Insights into biomonitoring of human exposure to polycyclic aromatic hydrocarbons with hair analysis: A case study in e-waste recycling area

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ARTICLE INFO

ABSTRACT

In this study, 96 pairs of hair and urine samples were collected from e-waste (EW) dismantling workers of an industrial park, as well as residents living in surrounding areas. The concentrations of polycyclic aromatic hydrocarbons (PAHs) and hydroxylated PAH metabolites (OH-PAHs) were analyzed . The results show that concentrations of Σ_{15}PAHs ranged from 6.24 to 692 ng/g dry weight (dw) and Σ_{12}OH-PAHs from undetected to 187 ng/g dw in hair external (hair-Ex), and ranged from 31.7 to 738 ng/g dw and 21.6 to 1887 ng/g dw in hair internal (hair-In). There was no significant difference in exposure levels between EW dismantling workers and residents of the surrounding area. For the parent PAHs, the concentrations of Σ_{15}PAHs of hair-In were comparable with those of hair-Ex for all populations except for the child residents. On the contrary, for the OH-PAHs, the concentrations of Σ_{12}OH-PAHs of hair-In were 9–37 times higher than those of hair-Ex for populations. Moreover, the congener profiles of OH-PAHs of hair-In were different from those of hair-Ex, but similar to that of urine. Particularly, 3-OH-Bap, which is a carcinogenic metabolite, was only detected in the hair-In. These results indicate that OH-PAHs in hair-In, just like in urine, are mainly derived from endogenous metabolism and could be considered as reliable biomarkers for PAHs exposure. However, there was almost no significant correlations between hair-In and urine for OH-PAHs. This indicates that more attention should be paid to OH-PAHs when conducting PAHs exposure risk assessment using hair, which will help to obtain more reliable and comprehensive information on health risk assessments.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are associated with various cancers, inflammation and respiratory disease in humans (Koike et al., 2014; Luo et al., 2015; Podechard et al., 2008). Many studies have reported the levels of PAHs in various environmental media and accordingly assessed their exposure levels and human health risk. However, the equivalent exposure risk to humans may be overestimated or underestimated due to the differences in bioavailability and pharmacokinetic properties of the compounds (Calafat et al., 2005; Fent, 2004).

Over the last few decades, a series of reliable methods have been developed to assess the level and hazard for human PAHs exposure. For

instance, PAH–DNA adducts that form in white blood cells were used to estimate the biologically effective dose and genotoxic effects of PAHs (Demetriou et al., 2012; Yi et al., 2015). Urinary hydroxylated PAH metabolites (OH-PAHs) were used for human biomonitoring of PAHs exposure (Motorykin et al., 2015). However, the levels of PAHs and their blood or urine metabolites indicate only recent exposure due to the generally short half-lives of these compounds (Li et al., 2012). Recently, hair was introduced as a potential bioindicator to assess human exposure to PAHs owing to its stability, non-invasive collection and wider detection window.

Many studies have achieved and confirmed that human hair can be a useful indicator for evaluating the exposure to PAHs. Toriba et al. first developed a method for PAHs quantification in human hair and

subsequently reported the hair PAHs concentrations in smokers and non-smokers (Toriba et al., 2003). Since then, several studies have been done to investigate the association of PAHs concentration between the environment matrix and human hair (Hasei et al., 2011; Wang et al., 2013a; Wang et al., 2013b). OH-PAHs were first investigated in human hair by Schummer et al. (2009). Recently, both parent PAHs and their metabolites were simultaneously measured in human hair due to improved analytical sensitivity (Palazzi et al., 2019, 2018), which provides more comprehensive information on PAHs exposure and the human health risk. In addition, to confirm the incorporation of OH-PAHs in hair, rat models were established to analyze 52 OH-PAHs in hair after intraperitoneal administration of the corresponding 12 parent PAHs (Grova et al., 2013). The results found a linkage of the PAH metabolite levels between hair and urine in the rat models. This showed that the monitoring of OH-PAHs in urine and hair allows for the appraisal of internal PAH exposure on an animal model under controlled external exposure (Grova et al., 2018). However, the association between hair and urine needs to be further confirmed with human samples due to the differences in the species.

PAHs can be generated by anthropogenic activities, such as incomplete burning of coal, wood biomass and waste. The electronic-waste (EW) recycling and dismantling industry has been active in China since 1990s. A great variety of toxic chemicals, including PAHs, escape into the environment during the dismantling of EW. Within the EW dismantling areas, high concentrations of PAHs are present in the air, soil, sediments and biological samples, including fish muscle and human samples, such as human blood, placenta, breast milk, umbilical cord blood and urine (Asamoah et al., 2019; Shi et al., 2016; Wang et al., 2012; Xu et al., 2015, 2013; Yu et al., 2006; Zhang et al., 2011; Zheng et al., 2016). Moreover, human hair has been used to assess the exposure of polyhalogenated aromatic hydrocarbons in EW areas (Ma et al., 2011; Zhao et al., 2008; Zheng et al., 2011; Zheng et al., 2010), while little data is available on the simultaneous assessment of PAHs and its metabolites in hair samples from these areas.

In addition, the difference between external and internal exposure of PAHs and OH-PAHs in hair is still unclear. Researchers have made great efforts to develop washing procedures to differentiate between internal and external pollutants, which is the major difficulty for hair analysis. Recently, our research group developed a reliable method to separately measure the levels of compounds in hair external (hair-Ex) and hair internal (hair-In) (Lin et al., 2019).

In this study, pairs of human hair and urine samples were collected from an EW dismantling area. Parent PAHs (n = 16) and OH-PAHs (n = 12) in both external and internal hair, as well as 12 OH-PAHs in urine samples, were analyzed. The objective was to assess the levels and patterns of the PAHs and OH-PAHs in hair-Ex, hair-In and urine from different populations, namely workers at the EW dismantling industrial park and residents (including adults and children) of surrounding areas. To validate the utility of hair as a bioindicator of internal exposure to OH-PAHs, the levels and profiles of PAHs and OH-PAHs in hair-In were then compared with those in hair-Ex and urine using partial least squares discriminant analysis (PLS-DA) and Spearman correlation analysis.

2. Materials and methods

2.1. Sample collection

Pairs of hair and urine samples were collected from 96 people in an EW recycling area in South China. The participants included 27 EW workers who directly engaged in EW dismantling activities, 29 non-EW workers who engaged in other activities at the EW dismantling industrial park and 40 residents living in the surrounding area (21 adults, > 14 years old; and 19 children, ≤14 years old). A detailed description of the sampling site has been provided elsewhere (Chen et al., 2019). The study was approved by the Ethics Committee of South

China Normal University. Consent was also obtained from all participants after they were clearly informed about the purpose of this study. For each participant, a short questionnaire and general physical examination were conducted and their demographics are listed in Table S1. During routine haircut sessions, approximately 2–3 g of hair was cut and collected using stainless steel scissors; wrapped in aluminum foil; and then sealed in polyethylene zip bags. The morning urine samples were collected and stored in polyethylene bottles and the creatinine concentration of each urine sample was determined immediately. The collected urine and hair samples were transferred to the laboratory and kept at $-80\,°C$ until chemical analysis. The hair and urine collection were finished within two days.

