Potential of Passive Sampling and Plant Absorption to Quantify Inhalation Exposure to Volatile Organic Compounds

Veerapas Na Roi-et¹ and Supawat Chaikasem²*

¹Faculty of Public Health, Thammamasat University, Hangchat, Lampang 52190, Thailand
²Faculty of International Maritime Studies, Kasetsart University, Sri Racha, Chonburi 20230, Thailand

1. INTRODUCTION

Volatile organic compounds (VOCs) are a ubiquitous group of harmful air pollutants that currently are the most common air pollutants existing in both indoor and outdoor air (Ari, 2020). The regulatory definition of VOCs used by the United States Environmental Protection Agency (U.S. EPA) is any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participate in atmospheric photochemical reactions (Srivastava and Majumdar, 2011). In the field of Indoor Air Quality (IAQ), U.S. EPA (2020a) clarifies that the term “volatile organic compounds” denotes any of thousands of organic (carbon-containing) chemicals that are present mostly as gases at room temperature. Inorganic carbon-containing gases such as carbon dioxide and carbon monoxide are excluded from this definition. VOCs are chemical compounds that arise by man-made or natural events. They include a very wide variety of types of molecules that can be categorized in many ways, such as by the types of chemical bonds (alkanes, alkenes, alkynes, saturated, unsaturated), by structure (e.g., straight-chained, branched, ring structures), by the function of specific parts of the molecules (e.g., aldehydes, ketones, alcohols, etc.), or by specific elements included (e.g., chlorinated hydrocarbons that contain chlorine, hydrogen, and carbon).

Hazardous air pollutants (HAPs) are air pollutants that are carcinogenic or have serious health effects, such as the cause of disability of a newborn baby or have a serious impact on the environment and ecosystem. Many VOCs are dangerous to human health (Kim et al., 2008; Na Roi-et et al., 2017) and are collectively named as hazardous VOCs. Short-term and long-term exposure to HAPs, even in low concentrations can cause harmful effects on human
health (i.e., cancerous illnesses, neurological disorders, central nervous system damage, respiratory irritation, and symptoms such as headaches, dizziness, fatigue, confusion, and nausea) (Durmusoglu et al., 2010; Na Roi-et et al., 2017; Saikomol et al., 2019; Sakai et al., 2017; Shrubsole et al., 2019; Xing et al., 2018; Zhang et al., 2019). The Clean Air Act amendments of 1990 identified 187 substances as HAPs published by the U.S. EPA for regulation of the emissions of HAPs. The important members of hazardous VOCs were benzene, dichloromethane, formaldehyde, chloroform, etc. (U.S. EPA, 2020b).

The presence of volatile organic compounds (VOCs) and the associated health risks in residential and public buildings are well reported (Delgado-Saborit et al., 2011; Hoskins, 2003; Shrubsole et al., 2019; Weschler, 2009). The Pollution Control Department (PCD) of Thailand notified the limit values of VOCs at 24 h in the atmosphere to limit harm to human health as Acetaldehyde <860 µg/m³, Acrolein <0.55 µg/m³, Acrylonitrile <10 µg/m³, Benzene <7.6 µg/m³, Benzyl chloride <12 µg/m³, 1,3-Butadiene <5.3 µg/m³, Bromomethane <190 µg/m³, Carbon tetrachloride <150 µg/m³, Chloroform <57 µg/m³, 1,2-Dibromoethane <370 µg/m³, 1,4-Dichloroethane <1,100 µg/m³, 1,2-Dichloroethane <48 µg/m³, Dichloromethane <210 µg/m³, 1,2-Dichloropropane <82 µg/m³, 1,4-Dioxane <860 µg/m³, Tetrachloroethylene <400 µg/m³, 1,1,2,2-Tetrachloroethylene <83 µg/m³, Vinyl chloride <20 µg/m³ (PCD, 2009), respectively. However, VOC concentration in indoor air is generally higher than the outdoor air by about 5-10 times (Dales et al., 2008). The concentration of VOCs of benzene, toluene, m,p-xylene, and aromatic hydrocarbons have the highest indoor air pollutant concentration (Wetzel and Doucette, 2015). Although individual VOC are observed even in low concentrations, the mixture can produce additive and probably synergistic effects (Orwell et al., 2004). WHO (2013) reported that the additive effects were considered as a significant mechanism driving the health impacts from combined or multiple exposures of VOCs. In this regard, it becomes an emerging threat to human health associated with chronic exposure to multiple VOCs. There is growing concern about potentially harmful pollutants that may be released from office productivity devices. Photocopiers and laser printers are important sources of VOCs, which derive from toners and printed circuit boards during the printing process (Tang et al., 2012). The VOCs emissions from photocopiers are much higher than other office equipment (Destaillets et al., 2008). As a result, photocopiers are major sources of exposure to VOCs and can lead to potential health impacts due to their proximity.

Photocopiers and laser printers are generally used as office equipment. Exposure of VOCs released during operation and maintenance of photocopiers and laser printers have been associated with the effects on human health. Furthermore, other sources of VOCs can be plastic materials and electronic components of photocopiers and laser printers (Destaillets et al., 2008; Kowalska et al., 2015). However, some VOC species may not only be an immediate hazard but also leading to long-term effects on human health. According to this regard, it is a necessity to understand the VOC species released to find the appropriate way to control the emissions.

