



Comparing pollution patterns and human exposure to atmospheric PBDEs and PCBs emitted from different e-waste dismantling processes



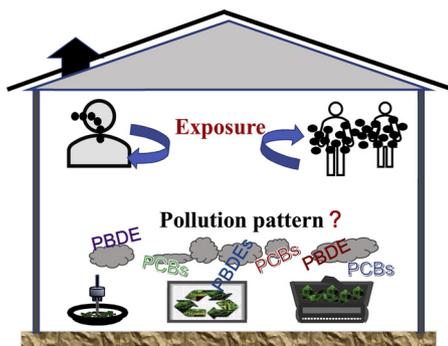
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GRAPHICAL ABSTRACT



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ABSTRACT

Waste electrical and electronic equipment (E-waste) recycling provides post-consumption economic opportunities, can also exert stress on environment and human health. This study investigated emissions, compositional profiles, and health risks associated with polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) at five workshops (electric blowers to treat mobile phones (EBMP), electric heating furnaces to treat televisions (EHFTV) and routers (EHFR), and rotatory incinerators to treat televisions (RITV) and hard disks (RIHD)) within an e-waste dismantling industrial park. Total suspended particulate (TSP), PBDE, and PCB concentrations were $490\text{--}1530\ \mu\text{g m}^{-3}$, $26.6\text{--}11,800\ \text{ng m}^{-3}$ and $6.4\text{--}19.8\ \text{ng m}^{-3}$ in different workshops, respectively. Tetra-BDEs were dominant in TV recycling workshops, whereas deca-BDEs were in other workshops. BDE-47, -99, and -209 were the most abundant PBDEs during e-waste recycling activities (except in RIHD workshop). Penta-CBs were present at high levels in TV workshops, as were tetra-CBs in RIHD workshop. Low brominated BDEs contributed a large portion during working and non-working time. The percentages of octa-BDEs and nona-BDEs were higher during non-working than working time. PBDEs posed a higher non-cancer risk; PCBs posed cancer risk to workers through inhalation in TV workshops. This study provides insights into environmental characterization of PBDEs and PCBs during e-waste recycling processes.

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1. Introduction

Waste electrical and electronic equipment (E-waste) has become a global environmental problem, and has been increasing annually at a rate of 3–5% [1–3]. The waste printed circuit board (WPCB) is the core part of the electronic device, offering particularly high recovery potential. This is because it contains significant amounts of valuable metals and materials [4–6]. This provides an opportunity for post-consumption economic activity with respect to WPCBs. However, recycling activities can also gradually increase stress on the environment as hazardous substances are released during recycling activities. This can adversely impact the eco-system and human beings [2,7–9].

E-waste hazards are among the emerging issues raising concerns in recent years [1,3]. Polybrominated diphenyl ether (PBDEs) and polychlorinated biphenyls (PCBs) are widely used in different electrical products and can be released from e-waste recycling or dismantling activities. Previous studies reported high levels of PBDEs in television WPCBs recycling workshops [10–12] and in the environments around the disposal areas [13–16]. Besides PBDEs, commercial PCBs congeners have been banned or restricted in many countries; however, recent evidence shows that there are elevated level of atmospheric PCBs in E-waste recycling sites [17–19], and e-waste workers have been exposed to risk of PCBs [17,20]. This makes it important to understand contemporary source factors of PCBs from primary or secondary emissions, to identify successful control measures.

However, very few studies have examined PCB contamination from the extensive dismantling of WPCBs, because most research has assumed that PCB emissions do not need to be considered during the WPCB dismantling processes. Very few studies have considered the emission characteristics of dismantling different kinds of WPCBs using typical techniques [12,21]. Such study is needed to deepen and refine the future development direction of WPCBs recycling [22]. Different types of WPCBs have their own specific recycling processes. Thus, more attention should be focused on the emission characteristics and fate behaviors of PBDEs and PCBs with respect to different types of e-waste sources and different recycling techniques. This could provide fundamental information on source apportionment, and would help update the emission inventory and abatement of PBDEs and PCBs.

High contamination levels of pollutants in the environment can create significant human exposure [23], especially for workers in e-waste recycling facilities [24]. Bi et al. [25] reported high PBDEs levels in the serum of dismantling workers in the town of Guiyu, China. High levels of PBDEs and PCBs contamination can disrupt the endocrine system [7], reproductive system [26], immune system [27] and also have other health effects [28,29]. Existing research on human health exposures at e-waste sites have mainly focused on inhalation, dust ingestion, and dietary ingestion. These studies show that there is a high exposure risk of PBDEs at e-waste dismantling sites [30–32]. However, there is limited detailed research on e-waste workers' exposure to persistent organic pollutants (POPs) contaminants using different dismantling techniques to recycle different WPCBs. Workers involved in e-recycling activities may face additional exposure to those contaminants as a result of environmental contamination. This makes it necessary to assess the potential health risks of exposure for e-waste workers in different workshops.