2.2. Chemicals and reagents

Sixteen PAHs and five surrogate standards were obtained from AccuStandard Inc. (New Heaven, USA). Twelve OH-PAHs and five internal standards were purchased from AccuStandard Inc., Dr. Ehrenstorfer (Augsburg, Germany), Chiron AS (Trondheim, Norway) and Toronto Research Chemicals, Inc. (North York, Canada). Hexane (Hex), methyl tert-butyl ether (MTBE), dichloromethane (DCM), acetone, ethyl acetate (EtAc), acetic acid (HAc) and sodium acetate (NaAC) were purchased from CNW (Technologies GmbH). Methanol was obtained from Merck (Darmstadt, Germany). Other reagents of pesticide residue grade or HPLC grade were used without further purification. All other chemicals and reagents are shown in Supplementary Information Text S1.

2.3. Sample preparation and analysis

The extraction and cleanup procedures of hair-In, hair-Ex and urine samples are provided in our previous study (Fan et al., 2012; Lin et al., 2019).

The sixteen parent PAHs were analyzed by gas chromatography – triple quadrupole mass spectrometry (Shimadzu TQ8040, Kyoto, Japan) using electron impact ionization. PAHs were chromatographically separated with a DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent Technologies). The twelve OH-PAHs were analyzed using an Agilent 1260 Infinity II HPLC coupled with a 6470 triple quadrupole mass spectrometer. The HPLC was equipped with a G7116A MCT, a G7129A vial sampler, and a G7112B binary pump. A Poroshell 120 EC-C18 reversed-phase analytical column (100 mm × 4.6 mm i.d., 2.7 μm particle diameter, Agilent Technologies) was used to separate the different OH-PAHs. The detailed analytical parameters of the instruments are presented in Supplementary Information Text S2. The typical chromatograms of PAHs and OH-PAHs from hair-Ex and hair-In samples were shown in Supplementary Information Figs. S1 and S2.

2.4. Quality assurance and quality control

Instrumental quality control (QC) included injection of solvent blanks and standard solutions with every batch of 10 field samples. For the method QC, procedural blanks and spiked matrices were processed with every batch of 10 filed samples. The target analytes were confirmed at below 5% in the blanks. The recovery of the target compounds in the standard spiked samples was 64.3%-136% for PAHs (expect for Nap in hair), 86.7%-143% for OH-PAHs in hair and 49.0%-145% for OH-PAHs in urine. The recovery of the surrogate standards in filed samples was $86.3 \pm 21.1\%$ for acenaphthene-d$_{10}$, $90.1 \pm 18.3\%$ for phenanthrene-d$_{10}$, $70.0 \pm 23.6\%$ for chrysene-d$_{12}$ and $71.5 \pm 12.6\%$ for perylene-d$_{12}$. Concentrations that were lower than the limit of detection (LOD), or not detected, were assigned a value of zero. The concentrations of the target compounds in the field samples were not corrected by the recovery but the corresponding procedural blank within the same batch was subtracted. In this study, Nap will not

Table 1
Concentrations of parent PAHs in hair-Ex and hair-In (ng/g dw).

	EW workers (n = 27)		Non-EW workers (n = 29)		Adult residents (n = 21)		Children residents (n = 19)		Total (n = 96)			
	Hair-Ex Mean (rang)	Hair-In Mean (rang)	Hair-Ex Mean (rang)	Hair-In Mean (rang)	Hair-Ex Mean (rang)	Hair-In Mean (rang)	Hair-Ex Mean (rang)	Hair-In Mean (rang)	Hair-Ex Mean (rang)	Freq.[a]	Hair-In Mean (rang)	Freq.[a]
Acy	0.04 (0.03–0.10)	1.33 (0.36–4.49)	0.03 (0.03–0.05)	1.20 (nd-6.48)	0.03 (0.03–0.04)	0.83 (0.34–1.65)	0.03 (0.03–0.04)	0.37 (0.02–0.88)	0.03 (0.03–0.10)	100%	0.99 (nd-6.48)	99%
Ace	4.83 (1.41–13.6)	4.06 (2.10–10.5)	3.82 (2.52–5.79)	4.22 (2.33–21.6)	4.07 (1.91–8.87)	3.40 (2.12–6.20)	2.57 (0.57–4.64)	3.35 (1.50–4.96)	3.91 (0.57–13.62)	100%	3.82 (1.50–21.6)	100%
Flu	10.1 (nd[b]-32.3)	11.4 (6.96–22.1)	9.64 (0.39–18.9)	10.1 (7.38–18.1)	9.80 (3.57–26.5)	7.78 (4.25–11.2)	4.70 (nd-11.0)	6.89 (4.34–11.5)	8.83 (nd-32.3)	98%	9.31 (4.25–22.1)	100%
Phe	30.0 (1.77–115)	45.0 (12.5–94.2)	26.1 (3.05–95.1)	50.0 (17.9–149)	26.5 (3.27–64.9)	36.9 (13.0–70.1)	9.68 (0.30–55.2)	30.7 (6.94–76.3)	24.0 (0.30–115)	100%	41.9 (6.94–149)	100%
Ant	1.82 (nd-14.4)	2.12 (0.14–10.6)	2.59 (0.10–11.5)	3.48 (0.56–17.6)	2.36 (0.22–12.7)	4.19 (0.43–46.1)	0.36 (0.01–1.83)	1.12 (0.08–2.66)	1.88 (nd-14.4)	97%	2.79 (0.08–46.1)	100%
Flua	55.7 (4.46–181)	58.1 (9.71–131)	46.1 (1.91–159)	37.4 (5.36–203)	51.1 (10.8–155)	43.2 (2.73–133)	15.6 (0.78–61.8)	37.2 (9.46–80.4)	43.9 (0.78–181)	100%	44.4 (2.73–203)	100%
Pyr	44.2 (3.69–165)	53.5 (8.77–134)	44.9 (1.53–197)	34.2 (6.45–168)	41.8 (3.44–117)	38.8 (3.30–106)	13.1 (0.44–49.6)	30.5 (8.77–73.4)	37.7 (0.44–197)	100%	39.9 (3.30–168)	100%
BaA	8.14 (0.65–37.9)	4.78 (0.32–14.4)	5.95 (0.13–24.7)	3.80 (0.35–37.5)	6.30 (0.23–18.8)	3.67 (0.16–9.47)	2.65 (0.14–9.37)	3.81 (0.55–12.9)	5.99 (0.13–37.9)	100%	4.05 (0.16–37.5)	100%
Chr	15.7 (1.48–54.7)	8.73 (0.83–28.9)	9.39 (0.36–37.7)	6.91 (0.7–60.5)	12.7 (0.44–49.4)	7.70 (0.37–26.1)	5.83 (0.60–16.4)	9.88 (1.26–40.9)	11.2 (0.36–54.7)	100%	8.18 (0.37–60.5)	100%
BbF	10.1 (0.91–41.1)	3.58 (0.24–11.9)	4.94 (0.23–26.7)	2.37 (0.15–32.0)	6.50 (0.10–30.6)	2.21 (0.08–6.12)	3.80 (0.55–9.41)	3.24 (0.29–16.4)	6.50 (0.10–41.1)	100%	2.85 (0.08–32.0)	100%
BkF	2.62 (0.21–9.98)	0.95 (0.07–3.15)	1.22 (0.06–6.33)	0.61 (0.04–7.99)	1.57 (0.03–7.15)	0.56 (0.02–1.53)	0.93 (0.13–2.63)	0.81 (0.09–3.65)	1.63 (0.03–9.98)	100%	0.73 (0.02–7.99)	100%
BaP	3.18 (0.22–16.32)	1.43 (0.07–4.08)	1.86 (0.12–7.70)	0.82 (0.07–9.16)	2.11 (0.12–5.31)	0.89 (0.03–2.79)	0.88 (0.23–3.20)	0.87 (0.13–3.60)	2.09 (0.12–16.3)	100%	1.02 (0.03–9.16)	100%
IcdP	2.90 (0.33–12.8)	1.17 (0.07–2.75)	1.38 (0.10–6.51)	0.63 (0.03–8.66)	1.57 (0.15–5.61)	0.51 (0.02–1.53)	0.87 (0.28–2.38)	0.71 (0.04–2.95)	1.75 (0.10–12.8)	100%	0.77 (0.02–8.66)	100%
DBahA	0.72 (0.07–3.73)	0.27 (0.02–0.80)	0.33 (0.02–2.10)	0.12 (0.01–1.56)	0.35 (0.03–1.24)	0.11 (nd-0.26)	0.15 (0.06–0.42)	0.11 (0.01–0.43)	0.41 (0.02–3.73)	100%	0.16 (nd-1.56)	99%
BghiP	4.30 (0.52–22.5)	2.34 (nd-10.7)	2.29 (0.03–12.8)	1.10 (nd-15.4)	2.40 (0.17–8.23)	1.11 (0.05–2.85)	1.26 (0.18–4.26)	1.18 (0.03–5.28)	2.68 (0.03–22.5)	100%	1.47 (nd-15.4)	97%
Σ_{15}PAHs	194 (20.8–692)	199 (54.0–393)	161 (11.5–527)	157 (47.3–738)	169 (25.0–453)	152 (31.7–344)	62.5 (6.24–220)	131 (39.4–294)	153 (6.24–692)	100%	162 (31.7–738)	100%

