals and reagents used in this study are described in the Supporting Information (SI), Section 1.

2.2. Sample Collection. Handwipes were sampled from 89 subjects in a typical e-waste dismantling area in South China in November 2018. The subjects included 29 EW (e-waste) dismantlers with the routine job of directly dismantling e-waste; 23 EW administrators who do other work like security, cleaning, and administration at the e-waste dismantling industrial park; 37 surrounding residents (19 juvenile residents, ≤ 14 years old; and 18 adult residents, >14 years old). Details about the sampling campaign are included in a previous publication.⁴⁵ Tables S1 and S2 summarize the characteristics of the study population. All subjects were requested to give informed consent before sampling, and this study was approved by the Ethics Committee of Guangdong University of Technology. Cotton twill wipes (7.5×7.5 cm, 2 mm thickness) were precleaned in a single 24 h Soxhlet extraction using methanol and dichloromethane. Prior to sampling, subjects undertook indoor activities and did not wash their hands for at least 60 min. A sterile twill wipe soaked in isopropanol (3 mL, $>99.5\%$) was used for wiping the both hands of each subject including the back of the hand, the palm, and between the fingers. The twill wipe was wrapped in a sealed bag with aluminum foil and stored at -20 °C until analysis. The paired urine samples were also collected from the same 89 subjects. Detailed information on the sampling protocols is in a previous publication.⁴³ The handwipes and urine samples of all subjects were collected simultaneously in the morning. All subjects were asked to collect urine during their first morning urination in a polypropylene bottle. The urine samples were stored at -20 °C until analysis.

2.3. Sample Preparation and Handwipe Analysis. Three typical types of SVOCs were analyzed, including 16 PAH congeners, 13 OPFR isomers, and 20 PBDE congeners in handwipes. Detailed sample preparation methods for measuring the three classes of SVOCs in handwipes are described as follows. First, a surrogate standard mixture (containing 10–40 ng) was added to cotton twill wipes, and then, the samples were extracted using about 60 mL of hexane/dichloromethane/acetone (2:2:1, v/v/v) in an ultrasonic bath for three times (10 min each). Second, the combined extracts were concentrated to approximately 1 mL using a rotary evaporator and cleaned using Florisil (12 mL, 2 g) solid phase extraction cartridges, eluting the fraction containing the targets with 10 mL of 1:1 ethyl acetate/dichloromethane (v/v). Finally, the collected fraction was dried under a nitrogen stream and reconstituted in 50 μ L of isoctane for the instrumental analysis based on a previous method^{27,46,47} after adding internal standards (3 ng). PAHs and OPFRs were quantified using gas chromatography–tandem mass spectrometry in the

electron ionization mode, and PBDEs were determined by gas chromatography–mass spectrometry in the negative chemical ionization mode, based on a previous method.^{27,46,47}

2.4. Analysis of Urine. The mOPFRs analyzed in urine samples included bis(1-chloro-2-propyl) phosphate (BCIPP), bis(2-chloroethyl) phosphate (BCEP), bis(1,3-dichloro-2-propyl) phosphate (BDCIPP), dibutyl phosphate (DBP), di-*o*-cresyl phosphate (DoCP), bis(2-butoxyethyl) phosphate (BBOEP), di-*p*-cresyl phosphate (DpCP), and diphenyl phosphate (DPhP). The 500 μ L urine samples were pretreated using a protein precipitation/dilution with acetonitrile (500 μ L) and 30 ng of internal standards (d_8 -BCEP, d_8 -BBOEP, d_{10} -BDCIPP, d_{10} -DPhP, d_{12} -BCIPP, d_{14} -DoCP, d_{14} -DpCP, and d_{18} -DBP). After protein precipitation, the sample was separated by centrifugation at 12 000 rpm for 10 min at 4 °C. Then, the supernatant was transferred to the auto sampler vial for further analysis. The analysis of mOPFRs was performed by high-performance liquid chromatography–tandem mass spectrometry (HPLC-MS/MS), and detailed instrumental analysis information is provided in the SI, Section 2 and Table S3. The sample preparation of BRPs and OH-PAHs in urine was based on previous research, and the analysis of OH-PAHs and BRPs was also performed using an HPLC-MS/MS-based method with the same instrumental conditions described previously.⁴³ Since the analysis methods of BRPs and OH-PAHs in urine have been reported previously, we will not describe them in detail in this study.