This study included the collection of air particles emitted from different WPCB recycling workshops using different typical dismantling techniques. The goal was to investigate the distribution, sources, and contamination profiles of PBDEs and PCBs during e-waste dismantling processes. To understand the diffusion and transformation mechanisms, the study examined PBDEs and PCBs during non-working time. Additionally, for the sake of health protection, the study compared e-waste workers' exposure associated with the inhalation and dermal exposure to PBDEs and PCBs through different dismantling techniques. This was done to better understand the significance of those pathways for overall human exposure and the resulting potential risk.

2. Material and methods

2.1. Study location

The study was conducted in an e-waste dismantling industrial park located in southern China. Five typical workshops using different dismantling techniques to recycle different WPCBs were chosen as the sources of emitted particulate matter (PM) as well as potential PBDEs and PCBs. Workshops used the following practices: one was using electric blowers to treat mobile phones (EBMP), two were using electric heating furnaces to treat televisions (EHFTV) and routers (EHFR), and some were using rotary incinerators to treat televisions (RITV) and hard disks (RIHD) (Table S1). A residential area near the e-waste recycling zone was selected as a control site. Detailed information about the typical processes used to recycle different WPCBs was reported in a separate study [33].

2.2. Sample collection and analysis

Twenty air samples were collected on a 20.3 cm × 25.4 cm pre-baked glass fiber filter (GFF) (Whatman, Maidstone, England) using a high-volume air sampler (Tianhong, China) at a flow of 0.15–0.25 m³ min⁻¹. Two samples were collected at each workshop. The two daily sampling times were approximately 8 h each, from 9:00 to 17:00 (working time) and from 21:00 to 5:00 (non-working time) during April and May 2013. Detailed information about the pre-treatment and treatment procedures after GFF sampling is provided in the supplementary information (SI).

All samples were spiked with surrogate standards and Soxhlet extraction, and then purified using a multilayer silica/alumina column [11]. Twenty PBDEs and 38 individual PCBs congeners were quantified using an Agilent 7890A gas chromatography coupled with a 5975C mass spectrometer. Chromatographic separation was performed on a DB-5HT capillary column (15 m × 0.25 mm × 0.1 μm, J&W Scientific, Folsom, CA) for PBDEs and on a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm, J&W Scientific, Folsom, CA) for PCBs. The quantitative analysis was performed in the selected ion monitoring mode. Ion fragments *m/z* 474, 476, and 478 were used for the internal standard (¹³C-PCB-208). The surrogate standard (¹³C-PCB-141 and ¹³C-PCB-209) were monitored at *m/z* 372, 374 and 376 and *m/z* 510 and 512, respectively. A detailed description of the analyses and characteristic ions of the target compounds for mass spectral analysis are provided in the SI.

2.3. Quality assurance and quality control

For each batch of 12 treated samples, a procedural blank and a spiked sample were processed to assess accuracy [21]. The analysis of the method blanks for the GFF analysis procedure identified only a very small amount of PBDE, including BDE-47 and -99; these levels were appropriately subtracted from the levels detected in the field samples. The recoveries of the surrogate standards of ¹³C₁₂-PCB-141 and ¹³C₁₂-PCB-209 were 103.4% ± 5.2% and 106.4% ± 4.2% in all blank samples, and 97.8% ± 22.8% and 103.9% ± 23.9% in the field samples, respectively. With a mean sample volume of 194 m³ and a final extract volume of 200 μL, the reported method detection limits were 1.0 pg m⁻³ for tri- to hepta-BDEs and 5.0 pg m⁻³ for octa- to deca-BDEs and PCBs, based on previous reports [11,32]. PBDEs concentrations were blank-corrected in all samples, but were not corrected by the surrogate standard recoveries. For each sampling site, the PBDEs and PCBs concentrations used for the study were the average of duplicate samples. Analyte concentrations below the reported method detection limits were set as zero when assessing health risk.

2.4. Risk assessment

The health risks associated with PBDEs and PCBs through inhalation and dermal exposure pathways were assessed using reported methods [20,34]. The non-cancer risk index (HI) of each compound was defined as the ratio of chronic daily intake (CDI_i) to its corresponding reference concentration (RfD_i) listed in Table S2 [32]:

$$HI_i = \frac{CDI_i}{RfD_i} \quad (1)$$

When HI is ≥ 1.0 , there is an adverse health effect for workers [32].

The lifetime cancer risk (LCR) was estimated using Eq. (2):

$$LCR_i = CDI_i \times CSF_i \quad (2)$$

In this expression, CSF is the cancer slope factor (kg day mg^{-1}), listed in the SI. A compound with a LCR lower than a range of 1.0×10^{-6} to 1.0×10^{-4} indicates a safe acceptable range [20,32].

