



Field study of PAHs with their derivatives emitted from e-waste dismantling processes and their comprehensive human exposure implications



Ranran Liu^{a,1}, Shengtao Ma^{a,b,1}, Yangyi Yu^a, Guiying Li^{a,b}, Yingxin Yu^a, Taicheng An^{a,*}

^a Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China

^b Synergy Innovation Institute of GDUT, Shantou 515100, China

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ABSTRACT

Extensive electronic waste (e-waste) recycling might be an important emission source of polycyclic aromatic hydrocarbons (PAHs) mixture, which might induce negative effects on the employees. In the present work, atmospheric pollution patterns of PAHs and their derivatives were determined in five different workshops to dismantle waste printed circuit boards (WPCBs) via thermal treatment. The results showed that mass concentrations of PAHs, chlorinated PAHs (ClPAHs), brominated PAHs (BrPAHs), oxy-PAHs (OPAHs) as well as carbazole (CBZ) were ranged from 1.53×10^4 – 2.02×10^5 , 32.3–364, 8.29– 1.13×10^3 , 923– 1.39×10^4 and 225– 1.95×10^3 pg·m⁻³, respectively. Electric heating furnaces (EHF) workshops emitted relatively higher contaminants than other disposal sectors. OPAHs was found to be the most predominant derivatives of PAHs with 9,10-anthraquinone (83.0%) has the absolute superior in EHFTV, while benzo(a)anthracene-7,12-dione (> 45.0%) was found to be the highest congener in other workshops, respectively. 9,10-Cl₂Phe exhibited the largest contributions to the ΣClPAHs whereas the composition profiles of BrPAHs varied among five workshops. In addition to direct chlorination of parent PAHs, thermal degradation of halogenated flame retardants incorporated into plastic materials might dominate the generation of Cl/BrPAHs from e-waste dismantling activities. The specific isomeric ratios of BrPAHs (3-BrFlu/1-BrPyr and 1-BrPyr/3-BrFlu) might be used to discriminate other emission sources from pyrolysis of WPCBs. However, their specific application as novel tracers for source identification should be further verified with more studies. The emitted PAHs mixture with their derivatives in all dismantling workshops posed carcinogenic risks to these dismantling workers via inhalation, particularly the workshop using electric heating furnaces to treat router. Nevertheless, new loadings of PAHs derivatives observed from e-waste dismantling activities, as well as their comprehensive health risk assessment provides us with a fresh perspective on the source appointment and potential adverse consequences of PAHs. More attention needs to be paid to the potential carcinogenic risks of exposure to PAHs and their derivatives from e-waste dismantling processes.

1. Introduction

The substantial increase in electronic wastes (e-waste) is of particular concern for global ecosystem. It has globally generated 44.7 Mt e-waste in 2016, which is anticipated to increase > 53 Mt in 2021 with steady growth rate of 4%–5% annually (Baldé et al., 2017; Chandrasekaran et al., 2018). In response to reduction in pollution and rational allocation of resources, e-waste recycling becomes rapidly growing industries in both developed and developing countries. E-waste, particularly waste printed circuit boards (WPCBs), offers a great potential for recovery of reusable materials and valuable metals (Hadi

et al., 2015; Tansel, 2017).

Challenge remain in hazardous substances released from thermal recycling activities. Priority has been given to the massive emission of volatile organic compounds and various fire retardants, such as polybrominated diphenyl ethers and dioxins (An et al., 2014; Chen et al., 2016a; Liu et al., 2019; Ren et al., 2014), while the quantitative emissions of polycyclic aromatic hydrocarbons (PAHs) from the incineration of WPCBs have rarely been reported (Zhang et al., 2011). Several studies have confirmed that environmental medias surrounding e-waste dismantling areas extremely contaminated by PAHs (Chen et al., 2019, 2016b; Luo et al., 2015; Wang et al., 2012). And increasing

* Corresponding author.

E-mail address: antc99@gdut.edu.cn (T. An).

¹ Both authors contributed equally to this work and were considered co-first authors.

number of researchers found associations between PAHs exposure with multiple adverse health effects and high levels of PAHs carcinogenic metabolite in populations working or living near e-waste recycling area (Lin et al., 2020; Lu et al., 2016). Thus, the emission characteristics of PAHs released from recycling activities need be further investigated despite their relatively lower emission factors compared with the burning of fossil fuels and biomass (Cai et al., 2018; Shen et al., 2011b, 2010b).

It is highly suspected that thermal processes might produce toxic by-products through PAHs precursors. Halogenated polycyclic aromatic hydrocarbons (HPAHs) are considered as an emerging group of persistent organic pollutants (Jin et al., 2020a, 2020b). Polar PAHs, such as oxygenated-PAHs (OPAHs) and carbazole (CBZ), displays greater toxicity compared to corresponding homocyclic PAHs (Idowu et al., 2019). Findings showed that e-waste dismantling constitute a significant source of HPAHs and those polar PAHs within e-waste zone (Ma et al., 2009; Tang et al., 2020; Wang et al., 2012; Wei et al., 2012). Fingerprints of HPAHs from several industries are now available. Currently, high HPAHs contamination in waste incinerators (Horii et al., 2008; Jin et al., 2017a) and metallurgical plants (Jin et al., 2017b; Xu et al., 2018) have repeatedly been reported. Importantly, polychlorinated naphthalene and dioxins with similar structure of HPAHs, have been proved to be markedly formed during WPCBs heating processes (Duan et al., 2011; Ren et al., 2014). OPAHs were mainly focused on un-completed combustion of wood, coal, and crop residues (Huang et al., 2014; Shen et al., 2011a; 2012) or laboratory condition (Huang et al., 2019). However, for the other important sources, e.g. e-waste dismantling which is an emerging source, such information is still lacking. In the future, the WPCBs recycling would be more in-depth and refined (Wang and Xu, 2015). Study of emitted substance patterns of primary PAHs derivatives sources, will serve as the basis for source apportionment and determination of emission strengths.

Growing findings showed that exposure to PAHs mixture might be related to deleterious health effects of people (Huo et al., 2019; Lu et al., 2016; Wu et al., 2020). Particularly, e-waste recycling workers may face additional exposure comparing with the control population (Ceballos and Dong, 2016; Julander et al., 2014). The potential exposure is highly variable and depends on emission sources in the occupational settings (Petit et al., 2019). Among tasks as potential co-factors of human exposure, the dismantling workers have the highest personal exposure (Gravel et al., 2019; Pettersson-Julander et al., 2004). Zhang et al. (2011) reported that PAHs exposures in a waste incineration field are 10-fold higher than other workplaces. In addition, research shows that part of the reason for exposure is the type of material and dismantling technologies used (An et al., 2014; He et al., 2015; Liu et al., 2019; Tang et al., 2020). However, few studies expanded to source apportionment and health risk assessment of PAHs mixture in different WPCBs disposal workshops.