2.5. Quality Assurance (QA) and Quality Control (QC). Instrumental QC included injecting standard solutions and solvent blanks with every batch of 10 field samples. Method QC included injecting spiked matrices and procedural blanks with every batch of 10 field samples. The target analytes were confirmed as being <5% in blanks of handwipe analysis. No mOPFRs were detected either in solvent blanks or procedural blanks of the urine analysis. The concentrations of target compounds in all samples were blank corrected on the basis of the average procedural blank concentration. The recoveries of target analytes in standard spiked samples of the handwipe analysis were 77.0–120% for PBDEs, 58.3–142% for PAHs (except for naphthalene), and 66.0–114% for OPFRs in handwipes. For PAHs, OPFRs, and PBDEs in handwipes, the instrument detection limits (IDLs) were defined as the signal level that was 3 times the noise level; the method detection limit (MDL) was defined as the average blank value plus three standard deviations, or a signal level that was 5 times the noise level. Detailed information is provided in Table S4. The recoveries of the surrogate standards for PAHs, PBDEs, and OPFRs are provided in the SI, Section 3. The recoveries of DBP, DPhP, BBOEP, BDCIPP, DoCP, and DpCP in the spiked samples of urine analysis were $108 \pm 19\%$, $101 \pm 6\%$, $115 \pm 3\%$, $102 \pm 35\%$, $101 \pm 5\%$, and $101 \pm 6\%$, respectively. For mOPFRs in urine, the MDL and IDL of all analytes, defined as a signal level that was 10 or 3 times the noise level, respectively, are listed in Table S5.

2.6. Statistical Analysis. The data were analyzed statistically using SPSS version 13.0 software. During statistical analysis, concentrations not detected (nd) were assigned a value of zero, and concentrations below the MDL were replaced by MDL divided by 2. A nonparametric statistical analysis was performed due to non-normally distributed SVOC concentrations in handwipes as tested by the Kolmogorov–Smirnov test of normality. A Mann–Whitney *U* test was used to assess significant differences of three classes of SVOC

concentrations in handwipes between two groups of population characteristics. A principle component analysis (PCA) was performed on all PAH, OPFR, and PBDE data in handwipes as one unit. Spearman correlation coefficients were calculated to estimate the associations between the concentrations of PAHs, PBDEs, and OPFRs in handwipes and the concentrations of their respective urinary metabolites for all populations. Only compounds with >50% detection are included in the spearman correlation analysis. A *p*-value less than 0.05 is considered to be with statistical significance.

2.7. Exposure Assessments. Handwipes are an effective assessment tool for evaluating exposures from direct surface contact, absorption through the dermal pathway, and from any hand-to-mouth activity.⁴⁸ The chemicals found in handwipes can enter our bodies through subsequent dermal absorption or hand-to-mouth contact (e.g., nail biting and finger sucking). This study focused on comparing dermal absorption, oral ingestion (hand-to-mouth ingestion), and dust ingestion exposure. Two methods are generally used to assess dermal contact and calculate the daily absorbed dose to the dermal layer: the relative absorption (percentage of dose) and permeability coefficient.⁴⁹ The permeability coefficient method assesses the effect of dermal lipids; however, the lipid content of hands was not measured for this study. As such, the relative absorption method was used to evaluate daily dermal exposure. Normalization of handwipe levels with hand surface area can control the difference in hand areas between individuals. Considering that the estimation of hand surface area without measuring the hand surface area may introduce additional differences, some studies also used handwipe levels without hand surface area normalization for skin exposure assessments.^{16,50} The calculation methods and parameters used to assess relative absorption were drawn from other studies.^{15,16,51} Exposures to PAHs, OPFRs, and PBDEs via dermal absorption, oral ingestion (hand-to-mouth ingestion), and dust ingestion were estimated based on the handwipe concentrations. The detailed calculation method is provided in the SI, Section 4 and Table S6. For the exposure via dermal adsorption, the dermal absorption rates were assumed based on previous studies^{52–55} (Table S6), and the hand wash frequency was set to 4 time/day.¹⁶ For the exposure via hand-to-mouth ingestion, we assumed that the proportion of the hand area contacted each time was 10%, the transfer efficiency was 50%, and the frequency of contact was set to 24 events per day.⁵¹ For the exposure via dust ingestion, it was assumed that the dust ingestion rate was 30 mg/day, and the daily time proportion was 0.5.¹⁵

3. RESULTS AND DISCUSSION

3.1. Levels of PAHs, OPFRs, and PBDEs in Handwipes.

The 15 target PAH isomers were all detected in >50% of handwipe samples (Table S7). The total concentrations of the 15 PAHs (Σ_{15} PAHs) in handwipes from all populations ranged from 2.38 to 814 ng/handwipe. The highest concentrations of PAHs in handwipes were found in EW dismantlers, at values from 5.73 to 507 ng/handwipe (median: 96.0 ng/handwipe). This was followed by adult residents, EW administrators, and juvenile residents with median PAH concentrations of 41.6, 36.1, and 3.31 ng/handwipe, respectively. The concentrations of Σ_{16} PAHs in EW dismantlers' handwipes were significantly higher compared to those of other study subjects (*p* < 0.05, except for adult residents) by approximately 2–29 times (Figure 1). This result demonstrated that e-waste dismantling

