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1 **Indoor use of essential oil-based cleaning products: Emission rate**  
2 **and indoor air quality impact assessment based on a realistic**  
3 **application methodology**

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22

23 **ABSTRACT**

24 Cleaning is performed to increase hygiene, esthetics and material preservation. Despite its  
25 benefits, cleaning also poses risks, potentially contributing to nearly 20 % of indoor pollution. As  
26 indoor air quality has become a major human health concern, “natural-scented” cleaning  
27 products, formulated with essential oils, have become market leaders among household products.  
28 However, these consumer products have benefitted from skillful marketing strategies based on  
29 the ambiguity of the words “green” and “natural”. The characterization of the emission processes  
30 studied through 1-m<sup>3</sup> chamber experiments under a realistic scenario suggests variable maximum  
31 total terpene concentrations from 150 to 300 ppb. The estimated emission rate profiles confirm  
32 that the liquid-to-gas transfer of terpenes is driven by (i) the formulation of the product matrix  
33 inducing specific chemical affinities, (ii) the liquid content of individual terpenes, and (iii) the  
34 intrinsic volatility of terpenes. A unique formaldehyde emission kinetics profile was observed,  
35 suggesting the presence of a unique emission source: formaldehyde-releasers. Consequently, the  
36 use of essential-oil-based cleaning products might generate a long-term increase in the indoor  
37 formaldehyde concentration, and the maximum levels might be sustained for several hours after  
38 cleaning. Thus, essential-oil-based cleaners should be seriously considered as versatile and  
39 significant sources of fragrance molecules and formaldehyde.

40

41 **KEYWORDS:** cleaning products; emission rates; indoor air quality; terpenes

42

43 **ABBREVIATIONS:** **TerVOCs** Terpenic volatile organic compounds; **AER** Air exchange rate;  
44 **OVOCs** Oxygenated volatile organic compounds; **VP** Vapor pressure; **PROBAS** Danish  
45 Product Register Database; **BNPC** National Database for Products and Compositions

46

## 47 1 INTRODUCTION

48 Major efforts have been focused on addressing indoor air problems since daily activities  
49 mostly occur in confined environments. Indoors, people are exposed to a wide variety of  
50 chemical, biological and physical pollutants that (i) infiltrate from outdoor air, (ii) are released  
51 from building materials and furnishing, and (iii) are generated by occupants and their indoor  
52 activities (Missia et al., 2012; Weschler, 2001). The scientific community has focused on  
53 chemical pollutants, principally volatile organic compounds (VOCs), defined as organic  
54 molecules with boiling points ranging from 50 to 100 °C on the low end and from 240 to 260 °C  
55 on the high end (Brown et al., 1994; World Health Organisation, 2010). Among indoor sources  
56 of pollutants, the main origins of chemical contaminants are linked to occupant activities, such as  
57 interior renovation or decoration, smoking, cooking, or housekeeping (Kirchner et al., 2001).

58 Among the thousands of cleaning products available and marketed, people are tempted to  
59 use scented products because a pleasant odor is associated with a cleaner environment.  
60 Therefore, despite all the benefits of cleaning activities, such as increased hygiene, esthetics, and  
61 material preservation, the chemical and physical pollutant exposure risks posed by such activities  
62 remain unclear. Previous studies (Nazaroff and Weschler, 2004; Wolkoff et al., 1998) have  
63 shown that atmospheric VOC emissions per capita from general purpose cleaners and air  
64 fresheners contribute the most to indoor VOC pollution, with values ranging from 200 to 230 mg  
65 per day. The intake fraction is defined as the pollutant mass inhaled per unit of pollutant mass  
66 emitted (Lai et al., 2000). A typical intake fraction from indoor emissions is on the order of  $10^{-3}$   
67 and  $10^{-1}$ , while that from outdoor emissions is on the order of  $10^{-6}$  and  $10^{-3}$ . These data highlight  
68 the fact that the proportion of emissions inhaled is higher when emissions occur indoors rather  
69 than outdoors (Nazaroff and Weschler, 2004).