The monitoring techniques of VOCs are generally composed of sampling, pretreatment, separation, and detection processes. Passive sampling techniques have been successfully applied to monitor VOC concentrations due to their simplicity, low cost, compactness, light weight, portability, and easy to implement (Sakurai et al., 2013). The early applications were for examining pollution in industrial sites, but over the past several years there has been significant progress in using passive sorbent samplers for measuring VOCs at the lower concentrations needed to assess human health risk onsite. Passive samplers have been shown to yield results equivalent to other established methods for many VOCs (Cocheo et al., 2009; Healy et al., 2018). The sampling protocols are simple and have several advantages over more traditional indoor air sampling techniques, for instance, U.S. EPA Methods TO-15 and TO-17 (U.S. EPA, 2009a). Passive samplers are small and lightweight compared with the canisters used in Method TO-15, and less expensive. This method provides accurate results for a large range of sampling durations, from daily to quarterly sampling periods for certain compounds (U.S. EPA, 2012). The ability to collect time-weighted average samples over longer durations than the 8 to 96 hours offered by the more traditional methods is an advantage because these longer periods can provide data that are more representative of the long-term average. Preferably, badge type passive samplers have greater adsorption rates than tube type passive samplers due to shorter diffusion length and larger surface area (Strandberg et
A passive sampler is particularly employed for the determination of time-weighted average (TWA) concentrations (Novic et al., 2017).

Plants used as a tool of environmental monitoring have many advantages over other systems: they are cheap, sensitive, and easy to sample. An indoor plant is often proposed as a passive approach for indoor air pollution mitigation. The use of the indoor plant to reduce potentially harmful pollutants such as VOCs has been studied for decades (Fukushi et al., 2005; Moya et al., 2019; Orwell et al., 2004; Wolverton et al., 1989). Epipremnum aureum (E. aureum) is widely used as an indoor plant because of its air pollution removal capacity, and tolerance to heat, humidity, and pests (Fukushi et al., 2005; Na Roi-et et al., 2017; Orwell et al., 2004). It can also grow in a water-filled container without any added nutrients and soil (Meshram and Srivastava, 2015). Gong et al. (2019) evaluated the benzene removal rate of four ornamental plants, namely Epipremnum aureum, Chlorophytum comosum, Hedera helix, and Echinopsis tubiflora, and they reported that the highest benzene removal rate was observed in E. aureum of about 1.10 µg/m³ cm². Yang et al. (2009) investigated twenty-eight indoor plant species for their ability to remove volatile organic pollutants and found that the total VOC removal efficiency of E. aureum was 6.71 µg/m³ m² h. In addition, E. aureum is a popular houseplant and native to tropical areas such as Thailand (Moya et al., 2019; Na Roi-et et al., 2017). Therefore, it was selected as a passive approach for pollutant removal of VOCs from office equipment.

To investigate the potential of using E. aureum to reduce VOC concentrations of indoor air pollutants, this study performed lab experiments with the aim to evaluate VOC species and concentrations released inside two different photocopy centers to further interpret the health impacts of VOCs exposure. Also, the appropriate mitigation measure to decrease potential health impacts by the use of E. aureum as a passive approach to remove VOCs was discussed.

### 2. METHODOLOGY

#### 2.1 Determination of VOCs with a passive approach

The indoor air quality of two photocopy centers was investigated for a broad range of VOCs utilizing passive samplers and plants for four times in February, 2020. The photocopy center was located at an educational institution, which is visited by approximately 50-200 people per working day. Each photocopy center consists of three employees and four photocopiers with similar manufacturer’s brands. The area of photocopy centers A and B was 9.39 m², 9.92 m², respectively. Both of them included one glass door for the entrance and four glass windows around the building to supply natural ventilation.

This study was a cross-sectional study to assess the risk of total VOC exposure. VOCs were collected using SKC passive sampling model 575, containing 350 mg of charcoal. The samples were collected during a 10 h working period from 07.30 a.m. to 05.30 p.m. using badge type passive samplers in both photocopy centers. Martin et al. (2017) reported that the workers in photocopy centers rarely spend their entire day at a single workstation, and they conduct a varying number of tasks, such as walking to and from the service counter to the copier to retrieve completed print jobs, light copier maintenance (e.g., replacing spent toner cartridges, refilling paper bins, and staples), and other tasks away from their workstation and copiers, such as document finishing (e.g., binding) and shipping. Hence, the passive samplers in our study were placed in the middle of the room at a distance of 1 m from the photocopiers which were laid out along the room walls. The passive sampler was hanging at a height of 1.5 m measured from the floor, which is the average breathing height.

The E. aureum or Golden Pothos were seedlings from local breeder stores. They were cultured inside compacted clean coconut husk in 10 cm diameter pots under clean conditions. At 30 days of age, a set of 25 healthy E. aureum with heights of 15-20 cm and average leaf areas of 2,600±141 cm² was used in the experiment. E. aureum was used as a passive approach. The absorption by plant leaf was collected from the photocopy centers A and B for 24 h. A pot of E. aureum was placed inside of the rooms to collected indoor air samples, with 1.5 m distance from the entrance, in a setting between the photocopiers which was least influenced by the outdoor environment, and in order not to obstruct the operation.

At each photocopy center, air samples were collected to represent the inhalation exposure from photocopiers and plant leaves were analysed to evaluate the potential of plant leaves as passive samplers for VOCs in the indoor environment. The schematic diagram of the position of E. aureum, photocopy machines (A and B), and passive samplers point is illustrated in Figure 1. After the end of the sampling, passive samplers and plant leaves were stored in an icebox and transferred to keep in a
refrigerator at 4°C before the extraction process. Then, the samples were examined by GC-MS/MS after the extraction process.

