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PAHs and their hydroxylated metabolites in the human fingernails from e-waste dismantlers: Implications for human non-invasive biomonitoring and exposure☆

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ABSTRACT

Non-invasive human biomonitoring methods using hair and fingernails as matrices are widely used to assess the exposure of organic contaminants. In this work, a total of 72 human fingernails were collected from workers and near-by residents from a typical electronic waste (e-waste) dismantling site, and were analyzed for human exposure to polycyclic aromatic hydrocarbons (PAHs) and their mono-hydroxyl metabolites (OH-PAHs). The concentrations of PAHs and OH-PAHs were obtained as 7.97–551 and 39.5–3280 ng/g for e-waste workers (EW workers), 7.05–431 and 27.3–3320 ng/g for non-EW workers, 7.93–289 and 124–779 ng/g for adult residents, and 8.88–1280 and 181–293 ng/g for child residents, respectively. The composition profiles of PAHs in the human fingernails of the four groups were similar, with isomers of Phe, Pyr and Fluo being the predominated congeners, while 2-OH-Nap accounted for more than 70% of the total OH-PAHs. These contaminants were found most in the fingernails of EW workers, followed by non-EW workers, adult residents, and child residents, indicating e-waste dismantling activities are the major sources of PAH exposure. However, significantly higher levels of PAHs with 4–6 rings were observed only in workers as opposed to the residents, and a significant correlation between 3-OH-Flu ($p < 0.05$) and 2-OH-Phe ($p < 0.01$) in the fingernails and urine was observed, but no significant correlation was found between the concentration of OH-PAHs in matched hair and fingernail samples. In addition, the levels of PAHs in fingernails increased with the age of EW workers. This is the first study to explore the accumulation and distribution of PAHs and OH-PAHs in human fingernails, which would provide valuable insight into non-invasive biomonitoring and health risk assessment of PAHs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous carcinogens, widely distributed in various matrixes such as air and dust, soil and sediment (Li et al., 2008). It is also claimed that they and their metabolites, are present in biotas such as fish (Baali et al., 2016) and cow (Zhu et al., 2019), as well as in human biological samples such as breast milk (Wang et al., 2018a) and urine (Guo et al., 2013). PAHs are hydrocarbons that contain multiple aromatic rings, and they are primarily emitted by anthropogenic activities related to the incomplete combustion of organic matter (Chen et al., 2019a). In general, humans' exposure to PAHs is associated with inhalation of atmospheric and particulate matter, dietary intake, and dermal absorption of soil/dust particles (Urbancova et al., 2017). After absorption, PAHs are metabolized in a

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number of organs to form free hydroxyl metabolites (OH-PAHs), which further react with glucuronic acid or sulfate, and subsequently increase water solubility and enhance renal excretion (Peng et al., 2020). The exposure to PAHs has been linked with a variety of human health problems, such as atherosclerosis (Hu et al., 2018) and lung cancer (Zhang et al., 2009). Khosravipour and Khosravipour (2020) suggested that there was a significant probability of a connection of urinary levels of OH-PAHs with diabetes. Poursafa et al. (2018) found that OH-PAHs in urine could possibly explain, in part, the association of obesity with cardiometabolic risk factors in children.

Due to the negative effects of PAHs, human biomonitoring is very important for assessing body burden, as well as the potential health risk related to PAH exposure. Since PAHs have a short half-life in the human body (Li et al., 2010), urinary concentrations of OH-PAHs have been commonly used to indicate body burden, especially in large-scale cohort studies. For example, the urinary concentrations of OH-PAHs were included in the National Health and Nutrition Examination Survey (NHANES), which was used to establish national reference levels for the US population, and to set benchmarks for future biomonitoring studies and epidemiological research (Li et al., 2008). OH-PAHs in urine samples from Asian countries were also detected and counted early (Guo et al., 2013). Urine is currently the preferred matrix used for the assessment of body burden of PAHs. However, as a biological sample, urine has several drawbacks. It needs to be stored at a strict temperature of −20 °C, or lower, to prevent the degradation of some target contaminants, which makes both sample storage and transportation problematic (Gaudreau et al., 2016). In addition, urinary creatinine is often used as a calculation basis for urine analytes, and needs to be measured quickly before it breaks down (Feldt et al., 2014). Urine can also be used as a spot sample to indicate metabolic rate in the human body, and the daily and even hourly fluctuations of urinary OH-PAHs have been measured (Li et al., 2010). It may be inaccurate to use instantaneous urinary levels to assess long-term body burden, as such levels are more susceptible to changes in body conditions.

Other non-invasive solid biological matrices, such as hair and nails, which could overcome the disadvantages of the storage and transportation of urine samples, have gained increasing attention recently (Alves et al., 2014). In contrast to urine, hair and nails give an average concentration of exposure over time and are not susceptible to short-term variations (Alves et al., 2016). In addition, hair and nails have a memory effect that can be used to trace the exposure characteristics of individuals over time (Esteban and Castano, 2009). Our previous work found that PAHs and OH-PAHs, which were widely detected in hair samples, especially PAHs metabolites that can be well protected from exogenous interference, can be used as the preferred indicators for long-term exposure to PAHs. Such an indicator might have fascinating consequences for human exposure monitoring (Lin et al., 2020). Qiao et al. (2019) have found a linear increase in concentrations of organic flame retardants along the hair shaft, with significant differences between each segment. Several studies also reported significantly higher concentrations of organic contaminants in women's hair than in men's, which were mostly attributed to greater exogenous exposure (He et al., 2017).