70 Unexpectedly, the largest indoor sources of terpene VOCs are not usually the recognized,  
71 regulated and controlled sources. Indeed, the composition of VOCs emitted from household  
72 products has been associated with health hazards to indoor occupants (Dimitroulopoulou et al.,  
73 2015; Nazaroff and Weschler, 2004; Steinemann, 2009, 2016; Trantallidi et al., 2015; Wolkoff et  
74 al., 1998). Nevertheless, limited information is available about the composition, quantification  
75 and emission dynamics associated with housekeeping activities in confined environments.  
76 Available scientific data are, in most cases, incomparable due to wide variations and  
77 heterogeneity in the experimental methodologies used for the evaluation of primary and  
78 secondary pollutant emissions from fragranced household products (Angulo et al., 2020). These  
79 variations are related to two key parameters: (i) the application protocol (quantity, mode of  
80 operation) and (ii) the test environment (air exchange rate (AER), temperature, chamber size, and  
81 relative humidity (RH)) (BEUC, 2005; Chesnais and Marchais, 2014; Colombo et al., 1991;  
82 Delmas et al., 2016; Höllbacher et al., 2017; Nicolas and Chiappini, 2013; Norgaard et al., 2014;  
83 Sarwar et al., 2004; Singer et al., 2006a, 2006b; Solal et al., 2014; Uhde and Schulz, 2015).  
84 Therefore, comparing the results from one investigation to those of another may be difficult and  
85 inaccurate.

86 Fragranced household products can be formulated with (i) synthetic fragrances, (ii) pure  
87 essential oils and (iii) mixtures of synthetic fragrances and essential oils to reduce production  
88 costs. Essential oils are used in “naturally” formulated cleaning products either to provide them  
89 with a pleasant odor, to hide odors from other chemicals in the formulation, or to enhance their  
90 antibacterial performance (Rastogi, 2002; Steinemann, 2009). Essential oils are extracted from  
91 plants by water vapor distillation, dry distillation or mechanical extraction, which does not  
92 involve temperature changes (Delmas et al., 2016). They usually contain more than 100 different

93 chemicals that compose their characteristic smell, and most of these chemicals are terpenes:  
94 monoterpenes, sesquiterpenes, terpene alcohols and terpenoids (denoted TerVOCs) (Babu et al.,  
95 2002; Lassen et al., 2008; Zuzarte and Salgueiro, 2015). The characteristic smell of an essential  
96 oil often originates from its major chemical components; therefore, the typical “scent” of an  
97 essential oil directly depends on its chemical composition. In contrast, fragrance mixtures  
98 combine differently sourced compounds (synthetic, natural-like or extracted) to replicate a  
99 “natural” scent (Teixeira et al., 2013; Zuzarte and Salgueiro, 2015).

100           Although diverse sanitation benefits of essential oil-based cleaning products have been  
101 recognized, several risks associated with their use in indoor environments are still questioned. *Is*  
102 *there a potential exposure risk to consumers posed by TerVOCs emitted from household*  
103 *products?*

104           This study is developed within the framework of the ESSENTIEL research project,  
105 aiming to characterize the impact of essential oil-based products on indoor air quality (IAQ)  
106 through investigation of their realistic emissions and indoor fate. The objectives of this  
107 investigation are to evaluate the correlation between the fragrance chemicals contained in  
108 cleaning products and their volatile fraction through determination of the gas-transferred  
109 concentration by micro-chamber testing and to characterize and assess their emissions in a 1 m<sup>3</sup>  
110 experimental chamber reflecting a realistic application scenario. The proposed experimental  
111 approach and the results provided in this study are required (i) to propose harmonized and  
112 realistic test protocols and (ii) to define risk scenarios and evaluate the human exposure to  
113 TerVOCs associated with the use of essential oil-based cleaning products.

114

115

116

## 117 **2 MATERIAL AND METHODS**

### 118 ***2.1 Cleaning product benchmarking***

119           To frame the approach of the present study, it is necessary to define the type of cleaning  
120 products considered. Essential oil-based cleaning products are defined in this work as naturally  
121 scented and certified organic products used in a nonpermanent way in indoor environments for  
122 housekeeping purposes. For their selection, a benchmark analysis was performed among cleaners  
123 certified as *ecological products* by different European labels. A total of 108 essential oil-based  
124 products were identified from the European market. Among them, 6 representative cleaning  
125 products were selected in the framework of this work and classified by category, i.e., intended  
126 use: (i) 2 kitchen degreasers, (ii) 2 general (multiuse) cleaners, (iii) 1 surface cleaner, and (iv) 1  
127 glass cleaner. This selection considered (i) diverse intended uses to assess the effect of different  
128 solvent formulations, (ii) a variety of application modes and (iii) a diversity of essential oils used  
129 as natural fragrances in the formulation of the cleaning products. The selected cleaning products  
130 were purchased from environmentally friendly and ecologically conscious retail stores in France.

131           Importantly, the solvent matrix composition could vary from one product to another in  
132 terms of the organic content (% ethanol) or the presence of texturing agents (gums). The contents  
133 of the fragrance chemicals and their volatile fractions were characterized for the six selected  
134 cleaning products, whereas only three products were considered for the 1 m<sup>3</sup> emission test. Table  
135 1 details the characteristics of the six selected products.

136

137 **Table 1.** Specifications of the selected cleaning products.