Chemical abbreviation: acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), fluoranthene (Flua), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DBahA), benzo[ghi]perylene (BghiP) and indeno[1,2,3-cd]pyrene (IcdP).

[a] Freq.: frequency detection.

[b] nd: not detected.

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be discussed due to its relatively high volatility and bad recovery in all field samples.

2.5. Statistical analysis

The statistical differences in concentrations between different populations were assessed by the Mann-Whitney U test. A PLS-DA based on log-transformed data was performed to differentiate target analytes between hair-Ex from hair-In. Correlations between OH-PAH concentrations in hair and urine were also performed using Spearman correlation. During the statistical analysis, concentrations that were lower than the LOD, or not detected, were assigned a value of zero. A p-value < 0.05 was regarded as statistically significant.

3. Results and discussion

3.1. Concentrations of PAHs in hair

3.1.1. PAH levels and profiles in hair-Ex

Of the 15 PAHs, all were identified at a 100% detection frequency in hair-Ex for all subjects except for Flu and Ant (Table 1). The sum concentrations of the 15 PAHs (Σ_{15}PAHs) in hair-Ex for all subjects ranged from 6.24 to 692 ng/g dry weight (dw). The highest level in hair-Ex was found in EW workers ranging from 20.8 to 692 ng/g dw (mean value: 194 $\pm$ 167 ng/g dw), followed by adult residents, non-EW workers and child residents with mean values of 169 $\pm$ 122, 161 $\pm$ 128 and 62.5 $\pm$ 52.3 ng/g dw, respectively. There was no significant difference in the Σ_{15}PAH concentrations between the EW workers, non-EW workers and adult residents ($p > 0.05$), but the mean concentration of child residents was 2.5 to 3 times lower than that of other subjects ($p < 0.001$).

No significant difference was obtained in PAH congener profiles between the different populations (Fig. 1A). Flua was the most abundant PAH in hair-Ex accounting for 21%-29% of the Σ_{15}PAHs. The concentration of Flua in hair-Ex was 55.7 $\pm$ 50.2 ng/g dw for EW workers, 46.1 $\pm$ 36.9 ng/g dw for non-EW workers, 51.2 $\pm$ 42.0 ng/g dw for adult residents and 15.6 $\pm$ 15.0 ng/g dw for child residents. The Flua concentration in children was 3 times lower than that for the other groups ($p < 0.05$). The second and third most abundant PAHs in hair-Ex were Pyr and Phe, accounting for 18%-25% and 13%-18% of the Σ_{15}PAHs, respectively (Fig. 1A). Similarly, the concentrations of Pyr and Phe for child residents were approximately 3 times lower than

those for other populations.

The high PAH concentrations in hair-Ex observed for EW workers and non-EW workers might be ascribed to the EW dismantling process, whereas other sources of PAHs, such as vehicle emissions, smoking and cooking, may primarily contribute to the high levels of PAHs in hair-Ex of the adult residents. Child residents those had less external exposure may be due to their mostly indoor activities. These results are in agreement with previous work demonstrating that the atmospheric PAH concentrations at this EW dismantling industrial park and roadside were significantly higher than those in the resident area (Chen et al., 2019). However, in our previous studies of atmospheric samples at the EW dismantling area, Phe was the most abundant PAH congener, follow by Flua and Pyr (Chen et al., 2019, 2016), which is inconsistent with the hair-Ex results. This may be attributed to the lower octanol-air partition coefficient (K_{OA}) of Phe, which is likely to be present in the gaseous phase (Zhang et al., 2011). Furthermore, it should be mentioned that the PAH levels in hair-Ex vary with the hair washing frequency. Therefore, PAH levels of hair-Ex were associated with short-term direct atmospheric precipitation as well as the physico-chemical properties of the PAHs.

