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Pollution characteristics and health risk assessment of volatile organic compounds emitted from different plastic solid waste recycling workshops



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ABSTRACT

The pollution profiles of volatile organic compounds (VOCs) emitted from different recycling workshops processing different types of plastic solid waste (PSW) and their health risks were investigated. A total of 64 VOCs including alkanes, alkenes, monoaromatics, oxygenated VOCs (OVOCs), chlorinated VOCs (ClVOCs) and acrylonitrile during the melting extrusion procedure were identified and quantified. The highest concentration of total VOCs (TVOC) occurred in the poly(acrylonitrile-butadiene styrene) (ABS) recycling workshop, followed by the polystyrene (PS), polypropylene (PP), polyamide (PA), polyvinyl chloride (PVC), polyethylene (PE) and polycarbonate (PC) workshops. Monoaromatics were found as the major component emitted from the ABS and PS recycling workshops, while alkanes were mainly emitted from the PE and PP recycling processes, and OVOCs from the PVC and PA recycling workshops. According to the occupational exposure limits' (OEL) assessment, the workers suffered acute and chronic health risks in the ABS and PS recycling workshops. Meanwhile, it was found that most VOCs in the indoor microenvironments were originated from the melting extrusion process, while the highest TVOC concentration was observed in the PS rather than in the ABS recycling workshop. Non-cancer hazard indices (HIs) of all individual VOCs were <1.0, whereas the total HI in the PS recycling workshop was 1.9, posing an adverse chronic health threat. Lifetime cancer risk assessment suggested that the residents also suffered from definite cancer risk in the PS, PA, ABS and PVC recycling workshops.

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1. Introduction

The global production of plastic and the associated plastic solid waste (PSW) generated by households and industries have grown exponentially in recent decades due to their low costs, easiness to mold, lightweight, and many other advantages (Nkwachukwu et al., 2013; Rochman et al., 2013). The growing amount of PSW can lead to various environmental problems, including “white pollution”. It is reported that marine litters consist of up to 60 to 80% of plastics (Moore, 2008), which also serve as a carrier of persistent organic pollutants (POPs) transferable to aquatic organisms (Koelmans et al., 2013). Dealing with these enormous PSW remains a challenging task in many countries. The widely-used traditional landfill is becoming an undesirable way of disposal due to legislation pressures, rising costs and the poor biodegradability of commonly used petroleum-based plastics (Achilias et al., 2007). The alternative, incineration, has been criticized for generating large amounts of bottom ash and various toxic air pollutants, like

polycyclic aromatic hydrocarbons, as well as dioxins in case of halogen-containing plastics (Shen et al., 2010; Vejerano et al., 2013). Therefore, the recycling of PSW is a highly desirable way for resource, energy conservation and reduction in waste gas emissions (Ignatyev et al., 2014). This is particularly important in the electronic waste (e-waste) dismantling industry, since plastics are one of the main components of e-waste (Wang and Xu, 2014).

The commonly adopted PSW recycling approaches include primary recycling, mechanical recycling, chemical recycling and energy recovery (Achilias and Karayannidis, 2004). The mechanical recycling is the main recycling approach in the e-waste dismantling process in Southern China, which is used to recover PSW for the reuse in manufacturing plastic products via the mechanical means. Mechanical recycling can be generally divided into several steps: collection, separation, milling, washing, agglutination, extrusion, quenching and granulation (Al-Salem et al., 2009). Among these steps, only during the extrusion process (Patel and Xanthos, 1995), PSW begin to melt and thermally degrade at a certain temperature, while other steps might not change the property of PSW. Previously, high temperature treatment processes like pyrolysis of thermoplastics

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were well studied (Aboulkas and El Bouadili, 2010; Elordi et al., 2011; Wang et al., 2013). At the high temperature (more than 400 °C), PSW could be converted into valuable substances, which can be used as either fuels or feedstock in the petrochemical industry (Williams, 2005). However, various toxic gases including alkanes, alkenes, as well as chlorinated and aromatic hydrocarbons could also be produced during this process. Although the melting temperature in the mechanical recycling is around 150–300 °C which is much lower than the pyrolysis, various volatile organic compounds (VOCs) might still be produced and released into the atmospheric environment at this temperature due to the aging, long thermal exposure, intrinsic sensitivity, and the interactions between the additives and polymers (Pospíšil et al., 2003). Furthermore, owing to the rather primitive and crude facilities used during the extrusion process, the VOCs are discharged directly into atmospheric environment without any ventilation or treatment in most PSW workshops in many developing countries. The VOC emission characteristics remain unclear during these recycling processes. Only a few studies were reported on the pollution characteristics of VOCs in the plastic waste recycling granulation step (Huang et al., 2013) without involving the extrusion process.

In addition, these VOCs may contain massive hazardous compounds posing health risks to workers and neighboring residents (An et al., 2014; Colman Lerner et al., 2012; Sax et al., 2006; Sofuoglu et al., 2011). The human health effects of VOCs can be classified as either non-cancer or cancer risks. The main non-cancer chronic effects of VOCs are sensory effects, damages to the liver, kidneys and central nervous system, asthma and other respiratory effects (Rumchev et al., 2007). The main cancer effects are lung, blood (leukemia and non-Hodgkin lymphoma), brain, liver, kidney and biliary tract cancers (WHO, 2000). For instance, benzene can induce not only non-cancer risks of hematotoxicity and aplastic anemia, but also cancer risks of acute myelogenous leukemia and lymphoma (Sarma et al., 2011). Thus, it is necessary to assess the health effects on the residents in the industrial areas. However, the risk assessment for human health has not yet become a routine task in the PSW recycling area, and most studies have only focused on VOC emission levels.

In this study, the VOC emission characteristics, health risks, and indoor microenvironment exposure during the melting extrusion of the recycling processes at seven different types of plastics were investigated in detail. The health risks of the emitted VOCs on the human beings were carried out in two ways: the occupational exposure limit assessment for workers in the extrusion assembly lines and the health risk assessment including non-cancer risks and cancer risks for the residents living near the PSW recycling workshops.

2. Materials and methods

2.1. Descriptions of the sampling sites

The recycling PSW can generally be divided into seven types: poly(acrylonitrile-butadiene styrene) (ABS), polystyrene (PS), polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyamide (PA), and polycarbonate (PC). Particularly, PA is a kind of thermoplastic polymers containing amide ($-NHCO-$) unit, where hydrocarbon segments between the amide groups could be aliphatic, partially aromatic, or wholly aromatic. In this study, PA 6 (monomer: caprolactam) and PA 66 (hexamethylenediamine and adipic acid) were the main recycling PSW in the PA workshop. The description for the structure, monomer and polymerization methods of the studied plastics is listed in Table 1.