Considering the importation and domestic production, China's amount of e-waste will reach 28.4 Mt in 2030 (Zeng et al., 2016). Subsequently, disposal activities invariably increased with significantly recycling potential within e-waste areas. It is reasonable to expect that e-waste dismantling can also be a significant emission source of PAHs mixture, although the emission inventory has not been published. The main goal of the present work was to report pollution profiles of PAHs mixture with their derivatives, for example OPAHs, HPAHs and CBZ, as well as to clarify the formation mechanism during WPCBs dismantling processes. Furthermore, the human exposure of these emitted PAHs mixture and their derivatives from above-mentioned dismantling workshops were also measured on the field, aiming to clarify the comprehensive occupational exposures in e-waste recycling industries.

2. Material and methods

2.1. Study location and sample collection

The sampling was carried out at five typical WPCBs disposal workshops with different operating techniques in a town located in south China. Pyrolytic processes included electric heating furnace to dismantle routers (EHFR) and televisions (EHFTV), electric blowers to dismantle mobile phones (EBMP), and rotatory incinerators to dismantle hard disks (RIHD) and televisions (RITV). Inconsistent protection with dust masks and gloves was noticed, however, no dismantlers wore respirators like N95 or otherwise during WPCBs recycling.

Indoor air samplers were deployed near to the workbenches for approximately 8 h at two periods between working-time (9:00–17:00) and off-working time (21:00–5:00). Air samples surrounding the e-waste dismantling zone was used to evaluate potential impact of source emissions on the surroundings. The details of sampling and dismantling procedure were referred the published works (An et al., 2014; Liu et al., 2019).

2.2. Preparation and analysis of samples

Pre-cleaning, extraction as well as cleanup of particles samples are provided elsewhere (Tang et al., 2020). Briefly, each sample was spiked with surrogate standards and Soxhlet extraction, and then purified with a neutral silica/alumina column. PAHs, HPAHs, OPAHs and CBZ were simultaneously determined by a gas chromatography coupled with an TQ8040 mass spectrometer (Shimadzu, Japan). Detailed parameters with regard to preparation and instrumental analysis are presented in [Supplementary Information](#).

2.3. Quality assurance and quality control

Each batch of six samples was followed by one procedural blank and one spiked matrix to evaluate the validity of the data. The surrogate recoveries were ranged from $39.2\% \pm 16.3\%$ for naphthalene- d_8 to $99.1\% \pm 10.9\%$ (mean \pm SD) for chrysene- d_{12} in all samples. Recoveries of target compounds in spiked samples were 61.0%–107.7% for PAHs, 59.4%–138.0% for OPAHs, 101.0%–165.9% for HPAHs and 85.3% for CBZ, respectively. Field results were blank corrected but not corrected by recoveries. The limit of quantification (LOQ) for HPAHs was estimated by the lowest level of the calibration standard based on air volumes of 194 m^3 on QFF. The LOQ for PAHs, OPAHs and CBZ were defined as 3 times the mean level of procedural blanks (Table S1).

2.4. Exposure evaluation

Exposure through dermal adsorption and inhalation was evaluated according to previous reported methodology (Wu et al., 2015; Zhang et al., 2019). Concentrations of individual PAHs and derivatives were converted to benzo(a)pyrene equivalent (BaP_{eq}) concentration based on toxicity equivalency factor (TEF) (Table S1). The average daily intake dose through inhalation (ADD_i , $\text{pg}\cdot\text{kg}\cdot\text{bw}^{-1}\cdot\text{day}^{-1}$) and dermal contact (ADD_d , $\text{pg}\cdot\text{kg}\cdot\text{bw}^{-1}\cdot\text{day}^{-1}$) were evaluated by Eqs. (1) and (2), with 100% absorption PAHs and derivatives was assumed (Aries et al., 2008; Hu et al., 2013).

$$\text{ADD}_i = \frac{C_{\text{eq},i} \times IR \times T \times EF \times ED}{AT \times BW} \quad (1)$$

$$\text{ADD}_d = \frac{C_{\text{eq},i} \times v_{d,h} \times SA \times f_{sa} \times T \times EF \times ED}{AT \times BW} \quad (2)$$

where $C_{\text{eq},i}$ is the BaP_{eq} concentration of contaminants ($\text{pg}\cdot\text{m}^{-3}$); IR is inhalation rate ($\text{m}^3\cdot\text{h}^{-1}$); T is time duration with exposure ($\text{h}\cdot\text{day}^{-1}$); EF is exposure frequency ($\text{days}\cdot\text{year}^{-1}$); ED is exposure duration (years);

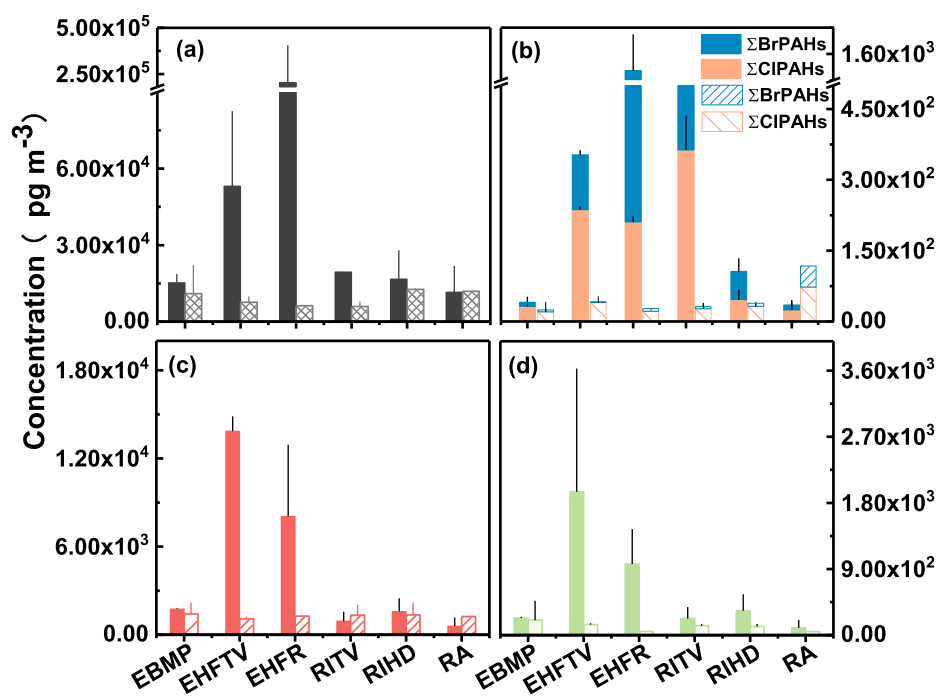


Fig. 1. Parent PAHs (a), HPAHs (b), OPAHs (c) and CBZ (d) concentrations at different WPCBs dismantling workshops and residential areas during working time (solid) and off-working time (hollow). Error bars represent standard deviation.

SA is skin surface area (m^2); f_{sa} is exposure fractions for skin surface area; $v_{d,h}$ is the average particle deposition velocity ($\text{m}\cdot\text{h}^{-1}$); BW (kg) and AT (days) is the body weight and the lifespan of carcinogens in 70 years, respectively. For details about the calculation formulas [Supplementary Information Text S2](#).