3.1.2. PAH levels and profiles in hair-In

The 15 PAHs were identified with a high detection frequency ranging from 97% to 100% in hair-In of all subjects (Table 1). The Σ_{15}PAHs concentration in hair-In of all subjects ranged from 31.7 to 738 ng/g dw. The mean concentrations of the different populations were 199 $\pm$ 86.7 ng/g dw for EW workers, 157 $\pm$ 125 ng/g dw for non-EW workers, 152 $\pm$ 72.3 ng/g dw for adult residents and 131 $\pm$ 74.3 ng/g dw for child residents. The mean concentrations of PAHs in hair-In was ordered as follows: EW workers > non-EW workers > adult residents > child residents. However, the difference in the Σ_{15}PAHs concentrations of hair-In for EW workers and adult residents were not significant ($p = 0.086$), which is consistent with the results of hair-Ex. This indicates that EW dismantling activity is not the only source of PAHs exposure in this EW dismantling area. For instance, vehicle emissions could also be an important contribution (Chen et al., 2019). However, the Σ_{15}PAHs concentrations of hair-In for the EW workers were significantly ($p < 0.05$) higher than those of non-EW workers. Our previous study also demonstrated that the total atmospheric PAHs concentration inside the EW workshop (where the EW workers are exposed) was higher than outside the EW workshop (where the non-EW workers are exposed) at the EW dismantling industrial park (Zhang
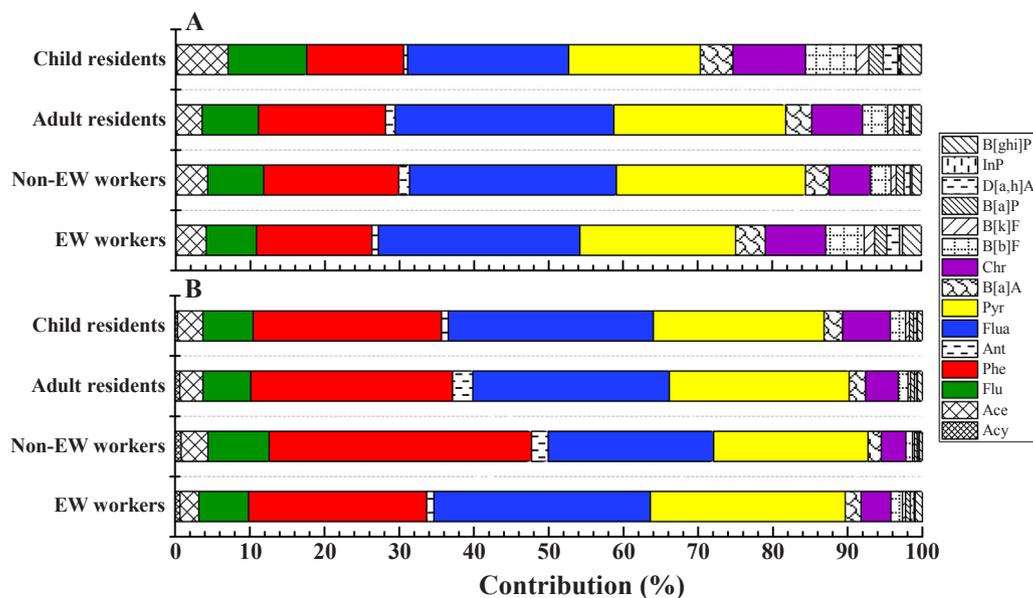

Fig. 1. Parent PAHs congener profiles in paired hair-Ex (A) and hair-In (B).

Table 2
Concentrations of OH-PAHs in hair-Ex and hair-In (ng/g dw).

	EW workers (n = 27)		Non-EW workers (n = 29)		Adult residents (n = 21)		Child residents (n = 19)		Total (n = 96)			
	Hair-Ex Mean (rang)	Hair-In Mean (rang)	Hair-Ex Mean (rang)	Hair-In Mean (rang)	Hair-Ex Mean (rang)	Hair-In Mean (rang)	Hair-Ex Mean (rang)	Hair-In Mean (rang)	Hair-Ex Mean (rang)	Freq.[a]	Hair-In Mean (rang)	Freq.[a]
1-OH-Nap	0.17 (nd[b]-2.56)	48.6 (nd-232)	7.01 (nd-54.9)	68.7 (2.62-204)	4.49 (nd-39.2)	141 (nd-1222)	0.94 (nd-9.92)	55.5 (7.91-190)	3.33 (nd-54.9)	41%	76.3 (nd-1221)	98%
2-OH-Nap	16.1 (nd-52.9)	175 (34.8-358)	19.1 (nd-116)	174 (15.1-631)	18.8 (nd-88.9)	181 (15.5-652)	1.21 (nd-14.6)	84.1 (35.2-249)	14.6 (nd-116)	66%	158 (15.1-652)	100%
2-OH-Flu	2.27 (nd-7.72)	18.6 (2.17-72.0)	2.30 (0.87-6.59)	13.0 (2.71-37.3)	2.22 (nd-6.45)	12.1 (2.69-33.2)	1.44 (0.83-2.80)	10.4 (3.89-28.8)	2.10 (nd-7.72)	95%	13.9 (2.17-72.0)	100%
3-OH-Flu	1.30 (nd-6.65)	17.0 (nd-71.8)	1.22 (nd-5.28)	11.6 (nd-30.4)	0.87 (nd-3.72)	9.50 (nd-26.6)	0.37 (nd-2.12)	8.61 (2.64-21.8)	1.00 (nd-6.65)	47%	12.1 (nd-71.8)	92%
2-OH-Phe	0.94 (nd-4.26)	6.40 (nd-20.6)	0.56 (nd-3.33)	4.89 (0.67-38.1)	0.65 (nd-2.49)	4.16 (0.14-16.7)	0.23 (nd-1.01)	4.83 (1.57-14.6)	0.62 (nd-4.26)	71%	5.14 (nd-38.1)	99%
3-OH-Phe	1.35 (nd-3.81)	5.94 (1.09-19.1)	0.98 (0.46-2.24)	4.36 (0.94-25.2)	1.06 (0.46-3.02)	4.35 (0.87-14.9)	0.71 (nd-1.67)	4.48 (1.80-12.4)	1.05 (nd-3.81)	98%	4.83 (0.87-25.2)	100%
4-OH-Phe	nd	0.70 (nd-5.64)	0.02 (nd-0.50)	0.83 (nd-4.93)	0.04 (nd-0.71)	1.39 (nd-10.4)	nd	1.05 (nd-4.85)	0.01 (nd-0.71)	4%	0.96 (nd-10.4)	64%
1/9-OH-Phe[c]	0.08 (nd-0.82)	3.31 (nd-14.1)	0.17 (nd-1.43)	2.34 (nd-7.60)	0.25 (nd-2.28)	3.69 (0.08-23.0)	0.06 (nd-0.75)	3.87 (0.80-12.7)	0.14 (nd-2.28)	27%	3.21 (nd-23.0)	98%
1-OH-Pyr	nd	2.94 (nd-9.60)	nd	3.05 (nd-14.4)	nd	1.88 (nd-11.9)	nd	1.94 (nd-7.76)	nd	0%	2.54 (nd-14.4)	91%
6-OH-Chr	nd	5.62 (nd-26.3)	nd	4.40 (nd-14.1)	nd	5.87 (nd-31.0)	nd	9.08 (nd-57.5)	nd	0%	5.99 (nd-57.5)	76%
3-OH-BaP	nd	2.47 (nd-33.2)	nd	2.06 (nd-13.4)	nd	1.51 (nd-10.1)	nd	1.73 (nd-12.8)	nd	0%	1.99 (nd-33.2)	41%
Σ_{12}OH-PAHs	22.2 (nd-71.6)	286 (56.8-596)	31.3 (1.32-187)	289 (32.2-873)	28.4 (0.71-131)	367 (21.6-1887)	4.95 (0.83-32.9)	186 (74.9-531)	22.9 (nd-187)	99%	285 (21.6-1887)	100%

Chemical abbreviation: 1-hydroxy-naphthalene (1-OH-Nap), 2-hydroxy-naphthalene (2-OH-Nap), 2-hydroxy-fluorene (2-OH-Flu), 3-hydroxy-fluorene (3-OH-Flu), 1-Hydroxy-phenanthrene (1-OH-Phe), 2-Hydroxy-phenanthrene (2-OH-Phe), 3-Hydroxy-phenanthrene (3-OH-Phe), 4-Hydroxy-phenanthrene (4-OH-Phe), 9-Hydroxy-phenanthrene (9-OH-Phe), 1-hydroxy-pyrene (1-OH-Pyr), 6-hydroxy-chrysene (6-OH-Chr) and 3-hydroxy-benzo[a]pyrene (3-OH-BaP).