All the exhausted gases were only fanned out and emitted through the outlet on the side-door or the roof (approximately 8 m above ground) of the workshops without any proper treatment. Sampling was conducted using 2.7 L vacuum Summa canisters at about 1 m away from the extruding machine during the extrusion process, as the workers stand at a similar distance in the workshops. The indoor

Table 1
Structure, monomer and polymerization methods of studied plastics.

Material	Monomer	Polymerization methods	Temperature (°C)	
			Decomposition	Extrusion
ABS	Styrene, 1,3-butadiene, acrylonitrile	AP ^a	290	200–300
PS	Styrene	AP	290	200–260
PE	Ethylene	AP	350	150–250
PP	Propylene	AP	350	150–250
PVC	Vinyl chloride	AP	210	150–200
PA	Diamine, dicarboxylic acid	AP/CP ^b	300–355	200–230
PC	Bisphenol A, carbonyl chloride	CP	>350	100–150

^a Addition polymerization.

^b Condensation polymerization.

microenvironment samples were simultaneously collected from three different sites in each of the workshops.

2.2. Analytical methods

The VOCs' samples were qualitatively and quantitatively detected by a Entech 7100 pre-concentrator (Entech Instruments Inc., CA, USA) and GC-MS (7890A GC-5975C MS, Agilent Technologies, USA) combined techniques with the USEPA TO-15 method (He et al., 2012; U.S. EPA, 1999). First, a volume of 150 mL of the VOCs from sampling Summa canisters was concentrated in the glass bead trap (module 1), which was maintained at 150 °C with liquid nitrogen. The trapped analytes were then desorbed at 20 °C and transferred to a Tenax-TA trap (module 2) maintained at -40 °C. The concentrated components were again desorbed at 190 °C and then focused at the cold top of the capillary column, which was cooled to -180 °C. After 2.5 min, the highly focused VOCs were quickly desorbed at 120 °C min^{-1} and swept into the column for the separation.

A DB-1 column (60 m \times 0.32 mm \times 0.25 μm , Agilent Technologies, USA) was used with the GC oven temperature program: initially 35 °C for 5 min, programmed to 150 °C at a rate of 5 °C min^{-1} , and then to 250 °C at a rate of 15 °C min^{-1} which was held for 2 min. The carrier gas was ultrahigh purity helium at a constant flow rate of 1.2 mL min^{-1} . Mass spectrometer conditions were as follows: temperature of the transfer line: 290 °C; ionizing energy: 70 eV; scan range: 45–260 me^{-1} . The concentrations of most VOCs were quantified by external standard calibration which was determined by standard samples Photochemical Assessment Monitoring Stations (PAMS) and TO-15 (Linde Spectra Environment Gases, USA). The calibration standards were prepared by dynamically diluting 100 ppbv PAMS standard mixture (33 compounds were detected) and 1 ppmv TO-15 standard mixture (30 compounds were detected) to 1, 5, 10, 15, 30 and 50 ppbv with high purity nitrogen. For some ketones (3-hexanone, cyclopentanone, 2-methylcyclopentanone, cyclohexanone and 2-ethylcyclopentanone), their concentrations were calculated using 2-hexanone as the reference compound due to their similar properties. For acrylonitrile and n-butanol, the concentrations were manually quantified to 342 and 245 ppbv, then they were dynamically diluted to five levels ranging from 1 to 30 ppbv. Each target VOC was identified by both retention time and mass spectra using the NIST 05 database (National Institute of Standards and Technology).

2.3. Quality control and assurance

Before sampling, all canisters were flushed at least five times by repeatedly filling and evacuating with high purity nitrogen. All canisters were evacuated after the cleansing procedures, re-filled with high purity nitrogen, stored in the laboratory for at least 24 h, and then analyzed in the same way as field samples to make sure that all the target VOC compounds were not present. All the samples were analyzed within 24 h after the collection. The target VOCs were identified based on

both their retention times and mass spectra, and quantified by the external calibration method.

The calibration curves were obtained by running the six diluted standards plus high purity nitrogen in the same way as the field samples. All the calibration standard curves were justified with the correlation coefficients (R^2) over 0.995 as listed in Table S1. The analytical system was checked daily with a one-point (typically 5 ppbv) calibration before running air samples. If the response was beyond $\pm 10\%$ of the initial calibration curve, the re-calibration was performed. The method detection limits (MDLs) for all VOC were maintained between $0.04 \mu\text{g m}^{-3}$ and $0.50 \mu\text{g m}^{-3}$ as presented in Table S1.

2.4. Risk assessment

2.4.1. Occupational exposure limits (OEL) for workers

The OEL for human is defined by the European directive, in accordance with the International Organization for Standardization (ISO) and American Conference of Industrial Hygienists (ACGIH), for some hazardous VOCs inhaled by workers (Romagnoli et al., 2014). Due to both acute and chronic health problems, ACGIH standards are updated annually to recommend maximum worker chemical exposure in workplaces but are not legally limited or regulated. ACGIH provides threshold limit values (TLV) according to short-term exposure limit and time-weighted average standards. TLV are based on a time-weighted average (TLV-TWA), meaning that an employee's exposure cannot exceed the TWA during 8-hour workday within a 40-hour work week (Purvis et al., 2001). Based on the VOC data in this study and TLV-TWA list in Table S2, a simple model of occupational exposure index (E_i) assessment is defined as (He et al., 2012):

$$E_i = \sum_i^n \frac{C_i}{TLV-TWA_i} \quad (1)$$

where C_i (mg m^{-3}) is the concentration of compound i ; $TLV-TWA_i$ values (mg m^{-3}) are provided by ACGIH. In workshop, VOCs with E_i above 1.0 are deemed to pose a potential health risk to the employees.

2.4.2. Health risk assessment for the residents

Health risk assessment has been developed to provide a basis to protect public health from the effects of air pollution in their everyday lives, which focused on the chronic exposure to VOCs that may cause cancer or other toxic effects, rather than acute toxicity (Yimrungruang et al., 2008). These human health effects can be classified as either non-cancer or cancer risks (Payne-Sturges et al., 2004). Since most PSW recycling are carried out in workshops or near residential areas, it is necessary to assess the non-cancer and cancer risks of VOCs to the residents.

For non-cancer risk, it is characterized in terms of a hazard index (HI) which is defined as the ratio of chronic daily intake (CDI, with a detailed description in the Supporting information) to the reference dose (RfD) listed in Table S2:

$$HI_i = \frac{CDI_i}{RfD_i} \quad (2)$$

When the HI is ≥ 1.0 , an adverse health effect is posed to human beings (Durmusoglu et al., 2010).

