

Legacy and Currently Used Organic Contaminants in Human Hair and Hand Wipes of Female E-Waste Dismantling Workers and Workplace Dust in South China

Lin Qiao,[†] Xiao-Bo Zheng,^{||} Jing Zheng,^{*,‡,§} She-Jun Chen,^{||} Chang-Qin Zhong,[‡] Jing-Hua Chen,[‡] Zhong-Yi Yang,^{*,§} and Bi-Xian Mai^{||}

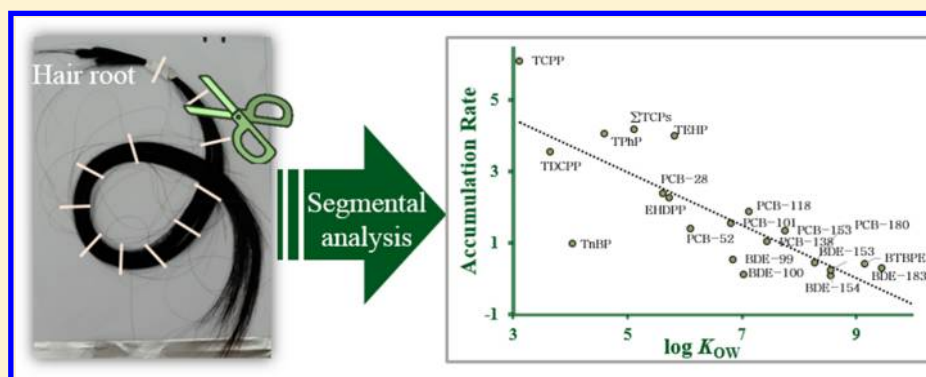
[†]College of Tourism and Exhibition, Henan University of Economics and Law, Zhengzhou 450046, China

[‡]State Environmental Protection Key Laboratory of Environmental Pollution Health Risk Assessment, South China Institute of Environmental Sciences, Ministry of Environmental Protection, Guangzhou 510655, China

[§]State Key Laboratory for Biocontrol, School of Life Sciences, Sun Yat-sen University, Guangzhou 510275, China

^{||}State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

Supporting Information



ABSTRACT: Legacy organic contaminants, such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), and several currently used organic contaminants, such as novel brominated retardants (NBFRs), organophosphate flame retardants (OPFRs), and Dechlorane Plus (DPs), were measured in the segmented hair and hand wipes of e-waste dismantling workers and in the dust from their workplace in an e-waste recycling site in South China to assess the accumulation and sources of organic contaminants in the hair shaft. The median concentrations of DPs, PBDEs, NBFRs, PCBs and OPFRs in hair samples were 23.5, 154, 156, 349, and 371 ng/g, respectively. A linear increase in organic contaminant concentrations was found along the hair shaft, with significant differences among each segment, while the age-related patterns were similar among the 7 hair segments. A linear relationship was found between the accumulation rates and the log K_{OW} , indicating that the accumulation rates of organic contaminants along the hair shaft decreased with increasing log K_{OW} values. Enantiomer fraction (EF) values of PCB-132 in distal segments were close to those in dust and air, while EFs in proximal segments were close to those in serum. The contributions of PCBs from external sources to hair increased with the distance from the scalp of hair segments, from 67.8% in 0–3 cm segments to 95.9% in 18–21 cm segments.

INTRODUCTION

Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) have been widely used in consumer and industrial products as flame retardants, insulating fluids or plasticizers,^{1,2} and they were listed under the Stockholm Convention on Persistent Organic Pollutants for phase out because of their persistence properties, bioaccumulation potential, and adverse effects on human and environmental health.^{3–5} A recent study in the US found much higher concentrations of airborne PCBs inside schools than outside, and children were thus exposed to considerable amounts of PCBs emitted from building materials via inhalation.⁶ Long-

term exposure to PCBs and PBDEs will continue due to their ubiquitous presence in the environment.

The restriction on these legacy organic contaminants gave rise to replacements with decabromodiphenylethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), and Dechlorane Plus (DP). Additionally, organophosphate flame retardants (OPFRs), also known as emerging flame

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retardants, have attracted growing concern in recent years because of the global occurrence in air, dust, soil, and sediment.^{7–9} OPFRs have also been found in human breast milk and placenta tissue,^{10,11} and metabolites of OPFRs have been found in human urine.^{12,13} Nevertheless, studies suggest that these replacements may also lead to hazardous effects to human health. It has been suggested that tris(1,3-dichloro-2-propyl)phosphate (TDCPP) and triphenyl phosphate (TPhP) could disturb the sex steroid hormone balance in human adrenal cells,¹⁴ and the concentrations of TDCPP and TPhP in dust were associated with altered hormone concentrations and decreased semen quality in men.¹⁵

Hair is one of the noninvasive matrices that has been increasingly used as an alternative biomarker due to its advantages of easy sampling and the low cost of storage and transportation. Several studies have demonstrated that concentrations of contaminants in hair could differentiate subject groups with different exposure levels.^{16–18} However, most studies have focused on exposure levels for risk assessment, and research on the accumulation of contaminants in the hair shaft is scarce.