2.2 Samples preparation and extraction

The SKC passive samplers (SKC 575-001, Lot 2000, containing 350 mg of charcoal) were used as passive samplers for VOCs determination. VOCs adsorbed on samplers were extracted using 5 mL carbon disulfide (AR grade, 99.9% CS₂, MW.76.13, Kemaus).

_E. aureum_ leaves without visible injury were randomly collected from the same plant using a gloved hand and ethanol-cleaned scissors. Three to five leaves were then cleaned with distilled water and dried with tissue paper. The plant leave samples were placed into a petri dish and cut into smaller pieces. The small pieces of _E. aureum_ leaves were then mixed to obtain 5 g of a final leaf sample weight. Methanol is commonly used as the extraction solvent of plant samples (Atawodi et al., 2010; Chaikasem and Na Roi- et, 2020; Geethangili and Ding, 2018; Larson et al., 2014; Parekh et al., 2005). Five milliliters of methanol (HPLC grade, ≥99.9% CH₃OH, MW.32.04, Sigma-Aldrich) were gently poured over the cut leaf for VOC extraction. After standing for 30 min, the extracted samples were collected.

All extracted samples were filtered through 0.2 µm PTFE syringe filters into amber glass vials with polyspring inserts and then analyzed for VOCs determination using gas chromatograph-mass spectrometer/mass spectrometer (GC-MS/MS).

![Figure 1. The schematic diagram of the position of _E. aureum_ and photocopiers (A and B).](image)

2.3 Analysis apparatus

The Thermo Scientific gas chromatography triple quadrupole mass spectrometry (TSQ 8000 Evo Triple Quadrupole GC-MS/MS, Thermo Scientific, USA) was employed for sample analysis. Analytes were separated on a DB-5MS Ultra Inert capillary gas chromatographic column (30 m × 0.25 mm × 0.25 µm), and the carrier gas was helium at a flow velocity of 1.0 mL/min. The GC-MS/MS conditions were as follows: The PTV (Programmed Temperature Vaporization) injector temperature was 290°C, the injection volume was 2 µL. The GC oven temperature was initially kept at 60°C for 0.5 min, then raised at a rate of 15°C/min to 300°C and held for 2 min.

The mass selective detector was operated using positive electron ionization (+EI) in the selected ion monitoring (SIM) mode. The collision gas (Argon) pressure was 1.5 mTorr. The value of the electron emission current was 50 µA. The ion source and transfer line temperatures were 250°C and 290°C, respectively.

The regression analysis, correlation coefficient ($R^2$), limit of detection (LOD), and limit of quantification (LOQ) of a calibration curve for VOCs covered the determination of 21 VOC species as presented in Table 1. A six-point calibration was carried out to quantify individual VOC species. Linear correlation between individual VOC concentrations and peak area was checked with correlation coefficients resulting from the six-point calibration curve. The correlation coefficient was greater than 0.99, indicating good linearity for the quantification of individual VOC species. The LOD and LOQ were calculated following the method described by Miller and Miller (2010).
TWAmix is to assume additive effects among the followings (Watts, 1997):

Contaminating gaseous pollution containing a mixture of hundreds of carbon-exposure limits. Also, VOCs are one component of air inhalation exposures to VOCs, the concentration of individual VOC species was compared to occupational weighted average concentrations derived from measured VOC concentrations and then adjusted based on the exposure scenario characteristics being evaluated (U.S. EPA, 2009b). The ECi was calculated in µg/m³ as follows:

\[
\text{ECi} = \frac{c_{m} \times \text{ET} \times \text{EF} \times \text{ED}}{\text{AT}}
\]

In this expression, \(c_{m}\) is the measured VOCs concentrations (µg/m³); ET is the exposure time (10 h/day); EF is the exposure frequency (168 days/year); ED is the exposure duration (5 years); AT is the averaging time (hours). For the hazard assessments of non-carcinogenic risk and carcinogenic risk, the averaged time (ED × 365 days/year × 24 h) and expected lifetime (70 years × 365 days/year × 24 h) are substituted for AT, respectively.

The inhalation exposure to non-carcinogenic and carcinogenic VOCs has followed the conventional approaches proposed by U.S. EPA (U.S. EPA, 2009b) and previous studies (Al-Zboon and Forton, 2019; Ari et al., 2020; El-Hashemy and Ali, 2018; Kitwattanavong et al., 2013; Loonsamrong et al., 2015; Xing et al., 2018). Health risk assessment

