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# The health risk attenuation by simultaneous elimination of atmospheric VOCs and POPs from an e-waste dismantling workshop by an integrated de-dusting with decontamination technique



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#### HIGHLIGHTS

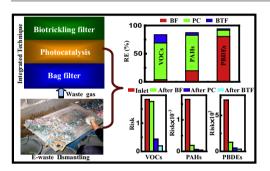
- Simultaneous removal of VOCs and POPs emitted from e-waste dismantling workshop.
- BF-PC-BTF integrated technique show high and stable removal to VOCs and POPs.
- Each technique contributes differently to REs and risk reduction of VOCs and POPs.
- The highest risk reduction efficiencies toward VOCs and PBDEs are PC and RF
- Higher TEFs of particle PAHs lead to highest risk attenuation ability of PAHs by BF.

# ARTICLE INFO

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#### GRAPHICAL ABSTRACT



# ABSTRACT

This study investigated the simultaneous abatement of atmospheric volatile organic compounds (VOCs) and persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs), using an integrated technique with a bag filter (BF), photocatalysis (PC) and biotrickling filter (BTF) in an electronic waste (e-waste) dismantling workshop. Approximately  $3.6 \times 10^5$ ,  $1.1 \times 10^3$ , and  $2.5 \times 10^3$  ng m $^{-3}$  of VOCs, PAHs, and PBDEs, respectively, were emitted from domestic stoves during a television dismantling process. During 30-day continuous treatment period, the treatment techniques eliminated 83.7%, 87.2% and 94.1% of VOCs, PAHs and PBDEs, respectively. Among three technologies, PC was responsible for the removal of 78.0% of VOCs and 72.3% of PAHs, while the BF technology removed 85.5% of PBDEs. The success assembling of different technologies depended on different gas-particle distributions of PAHs and PBDEs. Meanwhile, the decreased risk indices of all pollutants were also observed. The PC and BF treatment technologies reduced the cancer risks associated with the most VOCs and PBDEs (57.6% and 80.5%, respectively). The BF technology reduced risks from PAHs the most (86.1%), because of much higher toxic equivalency factors associated with particle-related-PAHs. After BTF treatment, the residual organic pollutants were further biodegraded and

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completely detoxified. This study indicated that the integrated technique, involving both excellent dedusting and decontamination capabilities, may provide an efficient alternative to current environment purification and human health protection practices.

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# 1. Introduction

The electronic waste (e-waste) recycling process causes significant pollution and harms to the environment and public health [1–4]. Since early 21st century, studies have focused on pollutant profiles and associated risks, particularly from air pollutants, both inside and outside e-waste recycling workshops [5–8]. Recent research revealed significant VOC emission during different activities associated with the e-waste dismantling process, and the severe emission was found particularly high in workshops using a rotary incinerator [9]. Another researcher observed that high levels of VOCs were emitted inside plastic waste recycling workshops [10]. These high concentrated VOCs could pose potential cancer and non-cancer risks on the workers through the inhalation exposure [11].

Besides VOCs, particles are also discharged to the air during the recycling process. Previous research reported that 24-h overall average concentration of total suspended particles (TSP) collected near e-waste recycling workshops in Guiyu town (124  $\mu$ g m<sup>-3</sup>) was almost twice the average level at Hong Kong (57.8–99.0  $\mu$ g m<sup>-3</sup>) urban site [5]. In fact, the particles generally were concerned of persistent organic pollutants (POPs) as well as heavy metals in e-waste regions. For example, polybrominated diphenyl ethers (PBDEs) within the particles were present at higher concentrations indoors in a Guiyu village (67,500 ng g<sup>-1</sup>) than in other cities of China (500–7500 ng g<sup>-1</sup>), Canada (2200 ng g<sup>-1</sup>), United Kingdom (2900 ng g<sup>-1</sup>) and United States (3500 ng g<sup>-1</sup>) [12]. Polycyclic aromatic hydrocarbon (PAHs) concentrations associated with TSP from Guiyu (from 40.0 to 347 ng m<sup>-3</sup>) were 3–28 times higher than levels obtained from Hong Kong (12.2 ng m<sup>-3</sup>) [13].