3. Results and discussion

3.1. Occurrence of the PAHs and their derivatives

3.1.1. PAHs

The $\Sigma_{16}\text{PAHs}$ concentrations in different workshops ranged from 1.53×10^4 – $2.02 \times 10^5 \text{ pg}\cdot\text{m}^{-3}$ (Fig. 1). Relatively higher concentrations were found in air particles collected from electric heating furnace workshops, with mean values of 2.02×10^5 and $5.31 \times 10^4 \text{ pg}\cdot\text{m}^{-3}$ in EHFR and EHFTV, respectively. In comparison, PAH concentrations emitted from other three workshops were all lower than $2.0 \times 10^4 \text{ pg}\cdot\text{m}^{-3}$, which might be ascribed to the closed platform and the relatively lower heating temperature applied in these workshops (Liu et al., 2019; Lu et al., 2009). Concentrations of PAHs in this work were comparable to previous studies conducted in other e-waste dismantling workshops with concentrations ranged from 2.45×10^4 – $5.48 \times 10^5 \text{ pg}\cdot\text{m}^{-3}$ (Chen et al., 2016a; Huang et al., 2013; Zhang et al., 2011), but were substantially lower than those in other emission sources such as carbon black manufacturing ($1.78 \times 10^6 \text{ pg}\cdot\text{m}^{-3}$) (Tsai et al., 2001) and fastener manufacturing ($2.30 \times 10^6 \text{ pg}\cdot\text{m}^{-3}$) (Goriaux et al., 2006). As compared with these dismantling workshops, the lowest level of PAHs was found in residential area (RA) ($1.16 \times 10^4 \text{ pg}\cdot\text{m}^{-3}$). Similarly, significantly lower levels of PAHs at control site were also observed than that of dismantling area (Chen et al., 2019). Those results indicate that the dismantling area have been largely affected by PAHs contaminants emitted from thermal processes of WPCBs. Our results further confirmed that high PAHs exposure might be ascribed to the e-waste disposal processes (Lin et al., 2020).

The composition profiles of PAHs among different e-waste workshops followed similar patterns, although their concentrations varied dramatically (Fig. S1). Median molecular weight PAHs (4 rings), for

example, Flu and Pyr were the most predominant isomers, and accounting for 4.79%–35.2% and 4.69%–32.4% of the total PAHs at different WPCBs treatment workshops. The results are in agreement with the conclusion of our previous work (Chen et al., 2019). Pyr and Flu were the extremely abundant atmospheric PAHs at an industrial park for e-waste dismantling (Chen et al., 2019), and were reported with higher proportion of contributions in external hair of e-waste workers (Lin et al., 2020). However, the most abundant species is Phe, accounting for 36% and 34% of total PAH amount in particulate phase for plastic casings and WPCBs, respectively (Cai et al., 2018) and air samples from an e-waste recycling area (Luo et al., 2015). Furthermore, Phe was also found as dominated PAH congener in atmospheric gaseous samples of e-waste recycling sites in previous reports (Chen et al., 2016a; Zhang et al., 2011). Gas-particle partitioning, dissimilar disposal conditions, and redistribution might all markedly affect the compositional profiles of freshly emitted PAHs during WPCBs recycling processes (Cai et al., 2018; Ding et al., 2012; Shen et al., 2010a).

3.1.2. Halogenated PAHs

Of the 31 HPAHs, 11 of C1PAHs and 7 of BrPAHs can be detected with frequencies > 50% at different WPCBs dismantling workshops. The concentrations of $\Sigma_{15}\text{C1PAHs}$ and $\Sigma_{16}\text{BrPAHs}$ were ranged from 32.3 – $364 \text{ pg}\cdot\text{m}^{-3}$ and 8.29 – $1.13 \times 10^3 \text{ pg}\cdot\text{m}^{-3}$ in air particles, respectively (Fig. 1). The highest level of $\Sigma_{15}\text{C1PAHs}$ was found in RITV workshop ($364 \text{ pg}\cdot\text{m}^{-3}$), followed by EHFTV and EHFR with mean values of 237 and 211 $\text{pg}\cdot\text{m}^{-3}$, respectively. For the BrPAHs, mean concentration of $\Sigma_{16}\text{BrPAHs}$ in EHFR ($1.13 \times 10^3 \text{ pg}\cdot\text{m}^{-3}$) workshop was almost higher by 10-fold than that of RITV ($159 \text{ pg}\cdot\text{m}^{-3}$) and EHFTV ($117 \text{ pg}\cdot\text{m}^{-3}$) workshops. Additionally, similar concentrations of HPAHs among EBMP and RIHD workshops as well as RA were also observed. Unexpectedly, RITV and EHFR emitted the highest concentrations of C1PAHs and BrPAHs, respectively. This was inconsistent with the emissions of other halogenated organic pollutants observed in our previous study, with the highest atmospheric levels of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) were reported in EHFTV workshop (Liu et al., 2019). These inconsistencies may be explained by different emission factors and

formation mechanisms of different pollutants. In addition, other unknown halogen sources may determine the formation of HPAHs.

Several studies have also reported the emissions of HPAHs from other sources. For example, the ClPAHs concentrations in stack gas from waste incineration ($0.28\text{--}8.41 \times 10^3 \text{ ng}\cdot\text{m}^{-3}$) (Jin et al., 2017a; Wang et al., 2018), metallurgical plants ($5.8\text{--}156 \text{ ng}\cdot\text{m}^{-3}$) (Jin et al., 2017b) and cement kiln co-processing solid waste process ($15.6\text{--}94.1 \text{ ng}\cdot\text{m}^{-3}$) (Jin et al., 2018) were all found to be obviously higher than that reported in our study. This suggests that these industries were the major emission sources of ClPAHs other than e-waste dismantling activities. However, for these automobile emissions, relatively lower concentrations were observed for ClPAHs from a road tunnel (3.4 and $29 \text{ pg}\cdot\text{m}^{-3}$ in 1996 and 1991, respectively) (Ishaq et al., 2003). In addition, findings have reported the concentrations of chlorine-substituted isomers were greater than that of bromine-substituted groups in waste (municipal, industrial, and hazardous operations) incineration processes (Horii et al., 2008) and metallurgical plants (Jin et al., 2017b; Xu et al., 2018). However, significantly higher concentrations of BrPAHs ($1.13 \times 10^3 \text{ pg}\cdot\text{m}^{-3}$) were observed in EHFR than that of ClPAHs ($211 \text{ pg}\cdot\text{m}^{-3}$) in the present study, which could be owing to the widely application of brominated flame retardants (BFRs) in e-waste materials. According to previous studies (Jin et al., 2017b; Tang et al., 2020; Xu et al., 2018), industrial thermal processes provide ideal conditions for the formation of HPAHs including carbon source, halogens, and various metals. However, apart from above mentioned, a high content of BFRs in e-waste materials (e.g. printed circuit boards and electronic components) compared with other wastes or metallurgical markedly affect the profiles of BrPAHs. High levels of BFRs releasing from e-waste recycling processes could provide bromine sources favoring the further formation of BrPAHs. Furthermore, BrPAHs concentrations exhibited a larger variation among different workshops, implying that the formation and emission of BrPAHs could be more sensitive to the combusted materials and decomposition conditions. However, the relatively lower emission factor of these brominated aromatics from mobile phone WPCBs treatment workshop was observed as compared with other workshops, which might be explained by the relatively lower bromine sources existed (Liu et al., 2019). Additional explanation may come from the relatively lower emission factor of PAHs from the combustion of printed circuit board as compared with plastic casing (Cai et al., 2018).