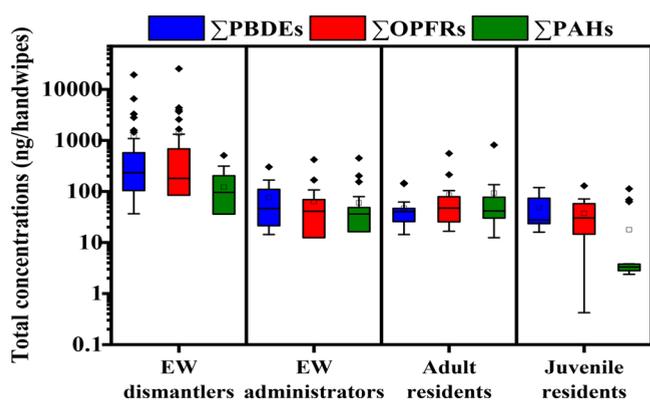


Figure 1. Total concentrations of PBDEs, OPFRs, and PAHs in handwipes of four different exposed populations.

activities may cause more PAHs to accumulate on EW dismantlers' hands. Notably, there was no significant difference in PAH concentration in the handwipe samples between smokers and nonsmokers, between those who do and do not eat barbecued food, or between people involved in high-temperature work and people not involved in high-temperature work. The concentration of phenanthrene (Phe) was the highest of all congeners in the handwipe samples from all populations, reaching as high as 22.2 ng/handwipe in the handwipes of EW dismantlers. Previous researchers found that the Phe was the main PAHs emitted during the dismantling of e-wastes, especially in the particulate phase (PM).⁵⁶ Fluorene (Flu) and pyrene (Pyr) were the most important isomers in the air particles of e-waste workshops.²⁹ This may explain the high concentrations of Phe, Flu, and Pyr in the handwipe samples of EW dismantlers in this study.

Among the 13 OPFRs analyzed, the following were detected in >50% of the handwipes: the chlorinated alkyl phosphates including tris(1-chloro-2-propyl) phosphate (TCPP), tris(2-chloroethyl) phosphate (TCEP), tris(2-iso-chlorophenyl) phosphate (TiCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), and the aryl phosphates, including TPhP and 2-ethylhexyl diphenyl phosphate (EDP) (Table S8). Total concentrations of the 13 OPFRs (Σ_{13} OPFRs) in handwipes from all populations ranged from 0.42 to 25 300 ng/handwipe (median: 43.8 ng/handwipe), with the highest concentration in the EW dismantlers' handwipes. The median concentrations of Σ_{13} OPFRs in the handwipes of EW dismantlers, EW administrators, adult residents, and juvenile residents were 183, 43.8, 34.3, and 18.9 ng/handwipe, respectively. The Σ OPFR concentrations in the handwipes of EW dismantlers were approximately 4–10 times higher compared to those of other populations ($p < 0.05$) (Figure 1). This result showed that e-waste dismantling activities may be a main cause of accumulating OPFRs on the hands of EW dismantlers. In particular, TPhP was found at considerably higher levels compared to other OPFRs in EW dismantlers' handwipes. This may be due to TPhP widely being added into the polyvinyl chloride (PVC) in the housings of household electronics³⁰ and electronic device wipes.⁵⁷ Furthermore, high TPhP concentrations in the PM extracts are discharged during the recycling of waste printed circuit boards.⁵⁸ This may cause TPhP to accumulate on EW dismantlers' hands during the e-waste dismantling process.

For PBDEs, the detection frequencies of BDE-209, BDE-206, BDE-207, BDE-208, and BDE-47 were all more than 50%

of the handwipes. The total concentrations of the 20 PBDEs (Σ_{20} PBDEs) in handwipes ranged from 14.3 to 19 300 ng/handwipe (median: 60.0 ng/handwipe) (Table S9) with median concentrations of 238, 50.1, 40.2, and 26.6 ng/handwipe for EW dismantlers, EW administrators, adult residents, and juvenile residents, respectively. In comparison, PBDE concentrations in the handwipes collected from EW dismantlers were approximately 5–9 times higher compared to the other groups ($p < 0.05$) (Figure 1). This result indicates that e-waste dismantling activities are important potential sources of PBDEs and may cause PBDEs to accumulate on the hands of EW dismantlers. In particular, BDE-209 levels in handwipes of all four groups were 1–3 orders of magnitude higher compared to other congeners. The previous study found that PBDEs on hands may be the result of contact with dust particles.¹⁵ Therefore, the distribution of PBDEs in handwipes may also reflect the distribution of PBDEs in environmental dust.