The lifetime cancer risk (LCR) is calculated using the equation:

$$LCR_i = CDI_i \times SF \quad (3)$$

where SF is the cancer slope factor in the unit of $\text{kg day}^{-1} \text{mg}^{-1}$ of a specific cancer substance. The values of SF are obtained from the Integrated Risk Information System (IRIS) developed by USEPA, which are also listed in Table S1. Compounds with LCRs more than 1×10^{-4} were considered as "definite risk", between 1×10^{-5} and 1×10^{-4} as

"probable risk", between 1×10^{-5} and 1×10^{-6} as "possible risk" and less than 1×10^{-6} as "negligible risk" (Durmusoglu et al., 2010; Li et al., 2013; Sexton et al., 2007).

When evaluating predicted health risks from multiple VOCs, the above models were used to estimate risks for each VOC and then sum these risks. These models yield an estimate of total health risks, which represent the cumulative predicted health risks for all toxic VOCs at the studied sites. However, it is noted that these two models for cumulative non-cancer or cancer risk assessment should assume that there are no synergistic or antagonistic chemical interactions and that all chemicals produce the same effect to human, including the same organ (U.S. EPA, 2009).

3. Results and discussion

3.1. VOC emissions from PSW extrusion process

Among the steps of PSW mechanical recycling, only the extrusion process had the potential to release VOCs (Patel and Xanthos, 1995). Hence, the VOC emissions from seven different types of PSW workshops during the extrusion were studied. A total of six groups (alkanes, alkenes, monoaromatics, oxygenated VOCs (OVOCs), chlorinated VOCs (ClVOCs) and acrylonitrile) including 64 kinds of VOCs were identified and quantified (Table S1). Based on the structure of polymers or monomers, the workshops were classified into three groups for discussion as follows.

3.1.1. ABS and PS recycling workshops

As the first group of PSW, both ABS and PS contained the same monomer, styrene. Thus, the pollution profiles and the concentrations of various types of VOCs emitted during the extrusion of ABS and PS

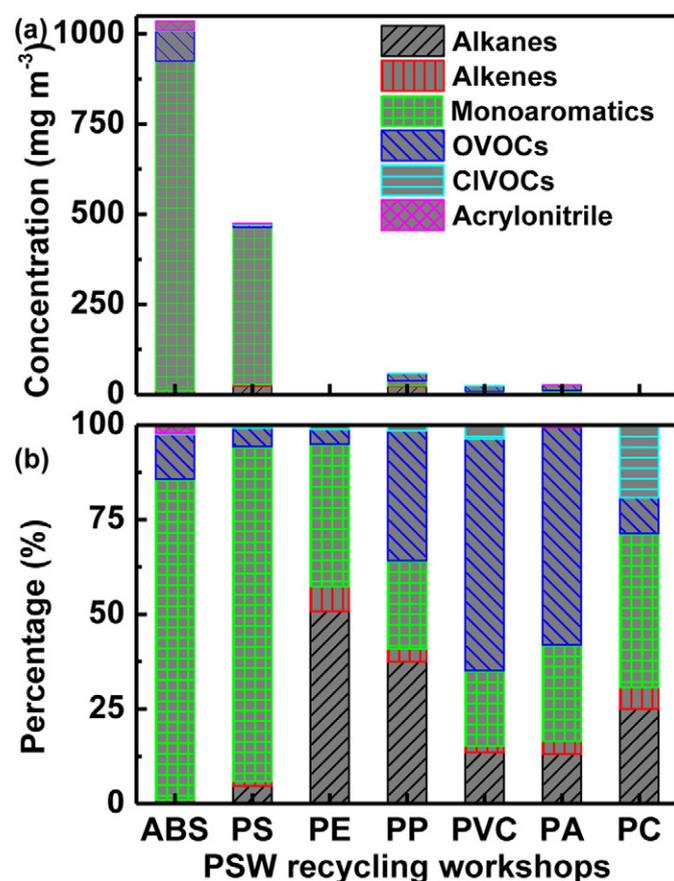


Fig. 1. Concentrations (a) and contributions (b) of six groups of VOCs emitted in seven PSW recycling workshops during extrusion processes.

were compared. As shown in Fig. 1, the total concentration of VOCs (TVOC) with a mean value of $1.0 \pm 0.4 \times 10^3 \text{ mg m}^{-3}$ in the ABS recycling workshop was much higher than that in the PS workshop ($4.7 \pm 1.0 \times 10^2 \text{ mg m}^{-3}$). Nevertheless, monoaromatics was the predominant group in both workshops ($\geq 84.7\%$). During the ABS recycling process (Table S3), styrene concentration was the highest with a mean value of $6.3 \pm 2.1 \times 10^2 \text{ mg m}^{-3}$, followed by ethylbenzene ($1.5 \pm 0.5 \times 10^2 \text{ mg m}^{-3}$), xylene ($54 \pm 22 \text{ mg m}^{-3}$), toluene ($31 \pm 14 \text{ mg m}^{-3}$) and i-propylbenzene ($28 \pm 9 \text{ mg m}^{-3}$), accounting for 60.9%, 14.5%, 5.2%, 3.0% and 2.7% of TVOCs, respectively (Fig. S1a). The main thermal decomposition mechanism of ABS consisted of three parts: depolymerization of polystyrene component; cyclization of polyacrylonitrile component; and cyclization of polybutadiene component (Wang and Zhang, 2013). It was suggested that the depolymerization of polystyrene component occurred by both end-chain scission and random chain scission, which were terminated in the formation of volatiles and conjugated structure (Day et al., 1999), and the monomer recovery was higher than 45% (Demirbas, 2004). Hence, massive styrene and other monoaromatics were easily formed by unzipping of polystyrene component. In the case of later two parts, cyclization, usually along with cross-linking and *cis-trans* isomerization reaction, could produce

nonvolatile macromolecules by thermal processes (Rahaman et al., 2007). As a result, low amounts of acrylonitrile monomer ($25 \pm 13 \text{ mg m}^{-3}$), alkanes ($3.0 \pm 1.0 \text{ mg m}^{-3}$) and alkenes ($7.4 \pm 5.4 \text{ mg m}^{-3}$) were detected. Surprisingly, methyl methacrylate concentration was the third highest VOC (6.7%) with a mean value of $70 \pm 33 \text{ mg m}^{-3}$, which might be produced from e-waste including unseparated polymethylmethacrylate (PMMA) or PMMA-ABS blend copolymers (An et al., 2013).