In addition to incorporation in hair through the blood (internal origin), environmental contaminants may enter the hair through external contamination from dust, air, or hair care products. Age, gender, and hair treatments may influence the incorporation of organic contaminants in hair.¹⁹ It is widely accepted that hair treatment (e.g., hair coloring) could reduce the concentrations of organic contaminants in hair.²⁰ However, inconsistent results have been observed on the relationships of organic contaminants between hair and serum in previous studies.^{21–24} In addition, the results on the age dependence and gender differences of organic contaminant concentrations in hair varied.^{18,25} A possible reason for these inconsistent results was the failure to differentiate the internal and external sources in hair. Our previous study found that organic contaminants in the proximal and distal segments of human hair showed different concentrations, profile patterns, and gender differences.^{26,27} Hair samples collected in most studies differed in the length and position of the shaft, which might have accounted for those inconsistent results. Thus, the diversity of hair length and its distance relative to the scalp need to be considered when comparing results (e.g., concentrations, congener profiles, and associations) from different studies. Research concentrating on the application of segmental analysis to solve questions in previous studies on hair is still needed.

In this study, hair samples were collected from female e-waste dismantling workers. The objectives were (1) to give a wide view of e-waste dismantling workers' body burden of both legacy and currently used organic contaminants, including concentration levels, congener profiles, age-related patterns, and temporal trends; (2) to explore the accumulation of the organic contaminants along the hair shaft and identify the factors that could affect the accumulation rate of organic contaminants along the hair shaft; and (3) to explore the chiral features of PCBs in different hair segments and distinguish sources of organic contaminants in hair segments.

MATERIALS AND METHODS

Sample Collection. Thirty-one female e-waste dismantling workers, with ages ranging from 20 to 50 years, were recruited from an e-waste recycling site in South China in August 2015. This is one of the largest e-waste recycling sites in China. A

detailed description of the site has been given elsewhere.²⁸ Nondyed hair was cut as close as possible to the scalp on the occipital area. Hand wipe samples were collected from 10 of these workers during their working time, typically at least 60 min after their last hand washing. Both the palms and backs of their hands from wrist to fingertips were wiped with a 22 × 14 cm sterile gauze pad immersed in isopropyl alcohol. Hand wipes could reflect the adsorption of contaminants to the hand surface both through gaseous phase and from contact with dust, e-waste, and electrical applications, which could provide integrated information about the external exposure for human. In addition, 10 indoor dust samples were obtained from the floor of the workers' workplace using brushes precleaned with ethyl alcohol. Both handwipe and dust samples are used to represent the source of organic contaminants in human hair from the external exposure pathway. Each sample was wrapped in aluminum foil, sealed in a plastic bag and stored at –20 °C. Participants answered a questionnaire regarding age and occupational history before sampling. The study was approved by the Ethics Committee in the School of Life Sciences, Sun Yat-sen University.

Selection of Organic Contaminants. PCBs, PBDEs, DBDPE, BTBPE, DP, and OPFRs were chosen in this study. Table S1 (Supporting Information (SI)) summarizes these organic contaminants and their abbreviations, the octanol–water partition coefficients (K_{OW}) and the octanol–air partition coefficients (K_{OA}).

Sample Preparation and Analysis. Only 0–21 cm of hair from the scalp (hair root) was used for analysis, which was sectioned into seven 3 cm segments. Details of the extraction and cleanup of hair samples is provided in the SI. The hand wipe samples were cut into pieces before the extraction and cleanup steps as described previously.²⁹ Dust samples were prepared using methods described previously.⁷ Instrumental analysis, quantification method for concentrations and chiral signatures, and statistical analysis are provided in the SI.

Quality Assurance and Quality Control. Procedure blanks, low-spiked matrices, and high-spiked matrices (a mixture of 8 PBDE congeners, 20 PCB congeners, 13 OPFR congeners, BTBPE, DBDPE, and DPs spiked in blank matrices, 5 ng of each compound for low concentration-spiked, and 50 ng of each compound for high concentration-spiked) were used for quality control. Only trace amounts were detected in the blanks, and they were subtracted from the sample extracts. The mean recoveries of the low-spiked matrices ($n = 4$) ranged from 83.1% to 110% for PBDEs, 71.4–96.4% for PCBs, 78.4–111% for OPFRs, and 102–119% for DPs, BTBPE, and DBDPE. The mean recoveries of the high-spiked matrices ($n = 4$) ranged from 79.0% to 109% for PBDEs, 70.4–107% for PCBs, 82.7–116% for OPFRs, and 106–126% for DPs, BTBPE and DBDPE. For instrumental QC, solvent blanks were injected every 6 samples, and standard solutions were injected every 12 samples (relative standard deviation <15%). The limits of quantification (LOQs) were calculated as the mean values of targets in procedure blanks plus three times those of standard deviations. For the undetected compounds in blanks, LOQs were estimated as a signal-to-noise ratio of 10. The LOQs of each compound are summarized in Table S2.

RESULTS

Concentrations and Profiles in Hair Samples. The concentrations of all organic contaminants analyzed in the 31 hair samples (whole segment) are listed in Table 1.