Furthermore, similar to VOCs, both TSP and associated POPs had much higher concentrations within on-site workshops than off-site ones during the working hours [14,15]. Inhaling particles with high POPs concentrations during recycling operations imposed significant health risks on the workers inside the workshop [3,16–18]. These risks included lung cancer risk from PAHs exposure [19], and cancer cell proliferation in female reproductive systems from PBDEs exposure [20]. Unfortunately, limited technology was reported to reduce the risks of the particles associated with these hazardous pollutants. Of course, these risks became more complex if VOCs and POPs-related-particles were emitted together, thus further complicating the threat to the on-site workers.

In our previous work, PC technology was found to be an effective detoxification method for gaseous aromatic VOCs [21,22]. Furthermore, typical PBDEs and PAHs (e.g., BDE-209 and phenanthrene) could be photocatalytically decomposed into aromatic ring opening intermediates, such as organic acids with lower toxicity [23,24]. Thus this work mainly pursued an integrated technique involving de-dusting with decontamination, by using a bag filter (BF) together with photocatalysis (PC)-biotrickling filter (BTF). The goal was to test the feasibility of this method to eliminate these complicated pollutants as well as reduce the risks of VOCs and POPs associated with TSP within e-waste dismantling workshops (PEWDW). The study tried to verify the hypothesis that BF efficiently blocked particles, reduced the concentration of POPs as well as its risk, and protected PC and BTF reactors from the negative effect of the particles. The particle-free gas then passed through the PC reactor, and VOCs as well as gaseous POPs with larger molecular weights were decomposed into easily biodegradable smaller substance, even to inorganic compounds. Finally, residual VOCs, PAHs, PBDEs, and other intermediates were completely biodegraded and detoxified using microorganism treatments [25–28]. Each technology's contribution to contaminant removal and risk reduction in the PEWDW was specified during 30-day operating period.

# 2. Experimental section

#### 2.1. Experimental setup

The experiment was conducted in a PEWDW, where e-waste dismantling equipment included domestic stoves, fed by fuel with honeycombed coal blocks. The e-waste mainly consisted of aged printed circuit board assemblies (PCBAs) from televisions. The detailed description of PEWDW was provided in Ref. [14]. As Fig. S1 shows, the integrated reactor used for these experiments included three sequentially connected parts: BF, PC and BTF reactor. The waste gas emitted from the dismantling process was first collected into BF through a gas-collecting cap, using a fan mounted between BF and PC reactor at a rate of 200 m<sup>3</sup> h<sup>-1</sup>. The gas was then successively introduced to PC reactor (up-flow mode) and BTF (down-flow mode). The experiment lasted for 30 days. More information about the experiment is available in Supporting Information.

# 2.2. Sample collection and analysis

To evaluate the pollutant levels and ability of the integrated technique to remove waste gas, four sampling intervals were established. Samples from day 1, 10, 20, and 30, were identified as the 1st, 2nd, 3rd, and 4th samples, respectively. Gaseous samples for VOC analysis were collected using vacuum Summa canisters (2.7 L, Entech Instruments Inc., CA, USA), and were thoroughly cleaned using high purity nitrogen before use.