Comparatively, the TVOC concentration in the pure PS recycling workshop was less than half of that of the ABS workshop, but the monoaromatics was also the most abundant VOC, accounting for 88.5% of TVOCs (Fig. 1). During the extrusion process for the PS (Table S3), the distribution pattern of VOCs was very similar to that of the ABS. Styrene level was also the highest with a mean value of $3.1 \pm 0.7 \times 10^2 \text{ mg m}^{-3}$, followed by ethylbenzene ($55 \pm 12 \text{ mg m}^{-3}$), accounting for 66.4% and 11.6% of TVOCs, respectively (Fig. S1b). The reason is that the pyrolytic mechanism of PS is similar to the polystyrene component of ABS. This result was in good agreement with another study that the major volatile products of pyrolysis of PS were styrene monomer and other monoaromatics including ethylbenzene, toluene, benzene, and xylene (Mehta et al., 1995). The low

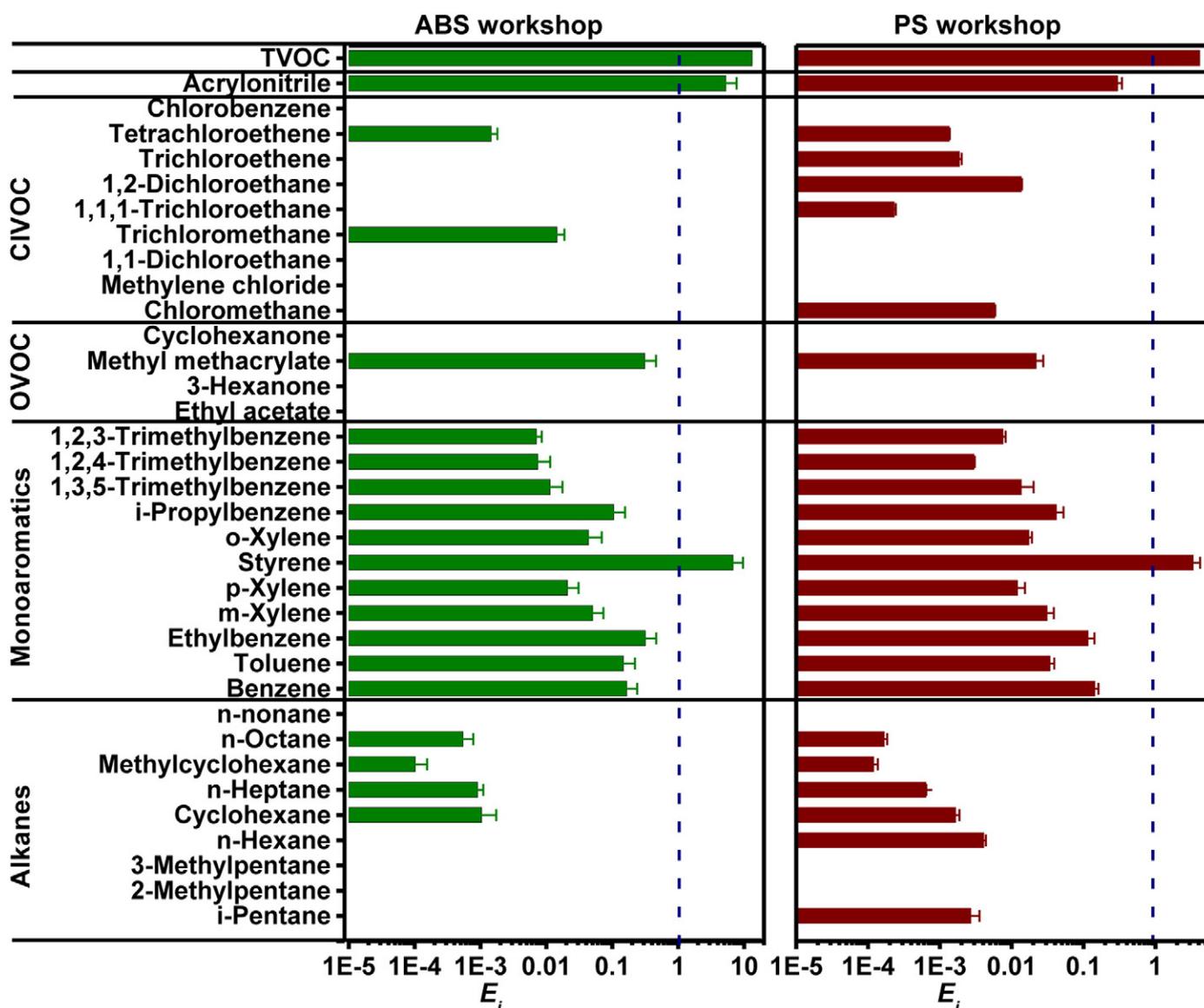


Fig. 2. The occupational exposure indexes (E_i) assessment of individual and total VOCs during extrusion in ABS and PS recycling workshops.

concentrations of VOCs implied that VOCs detected in the PS workshop were attributed to lower extrusion temperature (200–260 °C) than that in ABS workshop as listed in Table 1.

3.1.2. PE and PP recycling workshops

The second group of PSW included PE and PP, whose monomers were aliphatic olefins. Compared with the above two workshops, the TVOC concentrations in PE and PP recycling were much less, with the values of 2.8 ± 2.4 and $59 \pm 14 \text{ mg m}^{-3}$, respectively (Fig. 1a). Alkanes are the most abundant VOCs for polyolefins, contributing 50.8% and 37.5% to the PE and PP recycling VOC emissions (Fig. 1b), respectively. The significant decrease of TVOC concentrations was mainly attributed to the low melting temperature used (150–250 °C) in the PE and PP extrusion processes, but the pyrolytic temperature of virgin PE and PP was more than 350 °C (Kiran Ciliz et al., 2004; Peterson et al., 2001). However, due to the aging, long thermal exposure and the interactions between the additives and recycled PE and PP polymer waste, a small fraction of VOCs was still released during the melting extrusion process.

For the difference of emitted VOCs between these two polymers, it was also noted that the TVOC concentration during the PP extrusion was 20.7 times higher than that during the PE extrusion. Meanwhile, the OVOC concentration in the PP workshop was $20 \pm 7 \text{ mg m}^{-3}$, accounting for 34.4% of TVOC, whereas it was only $0.11 \pm 0.10 \text{ mg m}^{-3}$ in the PE workshop, accounting for 3.9% of TVOC (Fig. 1). As shown in Fig. S2, the three VOC species with the highest concentrations during the PP extrusion were cyclopentanone (20.6%), 3-hexanone (10.2%) and styrene (11.2%), while during the PE extrusion process they were i-pentane (20.4%), n-undecane (13.5%) and toluene (10.3%). Such a difference was mainly attributed to the different pyrolytic mechanisms between two polymers. It was believed that thermo-oxidative and thermo-mechanical degradation of PP occurred through the chain scission of the macromolecules, leading to a decrease in the molecular weight by a series of radical reactions: oxidation, fragmentation, disproportionation, etc. (Canevarolo, 2000; Hinsken et al., 1991). In the case of PE, the chain branching and the crosslinking took place simultaneously with the chain scission, resulting in the formation of more nonvolatile macromolecules (Camacho and Karlsson, 2002). Therefore, higher TVOC concentration and more OVOC were observed in the PP workshop than in the PE workshop.

