Impact of essential-oil-based cleaning products on indoor air quality: From liquid composition to test emission chamber

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Abstract. As society has become aware of health hazards related to the exposure to chemicals, major efforts have been made to address indoor air current problematic. Consequently, popularity of “green” cleaning products has upsurge. These products are formulated with essential-oils relying on their anti-bacterial properties to improve indoor air quality. Indeed, essential oils might contain a hundred of odorous molecules, mainly terpenes and terpenoids (TerVOCs) which acts as antibacterial agents. Nonetheless, do essential-oil-based products really contribute to indoor air quality improvement? This study is addressed to evaluate emissions from the use of essential-oils-based cleaning products by various scale experiments. Firstly, a correlation of liquid composition from 7 natural cleaning products with their emission potentials has been investigated. Volatile fractions are evaluated by using micro-chamber testing. A total of 28 terpenes are quantified among products in the liquid form. Nevertheless, only 22 species are detected in gas samples with a yield ranking from 9.1 \% to 99.8 \%. Results do not verified a direct correlation between liquid mass and emitted concentrations of terpenes. Indeed, chemical affinities between terpenes and solvent matrix in product formulation are evidenced. Then, 4 products from different cleaning purposes have been selected for emission evaluation in a test chamber of 1-m\textsuperscript{3}. Product application process are correlated to real case scenario regarding applied quantity and loading factor. Emitted terpenes and carbonyl compounds are quantified by off-line and on-line chromatography measurements. Results evidenced that peak concentrations from terpenes reached up to 1.5 h after cleaning activity. Major compound emitted concentration range from 121 to 152 µg/m\textsuperscript{3}, in the test chamber, for different product categories. Specific emission dynamic is evidenced for formaldehyde, in where continuous increasing concentration is revealed due to the presence of formaldehyde releasers. This study contributes to further assessment of exposure hazards related to cleaning activities.

1. Introduction

Major efforts have been made to assess indoor air current problematic since the daily activities of society are mostly developed in confined environments. [1], [2] As society has become aware of health hazard related to the exposure to chemicals, and notably concerned by the indoor air quality (ref 1-2), new habits aiming at decreasing the use of hazardous substances from industrial cleaning products tend to promote a “natural” housekeeping. Consequently, the popularity of “green” and “natural” scented household products has upsurge. These products are formulated with essential oils as natural fragrances, relying on their antibacterial properties in order to sanitize indoor air. Essential oils are known as a group of odorous or fragrant chemicals extracted from plants that might contain a hundred of molecules, mainly terpenes and terpenoids (TerVOCs). These molecules might indeed act as microbiological inhibitors. [3]–[8] Therefore, products containing essential oils take advantages from their so-called “natural” or ”green” formulations to promote an increase of indoor air quality by purifying and reducing synthetic chemical emissions. Do essential-oil-based household products effectively promote indoor air quality?
The composition of emissions from household products has been associated with health hazards for indoor occupants. [9]–[13] Nevertheless, limited information is available about composition and emissions associated to housekeeping activities in confined environments. The available scientific data are for most cases incomparable due to the wide variety in evaluation protocols. [14]–[18] This work is developed in the frame of the ESSENTIEL project, aiming at characterizing the impact of essential-oils-based products on indoor air quality through the investigation of their realistic emissions and indoor fate. Furthermore, the objective of this work is firstly, to evaluate the correlation between the fragrance chemicals present in cleaning products and their volatile fraction; secondly, to characterize and assess their emissions in a 1-m³ test chamber by conceiving a realistic application patterns from a real size room.

2. Materials and methods

2.1 Product Selection

A benchmark analysis was performed regarding European certified ecological cleaning products. A total of 108 essential-oils-based products were identified. Among them, 8 representative cleaning products were selected in the framework of the project ESSENTIEL. This selection has been done by considering (i) the diverse use purpose in order to assess the effect of different solvent formulations and (ii) the variety of application modes. Therefore, evaluated products are: (i) 2 kitchen degreasers, (ii) 2 general cleaners, (iii) 2 surface cleaners, (iv) 1 glass/window cleaner, and (v) 1 floor cleaner. In this work only 1 liquid surface cleaner fragranced with citrus oils is discussed.

2.2 Characterization of the liquid composition

For the evaluation of the terpene content in the citrus-oil-based surface cleaner, three consecutive liquid organic extractions were performed. Recovery tests revealed that close to 100 % of yield was found concerning the extraction of terpenes. Consecutively, samples were analyzed for identification and quantification using GC- FID/MS by direct liquid injection.

