



Pollution profiles and health risk assessment of VOCs emitted during e-waste dismantling processes associated with different dismantling methods



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ARTICLE INFO

Article history:

Received 10 February 2014

Accepted 24 July 2014

Available online 16 August 2014

Keywords:

VOCs

Pollution characteristic

Risk assessment

E-waste dismantling

Dismantling techniques

ABSTRACT

Pollution profiles of typical volatile organic compounds (VOCs) emitted during dismantling of various printed circuit board assemblies (PCBAs) of e-wastes using different methods were comparatively investigated in the real e-waste dismantling workshops in South China in April 2013. Similar pollution profiles and concentrations of VOCs were observed between dismantling mobile phone and hard disk PCBAs by using electric blowers and between dismantling television and power supplier PCBAs using electric heating furnaces. Aromatic hydrocarbons (accounting for >60% of the sum of VOCs) were the dominant group during using electric blowers, while aromatic (accounting for >44% of the sum of VOCs) and halogenated hydrocarbons (accounting for >48% of the sum of VOCs) were the two dominant groups which contributed equally using electric heating furnaces. However, the distribution profiles of VOCs emitted during dismantling of televisions, hard disks and micro motors using rotary incinerators varied greatly, though aromatic hydrocarbons were still the dominant group. The combustion of e-wastes led to the most severe contamination of VOCs, with total VOCs ($3.3 \times 10^4 \mu\text{g m}^{-3}$) using rotary incinerators about 190, 180, 139, and 40 times higher than those using mechanical cutting, electric soldering iron, electric blower, and electric heating furnace, respectively. Both cancer and non-cancer risks existed for workers due to exposure to on-site emitted VOCs in all workshops especially in those using rotary incinerators according to the USEPA methodology, whereas only cancer risks existed in rotary incinerator workshops according to the American Conference of Industrial Hygienists methodology.

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1. Introduction

Electrical and electronic waste (e-waste) is currently the fastest growing stream (about 4% growth a year) of hazardous wastes globally (Andersson et al., 2012; ILO 2012). Most parts of the electrical and electronic equipment, especially the essential parts and printed circuit board assemblies (PCBA), are dismantled and recycled (Duan et al., 2011). Nevertheless, various toxic compounds in e-wastes end up in air, water, soil, or workers, causing damages to human health and the environment during the recycling of electronic components and valuable metals using crude treatment methods (Alston and Arnold, 2011; Man et al., 2013; Sun et al., 2011). The main pollutants during e-waste dismantling processes are heavy metals and organic potentially hazardous substances (Fu et al., 2013; Man et al., 2013).

Existing research on the pollution profiles during these e-waste recycling processes has mainly focused on heavy metals or semi-

volatile organic compounds (SVOCs) in air, water, and soil (An et al., 2011; Hadi et al., 2013), and most of the work was carried out outside, instead of inside of the dismantling workshops. To date, in a strong contrast to pollution profiles of heavy metals and SVOCs, little is known regarding the pollution characteristics of volatile organic compounds (VOCs) during the e-waste dismantling processes (Huang et al., 2013). However, among various toxic wastes emitted, VOCs are one group of the inevitable components during the e-waste recycling processes even when experiments are conducted in a laboratory. For instance, the bulk of VOCs can be detected during pyrolysis of e-wastes including feedstock containing acrylonitrile–butadiene–styrene (ABS) and high impact polystyrene with high levels of additives and dense polymers (Alston et al., 2011) as well as PCBA waste (Quan et al., 2010). Although one study about the pollution characteristics of VOCs was carried out inside an actual workshop (Huang et al., 2013), only plastic waste recycling granulation was included without involving the whole e-waste dismantling process.

It is well-known that most of the organics associated with VOCs are toxic and can pose various threats to humans and the environment

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(Rohr, 2013; Su et al., 2014). Therefore, it is necessary to evaluate the potential risks of emitted VOCs to the employees in actual e-waste dismantling workshops. Potential risks calculated according to the reference values of organics have proven to be useful to assess the occupational exposure risks to the workers and neighborhood (Li et al., 2013; Ramírez et al., 2012), although it ignores the hazard effects from the other pollutants like heavy metals. For instance, cancer and non-cancer risks through the inhalation of pollutants can be evaluated according to the standard methodology of US Environmental Protection Agency (USEPA) and occupational exposure cancer risk through the inhalation, dermal contact and non-dietary ingestion of pollutants can be evaluated using the methodology of American Conference of Industrial Hygienists (ACGIH) (Alavanja et al., 1990; Ramírez et al., 2012). Nevertheless, no published work on the cancer risk assessment for VOCs emitted during actual on-site e-waste dismantling processes using a comparison of approaches of the ACGIH and USEPA can be found in the literature.

In this study, the components and concentrations of VOCs emitted during the dismantling of different PCBAs using various disassembling techniques were determined inside the workshops during the actual e-waste dismantling processes. In addition, two methodologies for the assessment of cancer risks of the emitted VOCs to workers were evaluated during actual e-waste dismantling processes. The findings of this study may be helpful for the establishment of feasible and reasonable pollution controls in e-waste workshops.

2. Materials and method

2.1. Study location

In April 2013, the study was conducted in a small town in Shantou City, South China where e-wastes have been treated for near 30 years. Ten typical workshops using various methods to dismantle different PCBAs were chosen as a range of potential VOC sources, and the description of the workshops is provided in Table S1. A residential area in Guangzhou city was chosen as a control site. The dismantling procedure of e-wastes is shown in Scheme S1 and the detailed procedure is described in Supporting Information.

2.2. Sample collection and analysis

To recycle the valuable electronic components from PCBAs, a series of rather primitive and crude e-waste dismantling methods are usually employed. Primarily, pliers, hammers or chisels are used to cut or disintegrate PCBAs and collect integrated chipsets during the mechanical/physical process. Then, heating process is applied to open solder connections and separate various types of metals, electronic components and board, with heating apparatus like electric soldering iron, electric blower, electric heating furnace or rotary incinerator (Duan and Li, 2010). The pollution profiles of VOCs emitted during the dismantling processes might vary significantly, because the required heating temperatures differ widely for various disassembling methods and different e-wastes to be dismantled.