To sample PAHs and PBDEs particulates, air volumes of  $108-180\,\mathrm{m}^3$  were drawn at  $0.15-0.25\,\mathrm{m}^3\,\mathrm{min}^{-1}$  for  $12\,\mathrm{h}$  through  $20.3\,\mathrm{cm} \times 25.4\,\mathrm{cm}$  glass fiber filters (GFFs) (Whatman, Maidstone, England). To collect the gaseous phase of these contaminants, the samples were subsequently drawn through  $6.5\,\mathrm{cm}$  in diameter  $\times$   $10.5\,\mathrm{cm}$  in thickness (a density of  $0.03\,\mathrm{g\,cm}^{-3}$ ) polyurethane foam (PUF) plugs, using a high-volume air sampler (Tianhong, China). GFFs were baked at  $450\,^{\circ}\mathrm{C}$  for  $12\,\mathrm{h}$  prior to sampling to remove organic contaminants, and PUF plugs were extracted with dichloromethane using Soxhlet for  $72\,\mathrm{h}$ . After sampling, loaded GFFs were wrapped in pre-baked aluminum foil and sealed in double-layer polyethylene bags, and PUF plugs were stored in solvent-cleaned glass jars with aluminum foil-lined lids. The samples were transported to the laboratory and stored at  $-20\,^{\circ}\mathrm{C}$  before the extraction.

VOCs were analyzed using an Entech 7100 pre-concentrator (Entech Instruments Inc., CA, USA) with an Agilent model 6890 N gas chromatography coupled with an Agilent model 5973 mass spectrometer (GC–MS), using U.S. Environmental Protection Agency (USEPA) TO-14 method. PAHs extraction and clean-up were done using previously reported methods [15,16]; samples were analyzed using a GC–MS system (GC6890N-MS5973). PBDEs

analysis was performed using a Shimadzu model 2010 GC coupled with a model QP2010 MS (Shimadzu, Japan), using negative chemical ionization in the selective ion monitoring mode with external standard and seven-point calibration curves. Detail analysis procedures of VOCs, PAHs, and PBDEs are summarized in Supporting Information.

# 2.3. Quality assurance and quality control

For VOCs, the standards in a mixture gas of 1.0 ppm were purchased from Linde Spectra Environmental Gases (Alpha, NJ). Target compounds were identified based on retention times and mass spectrum and quantified with a multi-point external calibration method. All calibrating reference standard points were run in duplicates or more. VOC calibrations had good dose–response correlation ( $R^2 > 0.99$ ) within the investigated concentration range.

For PAHs, procedural blanks were run every 5 samples to monitor potential contamination and interference [15]. Procedural and spiked blanks (including PUF and GFFs) were run before the extraction to quantify the recoveries. Two spiked blanks (one for PUF and the other for GFFs) were run for every ten samples. The correlation coefficients for all target compound and surrogate standard calibration curves were greater than 0.99. PAHs weren't presented in procedural blanks. PAHs recoveries ranged from 70.3% to 110.5%; surrogate recoveries ranged from 67.1% to 104.4%. The limit of quantification (LOQ) was set as the lowest concentration of the calibration standard (5  $\mu$ g L<sup>-1</sup> equal with 0.01 ng m<sup>-3</sup>).

For PBDEs, recoveries from eight spiking experiments ranged from 70.5% to 85.2% [14]. Two individual samples were subsampled from GFFs and then analyzed. Differences between duplicate samples were typically less than 20%. For PUF and GFF analysis method blanks (n = 3), only small amounts of BDE-47, -99, -190 and -209 were found, thus the data were not corrected. Surrogate recoveries ranged from 65.3% to 114.1% for  $^{13}$ C-PCB 141 and from 76.5% to 106.6% for  $^{13}$ C-PCB 209. The LOQ was set as the lowest calibration standard concentration (5 mg L $^{-1}$  equal to 0.01 ng m $^{-3}$  for tri- and hexa-BDEs, 10 mg L $^{-1}$  equal to 0.02 ng m $^{-3}$  for hepta-, octa-, nona- and deca-BDEs). Reported data weren't corrected by the recoveries.

# 2.4. Risk assessment

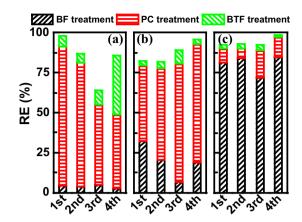
Cancer and non-cancer risks associated with the inhalation of VOCs, PAHs, and PBDEs for the worker were assessed using previously reported methods [9,14,29]. Detailed calculation methods are described in Supporting Information.