As a supplement to the hair, nails are less likely to show individual differences between genders or lengths. Nail growth is a continuous process that occurs throughout life, ranging from 0.05 to 1.2 mm per week (for human fingernails), and thus provides a long integration period for organic pollutants (Pan et al., 2020). The use of fingernail as an indicator of human exposure to heavy metals and drugs has long been recognized (Pan et al., 2020). However, there have been only few recent works using fingernails to assess the body burden of organic pollutants. For example, Liu et al. (2016) successfully detected several typical contaminants such as brominated and organophosphate flame retardants in paired nail and hair samples, and significant correlations between the concentrations of polybrominated diphenyl ethers (PBDEs) in hair and nail were observed with matched serum samples. Chen et al. (2019b) explored the relationship between concentrations of PBDEs, alternative flame retardants (AFRs) and organophosphate esters (OPEs) in paired samples of indoor dust and nails, and the results indicated that the content of PBDEs in male fingernails was significantly higher than that in female fingernails, while no gender-related differences were found for AFRs and OPEs. In fact, the accumulation and distribution characteristics of PAHs and their metabolites in nails have not been attempted yet until now.

In this study, 16 PAHs and 12 OH-PAHs were investigated in 72 human fingernail samples from a typical e-waste dismantling site. The fingernail samples were paired with previously analyzed hair and urine samples (Lin et al., 2019, 2020), which were collected at the same time. As a part of our ongoing research on the exposure to the organic contaminants from e-waste dismantling activities, the following aspects were studied. First, a new method was established for the simultaneous analysis of PAHs and OH-PAHs in human fingernail samples. Then, the concentration levels and pollution profiles of PAHs and OH-PAHs in the fingernails of workers exposed to e-waste and the residents who lived near the e-waste facilities were evaluated. Potential sources of these contaminants, and possible relationships between parental PAHs and their metabolites were also attempted. Finally, the accumulation and distribution of PAHs and OH-PAHs in matched human fingernail/hair/urine samples were also explored to gain insight into the potential markers for exposed groups.

2. Materials and methods

2.1. Characterization of the study population

Human fingernail samples were donated by 72 volunteers at a typical e-waste dismantling site, including 36 e-waste workers (EW workers), 16 non-EW workers, 14 adult residents not engaged in e-waste disposal (adult residents), and 6 child residents. Non-EW workers refer to those working in the vicinity but not directly involved in e-waste disposal, i.e., factory owners, security guards, cleaners etc. The study was approved by the Ethics Committee of Guangdong University of Technology, and all subjects agreed to the study after being informed of its purpose. A short questionnaire and a routine physical examination were carried out during sampling; volunteers' basic information is shown in Table S1. The questionnaire included questions about smoking (or secondhand smoke) and recent consumption of grilled food.

2.2. Sample collection

Human fingernail samples were cut with stainless steel clippers, and were then individually wrapped in aluminum foil, and stored at −20 °C in polyethylene zip-lock bags until the analysis. In order to avoid cross-contamination during sampling, the cutting edge of the stainless-steel nail clipper will be wiped clean by cotton ball soaked in isopropanol before use. The weights of fingernail samples donated by volunteers ranged from 0.0123 to 0.2793 g, with a median weight of 0.0658 g.

2.3. Chemicals and reagents

Sixteen PAH standards, five PAH surrogate standards, twelve OH-PAH standards and five OH-PAH internal standards were used

as same as those in our previous study (Lin et al., 2019). N-hexane (HEX), acetone, ethyl acetate (EtAc), dichloromethane (DCM) and methyl tert-butyl ether (MTBE) were purchased from CNW Technologies (Düsseldorf, Germany), and methanol of high-performance liquid chromatography (HPLC) grade was supplied by Merck KGaA (Darmstadt, Germany). Purified water (18.25 mΩ) was freshly prepared in our lab. Solid phase extraction (SPE) cartridges packed with silica gel (CNWBOND-Si, 1 g/6 mL) were purchased from CNW Technologies (Düsseldorf, Germany). Anhydrous sodium sulfate (previously baked at 450 °C for cleaning) was purchased from Sinopharm Chemical Reagent (Shanghai, China).

2.4. Sample preparation

2.4.1. Washing procedures

Fingernail samples with suitable levels of external contaminants were subjected to different washing procedures, in order to determine an acceptable washing solvent for the elimination of exogenous pollutants. Five identical mixed fingernail samples (0.1 g) were washed with acetone, ethyl acetate, dichloromethane, n-hexane, and water, respectively. The specific washing process was as follows: fingernail samples were cleaned ultrasonically three times for 5 min, using 5 mL of each solvent. A similar mixture of fingernail samples was not washed, as a control. After the washing process, all of the nail samples were kept under a fume hood for 2 days. The air-dried fingernail samples were scanned with an X-ray fluorescence (XRF) spectrometer (magnified 80 times). It can be seen that acetone washing causes little damage (preventing the endogenous compounds from escaping) to the fingernails (Fig. S1). Thus, the acetone washing solutions were further analyzed separately to identify PAHs and OH-PAHs. The same methods used for the quantitative analysis of endogenous PAHs and OH-PAHs were applied for washing extracts. Most of these PAH isomers were nondetectable in the solution used for the third wash, and only negligible amounts were detected with proportions less than 2% (Fig. S2). Except for 2-OH-Nap, the concentrations of OH-PAHs were below the detection limit in all the cleaning solutions, indicating that acetone cleaning could effectively remove exogenous pollutants and retain the endogenous components with little loss.