### Table 1. Regression analysis, correlation coefficient, LOD, and LOQ of calibration curves for all VOCs species

| Compounds               | Calibration curve | R²     | LOD (µg/m³) | LOQ (µg/m³) |
|-------------------------|-------------------|--------|-------------|-------------|
| Tetrachloroethene       | \(Y = 356614 + 2299.35X\) | 0.9944 | 0.25        | 0.83        |
| Styrene                 | \(Y = 1.82362 \times 10^{6} + 15696X\) | 0.9901 | 0.21        | 0.69        |
| Methylene chloride      | \(Y = 7.04441 \times 10^{6} + 6975.05X\) | 0.9912 | 48.73       | 162.43      |
| 1,2-Dichloroethane      | \(Y = 6.04807 \times 10^{6} + 19616.2X\) | 0.9958 | 0.18        | 0.59        |
| 1,1,1-Trichloroethane   | \(Y = 968965 + 5062.85X\) | 0.9989 | 0.09        | 0.29        |
| cis-1,2-Dichloroethene  | \(Y = 6.10499 \times 10^{6} + 1503.48X\) | 0.9970 | 0.22        | 0.72        |
| trans-1,2-Dichloroethene| \(Y = 729647 + 575.304X\) | 0.9963 | 0.73        | 2.44        |
| Carbon tetrachloride    | \(Y = 1.38908 \times 10^{6} + 15651.1X\) | 0.9957 | 4.48        | 14.94       |
| Toluene                 | \(Y = 1.85655 \times 10^{6} + 39080.9X\) | 0.9979 | 70.75       | 235.84      |
| Ethylbenzene            | \(Y = 85522.1 + 17287.8X\) | 0.9945 | 0.01        | 0.02        |
| 1,1-Dichloroethene      | \(Y = 5.65658 \times 10^{6} + 1661.65X\) | 0.9993 | 0.18        | 0.61        |
| Benzaldehyde            | \(Y = 980471 + 11399.7X\) | 0.9938 | 0.09        | 0.30        |
| 1,3-Dichloropropene     | \(Y = 9.30625 \times 10^{6} + 1373.73X\) | 0.9972 | 2.90        | 9.66        |
| 1,2-Dichloropropene     | \(Y = 9.63784 \times 10^{6} + 1777.48X\) | 0.9949 | 4.14        | 13.81       |
| 1,3-Dichloropropene     | \(Y = 1.81483 \times 10^{6} + 4147.92X\) | 0.9988 | 0.69        | 2.29        |
| Vinyl chloride          | \(Y = 1.02388 \times 10^{6} + 9413.95X\) | 0.9953 | 2.64        | 8.80        |
| Trichloroethene         | \(Y = 1.21394 \times 10^{6} + 5908.96X\) | 0.9950 | 0.05        | 0.16        |
| Benzene                 | \(Y = 2.2215 \times 10^{6} + 12135.9X\) | 0.9902 | 0.31        | 1.02        |
| o-Xylene                | \(Y = 126643 + 3414.45X\) | 0.9961 | 0.11        | 0.38        |
| m-Xylene                | \(Y = 4.65885 \times 10^{6} + 17399X\) | 0.9993 | 0.23        | 0.76        |
| p-Xylene                | \(Y = 4.65885 \times 10^{6} + 17399X\) | 0.9993 | 0.23        | 0.76        |

### 2.4 Quantitative risk assessment

Before evaluating potential health impacts from inhalation exposures to VOCs, the concentration of individual VOC species was compared to occupational exposure limits. Also, VOCs are one component of air pollution containing a mixture of hundreds of carbon-containing gaseous pollutants. Therefore, the most common method for evaluating Threshold Limit Values-Time Weighted Average for mixtures (TLV-TWAmix) is to assume additive effects among the VOC mixtures. The TLV-TWA was calculated as follows (Watts, 1997):

\[
\text{TLV} - \text{TWA} = \frac{\sum_{i=1}^{n} C_{i}}{\sum_{i=1}^{n} C_{i}^{\text{TLV-TWA}}}
\]

Where \(n\) is the number of VOCs; \(C_{i}\) is VOCs concentration, and Threshold Limit Values-Time Weighted Average (TLV-TWA) is the American Conference of Governmental Industrial Hygienists Threshold Limit Values (ACGIH TLV). The Risk Assessment Guidance for Superfund (RAGS): Part F was recommended for quantitative risk assessment to estimate the level of inhalation exposure to VOCs. Adjusted inhalation exposure to VOC concentrations (ECi) was proposed as a continuous exposure concentration for each person to calculate health risk based on U.S. EPA guidelines. The ECi are time-weighted average concentrations derived from measured VOC concentrations and then adjusted based on the exposure scenario characteristics being evaluated (U.S. EPA, 2009b).
associated with non-carcinogenic and carcinogenic risk caused by inhalation exposure to VOCs were estimated by combining EC\textsubscript{i} with the Reference Concentration for Inhalation Exposure (RfC) and Inhalation Unit Risk (IUR) obtained from the Integrated Risk Information System (IRIS) (U.S. EPA, 2016a), Department of Toxic Substances Control (DTSC) (DTSC, 2019), Office of Environmental Health Hazard Assessment (OEHHA) (OEHHA, 2011).

Non-carcinogenic risk assessment for the mixture of VOCs species was determined as the Hazard Index (HI), which is defined as follows:

\[
HI = \sum_{i=1}^{n} HQ_i
\]

Where HI is the hazard index of multiple VOC species, which is used to estimate potential health risk. The HI was acquired from the summing of Hazard Quotient (HQ\textsubscript{i}) for inhalation exposure to VOCs. The HQ\textsubscript{i} can be calculated by dividing the adjusted inhalation exposure to VOCs concentrations (EC\textsubscript{i}) by inhalation reference concentration (RfC\textsubscript{i}) expressed in µg/m\textsuperscript{3}:

\[
HQ_i = \frac{EC_i}{RfC_i}
\]

The HQ\textsubscript{i} greater than 1.0 would indicate the possibility of a non-carcinogenic effect from inhalation exposure. The HQ\textsubscript{i} lower than 1.0 provides acceptable risk; however, the cumulative acceptable risk for each VOC species must also be less than 1.0.