There is no remarkable difference in ClPAHs congener profiles among various dismantling workshops (Fig. 2a). 9,10-Cl₂Phe exhibited the largest contributions to the ΣClPAHs, accounting for 43.7%, 21.4%, 27.4% and 28.0% in EHFTV, EHFR, RITV and RIHD, respectively. The samples collected from EBMP workshop contained high fractions of 6-ClBaP (23.2%), which was similar to the profiles observed in RA. These contaminant patterns of ClPAHs in our study was different from the emission profiles from metallurgical facilities (Jin et al., 2017b; Xu et al., 2018), waste incinerators (Horii et al., 2008; Jin et al., 2017a), and chlor-alkali plant (Horii et al., 2009). Additionally, the compositional pattern was also different from ClPyr-prominent pattern found in e-waste soil (Tue et al., 2016), and dust/leaves (Ma et al., 2009), as well as ClAnt-prominent pattern reported in dust of e-waste recycling workshop (Tang et al., 2020).

The BrPAHs homologous at five workshops varied significantly among different e-waste workshops (Fig. 2b). 1,8-Br₂Ant was the most abundant isomer in EBMP and EHFR workshops, accounting for 62.1% and 49.2% of ΣBrPAHs, respectively. 5-BrAna (22.7%) was found to be the major congener, followed by 1,8-Br₂Ant (21.7%) in RIHD. For television WPCBs recycling workshop, 3-BrFlu (21.2%) and 9,10-Br₂Phe (35.6%) were found as the predominant homologues in EHFTV and RITV, respectively. The compositional patterns in our study were apparently different from that found in e-waste indoor dust, where the high-ring BrPAHs (BrPyr and BrBaA) were the prominent isomers (Tang et al., 2020). The BrPAHs profiles were also different with these reported from other industrial discharges (Horii et al., 2008; Xu et al.,

2018). Therefore, more studies are needed to clarify the pollution characteristics and formation mechanism of these ClPAHs and BrPAHs emitted from e-waste recycling processes, so as to be applied as potential indicators for sources appointment.

3.1.3. OPAHs

OPAHs concentration was approximately 10-fold lower than their parent PAHs in this study, but was apparently higher than those of the other derivatives of PAHs (Fig. 1). The highest concentrations of OPAHs were found in EHFTV ($1.39 \times 10^4 \text{ pg}\cdot\text{m}^{-3}$), followed by EHFR workshop ($8.05 \times 10^3 \text{ pg}\cdot\text{m}^{-3}$), while much lower OPAHs concentration were found in other three workshops, with mean values of 1.75×10^3 , 1.58×10^3 and $923 \text{ pg}\cdot\text{m}^{-3}$ in EBMP, RIHD, and RITV workshops, respectively. However, the concentration of OPAHs from our study was higher than that measured from an e-waste site in Qingyuan of southern China ($519\text{--}1.25 \times 10^3 \text{ pg}\cdot\text{m}^{-3}$) (Wei et al., 2012). The high levels found in EHFTV workshops from our study was also comparable or slightly lower than that released from solid fuel combustion ($23 \pm 20 \text{ ng}\cdot\text{m}^{-3}$) and motor vehicles emission ($29 \pm 24 \text{ ng}\cdot\text{m}^{-3}$) (Li et al., 2015). Previous study have demonstrated that OPAHs was the main derivative products emitted during pyrolytic disposal of electronic wastes (Huang et al., 2019), relatively higher emission factors were found for the thermal treatment of plastic casings ($32.6 \pm 18.1 \text{ mg}\cdot\text{kg}^{-1}$) than WPCBs ($3.37 \pm 4.10 \text{ mg}\cdot\text{kg}^{-1}$). However, the emission factors of the OPAHs in their study were nearly same levels as those of their parent PAHs. The relatively higher ratios of the levels of OPAHs to PAHs found from simulation study compared with field observations might be related to the relatively greater potential mobility of OPAHs (Idowu et al., 2019). With distance away from emission sources, the ratio of OPAHs/PAHs in flue gas was 10-fold higher than that of the workshops in our study, and was 2–3 orders of magnitude higher than that studied air sample collected in e-waste sites (Wei et al., 2012). Thus, the occurrences of OPAHs and its ratio to the parent PAHs could be used to indicate the e-waste contamination from fresh emission sources. Our findings highlighted e-waste recycling activities can be considered as a new source for OPAHs.

Of 4 OPAHs, benzo(a)anthracene-7,12-dione (BaAQ) was found to be the highest congener, accounting for 41.7%, 73.2%, 50.3% and 65.9% in EBMP, EHFR, RITV and RIHD workshops, respectively (Fig. S2). While in EHFTV workshop, 9,10-anthraquinone (ANTQ, accounting for 83.0%) was the absolute superior isomer. The relatively high contributions of ANTQ were also found in air particles from e-waste recycling zone (21.6% and 35.1% in summer and winter, respectively) (Wei et al., 2012) and traffic site (45.5%) (Ringuet et al., 2012). However, those field observations are inconsistent with the result obtain under laboratory-scale simulation, where 9FLO (69%) and ANTQ (27%) were the most abundant OPAH congeners (Huang et al., 2019). The different emission profiles of OPAHs might depend on the decomposition of different types of polymer plastics, as well as different thermal treatment conditions, such as temperature. In addition, the contribution of 9FLO in the present study (5.99%–18.8%) was also obviously lower than those of coal combustion (55.1%–92.7%) and biomass burning (41.9%–44.2%), where 9FLO was also found to be the most abundant specie (Huang et al., 2014).