Table 1. Summary of Organic Contaminant Concentrations in Whole-Segment Hair Samples (ng/g Dry Weight, n = 31)

	% Det	Range	Median	Mean	% Det	Range	Median	Mean	PCB-130	% Det	Range	Median	Mean
BDE-28	65.0	nd ^a -4.51	0.28	0.96	100	11.9-287	34.2	51.1	PCB-130	94.0	nd-5.85	1.94	2.30
BDE-47	84.0	nd-11.5	1.47	2.25	100	6.44-96.7	15.6	22.0	PCB-138	100	1.77-65.2	10.6	14.9
BDE-99	97.0	nd-23.8	2.56	5.04	0.00	nd	nd	nd	PCB-146	100	0.72-14.8	4.94	5.52
BDE-100	100	0.03-3.97	0.65	0.94	100	0.90-161	10.8	18.5	PCB-153	100	2.58-82.6	14.1	19.4
BDE-153	97.0	nd-6.64	1.40	1.89	100	4.15-99.5	14.0	19.8	PCB-158	74.0	nd-9.54	0.70	1.40
BDE-154	97.0	nd-1.94	0.54	0.71	100	12.6-748	67.2	92.9	PCB-164	100	9.61-26.3	17.1	17.0
BDE-183	97.0	nd-7.99	2.61	2.67	100	189-1558	371	431	PCB-170	97.0	nd-13.9	4.84	5.25
BDE-209	100	46.2-2049	136	256	100	14.0-296	52.9	67.7	PCB-171	100	7.18-19.2	11.2	11.6
\sum_6 PBDEs	100	49.8-2104	154	271	100	6.80-125	30.4	36.5	PCB-174	100	0.16-7.16	1.34	1.76
BTBPE	100	0.64-18.2	3.39	4.86	100	1.64-34.1	8.14	10.7	PCB-175	45.0	nd-3.45	nd	0.43
DBDPE	100	15.8-980	154	206	100	11.2-41.0	18.7	19.4	PCB-177	100	0.48-3.94	1.20	1.44
\sum NBFRs	100	16.4-991	156	211	100	5.95-60.1	20.6	24.8	PCB-180	100	0.38-15.2	3.95	4.72
a-DP	100	1.17-157	12.1	30.2	100	1.46-32.6	9.27	12.0	PCB-183	0.00	nd	nd	nd
s-DP	100	0.47-203	10.6	31.0	100	0.92-60.3	10.4	13.0	PCB-187	100	0.28-6.81	1.80	2.19
\sum DPs	100	1.64-360	23.5	61.3	71.0	nd-15.6	1.21	2.55	PCB-190	100	0.06-6.80	2.13	2.31
TtPrP	0.00	nd	nd	nd	100	7.64-50.8	17.6	19.8	PCB-194	100	1.70-4.19	2.66	2.88
TPPP	13.0	nd-0.34	nd	0.02	100	1.10-59.2	8.14	11.3	PCB-199	65.0	nd-4.04	0.49	0.84
TnBP	100	5.30-99.8	15.2	17.5	97.0	nd-110	17.1	22.3	PCB-203	100	1.83-4.83	3.20	3.19
TCEP	61.0	nd-51.6	1.88	8.47	100	1.63-78.0	11.3	15.5	PCB-206	100	1.71-81.0	3.94	14.4
TDCPP	100	7.48-166	31.4	40.1	100	1.76-118	22.7	26.4	PCB-208	74.0	nd-1.75	0.15	0.26
TBOEP	97.0	nd-341	80.6	97.5	100	3.35-150	21.0	29.9	PCB-209	100	0.03-2.76	0.50	0.73
TEHP	100	26.7-224	55.4	63.4	100	0.13-19.9	2.97	4.52	\sum_{36} PCBs	100	129-1186	349	429

^aNote: nd, not detected.

