

## Characterization of biogenic volatile organic compounds (BVOCs) in cleaning reagents and air fresheners in Hong Kong

Yu Huang<sup>a</sup>, Steven Sai Hang Ho<sup>b,c</sup>, Kin Fai Ho<sup>b</sup>, Shun Cheng Lee<sup>a,\*</sup>, Yuan Gao<sup>a</sup>, Yan Cheng<sup>a,d</sup>, C.S. Chan<sup>a</sup>

<sup>a</sup> Department of Civil and Structural Engineering, Research Center for Environmental Technology and Management, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, China

<sup>b</sup> SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China

<sup>c</sup> Division of Atmospheric Sciences, Desert Research Institute, Reno, NV 89512, USA

<sup>d</sup> Department of Environmental Science and Technology, School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, No.28 Xianning West Road, Xi'an, Shaanxi 710049, China

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### ABSTRACT

Biogenic volatile organic compounds (BVOCs) emitted from cleaning products and air fresheners indoors are prone to oxidation resulting in the formation of secondary pollutants that can pose health risks on residents. In this study, a solid phase microextraction (SPME) coupled with gas chromatography/mass spectrometry (SPME-GC/MS) method was applied for the determination of BVOCs compositions in three categories of cleaning products including floor cleaners (FC), kitchen cleaners (KC) and dishwashing detergents (DD), and also air fresheners (AF). The analysis results demonstrated that chemical composition and concentration of individual BVOC varied broadly with household products in the view of their different functions and scents as indicated on the labels. The concentration of total BVOCs for sample FC1 was the highest up to 4146.0  $\mu\text{g g}^{-1}$ , followed by FC2 of 264.6  $\mu\text{g g}^{-1}$ , FC4 of 249.3  $\mu\text{g g}^{-1}$  and FC3 of 139.2  $\mu\text{g g}^{-1}$ . *D*-limonene was the most abundant detected BVOCs in KC samples with the chemical composition varying from 19.6  $\pm$  1.0 to 1513.0  $\pm$  37.1  $\mu\text{g g}^{-1}$ . For dishwashing detergents, only *D*-limonene was detected and quantified. The BVOCs compositions of air freshener samples are much more complicated. It was estimated that the consumption of floor cleaners contributed 51% of the total BVOCs amount indoors in Hong Kong, followed by air fresheners 42%, kitchen cleaners 5% and dishwashing detergents 2%.

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### 1. Introduction

Study on indoor volatile organic compounds (VOCs) is essential. Concentrations of many VOCs are higher in indoor than those in outdoor due to existences of particular indoor emission sources (Weisel et al., 2008). The VOCs in a domestic environment originate from a variety of sources, including utilization of consumer household products (e.g., cleaning reagents and air fresheners), emissions from adhesives, furnishing, clothing and building materials, and incense burning (Guo et al., 2000; Lee and Wang, 2004). Among those indoor VOCs, some are classified as toxic air contaminants (TACs), while a few such as formaldehyde and benzene are evidenced to be carcinogenic. Long-term exposure to the VOCs can pose adverse health effects on occupants (Guo et al., 2009).

A few studies demonstrated that daily consumptions of household cleaning reagents and air fresheners would elevate indoor VOCs level (Singer et al., 2006). Recently, terpenes and terpene alcohols emitted from these household products have attracted more attentions because they are prone to oxidation and are probably associated with health risks for occupants and workers, even though such products offer substantial benefits (e.g., promotion of hygiene and aesthetics) to human life (Kwon et al., 2007; Nazaroff and Weschler, 2004). Besides, owing to their natural origin, terpenes and terpene alcohols are always classified as biogenic volatile organic compounds (BVOCs) that differentiate them from those generated by anthropogenic sources (AVOCs). Nazaroff and Weschler (2004) evidenced that household products such as floor cleaners and cleaning detergents are significant contributors for indoor air pollutants. BVOCs such as limonene,  $\alpha$ -pinene, and myrcene have been quantified with high frequency of occurrences in the cleaning reagents sold in Korea using headspace sampling technique (Kwon et al., 2007). Good correlation was also found between the abundances of BVOCs in a university building