2.4.2. Pretreatment procedures

The extraction and cleanup procedures for fingernail samples are similar to our previous study with minor change (Lin et al., 2019). In brief, after being cut it into pieces, fingernail samples were digested using 5 mL of 1 M NaOH at 40 °C for 12 h. The resulting digestion mixture was liquid-liquid extracted twice with 5 mL of HEX: MTBE (v/v, 1:1). The upper organic phase was collected and combined, and then 3 mL of 2 M HCl was used for the acidification of the extract mixture. Then the liquid-liquid extraction was repeated twice. The combined organic extract was washed with 1% KCl solution, and 5 mL of HEX was used to extract targets from the washed KCl solution twice. Then all of the organic phases were combined and concentrated to 1 mL, and passed through a 1 g silica gel solid phase extraction cartridge for separation of OH-PAHs from target PAHs. The SPE cartridge was preconditioned with 6 mL of EtAc, 6 mL of DCM and 12 mL of HEX. The first fraction containing PAHs was eluted with 10 mL of 5% EtAc in HEX, which was finally condensed into 50 μL of isooctane before adding internal standard (10 ng of hexamethylbenzene). The second fraction containing OH-PAHs was eluted with 10 mL of 50% EtAc in HEX, and concentrated to 200 μL of MeOH. Both were refrigerated in a 4 °C freezer before instrumental analysis. PAHs in the first fraction were analyzed using gas chromatography-tandem mass spectrometry (GC-MS/MS), and OH-PAHs in the second fraction were analyzed using liquid chromatography-tandem mass spectrometry (LC-MS/MS). Full details about the instrument set-up were given in our previous paper (Lin et al., 2019).

2.5. Quality assurance and quality control

A procedural blank and a spiked matrix sample were processed with every batch of 10 samples. The matrix sample was a mixed nail digestion solution made from nail samples of our lab colleagues. An aliquot of 0.1 g fingernail extract was spiked with 5 ng of PAHs, 50 ng of 2-OH-Nap, 10 ng of 1-OH-Nap and OH-Flu, as well as 5 ng of other OH-PAHs isomers. The recovery of PAHs and OH-PAHs from the spiked samples were 58%–107% and 50%–98%, respectively. The recovery of the surrogate standards in fingernail samples was 84.2 ± 19.5% for acenaphthene-d_{10}, 88.1 ± 16.1% for phenanthrene-d_{10}, 74.0 ± 22.1% for chrysene-d_{12} and 72.4 ± 14.8% for perylene-d_{12}, respectively. For the procedure blank, nail samples were replaced with anhydrous sodium sulfate and run through all the analytical procedure performed. The target PAHs were confirmed at less than 5% in the blank samples for those isomers with 2–3 rings and were blank-corrected, while OH-PAHs and PAHs with 4–6 rings were below the instrumental detection limits. For compounds that couldn't be detected, or with levels lower than the limit of detection (LOD), their concentrations were assigned a value of zero.

To check the stability of instrument response, 5 ng/mL of standard solution with each batch of 15 samples was injected. Eight level points for PAHs with the concentrations ranging from 10 to 3000 ng/mL were used to fit the calibration curve. Another 10-level point calibration curve for OH-PAHs included the concentrations in the range of 50–2500 ng/mL for 2-OH-Nap, 10–500 ng/mL for 1-OH-Nap and 2-OH-Flu, and 5–250 ng/mL for 5-OH-Phe, 1-OH-Pyr, 6-OH-Chr and 3-OH-BaP. As a result, the regression coefficients were all > 0.99. Information on LOD, limit of quantification (LOQ), method precision and accuracy are all shown in Table S2.

2.6. Statistical analysis

Since the concentration of the target compounds was not normally distributed, it was analyzed in relation to the concentration of samples and the age of subjects, using Spearman correlation and Pearson correlation, respectively. A Mann-Whitney *U* test was used to determine the existence of statistical differences between different populations. The statistical analysis was performed by SPSS version 13.0 software. A value of $p < 0.05$ was regarded as statistically significant. Compounds with a detection rate greater than 30% were included in the statistical analysis.

3. Results and discussion

3.1. Concentrations and composition profiles of PAHs in human fingernails

The median concentrations, ranges and detection frequencies (DFs) of PAHs in human fingernail samples are given in Table 1, showing that PAHs can be detected in all the fingernail samples, with DFs larger than 50% for most of target PAHs except for Ace (37%) and Flue (48%). For those 4–6 rings PAHs, the DFs of Fluo, Pyr, Chr, B[b]F, B[a]P and B[ghi]P were higher than 80%. In addition, the DFs of 4–6 rings PAHs were usually the highest in EW workers, followed by non-EW workers, and the lowest in adult residents. The total concentrations of 16 PAHs (∑PAHs) in fingernails ranged from 7.05 to 1280 ng/g, with a median value of 101 ng/g. There were no significant differences between the ∑PAH concentrations of EW Workers (median, 107 ng/g), non-EW workers (median, 90 ng/g), and adult residents (median, 93.9 ng/g), although slightly higher

Table 1
PAH concentrations (ng/g) in human fingernail samples collected from a typical e-waste dismantling area.