Product	Product category	Diffusion mode	Natural fragrance <sup>1</sup>	General product formulation <sup>2</sup>	Characterization performed		
					Liquid composition	Volatile fraction (micro-chamber)	Realistic emissions (1 m <sup>3</sup> test chamber)
KC – 1	Kitchen cleaner	Trigger spray	Lemon oil	< 5 % surfactant (anionic and nonanionic), citrus oil, citric acid, water, methylisothiazolone, 5-chloro-2-methyl-4-isothiazolin-3-one, nitrilotriacetic acid trisodium salt monohydrate	x	x	
KC – 2			Eucalyptus oil	< 5 % surfactant (nonanionic), essential oils (including eucalyptus oil <sup>2</sup> ), water, alcohol <sup>2</sup> , preservatives, acid correctors	x	x	x
MC – 1	Multiuse cleaner	Liquid	Citrus oil	< 5 % surfactant (anionic and nonanionic), water, alcohol, citrus oil <sup>2</sup> , citric acid	x	x	x
MC – 2			Lemon oil	< 5 % surfactant (anionic and nonanionic), water, alcohol, lemon oil <sup>2</sup> , lactic acid, fatty acids, sodium citrate, glyceryl caprylate	x	x	
SC – 1	Surface cleaner	Trigger spray	Lavender oil	70 % ethanol <sup>2</sup> , < 1 % lavender oil <sup>2</sup> , < 1 % sage oil <sup>2</sup> , water	x	x	x
GC – 1	Glass cleaner	Trigger spray	Eucalyptus oil	> 30 % water, 5 – 15 % alcohol <sup>2</sup> , < 5 % surfactant (anionic and nonanionic), citric acid, essential oils <sup>2</sup> (including eucalyptus oil), amphoteric surfactants	x	x	

138 *1: Certified organically grown*

139 *2: Based on information given by the manufacturer*

140



141 **2.2 Characterization of the liquid composition**

142 Several extraction parameters were optimized to maximize the extraction of terpenes: (i)  
143 the organic extraction solvent, (ii) the mass ratio of the cleaning product to the solvent, (iii) the  
144 contact time between the solvent and the cleaning product, and (iv) the number of consecutive  
145 extractions. The extraction procedure and the analytical methods and parameters are detailed in a  
146 supplementary information file (SI file).

147

148 **2.3 Determination of the gas-transferred concentration by micro-chamber testing**

