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

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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 μg $g^{-1}$, followed by FC2 of 264.6 μg $g^{-1}$, FC4 of 249.3 μg $g^{-1}$ and FC3 of 139.2 μg $g^{-1}$. D-limonene was the most abundant detected BVOCs in KC samples with the chemical composition varying from 19.6 ± 1.0 to 1513.0 ± 37.1 μg $g^{-1}$. 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%.



## 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, α-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

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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 (Destaillats 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 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.

**Table 1**
General information of studied cleaning products and air fresheners.

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

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

### 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 $min^{-1}$ to 95 °C and 10 °C $min^{-1}$ to 130 °C and 55 °C $min^{-1}$ 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