Compounds	EW workers (n = 36)		Non−EW workers (n = 16)		Adult residents (n = 14)		Child residents (n = 6)		Total (n = 72)	
	Median (range)	DF	Median (range)	DF	Median (range)	DF	Median (range)	DF	Median (range)	DF
Nap	0.09 (nd−3.21)	67%	0.12 (nd−1.73)	67%	0.30 (nd−2.19)	71%	4.51 (nd−14.9)	71%	0.15 (nd−14.9)	67%
Acy	0.40 (nd−3.11)	71%	0.32 (nd−1.96)	67%	0.21 (nd−2.54)	57%	nd (nd−1.89)	29%	0.19 (nd−3.11)	60%
Ace	nd (nd−6.24)	46%	2.11 (nd−6.24)	33%	nd (nd−7.65)	36%	nd (nd−2.23)	14%	nd (nd−7.65)	37%
Flu	1.15 (nd−30.4)	54%	nd (nd−15.5)	33%	0.11 (nd−45.9)	50%	nd (nd−98.5)	43%	nd (nd−98.5)	48%
Phe	27.4 (nd−215)	79%	15.3 (nd−86.6)	50%	1.53 (nd−97.7)	71%	1.52 (nd−249)	57%	16.7 (nd−249)	71%
Ant	1.90 (nd−24.1)	71%	2.66 (nd−6.83)	67%	2.01 (nd−16.6)	71%	28.91 (nd−171)	71%	2.75 (nd−171)	71%
Fluo	25.7 (nd−130)	83%	18.9 (5.08−40.1)	94%	14.22 (nd−127)	79%	33.5 (1.49−170)	100%	23.4 (nd−170)	88%
Pyr	22.4 (nd−168)	86%	19.9 (nd−55.3)	88%	10.31 (nd−63.3)	86%	114 (nd−417)	71%	20.4 (nd−417)	86%
B[a]A	2.11 (nd−26.2)	83%	0.80 (nd−20.2)	69%	0.69 (nd−26.2)	50%	nd (nd−17.0)	43%	1.31 (nd−26.2)	71%
Chr	8.02 (nd−42.1)	91%	1.02 (nd−165)	69%	3.66 (nd−28.5)	79%	3.42 (nd−35.4)	71%	4.17 (nd−165)	84%
B[b]F	5.87 (5.87−31.5)	100%	0.44 (nd−27.7)	63%	0.98 (nd−26.6)	64%	1.39 (nd−29.9)	71%	2.59 (nd−31.5)	84%
B[k]F	0.82 (nd−13.6)	91%	0.11 (nd−30.7)	69%	0.49 (nd−33.7)	57%	4.81 (nd−18.9)	57%	0.54 (nd−33.7)	78%
B[a]P	0.77 (nd−9.62)	91%	0.53 (nd−6.51)	81%	0.28 (nd−10.8)	64%	6.33 (nd−24.5)	86%	0.70 (nd−24.5)	85%
InP	1.14 (nd−8.02)	89%	0.31 (nd−1.69)	75%	0.19 (nd−4.82)	50%	2.75 (nd−16.3)	86%	0.64 (nd−16.3)	79%
D[a,h]A	0.41 (nd−3.09)	69%	nd (nd−4.19)	44%	nd (nd−3.59)	21%	nd (nd−7.23)	29%	0.09 (nd−7.23)	52%
B[ghi]P	1.97 (nd−22.4)	86%	1.07 (nd−7.79)	81%	4.84 (nd−13.2)	71%	34.1 (nd−127)	86%	1.83 (nd−127)	84%
$\sum_{16}$PAHs	**127 (7.92−551)**	**100%**	**63.2 (7.05−431)**	**100%**	**70.5 (7.93−289)**	**100%**	**509 (8.88−1275)**	**100%**	**101 (7.05−1275)**	**100%**

DF = detection frequency; nd = not detected.

concentrations of PAHs were found among EW workers. However, relatively higher concentrations were found in fingernails from child residents (median, 509 ng/g). The cause for this particularly higher concentration needs further investigation with a larger sample analysis, but it may be related to children's frequent touching of dusty surfaces (Tang et al., 2020), where the PAHs in the dust would further penetrate the nail plate. The penetration of triphenyl phosphate through the nail plate was also observed by Mendelsohn et al. (2016), which was confirmed as a significant source of dermal exposure. In contrast, the total concentration of PAHs with 4−6 rings ($\sum_{4-6r}$PAHs) in the fingernails of EW workers (median, 48.8 ng/g) was significantly higher than those of non-EW workers (median, 29.4 ng/g) and adult residents (median, 20.8 ng/g), while this was not the case for the low molecular weight PAHs with 2 or 3 rings. The result was consistent with our previous hair analysis (Lin et al., 2020), indicating that e-waste dismantling activities, together with other sources such as vehicle emissions, would jointly affect the exposure to PAHs (Chen et al., 2019a). Additionally, the highest median concentration of $\sum_{4-6r}$PAHs was also found among child residents (227 ng/g). No significant difference was observed in PAH concentration between smokers and non-smokers, or between barbecued food eaters and non-barbecued food eaters.

Since the accumulation of PAHs has never been studied in human fingernails, the comparison of pollution characteristics in different population groups was made tentatively using hair samples, as these two matrices are essentially composed of keratin (Alves et al., 2017). As reported previously, the concentration of PAHs in paired hair samples ranged from 31.7 to 738 ng/g with a mean value of 162 ng/g (Lin et al., 2020), which was comparable with that of fingernails. A similar order of concentration was also observed in three groups of adult subjects, but particularly high PAH concentrations were observed in fingernails of children. The composition profiles of PAHs in fingernail samples of the four different groups are similar, as shown in Fig. 1A. Phe is the congener accounting for the highest proportion, with 34% in EW workers' fingernails, 24% in non-EW workers' fingernails, 20% in adult residents' fingernails, and 20% in child residents' fingernails. In addition, Pyr also accounts for a large proportion of PAHs detected, that is, 15% for EW workers, 15% for non-EW workers, 29% for adult residents, and 18% for child residents. The three most predominant isomers Phe, Pyr and Fluo, accounted for 67.78%, 50.21%, 62.33% and 74.45% of the total PAHs in EW workers, non-EW workers, adult residents, and child residents, respectively. Similarly, results from hair analysis show these three isomers also accounting for 24%−35%, 22%−29% and 21%−26% of the total PAHs in hair, respectively (Lin et al., 2020). This suggests that nails and hair may share the same PAH sources, or the accumulation and distributions of PAHs in hair and nails are similar to some extent. Phe and Pyr were also found as the most prevalent PAH congeners in the aerosol from e-waste sites, accounting for about 70% of ∑PAHs (Chen et al., 2019a), which are also the main components found in the dust of different e-waste dismantling workshops (Tang et al., 2020).