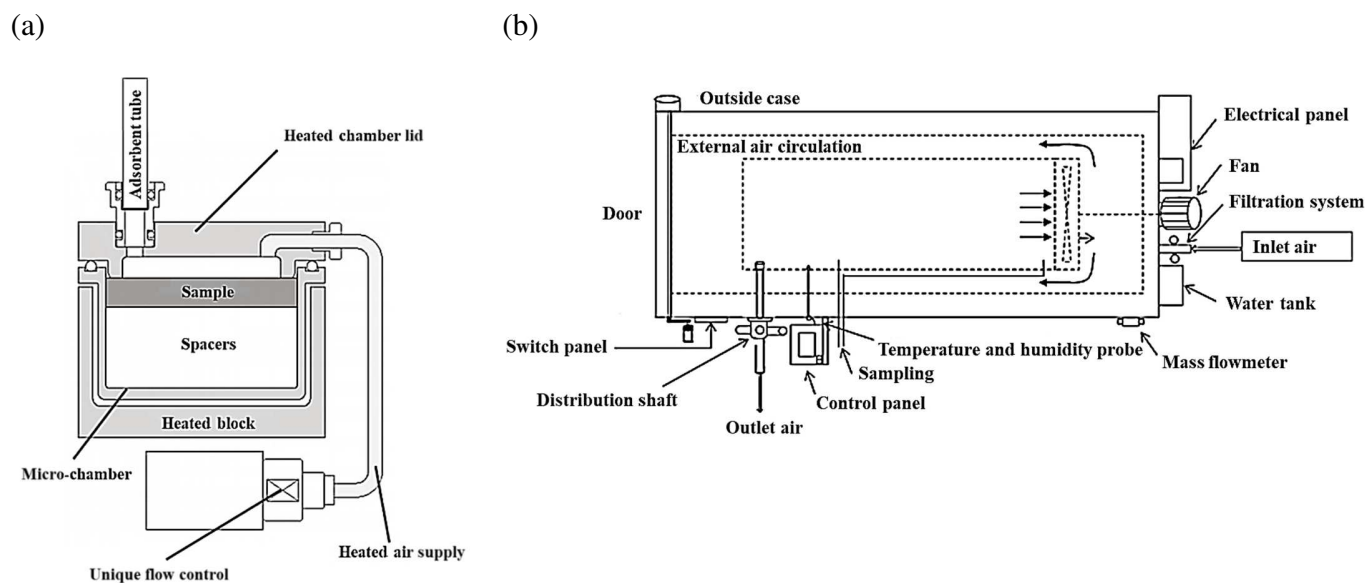
149

150 **2.3.1 Micro-chamber description**

151 The liquid-to-gas phase transfer capacity of each terpene identified in the cleaning products is  
152 defined as the gas-transferred concentration and was determined by using a stainless steel  
153 cylindrical micro-chamber with a 44 mL volume (M-CTE-120 Markes International®). The  
154 device was equipped with restrictors allowing the selection of a low-flow range and a high-flow  
155 range of 10 – 70 mL/min and 50 – 500 mL/min, respectively. In this work, the low-flow range  
156 was used and set at 50 mL/min. The dry air generation is ensured by an air compressor combined  
157 with membrane for humidity removal. Before entering the micro chamber, the dry air is purified  
158 by an activated carbon filter in order to remove particles and trace pollutants. The top of the  
159 chamber acts as a door and is sealed with a silicon gasket for leak control. After optimization, the  
160 temperature and air flow were set at 40 °C and 50 mL/min, respectively. Dry air flow enters each  
161 micro-chamber through the lid and is preheated to the micro-chamber temperature of 40 °C. A  
162 total volume of  $50 \pm 1$   $\mu$ L of each selected fragranced cleaner was introduced into the micro-  
163 chamber. Blank measurements were performed to determine the background levels of VOCs in  
164 the chamber outlet before running each set of experiments. Note that the mean concentration of

165 blank measurements in the micro-chamber did not exceed the quantification limits for the  
166 background concentrations of the individual target VOCs. The detailed characteristics of the  
167 micro-chamber are presented in Fig. 1a.

168



169 **Fig. 1.** (a) Schematic of the M-CTE-120 micro-chamber from Markes International®. (b)  
170 Schematic of the 1 m<sup>3</sup> emission chamber VCE1000 Classic from Vötsch.

171

### 172 2.3.2 Analytical strategy

173 The TerVOCs emitted from the investigated products inside each micro-chamber were  
174 monitored using an off-line device for their identification and quantification. Subsequently, two  
175 consecutive Tenax TA® cartridges collected volatilized compounds at the device outlet for 15  
176 minutes. The total sampled volume was 0.6 L. Afterward, these samples were desorbed at 280 °C  
177 under a helium flow of 50 mL/min using a PerkinElmer® thermal desorber (model: Turbo Matrix  
178 350). Then, the desorbed compounds were thermally transferred via the helium flow and  
179 refocused on a Carbotrap B/C trap at 5 °C with an outlet split flow of 70 mL/min. The gas

180 chromatographic analyses were performed using a 7890A instrument from Agilent Technologies  
181 equipped with a Restek 10189 chromatographic column (60 m x 320  $\mu\text{m}$ , 1  $\mu\text{m}$  film thickness)  
182 connected to two different detectors: (i) an FID and (ii) an MS (5975B inert MSD) from Agilent  
183 Technologies. The typical detection limit of this instrument for hydrocarbon VOCs with the  
184 abovementioned sampling conditions is 0.5  $\mu\text{g}/\text{m}^3$ . Calibration for the identified and quantified  
185 TerVOCs was achieved by individual liquid doping of the high-purity certified standards from  
186 Sigma-Aldrich<sup>®</sup> on Tenax TA<sup>®</sup> absorbent tubes.

187

#### 188 *2.4 Emission chamber test: simulation of a realistic scenario – correlation method for a* 189 *realistically sized room*

190

##### 191 *2.4.1 Emission chamber parameters*

192 The experiments reported in this paper were conducted in an experimental chamber with a 1  $\text{m}^3$   
193 volume (Vötsch VCE1000 Classic) that complied with the ISO 16000-9 (2006) standards. The  
194 chamber was operated at a controlled temperature, humidity and air exchange rate (AER) of  $23 \pm$   
195  $1 \text{ }^\circ\text{C}$ ,  $50 \pm 5 \%$  and  $0.3 \text{ h}^{-1} \pm 0.05$ , respectively. The humidity and temperature were set according  
196 to ISO 16000-9. The established AER corresponds to the 25<sup>th</sup> percentile reported in French  
197 dwellings by the Indoor Air Quality Observatory (OQAI) (Kirchner et al., 2001; Lucas et al.,  
198 2009). Detailed characteristics of the experimental chamber are presented in Fig. 1b. Before  
199 loading the test chamber with the selected product, blank measurements were performed to  
200 determine background levels of TerVOCs and oxygenated volatile organic compounds  
201 (OVOCs). Note that the mean concentration determined from blank measurements in the

202 experimental chamber did not exceed the standardized background concentrations of individual  
203 VOCs.