3.2. Composition Profiles of PAHs, OPFRs, and PBDEs in Handwipes. The difference was not statistically significant in the composition profiles of PAHs among four groups (Figure S1). The isomers with three and four aromatic rings were the dominant PAHs in all groups, accounting for 36–60% and 32–58% of total PAHs, respectively. The proportions of PAHs with six aromatic rings in EW dismantlers (9%) and EW administrators (10%) were slightly higher compared to those in adult residents (5%) and juvenile residents (7%). Among the 15 PAH isomers investigated, Phe (25%) was the most abundant PAH in handwipes for EW dismantlers, followed by fluoranthene (Flua) (22%) and Pyr (15%) (Figure S2); this is consistent with PAH levels in atmospheric samples collected from the same e-waste dismantling site.³ Thus, Phe, Flua, and Pyr are the compounds that most represent dermal exposure in the e-waste site. Further, there is evidence that SVOCs can directly travel from the air to the skin surface lipids.⁴⁸ As such, handwipes can capture the compounds on the skin surface lipid, indicating that pollutant exposure on the skin may be related to pollutant exposures in the atmosphere.

Among the OPFRs in handwipes, there were significant differences in OPFR congener profiles among the four groups. Σ aryl-OPFRs (69% and 83%, respectively) exhibited a higher contribution among all OPFRs, followed by Σ chloro-OPFRs (30% and 16%, respectively) in handwipes of EW dismantlers and EW administrators (Figure S1). These results indicated that aryl-OPFRs and chloro-OPFRs may be mainly emitted during e-waste dismantling activities. OPFR profiles in handwipes in this study were similar to levels observed in indoor dust collected from several e-waste recycling sites in South China, with aryl-OPFRs and chloro-OPFRs as the most abundant analogues.³³ The OPFR profiles for handwipes collected from EW dismantlers were dominated by TPhP, TCPP, TiCPP, and TDCIPP in this study (Figure S3). The TPhP was the most abundant, which may be due to its prevalence in e-waste as a plasticizer and flame retardant.

Unlike PAHs and OPFRs, slight differences in PBDE congener profiles were observed in the handwipes of the four group populations (Figure S1). Tri- to hepta-BDEs contributed the most in EW dismantlers (18%) and EW administrators (16%). Further, the highest contributor in the handwipes of EW dismantlers was BDE-209 (73%), followed by octa- to nona-BDEs (9%) and tri- to hepta-BDEs (18%). Similarly, high BDE-209 concentrations were observed in other exposed groups, reflecting the wide use of BDE-209 as FRs in

Table 1. Concentration (ng/mL Urine) of mOPFRs in Urine Samples from Different Exposed Populations

| compounds | median (range) | | | | | DF ^a (%) |
|-----------------------|---------------------------------|------------------------------------|----------------------------------|-------------------------------------|------------------------|---------------------|
| | EW dismantlers (<i>n</i> = 29) | EW administrators (<i>n</i> = 23) | adult residents (<i>n</i> = 18) | juvenile residents (<i>n</i> = 19) | total (<i>n</i> = 89) | |
| DBP | nd ^b (nd–1.37) | nd (nd–0.29) | nd (nd–0.29) | nd (nd–<MDL) | nd (nd–1.37) | 27% |
| DPhP | 1.82 (0.14–42.5) | 1.09 (0.29–11.9) | 0.89 (0.55–4.27) | 0.60 (0.96–2.01) | 1.04 (0.14–42.5) | 100% |
| BBOEP | <MDL (<MDL–0.35) | 0.31 (nd–0.35) | <MDL (<MDL–<MDL) | <MDL (<MDL–<MDL) | <MDL (nd–0.35) | 99% |
| BDCIPP | nd (nd–10.9) | nd (nd–0.62) | nd | nd (nd–0.81) | nd (nd–10.9) | 12% |
| D _o CP | nd (nd–0.65) | nd (nd–<MDL) | nd (nd–0.23) | nd (nd–0.34) | nd (nd–0.65) | 24% |
| D _p CP | <MDL (nd–1.65) | nd (nd–0.34) | nd (nd–0.31) | nd (nd–<MDL) | nd (nd–1.65) | 40% |
| ∑ ₆ mOPFRs | 2.74 (0.58–43.8) | 1.44 (nd–12.1) | 0.94 (0.59–4.69) | 1.09 (0.63–2.85) | 1.30 (0.58–43.8) | 100% |

^aDF: detection frequency. ^bnd: not detected.