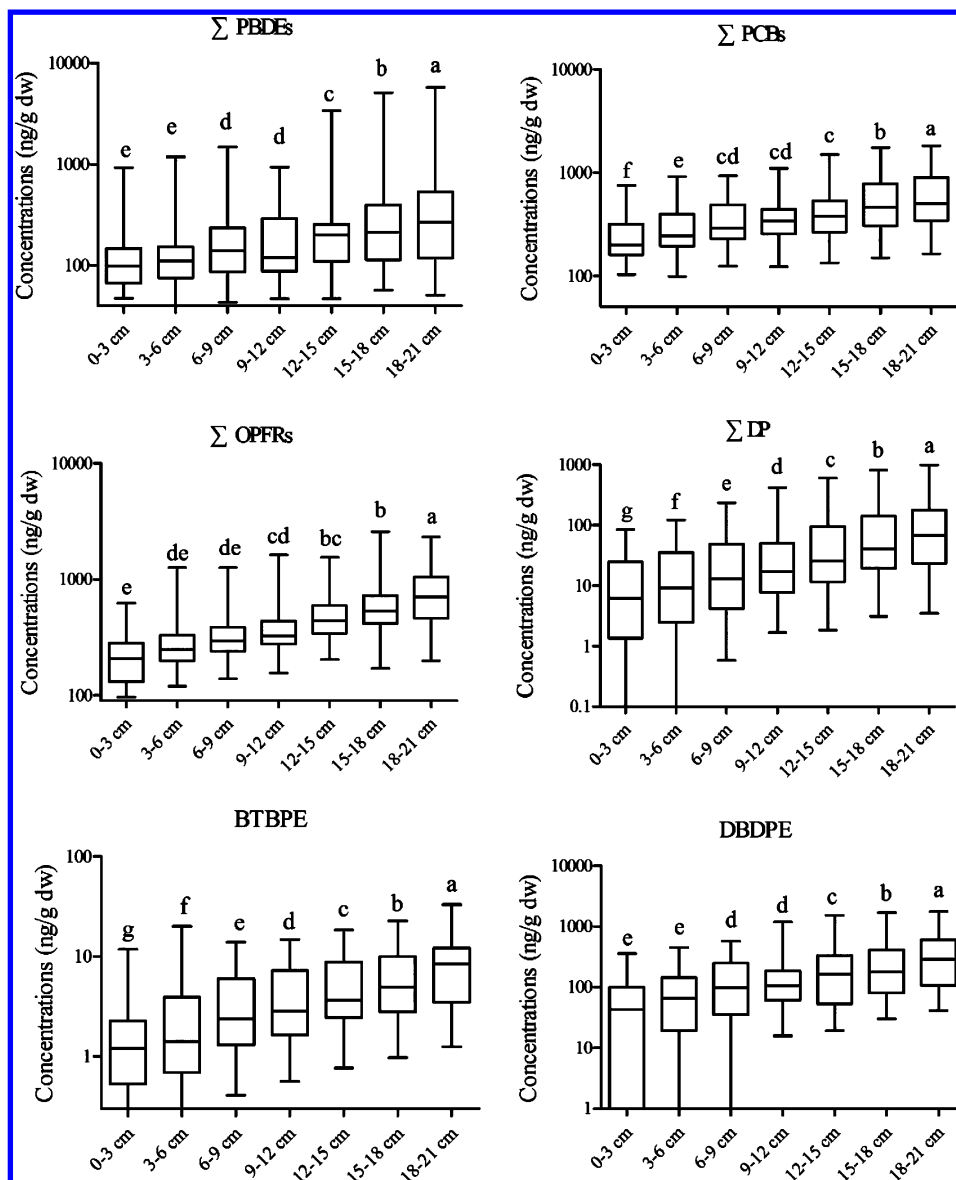


Figure 1. Organic contaminant concentrations in each segment ($n = 31 \times 7$). The boxes indicate the 25th and 75th percentiles, the whiskers indicate the minimum and maximum, and the lines in the box indicate the median concentrations. Different letters represent significant differences between hair segments at $p < 0.05$.

\sum_8 PBDE levels were in the range of 49.8–2104 ng/g, with a median of 154 ng/g. BDE-209 was the most abundant compound, accounting for 92.8% of total PBDEs. \sum_{36} PCB concentrations in hair were in the range of 129–1186 ng/g. Tri-, tetra-, and penta-CBs accounted for 70.4% of the total PCB concentrations, and PCB-28 and -52 were the most abundant congeners in the 36 PCB congeners analyzed. Eleven of the 13 measured OPFRs were detected in the hair, with predominant congeners of TBOEP, TCPP, TEHP, and TPhP (accounting for 24.2%, 18.7%, 15.9%, and 11.1% of the total OPFR concentrations, respectively). DPs were detected in all hair samples, in the range of 1.64–360 ng/g. The average isomer ratio of DP (f_{anti} , defined as the fraction of *anti*-DP in the total DP) in the hair samples was 0.49. This was lower than that in the commercial DP products (0.75), which can be explained by the metabolic processing of DP in dust, air, or the human body before incorporation into hair. In general, OPFRs accounted for 34.8% of all 61 organic contaminants analyzed,

followed by PCBs (32.6%), PBDEs (16.0%), NBFrs (13.2%), and DPs (3.47%).

No significant associations were observed between concentrations of these organic contaminants and occupational exposure time (Figure S1, $p > 0.05$). The concentrations of \sum_8 PBDEs, \sum NBFrs, \sum DPs, and \sum_{36} PCBs all occurred in the following order: middle-aged group (31–40 years old) > older group (41–50 years old) > younger group (20–30 years old) (Figure S2). Additionally, \sum_8 PBDE and \sum NBFR concentrations in the middle-aged group were significantly higher than in the younger group ($p < 0.05$). \sum_{13} OPFR concentrations did not show the same age-related patterns as other organic contaminants, and the OPFR compounds also showed different age-related patterns with each other (Figure S3).

Concentrations in Hair Segments. When comparing the concentrations by the distance from the scalp, we found that the concentrations increased from the first (0–3 cm from the

scalp) to the end segment (18–21 cm from the scalp) for all organic contaminants (Figure 1 and Table S3), with significant differences among the seven hair segments ($\chi^2(6) = 123$ for \sum_8 PBDEs, $\chi^2(6) = 148$ for DBDPE, $\chi^2(6) = 168$ for BTBPE, $\chi^2(6) = 173$ for \sum DPs; $\chi^2(6) = 145$, for \sum_{36} PCBs, and $F = 32.7$ for \sum_{13} OPFRs, with p values all less than 0.001). The median concentrations of the main organic contaminants (PBDEs, NBFRs, DPs, and OPFRs whose detection frequency >50%, and 7 indicator PCBs) in hair segments showed positive correlations with the distance from the scalp (Table S4, $p < 0.01$), indicating a linear accumulation ability for organic contaminants along the hair shaft.

A linear regression model was further conducted for the main individual organic contaminant concentrations in the hair segments and the distances to the scalp of the e-waste dismantling workers, separately. According to an average rate of hair growth of 1 cm per month,²⁰ each 3 cm segment was assumed to represent a 3-month exposure period. Thus, the slope of the linear regression equation of a compound could reflect its accumulation rate (R_A , ng/g/month) along the hair shaft per month. After excluding several data points whose p -values were above 0.05, we found that the organic contaminants accumulated in the hair shaft at different rates. Among the organic contaminants analyzed in this study, R_A of \sum DPs were the lowest, in the range of 0.18–54.7 ng/g/month (mean: 6.95 ng/g/month), and the R_A of \sum_{13} OPFRs was the highest, in the range of 13.3–94.9 ng/g/month (mean: 37.8 ng/g/month). R_A of \sum_8 PBDEs were similar to those of \sum_{36} PCBs, in the range of 2.04–76.0 ng/g/month (mean: 18.4 ng/g/month), and 3.45–74.2 ng/g/month (mean: 22.0 ng/g/month), respectively.