204

#### 205 *2.4.2 Definition of a realistic scenario for the use of essential oil-based household products*

206 The assessment of TerVOC emissions in the experimental test chamber has been primarily  
207 focused on *surface cleaning scenarios*. The product application procedure must be based on the  
208 typical consumer use pattern to mimic realistic application in the evaluation of cleaning product  
209 emissions. The key parameters required to define a specific and standardized product application  
210 procedure are (i) the quantity of product to apply and (ii) the surface to clean. These parameters  
211 were estimated from the loading factor and the final application yield of the cleaning product  
212 after wiping, called *product yield* in this study.

213

#### 214 *Loading factor*

215 The loading factor is defined as the ratio between the emissive surface area, i.e., the cleaned area,  
216 and the chamber volume. This is the key parameter to transfer the real application scenario at  
217 scale 1:1 to the 1m<sup>3</sup> test chamber. It has to be kept constant between both chamber volume as  
218 reported in Table 2. Conventionally, a reference room is used to extrapolate measured VOC  
219 concentrations in test chambers with small volumes when assessing human exposure. The  
220 reference room considered for the study is the IRINA experimental room characterized by a floor  
221 area of 12 m<sup>2</sup>, a ceiling height of 2.5 m and a volume of 40 m<sup>3</sup>. (Harb et al., 2016) In regard to  
222 the product application for surface cleaning, a typical table area of 2 m<sup>2</sup> was considered in the  
223 reference room. It results in a loading factor of 0.05 m<sup>2</sup>/m<sup>3</sup>. For the correlation between the 1 m<sup>3</sup>  
224 emission test chamber and the 40 m<sup>3</sup> reference room, the loading factor must be identical (Table

225 2). Based on this consideration, the *surface cleaning scenario* was defined and the surface to  
 226 clean was determined for the 1 m<sup>3</sup> emission test chamber as reported in Table 2, along with the  
 227 corresponding masses of cleaning products. Table 2.

228 **Table 2.** Application parameters for the surface cleaning scenario: reference values from the 40  
 229 m<sup>3</sup> room for the product yield and loading factor and subsequent quantities of products to be  
 230 applied in both chambers 40 m<sup>3</sup> and 1m<sup>3</sup>.

<i>Application parameters to mimic a 2 m<sup>2</sup> surface cleaning in a 40 m<sup>3</sup> room to the 1m<sup>3</sup> test chamber</i>			
	<b>(40 m<sup>3</sup>)</b>	<i>1 m<sup>3</sup></i>	
	<b>REFERENCE ROOM</b>	<i>TEST CHAMBER</i>	
SURFACE TO CLEAN	<b>2 m<sup>2</sup></b>	<i>0.05 m<sup>2</sup></i>	
LOADING FACTOR (m <sup>2</sup> /m <sup>3</sup> )	<b>0.05</b>	<b>0.05</b>	
PRODUCT YIELD	<b>SC - 1</b>	8.7 (g.m <sup>-2</sup> )	
	<b>MC -1</b>	7.2 (g.m <sup>-2</sup> )	
	<b>KC - 2</b>	12.0 (g.m <sup>-2</sup> )	
MASS APPLIED	<b>SC - 1</b>	<b>18.0 g</b>	3.2 g
	<b>MC -1</b>	<b>15.0 g</b>	4.4 g
	<b>KC - 2</b>	<b>24.0 g</b>	2.7 g

231

232 *Product yield*

233 The product yield is defined as the effective mass of product remaining on a 1 m<sup>2</sup> surface;  
 234 it includes the total mass applied balanced by the losses induced by wiping. This parameter was  
 235 estimated for each selected cleaning product. First, the average amount of cleaning product  
 236 required to clean 1 m<sup>2</sup> of surface was determined from the cleaning of a 1 m<sup>2</sup> surface by 10  
 237 different operators. Subsequently, the average mass of each product dispersed by a single spray  
 238 from each trigger spray mechanism was determined for a set of 15 successive sprays performed

239 by the same operator. Then the mass of product lost on wipes is determined by weighing. This  
240 procedure allows the estimation of the effective mass of product remaining on a 1 m<sup>2</sup> surface.  
241 The mass of product required for the *surface cleaning scenario* in the 1 m<sup>3</sup> emission test chamber  
242 is determined from this product yield by proportionality.

243 For each experiment, the calculated mass of product was evenly drizzled or sprayed on a  
244 0.05 m<sup>2</sup> stainless steel surface placed at the center of the 1 m<sup>3</sup> experimental chamber. Once the  
245 simulation of the cleaning activity was completed, the experimental chamber remained closed  
246 during the emission monitoring. For each cleaning product, a set of three experiments was  
247 performed to evaluate the repeatability of the experimental protocol. Additionally, during the  
248 experiment, t = 0 corresponded to the time when the application of the cleaning product was  
249 completed inside the chamber.