Emitted VOCs were collected using 2.7-L stainless steel canisters (ENTECH Instruments Inc., Silonite™) which were pre-cleaned five times using high purity nitrogen and pre-evacuated by a canister cleaner prior to sampling. The sampling canister, put near to the employee who dismantles the e-wastes, is about 60–80 cm away from the dismantling machine or heater and the sampling time is about 1.5 min for each sample. Three parallel samples were collected at each site. The samples were qualitatively and quantitatively detected using an Entech 7100 preconcentrator (Entech Instruments Inc., CA, USA) equipped with gas chromatography–mass spectrometer (7890A GC-5975C MS, Agilent technologies, USA) with the USEPA TO-15 method (He et al., 2012; Zhang et al., 2004). The concentrations of VOCs were quantified by external standard calibration using a standard sample

(TO-15, Linde Spectra Environment Gases, USA). Each target species was identified based on its retention time and mass spectra using the NIST 05 database. The detailed procedure is described in Supporting Information.

2.3. Quality assurance and quality control

Sampling sites were selected at random in the chosen town and three parallel samples were collected at each site. All samples were analyzed within 24 h after collection. Prior to measurements, all the experimental instruments were calibrated. Blank sample (ultra-nitrogen) analysis indicated that no target analytes existed in the analysis system.

Quality assurance and quality control including method detection limit (Table S2), field blanks, retention time, accuracy, precision duplications, and reference sample analyses, were all performed in accordance with the analytical procedure and requirements of USEPA Compendium Method TO-15 (USEPA 1999). The R^2 of the calibration curves for all compounds was >0.990. The method detection limit for each compound was less than $1.38 \mu\text{g m}^{-3}$. The relative standard deviation for all compounds of triplicates was <0.79% (Table S1).

2.4. Risk assessment

2.4.1. Assessment of non-cancer and cancer risk using the methodology of USEPA

Cancer and non-cancer risks of exposure to VOCs through inhalation were assessed according to the standard methodology of USEPA. The non-cancer risk of each compound (i) was calculated by dividing its daily concentration (C_i , $\mu\text{g m}^{-3}$) by its corresponding reference concentration (RfC , $\mu\text{g m}^{-3}$), regarded as hazard ratio (HR) according to $HR_i = \frac{C_i}{RfC_i}$. The reference concentrations for each VOC were taken from literature (Ramírez et al., 2012). Lifetime cancer risk (LCR) was calculated by multiplying each compound's unit risk (UR_i) values according to $LCR = C_i \times UR_i$. The unit risk data were obtained from USEPA (<http://www.epa.gov/iris/>).

2.4.2. Assessment of cancer risk of occupational exposure using the methodology of ACGIH

Cancer risk of occupational exposure to VOCs through the inhalation, dermal contact and non-dietary ingestion for workers was also evaluated according to the methodology from ACGIH (<http://www.acgih.org/>). The risk of occupational exposure (E_i) for each VOC was calculated as individual concentration divided by its time-weighted average (TWA_i), one of the three threshold limit values (Eq. 1). The total risk ($\sum E$) was calculated according to Eq. (2), where C_i ($\mu\text{g m}^{-3}$) is the detected concentration for each VOC. The TWA_i values were established under the assumption of working 8 h a day and 5 days per week for workers according to ACGIH, while the employees worked for at least 10 h a day and 6 days a week in these workshops. Hence, TWA_i (using 8 h a day and 5 days per week) was calibrated to TWA'_i (using 10 h a day and 6 days per week) here according to Eq. (3).

$$E_i = \frac{C_i}{TWA_i} \quad (1)$$

$$\sum E = \sum_i E_i \quad (2)$$

$$TWA'_i (\mu\text{g m}^{-3}) = TWA_i (\text{ppm}) \times \frac{M.W.}{24.45} \times 10^3 \times \frac{5 \times 8}{6 \times 10} \quad (3)$$

3. Results and discussion

3.1. Pollution profiles of VOCs

3.1.1. Electric blower workshops

The pollution profiles of emitted VOCs using electric blowers to melt soldering tin of different e-waste PCBAs are shown in Fig. 1. Workshops

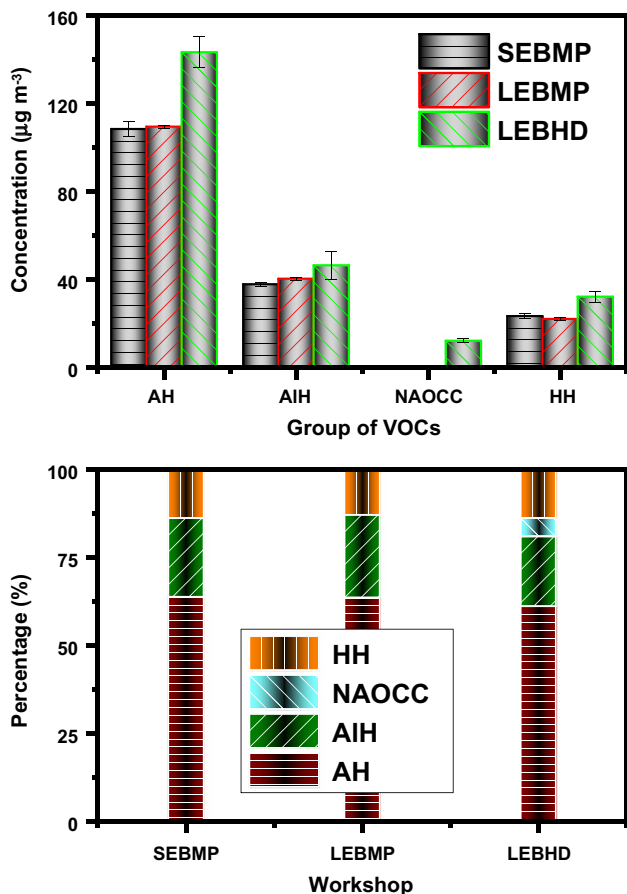


Fig. 1. Concentrations and contributions of four groups of VOCs emitted during the dismantling of different e-wastes using electric blowers (AHs: aromatic hydrocarbons; AIHs: aliphatic hydrocarbons; NAOCCs: nitrogen- and oxygen-containing compounds; HHs: halogenated hydrocarbons; SEBMP: small-bore electric blowers to treat mobile phones; LEBMP: large-bore electric blowers to treat mobile phones; LEBHD: large-bore electric blowers to treat hard disks).

included one using small-bore electric blowers to treat mobile phones (SEBMP), the other one using large-bore electric blowers to treat mobile phones (LEBMP) and the third one using large-bore electric blowers to treat hard disks (LEBHD) (Table S1). The difference between the small- and large-bore electric blowers is that the diameter of the blower bore is different, and thus the heating area is different. During the dismantling process, all three workshops were seriously contaminated by VOCs. The sum of VOC concentrations in SEBMP, LEBMP and LEBHD was $1.8 \times 10^2 (\pm 5.6)$, $1.7 \times 10^2 (\pm 2.0)$ and $2.3 \times 10^2 (\pm 2.4) \mu\text{g m}^{-3}$, respectively, which were 5.4–7.4 times higher than those at the control site (Table S3).