[a] Freq.: frequency detection; [b] nd: not detected.

[c] 1/9-OH-Phe: both 1- and 9-OH-Phe could not be separated chromatographically and were quantified together.

et al., 2011). This suggests that the EW workers accumulate more PAHs in hair-In due to a long-term higher exposure than the non-EW workers at the EW dismantling industrial park.

Phe, Flua and Pyr were the three most dominant PAH congeners in hair-In, accounting for 24%-35%, 22%-29% and 21%-26% of the total PAHs, respectively (Fig. 1B). For Phe, the concentrations for EW workers and non-EW workers were 45.0 ± 21.6 and 50.0 ± 25.6 ng/g dw, respectively, which were significantly ($p < 0.05$) higher than the concentrations for adult and child residents (36.9 ± 14.7 and 30.7 ± 17.8 ng/g dw, respectively). For Flua and Pyr, the concentrations for EW workers were 58.1 ± 27.1 and 53.5 ± 28.1 ng/g dw, respectively, which were higher than those for non-EW workers (37.4 ± 35.9 and 34.2 ± 30.3 ng/g dw, respectively), adult residents (43.2 ± 27.7 and 38.8 ± 23.3 ng/g dw, respectively) and child residents (37.2 ± 23.5 and 30.5 ± 19.8 ng/g dw, respectively). These hair-In PAHs patterns were different from those in hair-Ex.

When comparing hair-In with hair-Ex, no significant difference was obtained in the concentrations of Σ_{15}PAHs between hair-Ex and hair-In of EW workers, non-EW workers and adult residents. However, the concentration of Σ_{15}PAHs in hair-In of child residents was two times higher than that in hair-Ex ($p < 0.05$). The PAHs congener profiles were also different between hair-In and hair-Ex (Fig. 1), although Phe, Flua, and Pyr were the major contributors to both hair-In and hair-Ex. Moreover, the contribution of 5- and 6-ringed PAHs in hair-Ex (7%–16%) were approximately four times higher than those in hair-In (2%–4%).

In this study, the pollutants in hair-Ex mainly arose from the deposition of atmospheric fine particles and dust that adsorb onto or imbed into the hair shaft. In contrast, pollutants that enter the human body through respiration and diet are incorporated into the hair by passive diffusion from blood capillaries into growing cells (Pragst and Balikova, 2006). Pragst and Balikova proposed that cell membranes can be an impermeable barrier that stops organic ions of medium molecular mass from easily diffusing into the matrix of hair cells (Pragst and Balikova, 2006). Grova et al. studied the excretion kinetics of orally administered ^{14}C-PAHs in lactating goats, detecting in the feces and urine 88.2% and 6.3% of the ingested ^{14}C-BaP (molecular weight 253), respectively, but only 25.5% and 11.4% of the ^{14}C-Phe (molecular weight 179), respectively (Grova et al., 2002). Therefore, high molecular weight PAHs may tend to be excreted in feces instead of being retained in the human body and diffusing into the hair. Wang et al. found that 5- and 6-ringed PAHs dominated the total PAHs of dust, but had low contributions to the total PAHs in human hair (Wang et al., 2013b). Similar results were found for the profile of polychlorinated biphenyls in hair (Shi et al., 2016). The contribution of highly chlorinated congeners in serum were higher than that in human hair, which also suggests that high molecular weight chemicals have difficulty diffusing into the hair matrix.

Many studies have reported on the PAH levels in human hair and also found that Phe, Flua, and Pyr were the dominant PAHs in different polluted areas (Palazzi et al., 2018; Toriba et al., 2003; Wang et al., 2013a, b). The Phe concentrations in women's hair from Baoding and Dalian, China (ranging from 54.2 to 889 ng/g dw and 4.20–348 ng/g dw, respectively) (Palazzi et al., 2018); smokers and non-smokers from Japan (ranging from 50.3 to 208 ng/g dw and 28.9–255 ng/g dw, respectively) (Toriba et al., 2003); and the general population from Guangzhou, China (ranging from 5.93 to 441 ng/g dw) (Wang et al., 2013b) were all found to be higher than the level of hair-In reported in our study (ranging from 6.94 to 149 ng/g dw). In addition, the results of those studies were higher than the sum levels of hair-In and hair-Ex of this study. This might suggest that the PAHs exposure levels in those areas were all higher than in the EW dismantling area of this study. However, for children's hair in France, relatively lower concentrations were observed for Phe, Flua and Pyr, ranging from 0.30 to 32.4 ng/g dw, 1.66–21.3 ng/g dw and 1.94–17.9 ng/g dw, respectively (Palazzi et al., 2019).

Thus, it was concluded that EW dismantling activity is not the sole source of PAHs at the EW dismantling area, and that the characteristic congener profile of PAHs in hair-Ex and hair-In are both associated with the exposure duration and physico-chemical properties of the PAHs.

3.2. The exposure concentration of OH-PAHs in hair

3.2.1. OH-PAH levels and profiles in hair-Ex

In hair-Ex, 2-OH-Flu and 3-OH-Phe were the most frequently detected species in 95% and 98% of all subjects, respectively, followed by 2-OH-Phe and 2-OH-Nap with the frequency detection of 71% and 66%, respectively (Table 2). In contrast, 1-OH-Pyr, 6-OH-Chr and 3-OH-BaP were never detected in hair-Ex. The sum concentrations of the 12 OH-PAHs (Σ_{12}OH-PAHs) in hair-Ex ranged from not detected (nd) to 187 ng/g dw (mean value: 22.9 $\pm$ 31.7 ng/g dw). The mean concentrations of Σ_{12}OH-PAHs in hair-Ex of EW workers, non-EW workers, adult residents and child residents were 22.2 $\pm$ 19.0, 31.4 $\pm$ 43.0, 28.4 $\pm$ 33.4 and 4.95 $\pm$ 7.61 ng/g dw, respectively. The concentration for child residents was significantly lower ($p < 0.05$) thanthat for other populations, which is in line with the results of the parent PAHs in hair-Ex. OH-PAHs can be produced from coal combustion, traffic emissions and biomass burning, as well as by secondary formation in the atmosphere (Lin et al., 2015). The high OH-PAH concentrations in hair-Ex of EW workers and non-EW workers could be attributed to the EW dismantling process; however, the high OH-PAH concentrations in hair-Ex of adult residents maybe from frequent exposure to other emission sources of OH-PAHs during their daily life.