In addition, electric heating furnace thermal processes also yield relatively high levels of CBZ among five different dismantling workshops. The highest concentration of CBZ were also found in EHFTV ($1.95 \times 10^3 \text{ pg}\cdot\text{m}^{-3}$) workshop, followed by EHFR workshop ($966 \text{ pg}\cdot\text{m}^{-3}$). In the other three workshops, the concentrations of CBZ were much lower, with values of 233, 225 and $331 \text{ pg}\cdot\text{m}^{-3}$ in EBMP, RITV, and RIHD workshops, respectively. However, the data regarding the emission of CBZ from e-waste dismantling activities is not available. Nevertheless, the atmospheric concentration of CBZ from our study ($225\text{--}1.95 \times 10^3 \text{ pg}\cdot\text{m}^{-3}$) was relatively higher than that found in Southern European cities (Alves et al., 2017). In addition, CBZ is an important chemical raw material, mainly served as structural motifs in

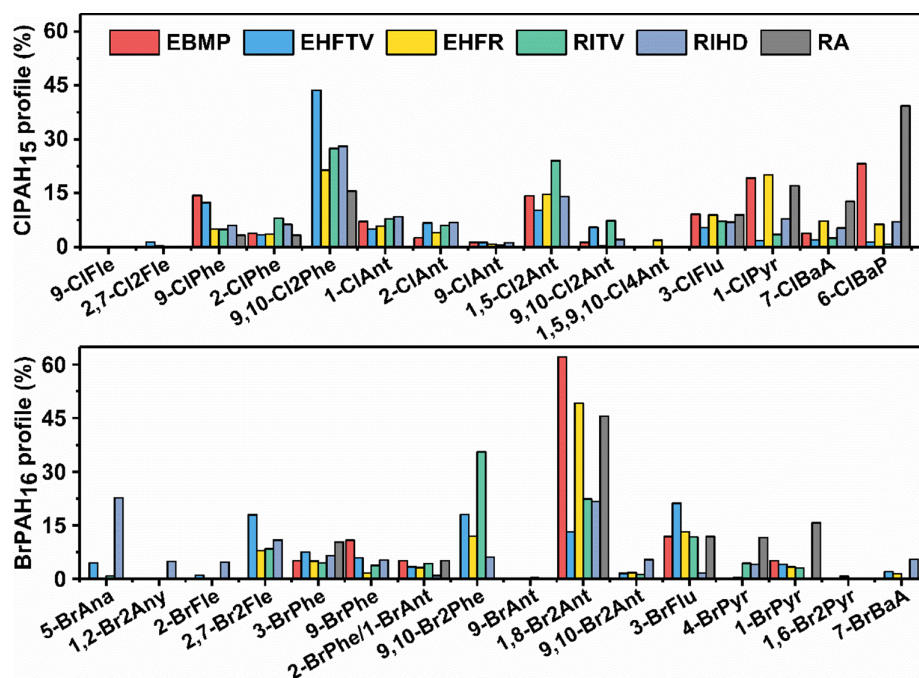


Fig. 2. Comparison of pollution profiles of (a) CIPAHs and (b) BrPAHs for different recycling processes.

various synthetic materials, which would be used in various e-waste materials (Salam et al., 2017). The universal presence of polyhalogenated carbazoles were also found in sediment from Sanmen Bay, East China Sea (Qiu et al., 2019). In addition, the emission of CBZ was also demonstrated from incineration of solid waste, as well as combustion of rubber, petroleum and coal (Salam et al., 2017). Thus, the extensively e-waste dismantling activities may lead to the atmospheric occurrences of CBZ. Concerning its relatively high concentration levels and potential toxicities, more attentions should be urgently paid to the emissions, fates as well as adverse health consequences of CBZ in e-waste recycling sites.

3.1.4. Diurnal variation

In general, the occurrences and distributions of PAHs and their derivatives shown a distinct diurnal variation in the most polluted workshops (EHFTV and EHFR), as depicted in Fig. 1. The levels of parent PAHs, CIPAHs, OPAHs as well as CBZ from off-working time were reduced by 5.99, 7.98, 11.8 and 12.6 times than those during the working time in EHFTV workshop, and were decreased by 31.3, 9.00, 5.34 and 18.6 times than those during the working time in EHFR workshop, respectively. While for the other e-waste dismantling workshops, the levels of parent PAHs, CIPAHs, OPAHs and CBZ from off-working time were 0.68 to 13.7 times lower than those from working time. Particularly, the concentrations of BrPAHs from off-working time were 212, 186, 31.7, 9.22, and 2.21 times lower than those from working time in EHFTV, EHFR, RITV, RIHD, and EBMP, respectively. The atmospheric concentrations of PAHs and their derivatives during working time varied significantly owing to the different emission sources existed in different workshops. However, at off-working time at night, the variation of the concentration of pollutants in different workshops becomes negligible. This result further indicates that e-waste recycling activities are a vital source of these PAHs as well as their derivatives, especially for these BrPAHs.

The different source distributions between working time and off-working time could also alter the profile of parent PAHs and derivatived PAHs. Remarkably, the contribution of high molecular weight PAHs and their derivatives shown significant increase due to partition as well as the deposition of particulates after its emission. In comparison with the working time, a normalized profile of PAHs and derivatives was

presented during the off-working time (except for BrPAHs). BkF, IcdP and BghiP were found to be the most predominant pollutants for PAHs (Fig. S1). BaAQ (> 40%) was obtained to be higher than other three OPAHs (Fig. S2). Furthermore, the percentage of 6-ClBaP increased from 1.34% to 21.2% in EHFTV and from 0.77% to 12.0% in RITV workshops, respectively (Fig. S3). This pattern is consistent with our previous findings on PBDEs and PCBs samples collected from WPCBs burning at atmospheric samples (Liu et al., 2019).

3.2. Correlations of derivatived PAHs with parent PAHs

Correlation coefficients between CIPAH, BrPAH congeners and their corresponding parent PAH congeners were evaluated for possible formation mechanisms (Table S2). Significant positive correlations were found between 9-ClPhe, 2,7-Cl₂Flu, 7-ClBaA, 3-BrFlu and 7-BrBaA and their parent PAHs ($p < 0.01$). Furthermore, the concentrations of 9-ClAnt, 3-BrPhe, 2,7-Br₂Flu and 1-BrPyr were also significantly correlated with parent PAHs during dismantling processes ($p < 0.05$). The significantly associations between HPAHs and their corresponding parent PAH species suggesting WPCBs dismantling activities was the dominant source of these pollutants. However, for the rest of the individual PAHs derivatives, no significant correlation was observed ($p > 0.05$), indicating another unknown emission sources or transformation mechanism might dominant the formation of these CIPAH and BrPAH congeners. This was agreement with the results obtained during the metallurgical smelting process (Jin et al., 2017b; Xu et al., 2018).

Published works questioned that dominant formation pathway of HPAHs are derived from direct chlorination parent PAH precursor. Based on the relative Gibbs free energies, monochlorinated PAHs isomers, such as 9-ClPhe and 1-ClAnt are more easily to be generated through direct chlorination of their parent PAHs than dichlorinated PAHs isomers (Jin et al., 2017b). However, 1,5-Cl₂Ant and 9,10-Cl₂Phe which require the much higher energy for direct formation from Ant and Phe, were the predominant species in profile of CIPAHs, and displayed no correlation with Phe ($r = 0.486$, $p > 0.05$) and Ant ($r = 0.539$, $p > 0.05$), respectively. Similar observation has also reported in e-waste contaminated soils collected from open burning site in Agbogboshie of Africa (Tue et al., 2016). It was speculated that