\* Corresponding author. Tel.: +852 27666011; fax: +852 23346389.  
E-mail addresses: [ceslee@inet.polyu.edu.hk](mailto:ceslee@inet.polyu.edu.hk), [ceslee@polyu.edu.hk](mailto:ceslee@polyu.edu.hk) (S.C. Lee).

and the frequency of cleaning activities, suggesting that the usage of household cleaning reagents can pose occupants on high pollutant level exposure (Solomon et al., 2008). These BVOCs emitted from cleaning reagents and air fresheners can react rapidly with indoor ozone, resulting in the formation of secondary pollutants such as reactive radicals, airborne formaldehyde, and secondary organic aerosols (SOAs) (Coleman et al., 2008; Fan et al., 2003). The formation of SOAs has been evidenced from ozonolysis of indoor emissions from building materials (Aoki and Tanabe, 2007), terpene-rich household products (Coleman et al., 2008), cleaning reagents and air fresheners (Destailats et al., 2006), and wood-based materials (Toftum et al., 2008). Additionally, the products generated from oxidations of fragrance terpenes contributed greatly to fragrance allergy and upper airway irritation (Matura et al., 2005; Wolkoff et al., 2000). Such secondary formation pollutants possibly contain multiple oxygen groups that can even cause adverse health effects (Forester and Wells, 2009; Jarvis et al., 2005).

In order to reduce the posed health risk on building occupants and cleaning personals, regulations to control VOC emissions from the household products have been established by several governmental authorities such as United States Environmental Protection Agency (U.S.EPA), the California Air Resources Board (CARB) and the Hong Kong Environmental Protection Department (HKEPD) (CARB, 2009; EPA, 1998; EPD, 2007). In order to understand the roles of BVOCs associated with the consumption of cleaning reagents and air fresheners in indoor chemistry, it is important to characterize and quantify the BVOCs composition profiles in the related products. Solid-phase microextraction (SPME) is an alternative approach for environmental monitoring that integrates sampling, isolation, and concentration for analysis with chromatographic methods (Adam et al., 2005; Bouvier-Brown et al., 2007; Nicolle et al., 2008; Zeng et al., 2008). We have demonstrated its feasibility in determination of BVOCs coupled with gas chromatography/mass spectrometric detection (SPME-GC/MS) (Huang et al., 2011).

The objectives of this study are to evaluate the concentrations and compositions of BVOCs in cleaning reagents and air fresheners sold in Hong Kong and to estimate the indoor BVOCs concentrations related to the use of these products. To our best knowledge, only limited research has been carried out to quantify the mass concentrations of BVOCs in the cleaning reagents and air fresheners, and none of them has been reported on our local products. The study is thus critical for the establishment of any regulation subject to indoor BVOCs emissions.

## 2. Experimental

### 2.1. Selection of testing samples

Four categories of household products including floor cleaners (FC), kitchen cleaners (KC), dishwashing detergents (DD), and air fresheners (AF) were examined in this study. The samples were selected based on the extent of product consumption in Hong Kong and the scent of the products shown on the label of their containers. Cleaning products consisting of lemon and pine oil were selected because they are expected to release substantial levels of reactive terpenes and related terpene alcohols. Four samples of FC, KC and DD and three samples of AF were tested and their general information was presented in Table 1.

### 2.2. Sample preparation

Three milliliter of each aqueous household samples was extracted respectively with 2 ml of cyclohexane. Recovery test shows that a close to 100% of efficiency was found in the

**Table 1**

General information of studied cleaning products and air fresheners.