2.3 Determination of the volatile fraction using the µ-chamber

A total volume of 50 µl of the citrus-fragranced cleaner was introduced into a µ-chamber of 40 ml volume (M- CTE-250, Markers International®). Several experimental conditions were optimized, then temperature and air flow were set at 40°C and 50 ml/min, respectively. Furthermore, micro-chamber gas phase concentration and mass concentration allowed the evaluation of the liquid/gas transfer yield for each terpene, thus their volatile fraction.

2.4 Evaluation of terpene emissions: 1 m³ experimental chamber

Emissions from selected cleaning agent were evaluated in a stainless steel test chamber with a volume of 1-m³ (Vötsch VCE1000 Classic). Tests were conducted under controlled relative humidity, temperature and air exchange rate of 50 %, 23°C, and 0.3 h-1, respectively. Moreover, the product application procedure aimed at simulating a realistic scenario: the application parameters, namely the quantity of product applied and the cleaned surface were sized based on a real scale scenario selected as reference. The product was applied on a stainless steel surface, according to product application instructions and simulating the wiping process. Table 1 details the parameters of the selected reference room and the 1-m3 chamber.

| Table 1. Correlation for application patterns: from a real room to a test chamber |
|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Loading (Cleaned surface / Chamber volume)      | Real size room (40 m³)                          | Test chamber (1-m³)                             |
| Determined product yield (From wiping lost)     | 0.05 m²/m³                                      | 0.37 m²/m³                                     |
|                                                | 12 g per cleaned m²                            |                                                 |
Surface ($S = L \times V$)  
|          | 2.00 m$^2$ | 0.37 m$^2$ |
|----------|------------|------------|
| Correlated mass of product (Table surface: 2 m$^2$) | 24.00 g | 4.44 g | (Considering product yield) |

Regarding analytical methods, emissions of TerVOCs were sampled on Tenax-TA and analyzed using TD/GC- FID/MS according to ISO-16000-6. Additionally, carbonyl compounds were derivatized on DNPH cartridges and analyzed using HPLC according to ISO-16000-3.

3. Results and discussion

3.1 Liquid composition vs. Volatile fraction

Only the presence of citral and limonene in the liquid format was indicated by the manufacturer; however a diversity of 11 terpenes was detected in the composition of this product. The major TerVOCs detected were limonene, eucalyptol, ρ-cymene, and β-pinene. Concerning the volatile fraction of the tested product, only 6 terpenes were identified in the gas phase. Nevertheless, the major emitted compounds correspond to the major species reported in the liquid phase. Moreover, Table 2 presents the ratio of the relative abundances between liquid phase and volatile fraction.

**Table 2. Correlation between liquid mass composition and volatile fraction**

| Major Terpenes | Ratio- Volatile fraction / Mass fraction | VP (Pa) | [Reference] |
|----------------|----------------------------------------|---------|-------------|
| Limonene       | 1.15                                   | 202     | [19]        |
| Eucalyptol     | 1.26                                   | 254     | [20]        |
| Cymene         | 0.58                                   | 192     | [21]        |

According to Table 2, eucalyptol has the highest ratio between its volatile fraction and liquid mass content. This observation is in agreement with the fact that eucalyptol has the highest vapor pressure compared to other terpenes. On the contrary, other terpenes, such as cymene, are known for their lower volatility, and accordingly characterized by a ratio lower than 1. It is expected that the transfer of these molecules to the gas phase might be limited under realistic conditions. Finally, µ-chamber tests allowed the screening of major emitted compounds transferred to the gas phase. Nonetheless, it is important to associate these results to a realistic emission evaluation for a complete assessment of the impact of the cleaning products on indoor air quality.

3.2 Emission dynamics and concentration: test chamber results

Emission kinetics were evaluated for terpenes and carbonyl compounds over 3.5 h after the cleaning activity is completed. Figure 1 presents the concentration profiles of formaldehyde and the four major terpenes identified. Concerning the diversity of the species emitted, a total of 7 out of the 22 terpenes contained in the product were identified in the gas phase. Regarding the major emitted terpenes, limonene and eucalyptol reached a peak concentration of 144 ppb and 138 ppb, respectively 0.63 h and 0.38 h after application. Other detected terpenes at lower concentrations, nearly 20 ppb, were cymene and α-pinene. Generally, the maximum emitted concentration of total TerVOCs reached ca. 300 ppb within the first half-hour after application.

Concerning formaldehyde, the emission profile evidenced a specific behavior. Despite that formaldehyde concentrations remained below 20 ppb, its concentration profile is characterized by a continuous increase till 3.5 h, while TerVOCs were depleted by 75% of their maximum concentration. This behavior is suggested to be attributed the presence of various formaldehyde releasers in the cleaning product. These compounds are used in industrial formulations as biocide and conservatives, being Bronopol the...
main formaldehyde releaser used in toiletries [22], [23]. Likewise, Solar et al. [15] verified a linear increase of formaldehyde concentration several hours after the application of different cleaning products such as a toilet cleaner. Consequently, this specific dynamic of formaldehyde emission might extend the impact indoor air quality several hours after the cleaning activity is completed.