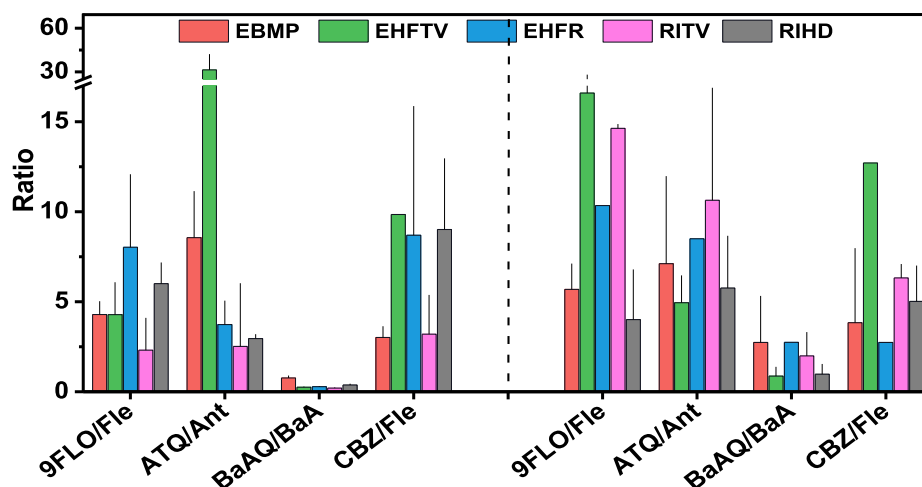


Fig. 3. Ratios of individual OPAH/parent PAH and CBZ/parent PAH among different workshops during working time (left panel) and off-working time (right panel). Error bars represent standard deviations.

another formation mechanism might dominate the generation of HPAHs, apart from direct chlorination of PAHs. Some highly chlorinated/brominated flame retardants might also serve as potential precursors to form HPAHs. For example, brominated-Phe with up to four bromine were identified as thermal degradation products of decabromodiphenyl ethane (Grause et al., 2011). Thus, further studies related to the formation mechanism of HPAHs are needed.

For these OPAHs, 9FLO, ANTQ and BaAQ were significantly correlated with their corresponding parent PAHs, Flu ($r = 0.855$, $p < 0.01$), Ant ($r = 0.636$, $p < 0.05$), and BaA ($r = 0.673$, $p < 0.05$) (Table S2) in working time, respectively. This result was consistent with the bench-scale simulation of e-waste combustion (Huang et al., 2019). However, no correlation was found between nighttime concentrations of PAHs and OPAHs, indicating that the nighttime sources of OPAHs might be differed from PAHs. At nighttime, the main formation process of OPAHs might be related with NO_3 -radical-initiated reaction in ambient air (Tsapakidis and Stephanou, 2007). A similar formation mechanism has also been demonstrated at e-waste dismantling area (Wei et al., 2012). Ratios of the OPAHs and CBZ to their corresponding parent PAHs (Ro) were evaluated. As Fig. 3 shows, the Ro values of 9FLO/Flu, ATQ/Ant, BaAQ/BaA and CBZ/Flu were ranged from 2.31–8.02, 2.52–31.4, 0.20–0.76 and 3.01–9.85 among five dismantling workshops, respectively. Comparatively, the Ro during the off-working time were higher than those during the working time. For example, the ratio of BaAQ/BaA during the off-working time was significantly higher than that of during working times ($p < 0.05$). This indicates that greater secondary formation of OPAHs was also occurred.

3.3. Distinguishing of E-waste recycling from other sources

Ratios of parent PAHs, such as Ant/(Ant + Phe), Flu/(Flu + Pyr), IcdP/(IcdP + BghiP), BaA/(BaA + Chr), BbF/(BbF + BkF), as well as BaA/(BaA + BghiP), can be acted as specific indicators to apportion the source of PAHs. Previous works on source apportionment of PAHs rarely take into account the emission of PAHs from pyrolysis of e-waste. The present study compared the ratio based on pyrolysis of e-waste with those from other major particle matter emission sources (Table S3). Obviously, none of these ratios can effectively distinguish the sources since each type of source differs greatly and full overlap occur among various sources.

Diagnostic ratios of typical PAH isomer pairs were further compared by cross plots (Fig. 4). The dots of e-waste recycling emission displayed extraordinary overlap with biomass burning and coal combustion but could greatly separate from that of cigarette smoke. The results indicated that PAH isomer pairs can potentially differentiate e-waste

recycling emission from cigarette smoke. Previous studies found that PAHs were originated from the combustion of biomass and coal within e-waste recycling area (Chen et al., 2019, 2016b). As such, there may be a risk of misdiagnosis, if the mentioned above diagnostic ratios are selected. More recently, Cai et al proposed that using ratios of IcdP/(IcdP + BghiP) and BaA/(BaA + BghiP) can distinguish other emission sources from sources of e-waste pyrolysis, and might serve as preliminary diagnostic ratios (Cai et al., 2018). Nevertheless, our observation from field samples do not support their speculation. Ratio of BbF/(BbF + BkF) was 0.72 ± 0.06 among different workshops. Caution is needed for ambient data because these ratios can change during the transport owing to differential partitioning, scavenging and degradation (Sheesley et al., 2011).

The ratios of paired isomers in different receiving media were usually compared to those in various emission sources to distinguish original sources of HPAHs. A summary of HPAH congener ratios collected from different sources are also listed in Table S4, which shows various differences in the ratios among these studies. The isomeric ratios of HPAHs from pyrolysis of WPCBs in the present work belongs to the same or approximate range or overlaps with thresholds of other emission sources. Hence, new threshold values of isomer ratios which could differentiate source of e-waste recycling processes from others are required. According to Table S4, the paired ratios of 3-BrFlu/1-BrPyr and 1-BrPyr/3-BrFlu could, overall, differentiate pyrolysis of WPCBs from other emission sources, and may act as important fingerprint for source identification and allocation of PAHs from e-waste dismantling. Principal component analysis of these ratios of congener profiles of ClPAHs as well as BrPAHs for the e-waste recycling and other sources is illustrated in Fig. 5. The ClPAHs and BrPAHs ratios show specificities among different sources. These results show that dismantling of e-waste are significant sources of ClPAHs and BrPAHs, and the congener profiles reported in this study can be used as fingerprints for source traceability of ClPAHs and BrPAHs in the environment.

3.4. Potential human health risks

Carcinogenic risks via inhalation and dermal exposure were assessed due to negative effects of PAHs mixture on workers' health. With the deterministic TEFs, the results find that the ADD of BaP_{eq31} ranges 345 to 9959 $\text{pg}\cdot\text{kg}\cdot\text{bw}^{-1}\cdot\text{day}^{-1}$ and 0.69 to 20.4 $\text{pg}\cdot\text{kg}\cdot\text{bw}^{-1}\cdot\text{day}^{-1}$ through inhalation and dermal absorption for male workers during the working hours, respectively (Tables S5 and S6). No significance difference was obtained in ADD between male and female workers during different dismantling workshops. For exposure route, the risk from inhalation made up $> 99\%$ of total risk to male and female workers,