3. Results and discussion

3.1. TSP Concentration comparison at different dismantling workshops

Fig. 1 summarizes the total suspended particulate (TSP) concentrations found in five typical dismantling workshops and the residential area. During the working time, TSP concentrations ranged from 490 ± 14.9 to $1530 \pm 340 \mu\text{g m}^{-3}$; these levels were 4 to 13 times greater than the threshold set by the primary China national standards GB3095-2012 ($120 \mu\text{g m}^{-3}$). This demonstrates that WPCBs recycling workshops face significant ambient TSP pollution. Particle concentrations were significantly lower during non-working time, compared with the working time. For example, the TSP concentration decreased significantly, from 1530 ± 340 to $140 \pm 18.9 \mu\text{g m}^{-3}$ in the EHFTV workshop between working and non-working times. In addition, particle matter levels remained relatively stable during non-working time, and there were no significant differences between different workshops and the residential area. This result can be partly attributed to the atmospheric diffusion and enhanced deposition at lower temperatures when WPCBs recycling activities were temporarily stopped at night.

However, TSP concentrations differed significantly at different recycling workshops using different dismantling techniques for different WPCBs. The highest TSP concentration ($1530 \pm 340 \mu\text{g m}^{-3}$) was found in the EHFTV workshop, followed by the RITV workshop ($980 \pm 390 \mu\text{g m}^{-3}$), EHFR workshop ($920 \pm 110 \mu\text{g m}^{-3}$), RIHD

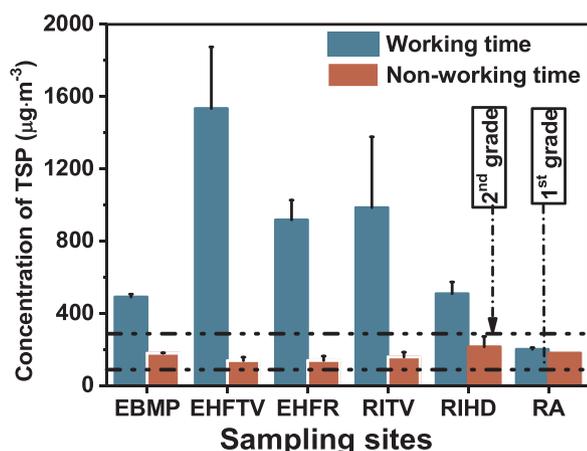


Fig. 1. TSP concentration at different WPCB dismantling workshops and residential areas during working and non-working time (the 2 dashed lines mean the 1st and 2nd grades of TSP concentration defined by Chinese ambient air quality control criteria GB3095-2012).

workshop ($510 \pm 64.3 \mu\text{g m}^{-3}$), and EBMP workshop ($490 \pm 14.9 \mu\text{g m}^{-3}$) workshops. The different types of WPCBs originating from different e-waste may mainly explain the fluctuation in TSP concentrations. The TV WPCBs recycled in the EHFTV workshop were used for a long time, and significant amounts of dust deposited in the TV cabinet may be rereleased into the atmosphere during dismantling processes. Furthermore, the operating platform of the EHFTV workshop was an open system, with electronic components manually removed using mechanical cracking. This process also resulted in a relatively higher PM emission level.

TSP concentrations in the EHFTV workshop in this study were comparable to the result obtained by a previous study at the town of Guiyu ($2210 \mu\text{g m}^{-3}$) [11], and from other e-waste recycling workshops, such as in Shanghai, China ($1790 \mu\text{g m}^{-3}$) [12] and Sweden ($3300 \mu\text{g m}^{-3}$) [35]. Comparatively, relatively lower TSP concentrations were found in the RITV workshop, which also dismantled TV WPCBs. This may be because the closed incinerator was used in this workshop during dismantling processes, and the waste gas was only emitted when opening the incinerator to replace WPCBs materials. This result suggests that a closed incinerator system, with an appropriate exhaust gas treatment device, can significantly reduce particulate emissions. The PM concentrations in RIHD and EBMP workshops were the lowest, because the WPCBs coming from these e-wastes were of small sizes and a fine structure. In summary, the recycling processes and the types of WPCBs dismantled in recycling facilities may determine particle concentrations.

3.2. Emission patterns of PBDEs and PCBs using different dismantling techniques

Table 1 provides the pollution levels of emitted PBDEs and PCBs at five different e-waste dismantling workshops using different dismantling techniques. The highest PBDE concentrations were detected at average concentrations of $11,800 \text{ ng m}^{-3}$ in the EHFTV workshop, followed by concentrations of 740 ng m^{-3} in the RITV workshop. Lower levels were found at the other three workshops; in decreasing order, these levels were: EHFR (170 ng m^{-3}); RIHD (140 ng m^{-3}); and EBMP (26.6 ng m^{-3}). PBDE concentrations in all workshops were much higher than at the residential area (6.5 ng m^{-3}).