In comparison with other indoor sources of terpenes, Harb et al. [24] evaluated the emission from a wood based construction material. Author verified that the total peak concentration of TerVOCs detected under real conditions reached values ca. 80 ppb. In agreement with this study, S.K. Brown [25] identified similar emitted concentrations from a 16-mm pine softwood particleboard. As a consequence, cleaning activities can contribute to indoor concentrations of TerVOCs more than wood-based materials. Nevertheless, it is important to highlight that emissions of cleaning products are characterized by different dynamics compared to indoor material emissions. Actually, they mostly act as punctual or transient sources of pollutants, thus long-term exposure is directly related with cleaning occurrence and human factor, while sources constituted by wood-based material mostly act as long term and continuous emission sources.

In a controlled environment, emission rates are calculated through the mass conservation equation, in where reactivity and outside influence are considered as negligible. Therefore, the concentration decay is supposed to be mainly contributed by the natural decay, i.e. the air renewal and possible but minor sink effect on the chamber walls. Figure 2 reports a comparison between mass fraction composition, volatile fraction and mass emission rate abundance 15 min after application (ppb. h\(^{-1}\).g\(^{-1}\)). Focusing on the emission rate values regarding eucalyptol and limonene, they are equally emitted under realistic conditions. Nevertheless, their contribution in liquid composition were noticeably contrasted. This observation was expected due to the fact that eucalyptol is the compound presenting the highest vapor pressure, and considering data from volatile fraction assessment. In the case of limonene, the high contribution to the volatile fraction is related to the temperature increment forcing the emission of compound with relative lower vapor pressure. Similar behavior was observed for cymene evidencing that evidenced that the direct transfer from the liquid phase to the gas phase is mainly driven by (i) the mass content in the cleaning agent and (ii) the physical and chemical properties of involved species. However, different formulation from other household product categories might present a particular solvent matrix that might have a direct effect in the emitted concentrations. [26]
4. Conclusions and Perspectives
This work has evidenced that the largest contributors of terpenes to indoor air are not only recognized, regulated and controlled sources, namely building materials. Household products have to be seriously envisaged as versatile and high impact sources. Sources of fragrance chemicals, these molecules are classified as allergens responsible to skin irritations, allergic rhinitis, and asthma \[27\], are primarily associated to the use of cleaning products, air fresheners and purifiers. These products might release concentration levels of several tens to hundreds of micrograms per cubic meter of TerVOCs, exceeding exposure limits established by the European Union and the United States.

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References
[1] S. K. Brown, M. R. Sim, M. J. Abramson, et C. N. Gray, « Concentrations of Volatile Organic Compounds in Indoor Air – A Review », *Indoor Air*, vol. 4, n° 2, p. 123–134, 1994.
[2] J. Namieśnik, T. Gorecki, B. Kozdroń-Zabiegała, et J. Łukasiak, « Indoor air quality (IAQ), pollutants, their sources and concentration levels », *Build. Environ.*, vol. 27, n° 3, p. 339-356, juill. 1992.
[3] B. Teixeira et al., « Chemical composition and antibacterial and antioxidant properties of commercial essential oils », *Ind. Crops Prod.*, vol. 43, p. 587-595, mai 2013.
[4] L. Harkat-Madouri et al., « Chemical composition, antibacterial and antioxidant activities of essential oil of Eucalyptus globulus from Algeria », *Ind. Crops Prod.*, vol. 78, p. 148-153, déc. 2015.
[5] A. Luis, A. Duarte, J. Gominho, F. Domingues, et A. P. Duarte, « Chemical composition, antioxidant, antibacterial and anti-quorum sensing activities of Eucalyptus globulus and Eucalyptus radiata essential oils », *Ind. Crops Prod.*, vol. 79, p. 274-282, janv. 2016.
[6] J. Guo, Z. Gao, J. Xia, M. A. Ritenour, G. Li, et Y. Shan, « Comparative analysis of chemical composition, antimicrobial and antioxidant activity of citrus essential oils from the main cultivated varieties in China », *LWT*, août 2018.
7] K. G. D. Babu, B. Singh, V. P. Joshi, et V. Singh, « Essential oil composition of Damask rose (Rosa damascena Mill.) distilled under different pressures and temperatures », Flavour Fragr. J., vol. 17, n° 2, p. 136-140, mars 2002.