In this work, a total of 81 VOCs were detected. For convenience, VOCs were categorized into four groups: aromatic hydrocarbons (AHs), aliphatic hydrocarbons (AIHs), halogenated hydrocarbons (HHs) and nitrogen- and oxygen-containing compounds (NAOCCs) as listed in Table S2. During dismantling PCBAs using electric blowers, AHs were found as the dominant group in all three workshops, with total concentrations of $1.1 \times 10^2 (\pm 3.5)$, $1.1 \times 10^2 (\pm 0.6)$, and $1.4 \times 10^2 (\pm 7.1) \mu\text{g m}^{-3}$ in SEBMP, LEBMP and LEBHD, respectively, accounting for more than 60% of the sum of VOCs (Fig. 1). AIHs, including alkyl hydrocarbons and cyclo-hydrocarbons, were the second most abundant group (accounting for ~20% of the sum of VOCs), followed by HHs (accounting for ~13%). The least abundant group was the NAOCCs, with up to 5.2% of the sum of VOCs in LEBHD. The predominance of AHs in all three workshops was due to the ingredient of PCBAs of mobile phones and hard disks of epoxy resin with its monomer bisphenol A. Because of the stability of phenyl ring, the single bond

between carbon atom and benzene ring in bisphenol A might be broken or be substituted by other radicals during heating, causing the release of a large amount of aromatics (Grause et al., 2008). This can be partly demonstrated by the reported findings that phenol and its derivatives were the most abundant congeners in the pyrolysis oil of printed circuit boards (Alston et al., 2011; Sun et al., 2011).

Contributions of different AH components in these three workshops using electric blowers to dismantle PCBAs are demonstrated in Fig. S1. Toluene was the most abundant component, while $\sum(o/m/p)$ -xylene and $\sum(1,2,3/1,2,4/1,3,5)$ -trimethylbenzene were the other two most abundant components in these three workshops. Small amount of trimethylbenzene (<3.1%), diethylbenzene (<3.4%), ethylbenzene (<6.7%), benzene (<4.5%), styrene (<2.1%), and propylbenzene (<2.2%) was also observed. AHs including benzene, toluene, ethylbenzene, xylene and styrene were also reported as the major emitted components during the pyrolysis of computer or mobile phone PCBAs or plastics (Molto et al., 2011; Sun et al., 2011).

Contributions of different components of AIHs and HHs in the three workshops are illustrated in Figs. S2 and S3, respectively. Among AIHs, the most abundant component was i-pentane (accounting for ~50% of AIHs), while the other two major components were n-hexane and n-heptane. Among HHs, dichloromethane was the predominant species, with $16 (\pm 1.4)$, $15 (\pm 0.6)$ and $24 (\pm 2.1) \mu\text{g m}^{-3}$ in SEBMP, LEBMP and LEBHD, respectively.

In summary, the results showed that both pollution profiles and percentages of VOCs emitted were similar for different electric blowers employed to melt the soldering tin of mobile phone mainframes in two workshops. Meanwhile, the concentration for sum of VOCs in LEBHD was $50 \mu\text{g m}^{-3}$ higher than those in the former two.

3.1.2. Electric heating furnace workshops

Individual VOCs and their concentrations emitted in two workshops, including one using electric heating furnaces to treat televisions (EHF-TV) and another using electric heating furnaces to treat power suppliers (EHF-PS) (Table S1), are shown in Fig. 2. The VOC components using electric heating furnaces were fewer than those using electric blowers, and the components were very similar in EHF-TV and EHF-PS with slight exception. That is, AHs and HHs almost had equal shares of the whole sum of VOCs, and the only difference was that little of methyl isobutyl ketone ($33 (\pm 1.1) \mu\text{g m}^{-3}$), chloroform ($2.9 (\pm 0.20) \mu\text{g m}^{-3}$) and α -pinene ($0.8 (\pm 0.01) \mu\text{g m}^{-3}$), and no n-undecane was detected in the EHF-TV. However, no methyl isobutyl ketone, chloroform and α -pinene, but partial of n-undecane ($40 (\pm 9.8) \mu\text{g m}^{-3}$) was emitted in EHF-PS.

Among the major groups of VOCs emitted, AHs and HHs were the two predominant groups, accounting for 45.3% and 50.5% of the sum of VOCs in EHF-TV ($8.0 \times 10^2 \mu\text{g m}^{-3}$), and 44.2% and 48.3% of the sum of VOCs in EHF-PS ($5.3 \times 10^2 \mu\text{g m}^{-3}$), respectively. In both workshops, toluene and bromomethane were the dominant constituents, accounting for 34.7% and 44.7% of the sum of VOCs (76.7% of AHs and 88.5% of HHs) in EHF-TV and 21.2% and 42.2% of the sum of VOCs (47.9% of AHs and 87.3% of HHs) in EHF-PS, respectively. Other components included styrene, chloromethane and methyl isobutyl ketone in EHF-TV, and benzene, n-undecane, chloromethane as well as xylene in EHF-PS.

3.1.3. Rotary incinerator workshops

Employing rotary incinerator to dismantle e-wastes is also a widely used approach to recycle precious metals. Fig. 3 demonstrates the concentrations of four groups of VOCs emitted during the combustion of various PCBAs using rotary incinerators. Workshops included those using rotary incinerators to treat televisions (RI-TV), hard disks (RI-HD) and micro motors (RI-MM), respectively (Table S1). There was considerable variation in the sum of VOC concentrations in workshops dismantling different PCBAs using this same dismantling method. Concentration of sum of VOCs in RI-TV ($3.3 \times 10^4 \mu\text{g m}^{-3}$) was the highest, followed by that in RI-MM ($1.1 \times 10^4 \mu\text{g m}^{-3}$). Comparatively, the sum of VOC