No significant correlations were observed between the R_A s of organic contaminants and the ages of the e-waste dismantling workers ($p > 0.05$) or the occupational exposure time ($p > 0.05$). However, the R_A s of organic contaminants were significantly associated with the concentrations of the whole segment of hair (Figure S4, $p < 0.001$ for \sum_8 PBDEs, \sum_{36} PCBs, and \sum_{13} OPFRs), suggesting that organic contaminants accumulated faster along the hair shaft of individuals with higher exposure levels.

The relationships between the R_A and physicochemical parameters of the organic contaminants were also explored. As seen in Figure 2A, except for BDE-209, DP, DBDPE, and TBOEP (which had outliers in the concentration data), the R_A s of other organic contaminants decreased significantly as the $\log K_{OW}$ increased ($R_A = -0.74 \times \log K_{OW} + 6.69$; $R^2 = 0.63$). Meanwhile, the R_A s of PCBs were significantly associated with the \log vapor pressure ($R_A = 0.66 \times \log VP + 3.81$; $R^2 = 0.77$, Figure 2B). For the other organic contaminants, R_A also increased with the rise of \log vapor pressure, but the association did not reach statistical significance (Figure S5).

Concentrations and Profiles in Dust and Hand Wipes.

The median PBDE concentrations in dust and hand wipe samples in the hair sampling area were 126 944 ng/g and 238 ng/sample, respectively, which were slightly higher than those of NBFRs (25 341 ng/g for dust, and 143 ng/sample for hand wipes) and much higher than those of PCBs (13 961 ng/g for dust and 23.3 ng/sample for hand wipes). OPFRs were also detected in most dust and hand wipe samples, with a median of 5297 ng/g and 252 ng/sample, respectively. BDE-209 was the most abundant PBDE congener, with a proportion of 97.6% in the dust samples and 90.0% in the hand wipe samples, which

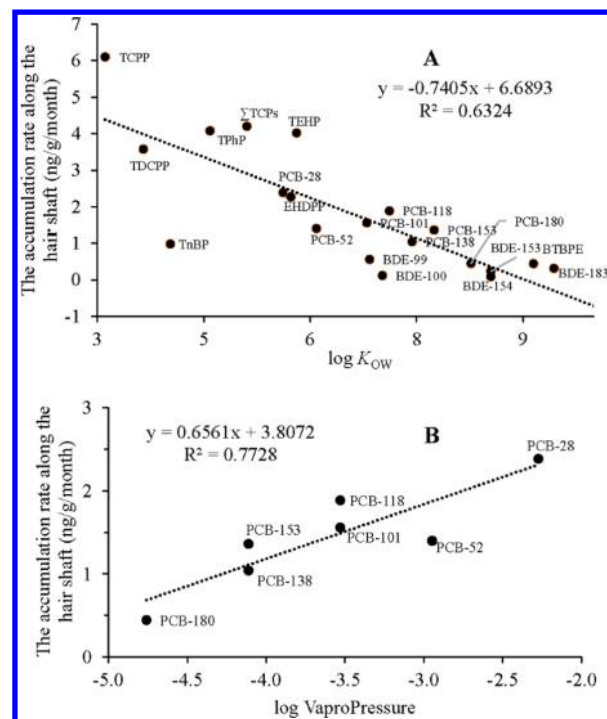


Figure 2. Relationships between the accumulation rate and $\log K_{OW}$ of all organic contaminants except BDE-209, DBDPE, DP, and TBOEP (A). Relationships between the accumulation rate and vapor pressures of PCBs (B).

was inconsistent with those in the hair segments. Tri-, tetra-, and penta-CBs accounted for 78.0% of the total PCB concentrations in dust samples and 70.0% in hand wipe samples, which were similar to those in hair samples. PCB-28 was the predominant congener of 7 PCB indicators, accounting for 26.6% in dust and 42.9% in hand wipes. Compared to dust samples, the OPFR congener profiles in hand wipe samples were more similar to those in hair samples (Figure S6 and Figure S7).

Chiral Signatures of PCBs. The enantiomer fractions (EFs) of four chiral PCB enantiomers (PCB-95, -132, -135, and -149) were investigated in the 7 hair segments, dust, and hand wipe samples (Figure 3). The chiral signatures of PCB-95, -135, and -149 were racemic or near-racemic in all hair segments, with no significant differences among the segments ($p > 0.05$). Similarly, the chiral signatures of PCB-95, -135, and -149 showed racemic or near-racemic configurations in the dust and hand wipes. The EF values of PCB-132 in 0–3 cm, 3–6 cm, and 6–9 cm hair were significantly higher than those in 15–18 cm and 18–21 cm hair ($p < 0.05$, Figure S8). In addition, the EF values of PCB-132 in 0–9 cm hair (0.49 ± 0.05 in 0–3 cm, 0.49 ± 0.04 in 3–6 cm and 6–9 cm) were significantly different from those in dust samples (0.43 ± 0.01) ($p < 0.05$).