#### 3. Results and discussion

# 3.1. Simultaneous elimination of VOCs and POPs

Table S1 lists VOC concentrations and components generated during e-waste recycling process. Benzene, toluene, ethylbenzene, m/p-xylene and o-xylene were the top five dominant VOCs. Total VOC (TVOC) concentrations ranged from 48 to  $9.2 \times 10^2 \, \mu g \, m^{-3}$ , and toluene made up an average of 57.9% of TVOC (Fig. S2). These results are consistent with previous studies from electric heating furnaces (similar dismantling processes) [9].

Television PCBAs are mainly manufactured with epoxy or phenol resin containing a fire retardant; the single bond between the carbon atom and benzene ring is easily broken then releasing aromatics when heated [11]. Applying the integrated technique (Fig. 1a) could remove an average of 83.7% of TVOC over 30-day operation period. Specifically, PC technology removed approxi-



**Fig. 1.** Eliminating TVOC (a),  $\Sigma$ PAHs (b), and  $\Sigma$ PBDEs (c) using the integrated technique, across the four sampling events.

mately 65.3% of TVOC, followed by BTF (14.6%) and BF (3.8%) technology. This result consistent with previous research [11], suggesting that PC contributed the most to VOC removal due to its aromatic degradation abilities [21,22]. The de-dusting technology was less effective to VOCs.

Similar results were obtained for individual VOCs. Fig. S3 shows that the average removal efficiencies of benzene, toluene, ethylbenzene, m/p-xylene and o-xylene were measured as 75.2%, 84.8%, 82.2%, 80.2% and 83.2% using the integrated technologies, respectively. Benzene was the hardest to eliminate using the integrated technique, because benzene is also degraded intermediate when other large molecular weight aromatics, such as toluene, degrade [21,30]. Approximately 56.9–67.4% of these five VOCs were removed by PC technology, followed by BTF technology (14.8%) and BF technology (4.2%), which is consistent with TVOC removal results.

Using toluene as an example, the data show that the technologies changed in their abilities to remove individual VOCs as treatment time progressed. For example, the efficiency of PC in treating toluene decreased from 89.4% to 51.3%, while the removal efficiency of BTF increased from 6.4% to 40.5%. This may be because at the beginning of the treatment, the catalysts and ultraviolet lamps in PC reactor are at peak conditions, with a high ability to eliminate VOCs. However, after long treatment time in complex conditions, fine particles and refractory intermediates may stain catalyst and lamp surfaces, decreasing effective contact between the catalysts and lamps, and then decreasing the removal efficiencies. Similar tread is also observed for TVOC that the efficiency of PC decreased from 87.4% to 46.3%, while the removal efficiency of BTF increased from 6.8% to 37.1%, again supporting the above hypothesis.

Conversely, at the start of the treatment period, BTF is in start-up mode, with limited VOC removal capability. As biofilm grows on the packing materials, microorganisms help reduce VOCs. As such, using both PC and BTF technologies to remove VOCs leads to the best overall results. This trend is consistent with previous research applying BTF-PC techniques to treat organic waste gas emitted from a paint factory [31].

For PAHs, total PAH ( $\sum$ PAHs, gaseous plus particulate phase) concentrations ranged from  $9.4 \times 10^2$  to  $1.2 \times 10^3$  ng m<sup>-3</sup> before treatment, and approximately 67.0–95.9% of PAHs was in a gaseous phase (Fig. S4a). The four dominant PAH compounds were phenanthrene (Phe, accounting for an average of 36.6%), fluoranthene (Flua, average: 18.1%), naphthalene (Nap, average: 15.6%), and pyrene (Pyr, average: 12.4%) (Fig. S5a) due to the heat of television PCBA with the smoldering of honeycomb coals [14,15].