Table 2. Spearman Correlation Coefficient of PAHs, OPFRs, and PBDEs in Handwipes and Their Urinary Metabolites for All Exposed Populations in the E-Waste Dismantling Area^a

| urine (<i>n</i> = 89) | Spearman Coefficient | | | | | |
|------------------------|----------------------------|----------------|----------------|---------------|----------------|----------------|
| | handwipes (<i>n</i> = 89) | | | | | |
| | Flu | Phe | Pyr | | | |
| ∑ ₂ OH-Flu | 0.305** | 0.348** | 0.359** | | | |
| ∑ ₅ OH-Phe | 0.409** | 0.414** | 0.378** | | | |
| 1-OH-Pyr | 0.450** | 0.476** | 0.491** | | | |
| | TCEP | TCPP | TiCPP | TDCIPP | TPhP | EDP |
| DPhP | 0.400** | 0.492** | 0.514** | 0.360** | 0.600** | 0.197 |
| BBOEP | 0.282** | 0.315** | 0.314** | 0.313** | 0.241* | 0.063 |
| | BDE-47 | BDE-99 | BDE-208 | BDE-207 | BDE-206 | BDE-209 |
| 2,4-diBRP | 0.220* | 0.229* | 0.160 | 0.231* | 0.200 | 0.132 |
| 2,4,6-triBRP | 0.076 | 0.151 | 0.121 | 0.191 | 0.175 | 0.275** |
| 2,4,5-triBRP | 0.046 | 0.027 | 0.221* | 0.224* | 0.210* | 0.172 |

^aBold text indicates significant ($p < 0.01$) correlations. **: Correlation is significant at the 0.01 level (2-tailed). *: Correlation is significant at the 0.05 level (2-tailed).

household and office appliances frequently used by people in China. Tri- to hepta-BDEs, especially BDE-47 and BDE-99, were found to have a higher contribution in the handwipes of EW dismantlers and EW administrators (Figure S4); this may be because low-brominated PBDEs were emitted from the e-waste dismantling processes at the same e-waste dismantling area.²⁷ This result may be attributed to the dismantling of early imported e-waste mainly containing BDE-99 and BDE-47.⁵⁹

Overall, the median concentrations of target compounds in the handwipes of EW dismantlers were ranked as follows, in decreasing concentrations: ∑₂₀PBDEs > ∑₁₃OPFRs > ∑₁₅PAHs. The results indicated that a high PBDE concentration in EW dismantlers' handwipes may be due to the emission of a great quantity of PBDEs during e-waste dismantling. In addition, PCA was performed to evaluate PAHs, PBDEs, and OPFRs in the handwipes of the exposed population (Figure S5). TBOEP and TEHP were not analyzed, because they were not detected in the handwipes. The results indicated that BDE-209 and TPhP detected mainly in the handwipes were coexisting and might have similar sources of the e-waste dismantling. Therefore, as reported in a previous study, BDE-209 and TPhP, used as FRs, are widely present in e-waste.³³

However, the PCA results may also indicate that PAHs had different sources compared to the OPFRs and PBDEs. There may have been many sources of PAHs, including open burning or thermal treatment of e-waste, and from automobile exhaust emissions and biomass combustion.³ This explains why the sources of PAHs may have differed from OPFR and PBDE

sources. In addition, this study found significant correlations between individual chemicals with detection frequencies >50% within group of PAHs, OPFRs, or PBDEs (Tables S10–S12), and there were correlations among the monomers of PAHs, OPFRs, and PBDEs. This indicated that their corresponding monomers shared common sources.

3.3. Correlations between Handwipe Pollutants with the Metabolites of PAHs, OPFRs, and PBDEs in Urine. In this study, the corresponding metabolites of PAHs, OPFRs, and PBDEs in urine of all populations from the e-waste dismantling area were measured to further analyze the correlation between urinary metabolites and the parent compounds in handwipes. Detailed information about concentrations and composition profiles of OH-PAHs and BRPs in the urine samples has been discussed in previous studies, which analyzed 12 OH-PAHs and 16 BRPs in urine, and 2-OH-Nap, 2-OH-Flu, 2-OH-Phe, 3-OH-Phe, 4-BRP, and 2,4,6-triBRP were the main pollutants detected.^{43,45} In this study, mOPFR concentrations in urine samples were paired with the handwipe samples of EW dismantlers, EW administrators, adult residents, and juvenile residents, and the comparative results were analyzed. Table 1 presents levels (median, mean, and range) of mOPFRs in the urine. Due to the low response of BCEP and BCIPP by HPLC-MS/MS, those two compounds were not further evaluated. DPhP and BBOEP were detected in 100% and 99% of samples, respectively. The highest DPhP concentrations were found in the urine of EW dismantlers and ranged from 0.14 to 42.5 ng/mL (median: 1.82 ng/mL), followed by EW administrators,