For EW workers, non-EW workers and adult residents, 2-OH-Nap was the most abundant OH-PAH congener in hair-Ex, accounting for 58%, 42% and 48% of the Σ_{12}OH-PAHs, respectively (Fig. 2A). However, 2-OH-Flu was the most abundant OH-PAH congener in hair-Ex for child residents, accounting for 54% of the Σ_{12}OH-PAHs, while 2-OH-Nap only accounted for 7%. Therefore, the difference of OH-PAH profiles between child residents and other populations was significant. Nap, the most volatile and abundant PAH in the atmosphere, undergoes direct photo-oxidation to produce more hydrophilic oxygenated compounds (Zhang et al., 2012). Therefore, the high abundance of 2-OH-Nap in the hair-Ex of EW workers, non-EW workers and adult residents might be attributed to the higher frequency of occupational and outdoor exposure than the child residents.

3.2.2. OH-PAH levels and profiles in hair-In

Of the 12 OH-PAHs, 9 were identified at more than 90% detection frequency in hair-In (Table 2). Moreover, 2-OH-Nap, 2-OH-Flu and 3-OH-Phe were detected in 100%, while 1-OH-Pyr, 6-OH-Chr and 3-OH-BaP were detected in 91%, 76% and 41%, respectively, but were not detected in hair-Ex. The detection frequencies in hair-In were much higher than those in hair-Ex with the Σ_{12}OH-PAHs concentrations of all subjects ranging from 21.6 to 1887 ng/g dw (mean value: 285 $\pm$ 256 ng/g dw). The Σ_{12}OH-PAHs concentrations in hair-In of the EW workers, non-EW workers, adult residents and child residents were 286 $\pm$ 167, 289 $\pm$ 231, 367 $\pm$ 400 and 186 $\pm$ 126 ng/g dw, respectively, which were 9–37 times higher than the concentrations in hair-Ex. No significant differences were found in the OH-PAH concentrations of hair-In between EW workers, non-EW workers and adult residents.

The congener profiles of OH-PAHs were similar between the different populations (Fig. 2B). 2-OH-Nap was the most dominant PAH metabolite in hair-In, accounting for 47%-63% of the total OH-PAHs, with a mean concentration of 175 $\pm$ 98.0 ng/g dw for EW workers, 174 $\pm$ 160 ng/g dw for non-EW workers, 181 $\pm$ 152 ng/g dw for adult residents and 84.1 $\pm$ 54.6 ng/g dw for child residents. The second most dominant OH-PAH in hair-In was 1-OH-Nap, accounting for 16%-28% the total OH-PAHs, with a mean concentration of 48.6 $\pm$ 49.2, 68.7 $\pm$ 62.3, 141 $\pm$ 257 and 55.5 $\pm$ 52.4 ng/g dw for EW workers, non-EW workers, adult residents and child residents, respectively.

The standard deviations of the Σ_{12}OH-PAH concentrations of adult residents were much higher than other populations, which was attributed to the high standard deviation of 1-OH-Nap. This indicates a high dispersion degree for adult residents, thereby suggesting more complex sources of PAHs exposure for the adult residents, which may be associated with their job diversity. However, EW workers engaged in professional EW dismantling activities and the child residents attended school, explaining the lower standard deviations for their OH-PAH concentrations.

Limited studies are available on OH-PAHs determination in human hair. Although there are few studies to report the levels of PAH metabolites in human hair, low positive detection rates were obtained in earlier studies due to limited analytical sensitivity (Appenzeller and Tsatsakis, 2012; Schummer et al., 2009). The most abundant congener was observed for 2-OH-Nap in the hair of Chinese women (ranging from
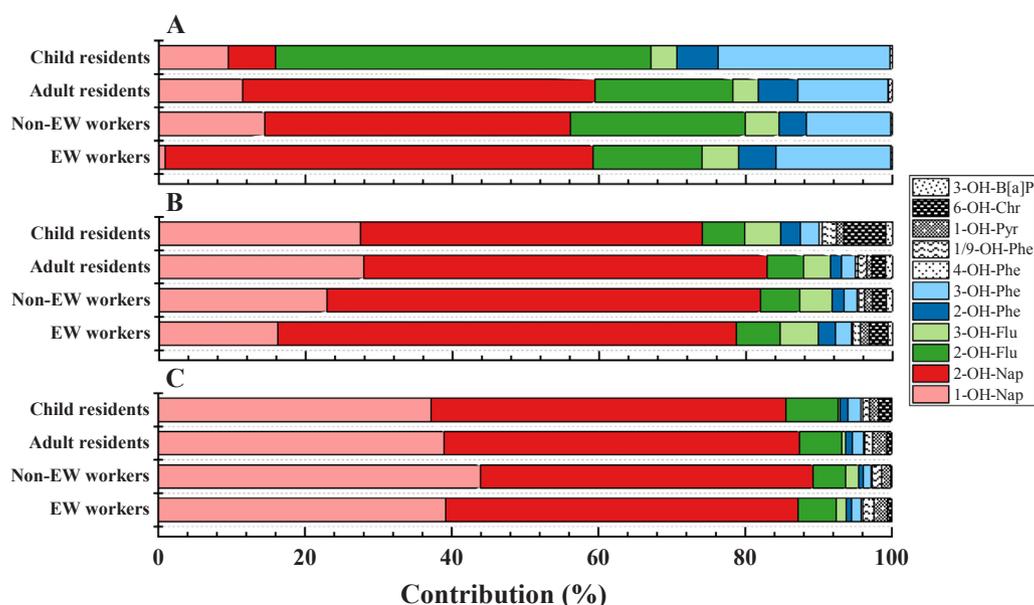

Fig. 2. OH-PAHs congener profiles in paired hair-Ex (A), hair-In (B) and urine (C).
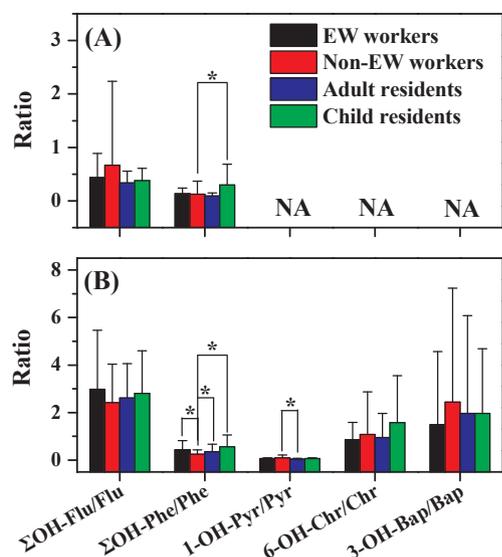
Fig. 3. The ratios of OH-PAH to parent PAH in hair-Ex (A) and hair-In (B). (NA represents date not available due to the zero detection of 1-OH-Pyr, 6-OH-Chr and 3-OH-Bap in hair-Ex; ΣOH-Flu = 2-OH-Flu + 3-OH-Flu; ΣOH-Phe = 1/9-OH-Phe + 2-OH-Phe + 3-OH-Phe + 4-OH-Phe; * means significant difference between two groups at the 0.05 level).