3.2. Concentrations and composition profiles of OH-PAHs in human fingernails

The DFs of 12 OH-PAHs in human fingernails are shown in Table 2. 2-OH-Nap, 2-OH-Phe and 3-OH-Phe were detected in all fingernail samples, with DFs higher than 50% for 1-OH-Nap, 3-OH-Flu and 4-OH-Phe. Those OH-PAHs with 4−5 rings were mainly detected in EW workers and non-EW workers, but not in child residents. Specifically, 3-OH-BaP was only detected in small groups of EW workers (with a DF of 4%), non-EW workers (9%), and adult residents (6%). Compared with paired hair and urine samples, the DF of 3-OH-BaP in human fingernails was lower than that in hair (41%), but significantly higher than that in urine (non-detectable) (Lin et al., 2020). As for parental PAHs, the DFs of OH-PAHs in EW workers were also apparently higher than those in other groups.

The total concentrations of 12 OH-PAHs (∑OH-PAHs) in human fingernail samples ranged from 27.3 to 3282 ng/g, with a median value of 261 ng/g. The concentrations of ∑OH-PAHs in the fingernails of EW workers (median, 375 ng/g) were significantly higher than those of the other three groups. There was little difference in concentrations between other populations. In contrast to the highest concentration of PAHs found in children's fingernails, the concentration of OH-PAHs (230 ng/g) in the same samples was obtained the lowest one. Our previous study indicated that the concentrations of OH-PAHs in children's hair and urine samples were also lower than that of other populations (Lin et al., 2020). Considering the relatively higher metabolic capacity of a child (National Research Council (NRC), 1993), the particularly high concentration of PAHs in children's nails may be more likely to be affected by exogenous penetration, rather than by distribution/transport of endogenous PAHs from blood perfusion. This further indicates that the detection of hydroxyl metabolites can more

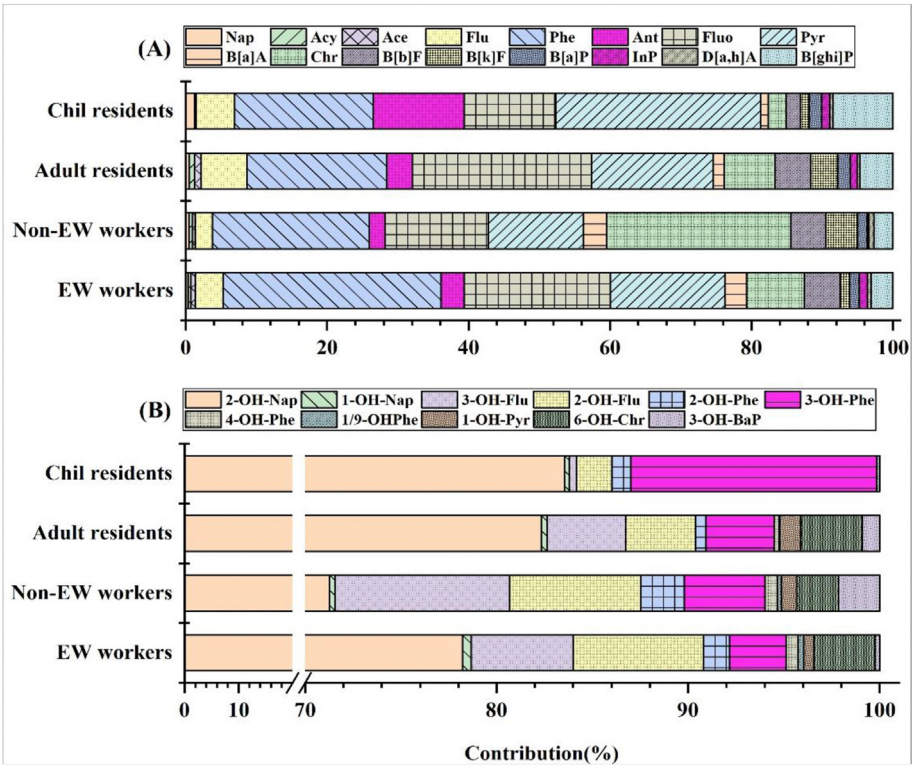

Fig. 1. Composition profiles of PAHs (A) and OH-PAHs (B) in human fingernail samples collected from a typical e-waste dismantling area.

Table 2
OH-PAH concentrations (ng/g) in human fingernail samples collected from a typical e-waste dismantling area.