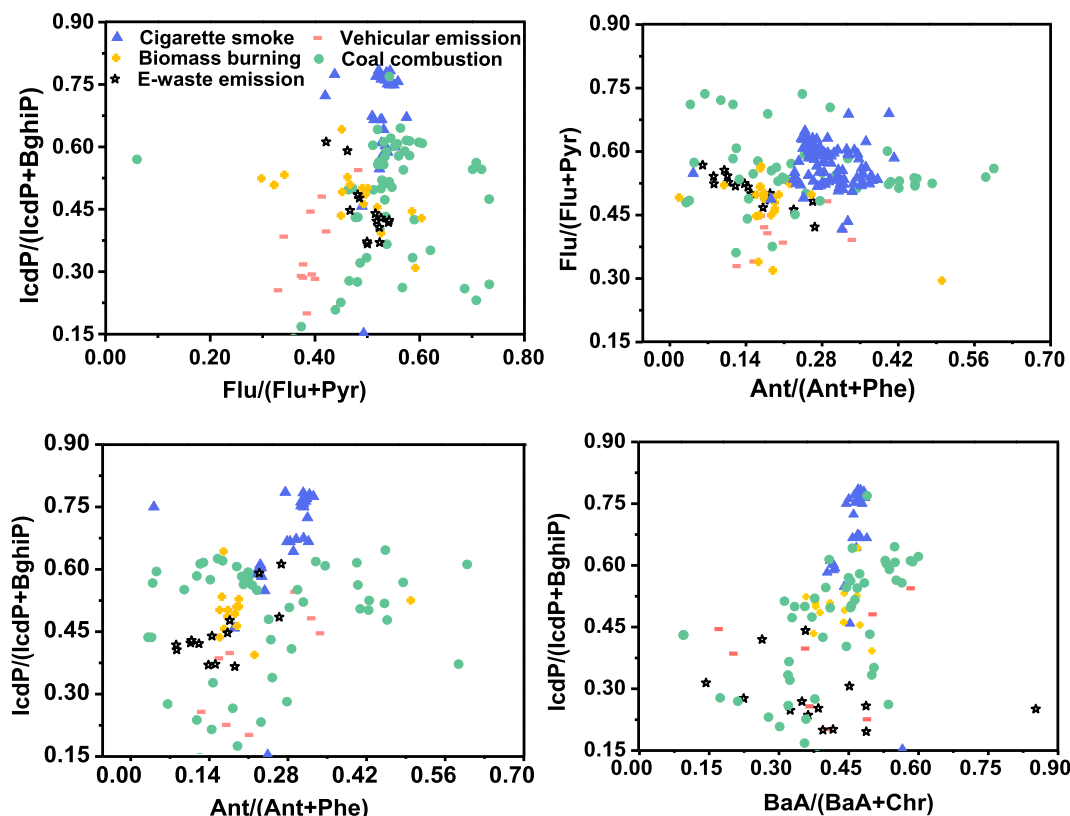


Fig. 4. Cross plots for parent PAH ratios in e-waste recycling, cigarette smoke, vehicular emission, biomass burning, and coal combustion.

demonstrating that inhalation exposure was main chemical exposure pathway for e-waste recycling workers. Similar results have also been obtained by other researchers (Shi and Zhao, 2014). However, previous research showed that skin contact is the principal input way of PAHs in air for firefighters (Fent et al., 2014). In addition, a report found that total fluxes due to dermal contact were equivalent to or greater than those through inhalation when considering the attribution of gaseous PAHs (Wu et al., 2015). As such, although dermal exposure cannot be ignored, inhalation seems as a main exposure way in this study.

The highest BaP_{eq} concentration in EHFR workshops ($126 \text{ ng}\cdot\text{m}^{-3}$) was obtained as 50.4 times higher than that of new standard of China, while it was 15.7, 19.2, 19.5, and 28.9 times higher than those in EBMP, EHFTV, RITV, and RIHD, respectively (Table S7). This result was comparable with e-waste incineration field during the working day

(Zhang et al., 2011). BaP_{eq} in all workshops outnumbered the China national daily BaP_{eq} standard ($2.5 \text{ ng}\cdot\text{m}^{-3}$), the WHO guideline level ($1 \text{ ng}\cdot\text{m}^{-3}$), as well as the European Union's annual average BaP_{eq} standard ($1 \text{ ng}\cdot\text{m}^{-3}$) (Wang et al., 2012). This suggests that these workers are subjected to high exposure doses of these emitted contaminants during dismantling activities. This also confirmed that burning of WPCBs result in the exposure of considerable PAHs and derivatives, besides other toxic chemicals (An et al., 2014; He et al., 2015; Liu et al., 2019; Ren et al., 2014). The risks from parent PAHs were the highest, and accounted for a significant contribution ($> 95\%$) to the total concentrations of BaP_{eq} in all five workshops. This was due to their relatively high concentrations and the high relative potency factors values. Since the authentic relative potency factors values were only available for a few HPAHs (Table S2), these roughly estimated

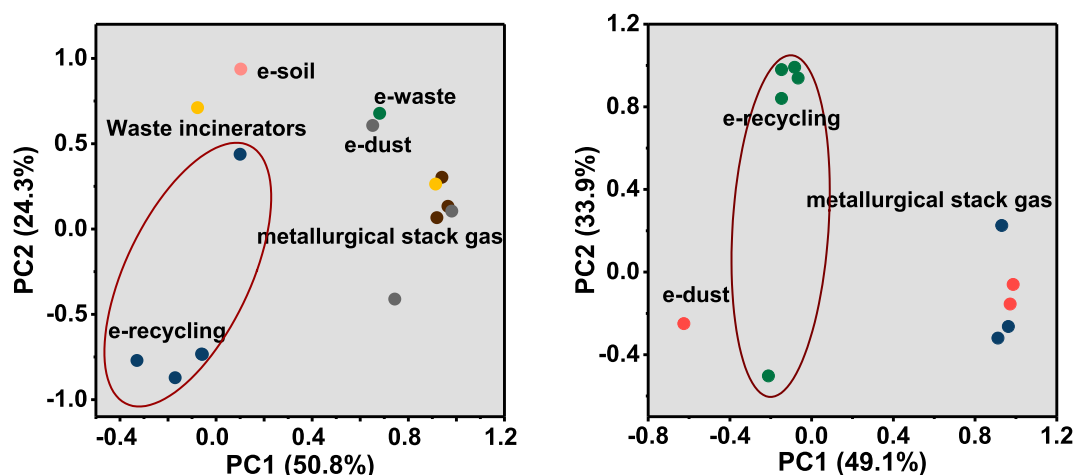


Fig. 5. PCA of specific congener ratios in samples collected from different sources.