Household Products	Status	Fragrance	Origin	Main function
<b>Floor Cleaners (FC)</b>				
FC 1	Liquid	–	Taiwan	To clean and disinfect the floor, effective in killing germs
FC 2		Lemon	Taiwan	
FC 3		Pinene scent	Hong Kong	
FC 4		–	Hong Kong	
<b>Kitchen Cleaners (KC)</b>				
KC1	Liquid	Lemon	Hong Kong	To remove stubborn dirt in kitchen
KC2		Lemon	Taiwan	
KC3		–	Taiwan	
KC4		–	Hong Kong	
<b>Dishwashing Detergents (DD)</b>				
DD1	Liquid	Lemon & Aloe	Hong Kong	To remove tough grease from dishes
DD2		Lemon	Hong Kong	
DD3		Lemon	Hong Kong	
DD4		–	Hong Kong	
<b>Air Fresheners (AF)</b>				
AF1	Liquid	Lemon	Japan	To remove dust, pollen, virus, bacteria, and odor
AF2		Jasmine Flower	China	
AF3		Jasmine Flower	Taiwan	

–No fragrance was labeled on the brand of these household products.

liquid–liquid extraction for BVOCs. The supernatant (cyclohexane) layer was transferred into a clean capped vial. A 12-L Tedlar bag (SKC Inc., Eighty Four, PA) was cleaned by filling it with air supplied by a zero air generator (Model 111, Thermo Environmental Inc., Sugar Land, TX) and evacuating it with laboratory suction at least four times before use. The clean bag was then filled with 10 L of the zero air monitored by a calibrated flow meter. Ten microliters of the extract was injected into the clean bag with a micro-syringe (Hamilton, Reno, NV) through a septum. Liquid vaporization was allowed by keeping the filled bag in a temperature-regulated environmental chamber at 23 °C for 2 h. All discharges from the Tedlar bag were directed into a fume hood as safety measure.

### 2.3. Solid-phase microextraction (SPME) method

A manual SPME sampling holder consists of a 75 µm Carboxen-PDMS fiber (Supelco, Bellefonte, PA). New fiber was heated in a GC injection port (6890 GC, Hewlett–Packard, Santa Clara, CA) at a continuous helium (He) gas flow at 300 °C for 1 h, aiming to thermally desorb any impurities. The conditioned fibers were stored properly inside a clean box in laboratory. Before sample collection, each fiber was reconditioned in the GC injection port at 300 °C for 10 min. Experimental results show that no significant amount of BVOCs remained on the fiber. Each conditioned fiber was exposed in the test atmosphere for 5 min.

### 2.4. Sample analysis

Once the sampling completed, the fiber was stored and then inserted into the GC injection port at 280 °C for 4 min. During the desorption period, the GC oven temperature was kept at 50 °C. Such a temperature condition would allow the analytes released from the SPME fiber on the head of the GC column in a narrow band. The injector was kept in the splitless mode for the first 2 min and then switched to the split mode until the end of the GC oven temperature program. The GC oven temperature program was then started, which was initially set at 50 °C and held at this temperature for 3 min, ramped at a rate of 5 °C min<sup>-1</sup> to 95 °C and 10 °C min<sup>-1</sup> to 130 °C and 55 °C min<sup>-1</sup> to 290 °C, and then held at the final temperature of 290 °C for 3 min. A DB-5MS UI column (J&W, Agilent Technologies, Inc., Santa Clara, CA, 30 m × 25 mm i.d. × 25 µm film

thickness) were adopted for the analytes separation. The GC injector temperature was kept at 280 °C throughout the analysis. The carrier gas was He (ultra-high purity grade) held at a constant flow of 1.0 ml min<sup>-1</sup>. The analytes after the GC separation were detected using an MS (5973 MS, Hewlett–Packard), which was operated at an ion source temperature of 230 °C and 70 eV for electron ionization (EI). The mass scan range was from 50 to 200 amu. Identification was achieved by comparing the mass spectra with NIST 08 MS library and retention times of the chromatographic peaks with those of calibration standards. The two or three most abundant ion fragments of each BVOC were selected as extract ions for the targeted BVOCs.

### 2.5. Calibrations

The highest purity of BVOCs standards of  $\alpha$ -pinene, camphene,  $\beta$ -pinene, myrcene, 3-carene, p-cymene, d-limonene, eucalyptol,  $\gamma$ -terpinene, terpinolene, linalool and  $\alpha$ -terpineol were purchased from Aldrich (Milwaukee, WI) and Fluka (Buchs, SG, Switzerland). The standards were diluted with cyclohexane (AR grade, Pestinorm, BDH, Poole, UK). A known amount of diluted standard solution was injected into the zero-air filled bag. The air bag was conditioned in a large environmental chamber at temperature of 23 °C for 2 h. Both sample collection and analytical protocol were the same as those applied for the sample determination.