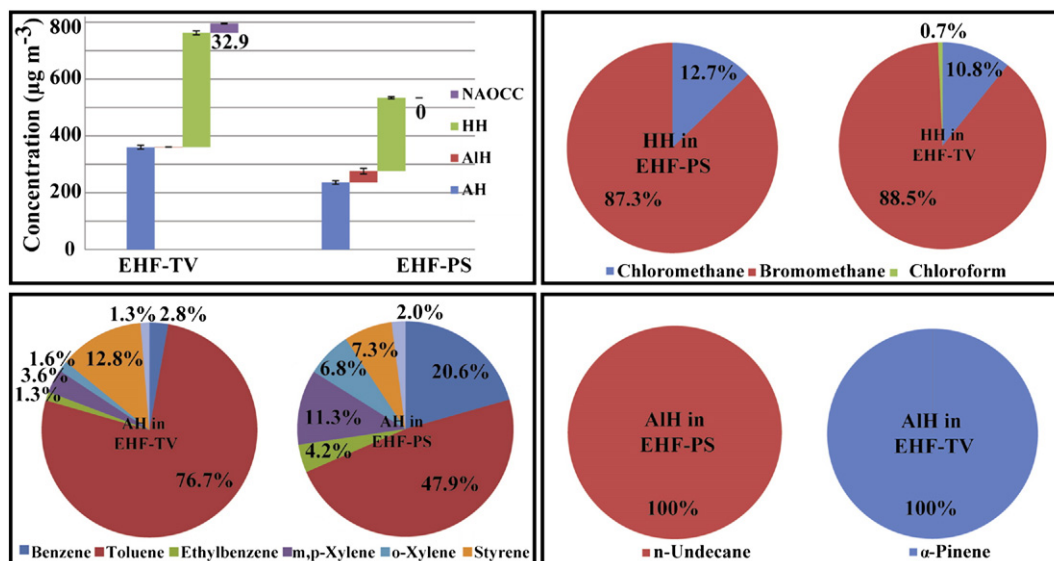


Fig. 2. Pollution profiles and contributions of VOCs emitted during the dismantling of different e-wastes using electric heating furnaces (AHs: aromatic hydrocarbons; AIHs: aliphatic hydrocarbons; NAOCCs: nitrogen- and oxygen-containing compounds; HHs: halogenated hydrocarbons; EHF-TV: electric heating furnaces to treat televisions; EHF-PS: electric heating furnaces to treat power suppliers).

concentration in RI-HD ($3.3 \times 10^3 \mu\text{g m}^{-3}$) was the lowest, which was about 10 and 3 times lower than that in RI-TV and RI-MM, respectively. Similar results were reported that much lower amounts of light hydrocarbons were emitted during pyrolysis dismantling of mobile phone PCBAs than those of mobile phones and the mixture of two (Molto et al., 2011). The dramatic distinction of sum of VOC concentrations in these workshops was probably caused by the following reasons: During the dismantling process, part of TV casings were mixed with TV PCBAs in RI-TV; electric wires in micro motors made from thermoplastics emitted much more VOCs than those of thermosets during the combustion, while epoxy resin (thermosets) was mainly used for hard disk PCBAs. All of these may have caused the highest sum of VOCs in RI-TV and then in RI-MM and the lowest in RI-HD.

From Fig. 3, it can also be found that AHs were the most dominant group (>54% of the sum of VOCs) and AIHs ranked the least (<4% of the sum of VOCs) in all three workshops. According to the literature (Blazso et al., 2002), the combustion temperature in an incinerator is

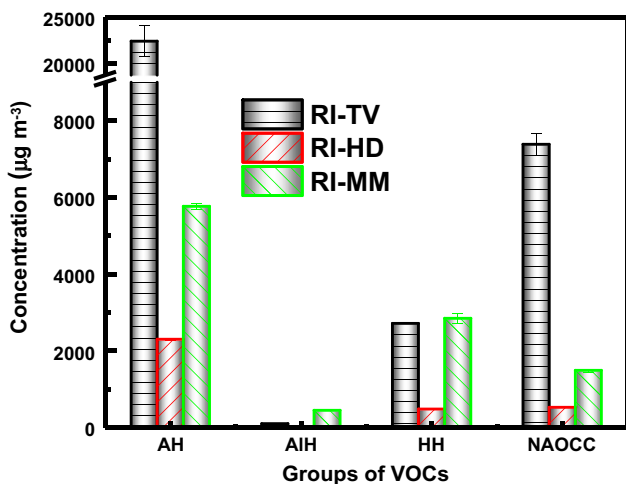


Fig. 3. Concentrations of four groups of VOCs emitted in workshops using rotary incinerators to dismantle e-wastes (AHs: aromatic hydrocarbons; AIHs: aliphatic hydrocarbons; NAOCCs: nitrogen- and oxygen-containing compounds; HHs: halogenated hydrocarbons; RI-TV: rotary incinerators to treat televisions; RI-HD: rotary incinerators to treat hard disks; RI-MM: rotary incinerators to treat micro motors).

>400 °C, which can decompose a large amount of organics and aromatics as well as aliphatics can be released from the e-wastes. The detected concentration of AHs was far higher than that of AIHs, since AIHs are apt to be oxidized while the phenyl ring in AHs is stable. Furthermore, AHs and NAOCCs in RI-TV were far higher than those in RI-MM and RI-HD, with approximately 3.9 and 9.8 times higher for AHs and 4.9 and 14.0 times higher for NAOCCs, respectively. In contrast, the concentrations of AIHs and HHs in RI-MM were higher than those in RI-TV and RI-HD. This might be ascribed to the fact that the electric wires in micro motors are made from polyvinyl chloride. It is worth noting that no AIH was detected in RI-HD.

More details of VOC components are shown in Fig. S4. In RI-TV and RI-MM, the main compositions of AHs were styrene (61.3% and 43.1%), followed by toluene (>12%), ethylbenzene (>11%) and benzene (8.2% and 6.7%). Concentrations for the other components were very low (0–3.7% in RI-TV; 0–2.1% in RI-MM) except for xylene in RI-MM. These results were in good agreement with literatures. For instance, styrene was the most significant constituent during the pyrolysis and combustion of mobile phones (PCBAs and casing) and PCBAs alone (Moltó et al., 2009). Similarly, both the casings and keyboards of computers provide mainly aromatic derivatives, especially styrene and ethylbenzene and then toluene during pyrolysis (Vasile et al., 2006). In contrast, the predominant constituent of AHs was toluene (86.3%) in RI-HD, and the others are trivial (0–1.2%) except benzene (4.9%) and styrene (4.6%), which is different from the reported results of (Vasile et al., 2006) suggesting that phenol and its derivatives were the most abundant compositions during the pyrolysis of computer PCBAs. This difference is due to the poor volatility of phenol leading low detected concentration in gas phase. However, the results of this study are similar to the others. Besides phenol, toluene and ethylbenzene were found as the main AH components; styrene, benzene and xylene were also observed during pyrolysis. The predominance of styrene in RI-TV and RI-MM is related to the e-waste materials being treated. The bulk of thermoplastic casings of TV, components in TV PCBAs, and electric wires in micro motors are mainly made from ABS or high impact polystyrene (HIPS) or polystyrene (PS) which may release plenty of styrene during combustion.