Total PBDE ( $\sum$ PBDEs) concentrations ranged from  $8.5 \times 10^2$  to  $4.8 \times 10^3$  ng m<sup>-3</sup> (ca. 90.2% in particulate phase and 9.8% in gaseous phase) before treatment (Fig. S4b). The top three PBDEs were BDE-209, -99, and -47, accounting for average proportions of 21.7%, 19.2%, and 18.4%, respectively (Fig. S5b). These PBDEs were used as additive flame-retardants in television PCBAs produced decades ago [14,15,32,33].

In summary, VOCs and typical POPs such as PAHs and PBDEs, were presented at significant levels in PEWDW. Once PAHs and PBDEs are released into atmosphere, these persistent pollutants are distributed in both gaseous and particulate forms. They can, however, be effectively eliminated with the integrated techniques of BF-PC-BTF. First, BF efficiently blocks particles, reducing POPs concentrations. BF treatment removed an average of 86.0% (decrease from 2.20 to 0.31 mg m<sup>-3</sup>) of TSP, efficiently eliminating particulate-based PBDEs and PAHs, and protecting PC and BTF reactors from the negative effect of particles. The particle-free polluted waste gas then enters PC reactor, where PAHs and PBDEs are decomposed, or even mineralized. Finally, microorganisms also possess the ability of efficient biodegradation to the organics.

Fig. 1b and c shows that the integrated technique achieved average removal efficiencies of 87.2% and 94.1% for  $\Sigma$ PAHs and  $\Sigma$ PBDEs, respectively, during the 30-day operation. This again confirms the success of the integrated technique in eliminating POPs. PC and BF contributed the most in reducing  $\Sigma$ PAHs and  $\Sigma$ PBDEs, at 63.2% and 80.5%, respectively. This difference relates to the different particlegas distribution of PAHs and PBDEs. As discussed above, most PAHs were in the gaseous phase (83.7% on average), which could be efficiently removed by PC technology (average reduction efficiency: 69.9%) (Fig. S6); BF was highly efficient in removing minor PAHs in the particulate phase (average reduction: 93.3%) (Fig. S7).

Conversely, approximately 90.2% of PBDEs were distributed on particles, which were well captured by BF technology (average removal efficiency: 84.0%) (Fig. S8). Similar to gaseous PAHs, PC achieved the highest removal efficiency for gaseous PBDEs (48.9%); residual POPs could be eliminated by the subsequent BTF. The integrated technique therefore achieves a high POPs removal efficiency.

A similar trend was seen for the removal of dominant POPs. For PAHs, the integrated technique achieved the highest average removal efficiency for Nap (95.7%), followed by Phe (85.9%), Pyr (81.3%), and Flua (77.7%). This suggests that PAHs with fewer rings are more easily removed than PAHs with more rings using the integrated technique. This aligns with other reported observations [34]. Moreover, PC played a primary role compared with BF (10.4–22.9%) and BTF (1.8–6.6%) in reducing the four dominant PAHs (51.8–82.7%) (Fig. S10), again showing the high capability of PC to eliminate PAHs.

For the top three PBDE contributors (BDE-47, -99, and -209) (Fig. S11), the integrated treatment efficiently eliminated almost all dominant PBDEs, achieving average reduction efficiencies of 94.9%, 95.9%, and 88.6%, respectively. As with  $\Sigma$ PBDEs, BF contributed the highest reduction efficiencies for these dominant substances compared to other technologies (78.5% in average), followed by PC (11.8% in average) and BTF (2.8% in average).

In summary, BF was very successful in removing particulate POPs; PC achieved a high elimination of VOCs and gaseous POPs; and BTF contributed additional biodegradation. The combined BF-PC-BTF technique effectively and simultaneously eliminated both VOCs and POPs, demonstrating the ability of this technique to purify the atmosphere at e-waste recycling sites.