3.1.3. Other PSW recycling workshops

The third group of PSW included PVC, PA and PC, whose monomers contained heteroatoms. During the extrusion of these three types of PSW, the TVOC emissions were also much lower than those of the ABS and PS recycling processes, but not so much different from the PP and PE recycling processes. During the PVC extrusion process, the TVOC concentration was $25 \pm 1 \text{ mg m}^{-3}$, of which OVOC was the most abundant group, followed by monoaromatics, alkanes, CIVOC and alkenes, contributing 61.2%, 19.8%, 13.5%, 3.7% and 1.7% of VOC emissions, respectively (Fig. 1). The OVOC mainly contained the cyclopentanone, n-butanol and methyl methacrylate with the mean concentrations of 8.2 ± 0.2 , 5.5 ± 0.1 and $1.2 \pm 0.0 \text{ mg m}^{-3}$ (Table S3), accounting for 33.1%, 22.1% and 4.8% (Fig. S3a), respectively. These results implied that PVC tended to be oxidized by the heat at the operating temperature (150–200 °C). However, only a small amount of CIVOC (3.7%) appeared, although PVC contained Cl atom. It was suggested that the first step of PVC thermal decomposition was the dehydrochlorination at low temperature (<300 °C), leading to the formation of HCl as well as polyene free radicals (Blazso and Jakab, 1999; Close et al., 1977; Jafari and Donaldson, 2009; Kim, 2001). Owing to the oxidation and the cyclization reactions, these radicals could be transferred to OVOC, monoaromatics and other products (Starnes, 2002), with less CIVOC.

Similar to PVC, the emitted VOCs (TVOC concentrations: $26 \pm 12 \text{ mg m}^{-3}$) during the PA extrusion could be divided into three major groups: OVOC (57.5%), monoaromatics (25.4%) and alkanes (13.1%) (Fig. 1). Furthermore, OVOC was dominated by ketones,

where cyclopentanone ($6.6 \pm 5.4 \text{ mg m}^{-3}$) was found to be the most abundant OVOC, followed by 2-ethyl-cyclopentanone ($2.9 \pm 2.0 \text{ mg m}^{-3}$), methyl methacrylate ($1.9 \pm 0.3 \text{ mg m}^{-3}$) and 2-methylcyclopentanone ($1.3 \pm 0.3 \text{ mg m}^{-3}$), accounting for 25.1%, 10.8%, 7.2% and 4.8% of TVOC (Fig. S3b), respectively. The result was in good agreement with a previous study that the pyrolysis of PA 66 could mainly yield cyclopentanone, which was formed by radical scission and CO elimination from the adipic acid moieties (Ballistreri et al., 1987). The minor monoaromatics were originated from some aromatic polyamides. Furthermore, it was also noted that acrylonitrile with $0.17 \pm 0.05 \text{ mg m}^{-3}$ was the only detected nitrogen containing VOC. According to previous studies (Beyler and Hirschler, 2002; Herrera et al., 2001), the C–N bonds of PA were the weakest bond among the chains. Thus, at low operating temperature, most decomposed gaseous N-containing products were the organic gases, NH_3 and HCN, which was also confirmed by many other researchers (Beyler and Hirschler, 2002; Herrera et al., 2000; Nielsen et al., 1995).

In the case of the PC workshop, the lowest TVOC concentration with the value of $0.99 \pm 0.21 \text{ mg m}^{-3}$ was determined during the extrusion process among the studied workshops, which was more than 1000 times lower than that during the ABS extrusion. This might be caused by that PC could not be decomposed at the operating temperature of 180–230 °C. The PC showed no weight loss at the temperature below 450 °C, proving that PC had good thermal stability and high heat distortion temperature (Jang and Wilkie, 2004). Because most PC was used for compact disks with the additives of metal film and organic dyes on the surface, which were washed before the extrusion, VOCs' emission during the PC extrusion was much less than any other plastics.

Generally, VOCs could be emitted from polymers and additive pyrolysis at the operating temperature, and the types and concentrations of VOCs emitted mainly depended on the plastic composition during the extrusion process. For example, a large amount of monoaromatics were emitted from thermal degradation of the plastic containing styrene monomer, whereas few VOCs were emitted from polyolefin plastics. With respect to additives, they were usually applied for some special functions, including plasticizers, UV stabilizers and antioxidants, and might have produced extraordinary VOCs found in this study. It was noted that alkane concentration in the PS workshop was much higher than that of the ABS workshop, which was presumably evolved from the additive of PS. Moreover, the operating temperature was another important factor affecting VOC emissions. In addition, the aging, long

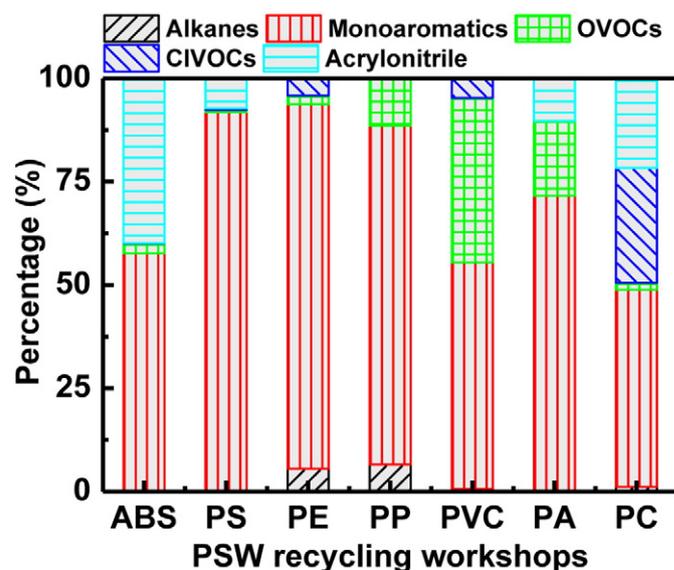


Fig. 3. Percent contribution of different VOC groups to occupational exposure hazard indexes in extrusion process of studied workshops.

thermal exposure, unseparated plastics and interactions between polymer components would also affect the VOC emissions.

3.2. OEL assessment for the PSW extrusion process

High pollution levels of VOCs might have acute and chronic risks to the workers in the extrusion workshops. Hence, OEL of emitted VOCs was assessed. According to the ACGIH standards (Table S2), TWA–TLV of 34 out of 64 quantified VOCs were evaluated for occupational exposure effects in this study.