Compared with other e-waste dismantling workshops, the PBDEs concentrations in this study (except the EBMP workshop) were much higher than levels reported in the United States (USA) (93.0 ng m^{-3}) [36], Sweden (63.7 ng m^{-3}) [35], and Korea (16.9 ng m^{-3}) [37]. In this study, the levels in the EHFTV workshop were much higher than previously measured at the same e-waste site [10,11]. Different disassembly conditions and recovery technologies may explain the different pollution emission characteristics. However, these results indicate that recycling WPCBs may be a potential important source of

Table 1

PBDEs and PCBs concentrations (Mean \pm SD, ng m^{-3}) during different recycling workshops and residential area.

Workshops	PBDEs		PCBs	
	Working time	Non-working time	Working time	Non-working time
EBMP	26.6 ± 9.4	9.6 ± 0.1	nd	nd
EHFTV	$11,800 \pm 170$	17.6 ± 9.9	$22. \pm 0.8$	nd
EHFR	170 ± 38.5	6.4 ± 1.3	nd	nd
RITV	740 ± 56.7	8.6 ± 1.1	12.4 ± 1.4	nd
RIHD	140 ± 53.6	19.8 ± 2.0	1.3 ± 0.0	nd
RA	6.5 ± 1.1	16.5 ± 0.0	nd	nd

EBMP: electric blowers to treat mobile phone; EHFR: electric heating furnaces to treat router; EHFTV: electric heating furnaces to treat televisions; RITV: rotary incinerators to treat televisions; RIHD: rotary incinerators to treat hard dishes, RA: residential area. nd, under detection limit.

organo-halogen pollutants, such as PBDEs.

Compared with PBDEs, PCBs concentrations were lower in this study. This was consistent with other studies focused on e-waste dismantling related pollution [38]. PCBs were found only in the EHFTV, RITV, and RIHD workshops, suggesting partial contamination across different WPCB recycling facilities. The highest PCB concentrations were found in the EHFTV workshop (22.9 ng m^{-3}), followed by RITV (12.4 ng m^{-3}) and RIHD (1.3 ng m^{-3}). This may be because PCB-contaminated electrical components were used in those TV printed circuit boards. PCBs have also been reported as being used for heat transfer and insulating fluid in old electrical transformers, capacitors, and plasticizers [39,40].

Few studies have reported the presence of PCBs in e-waste workshops in recent years [20,41], and PCB levels in this study were comparable to data reported for another large e-waste dismantling site in Taizhou, China (10.3 [20] and 17.6 ng m^{-3} [41]). However, PCBs levels were lower than that in Qingyuan, China ($7.83\text{--}76.3 \text{ ng m}^{-3}$) [19]. The lower PCB concentrations in e-waste recycling sites may be because PCB production and use are much lower around the world due to their prohibition.

3.2.1. Electric blower workshop

Fig. 2 shows the contributions of different PBDEs congeners in the EBMP workshop. When WPCBs were dismantled using electric blowers, deca-BDEs were the dominant group, accounting for 31.0% of the total PBDEs. Penta-BDEs were the second most abundant group (accounting for 23.4% of the total PBDEs), followed by tetra-BDEs (accounting for 17.2%). The congener profiles in the indoor air differed from the profiles associated with known technical products. This suggests that they came from a mixed source [42]. Fig. S1 shows the contribution of different BDEs components; BDE-209 was the most abundant component (31.0%); BDE-99 and -47 were the other two most abundant components in this workshop, accounting for 20.2% and 12.6% of total PBDEs, respectively.

3.2.2. Electric heating workshops

The electric heating furnace is the most widely-used heating machine to dismantle different WPCBs. PBDEs concentrations in EHFR and EHFTV workshops were approximately 6 and 443 times higher compared to the electric blower workshop. The significant increase was mainly attributed to the higher heating temperature used ($> 250 \text{ }^\circ\text{C}$) during the dismantling processes [12,16]. In addition, the open operating platform and intensive recycling activities may also lead to the increased emission of these semi-volatile organic contaminants.

In the EHFTV workshop, tetra-BDEs (mainly BDE-47) were the highest congeners, accounting for 46.4% of the total PBDEs, followed by penta-BDEs (mainly BDE-99, accounting for 22.5%) (Figs. 2 and S1). Additionally, BDE-209 was observed by far less than tetra- and penta-BDEs congeners, accounting for 16.9% of the total PBDEs. However, the

proportion of BDE-209 (50.4%) was clearly dominant in the EHFR workshop. The large difference may be associated with the different PBDE contents added into different WPCBs materials. Technical penta-BDEs was mainly used in TV WPCBs, whereas deca-BDEs might be usually used in router WPCBs.