The calibration curves for the tested BVOCs were constructed by exposing the SPME fiber in the gaseous BVOC mixture of known mixing ratios for 4 min. The mixing ratios of individual BVOCs in the Tedlar sampling bags ranged from 10 to 120 ppbv at the temperature of 23 °C and RH of 18%. The calibration curves were plotted as the total peak areas of the respective quantification ions versus the mixing ratio of BVOCs in the standard atmosphere. Even though many targeted BVOCs are constitutional or spatial isomers, their EI mass spectra are generally distinguishable. The two or three most abundant fragment ions were selected as quantification ions for each compound. The  $m/z$  93 ion is the base peak in EI mass spectra of most but not for p-cymene and eucalyptol. The coefficients of determination are >0.98, except myrcene (0.971), linalool (0.973), p-cymene (0.975) and  $\alpha$ -terpineol (0.978). The values demonstrate that the SPME method is reliable for quantification of BVOCs at standard conditions.

The limit of detection (LOD) of the method is defined as the minimum amount of a selected standard that generates the minimum distinguishable signal plus three times the standard deviation of the blank signals. No peaks were detected for the BVOCs in the blank calibration samples. Hence, we approximated the mean blank signal with the calibration line intercept and the blank signal standard deviation with the standard error for the  $y$  (peak area ratio) estimate (Miller and Miller, 1993). The LODs in mixing ratio were 0.31–0.50 ppbv for the 12 BVOCs and the observed RSD ranged from 1.1 to 6.7%.

## 3. Results and discussion

### 3.1. Chemical compositions

Table 2 lists the mass concentrations of BVOCs in the four categories of household products (expressed as microgram of the compound in per gram of the sample) measured with the SPME-GC/MS method. Large variations in the concentrations were showed. For FC, the highest total quantified BVOCs concentration was seen in FC#1 with a mean of 4146.0  $\mu\text{g g}^{-1}$ , which is at >15 times higher than that in the other three samples, ranging from 139.2 to 264.6  $\mu\text{g g}^{-1}$ . d-Limonene, eucalyptol, linalool and  $\alpha$ -terpineol are the major quantified BVOCs in FC. Among these compounds, eucalyptol is a sole compound which can be detected in all FC samples. Its mass concentrations ranged from 20.0  $\pm$  0.7 to 210.0  $\pm$  50.1  $\mu\text{g g}^{-1}$ . Only in FC#1, other monoterpenes such as  $\beta$ -pinene (11.0  $\pm$  4.5  $\mu\text{g g}^{-1}$ ), myrcene (215.0  $\pm$  12.1  $\mu\text{g g}^{-1}$ ), and p-cymene (142.8  $\pm$  13.1  $\mu\text{g g}^{-1}$ ) were quantified, while they were undetectable in the rest of samples. Linalool and d-limonene were the two most abundant BVOCs in FC#1, which contributed 55.9% and 30.2%, respectively, to the total quantified BVOCs concentration. However, the contribution of linalool was significantly small in the FC#2 (35.8%) and FC#3 (21.3%) and even no linalool was found in the FC#4. For d-limonene, it only contributed 8.9% in the FC#2 and none was found in FC#3 and FC#4. It should be noted that  $\alpha$ -terpineol was the most abundant BVOCs in FC#2–FC#4, contributing 43.0–83.7% to the total quantified concentration, but cannot be detected in FC#1. The concentrations and compositions of monoterpenes and monoterpenoids do not indicate any relationship with the fragrance presented in the FC samples. According

**Table 2**  
BVOCs composition of cleaning products and air fresheners (in the unit of  $\mu\text{g BVOC g}^{-1}$  household products).