Based on the TWA–TLV of individual VOC as mentioned above, the occupational exposure indices E_i for all the investigated VOCs during the extrusion process in the different PSW recycling workshops are given in Figs. 2 and S4. It can be found that, only in the ABS and PS workshops, the E_i for TVOCs were more than 1.0, indicating that workers in these two workshops might suffer from potential health risks from the emitted VOCs. Specifically, styrene and acrylonitrile with the highest mean E_i of 6.8 and 5.3 contributed 51.1% and 39.8% of TVOC E_i in the ABS recycling workshop, respectively; while styrene E_i was 3.4, accounting for 72.1% of TVOC E_i in the PS recycling workshop. Other E_i values for

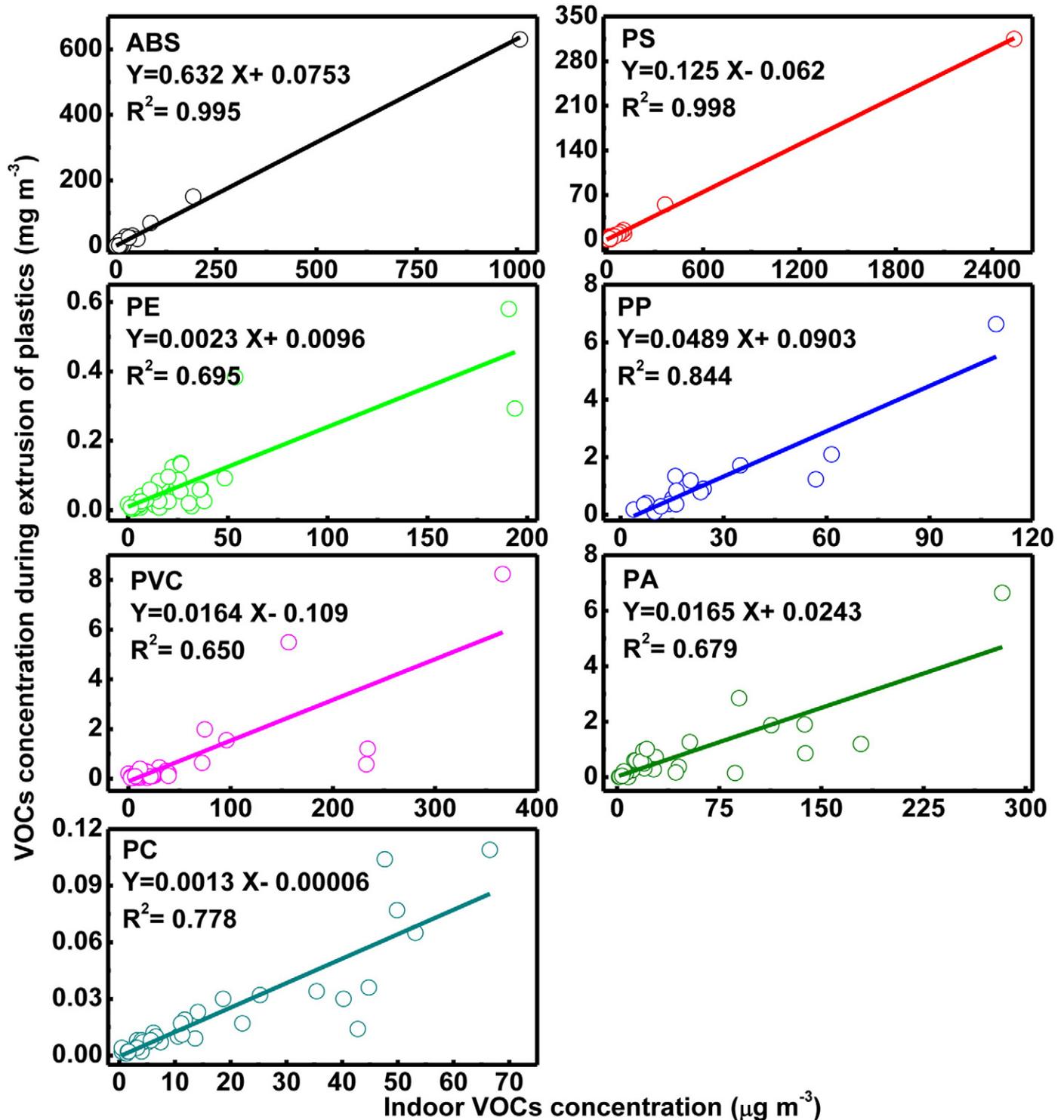


Fig. 4. The correlation between indoor VOC concentrations and their corresponding concentrations in extrusion processes for each workshop.

individual VOCs were less than 1.0 in all the other workshops. For the other workshops, due to its low TWA-TLV (0.0017 mg m^{-3}), benzene contributed to the majority of E_i (0.0042–0.21), accounting for 67.1%, 43.4%, 42.7%, 62.9% and 41.7% of TVOC E_i in the PE, PP, PVC, PA and PC workshops, respectively (Fig. S4). In addition, the contributions of different VOC groups to E_i in all the investigated workshops are given in Fig. 3. Monoaromatics was the main contributor to TVOC E_i in all the workshops, ranging from 47.7% to 91.6%. Other groups also showed substantial contribution to TVOC E_i . For example, OVOC contributed to 39.8% and 18.2% of occupational exposure in the PVC and PA workshops, respectively. Overall, the sums of E_i for all VOCs in the different workshops were ranked in the following order: ABS (13) > PS (4.2) > PA (0.34) > PVC (0.25) > PP (0.24) > PE (0.014) > PC (0.010). Obviously, the workers should wear protective equipment like respirator, or additional engineering controls should be implemented in the ABS and PS recycling workshops during the extrusion process. Although the E_i

values of other workshops were <1.0, their potential health impacts could not be completely ignored.

3.3. Correlation of VOCs in residential indoor microenvironments with PSW extrusion process

As mentioned earlier, due to the rather primitive and crude facilities used during the extrusion of plastics, VOCs produced during the process might be discharged directly into the residential indoor microenvironments and directly exposed to the people who lived in or near the workshops. Therefore, the indoor VOC pollution profiles for the different PSW recycling workshops were investigated in detail. A total of 69 VOCs including 20 alkanes, 10 alkenes, 20 monoaromatics, 9 OVOCs, 9 CIVOCs and acrylonitrile were identified and quantified in seven residential indoor microenvironments (Table S4). Besides the 63 VOCs observed near the extrusion machines mentioned earlier, six VOCs including 2-