Compounds	EW workers (n = 36)		Non-EW workers (n = 16)		Adult residents (n = 14)		Child residents (n = 6)		Total (n = 72)	
	Median (range)	DF	Median (range)	DF	Median (range)	DF	Median (range)	DF	Median (range)	DF
2-OH-Nap	289 (23.6–2452)	100%	86.6 (17.6–2004)	100%	244 (101–549)	100%	196 (140–264)	100%	220 (17.63–2452)	100%
1-OH-Nap	0.26 (nd–38.4)	58%	nd (nd–8.37)	44%	0.92 (nd–3.94)	57%	nd (nd–3.71)	17%	0.09 (nd–38.4)	51%
3-OH-Flu	12.9 (nd–275)	86%	3.90 (nd–399)	75%	10.8 (nd–33.8)	71%	nd (nd–4.98)	17%	8.40 (nd–399)	75%
2-OH-Flu	nd (nd–575)	19%	nd (nd–345)	13%	nd (nd–100)	29%	nd (nd–26.0)	17%	nd (nd–575)	19%
2-OH-Phe	2.05 (0.68–63.7)	100%	0.79 (0.23–123)	100%	1.58 (0.48–4.34)	100%	1.32 (0.38–7.37)	100%	1.58 (0.23–125)	100%
3-OH-Phe	8.68 (2.45–56.0)	100%	7.55 (4.91–96.8)	100%	15.2 (4.56–31.7)	100%	32.0 (12.0–47.8)	100%	10.16 (2.45–96.8)	100%
4-OH-Phe	0.42 (nd–46.8)	56%	0.19 (nd–34.0)	63%	0.82 (nd–2.99)	57%	nd	0%	0.19 (nd–46.8)	53%
1/9-OH-Phe	nd (nd–21.3)	42%	0.02 (nd–11.6)	50%	nd (nd–0.90)	14%	nd (nd–2.21)	17%	nd (nd–21.3)	36%
1-OH-Pyr	nd (nd–42.2)	17%	nd (nd–32.8)	31%	nd (nd–72.9)	7%	nd	0%	nd (nd–72.9)	17%
6-OH-Chr	nd (nd–201)	31%	nd (nd–45.1)	13%	nd (nd–152)	7%	nd	0%	nd (nd–201)	19%
3-OH-BaP	nd (nd–18.5)	6%	nd (nd–127)	13%	nd (nd–61.3)	7%	nd	0%	nd (nd–126)	7%
$\sum_{12}$OH-PAHs	**375 (39.5–3282)**	**100%**	**107 (27.3–3116)**	**100%**	**283 (124–576)**	**100%**	**230 (181–293)**	**100%**	**261 (27.25–3282)**	**100%**

DF = detection frequency; nd = not detected.

accurately reflect the exposure characteristics of PAHs. However, the sample size of children's fingernails in this study was small, and further research on larger population is still needed to clarify the sources of the found PAHs.

In general, the levels of ∑OH-PAHs in the human fingernail samples are found to be similar to those in the matched hair samples (ranging from 21.6 to 1887 ng/g). However, significantly higher concentrations of OH-PAHs were found in EW workers, while no significant differences were found in hair (Lin et al., 2020). In addition, the concentrations of various OH-PAH in human fingernails of children from our study were also higher than those in the hair of French children (Palazzi et al., 2019).

2-OH-Nap accounted for the highest proportion of OH-PAHs reported, accounting for over 70% in all the four groups (Fig. 1B). This conclusion is similar to our previous hair analysis results, where 2-OH-Nap was also the most predominant OH-PAH isomer (Lin et al., 2020). However, the prevalence of 1-OH-Nap in human fingernails is quite different from that in hair and urine (as shown in Fig. S3). In urine samples, the proportions of 1-OH-Nap and 2-OH-Nap were found to be equal. In hair, the percentage of 1-OH-Nap is slightly lower, about half that of 2-OH-Nap. In fingernails, 2-OH-Nap contributes almost all of the monohydroxy naphthalene, while 1-OH-Nap contributes less than 1% in any population. The reason why only 2-OH-Nap exists remains unknown, and may be related to specific metabolic characteristics and special distribution of 2-OH-Nap in fingernails. Studies have also shown different composition profiles of perfluoroalkyl substances in paired nail, hair, urine and serum samples (Li et al., 2013; Wang et al., 2018b, 2018c). Except for 1-OH-Nap, the congener profiles of OH-PAHs were similar among different populations (Fig. 1B). The proportion of 4–5 ring OH-PAHs (1-OH-Pyr, 6-OH-Chr and 3-OH-BaP) in human fingernail samples was very low, accounting for 4.1% in EW workers samples, 5.0% in

non-EW workers samples, 5.6% in adult residents' samples, and none in child residents' samples. The differences between these populations were more pronounced in fingernail samples than those in hair and urine samples, especially for child residents. This may indicate that OH-PAHs in fingernails are more suitable biomarkers for demonstrating how different occupations are affected by PAHs. However, more evidence from large population is still needed to confirm this.

3.3. Relationships between PAHs and OH-PAHs in fingernails

The correlation between the concentrations of 16 PAHs and 12 OH-PAHs in human fingernails are shown in Fig. 2. For those PAHs with four or more rings, as well as Acy and Ace, the concentrations of all studied groups correlated well with each other. In addition, the concentration correlation between PAH isomers in EW workers is obviously stronger than that in the other three groups. This further indicates that PAH exposure of EW workers might derive from the same source as e-waste dismantling activities. With significantly higher concentrations of $\sum_{4-6r}$PAHs found in EW workers, our study suggests that primitive e-waste disposal may be a more significant source for high molecular weight PAHs. Specifically, strong correlations between B[a]A, Chr, and B[b]F were also observed in four groups ($R > 0.64$, $p < 0.01$, as shown in Table S3). It