The composition of HHs was very complicated and varied significantly among these three workshops (Fig. S5). In RI-TV, the major components were bromomethane (37.5%) and benzyl chloride (29.9%), followed by chlorobenzene (11.8%), m/p/o-dichlorobenzene (14.6%)

and chloromethane (6.2%). However, four components of HHs including 1,2,2-trifluoro-1,1,2-trichloroethane, 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene were not detected. Comparatively, the composition of HHs in RI-MM is very different from that in RI-TV. Contrary to that in RI-TV, the majority compounds are 1,2,2-trifluoro-1,1,2-trichloroethane (47.3%) and trichloroethene (40.4%), while bromomethane, m/p/o-dichlorobenzene, and benzyl chloride were not detected in RI-MM. Unlike the pollutant profiles of other two workshops, only two HH components, large quantity of bromomethane (91.4%) and a small portion of chloromethane (8.6%) were emitted in RI-HD.

Compared with HHs, the compositions of AIHs and NAOCCs were relatively less complicated in these workshops (Fig. S6). For AIHs, only n-hexene (86.4%) and cyclopentene (13.6%) in RI-TV, six components in RI-MM and none in RI-HD were detected. For NAOCCs, the compositions were very simple and their percentages varied among three workshops. Both benzaldehyde and methyl methacrylate were detected in all three workshops except extra acrylonitrile in RI-TV. Besides aromatics like benzene, toluene, styrene and chlorobenzene, acrylonitrile was reported as other main component during pyrolysis of styrenic polymers such as ABS, HIPS, and styrene-acrylonitrile (SAN) (Hall and Williams, 2006; Karaduman et al., 2001). The only release of acrylonitrile in RI-TV might be resulted from the bulk components in TV PCBAs and mixed TV cases made from ABS and the decomposition of ABS. Whereas the wires in micro motors are composed of other thermoplastics, and hard disk PCBAs are consisted of epoxy resin, leading to the absence of acrylonitrile during the dismantling of PCBAs of micro motors and hard disks.

In summary, using rotary incinerators to dismantle e-wastes can lead to heavy pollution of VOCs. The major group of VOCs was AHs, among which styrene was the major component in both RI-TV and RI-MM while toluene was the major component in RI-HD.

3.1.4. Workshops using different dismantling methods

Based on the results above, it can be found that the pollution profiles of VOCs varied greatly among different dismantling methods. The whole e-waste dismantling procedure includes mechanical cutting (MC, using cutting-off machine), melting soldering tin (using electric soldering iron (ESI), electric blower or electric heating furnace), and combusting PCBAs (using rotary incinerator). Therefore, to further investigate the pollution characteristics of VOCs during the actual dismantling procedure of e-wastes employing different methods, results of the above representative workshops (LEBHD, EHF-TV, and RI-TV) were compared with two others methods, MC and ESI to dismantle personal computer motherboards (Table S1).

The compositions of VOCs and their corresponding concentrations generated in the five different dismantling workshops are shown in Fig. 4. Using rotary incinerators to combust TV mainframes was the most severe method to produce VOCs. The sum of VOCs ($3.3 \times 10^4 \mu\text{g m}^{-3}$) in RI-TV was about 190, 180, 139, and 40 times higher than that in MC, ESI, LEBHD, and EHF-TV, respectively. The concentrations for each of four groups, especially NAOCCs and HHs in RI-TV were far higher than those in other four workshops. The concentration of NAOCCs in RI-TV was 1132, 600 and 224 times higher than that in MC, LEBHD and EHF-TV, respectively; HHs in RI-TV were 538, 509, 84 and 6.8 times higher than those in MC, ESI, LEBHD and EHF-TV, respectively. The high concentrations of NAOCCs and HHs are due to the highest temperature of rotary incinerators among these workshops elevating the amounts of chlorinated species and NAOCCs evolved with all the studied materials (Molto et al., 2011). Despite of all these differences in concentrations, a similar feature was shared by all the workshops that AHs were mainly composed of toluene, xylene, ethylbenzene, and styrene, which was the predominant group among VOCs.

As for the contributions of four VOC groups using different dismantling methods, AHs were the biggest contributor in four workshops, particularly in MC (84.9%) (Fig. S7), except in EHF-TV, where AHs and HHs almost had equal shares of the whole sum of VOCs besides a

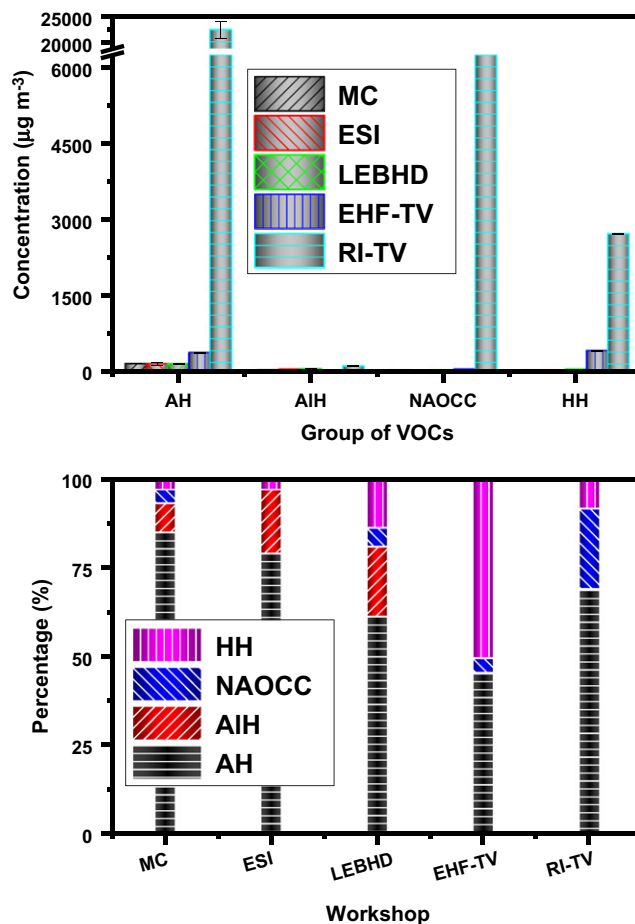


Fig. 4. Concentrations and contributions of four groups of VOCs during the dismantling of e-wastes using different methods (AHs: aromatic hydrocarbons; AIHs: aliphatic hydrocarbons; NAOCCs: nitrogen- and oxygen-containing compounds; HHs: halogenated hydrocarbons; MC: mechanical cutting; ESI: electric soldering iron; LEBHD: large-bore electric blowers to treat hard disks; EHF-TV: electric heating furnaces to treat televisions; RI-TV: rotary incinerators to treat televisions).

small portion of NAOCCs (4.1%) (Fig. 2). Furthermore, besides in LEBHD, EHF-TV and RI-TV, the percentages of all components of sum of VOCs in MC and ESI were also analyzed. In the most predominant group-AH in MC (Fig. S7), m,p-xylene (27.2% of AHs) and ethylbenzene (21.3% of AHs) were the most abundant, followed by toluene (11.6% of AHs) and o-xylene (9.9% of AHs). All the other AH components were less than 5%. In the AIH group, the compositions were simple, with almost half of AIHs contributed by n-heptane and another half almost equally contributed by n-hexane and i-pentane. However, the simplest groups in MC were NAOCCs and HHs, where only methyl methacrylate and 1,2-dichloroethane were detected, respectively.