0.68 to 811 ng/g dw, mean of 29.53 ng/g dw) (Palazzi et al., 2018) and French children (ranging from 1.94 to 9.39 ng/g dw) (Palazzi et al., 2019). These reported concentrations were lower than the 2-OH-Nap level of hair-In in the present work, which ranged from 15.1 to 652 ng/g dw (mean of 158 ng/g dw).

When comparing hair-Ex with hair-In, significant differences in concentrations and congener profiles of OH-PAHs were obtained. The ratios of OH-PAH to parent PAH were also significantly different between hair-Ex and hair-In (Fig. 3). The ratios of ΣOH-Flu/Flu and ΣOH-Phe/Phe for hair-In were 2.69 ± 1.92 and 0.38 ± 0.37, respectively, which were higher than those for hair-Ex (0.47 ± 0.92 and 0.15 ± 0.24, respectively). The ratios of 1-OH-Pyr/Pyr, 6-OH-Chr/Chr and 3-OH-Bap/Bap for hair-Ex were not available due to the zero detection frequencies of 1-OH-Pyr, 6-OH-Chr and 3-OH-Bap; however, their ratios for hair-In were 0.06 ± 0.07, 1.09 ± 1.48 and 1.97 ± 3.86, respectively. Therefore, the sources of OH-PAHs in hair-In were different from those in hair-Ex. Moreover, that the ratios of ΣOH-Flu/Flu, 6-OH-Chr/Chr and 3-OH-Bap/Bap in hair-In were greater than 1, and were comparable for the different populations. This suggests that a relative persistence of OH-Flu, 6-OH-Chr and 3-OH-Bap occurs in the human body. Therefore, the OH-PAHs of hair-In, especially the carcinogenic metabolite 3-OH-Bap, may provide some insights when investigating the major human health risks from long-term PAHs exposure.

Using the parent and metabolite PAH concentrations, our previously developed partial least-squares discriminant analysis (PLS-DA) method was used to separate chemicals of hair-Ex and hair-In (Fig. 4A). As shown in Fig. 4B, all OH-PAHs were located on the right side of the chart, which indicates a positive correlation with the internal exposure of hair. Furthermore, the value of variable importance of each OH-PAH for the projection was greater than 1 (Fig. S3), which further suggests that OH-PAHs can be considered as contributors to the internal exposure of hair. In other words, the OH-PAHs in hair-In were mainly derived from endogenous metabolism. Above all, it could be concluded that OH-PAHs are more reliable biomarkers than parent PAHs when hair is used as an indicator for PAHs exposure assessment.

3.3. OH-PAH levels and profiles in urine

Urine has been frequently used to measure OH-PAHs for PAHs exposure assessment due to the strong water solubility of OH-PAHs. Table S2 provides the levels of each OH-PAH in the paired urine samples, which are adjusted by the concentration of urinary creatinine. 1-OH-Nap, 2-OH-Nap, 2-OH-Flu, 2-OH-Phe and 3-OH-Phe had the highest detection frequency in 100% of the samples, follow by 1-OH-Pyr (98%) and 1/9-OH-Phe (97%), while 3-OH-BaP was not detected in all urine samples. The levels of Σ_{12}OH-PAHs of all subjects ranged from 0.52 to 155 µg/g creatinine, with a mean value of 31.5 ± 33.3 µg/g creatinine. The mean Σ_{12}OH-PAH concentrations in urine were 39.1 ± 38.5 µg/g creatinine for EW workers, 30.7 ± 22.9 µg/g creatinine for non-EW workers, 33.3 ± 37.0 µg/g creatinine for adult residents and 22.1 ± 31.2 µg/g creatinine for child residents. No significant difference was observed in the urinary Σ_{12}OH-PAH concentrations between the different populations ($p > 0.05$), except between the EW workers and child residents. This was similar to the results of hair-In, in that no significant differences in the Σ_{12}OH-PAH concentrations were found between EW workers and non-EW workers and adult residents.

The congener profiles of urinary OH-PAHs were similar between the different populations (Fig. 2C). 2-OH-Nap was the predominant congener making up 45%-49% of the Σ_{12}OH-PAH concentrations, with a mean concentration of 17.6 ± 15.0 µg/g creatinine for EW workers, 15.0 ± 12.3 µg/g creatinine for non-EW workers, 16.4 ± 18.7 µg/g creatinine for adult residents and 10.6 ± 12.7 µg/g creatinine for child residents. 1-OH-Nap accounted for 37%-44% of the Σ_{12}OH-PAH concentrations, with a mean concentration of 16.4 ± 19.4, 13.5 ± 11.0, 14.3 ± 17.4 and 9.55 ± 20.0 µg/g creatinine for EW workers, non-EW workers, adult residents and child residents, respectively.

When comparing urine with hair, the profiles of OH-PAHs in urine were similar to those in hair-In, but different from those in hair-Ex. However, more PAH metabolites were detected in hair-In than in urine, including the carcinogenic metabolite 3-OH-Bap. This further indicates that the OH-PAHs in hair-In, just like in urine, are derived from the endogenous metabolism of parent PAHs.

3.4. The relationship between the OH-PAHs of hair-In and urine

The concentrations of Σ_{12}OH-PAHs were not significantly correlated between the hair-In and urine of EW workers (r = -0.156, p = 0.438), non-EW workers (r = 0.356, p = 0.063), adult residents (r = 0.359, p = 0.120) and child residents (r = 0.087, p = 0.724) (Table 3). For 2-OH-Nap, moderate positive correlations were found between hair-In and urine of non-EW workers (r = 0.403, p = 0.034) and adult residents (r = 0.374, p = 0.104), but only the correlation for non-EW workers was significant. The concentrations of 2-OH-Nap also insignificantly correlated between the hair-In and urine of both EW workers and child residents. Furthermore, for the rest of the individual OH-PAH concentrations, there was no significant correlation observed between hair-In and urine for the different populations (r = −0.382-0.376, p > 0.05). This might suggest differences in the biotransformation and enrichment behaviors of OH-PAHs between hair-In and urine, although the OH-PAHs of hair-In and urine are both from the endogenous metabolism of parent PAHs.