# 3.2. Risk attenuation of VOCs and POPs

The non-cancer risk associated with VOCs in PEWDW was compared before and after the treatment. As Fig. 2 shows, before the treatment, the hazard ratios of benzene (3.46) on day 1 and

m/p-xylene (1.07) on day 10 were both higher than 1. This indicates that their concentrations exceed the reference levels of concern [35,36]. Other VOCs had hazard ratios ranging from 0.1 to 1, including m/p-xylene (0.79 on day 1), benzene (0.55, 0.12 and 0.15 on days 10, 20 and 30), o-xylene (0.34 and 0.32 on days 1 and 10), and toluene (0.13 on day 1). These results indicate a potential non-cancer threat associated with VOCs to the workers [37].

For VOCs, the lifetime cancer risk (LCR) of (Fig. 3) benzene (day 1:  $6.24 \times 10^{-4}$ ) and ethylbenzene (days 1 and 10:  $1.69 \times 10^{-4}$  and  $1.92 \times 10^{-4}$ , respectively) exceeded  $10^{-4}$ . These results indicate very high cancer risks at the current concentrations compared to reference levels [38]. The LCRs of benzene on days 10 ( $9.85 \times 10^{-5}$ ), 20 ( $2.13 \times 10^{-5}$ ) and 30 ( $2.71 \times 10^{-5}$ ) as well as ethylbenzene on day 20 ( $1.89 \times 10^{-5}$ ) ranged between  $10^{-5}$  and  $10^{-4}$ , indicating probable cancer risks [38]. In addition, the risk associated with ethylbenzene on day 30 ( $8.43 \times 10^{-6}$ ) was between  $10^{-5}$  and  $10^{-6}$ , indicating possible risks. Overall, these results show that non-cancer and cancer risks are danger to the worker with the exposure to VOCs, and these risks should be considered and proper treatment approaches should be selected before the waste gas discharged.

Figs. 2 and 3 indicated no obvious decreases in non-cancer and cancer risks after BF treatment, suggesting that de-dusting technology doesn't offer a significant reducing risks from VOCs. These results are similar with previous study, indicating that different de-dusting technologies contribute little to VOCs elimination [11].

In contrast, the decontamination techniques (PC–BTF) demonstrate significant risk reduction ability. PC treatment greatly reduced both non-cancer and cancer risk indices for all investigated VOCs. For example, the cancer risk index for benzene decreased from 3.34 to 0.51 on day 1 and from 0.11 to 0.05 on day 20. The toluene risk index decreased from 0.12 to 0.01 on day 1 for non-cancer risk. For non-cancer risks, benzene dropped from  $6.01 \times 10^{-4}$  to  $9.15 \times 10^{-5}$  on day 1 and from  $2.04 \times 10^{-5}$  to  $9.53 \times 10^{-6}$  on day 20). Cancer-related risks associated with ethylbenzene also dropped (from  $1.63 \times 10^{-4}$ ,  $1.84 \times 10^{-4}$  and  $1.83 \times 10^{-5}$  to  $2.65 \times 10^{-5}$ ,  $3.77 \times 10^{-5}$  and  $8.49 \times 10^{-6}$  on days 1, 10 and 20, respectively).

The LCRs of selected VOCs were all below 10<sup>-4</sup> after PC treatment, indicating that PC technology has a significant ability to reduce risks. Due to VOC concentrations were very high before PC treatment, the hazard ratios of benzene (0.51, 0.20 and 0.10 at days 1, 10 and 30) and toluene (0.14 and 0.27 on days 1 and 10) remained higher than 0.1 after treatment. Nevertheless, the fact that hazard indices of these VOCs were mostly below 0.1 after subsequent BTF treatment to support the success of the integrated PC–BTF decontamination technique.