DISCUSSION

Temporal Trend of Organic Contaminants in Dust and Hair samples. The location of the e-waste recycling site was the same as our previous studies sampling in 2009, 2011, and 2013,^{18,21,30–34} which made it possible to analyze the temporal trend of organic contaminant concentrations in hair and dust at this site (Table S5). Compared to the dust samples collected in 2009, the PCB concentrations in dust decreased

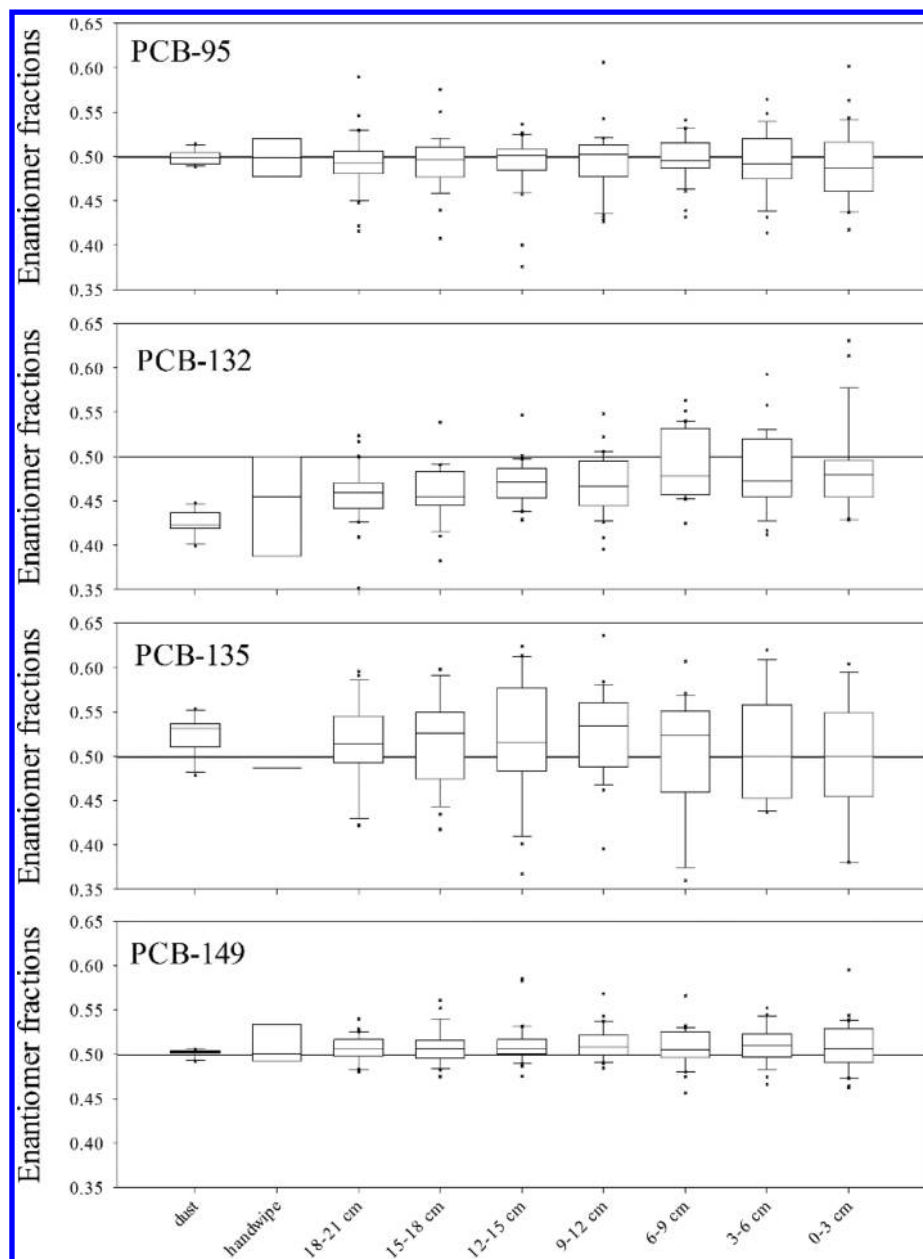


Figure 3. Enantiomer fractions of chiral PCBs in the 7 hair segments, dust, and hand wipe samples. The flat line represents EF = 0.5.

notably, while concentrations of PBDEs, DP, BTBPE, and DBDPE increased over time. Zheng et al.³⁵ also found increased concentrations of PBDEs, BTBPE, and DBDPE but decreased concentrations of PCB compared to those collected in 2008 in dust at another e-waste recycling site in South China. The decreased dust PCB concentrations suggest that increased newer electrical wastes were introduced to e-waste recycling areas in Guangdong, and the proportion of obsolete transformers decreased accordingly. In contrast, the increasing PBDE levels over the years reminded us that PBDEs were still being released into the environment in e-waste recycling areas, although they have been prohibited by the Stockholm Convention.

The temporal trend of PBDE concentration in the hair samples was the same as that in the dust. However, PCB and DP levels in the hair samples increased from 2009 to 2011 but decreased from 2011 to 2015. The hair samples and dust samples were all collected at the same e-waste recycling area

using same dust collecting method. However, the hair samples collected in 2009 were from male workers, which was short and collected near the scalp. Most of the hair samples analyzed in 2011 were distal hair segments with varying distances from the scalp. In this study, we cut hair samples 0–21 cm away from the scalp, and found that concentrations of organic contaminants in the distal segments were higher than those in the proximal segments. Thus, the inconsistent temporal trend of DP and PCB levels between hair and dust might have been caused by the difference in hair collecting methods. This result also indicated that inconsistent hair sample collection methods would introduce confusion to the analysis of temporal trends. Thus, it is important to consider the diversity of hair length and its location related to the scalp when using hair as a biomonitoring matrix.