Overall, the congener profiles differed from compositions in the technical penta-BDEs and deca-BDEs mixtures. This may be due to the evaporation of less brominated congeners and the degradation of higher brominated BDEs. In addition, a mixture of technical penta-BDEs and deca-BDEs may be used in those e-waste [10,12,43]. A penta-BDEs commercial product has been listed as POPs and had been gradually phased-out worldwide [44]; however, our results indicated that high levels of penta-BDEs were released into the atmospheric environment during WPCB recycling processes.

Table S3 also shows the relative abundance of PCBs in the EHFTV workshop. Penta-CB constituted the greatest homologue group (over 80%) in the particle phase, followed by tetra-CB (8.9%). Tri-CB, hexa-CB and hepta-CB made up a smaller proportion (1.2–3.9% in total). These results were not consistent with a previous study on PCBs in e-waste recycling factories in Taizhou, China, where tri-CB and tetra-CB were the primary homologue groups [20]. This may be due to different kinds of e-waste being used in different workshops. For the congener-specific analysis of PCBs, CB-82 and -118 were much higher than other observed PCB components. This indicates that sources such as Aroclor 1254 or Clophen A50 were added in those E-waste WPCBs, as well as the crucial objects which needed to be focused on when the waste was being preferentially treated. However, the percentage of those congeners were much higher in this study than in commercial products [45]. Gas-particle partition, volatilization or/and redistribution, transformation or/and degradation, and other emission sources may have contributed to these changes [20,46–48]. Similar results were seen for CB-77 and CB-126.

In summary, the pollutant emission characteristics of PBDEs and PCBs differed when different types of e-waste WPCBs was dismantled, even when same electric heating furnace treatment process was used.

3.2.3. Rotary incinerator workshops

The total PBDEs concentration in the RITV workshop ($740 \pm 56.7 \text{ ng m}^{-3}$) was much higher than that in the RIHD workshop ($140 \pm 53.6 \text{ ng m}^{-3}$) (Table 1). Similar to the EHFTV workshop, tetra-BDEs (40.7%) and penta-BDEs congeners (21.7%) also governed the PBDE patterns in the RITV workshop; the total proportion of octa-BDEs, nona-BDEs, and deca-BDEs increased to 1.33%, 5.95%, and 19.5%, respectively (Fig. 2). This may be because different heating temperatures were used during different recycling processes. The high temperatures used in the rotary incinerator workshop facilitated the release of heavily higher brominated congeners into atmospheric environments. One exception occurred in the compositional profile in RIHD workshop, where tri-BDEs components contributed to approximately 22.9% of the total amount and became the dominant components, followed deca-BDEs (29.3%) and tetra-BDEs (26.5%) (Fig. 2).

The PCBs at two types of WPCBs exhibited a different composition of homologue groups (Table S3). Results indicated that penta-CBs and hexa-CBs were the two predominant groups, accounting for 39.4% and 33.0% of total PCBs, respectively, in the RITV workshop. In the RIHD workshop, tetra-CB (42.3%) was the most prevalent homologue group in the samples, followed by hexa-CB (36.1%). These results reflected the different sources of PCBs in the two types of WPCBs. However, CB-138 was found to be the dominant constituent congener in the RITV and RIHD workshops, accounting for 11.4% and 20.3% of the total PCBs, respectively. This suggests their greater abundance in WPCBs samples. Compared to PBDEs, a similar outcome was seen in the distribution of PCBs, in which higher chlorinated congeners contributed relatively more proportion of total PCBs compared with the electric heating workshops. For example, hexa-CBs and hepta-CBs made up 33.0% and 13.5% of total PCBs, respectively, in the RITV workshops, which were

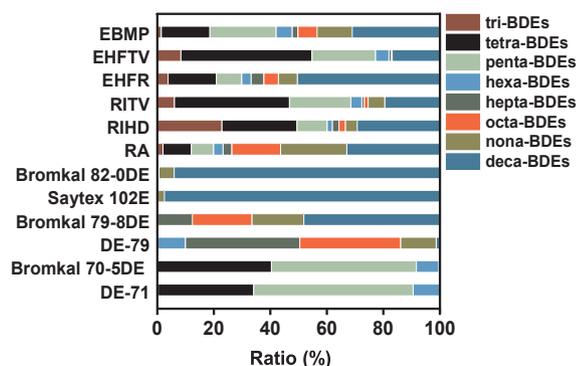


Fig. 2. Comparison of PBDE isomer patterns in the atmospheric samples from different recycling processes with technical PBDE products.