Fig. 4a shows the cancer risk associated with  $\Sigma$ PAHs before treatment. The calculated lifetime cancer risk indexes associated with particulate PAHs  $(1.47 \times 10^{-3} \text{ in average})$  were higher than the significant risk level  $(10^{-3} \text{ is considered acceptable})$  [39]; the gaseous phase PAHs  $(1.74 \times 10^{-4} \text{ average})$ , however, showed a very low risk level. This result suggests that lower percentages of particulate PAHs are associated with a higher cancer risk, because particulate PAHs have much higher toxic equivalency factors (TEFs, Table S2). Hence, to decrease the toxicity of  $\Sigma$ PAHs, eliminating particulate phase PAHs is critical.

Fig. 4 shows that the average cancer risk indexes from particulate and gaseous PAHs decreased to  $4.41\times10^{-5}$  and  $1.49\times10^{-4}$ , respectively, after BF treatment. This indicates that BF technology can more efficiently reduce the risk associated with particulate PAHs than gaseous PAHs. After PC treatment, the cancer risk index associated with gaseous PAHs significantly reduced to  $3.36\times10^{-5}$ . With subsequent BTF treatment, the risk indexes were further reduced to  $2.54\times10^{-5}$  and  $1.73\times10^{-5}$  for PAHs in particulate

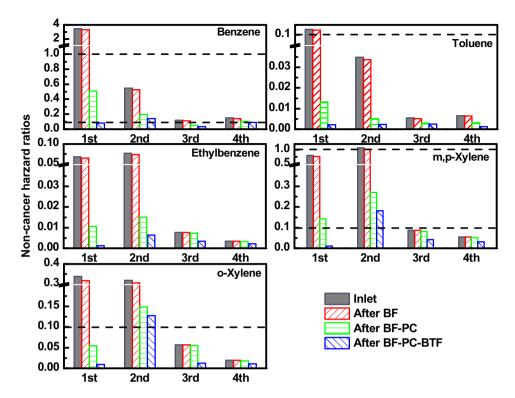
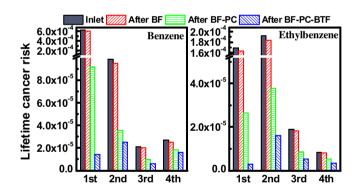
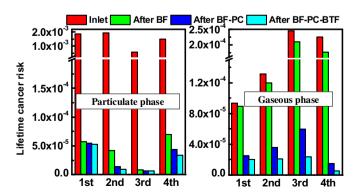


Fig. 2. Non-cancer hazard risk reduction of VOCs across the four sampling events using the integrated technique.

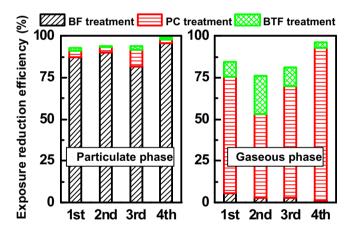


**Fig. 3.** Cancer hazard risk reduction of VOCs across the four sampling events, using the integrated technique.



**Fig. 4.** Cancer risks reduction of  $\sum$ PAHs by the integrated technique.

and gaseous phases, respectively. These levels were much lower than that before treatment, and were below the significant risk



 $\begin{tabular}{ll} \textbf{Fig. 5.} & $ \searrow $ \texttt{PBDEs} $ exposure $ reduction $ across $ the four sampling events $ after $ the integrated technique. \end{tabular}$ 

level ( $10^{-3}$  is considered acceptable). Fig. S12 shows similar results for carcinogenic  $\Sigma$ PAHs.