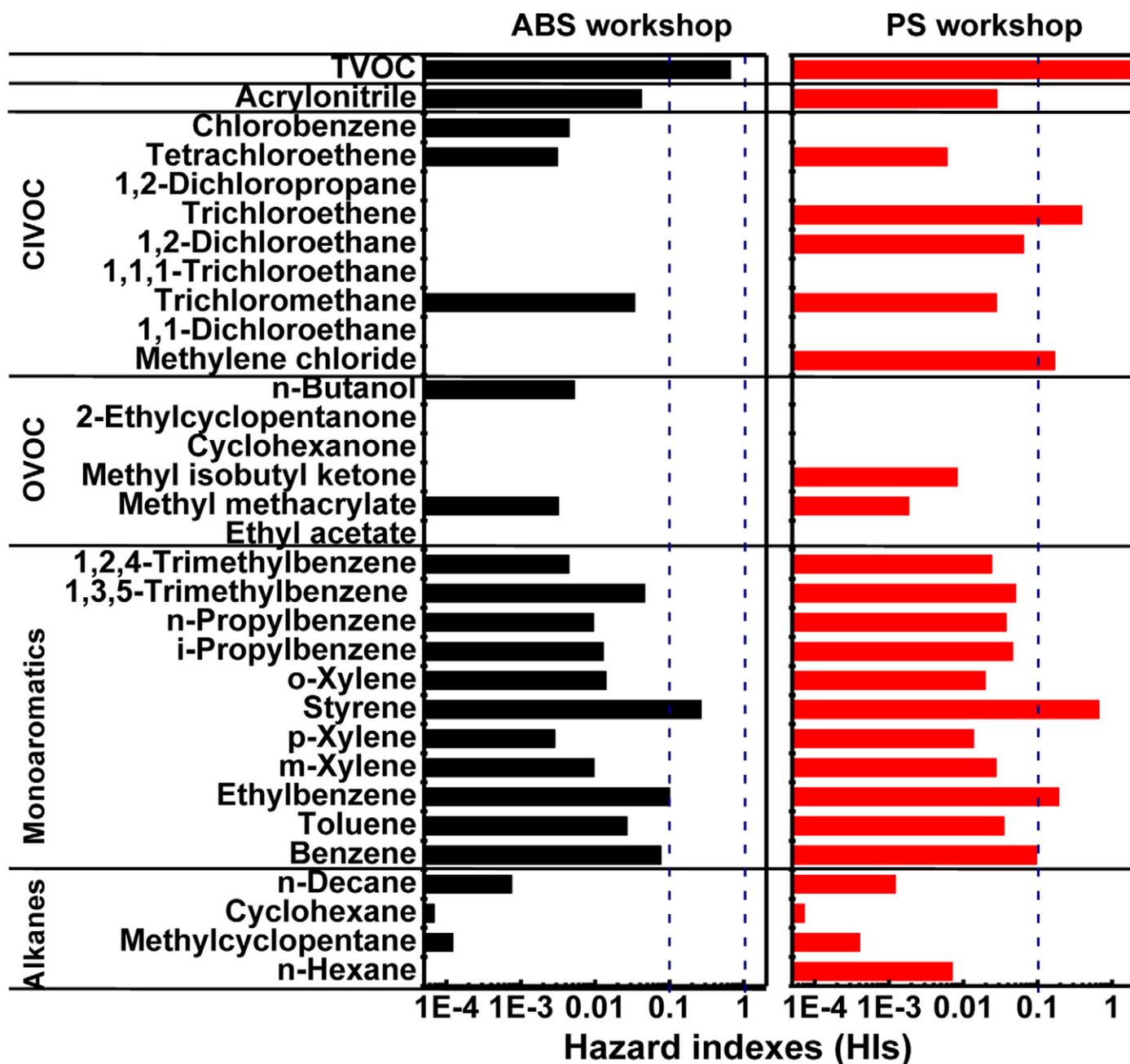


Fig. 5. Indoor VOC non-cancer hazard indexes for the residents in ABS and PS recycling workshops.

pentene, α - and β -pinene, m/p-diethylbenzene, 1,2-dichloropropane were newly detected in these indoor microenvironments.

It was noted that the highest TVOC concentration was found in the PS indoor workshop with a mean concentration of 3.9 mg m^{-3} , followed by PA (2.1 mg m^{-3}), PVC (1.9 mg m^{-3}), ABS (1.8 mg m^{-3}), PP (1.2 mg m^{-3}), PE (1.1 mg m^{-3}) and PC (0.60 mg m^{-3}) indoor workshops (Table S4). TVOC concentrations in residential indoor microenvironments of PSW workshops were approximately 7 to 42 times greater than indoor TVOC concentration reported of the living room in an urban city of Southern China (Ohura et al., 2009), and even much higher than in indoor air of highly industrialized city whose TVOC concentration was 0.13 mg m^{-3} (Jia et al., 2008). It was likely that massive VOCs were discharged into indoor microenvironments due to poor ventilation or no treatment in most PSW workshops. By evaluating the correlation between the 63 VOC concentrations in the extrusion process and indoor microenvironments (Fig. 4), it was possible to estimate the VOC emission sources based on the linear coefficients (R^2). For all the sites, the R^2 were higher than 0.650, indicating that VOCs in these indoor microenvironments predominately originated from the extrusion process. The result was also confirmed by the VOC composition patterns (Fig. S5), revealing that the percentages of major VOC groups in indoor microenvironments were similar to those in the recycling workshops (Fig. 1). As for ABS and PS, the R^2 were very high (0.995 and 0.998, respectively), indicating that the VOCs were from single sources. With lower R^2 for the others sites, it seemed that other VOC emission sources existed such as injection molding, other adjacent workshops or natural sources, which released α - and β -pinene by plants (Kansal, 2009). The indoor VOC emission impact factors were also expressed by the slopes of the lines. The highest slope of 0.632 was obtained for the ABS recycling workshop due to its excellent ventilation system. Therefore, the indoor VOC concentrations for the ABS recycling workshop were dramatically reduced in comparison with the others during the extrusion process.

3.4. Health risk assessment for the residents

A total of 31 quantified VOCs were assessed according to the reference dose values for non-cancer effects (Table S2). Based on the indoor concentrations (Table S4), the non-cancer hazard indices (HIs) of VOCs for the residents lived near these PSW recycling workshops are presented in Figs. 5 and S6. The maximum total HI with a value of 1.90 for the

investigated VOCs was obtained in the PS indoor workshop, followed by PA (0.97), PC (0.74), PVC (0.74), ABS (0.66), PE (0.56) and PP (0.25) workshops. With the HI above 1.0, a non-cancer risk might be posed to the residents by VOCs emitted from the PS recycling workshops, where top four species for HIs were styrene (0.66), trichloroethylene (0.39), ethylbenzene (0.19) and methylene chloride (0.17), accounting for 37.8%, 20.5%, 10.0% and 8.8% of total HI, respectively. As for the other workshops, with the total HI values less than 1.0, the non-cancer risks of VOCs were unlikely to affect the residents. Nevertheless, it was considered that the compounds still posed potential risks to the residents' health with the HI values between 0.1 and 1 (McCarthy et al., 2009; Ramirez et al., 2012). In the indoor microenvironment of the PA recycling workshop, the HIs associated with benzene (0.59) and methylene chloride (0.16) were above 0.1, contributing 60.7% and 16.0% of the total non-cancer risk. In addition, methylene chloride (0.46) also contributed 62.3% of the no-cancer risk in the indoor PC recycling workshop. In the indoor microenvironment of the PVC and PE recycling workshops, benzene was also the main contributor (accounting for 39.1% and 38.9% of total HIs) with the highest HIs of 0.29 and 0.22, respectively. In the ABS workshop, the highest non-cancer risks were originated from styrene (0.26) and ethylbenzene (0.10), while the highest risks were from 1,3,5-trimethylbenzene (0.044), benzene (0.050) and toluene (0.0037) in the PP workshop.