	$\alpha$ -Pinene		$\beta$ -Pinene		Myrcene		p-Cymene		d-Limonene		Eucalyptol		$\gamma$ -Terpinene		Terpinolene		Linalool		$\alpha$ -Terpineol		Total	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD		
Floor Cleaners (FC)																						
FC1			11.0	4.5	215.0	12.1	142.8	13.1	1250.0	236.5	210.0	50.1					2317.2	571.6			4146.0	
FC2									23.6	3.1	32.5	3.3					94.7	8.4	113.8	9.8	264.6	
FC3											20.0	0.7					29.7	2.1	89.6	1.1	139.2	
FC4											40.7	9.6							208.6	28.1	249.3	
Kitchen Cleaners(KC)																						
KC1							19.8	0.5	1513.0	37.1				72.4	0.8	14.5	0.9	7.6	0.2		1627.3	
KC2									805.6	94.9											805.6	
KC3									19.6	1.0									8.3	0.5	27.8	
KC4							5.6	1.1	51.4	1.8	22.8	4.2							34.6	1.1	114.3	
Dishwashing Detergents (DD)																						
DD1									71.8	3.9											71.8	
DD2									209.1	10.0											209.1	
DD3									143.0	17.8											143.0	
DD4									299.0	14.4											299.0	
Air Fresheners (AF)																						
AF1									362.0	5.9							627.0	26.4			989.0	
AF2									114.5	1.6							1349.2	49.2	18.7	0.6	1482.4	
AF3	262.4	6.9	1377.9	30.2	997.9	40.3	1598.1	82.1	12980.4	412.6			497.5	75.3			9166.2	1309.0			26880.4	

to the information provided by the manufacturers, none of fragrance was added in FC#1 and FC#4 but no similarity was seen on their composition profiles. For FC#2 and FC#3, both were added with lemon and pinene scent respectively. And again, the mass concentrations and contributions of BVOCs were varied greatly. The results demonstrate that the fragrance should not be a major contributor to the BVOCs emission from the FC.

KC and DD are the two categories of household cleaning products which are limited for uses in kitchens or cooking places. The highest total quantified BVOCs concentration ( $1627.3 \mu\text{g g}^{-1}$ ) was seen in KC#1, while KC#3 had the lowest of  $27.8 \mu\text{g g}^{-1}$  (Table 2). *D*-Limonene was the most abundant BVOCs in all KC samples, with the mass concentrations ranging from  $19.6 \pm 1.0$  to  $1513 \pm 37.1 \mu\text{g g}^{-1}$ . Its contributions ranged from 44.9% to 100% to the total quantified concentrations. A few more BVOCs including *p*-cymene ( $19.8 \pm 0.5 \mu\text{g g}^{-1}$ ), terpinolene ( $72.4 \pm 0.8 \mu\text{g g}^{-1}$ ), linalool ( $14.5 \pm 0.9 \mu\text{g g}^{-1}$ ), and  $\alpha$ -terpineol ( $7.6 \pm 0.2 \mu\text{g g}^{-1}$ ) were quantified in KC#1. *D*-Limonene is the sole monoterpene quantified in KC#2. Eucalyptol was only detected in FC#4 with the mass concentration of  $22.8 \pm 4.2 \mu\text{g g}^{-1}$ . In general, higher mass concentration of *D*-limonene was seen for the samples containing fragrance of lemon (i.e., KC#1 and KC#2). No specific fragrance presented in KC#3 and KC#4 according to the package label provided by the manufacturers.

For the category of DD, only *d*-limonene was quantified in the four testing samples. The highest mass concentration of  $299 \pm 14.4 \mu\text{g g}^{-1}$  was seen in DD#4 in which without any fragrance. *d*-Limonene had the lowest mass concentration of  $71.8 \pm 3.9 \mu\text{g g}^{-1}$  in DD#1, which contains fragrances of lemon and aloe. Our results, again, prove that no association was shown between the presence of fragrance and the BVOC mass concentrations.