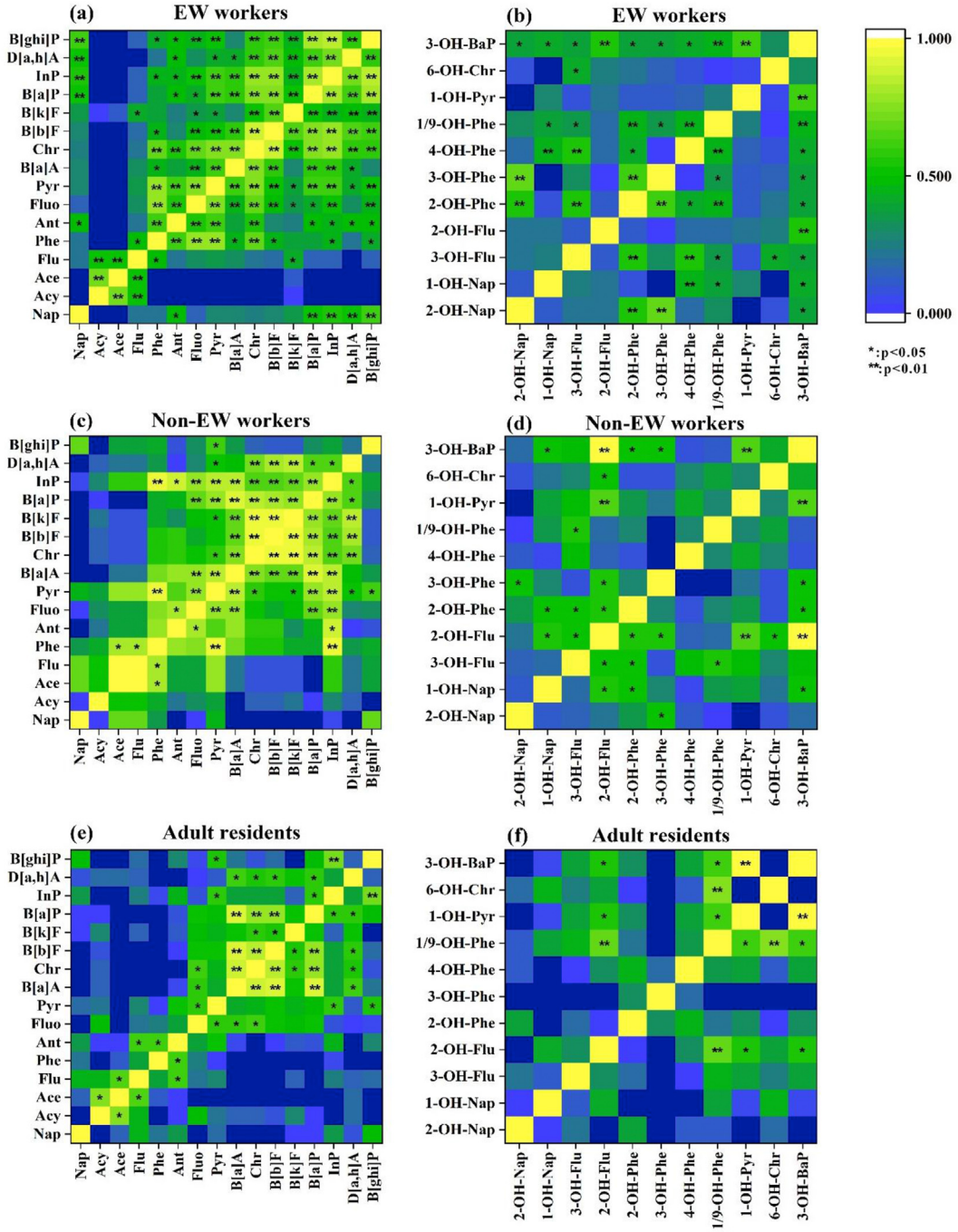

Fig. 2. Spearman correlation coefficients of PAHs and OH-PAHs concentrations in fingernails from study population.

is thus speculated that the source, distribution and accumulation of these chemicals, are similar within human body.

Similarly, the concentration correlation of OH-PAHs in the fingernails of EW workers was stronger than that of non-EW workers and adult residents (Fig. 2), while there was almost no correlation with child residents mainly due to limited data available. Compared to PAHs, relatively weaker correlations were found for OH-PAHs. Since there are very few OH-PAHs obtained in the environment, the OH-PAHs in human fingernails could largely be ascribed to being transported through blood after the metabolism of PAHs in the body, rather than penetrating the nail from external sources. On the other hand, the correlations between concentrations of OH-PAHs might be influenced by individual specific differences in the metabolism and distribution of chemicals within a human's body (Zheng et al., 2014; Wang et al., 2018a, b, c).

In addition, similar to that found in hair analysis (Lin et al., 2020), no correlation was found between PAHs and OH-PAHs in human fingernails. This is mainly attributed to the fact that PAHs in nails may be derived from both exogenous and endogenous sources, while OH-PAHs were almost exclusively from endogenous source. On the other hand, it may be related to the differences between the distribution and accumulation of PAHs and OH-PAHs in the human body.

3.4. The relationship of OH-PAHs in human fingernail, hair, and urine

To further explore the distribution and accumulation of OH-PAHs in different human biological tissues, a correlation analysis was also carried out on OH-PAHs in human fingernails, hair, and urine. Only a significant correlation was observed between 3-OH-Flu ($p < 0.05$) and 2-OH-Phe ($p < 0.01$) in fingernails and urine (Table S4). As mentioned above, urine and fingernails are found to be the biomarkers that reflect short-term and long-term exposure to chemicals in the human body, respectively. In addition, these chemicals may be distributed and accumulated differently in different human biological tissues such as nails, urine, and hair. Organic compounds in nails are transported to nail plates by blood and skin cells, and can also be absorbed from external sources (Gupta et al., 2018). The compounds in urine are only extracted from the blood by the kidneys (Bouatra et al., 2013). Therefore, it is reasonable that no significant correlation was observed between most OH-PAH isomers in fingernails and urine. In fact, no correlation was either observed for most phthalate metabolites, except for monoethyl phthalate, in paired nails and urine samples from the residents of Oslo, Norway (Giovanoulis et al., 2016). In addition, moderate positive correlations were obtained between 3-OH-Flu and 2-OH-Phe in fingernails and urine, which may be due to continuous long-term exposure to these chemicals in the e-waste dismantling area.