Carcinogenic risk assessment was estimated using the following equation:

\[
R_i = EC_i \times IUR_i
\]

Where R\textsubscript{i} is the estimated inhalation carcinogenic risk; EC\textsubscript{i} is the adjusted inhalation exposure to VOC concentrations, and IUR\textsubscript{i} is the inhalation unit risk (m\textsuperscript{3}/µg) of carcinogenic compounds as a result of the continuous exposure concentration to that contaminants at 1.0 µg/m\textsuperscript{3} (assuming 70 kg body weight and inhalation rate of 20 m\textsuperscript{3}/d over 70 year lifetimes). The acceptable value of cancer risk is less than 1.0×10\textsuperscript{-6}. This indicates no potential carcinogenic risk resulting from exposure to carcinogenic substances. Likewise, the total risk was determined by summing individual cancer risk. The total carcinogenic risk of inhalation exposure to VOCs lower than 1.0×10\textsuperscript{-6} represents an acceptable level.

3. RESULTS AND DISCUSSION

3.1 VOCs concentrations

During the printing process, VOC emissions can result from heating the drum and toner to temperature levels observed inside printing equipment to compress the toner on paper. The VOC emissions by the use of printers and copiers were caused by circuit boards, toners and inks, paper, and plastic construction materials. Kowalska et al. (2015) studied the characteristic of VOCs emitted from seven office devices (office printers and copying devices) and found that all of them release VOCs with a difference in individual VOCs species and concentrations. The dominant VOC species related to the printing process were chlorinated VOCs, styrene, xylenes, ethylbenzene, acetophenone, benzaldehyde, and many other benzene derivatives (El-Hashemy and Ali, 2018; Henschel et al., 2001; Kowalska et al., 2015).

VOCs were grouped into two categories according to their chemical structure characteristics namely; non-halogenated hydrocarbons and halogenated hydrocarbons. Concentrations of halogenated hydrocarbons were the dominant components of the detected VOCs. The halogenated hydrocarbons and the non-halogenated hydrocarbon concentrations were 1.11×10\textsuperscript{3}, 2.18×10\textsuperscript{4} and 1.73×10\textsuperscript{3}, 2.15×10\textsuperscript{4} µg/m\textsuperscript{3} in photocopy centers A and B, respectively.

The total VOCs concentrations were 2.29×10\textsuperscript{4} and 2.32×10\textsuperscript{4} µg/m\textsuperscript{3} for photocopy centers A and B, respectively. Figure 2(a), (b) illustrated the concentration distributions of detected VOC in the photocopy centers. Of these, halogenated hydrocarbons were the dominant component of detected VOCs, contributing 95.16% and 92.54% of total VOCs. Among the halogenated hydrocarbons, tran-1,2-Dichloroethene was the most prevalent VOC in emissions from printing equipment. Additionally, the highest concentrations of m-Xylene, p-Xylene, and trans-1,2-Dichloroethene observed in photocopy center A were 4.89×10\textsuperscript{2}, 6.20×10\textsuperscript{2}, and 2.18×10\textsuperscript{4} µg/m\textsuperscript{3}, and the highest concentration of m-Xylene, p-Xylene, and trans-1,2-Dichloroethene in photocopy center B were determined as 7.97×10\textsuperscript{2}, 9.36×10\textsuperscript{2}, and 2.15×10\textsuperscript{4} µg/ m\textsuperscript{3}, respectively. The mean indoor air concentrations for the total VOCs detected at photocopy center B were greater than photocopy center A. These findings suggest that the number of works at photocopy center B was greater than A. Wang et al. (2011) proved that while the copier and laser printer are printing, there will be an increase in...
the amount of m-Xylene, p-Xylene, and trans-1,2-Dichloroethene concentrations. The increase of the total VOC concentration of toner is caused by the VOCs released by the heated fuser (El-Hashemy and Ali, 2018). The highest concentration of VOC found in this study was trans-1,2-Dichloroethene, which is largely used in the industrial sector, for example as a solvent of polymer products, chemical spills, burning vinyl objects, chemicals transformations, etc. The sources of trans-1,2-Dichloroethene in photocopy centers may be released from toner, typewriter fluid, document protectors, file folders, PVC furniture, insulation of power cables, etc. (Kowalska and Gierczak, 2013).

VOCs are classified as HAPs due to their malodorous and hazardous properties (Durmusoglu et al., 2010). Exposure to HAPs can cause potential short-term and long-term adverse effects on human health. In this study, 21 species of VOCs were analyzed using GC-MS/MS. The summary lists for the 21 species of VOCs and total VOC concentrations are presented in Table 2. However, only three of the 21 total VOCs were quantified and identified because the concentrations of the remaining 18 VOCs were below LOD values.

Figure 2. The characteristics and distributions of detected VOCs groups: (a) Photocopy center A; (b) Photocopy center B.

Table 2. The summary lists for the 21 species of VOCs and total VOCs concentration