Comparison with Other Sites. The concentrations of legacy organic contaminants (PCBs and PBDEs) in dust samples were much higher than those in Dali and Guiyu,³⁵

which are other two famous e-waste recycling sites in China. For the currently used contaminants, dust concentrations of BTBPE, DPDPE, and OPFR in this study were much lower than those in Dali and Guiyu. The congener profiles of PBDEs and OPFRs were similar among the three sites, with BDE-209, TPhP, and TCPP being the predominant congeners. However, the main PCB congener in Dali and Guiyu was PCB-118, while PCB-28 was the predominant congener in this study. Our previous studies^{31,32} also found that PCB-28 was the dominant congener of total PCBs in the dust samples in the same e-waste recycling site. These results indicated that e-waste containing flame retardants in the three sites may have common sources, while e-wastes containing PCBs were probably from different applications (transformers, capacitors, and adhesives, etc.).

There were few studies on organic contaminants in hand wipe samples, and comparison with hand wipes in other e-waste sites is impossible. BDE-209 concentrations in the hand wipes of workers in this study were much higher than those in the hand wipes of urban residents in the US³⁶ and Holland,³⁷ while penta-BDE concentrations were much lower than those in the hand wipes of residents in the US. This interesting result might have accounted for the application and usage of penta-BDEs. Penta-BDEs are usually used in products with long life cycles, such as carpet underlay, vehicle interiors, furniture, and bedding,³⁸ and their demand in North America is larger than in other countries.³⁹ Thus, the level of dermal exposure to penta-BDEs of residents of the US exceeded that of e-waste workers in this study. Concentrations of TCEP, TCPP, and TDCPP in hand wipes of workers in this study were lower than those in the US^{36,40} and Holland,³⁷ while TPhP and TCP concentrations were much higher than those in Holland,³⁷ which might have been due to the regional disparities between market shares of different OPFR compounds.

Segmental Hair Analysis and Age-Related Organic Contaminant Patterns. Previous studies have found strong associations between age and organic contaminant concentrations in human serum. Park et al.⁴¹ and Zubero et al.⁴² both reported that PCB concentrations increased with age. Sjödin et al.⁴³ found that PBDE concentrations increased with age. This could be explained by the longer-term exposure to pollutants and/or lower biotransformation/elimination process for older people.⁴⁴ However, there were only a few studies on associations between age and organic contaminant concentrations in hair, and the conclusions were inconsistent. Malarvannan et al.²⁵ reported that there were no correlations between age and PBDEs/PCBs concentrations in hair, and Covaci et al.⁴⁵ and Behrooz et al.⁴⁶ also reported the age nondependency. Zheng et al.¹⁸ found PBDE concentrations in hair of the elderly and children were higher than those of adults, while Tang et al.⁴⁷ found that PBDE concentrations in adults were higher than those of children.

In this study, the age-related patterns of organic contaminants were similar among the 7 hair segments. For the same hair segment, organic contaminant concentrations (except OPFRs) in the hair of the middle-aged group were higher than those in the older group and younger group. The results suggested that segmental analysis would not affect the results of age-related patterns. Inconsistent age-related patterns in hair in different studies may be due to the inconsistent hair collecting method, and may be due to contaminants in the hair representing both internal and external exposures, leading to age-related patterns in the hair that are more complex than serum analysis, which only represents internal exposure.

Accumulation of Organic Contaminants along the Hair Shaft. Few studies have explored the accumulation of contaminants along the hair shaft. In our previous research on hair of university students, concentrations of organic contaminants increased significantly from the 0–5 cm close to the scalp to the sample 5–10 cm from the scalp.^{26,27} In this study on the hair of e-waste dismantling workers, linear increasing trends of all organic contaminants were found along the hair shaft from the scalp to 21 cm outward, with significant differences among each 3 cm segment. This could be explained by the longer exposure time of the distal segments, which enabled a higher extent of binding from both internal and external sources. It also showed that the segmental difference of contaminants in hair was universal for these organic contaminants.

As the accumulation rate could reflect the difficulty of a target compound's incorporation into hair, it was worthwhile to explore the factors influencing it. It is interesting that the age or occupational exposure time of the workers did not influence the accumulation rate of organic contaminants along the hair shaft, while the physicochemical parameters of the organic contaminants influenced the accumulation rate. The R_A s of most organic contaminants decreased with the increase of $\log K_{OW}$, probably because organic contaminants with high $\log K_{OW}$ do not escape easily from dust particles to be absorbed on the hair shaft.²¹ The significant associations between the $\log K_{OW}$ of organic contaminants and the accumulation rate suggested that exposure through the deposition of dust or fine particles in air might be an important pathway for the entry of most of these organic contaminants into hair. Fang et al. reported similar relationships between $\log K_{OW}$ and the bioaccessibility of several flame retardants (OPFRs, PBDEs, EH-TBB, and BEH-TEBP).⁴⁸ The bioaccessibility, referring to the fraction that dissolves in the gastrointestinal tract and is available for absorption,⁴⁹ could reflect the distribution/partition of contaminants between dust particles and the intestinal wall. Although the physiological structure of hair shaft and the process of contaminants' entry into hair were different from those of the gastrointestinal tract, these results suggest that the $\log K_{OW}$ is also a good predictor of the accumulation rate of the organic contaminants along the hair shaft.