#### 250 *2.4.3 Sampling and analytical parameters*

251 Regarding the analytical methodology, the temporal dynamics of the TerVOC and OVOC  
252 concentrations inside the experimental chamber were monitored using off-line devices that  
253 allowed their quantification with high temporal resolution. Several preliminary tests were  
254 performed to optimize the experiment duration depending on the cleaning product. On the basis  
255 of these preliminary results, the duration of a typical emission experiment was 5 hours.

256 Off-line sampling was performed according to ISO 16000-3 and 16000-6 by using (i)  
257 Tenax TA<sup>®</sup> cartridges for terpene compounds and (ii) 2,4-dinitrophenylhydrazine (DNPH)-  
258 impregnated silica cartridges (Sep-Pak DNPH-Silica Plus Short Cartridges, Waters) for carbonyl  
259 compounds. Sampling was performed using a pump (KNF<sup>®</sup>) connected to a mass flow controller  
260 with specific flow rates and durations optimized for each cleaning product tested, as described in  
261 Table 3.

262 **Table 3.** Experimental protocol and optimized parameters for the off-line sampling systems.

<i>Evaluation of emissions from cleaning products</i>		
<b>Sampling device</b>	<i>Terpenes (TerVOCs):</i> Tenax TA <sup>®</sup> adsorbent <i>Carbonyl Compounds (OVOCs):</i> DNPH cartridges	
<b>Duration of experiment* (h)</b>	5 h	
<b>Sampling flow*</b>	<i>TerVOCs</i>	0.150 L/min
	<i>Carbonyl compounds</i>	0.800 L/min
<b>Sampling duration (min) and time interval (h)*</b>		From 0 to 1 hour; continuous sampling for 15 minutes; total of 4 samples From 1 – 5 hour; continuous sampling for 60 minutes; total of 4 samples

263 \*Experimental parameters that were optimized

264

265 The analytical protocol to quantify TerVOCs was the same as that reported in section 2.3

266 for the gas-transferred concentration determination. In contrast, derivatized carbonyl compounds

267 (OVOCs) were extracted from DNPH cartridges with 3 mL of acetonitrile and analyzed with a

268 Thermo Dionex Ultimate U3000 liquid chromatograph. Compounds were eluted on an Acclaim

269 RSLC Carbonyl column (2.1 x 150 mm) and detected by RS variable-wavelength UV

270 absorption. The acquisition was performed at 365 nm wavelength. Calibration for the carbonyl

271 compounds was achieved using high-purity certified standard solutions (Aldehyde/Ketone-

272 DNPH Stock Standard-13). Under these conditions, the detection limit for the carbonyl

273 compounds was 0.01 ppb.

274

275 **3 RESULTS AND DISCUSSION**

276

277 **3.1 Chemical composition: terpene (TerVOC) content of natural, certified organic cleaning**

278 **products**

279 The terpene contents of the six selected cleaning products are listed in Table 4. Note that of the  
 280 identified compounds, the predominant terpenes are written in bold. The most frequently  
 281 identified terpenes were limonene, linalool, and  $\alpha$ -terpineol, which were present in all the  
 282 evaluated cleaning products. To date, five studies have assessed the presence of fragrance  
 283 chemicals in cleaning product formulations on the European market. Among the 121 cleaning  
 284 products evaluated, limonene and linalool have been reported with the highest occurrence rates:  
 285 84.2 % and 60.8 %, respectively (Nicolas and Chiappini, 2013; Pors and Fuhlendorff, 2003;  
 286 Rastogi, 2002; Rastogi et al., 2001; Uhde and Schulz, 2015). Worldwide, the most commonly  
 287 used essential oils in household product formulations are citrus oil, lavender oil, pine oil,  
 288 eucalyptus oil, tea tree oil and rose oil. In contrast, several terpene derivatives, such as camphor  
 289 and bergamol, detected in SC-1 and KC-2, have been more rarely reported (Ezendam et al.,  
 290 2009; Huang et al., 2011; Jo et al., 2008; Kwon et al., 2007).

291 **Table 4.** Liquid composition (expressed in  $\mu\text{g}$  of terpene per g of product:  $\mu\text{g/g}$ ) of the six  
 292 selected cleaning products and their occurrence rate in the literature. NB: the mass concentration  
 293 of the predominant TerVOCs in each cleaning product is written in bold.