Many studies have reported that parent PAHs experience two phases of biotransformation after entering the human body (Grover, 1986). During phase I, the parent PAHs are metabolized into OH-PAHs. Then, they are rapidly detoxified to glucuronide and sulfate conjugates during phase II. The later metabolites are mostly excreted in urine and feces (Ramesh et al., 2004). Gaudreau et al. found that PAH metabolites were excreted either as free compounds or in conjugated form, with the later accounting for more than 90% of the total OH-PAH in urine samples (Gaudreau et al., 2016). Additionally, Schummer et al. suggested that hair does not contain or only contains a negligible level of
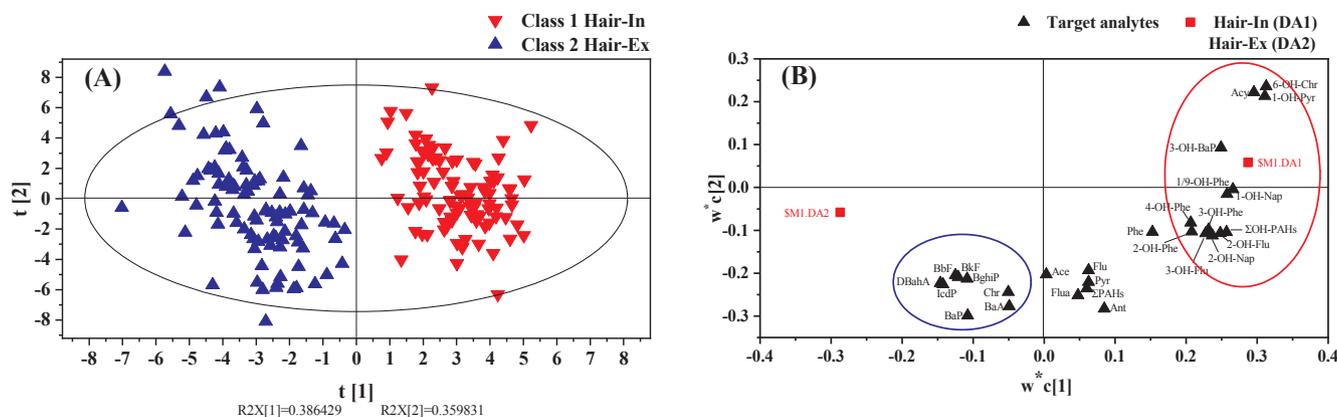
Fig. 4. Plot of PLS-DA model. (A) First and second score plot of PLS-DA for external exposure and internal exposure of hair according to the concentrations of parent PAHs and OH-PAHs; (B) Loading plot obtained using Pareto scaling.

glucuronidated metabolites when compared to hydroxylated compounds (Schummer et al., 2009). Therefore, the OH-PAHs in hair-In were probably from phase I metabolism.

Moreover, the concentrations of OH-PAHs in urine only represent recent exposure due to the short half-lives of OH-PAHs in human body. For example, the half-life of urinary 1-OH-Pyr in humans is estimated to be 6–35 h (Jongeneelen et al., 1990). The half-life of 2-OH-Nap is in the range of 4.9–12.2 h, and 2- and 3-OH-Flu have half-lives of 4.1 $\pm$ 1.1 h and 8.2 $\pm$ 4.1 h, respectively (St Helen et al., 2012). Moreover, urine samples are generally taken randomly, which is influenced by short-term variations in exposure. Li et al. investigated the variability of PAH metabolite concentrations in urine in the general population and the results showed that the within-week variability was 41%-60% and the within-day variability was 60%–84% (Li et al., 2010). Conversely, hair reflects long-term exposure due to its low growth rate and continuous incorporation into the hair shaft. The level in hair-In represents an average level of PAH exposure for a period. Therefore, the OH-PAH concentrations in urine did not match those in hair-In, resulting in a weak or non-significant correlation between urine and hair.

Similar results have been reported in hair and urine or other internal tissues. Grova et al. detected 26 OH-PAHs in hair and 33 OH-PAHs in urine using a rat model and found that only 3-OH-Chr presented a significant correlation ($p < 0.001$) between hair and urine (Grova et al., 2018). Sauve et al. found only a weak positive correlation in cortisol levels between hair and 24-hour urine of humans ($r = 0.33$, $p = 0.041$) (Sauve et al., 2007).

Above all, the OH-PAHs of hair-In and urine reflect different toxicokinetic processes, which could be significant for exposure risk assessment of human health. For long-term exposure risk assessment, the OH-PAHs in hair-In are a more reliable species than the OH-PAHs in

urine for use as biomarkers for PAHs biomonitoring.

4. Conclusion

The present study analyzed the concentrations and exposure patterns of both PAHs and their hydroxylated metabolites in hair-Ex, hair-In and urine. Irrespective of the sample (hair-Ex, hair-In or urine) the concentrations of both Σ_{15}PAHs and Σ_{12}OH-PAHs of EW workers were comparable to those of non-EW workers and adult residents ($p > 0.05$). There were multiple sources of PAHs at this EW dismantling area, and the concentrations and congener profiles of the parent PAHs in hair-Ex were similar to those of hair-In for all populations, except for the child residents. Significant differences were found in the concentrations and congener profiles of OH-PAHs between hair-Ex and hair-In of all populations. Moreover, the OH-PAH congener profiles of hair-In and urine pairs were similar, suggesting that OH-PAHs are mainly derived from endogenous metabolism and are reliable biomarkers for hair analysis. Additionally, no significant correlations of OH-PAH concentrations between hair-In and urine were found for PAHs, which could be attributed to the difference in the representative exposure duration and biotransformation processes of OH-PAHs between hair-In and urine. These results suggest that more attention should be paid to metabolic compounds when conducting hair analysis. Finally, the toxicokinetic characteristics of OH-PAHs in hair-In need to be further confirmed and clarified, which will help to establish a more comprehensive PAHs exposure risk assessment system.

CRediT authorship contribution statement

Meiqing Lin: Formal analysis, Methodology, Writing-original draft.

Table 3
Pearson correlation coefficients between for OH-PAH in hair-In and urine (levels of compounds were log-transformed and standardized beforehand).

	EW workers		Non-EW workers		Adult residents		Child residents	
	r	p	r	p	r	p	r	p
1-OH-Nap	−0.026	0.899	0.376	0.090	0.251	0.286	0.007	0.977
2-OH-Nap	−0.146	0.468	0.403	0.034	0.374	0.104	0.104	0.670
2-OH-Flu	0.127	0.528	0.320	0.097	0.150	0.527	−0.163	0.504
3-OH-Flu	0.072	0.720	0.0119	0.548	0.266	0.257	0.157	0.522
2-OH-Phe	0.198	0.323	0.237	0.224	−0.364	0.115	−0.292	0.225
3-OH-Phe	0.063	0.753	0.166	0.397	0.057	0.811	0.124	0.614
4-OH-Phe	0.257	0.195	0.040	0.839	−0.382	0.097	0.017	0.946
1/9-OH-Phe [a]	−0.063	0.753	0.013	0.947	0.129	0.587	−0.354	0.137
1-OH-Pyr	0.203	0.310	0.096	0.626	−0.173	0.467	0.073	0.767
6-OH-Chr	−0.237	0.233	0.138	0.483	0.321	0.168	0.287	0.234
Σ_{12}OH-PAHs	−0.156	0.438	0.356	0.063	0.359	0.120	0.087	0.724

[a] 1/9-OH-Phe: both 1- and 9-OH-Phe could not be separated chromatographically and were quantified together.

Jian Tang: Formal analysis, Methodology . **Shengtao Ma:** Methodology, Data curation. **Yingxin Yu:** Visualization, Investigation. **Guiying Li:** Writing - review & editing. **Ruifang Fan:** Validation. **Bixian Mai:** Supervision. **Taicheng An:** Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A

Supplementary material

Appendix B. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2019.105432.

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