According to the International Agency for Research on Cancer (IARC, 2014), nine of the investigated VOCs are classified into three cancerigenic categories: human carcinogens (Group 1: benzene), probable carcinogens (Group 2A: trichloroethylene and tetrachloroethylene) and possible carcinogens (Group 2B: ethylbenzene, styrene, methylene chloride, trichloromethane, 1,2-dichloromethane and acrylonitrile). Fig. 6 shows the lifetime cancer risks of these VOCs to the residents near the investigated PSW recycling workshops. The highest cumulative LCR (1.29×10^{-3}) occurred in the indoor microenvironment of the PS workshop, followed by in PA (1.28×10^{-3}), ABS (1.18×10^{-3}), PVC (1.01×10^{-4}), PE (5.56×10^{-5}), PC (5.25×10^{-5}), and PP (3.02×10^{-5}) workshops. It was noted that the residents have been posed definite cancer risks near the PS, PA, ABS and PVC recycling workshops when posed probable risk in other workshops. In the former three workshops, the cumulative LCRs were mainly contributed by acrylonitrile (accounting for 47.1%, 94.8% and 76.3% of the total LCRs, respectively) whose LCR values exceeded a level of 10^{-4} . Besides, styrene with LCRs of 4.63×10^{-4} and 1.84×10^{-4} near PS and ABS recycling workshops as

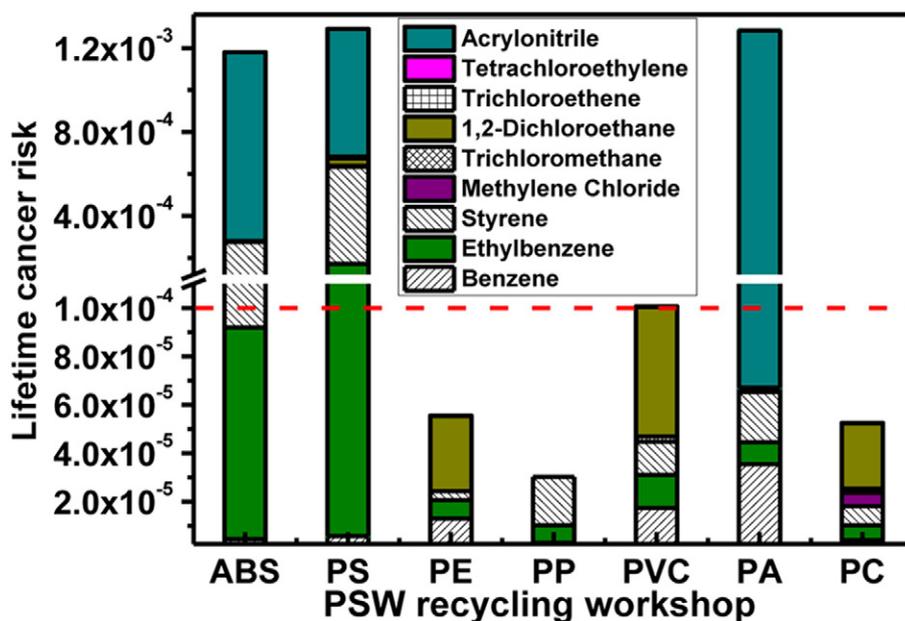


Fig. 6. LCRs of the carcinogenic VOCs for residents in seven PSW recycling workshops.

well as ethylbenzene with LCR of 1.65×10^{-4} near PS recycling workshops were estimated, respectively. These compounds were demonstrated unacceptable to the residents near corresponding workshops. Referring to PVC, PE and PC recycling workshops, 1,2-dichloromethane was the main contributor (contributing 53.1%, 55.9% and 51.5% of the total LCRs, respectively). With the LCR values greater than 10^{-5} , 1,2-dichloromethane was defined as a probable risk. In the PP workshop, styrene contributed 66.1% to total LCRs. Additionally, as for Group 1 carcinogen benzene, the LCRs in all the workshops ranged from 4.05×10^{-6} to 3.55×10^{-5} , indicating that the benzene related cancer risk was not negligible to the residents near all the recycling workshops.

Generally, for the non-cancer risk, benzene, toluene, ethylbenzene, styrene, methylene chloride and trichloroethylene were the major contributors to the chronic health effects in these workshops; while acrylonitrile, styrene, ethylbenzene and 1,2-dichloromethane verified as Group 2B were the major contributors to cancer risks, like tumor of the lungs, liver, kidneys, and brain via inhalation exposure (Achanzar and Mangipudy, 2014; David et al., 2006; Huff et al., 2010). Therefore, the VOCs' exposure was at a high level in these workshops, and some management strategy should be taken to reduce the pollution and to protect the residents from the non-cancer and cancer risks. Furthermore, VOCs' effluent should be taken into account for future health risk legislations.

4. Conclusions

The melting extrusion of seven different thermoplastics could produce massive VOCs. The TVOC concentrations emitted during PSW recycling were in the following order: ABS > PS > PP > PA > PVC > PE > PC. Monoaromatics was found as the main contributor in the ABS, PS and PC workshops, while the most abundant VOC group was found to be alkanes in the PE and PP workshops, and OVOCs in the PVC and PA workshops. OEL assessment indicated that the workers might suffer from acute and chronic health risks in the ABS and PS recycling workshops. For indoor microenvironment, most VOCs were originated from the melting extrusion process while the TVOC concentration order was quite different: PS > PA > PVC > ABS > PP > PE > PC. For the non-cancer risk, only the HI of the PS workshop was more than 1.0, posing an adverse chronic health effect on residents. For the lifetime cancer risk, the values near PS, PA, ABS and PVC recycling workshops were higher than 10^{-4} , suggesting definite cancer risks to the residents nearby. Therefore, some management strategies should be taken to protect the residents from non-cancer and cancer risks.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.envint.2015.01.004>.

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