adult residents, and juvenile residents. DPhP concentrations in the urine of juvenile residents in this study were lower than levels detected in children (1.1 ng/mL) in the Norwegian general population,⁶⁰ while similar levels were found in the urine (0.56 ng/mL urine) of participants living in an e-waste dismantling area.⁶¹ Among mOPFRs, DPhP was the most abundant compound in the four different exposed populations, accounting for 75–92% of the total amount of mOPFRs (Figure S6).

Table 2 shows the Spearman correlation coefficients of the parent compounds and their metabolites OH-PAHs. Generally, 1-OH-Pyr acts as a biomarker of occupational exposure to PAHs and has been frequently analyzed in biomonitoring studies.^{62,63} In this study, a significant positive correlation was also found between the concentrations of Pyr and 1-OH-Pyr ($r_s = 0.491$, $p < 0.01$) in all populations (Table 2). However, weak correlations were observed between Pyr and 1-OH-Pyr for adult residents ($r_s = 0.496$, $p < 0.05$) (Table S13), while no correlation was observed in the other three groups. This showed that the dermal exposure to Pyr may have other main sources besides dermal contact for the adult residents. Importantly, Flu concentrations were associated with $\sum_2\text{OH-Flu}$ ($r_s = 0.305$, $p < 0.01$), and Phe concentrations were associated with $\sum_5\text{OH-Phe}$ ($r_s = 0.414$, $p < 0.01$) (Table 2). Interestingly, 4-OH-Phe ($r_s = 0.669$, $p < 0.01$), 1-/9-OH-Phe ($r_s = 0.467$, $p < 0.05$), and 3-OH-Phe ($r_s = 0.458$, $p < 0.05$) all had higher positive associations with Phe in EW administrators compared to the other groups, except for 2-OH-Phe (Table S13). These results implied that dermal absorption may be an important PAH exposure route in e-waste dismantling areas. However, due to differences in the exposure pathways of each individual PAH isomer, the correlations are different. Nevertheless, this study showed that total PAHs in handwipes can be used as a measure for the dermal exposure to PAHs for occupational workers; however, specific PAH and OH-PAH biomarkers need to be further studied and clarified for exposure assessments.

For OPFRs and their metabolites mOPFRs, there were different correlations between individual chemicals in the handwipes with the urine samples. Table 2 shows that TCEP, TCPP, TiCPP, and TDCIPP were all significantly correlated with DPhP and BBOEP ($p < 0.01$; Table 2). In particular, there were significant correlations between concentrations of TPhP in handwipes and DPhP in urine ($r_s = 0.600$, $p < 0.01$; Table 2) for all exposed populations from the e-waste dismantling area. This indicates that handwipes could be used to effectively predict TPhP excretion in urine. As previously reported, DPhP is a nonspecific biomarker for TPhP and may form as a degradation product of EDP.^{57,64} In this study, TPhP and EDP were significantly correlated in handwipe samples ($r_s = 0.595$, $p < 0.01$; Table S11) and may share similar sources. However, unlike TPhP, EDP in handwipes was not associated with DPhP in paired urine samples (Table 2). This may be because DPhP is not the main or most abundant metabolite of EDP.^{65,66} In addition, previous research reported that over 95% of the total EDP exposure was estimated to be exposed via diet.⁶⁷ Otherwise, DPhP concentrations in urine were significantly correlated with TPhP concentrations in handwipes for EW dismantlers ($r_s = 0.679$, $p < 0.01$). No associations were observed for EW administrators ($r_s = 0.417$, $p > 0.05$), adult residents ($r_s = 0.137$, $p > 0.05$), and juvenile residents ($r_s = 0.012$, $p > 0.05$) (Figure 2). Together with a higher proportion of TPhP in