| Compounds                | Photocopy center (µg/m³) | Occupational exposure limits (µg/m³) |
|--------------------------|--------------------------|-------------------------------------|
|                          | A                        | B                                   | ACGIH^{c} TLV | NIOSH^{c} REL | OSHA^{c} PEL | DLPW^{d} |
| Non-Halogenated hydrocarbons |
| Styrene                  | <0.21                    | <0.21                               | 8.52x10^4     | 2.15x10^5     | 4.26x10^5     | 4.26x10^5 |
| Toluene                  | <70.75                   | <70.75                              | 7.54x10^4     | 3.75x10^4     | 7.54x10^5     | 7.54x10^5 |
| Ethylbenzene             | <0.01                    | <0.01                               | 8.68x10^4     | 4.35x10^5     | 4.35x10^5     | 4.35x10^5 |
| Benzo(a) pyrene          | <0.09                    | <0.09                               | -             | -             | 2.00x10^2     | -         |
| Benzene                  | <0.31                    | <0.31                               | 1.60x10^3     | 3.19x10^3     | 3.19x10^3     | 3.19x10^3 |
| o-Xylene                 | <1.11                    | <1.11                               | 4.35x10^3     | 4.35x10^3     | 4.35x10^3     | 4.35x10^3 |
| m-Xylene                 | <2.3x10^2               | <2.3x10^2                           | 4.35x10^3     | 4.35x10^3     | 4.35x10^3     | 4.35x10^3 |
| p-Xylene                 | <2.3x10^2               | <2.3x10^2                           | 4.35x10^3     | 4.35x10^3     | 4.35x10^3     | 4.35x10^3 |
| Halogenated hydrocarbons |
| Tetrachloroethene        | <0.25                    | <0.25                               | 1.70x10^5     | -             | 6.78x10^5     | 6.78x10^5 |
| Methylene chloride       | <48.73                   | <48.73                              | 1.74x10^5     | -             | 8.68x10^4     | 8.68x10^4 |
| 1,2-Dichloroethane       | <0.18                    | <0.18                               | 4.05x10^4     | 4.00x10^4     | 2.02x10^5     | 2.02x10^5 |
| 1,1,1-Trichloroethane    | <0.09                    | <0.09                               | 1.90x10^6     | 1.90x10^6     | 1.90x10^6     | 1.90x10^6 |
| cis-1,2-Dichloroethene   | <0.22                    | <0.22                               | 7.90x10^5     | 7.90x10^5     | 7.90x10^5     | 7.90x10^5 |
| trans-1,2-Dichloroethene | <0.73x10^4              | <0.73x10^4                          | 7.90x10^5     | 7.90x10^5     | 7.90x10^5     | 7.90x10^5 |
According to Table 2, the individual VOC species concentrations measured in this study were lower than the occupational exposure limits set by ACGIH (ACGIH, 2019), NIOSH (NIOSH, 2019), OSHA (OSHA, 2019), and DLPW (DLPW, 2017). Although the concentration of individual VOC species was below the limits of their respective standard of 8-hour time-weighted average (TWA), their potential health effects on workers cannot be disqualified. The major pathway of exposure from VOCs in the environment occurs by inhalation. Although the concentrations are very low (in µg/m³ level), they are still toxic to a worker in office due to their chronic exposure to the low level of VOCs. In this regard, risk assessment was employed to evaluate the potential effects on human health of the concentrations of individual and cumulative VOC exposures via inhalation for workers.

### 3.2 Inhalation exposure risks to VOCs

The concentration of individual VOC species was measured in photocopy centers by passive sampling at the worker’s breathing zone for the whole workday. The TLV-TWA_	ext{mix} was computed using all of the detectable VOCs: 4.89×10³ µg/m³ m-Xylene, 6.20×10³ µg/m³ p-Xylene, 2.18×10⁴ µg/m³ trans-1,2-Dichloroethene and 7.97×10² µg/m³ m-Xylene, 9.36×10² µg/m³ p-Xylene, 2.15×10⁴ µg/m³ trans-1,2-Dichloroethene in photocopy centers A and B, respectively. The results indicated that 7.62×10⁵ and 7.47×10⁵ µg/m³ of TLV-TWA_	ext{mix} were observed in photocopy centers A and B, respectively. The inhalation exposure to total VOC concentrations of 2.29×10⁴ and 2.32×10⁴ µg/m³ is lower than TLV-TWA_	ext{mix} of 7.62×10⁵ and 7.47×10⁵ µg/m³. This means that inhalation exposure to total VOC concentrations in both photocopy centers is not harmful to human health based on TLV-TWA_	ext{mix}. However, chronic toxicity is often incurred by long-term exposure to low concentrations of VOCs. Therefore, there is a need to investigate the effects on health by prolonged exposure to low concentrations of VOCs.

As aforementioned, the occupational exposure of VOC species concentration was present in low concentrations under the exposure limits and TLV-TWA_	ext{mix}. However, VOC mixtures can produce additive effects. Therefore, there is a need to investigate the health risk assessment of inhalation exposure to VOCs. Considering the twenty one components of standards VOCs, three VOCs species were detected at both photocopy centers (m-Xylene, p-Xylene, and trans-1,2-Dichloroethene) and were used to assess the risk of inhalation exposure to VOCs. Table 3 illustrated the available toxicological data associated with target health-related VOCs used in this study and their source.

### Table 3. Toxicity values associated with target health-related VOCs

| Compounds         | CAS Number | IARC Group | RfC (µg/m³) Values | IUR (m³/µg) Values | Source | Source |
|--------------------|------------|------------|-------------------|-------------------|--------|--------|
| Tetrachloroethene  | 127-18-4   | 2A         | 40                | 2.6×10⁻⁷          | IRIS   |
| Styrene            | 100-42-5   | 2B         | 1.000             | -                 | IRIS   |
| Methylene chloride | 75-09-2    | 2B         | 600               | 1.0×10⁻⁶          | OEHHA  |
Table 3. Toxicity values associated with target health-related VOCs (cont.)