[8] Z. Bey-Ould Si Said et al., « Essential oils composition, antibacterial and antioxidant activities of hydrodistilled extract of Eucalyptus globulus fruits », Ind. Crops Prod., vol. 89, p. 167-175, oct. 2016.

[9] M. Trantallidi, C. Dimitroulopoulou, P. Wolkoff, S. Kephalopoulos, et P. Carrer, « EPHECT III: Health risk assessment of exposure to household consumer products », Sci. Total Environ., vol. 536, p. 903-913, déc. 2015.

[10] A. Steinemann, « Fragranced consumer products: exposures and effects from emissions », Air Qual. Atmosphere Health, vol. 9, n° 8, p. 861-866, déc. 2016.

[11] P. Wolkoff, T. Schneider, J. Kildeso, R. Degerth, M. Jaroszewski, et H. Schunk, « Risk in cleaning: chemical and physical exposure », Sci. Total Environ., vol. 215, n° 1-2, p. 135-156, avr. 1998.

[12] W. W. Nazaroff et C. J. Weschler, « Cleaning products and air fresheners: exposure to primary and secondary air pollutants », Atmos. Environ., vol. 38, n° 18, p. 2841-2865, juin 2004.

[13] C. Dimitroulopoulou, M. Trantallidi, P. Carrer, G. C. Efthimiou, et J. G. Bartzis, « EPHECT II: Exposure assessment to household consumer products », Sci. Total Environ., vol. 536, p. 890-902, déc. 2015.

[14] E. Chesnais et M. Marchais, « Sprays assainissants et désodorisants - Notre intérieur dégradé », vol. 530, 11/2014, p. 50-53, nov. 2014.

[15] C. Solal, C. Rousselle, C. Mandin, J. Manel, et F. Maupetit, « VOC’s and formaldehyde emissions from cleaning products and air freshener », Int. Conf. Indoor Qual. Clim., vol. 11, avr. 2014.

[16] E. Uhde et N. Schulz, « Impact of room fragrance products on indoor air quality », Atmos. Environ., vol. 106, p. 492-502, avr. 2015.

[17] K.-D. Kwon, W.-K. Jo, H.-J. Lim, et W.-S. Jeong, « Volatile pollutants emitted from selected liquid household products », Environ. Sci. Pollut. Res., vol. 15, n° 6, p. 521-526, 2008.

[18] J. Bartzis et al., « On organic emissions testing from indoor consumer products’ use », J. Hazard. Mater., vol. 285, p. 37-45, mars 2015.

[19] J. Li, E. M. Perdue, S. G. Pavlostathis, et R. Araujo, « Physicochemical properties of selected monoterpenes », Environ. Int., vol. 24, n° 3, p. 353-358, avr. 1998.

[20] V. Štejfa, M. Fulem, K. Růžička, et C. Červinka, « Thermodynamic study of selected monoterpenes III », J. Chem. Thermodyn., vol. 79, n° Supplement C, p. 280-289, déc. 2014.

[21] M. Hoskovec et al., « Determining the vapour pressures of plant volatiles from gas chromatographic retention data », J. Chromatogr. A, vol. 1083, n° 1, p. 161-172, août 2005.

[22] A. C. De Groot, M.-A. Flyvholm, G. Lensen, T. Menné, et P.-J. Coenraads, « Formaldehyde-releasers: relationship to formaldehyde contact allergy. Contact allergy to formaldehyde and inventory of formaldehyde-releasers », Contact Dermatitis, vol. 61, n° 2, p. 63-85, août 2009.

[23] K. Kajimura, T. Tagami, T. Yamamoto, et S. Iwagami, « The Release of Formaldehyde upon Decomposition of 2-Bromo-2-nitropropan-1, 3-diol (Bronopol) », J. Health Sci., vol. 54, n° 4, p. 488-492, 2008.

[24] P. Harb, N. Locoge, et F. Thevenet, « Emissions and treatment of VOCs emitted from wood-based construction materials: Impact on indoor air quality », Chem. Eng. J., vol. 354, p. 641-652, déc. 2018.

[25] S. K. Brown, « Chamber Assessment of Formaldehyde and VOC Emissions from Wood-Based Panels », Indoor Air, vol. 9, n° 3, p. 209-215, avr. 2004.

[26] K.-D. Kwon et W.-K. Jo, « Indoor Emission Characteristics of Liquid Household Products using Purge-and-Trap Method », Environ. Eng. Res., vol. 12, n° 5, p. 203-210, déc. 2007.

[27] P. Wolkoff et G. D. Nielsen, « Effects by inhalation of abundant fragrances in indoor air – An overview », Environ. Int., vol. 101, p. 96-107, avr. 2017.