Similar to MC, the most abundant component of AHs in ESI (Fig. 5) was m,p-xylene (22.7% of AH), while m-diethylbenzene and o-diethylbenzene were not present. As mentioned previously, both of the latter two VOCs were not detected in EHF-TV and RI-TV either. The compositions of NAOCCs and HHs in ESI were also very simple, with only 1,2-dichloroethane detected in HHs and none in NAOCCs. The largest difference in sum of VOC compositions was observed in NAOCCs, with the main contributor varied greatly in all five different workshops. This might be caused by the oxidation of emitted hydrocarbons at high temperatures.

To better understand the VOC profiles of five workshops using different dismantling methods, the contributions of four VOC groups are

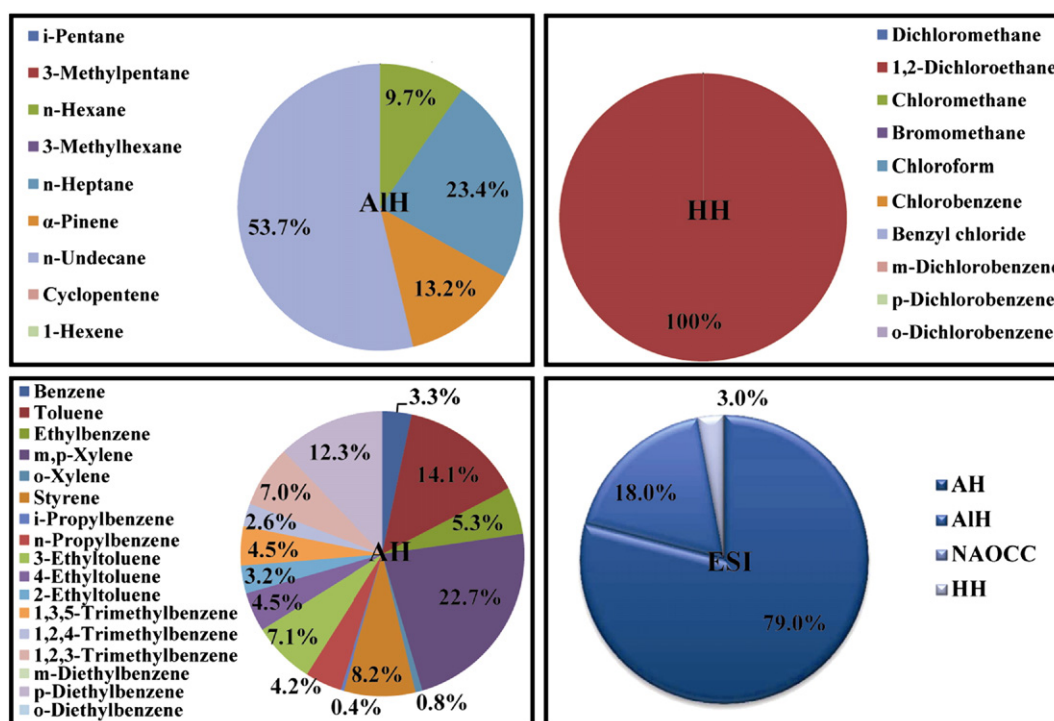


Fig. 5. Percentage of main constituents to sum of VOCs as well as the specific contribution of three groups of VOCs emitted in ESI workshop (AHs: aromatic hydrocarbons; AIHs: aliphatic hydrocarbons; HHs: halogenated hydrocarbons; ESI: electric soldering iron).

compared (Fig. 4). Among the sum of VOCs, the percentage of AHs, especially for xylene, ethylbenzene, propylbenzene, ethyltoluene and trimethylbenzene, decreased gradually in the order of MC, ESI, LEBHD, and EHF-TV (sum of the former five species accounted in sum of VOC decreased from 69.5% (in MC), to 57.2% (in ESI), then to 36.1% (in LEBHD) and finally to 12.3% (in RI-TV)), while the proportion of styrene in the sum of VOCs increased gradually (from ~2% in MC, ESI and LEBHD to 42.3% in RI-TV) in these four workshops with the highest value in RI-TV. The possible reason can be explained as follows. The longer the alkyl chain is, the easier it can be broken. The more side chains are attached to phenyl ring, the easier the side chains can be eliminated or substituted. With the increase of processing temperature and the enlargement of heating area, a descending trend existed for the contributions of xylene, ethylbenzene, ethyltoluene and trimethylbenzene. In contrast, the changing trend of HH contribution was just opposite to that of AHs in the former four workshops. As described, an increase in processing temperature can cause the increase in the amounts of chlorinated species, and the release and break down of halogenated flame retardants. Moreover, the hydrogen atom in hydrocarbons can be substituted by halogens at high temperatures. As for NAOCCs, its contribution to the sum of VOCs in RI-TV was far higher ($7.4 \times 10^3 \mu\text{g m}^{-3}$) than that of the other four workshops, indicating that high heating temperature could promote the emission of NAOCCs like benzaldehyde, acrylonitrile and methyl methacrylate from e-wastes due to the incomplete oxygenation of aromatic hydrocarbons and decomposition of styrenic polymer under high temperatures. The contributions of AIHs in EHF-TV and RI-TV were very small ($\leq 0.3\%$), suggesting that high temperatures and large heating area rarely boost AIH production.

In summary, the higher of processing temperature was and the larger of heating area was, the more VOCs were produced. As listed in Table S4, the amount of VOCs formed in the workshops followed the ascending order of LEBHD < EHF-TV << RI-TV. Due to small heating area and low processing temperature applied to dismantle PCBAs in MC, ESI and LEBHD, the compositions of VOCs and their corresponding amounts rarely changed.