The mass concentrations and compositions of BVOCs were quite different along the AF samples as well. The highest total quantified BVOCs concentration of  $26,880.4 \mu\text{g g}^{-1}$  was found in AF#3 which is >18 times higher than AF#1 and AF#2. *D*-Limonene was the most abundant BVOCs in AF#3 with a mean mass concentration of  $12,980.4 \pm 412.6 \mu\text{g g}^{-1}$ , contributing the highest of 48.3% to the total quantified BVOCs. However, *D*-limonene contributed only 7.8–36.6% in the other two samples. Linalool was the most abundant BVOC in AF#1 and AF#2, with a mean mass concentration of  $627.0 \pm 26.4 \mu\text{g g}^{-1}$  and  $1349.2 \pm 49.2 \mu\text{g g}^{-1}$ , respectively, contributing 63.3–91.0% to the total quantified BVOCs. Its contribution was only 34.1% in AF#3.  $\alpha$ -Terpineol was only seen in AF#2, with a mean of  $18.7 \pm 0.6 \mu\text{g g}^{-1}$ . More BVOCs including  $\alpha$ -pinene,

$\beta$ -pinene, myrcene, *p*-cymene, and  $\gamma$ -terpinene were found in AF#3. Both of the AF samples contain fragrance such as lemon and jasmine flower, but their presences do not show any obvious association with either the mass concentrations or composition profiles.

### 3.2. Comparison with literature data

The mass concentrations in the household products in Hong Kong were compared with those reported in U.S. products (Table 3). Our unit has been converted to microgram of BVOC per milliliter of household sample for the comparison purpose. The density of each sample was measured from its weight over volume at the standard environment. On average, the mass concentrations of BVOCs in U.S. household products were at least one magnitude higher than those in our test samples, except myrcene and linalool. *D*-Limonene was the most abundant BVOC in the Hong Kong samples but it was still >30% lower than the mean values of 14.7 and 17.0 mg mL<sup>-1</sup>, respectively, in the U.S. cleaning products and air fresheners (Singer et al., 2006).  $\alpha$ -Terpineol was the most abundant BVOC in the U.S. cleaning products but none was found in air fresheners. In contrast, linalool was the most abundant BVOC in the U.S. air fresheners but was undetectable in the cleaning products. Such differentiation could not be seen in the Hong Kong samples in which both  $\alpha$ -terpineol and linalool co-existed. It is also noted that a wider variety of BVOCs was seen in the air fresheners in Hong Kong, compared to only limonene and  $\alpha$ -terpineol were found in the U.S. products. The comparisons demonstrate large deviations in the chemical compositions of the household products manufactured in the countries.

As a majority of cosmetic products and household products are scented, an exposure to fragrance chemicals is immense in the population. Even though major constituents of terpenes (e.g., 3-carene, *D*-limonene,  $\alpha$ -pinene, and  $\alpha$ -terpineol) emitted from Nordic soft woods can probably be ruled out as cause of acute eye irritation indoors (Molhave et al., 2000), products generated from the oxidation of fragrance terpenes contributes greatly to fragrance allergy (Matura et al., 2005). Karlberg and Dooms-Goossens (1997) also found that the exposure to *D*-limonene containing allergenic oxidation products might result in contact sensitization and dermatitis. Table 3 displays the second-order rate constants for the reactions between the quantified BVOCs and hydroxyl radical ( $\cdot\text{OH}$ ) at 298 K. In contrast to the rate constants for the reactions with ozone, those for the reactions with  $\cdot\text{OH}$  span a relatively narrow

**Table 3**  
Rate constants of BVOCs with ozone and OH radical, and comparison of BVOCs compositions in cleaning products and air fresheners with literature.