Identified Terpenes	Mass of individual TerVOCs (this work)						Occurrence rate (%) in the literature
	Mass $\pm$ SD ( $\mu\text{g/g}$ )						
	MC -1	MC -2	SC - 1	KC - 1	KC - 2	GC - 1	
<i>Diffusion mode</i>	<i>Liquid</i>	<i>Liquid</i>	<i>Spray</i>	<i>Spray</i>	<i>Spray</i>	<i>Spray</i>	[121 cleaning products] (Nicolas and Chiappini, 2013; Rastogi, 2002; Rastogi et al., 2001; Uhde and Schulz, 2015)
$\alpha$ -Pinene	24.2 $\pm$ 6.2	23.3 $\pm$ 4.8	37.6 $\pm$ 5.0	-	35.6 $\pm$ 3.8	-	36 %
Limonene	<b>852.9 <math>\pm</math> 32.9</b>	<b>472.0 <math>\pm</math> 8.2</b>	25.5 $\pm$ 0.7	6.3 $\pm$ 0.5	173.3 $\pm$ 36.1	2.2 $\pm$ 0.3	84 %
Linalool	10.2 $\pm$ 0.6	6.0 $\pm$ 0.9	<b>390.0 <math>\pm</math> 5.0</b>	6.5 $\pm$ 0.5	4.3 $\pm$ 0.7	1.5 $\pm$ 0.3	61 %



Eucalyptol	424.1 ± 37.0	-	213.4 ± 4.7	-	<b>2230.8 ± 71.4</b>	<b>18.0 ± 1.5</b>	38 %
Cymene	158.7 ± 23.9	8.5 ± 0.2	-	-	76.2 ± 11.5	-	26 %
Bergamol	-	-	279.0 ± 2.0	-	-	-	NS
Camphor	-	-	256.8 ± 2.5	-	19.3 ± 2.5	-	NS
β-Pinene	69.9 ± 3.6	146.2 ± 5.0	21.8 ± 0.4	3.4 ± 0.4	3.1 ± 1.4	-	40 %
γ-Terpinene	15.9 ± 2.6	61.4 ± 5.7	2.6 ± 0.2	-	7.5 ± 0.5	-	20 %
α-Terpineol	29.7 ± 7.4	2.9 ± 0.8	16.4 ± 0.5	<b>10.0 ± 0.3</b>	18.2 ± 0.8	12.8 ± 2.0	NS
Menthol	-	-	-	1.0 ± 0.3	570.9 ± 25.2	3.3 ± 0.7	NS
Other TerVOCs	121.5 ± 15.8	79.1 ± 7.4	247.9 ± 6.9	10.3 ± 0.6	77.2 ± 18.5	1.30 ± 0.3	-
<b>TOTAL TerVOCs</b>	<b>1682.8 ± 131.3</b>	<b>776.0 ± 28.1</b>	<b>1453.7 ± 22.6</b>	<b>37.6 ± 2.5</b>	<b>3180.7 ± 200.5</b>	<b>39.1 ± 4.5</b>	

294

### 295 3.1.1 Total TerVOC mass concentration

296 Regarding the total terpene content in household products, the mass concentrations varied  
297 widely, ranging from  $37.6 \pm 2.5$  to  $3180.7 \pm 200.5$   $\mu\text{g/g}$  (of product). Nevertheless, these  
298 concentrations accounted for only 0.01 % to 0.17 % w/w of the total composition of the selected  
299 products, as shown in Table 4. Sarwar et al. (2004) reported the quantification of TerVOCs in  
300 four different types of cleaning products used as floor cleaners and general purpose cleaners. The  
301 main detected terpenes were  $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, limonene and  $\alpha$ -terpinene, with  
302 individual mass concentrations ranging from 0.2 % w/w to 2.0 % w/w. The proportions of  
303 fragrance chemicals in industrial formulations of cleaning products do not exceed 5.0 % w/w  
304 (Ezendam et al., 2009; Rastogi, 2002; Steinemann, 2009; Steinemann et al., 2011).

305

306 *3.1.2 Individual mass concentration of TerVOCs*

307 Among the selected cleaning products, a total of 27 terpenes were detected: (i) 14 monoterpenes,  
308 (ii) 8 terpene alcohols, (iii) 4 terpene derivatives, and (iv) 1 sesquiterpene. Per product, the  
309 diversity of odorous chemicals varied from 6 to 20 different species. Furthermore, all tested  
310 products, except for KC – 1, showed a correlation between the predominant terpene detected and  
311 the essential oil indicated by the manufacturer. KC – 1 was reportedly formulated with lemon oil;  
312 however, the major terpene was  $\alpha$ -terpineol instead of limonene. In terms of the product  
313 categories, limonene was the predominant terpene contained in the multiuse cleaners, both  
314 fragranced with citrus oils. In the kitchen cleaners tested, the main detected terpene differed:  
315 eucalyptol in KC – 2 and  $\alpha$ -terpineol in KC – 1. Concerning the mass concentration of terpenes,  
316 the predominant species in the selected products were limonene, linalool, eucalyptol, and  $\alpha$ -  
317 terpineol, detected at concentrations ranging from  $10.0 \pm 0.3 \mu\text{g/g}$  to  $2230.8 \pm 71.4 \mu\text{g/g}$ .