3.2. Risk assessment

3.2.1. Assessment of non-cancer and cancer risks using the methodology of USEPA

Because of the ubiquitous presence of VOCs in the air of e-waste dismantling workshops, the potential chronic health effects (non-cancer and cancer risks) of exposure to VOCs by means of inhalation were assessed according to our previous study using the methodology of USEPA (Li et al., 2013). In this study, for all the detected and quantified VOCs, only 20 (in following description, m,p-xylene and o-xylene called xylene, and 1,3,5-, 1,2,4-, 1,2,3-trimethylbenzene called trimethylbenzene (the HR of each individual trimethylbenzene or xylene was calculated and then summarized), so total of 17 were calculated) and 7 VOCs were selected to assess non-cancer and cancer risk, respectively, due to the lack of reference concentrations and unit risk values of others.

The non-cancer hazard ratios (HR) of individual and sum of VOCs using different dismantling methods is shown in Fig. 6. As expected, the non-cancer risk in RI-TV was the highest, and the total HR was up to 1.8×10^3 , which was 213, 223, 278, and 24 times higher than that in MC, ESI, LEBHD, and EHF-TV, respectively. In RI-TV, HRs of 12 VOCs exceeded 1, and four of them were $1 > \text{HR} > 0.1$, meaning that these VOC concentrations were all above the level of concern (Ramírez et al., 2012) and potential concern (McCarthy et al., 2009), respectively. It must be mentioned that the highest HR in RI-TV was methyl methacrylate with a value of up to 1.4×10^3 , which accounted for ~79% of the total HR in RI-TV. What's more, the total HRs of each group especially for HHs in RI-TV were also much higher than those of corresponding groups in other workshops, which were about 100332, 95293, 4806, and 3 times higher than those in MC, ESI, LEBHD, and EHF-TV, respectively. Hence, more attention should be paid to employees in the rotary incinerator workshop.

Among VOCs, trimethylbenzene was an important hazardous pollutant, whose HR was higher than 1 in MC (1.9), ESI (3.6), LEBHD (2.7), and RI-TV (32) and was up to 0.68 in EHF-TV. Apart from RI-TV, HR of individual VOCs in other workshops rarely over 1 except bromomethane

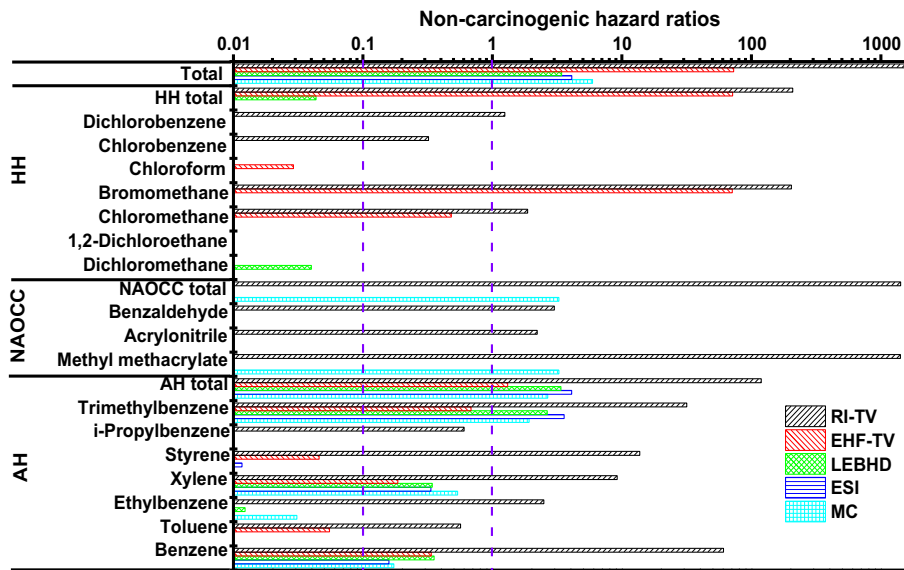


Fig. 6. Non-cancer risk of VOCs emitted in workshops using different methods to dismantle e-wastes (AHs: aromatic hydrocarbons; NAOCCs: nitrogen- and oxygen-containing compounds; HHs: halogenated hydrocarbons; MC: mechanical cutting; ESI: electric soldering iron; LEBHD: large-bore electric blowers to treat hard disks; EHF-TV: electric heating furnaces to treat televisions; RI-TV: rotary incinerators to treat televisions).

(71) in EHF-TV and methyl methacrylate (3.3) in MC. In addition, other two important hazardous VOCs were benzene and xylene, whose HRs were all between 0.1 and 1 in the other four workshops, demonstrating that benzene and xylene might pose non-cancer threats to workers.

The lifetime cancer risk in various workshops was also evaluated. According to the reference (Sexton et al., 2007), compounds with $LCR > 10^{-4}$ were labeled as “definite risk”, $10^{-4} > LCR > 10^{-5}$ as “probable risk” and $10^{-5} > LCR > 10^{-6}$ as “possible risk”. From Table S5, the cancer risk in RI-TV was very high, and all detected VOCs in RI-TV, referred to acrylonitrile (1.1×10^{-1}), benzene (1.1×10^{-2}), ethylbenzene (6.2×10^{-3}) and p-dichlorobenzene (1.1×10^{-3}), were regarded as definite risk. $\sum LCR_i$ in RI-TV was the highest (1.2×10^{-1}), which was

approximately 19, 666, 400 and 900 times higher than that of MC, ESI, LEBHD, and EHF-TV, respectively, 124,000 times higher than the acceptance LCR for carcinogens (1×10^{-6}) established by USEPA and 2480 times higher than the maximum acceptance LCR (5×10^{-5}) recommended by the International Commission on Radiological Protection (ICRP). Although the cancer risks in other four workshops were 3 orders of magnitude lower than that in RI-TV, their $\sum LCR_i$ were all beyond the definite risk. In MC, ESI, and LEBHD, the most important cancer risk contributor was 1,2-dichloroethane ($LCR > 10^{-4}$), while in EHF-TV and RI-TV, 1,2-dichloroethane was not detected. Additionally, the LCRs of both benzene and ethylbenzene were also considered as probable risk in MC, ESI, LEBHD and EHF-TV. It is worth noting that though the concentration