Figure 2B shows that PCBs with lower vapor pressure accumulated slower in the hair than those with higher vapor pressure, indicating that vapor pressure plays a key role in the accumulation of PCBs in hair. The results also indicated that exposure from the gaseous phase might be the main source of PCBs in hair. In a designed exposure experiment reported by Kucharska et al.,⁵⁰ PBDEs and OPFRs with lower vapor pressure had lower transfer efficiencies from the gaseous phase to hair. Barghi et al.⁵¹ found that the concentrations of HBCD and TBBPA in hair samples showed no increase after a one-week gaseous phase exposure experiment due to their lower vapor pressure. The OPFR or PBDE congeners varied much in vapor pressure (0.0000629–0.46 for OPFRs; 6.23×10^{-10} –0.000144 for PBDEs), which might be the reason why their accumulation rates were not associated significantly with \log vapor pressure, revealing that the accumulation of PBDEs and OPFRs along the hair shaft was more complicated than that of PCBs.

Contribution of Contaminants in Hair through External Sources. The enantiomer fractions (EFs) analysis of chiral chemicals was an effective way to assess the source of

contaminants in the environment. Physical (e.g., air–water exchange, sorption, etc.) and chemical processes (e.g., abiotic transformation) do not change enantiomeric ratios because abiotic processes are the same for both enantiomers, making the measurement of enantiomeric composition an easy and conclusive indicator of biological processing.

PCBs are released as racemic enantiomers in environmental matrices, and their enantiomer patterns can only be affected by biotransformation.⁵² The EF values of PCB-132 showed a significant decreasing trend from the proximal hair segments to the distal hair segments. In previous studies, we measured the EFs of PCB-132 in air and human serum in this e-waste recycling area, with EFs of 0.484 ± 0.022 and 0.554 ± 0.058 , respectively.^{34,53} Thus, the higher EF values of PCB-132 in the proximal segments suggested that the proximal segments of hair were probably influenced by the internal source (blood), which has a preference for the (+)-enantiomer accumulation of PCB-132.

Based on the assumption that no alteration of EFs would occur in and after the process of getting into hair, the EF value of PCB-132 was taken as an index to quantify the contribution of PCB-132 in hair through external sources using a two-end member linear mixture model. The average EF value of PCB-132 in the serum of e-waste workers (0.554) at the same sampling place reported by Zheng et al.³⁴ was considered as that of the internal source. The results (Figure S9) showed that the contributions of PCB-132 in hair through external sources increased with the distance of the hair segment from the scalp. The average contributions increased from 53.0% for the 0–3 cm segment to 75.1% in the 18–21 cm segment using the EF of PCB-132 in dust samples as the external source, and from 65.6% in the 0–3 cm segment to 92.8% in the 18–21 cm segment using the EF of PCB-132 in hand wipe samples as the external source. These results suggested that external contaminants were the main exposure sources of PCBs in hair, especially for the distal segments of hair.

Correlations between Contaminants in Hair and Hand Wipe Samples. Taking into account that higher proportions of the external sources were obtained when using EFs of hand wipe samples compared to EFs of dust samples and that the OPFR congener profiles in hand wipe samples were more similar to those in hair samples (Figure S6 and S7), hand wipe samples are recommended to represent information regarding external exposure to hair in further studies. A previous study showed that the congener profiles of organic contaminants in dust on electrical products' surfaces, windows, floors, and beds were different from each other.⁷ Therefore, the dust samples collected from the floor in this study reflected only one external exposure route, while hand wipes could give an integrated view on the external exposure, reflecting the adsorption of chemicals to the hand both through the gaseous phase and from contact with dust, e-waste, and electrical applications (such as phones, TVs, and air conditioners). However, no significant relationships were found between organic contaminants in the paired hand wipe samples and hair segments, which could be due to the small paired sample size (10 paired hand wipe and hair samples) or effects from the internal source of exposure.

This study found a linear accumulation ability of organic contaminants along the hair shaft from the scalp outward, and the $\log K_{OW}$ value is a good predictor of the accumulation rate of the contaminants along the hair shaft in future work. As the contributions of PCB-132 in hair through external sources

increased with the distance of the hair segment from the scalp, short haircuts and hats were recommended to decrease the external exposure among e-waste dismantling workers. In addition, wearing gloves was highly recommended because high concentrations of contaminants were found in the hand wipe samples. As this study found that inconsistent hair sampling methods would complicate the analysis of the temporal trend of contaminants, consistent methods for hair sample collection (such as the distance from the hair root, the length of hair, and the sampling position on the head) are recommended in international investigations when using hair as a biomonitoring matrix.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b05503.

Detailed descriptions of hair sample extraction and cleanup and a detailed description of instrumental analysis (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhengjing@scies.org. Phone: +86 20 29119884. Fax: +86 20 29119308.

*E-mail: adszyzy@mail.sysu.edu.cn. Phone: +86 20 84112008. Fax: +86 20 84112008.

ORCID

Jing Zheng: 0000-0003-0693-9839

She-Jun Chen: 0000-0002-7660-739X

Zhong-Yi Yang: 0000-0002-5187-3296

Bi-Xian Mai: 0000-0001-6358-8698

Notes

The authors declare no competing financial interest.

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