8.5 and 10.8 times higher, respectively, than in EHFTV workshop.

Overall, the concentrations and congener profiles of PBDEs and PCBs emitted from WPCBs depended on the kinds of commercial mixtures added into the WPCBs and recycling technology used. For example, several penta-BDEs were found in atmospheric samples from a TV WPCBs dismantling workshop; these may be from penta-BDEs commercial products. The operating temperature in different dismantling techniques was another important factor affecting PBDEs and PCBs emissions. Finally, the life cycle of the discarded electronics products and exhaust recycling platform may also significantly impact PBDE and PCB emissions.

3.3. Comparison of PBDE and PCB concentrations and congener profiles during working and non-working time

As discussed above, the ambient air in the workshops was significantly contaminated as a result of different recycling activities; however, significant decreases in PBDE and PCB concentrations were found during the non-working time (Table 1). The highest concentration of PBDEs during non-working time was found in the RIHD workshop, with a mean value of $19.8 \pm 2.0 \text{ ng m}^{-3}$. This level was comparable with the residential area (16.5 ng m^{-3}), and was 7 times lower than detected during the working time. Similar results were seen in other workshops; the emission levels of PBDEs at non-working times were approximately 3–670 times lower compared to working times. PCBs were not detected during any non-working time in any workshop. The dramatic decrease of PBDE and PCB concentrations during non-working times indicated that the dismantling of WPCBs is an important source of both pollutants. This conclusion increases concerns that e-waste recyclers may be exposed to toxic levels of these emitted POPs during dismantling activities.

For the lower brominated tri- to hepta-BDEs, the congeners were dominated by BDE-47 and -99. There was no significant difference between working and non-working time (except for EBMP workshop during non-working time) (Figs. 3 and S1). However, the proportion of lower brominated PBDEs decreased, whereas the corresponding higher brominated congeners increased during non-working time. The ratios of octa- and nona-BDEs/deca-BDEs were 0.62, 0.02, 0.24, 0.37 and 0.23 in the EBMP, EHFTV, EHFR, RITV, and RIHD workshops, respectively, during recycling processes. However, the values increased to 1.32, 0.59, 1.33, 1.35, and 0.73 for the same workshops during non-working time. For example, the contribution of tetra-BDEs and penta-BDEs decreased from 40.7% to 21.0% and from 21.7% to 10.5% in RITV workshop; the octa-BDEs and nona-BDEs increased from 1.33% to 13.9% and from

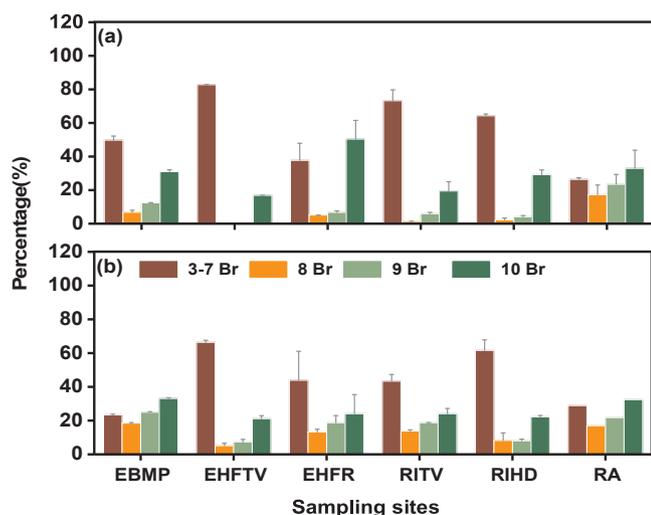


Fig. 3. PBDEs compositions during working (a) and non-working time (b). Error bars represent standard deviations.

5.95% to 18.7%, respectively (Figs. 2 and S2). In addition, nona-BDEs congeners and octa-BDEs congeners became the dominant species, and BDE-209 (33.1%), BDE-207 (10.0%), and BDE-206 (8.3%) were the dominant compounds in the EBMP workshop, respectively (Figs. S1 and S2).

Particle-bound lightly brominated congeners are mainly derived from evaporation and reabsorption [16,49]; high recycling temperatures facilitate the volatilization of lower brominated congeners. This results in greater fractions of lightly brominated congeners in atmospheric environments during the dismantling processes. PBDEs are semi-volatile organic compounds, and the estimated solid phase vapor pressures (Ps) increase with the decrease in the degree of bromination [12]. Lightly brominated congeners volatilize from particles into the air more easily. Higher brominated congeners trapped in the particle phase contribute a higher percentage of higher brominated BDE congeners during the non-working time. In addition, debromination from technical deca-BDEs congeners to lower brominated congeners has been seen in sunlight and thermal processes [50–52]. Many studies on atmospheric PBDEs transformation have indicated the debromination of highly brominated BDEs [16,49].