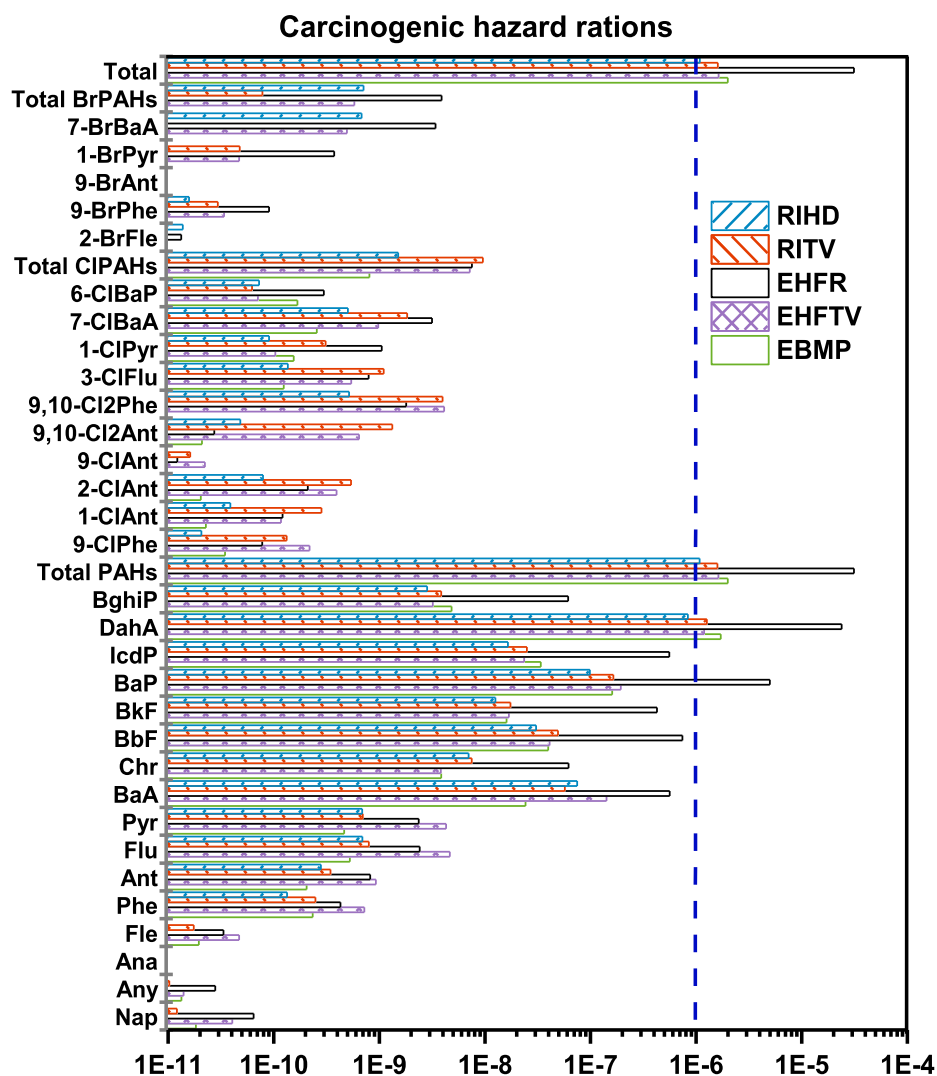


Fig. 6. Cancer risks of male workers associated with PAHs mixture with their derivatives through inhalation in different workshops during working time.

concentrations may be underestimated the exposure risk in this study.

The elevated atmospheric concentrations in different workshops pose a high risk of potential exposure to dismantling workers. Chronic exposure to PAHs resulted in high concentrations of metabolites in urine of the workers and non-occupationally exposed people (Lin et al., 2020; Lu et al., 2016). As Fig. 6 shows, the highest risk via inhalation (3.13×10^{-5}) among was observed at EHFR workshop, followed by EBMP of 1.99×10^{-6} . In the other three workshops, the risk values were 1.63×10^{-6} , 1.60×10^{-6} , and 1.08×10^{-6} in EHFTV, RITV and RIHD, respectively. Similar results were also observed for female workers (Fig. S4). This is not in consistent with their pollution trends discussed above, which EBMP contained the least content of parent PAHs and HPAHs (Fig. 1). This phenomenon was attributed to high percentage of toxic PAH components existed in EBMP workshop. The cancer levels of all five workshops are higher than the acceptable range of EPA ($10^{-6} - 10^{-4}$), indicating that more attention needs to be paid on the carcinogenic risks of PAHs mixture during WPCBs dismantling. For a congener-specific analysis of those contaminants, DahA and BaP account for approximately $> 85.2\%$ of total in five workshops. Thus, in order to reduce the cancer risk for occupational exposed workers, some detoxification technology should be mandatory introduced, for example, to removal particle-bound DahA and BaP emission from e-waste fumes by integrated de-dusting with decontamination facilities (Chen et al., 2016a). Exposure to median molecular weight compounds was not significantly, although higher levels were published in many

studied workshops. Compared with inhalation, cancer risks via dermal contact was all lower than the acceptable range ($10^{-6} - 10^{-4}$), with the highest risk was only 6.29×10^{-8} and 6.17×10^{-8} for male and female workers, respectively (Figs. S5 and S6).

Overall, the above-mentioned cancer risk assessment through inhalation and dermal exposure in the present study has several uncertainties and limitations. Firstly, relatively small samples were collected, and may not be representative for long-term disposal variability from e-waste activities. Secondly, limitations also include the accuracy of parameters used in the present study. For instance, 100% adsorption of parent and derivative PAHs without considering about external and internal interception of human body might greatly overestimate the exposure assessment in this study. The inhaled efficiencies and deposited fraction for particle-bound PAHs in the human respiratory tract were highly particle-size dependent (Chen et al., 2019; Luo et al., 2015). Additionally, dermal absorption is related to time-dependent concentrations on the skin surface and gender difference (Cao et al., 2019; Gong et al., 2014). However, a constant transdermal coefficient was used and the same skin properties were also assumed, which might also add uncertainty to the dermal absorption. Finally, deterministic risk assessment also produces underestimated or overrated evaluation results due to complex and changeable parameters in workplaces. Nevertheless, our study gains a new perspective on the potential health risk resulting from the exposure to the diverse contaminants emitted from e-waste dismantling activities.

4. Conclusions

The pollution profiles of parent PAHs, Cl/BrPAHs, OPAHs and CBZ were systematically investigated in five e-waste recycling workshops. Findings showed that high atmospheric level of parent and derivatized PAHs emitted from different workshops, which could be identified as new sources of HPAHs and OPAHs. Emissions of those pollutants from electric heating workshops were much higher than those from other workshops, indicating that the priority to control and reduce their emission. E-waste recycling processes were facilitated the formation of OPAHs than other derivatized PAHs. Congener profiles of specific distribution among WPCBs recycling can be served as possible fingerprints and source apportionments of environmental tracing. High carcinogenic risk via inhalation of parent PAHs in the dismantling workshops indicated that the need to consider combustion by-product besides additive flame retardants in future studies on health implications for e-waste workers. Our results indicate that we need to center on the PAHs mixture contamination. Finally, to develop a more comprehensive risk evaluation system for the exposure of PAHs mixture, critical exposure pathways, unexpected sources and environmental fates of emerging contaminants need further confirmation and clarification.

CRediT authorship contribution statement

Ranran Liu: Formal analysis, Methodology, Writing - original draft. **Shengtao Ma:** Writing - review & editing. **Yangyi Yu:** Formal analysis, Methodology. **Guiying Li:** Writing - review & editing. **Yingxin Yu:** Visualization, Investigation. **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 material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envint.2020.106059>.

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