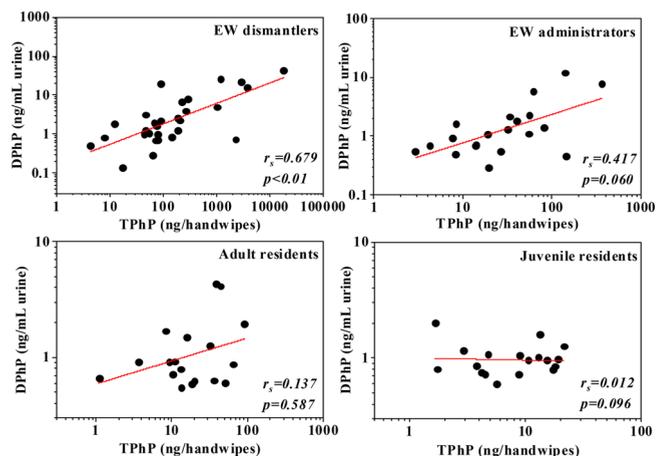


Figure 2. Scatter plots (logarithmic scale) of spearman correlations between TPhP levels in handwipes and DPhP levels in urine of EW dismantlers ($n = 29$), EW administrators ($n = 23$), adult residents ($n = 18$), and juvenile residents ($n = 19$).

handwipes (68%) and DPhP in urine (89%) found in EW dismantlers (Figures S3 and S6), the results indicated that DPhP may be used as a biomarker of dermal exposure to TPhP for those EW dismantlers. As such, the handwipe samples may provide preliminary insights into occupational worker exposure to e-waste, especially for TPhP.

For PBDEs in handwipes and their metabolites BRPs in urine, 2,4-diBRP was a positive correlation with BDE-47 ($r_s = 0.220$, $p < 0.05$) and BDE-99 ($r_s = 0.229$, $p < 0.05$); however, the coefficients were low (Table 2). Additionally, there were significant associations between BDE-209 and 2,4,6-triBRP ($r_s = 0.275$, $p < 0.01$) in all exposed populations in the e-waste dismantling area. However, there was no correlation between BDE-209 and 2,4,6-triBRP for EW dismantlers ($r_s = 0.356$, $p > 0.05$, Table S13). Two chemicals, 2,4,6-triBRP and 2,4-diBRP, have been also found in e-waste raw materials;⁶⁸ these are used as FRs and are metabolites of BDE-47, BDE-100, and BDE-154 in humans⁶⁹ and rats.⁷⁰ In particular, BDE-209 has been confirmed to be an e-waste priority pollutant; however, for occupationally exposed EW dismantlers, there was no correlation between target compounds in handwipes with their urinary metabolites. This may be mainly due to a low transdermal permeability of BDE-209 (Molecular weight = 959.2, $K_{ow} = 10.3$). As such, dermal contact may not be the primary exposure pathway for high-molecular-weight PBDEs. In addition, a previous study has reported that BDE-209 was excreted in feces or accumulated in serum;⁷¹ however, few studies have reported finding BDE-209 in urine, and its characteristic urinary metabolites remain unknown. It may be that the metabolites in urine detected in this study were not the main exposure markers of BDE-209 in humans. Further, some works have confirmed a correlation between PBDEs in dust and serum, and in handwipes and serum. This indicates that the exposure to PBDEs may contribute to PBDEs accumulated in human serum, instead of being metabolized into BRPs and then excreted in urine.^{20,72} Furthermore, for PBDEs with longer half-lives, the serum metabolites OH-PBDEs may reflect relatively earlier skin exposure. More evidence based on serum levels is needed to clarify the contribution of skin exposure to the body burden.

In summary, the strongest association was found between OPFRs in handwipes and their urinary metabolites, followed

by the correlation between PAHs in handwipes and their urinary metabolites. The weakest correlation was found between PBDEs in handwipes and their urinary metabolites for all exposed populations. Compared with PBDEs, OPFRs were more easily metabolized and further excreted mainly via urine with shorter half-lives (hours to days).³⁵ In contrast, most BDE-209 is usually accumulated in adipose tissue such as serum in humans with longer half-lives (1–2 weeks).⁷³ Compared with PAHs, the exposure of OPFRs mainly came from e-waste dismantling activities in the e-waste dismantling area; in contrast, the exposure of PAHs was mainly due to the combined effects of e-waste dismantling activities and other sources (such as vehicle emissions).³ Therefore, handwipes may better reflect exposure to OPFRs.

3.4. Identification of the Significant Exposure Pathways of Typical SVOCs. Due to their high exposure levels and their dominance in the handwipes of EW dismantlers, Phe, Pyr, TPhP, and BDE-209 were selected to assess the daily dermal exposure to these SVOCs. Table S14 lists the absorption and intake exposure to Phe, Pyr, TPhP, and BDE-209 via dermal absorption, hand-to-mouth ingestion, and dust ingestion. The sums of the exposure estimations of dermal absorption and hand-to-mouth ingestion of Phe, Pyr, TPhP, and BDE-209 from EW dismantlers were 0.62, 0.43, 2.07, and 3.03 ng/(kg_{bw} day), respectively (Table S14). In addition, we calculated and compared the contribution of dermal exposure to the total exposure through the three routes for these four SVOCs. Results showed that the TPhP (62%) contribution was the highest exposure proportion to EW dismantlers through dermal absorption and hand-to-mouth ingestion, followed by Phe (45%), Pyr (36%), and BDE-209 (13%) (Figure 3). This result suggests that dermal absorption