No significant correlations were found between all OH-PAHs in matched pairs of hair and fingernails ($p > 0.05$). As mentioned above, both fingernails and hair are derived from skin and mostly composed of keratin (Sakamoto et al., 2015). However, some studies have suggested that PAHs are bound to melanin, thus the amount and type of melanin present are major factors in determining how much PAHs enters hair after the exposure (Larsson, 1993), while this is not the case for the nails as they do not contain melanin. In addition, any measurements of hair samples are more affected by hair length and growth time (Qiao et al., 2019). The rate of fingernail growth is similar for individuals, about 0.05–1.2 mm per week for adults (Pan et al., 2020), and thus can reflect exposure characteristics during the few past weeks. However, the exposure window represented by different lengths of hair can vary by months or even a year. Thus, fingernails and hair samples from the same individual might represent different exposure durations. On the other hand, mixed complex sources as well as different exposures routes might also influence the incorporation/deposition of OH-PAHs in hair and nails, thus affecting the correlation of OH-PAHs in the samples. This can also be verified by the different composition profiles of 1-OH-Nap in fingernails, hair and urine as mentioned. In fact, there have been reported positive correlations with triclosan between matched nails and urine (Yin et al., 2015), and with organophosphorus flame retardants between nails and hair (Alves et al., 2017). Nevertheless, the pollution characteristics of PAHs in fingernails and other biological tissues need to be further clarified with a larger sampling study.

3.5. Implications in human non-invasive biomonitoring studies

It was found that OH-PAHs in fingernails of EW workers were positively associated with age (Fig. S4, $p < 0.5$), while no correlation was found in other three groups. Specifically, all of these targeted OH-PAHs (except for 2-OH-Flu and 6-OH-Chr) were positively correlated with the age of EW workers. The Pearson correlation coefficients of 2-OH-Nap, 3-OH-Flu, 2-OH-Phe and 1-OH-Pyr were obtained as 0.340 ($p < 0.05$), 0.356 ($p < 0.05$), 0.448 ($p < 0.01$) and 0.409 ($p < 0.05$), respectively. This indicated that the accumulation of OH-PAHs in human fingernails increased with the age, although this was not the case for the matched hair (Lin et al., 2020). In general, when the absorption rate of a chemical is greater than its excretion rate, this chemical will always accumulate over the exposure time (Zhu et al., 2009). During e-waste dismantling activities, these workers were exposed to PAHs over the long-term. As compared with older dismantlers, these younger workers are preferring to work in a cleaner, less polluted workshop, thus might be less exposed to airborne PAHs and more protected, which resulted in a relatively lower concentrations of OH-PAHs found in fingernails of younger workers. However, Palazzi et al. (2019) found a negative correlation of the accumulation of multiple OH-PAHs in the hair with the age of children. In addition, no correlations were found between the concentration in human fingernails and years of employment.

The analysis of paired nail/hair/urine samples is valuable for exploring the distribution and accumulation of PAHs and OH-PAHs in the human body, and can be applied to non-invasive human biological monitoring. In general, fingernails reflect exposure over the past few weeks, and the gender difference derived from sampling is insignificant, as confirmed by our study. No gender differences were found in these target PAHs and OH-PAHs in human fingernail samples, but the results of hair analysis showed that gender differences were significantly affected (He et al., 2017), possibly because the hair samples were mostly taken from men with short hair. In order to collect hair samples from women with the same exposure time window as men, hair segments closer to the scalp should be collected, which would greatly increase the difficulty of sampling and limit the amount of hair samples available for quantitative analysis. Therefore, fingernails provide unique sampling advantages and are an important supplement for hair analysis in human biomonitoring. On the other hand, due to long-term direct exposure of nails to aerosols and indoor dust, the penetration of exogenous pollution into the nails may also cause an overestimation of the parental PAHs, especially for children who are frequently in contact with dust. The nail unit is rich in blood and lymphatic vessels, and thus might amplify the absorption of exogenous pollutants through skin penetration (Alves et al., 2017).

The analysis of hydroxylated metabolites can effectively eliminate the interference caused by exogenous pollutants, which is similar to the advantages of analyzing OH-PAHs in hair (Lin et al., 2020). However, a quite different distribution of 1-OH-Nap in

paired nail/hair/urine samples was also observed, so more studies are really needed to clarify the mechanisms of incorporation and deposition into fingernail and hair. This would further facilitate widespread and accurate application of nail and hair analysis in human non-invasive biomonitoring studies.

4. Conclusion

In this study, the accumulation and distribution of PAHs and OH-PAHs were investigated in fingernails of EW workers and near-by residents in an e-waste dismantling area. The results showed that concentrations of high molecular weight PAHs (four or more rings) and OH-PAHs in fingernails of these EW workers were found to be significantly higher than those of non-EW workers and near-by residents. The concentrations and composition profiles of PAHs and OH-PAHs in fingernails were similar to hair samples from the same subjects. However, only weak correlations were found between concentrations of OH-Flu and 2-OH-Phe in matched fingernails and urine samples, while no correlations were found between the concentrations of OH-PAHs in matched nail and hair samples. This may be due to different exposure time windows for the nails and hair samples examined, as well as the individual specific metabolism and accumulation of PAHs. This study is the first study to investigate the accumulation and distribution PAHs and OH-PAHs in human fingernails, although the sample size is limited. More evidence from larger populations is still urgently needed to clarify the mechanism of exposure and deposition of organic compounds in fingernails in order to use fingernails as non-invasive matrices for human biomonitoring studies.

Author statement

Shengtao Ma: Methodology, Formal analysis, Writing-original draft. **Zihuan Zeng:** Methodology, Formal analysis. **Meiqing Lin:** Methodology, Formal analysis. **Jian Tang:** Methodology, Data curation. **Yan Yang:** Visualization, Investigation. **Yingxin Yu:** Visualization, Investigation. **Guiying Li:** Writing- Reviewing and Editing. **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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117059.

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