| Compounds                  | CAS Number | IARC Group | RIC (µg/m³) Values | Source | IUR (m³/µg) Values | Source |
|----------------------------|------------|------------|--------------------|--------|--------------------|--------|
| 1,2-Dichloroethane         | 107-06-2   | 2B         | -                  | -      | 2.6×10⁻⁵           | IRIS   |
| 1,1,1-Trichloroethane      | 71-55-6    | 3          | 5.000              | IRIS   | -                  | -      |
| cis-1,2-Dichloroethene     | 159-59-2   | 3          | 8                  | DTSC   | -                  | -      |
| trans-1,2-Dichloroethene   | 156-60-5   | 3          | 80                 | DTSC   | -                  | -      |
| Carbon tetrachloride       | 56-23-5    | 2B         | 100                | IRIS   | 6.0×10⁻⁶           | IRIS   |
| Toluene                    | 108-88-3   | 3          | 5.000              | IRIS   | -                  | -      |
| Ethylbenzene               | 100-41-4   | 2B         | 1.000              | IRIS   | 2.5×10⁻⁶           | OEHHA  |
| 1,1-Dichloroethene         | 75-35-4    | 3          | 200                | IRIS   | -                  | -      |
| Benzo(a)pyrene             | 50-32-8    | 2A         | 0.002              | IRIS   | 1.1×10⁻³           | OEHHA  |
| 1,3-Dichloropropene        | 142-28-9   | -          | 80                 | DTSC   | -                  | -      |
| 1,2-Dichloropropane        | 78-87-5    | 1          | 4                  | IRIS   | 1.0×10⁻⁵           | OEHHA  |
| Vinyl chloride             | 75-01-4    | 1          | 100                | IRIS   | 7.8×10⁻⁶           | OEHHA  |
| Trichloroethene            | 79-01-6    | 1          | 2                  | IRIS   | 4.1×10⁻⁶           | IRIS   |
| Benzene                    | 71-43-2    | 1          | 30                 | IRIS   | 2.2×10⁻⁶           | IRIS   |
| o-Xylene                   | 95-47-6    | 3          | 100                | IRIS   | -                  | -      |
| m-Xylene                   | 108-38-3   | 3          | 100                | IRIS   | -                  | -      |
| p-Xylene                   | 106-42-3   | 3          | 100                | IRIS   | -                  | -      |

Note: IARC: Group 1-Carcinogenic to humans; Group 2A-Probably carcinogenic to humans; Group 2B-Possibly carcinogenic to humans; Group 3-Not classifiable as to its carcinogenicity to humans; Group 4-Probably not carcinogenic to humans (Source: DTSC (2019); OEHHA (2009); OEHHA (2011); U.S. EPA (2016a))

The detectable VOCs with available toxicological data characterizing their risk are provided in Table 4. Only RfC values are reported, because there were no published IUR values for m-Xylene, p-Xylene, and trans-1,2-Dichloroethene. Therefore, cancer risks as a result of lifetime inhalation exposure to detected VOCs were not determined.

Table 4. The non-carcinogenic and carcinogenic risk of inhalation exposure to VOCs

| Risk characterization | Compounds        | Photocopy center A | Photocopy center B |
|----------------------|------------------|--------------------|--------------------|
|                      | EC (µg/m³)       | RIC (µg/m³)        | HQ                 | EC (µg/m³)       | RIC (µg/m³)        | HQ |
| Non-cancer risk      | m-Xylene         | 9.37×10⁻⁴         | 100                | 0.94             | 1.53×10⁻⁴         | 100 | 1.53 |
|                      | p-Xylene         | 1.19×10⁻²         | 100                | 1.19             | 1.79×10⁻²         | 100 | 1.79 |
|                      | trans-1,2-       | 4.18×10⁻³         | 80                 | 52.23            | 4.12×10⁻³         | 80  | 51.54 |
|                      | Dichloroethene   |                   |                    |                  |                   |     |
| Hazard Index (HI)    |                  | 54.36              | 54.86              |
| Cancer risk          | m-Xylene         | 6.70               | -                  | -                | 1.09×10⁻¹         | -   | -   |
|                      | p-Xylene         | 8.49               | -                  | -                | 1.28×10⁻¹         | -   | -   |
|                      | trans-1,2-       | 2.98×10⁻²         | -                  | -                | 2.94×10⁻²         | -   | -   |
|                      | Dichloroethene   |                   |                    |                  |                   |     |
| Total Risk (R)       |                  | -                  | -                  |

Source: DTSC (2019); OEHHA (2011); U.S. EPA (2016a)

In addition, the non-carcinogenic risk assessment of inhalation exposure to VOCs is presented in Table 4 and Figure 3(a) and (b). The results reveal that the HQ of m-Xylene, p-Xylene, and trans-1,2-Dichloroethene were 0.94, 1.19, and 52.23, respectively. Regarding the HI of total VOCs, it reached 54.36, thus exceeding the threshold (HI>1.0) in photocopy center A. Likewise, the calculated HQ of photocopy center B was 1.53, 1.79, and 51.54 for m-Xylene, p-Xylene, and trans-1,2-Dichloroethene,
respectively, resulting in the HI of total VOCs reaching 54.86, thus exceeding the acceptable value of 1.0. This indicated that the risk of non-carcinogenic effects may occur and it’s probably higher as HI value increases. Figure 3(a) and (b) also shows the distribution of each HQ to HI value. The HQ to HI value of trans-1,2-Dichloroethene (96.09% and 93.94%) was the dominant contributor, followed by p-Xylene (2.19% and 3.27%), and m-Xylene (1.72% and 2.79%) in photocopy centers A and B, respectively. This finding implies that the measures to decrease the inhalation exposure to VOCs should be taken into account options such as an indoor plant for passive removal for VOCs.

Figure 3(a). The distributions of non-carcinogenic risk estimates for inhalation exposure to VOCs: (a) Photocopy center A; (b) Photocopy center B.