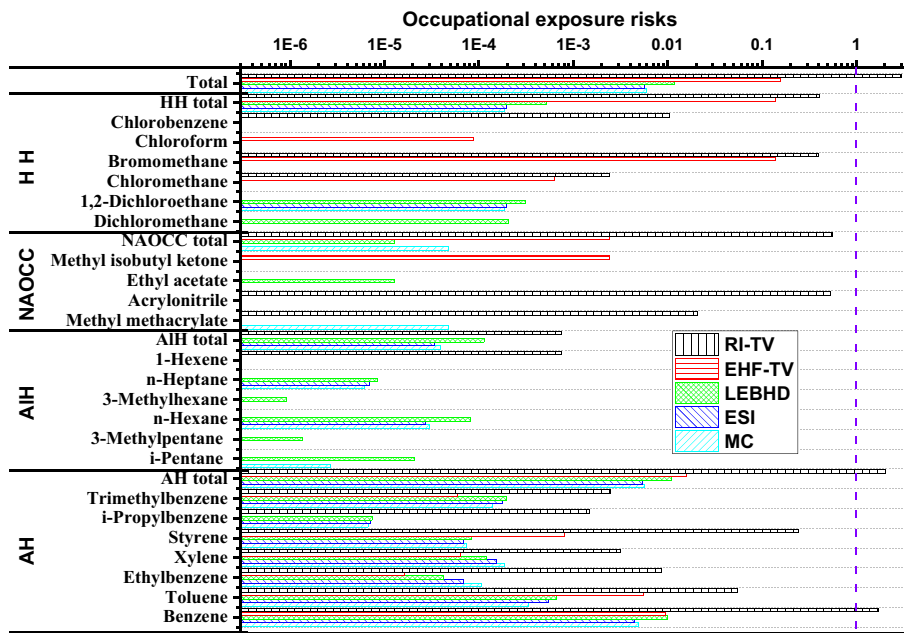


Fig. 7. Occupation exposure risk for 23 VOCs emitted in workshops using different methods to dismantle e-wastes (AHs: aromatic hydrocarbons; AIHs: aliphatic hydrocarbons; NAOCCs: nitrogen- and oxygen-containing compounds; HHs: halogenated hydrocarbons; MC: mechanical cutting; ESI: electric soldering iron; LEBHD: large-bore electric blowers to treat hard disks; EHF-TV: electric heating furnaces to treat televisions; RI-TV: rotary incinerators to treat televisions).

of sum of VOCs in EHF-TV was much higher than that in the former three workshops, its $\sum LCR_i$ was lower. The possible reasons can be summarized as: the major constituents of VOCs in EHF-TV were bromomethane and toluene, which accounted for 85.2% of the sum of VOCs. However, the lack of definite unit risk for bromomethane and no carcinogenicity effect for toluene led to underestimate $\sum LCR_i$ value in EHF-TV.

In summary, using the methodology of USEPA, both cancer and non-cancer risks of VOCs generated in the five workshops especially in RI-TV were very high. All of $\sum HRs$ were beyond 1, and $\sum LCR_i$ was $>10^{-4}$, indicating that VOCs emitted during e-waste dismantling processes would exert extreme cancer and non-cancer risks on employees in these workshops.

3.2.2. Assessment of occupational exposure cancer risk using the methodology of ACGIH

Occupational exposure cancer risk was also evaluated according to ACGIH and E_i values for 23 VOCs from TWA (Table S6), due to the lack of others. The E_i values of VOCs are shown in Fig. 7. Similar to the abovementioned risks using the methodology of USEPA, the occupational exposure cancer risks of individual VOCs in RI-TV were also much higher than those of other four workshops. Nevertheless, only E_i of benzene (1.7, categorized into A1-definite human carcinogens) formed in RI-TV exceeded 1, suggesting that benzene at this pollution level posed a cancer threat to workers in RI-TV (ACGIH 2010). The E_i values of other major pollutants like acrylonitrile (5.4×10^{-1}), bromomethane (3.9×10^{-1}) and styrene (2.4×10^{-1}), falling under groups A2 or A3 that can't be regarded as carcinogens, were all above 0.1 in RI-TV. Comparatively, the E_i values of individual VOCs in MC, ESI, LEBHD and EHF-TV were all below 0.1, except for bromomethane in EHF-TV (1.4×10^{-1}). And except in EHF-TV (1.6×10^{-1}), the $\sum E_i$ for all investigated VOCs were all below 0.1 (6.0×10^{-3} , 5.7×10^{-3} , and 1.2×10^{-2} in MC, ESI and LEBHD, respectively), indicating that VOCs produced in these workshops would not exert obvious harmful effects on employees if they were well equipped or sheltered.

Comparatively, the risk assessment results using the two different methods varied greatly. According to the USEPA methodology, in all workshops, cancer and non-cancer risks existed to workers by exposure of VOCs. While only RI-TV would definitely pose detrimental effects on workers according to ACGIH methodology. These might be ascribed to the difference of exposure time; that is, the cancer risk obtained from the USEPA is the lifetime cancer risk, while the cancer risk obtained from the ACGIH is only to assess the cancer risk related to an occupational exposure. However, despite of the differences between the two methods, the health risk from VOCs emitted in RI-TV was all beyond the acceptance level, with its risk much higher than the other workshops. Therefore, to ensure the security of workers in RI-TV, one way forward is to develop the gas-tightness of rotary incinerators and to collect the waste gases for further treatment.

4. Conclusions

With the increase of processing temperature and the enlargement of heating area for dismantling methods, all the concentrations of AHs, NAOCCs and HHs formed in the workshops increased significantly, while that of AIHs only increased slightly. Generally, the amount of sum of VOCs produced in different workshops followed the ascending order of EB < EHF < RI, and AH was always the predominant group in VOCs. For VOCs emitted during actual e-waste dismantling processes applying various methods, the following conclusions can be drawn:

1. Compositions of VOCs emitted during applying the electric blowers to dismantle various PCBAs were almost the same. AHs were the main contributor of VOCs and its composition was the most complicated, where toluene, xylene, ethyltoluene, trimethylbenzene, i-pentane and dichloromethane were the most abundant components.
2. Using electric heating furnaces to melt soldering tin of TVs and power supplier boards, we found that the VOC components produced were also very similar. AHs and HHs were the main and equal contributors of sum of VOCs.
3. Using rotary incinerators to dismantle a variety of PCBAs, we found that constituents of VOCs varied greatly, but a same trend existed in these workshops with a descending order of AHs > NAOCCs > HHs > AIHs.
4. Comparatively, VOCs emitted during using different dismantling methods were all severely contaminated and extreme health risks on workers could be posed, especially in workshops using rotary incinerator to dismantle e-wastes.

Acknowledgments

This is contribution No. IS-1879 from GIGCAS. This work was financially supported by Science and Technology Project of Guangdong Province, China (2012A032300017 and 2009A030902003), Team Project from the Natural Science Foundation of Guangdong Province, China (S2012030006604), the Cooperation Projects of the Chinese Academy of Science with Foshan Government (2012HY100101) and NSFC (41373102).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.envint.2014.07.019>.

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