3.4. Health risk assessment with different dismantling techniques and uncertainty analysis

This study compared the non-cancer hazard indices (HI) of individual and total PBDEs and PCBs associated with inhalation exposure to different WPCBs using different dismantling processes during working times. Fig. 4 shows that the highest non-cancer risk was seen in the EHFTV workshop at an HI value of 23.7. This level was 790, 158, 18, and 108 times higher than for the EBMP (0.03), EHFR (0.15), RITV (1.32) and RIHD (0.22) workshops, respectively. Only the inhalation HI of PBDEs in EHFTV and RITV workshops exceeded 1.0, indicating that PBDEs at this pollution level posed a non-cancer risk to the dismantling workers [32]. The non-cancer risk in the other three workshops were lower than 1.0; however, the HI of PBDEs in EHFR and RIHD workshops all exceeded the potential risk level (≥ 0.1). In addition, the PCBs in the RITV (0.16) and EHFTV (0.29) workshops also posed a potential risk. The results indicated that TV recycling workshops were the sites with the highest PBDE and PCB exposures; and recycling workers face a high risk of occupational exposure at these sites (Fig. 5).

Non-cancer risks were assessed based on PBDE and PCB dermal exposure levels (Figs. S3–S5). For PBDEs, the HI values were

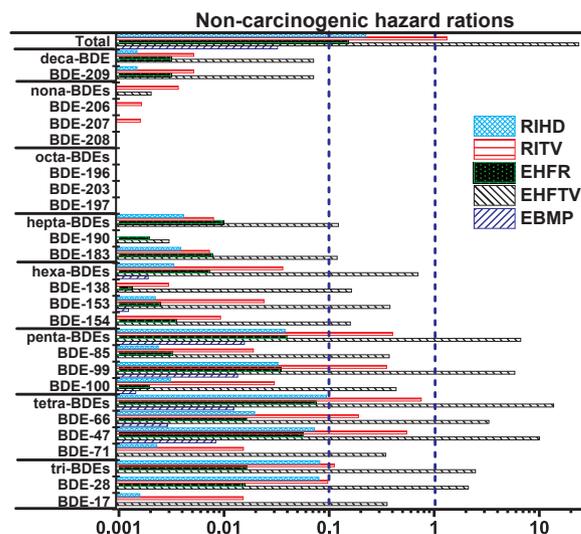


Fig. 4. Non-cancer risks associated with PBDEs through the inhalation in different workshops during working time (the dashed lines mean an adverse health effect posed to recycling workers).

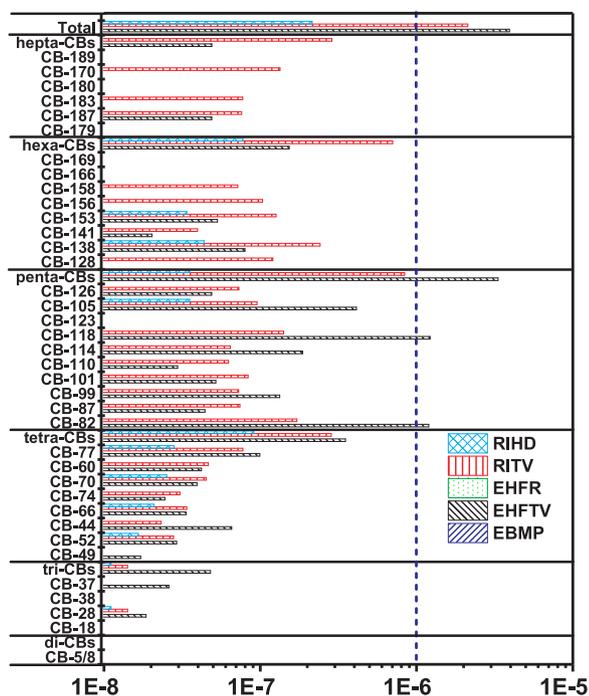


Fig. 5. Cancer risks associated with PCBs through the inhalation in different workshops during working time (the dashed lines mean an adverse health effect posed to recycling workers).

1.3×10^{-5} , 8.9×10^{-3} , 5.7×10^{-5} , 5.0×10^{-4} , and 8.5×10^{-5} in the EBMP, EHFTV, EHFR, RITV and RIHD workshops, respectively. The contributions of PCBs to dermal exposure were 1.1×10^{-4} , 5.9×10^{-5} , and 5.9×10^{-6} in the EHFTV, RITV, and RIHD workshops, respectively. This suggests that the total HI of dermal exposure of PBDEs and PCBs were all below the risk level of 1.0. This means that those contaminants from PBDEs and PCBs may not exhibit significant occupational threats to the dismantling workers.