Figs. 5 and S13 show the exposure risk to workers from inhaling PBDEs before and after the integrated treatment. Fig. S13 shows that the workers' average exposure index in the PEWDW from particulate phase PBDEs was 639.43 ng kg<sup>-1</sup> day<sup>-1</sup>, which was approximately 9 times in the gaseous phase (73.35 ng kg<sup>-1</sup> day<sup>-1</sup>). This indicates that particle related PBDEs impose a higher exposure risk on the workers. After BF treatment, the exposure risk index decreased to 55.55 ng kg<sup>-1</sup> day<sup>-1</sup> for particulate phase PBDEs, again demonstrating BF's ability to reduce risks associated with POPs distributed on particles. The exposure risk index associated with gaseous PBDEs decreased to 15.11 ng kg<sup>-1</sup> day<sup>-1</sup> after PC treatment, indicating PC's ability to reduce risks associated with PBDEs in the gaseous phase. Overall, the risk reduction efficiencies

of particulate and gaseous PBDEs reached 95.0% and 84.6%, respectively, using the integrated BF-PC-BTF technique (Fig. 5). These results suggest that the integrated technique can efficiently reduce exposure risk from PBDE inhalation.

Similar results are obtained for the carcinogenic hazard indices of dominant PBDEs in Figs. S14 and S15. The hazard quotients of BDE-47, -99, and -209 were calculated using the reference dose (RfD), as reported by USEPA Integrated Risk Information System Toxicological Evaluations [40]; the draft RfD values were 7  $\mu g \ kg^{-1} \ day^{-1}$  for BDE-209 and 0.1  $\mu g \ kg^{-1} \ day^{-1}$  for both BDE-99 and BDE-47. The average hazard indices of BDE-47, -99 and -209 in particulate phase were 1.04, 1.33 and 1.50  $\times$  10 $^{-2}$ , respectively. Gaseous phase risks were significantly lower, at 2.86  $\times$  10 $^{-1}$ , 5.82  $\times$  10 $^{-2}$  and 4.55  $\times$  10 $^{-5}$ , respectively (Fig. S15). This indicates that the particulate phase of BDE-47, -99, and -209 impose the greatest threat. Similar to the exposure risk, BF treatment resulted in average reduction efficiencies of the particulate BDE-47, -99, and -209 hazard indices of 95.7%, 90.6% and 76.6%. This accounted for 97.5%, 94.0% and 86.5% of the total hazard index reduction (Fig. S14).

BF didn't do well for the reduction of the risks associated with gaseous BDE-47, -99, and -209 with only 2.2%, 7.7% and 23.2% of the hazard indices, respectively. The subsequent PC technology did efficiently reduce the risks, achieving 74.4%, 69.2% and 72.5% for reduction efficiencies. These efficiencies further increased to greater than 85.2% after the subsequent BTF treatment. Finally, the results prove the excellent risks reduction ability of gas and particulate POPs by employed this integrated technique.

### 4. Conclusions

In summary, this study evaluated the simultaneous elimination of both VOCs and POPs (PAHs and PBDEs) emitted from an e-waste dismantling process, and evaluated the reduction in risks achieved with an intergraded technique. Before the treatment, toluene, phenanthrene, and BDE-209 were the dominant VOC, PAH, and PBDE components, respectively. The integrated BF-PC-BTF technique achieved removal efficiencies of approximately 83.7%, 87.2% and 94.1% for TVOC,  $\Sigma$ PAHs, and  $\Sigma$ PBDEs, respectively, over 30-day operating period. Specifically, PC had a removal efficiency of 78.0% and 72.3% for VOCs and PAHs, respectively, while BF eliminated 85.5% of PBDEs. These differences were due to different distributions and characteristics of pollutant in gaseous and particulate phases. PC and BF contributed the most to reduce risks associated with VOCs and PBDEs. However, BF reduced more of the risks from PAHs than PC, due to higher risk from PAHs in the particulate phase with higher TEFs. Overall, the worker health risks from VOCs, PAHs, and PBDEs dropped significantly after the treatment of the integrated technique. All these results demonstrate that this integrated technique may provide an efficient way to purify the atmospheric VOCs and POPs, and improve human health on-site in e-waste recycling workshops, which should be of highly significance to fulfill the environmental pollution and pollution control field.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2016.05.013.

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