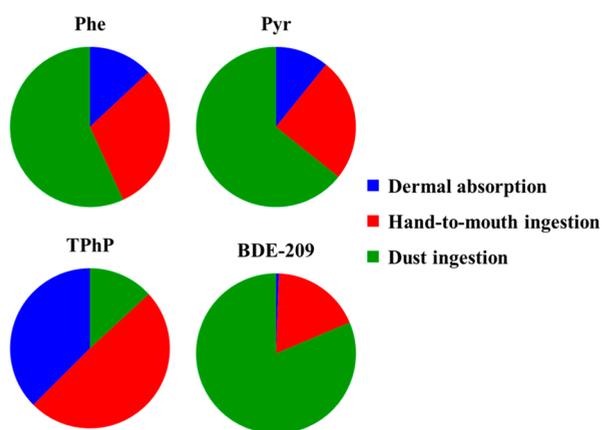


Figure 3. Comparison of the exposure estimation of Phe, Pyr, TPhP, and BDE-209 via different pathways, including dermal absorption via handwipes, hand-to-mouth ingestion, and dust ingestion.

exposure and hand-to-mouth ingestion are the most significant exposure pathways for TPhP. As such, handwipes can effectively predict the dermal contact exposure to TPhP, particularly for occupationally exposed EW dismantlers.

Notably, the dust ingestion of BDE-209 was 1–2 orders of magnitude higher than those of other compounds (Table S14), and the estimated exposure contribution accounted for up to 81% of all three exposure pathways (Figure 3). BDE-209 was also dominant in the handwipes and accumulated in high concentrations on the skin; however, a low dermal absorption rate and low dermal bioavailability resulted in almost negligible

dermal absorption via handwipe exposure.⁷⁴ In this study, PAHs, PBDEs, and OPFRs were all detected in handwipes, showing that these three groups of SVOCs were adsorbed onto the hand surface area and are more likely to create exposures from contact with dust or object surfaces, particle deposition, and air penetration from more than one microenvironment.⁴⁹ However, only considering the use of handwipes to estimate dermal absorption exposure might underestimate the actual exposure risks, as it only limits exposure through the skin of the hand. Also, if exposed workers wear short-sleeved T-shirts for a long time, their arms, face, neck, and other exposed skin are also exposed, leading to an underestimated skin exposure. Nevertheless, the dermal exposure of the occupationally exposed population draws significant attention.

In conclusion, three typical SVOCs, including PAHs, OPFRs, and PBDEs, of different exposed groups in an e-waste dismantling area were analyzed using handwipes and an analysis of possible metabolites in paired urine samples. A significant correlation was found between TPhP in handwipes and DPhP in urine, indicating that handwipes can be used as a noninvasive indicator of dermal exposure, and TPhP can serve as a characteristic marker of OPFR dermal exposure. Partial PAHs in handwipes were also correlated with their urinary metabolites, indicating that dermal exposure was also an important pathway for PAHs. In contrast, only a small amount of BDE-209 was found to be contributed from dermal exposure. The distinct properties of different compounds led to various proportions of dermal exposure contributions. Notably, the air inhalation is also important to human exposure. Due to the relative difficulty of collecting air samples (indoor stationary air and personal ambient air) and the uncertainty of human daily activities, collecting these paired environmental samples presents great challenges. This factor needs to be considered in our further research.

Dermal exposure is an important exposure pathway. This study, however, showed that a comprehensive internal and external exposure sample analysis is needed to accurately assess the exposure pathways of different organic pollutants. This highlights the need to simultaneously analyze multiple internal and external exposure markers when studying dermal contact exposure via handwipe samples. We believe that this is a systematic research work evaluating dermal exposure to different characteristic pollutants for high-exposure occupational EW dismantlers, from the perspectives of internal exposure based on urinary metabolites and external exposure based on handwipes. The findings on the characteristics of different SVOCs exposed by the dermal contact for EW dismantlers provide valuable insights into human biomonitoring and exposure assessment of organic pollutants. Due to the limitation of sampling methods and the number of study population samples, large-scale sampling and more comprehensive studies are needed to accurately assess the risks caused by exposure using wipes and the potential for using wipes to indicate biomarkers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.1c02562>.

Additional data and figures including contributions of PBDEs, OPFRs and PAHs in handwipes, congener profiles, and PCAs (PDF)

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Notes

The authors declare no competing financial interest.

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