High pollution levels led to significantly higher exposures from tetra-BDEs and penta-BDEs congeners, both from inhalation and dermal exposure to PBDEs. In the EHFTV workshop, the contribution of tetra-BDEs to inhalation exposure was 13.7, accounting for 58% of total HI. Penta-BDEs substantially contributed to the HI of the total PBDEs (6.6); this indicated those compounds might also pose a health threat to the dismantling workers. For a congener-specific analysis of PBDEs, BDE-47 and -99 were two important hazardous pollutants, with HI values of 10.1 and 5.9 in the EHFTV workshop, and values of 0.55 and 0.36 in RITV workshop, respectively. Exposure to deca-BDE (BDE-209) was substantially low, despite higher concentrations reported in the most investigated workshops. However, lower brominated homologs such as BDE-47 and -99 are more easily distributed in the gas phase [51]; as such, the actual exposure risk to e-waste workers may be underestimated.

The LCR of both individual and total PBDEs and PCBs were also evaluated. The cancer risk of BDE-209 through the inhalation and dermal exposure pathways were all below the acceptable risk level (1.0×10^{-6}), for PBDEs and PCBs, as follows: in the EBMP workshop (4.9×10^{-10} and 1.9×10^{-13}), EHFTV (1.2×10^{-7} and 4.5×10^{-11}), EHFR (5.2×10^{-9} and 2.0×10^{-12}), RITV (8.6×10^{-9} and 3.3×10^{-12}), and RIHD (2.5×10^{-9} and 9.5×10^{-13}) (Table S4). The highest total cancer risk from PCBs through inhalation was in the EHFTV workshop (3.9×10^{-6}); this risk which was approximately 2 and 19 times greater than the risks seem for the RITV (2.1×10^{-6}) and RIHD (2.1×10^{-7}) workshops, respectively (Fig. 5).

These results demonstrated that the LCR of total PCBs through the inhalation pathway in TV recycling workshops was higher than the

acceptable LCR for carcinogens (1.0×10^{-6}). In the EHFTV workshop, the most important contributors to cancer risk were penta-CBs (3.3×10^{-6}), accounting for 85% of the total LCR. In addition, two important hazardous PCBs were CB-82 and -118, with LCRs of 1.2×10^{-6} and 1.2×10^{-6} , respectively. This demonstrated that those two contaminants may pose cancer threats to the dismantling workers in the EHFTV workshop. As for dermal cancer risk, adverse health effects are not expected across the five recycling workshops (Fig. S6).

The models for cumulative non-cancer or cancer risk assessment in this study assume that there are no synergistic or antagonistic chemical interactions between different chemicals and that all chemicals have the same effect on e-waste dismantling workers. This adds uncertainty to the risk estimates. In addition, inhalation exposure assessments should account for particle size distribution, as organic contaminants are highly particle size-dependent [32]. In this assessment, the concentration of PBDEs and PCBs were obtained from TSP; as such, this may overestimate contaminant uptake and the associated potential health risks.

Further, this study did not correct the PBDE concentrations in field samples to mitigate surrogate standard recoveries. This may create some bias with respect to the PBDE risk assessment. Additionally, only the particle-phase concentrations were evaluated; however, the permeability of the skin exposed and the exposed surface area can affect directly the accuracy of calculate risk to humans. This may lead to a difference between the calculated risks for inhalation and dermal exposure routes. For example, this study found that the estimated risks from inhalation were higher than those from dermal contact.

These conclusions align with those of Luo and Wu [32,34]. However, this conclusion is not fully aligned with other studies [53,54], which found the dermal uptake was roughly equal to or greater than uptake from inhalation exposure. Moreover, the f_{sa} of 25% represented the portion of the dermal area, based on the hypothesis that thick cloths provide resistance to organic compound transport from the air to skin. This may underestimate contaminant exposure, because clothes with adsorbed pollutants may significantly enhance the dermal uptake of SVOCs compared with bare skin [55]. Therefore, the exposure results associated with dermal exposure remains of special concern and further research is recommended to improve the overall accurate risk assessment.

4. Conclusions

WPCB recycling workshops face significant ambient TSP, PBDE, and PCB pollution. Both the WPCB types and operating platforms could affect contaminant releases. Pollutant emission profiles of PBDEs and PCBs mainly depend on the types of commercial mixtures added into the WPCBs. High-temperatures used during the dismantling process may facilitate the heavily higher releases of chlorinated/brominated congeners into atmospheric environments. The PBDE emission levels of during non-working time differed from during working-times, due to evaporation and reabsorption. The released PBDEs and PCBs pose different health risks for e-waste recycling workers in TV workshops. More attention should be paid to protect dismantling workers from the exposure of these potential carcinogens.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jhazmat.2019.02.029>.

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