	Reaction with OH radicals	Reaction with Ozone	This study (mg mL <sup>-1</sup> )		Singer et al., 2006 <sup>b</sup> (mg mL <sup>-1</sup> )	
	$10^{12} \times k$ (298 K) (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$10^{17} \times k$ (298 K) (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	Cleaning products	Air fresheners	Cleaning products	Air fresheners
$\alpha$ -Pinene	52.3 <sup>a</sup>	8.4 <sup>a</sup>	ND	0.239	1.1	No data
$\beta$ -Pinene	74.3 <sup>a</sup>	1.5 <sup>a</sup>	0.011	1.25	0.13	No data
Myrcene	215 <sup>a</sup>	47(296 K) <sup>a</sup>	0.21	0.91	No data	No data
<i>p</i> -Cymene	15.1 <sup>c</sup>	<0.005 <sup>d</sup>	0.007–0.14	1.45	1.9	No data
<i>D</i> -Limonene	164 <sup>a</sup>	21 <sup>a</sup>	0.019–1.2	0.035–11.81	14.7	17
Eucalyptol	11.1 <sup>c</sup>	<0.015 <sup>d</sup>	0.015–0.202	ND	4.1	No data
$\gamma$ -Terpinene	177 <sup>a</sup>	14 <sup>a</sup>	ND	0.45	1.8	No data
Terpinolene	225 <sup>a</sup>	190 <sup>a</sup>	0.1	ND	23	No data
Linalool	159 <sup>e</sup>	43 <sup>e</sup>	0.20–2.22	0.61–8.34	No data	65
$\alpha$ -Terpineol	190 <sup>f</sup>	30 <sup>f</sup>	0.008–0.204	0.018	67	No data

<sup>a</sup> (Atkinson and Arey, 2003)

<sup>b</sup> (Nazaroff and Weschler, 2004)

<sup>c</sup> (Corchnoy and Atkinson, 1990)

<sup>d</sup> (Atkinson et al., 1990)

<sup>e</sup> (Wells, 2005)

<sup>f</sup> (Atkinson et al., 1995).

range, approximately an order of magnitude. The reaction rate constants for terpinolene, myrcene, linalool,  $\alpha$ -limonene and  $\alpha$ -terpineol with ozone are in descending order. For a gas-phase reaction between ozone and any BVOC emitted from the household products, it must occur at a rate competitive with air exchange, ventilation, or other removal processes (Nazaroff and Weschler, 2004; Weschler and Shields, 2000). As a result, the rate constant plays an important role on the resulting products and associated adverse health impact. Additionally, a large variety in BVOCs composition profiles may result in complex health effects because each of them possesses different paths and rates in the reactions between ozone and  $\cdot\text{OH}$ . The discussion on potential formation of secondary pollutants associated with the consumption of cleaning products and air fresheners was present in the following part.

### 3.3. Estimation of indoor BVOC emissions in Hong Kong

Hong Kong is a famous densely-populated city where >70% people live in a small apartment with a building area <70 m<sup>2</sup> (Li et al., 2006). Due to limited landscape, tall commercial and residential buildings are closely developed that blocks natural winds and leads to inefficient air exchanges from indoor to outdoor environments. Any indoor residential emission sources such as use of household chemicals would thus greatly affect the indoor air quality (IAQ) in Hong Kong. The median air exchange rate (AER) in residences in three urban U.S. metropolitan areas was 0.71 h<sup>-1</sup> (Yamamoto et al., 1999–2001), while that in 390 Swedish homes were <0.5 h<sup>-1</sup> (Bornehag et al., 2005). Because there was no report on the residential AER in Hong Kong, an AER of 0.5 h<sup>-1</sup> is thus assumed in this study. BVOCs concentrations in Hong Kong residential homes caused by the consumption of cleaning products and air fresheners were estimated. According to the assumptions made by Habib et al. (2006) and Nazaroff (2004), the daily consumptions (R, in the unit of gram per day) of FC, KC, DD, and AF are 50, 10, 10 and 15 g day<sup>-1</sup>, respectively, in one household unit. We here assume that there is no significant variation in the consumption rates between the countries. The daily emission amount of an individual BVOC ( $W_i$ , in the unit of microgram) from one category of household product (i) is calculated as:

$$W_i = C_i \times R_i \quad (1)$$

where  $C_i$  (in unit of  $\mu\text{g g}^{-1}$ ) is the mean concentration of an individual BVOC component in one category of the household products as determined in this study. The daily emission amount of BVOCs from all consumed household products can be thus calculated as:

$$W = W_{\text{FC}} + W_{\text{KC}} + W_{\text{DD}} + W_{\text{AF}} \quad (2)$$

The size of the apartment is also assumed with an area of 70 m<sup>2</sup> and 2.8 m in height (the total volume is 196 m<sup>3</sup>). Based on these assumptions and the mass concentrations measured from the testing samples, the corresponding daily BVOCs emissions from the consumption of cleaning products and air fresheners in a local family were estimated. As indicated in Fig. 1, the highest BVOCs concentration in residential homes is caused by the floor cleaner usage (204.0  $\mu\text{g m}^{-3}$ ), followed by air fresheners (166.4  $\mu\text{g m}^{-3}$ ), kitchen cleaners (21.9  $\mu\text{g m}^{-3}$ ) and dishwashing detergents (6.2  $\mu\text{g m}^{-3}$ ). The ratio of BVOCs amount caused by the consumption of floor cleaners to the total amount caused by the usage of these four categories household products weighted about 51%, followed by air fresheners 42%, kitchen cleaners 5% and dishwashing detergents 2%. The combined product of indoor BVOC concentrations ( $C_i$ ) and their reaction rates with ozone ( $k_i$ ) (as shown in Table 3), namely  $\sum C_i k_i$ , was used to predict the potential on secondary pollutants formation (Destailats et al., 2006). The product varied in the order

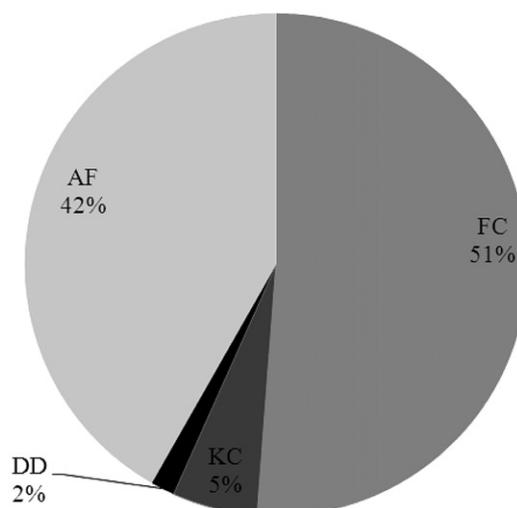
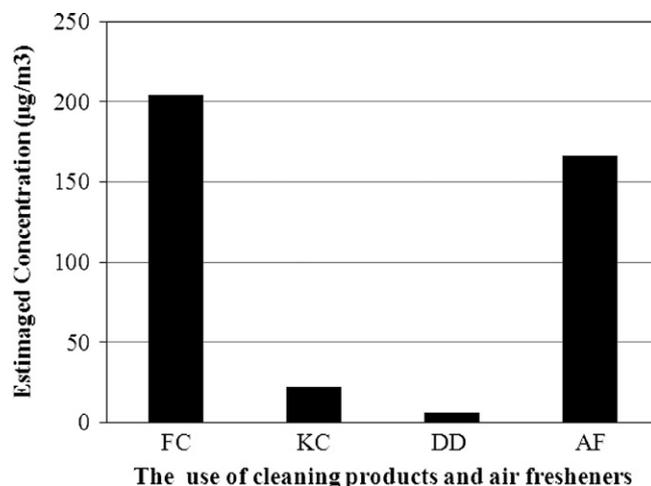


Fig. 1. The estimated mass concentrations (a) and fractions (b) of BVOCs caused by the consumption of cleaning products and air fresheners in residential homes in Hong Kong.

AF > FC > KC > DD, suggesting the consumption of air fresheners pose high risks on secondary pollutants formation indoors.

## 4. Conclusion

In this study, the characteristics of BVOCs composition in three categories of general purpose cleaning products including floor cleaners (FL), kitchen cleaners (KC) and dishwashing detergents (DD), and also air fresheners (AF) were examined by SPME-GC/MS method. The chemical composition and concentrations of individual BVOCs varied broadly with household products due to their different functions and scents. The consumption of floor cleaners was estimated to contribute most to total indoor BVOCs in Hong Kong. Secondary products formation potential associated with the use of these household products varied in the order AF > FC > KC > DD in the presence of ozone. The findings obtained in this study can significantly enhance our understanding on indoor levels of BVOCs associated with the consumption of household products. The experimental results can also assist residents to improve indoor air quality (IAQ) by means of reducing usage or choosing appropriate household cleaning products.

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