### 3.3 Potential of *E. aureum* for passive removal of VOCs

The main point on phytoremediation mechanisms of air pollutions is the plant’s aerial parts such as the cuticle and stomata. The most explicit route is the mechanical collection of deposits on plant parts like flowers, stems, leaves, etc. (Agarwal et al., 2019). The major absorption of the lipophilic semi-volatile compounds are obtained through the cuticle by leaf surface adsorption (Gawronski et al., 2017). When the volatiles are absorbed by the plant tissue within the stomatal cavity, a concentration gradient occurs and subsequently gravitates into the leaf by diffusion. *E. aureum* were studied for their possibility of absorbing VOCs during exposure for 24 h. The *E. aureum* was placed in the photocopy center to mitigate the amount of VOCs.

The results showed the differences in the absorption of individual VOC species between the tested and controlled *E. aureum*. The concentrations of chlorinated hydrocarbons as trans-1,2-Dichloroethene and Tetrachloroethene observed in photocopy center A were an average of 9.47×10³ µg/m³. In the photocopy center B, the average was determined as 5.07×10³ µg/m³. The analysis of total VOCs in leaf specimens is shown in Figure 4. At time 0 h, the result presented the plant contaminated with VOCs before the study. Meanwhile, results at 24 h show that the plants could absorb more VOCs in their leaves. According to Mishra and Pandey (2019), the bio-concentration factor (BCF) was calculated to describe the ability of plants for elemental accumulation from total VOCs using the following equation:

\[
BCF = \frac{\text{Total VOCs}_{24}}{\text{Total VOCs}_{0}}
\]

Where; BCF is the bio-concentration factor of total VOCs in the plant’s leaves. Total VOCs24 represents the amount of total VOCs found in the plant’s leaves at 24 h. Total VOCs0 is the amount of total VOCs observed in the plant’s leaves at 0 h. The concentrations in the plant leaves were determined on a dry-weight basis and made equivalent to volume by assuming the density as 1.0 (1 g leaves dry-weight=1 mL).

The removal of VOCs involves a combination of biotransformation and absorption mechanisms which may be achieved by different plant parts. Both the stomata and cuticules participate in the VOC removal process. Benzene penetrates more easily through the cuticle, while formaldehyde, a hydrophilic VOC, enters more easily through stomatal openings.
The ease of penetration through the stomata depends on stomatal size and associated factors, while the molecular size of VOCs is more important in the case of entry through the cuticle (Gawronska et al., 2017; Gong et al., 2019). The bio-concentration levels of total volatile organic compounds in *E. aureum* were noted from high to low as 174.42-74.71. Their ability was detected with a relatively good correlation coefficient ($R^2=0.723$) that represents the relationship between the level of VOCs observed in the air and the plant’s leaves. The correlation is significant at 0.01 (two-tailed). The relation showed that the types and levels of VOCs as trans-1,2-Dichloroethene detected in the passive samplers were consistent with levels discovered within the *E. aureum*. The ability of the plant to absorb VOCs is related to the exposure time. The passive sampler and plant absorption can potentially be used to monitor low concentration VOCs. When compared to other species for the bio-concentration level of m-Xylene, p-Xylene, and Tetrachloroethene, *E. aureum* had the same range of accumulation as holly or *Ilex aquifolium* (U.S. EPA, 2016b). Furthermore, the higher bio-concentration of VOCs in leaves indicate their infiltration into tissues by air pollution uptake (Agarwal et al., 2019). *E. aureum* is effective for removing VOCs, especially in indoor areas by adsorbing particulates on their leaves.

**Figure 4.** Bio-concentration factor of *E. aureum* for passive removal of VOCs.

The photocopy centers should be designed with sufficient ventilation and engineering controls ought to be implemented to mitigate emissions at the source. The air conditioner is adjusted to guidance temperature to reduce the amount of volatile organic compounds released in the event of high heat. Try to choose ink cartridges that are natural inks to reduce the impact on operators and customers. Furthermore, employees should be informed of the potential hazards and guidelines of such emissions. Workers should protect themselves by wearing suitable protective gloves and masks to avoid direct and indirect contact with VOCs. Indoor plant cultivation has the potential to improve air quality by removing specific air pollutants.

**4. CONCLUSION**

This study investigated the VOC characteristics and risk assessment associated with emissions from photocopy centers. The obtained results indicate that the total VOCs concentrations were $2.92 \times 10^4$ and $2.32 \times 10^4 \mu g/m^3$ which include three substances (m-Xylene, p-Xylene, and trans-1,2-Dichloroethene) in photocopy centers A and B, respectively. The trans-1,2-Dichloroethene was the most abundant among VOC profiles. It was observed that VOC species concentrations were lower than recommended limit values set by ACGIH, NIOSH, OSHA, and DLPW. Long-term exposure to VOCs even at lower concentrations than its limit value poses a potential health risk. The non-carcinogenic and carcinogenic risks due to inhalation exposure were also determined. However, the toxicity values associated with observed VOCs were not reported. Therefore only the risk of non-carcinogenic VOCs was determined. The non-cancer risk associated with non-carcinogenic VOCs as indicated by HI exceeded the acceptable limit value in both photocopy centers, indicating that exposed VOCs...
posed a probable health threat of non-carcinogenic effects to workers. Hence, *E. aureum* or Golden Pothos for the passive VOCs removal at the photocopy center further reduces VOCs concentrations and provides risk abatement resulting in reduced exposure to VOCs of workers.

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