318 The chemical composition of a cleaning product might vary widely depending on its  
319 usage purpose and diffusion mode. For instance, when a cleaning product emphasizes a  
320 disinfecting property, complementary chemicals are added to its formulation to suppress or  
321 inhibit microbial activity. In so-called “green” cleaning product formulations, specific essential  
322 oils might be added to increase the concentration of terpenes with antibacterial and antiseptic  
323 activity, such as eucalyptol and geraniol. Therefore, no correlation was evidenced between the  
324 diffusion mode of the selected cleaning products and their total terpene mass concentration. This  
325 finding is suggested to result from the intrinsic industrial formulations designed to achieve a  
326 particular performance.

327 Finally, the contrasting terpene contents bring up questions about the intrinsic emission  
328 potential of the cleaning products. The diversity in the constituent volatility affects the emission  
329 dynamics associated with the cleaning activity. *Does a high terpene content necessarily imply*  
330 *high emission levels? What is the effective amount of terpenes eventually transferred to the gas*  
331 *phase? What is the impact of the cleaning product matrix on the gas phase transfer? How long is*  
332 *the user impacted by the emissions?*

333 To provide key elements needed to answer these questions, a screening of their ability to  
334 be transferred from the liquid to the gas phase, defined in this paper as the gas-transferred  
335 concentration, was performed to identify the emission potential of each cleaning product.

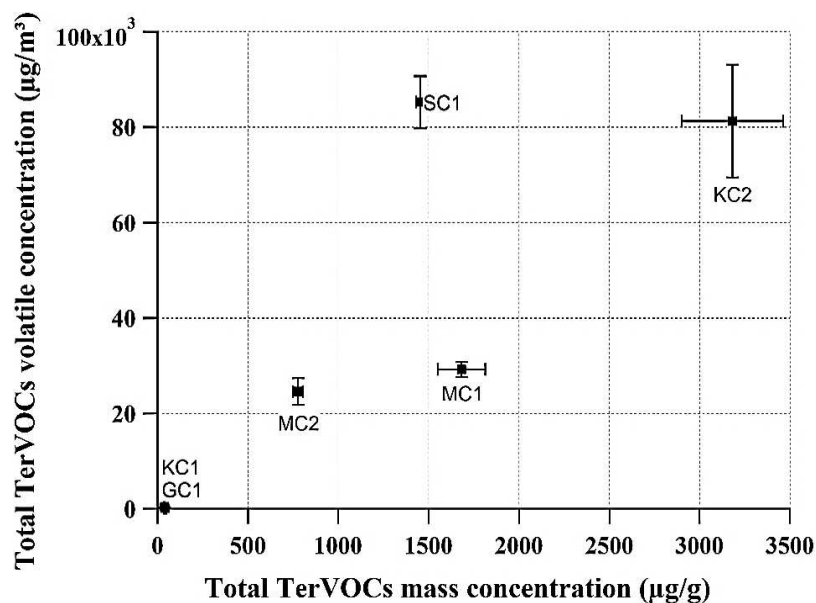
336

### 337 ***3.2 Gas-transferred concentration vs. liquid composition***

#### 338 *3.2.1 Total gas-transferred concentration*

339 The total gas-transferred concentration of terpenes corresponds to the sum of the concentrations,  
340 subsequently expressed in  $\mu\text{g}/\text{m}^3$ , of terpenes collected at the outlet of the micro-chamber setup.  
341 This concentration can be used to assess the ability of a given cleaning product to release  
342 terpenes to the gas phase. Comparison of the six selected products revealed very different total  
343 gas-transferred concentrations, ranging from  $125 \pm 15$  to  $85\,225 \pm 5\,500 \mu\text{g}/\text{m}^3$ . The glass  
344 cleaner GC – 1 was the least emissive product, with a total gas-transferred concentration of  $125$   
345  $\pm 15 \mu\text{g}/\text{m}^3$ , while the gas-transferred concentrations of the surface cleaner SC – 1 and the  
346 kitchen cleaner KC – 2 were higher by 2 orders of magnitude. These two products transferred  
347 analogous total terpene concentrations to the gas phase, considering the standard deviation:  
348  $85\,000 \pm 5\,500 \mu\text{g}/\text{m}^3$  and  $81\,000 \pm 12\,000 \mu\text{g}/\text{m}^3$ , respectively.

349 Fig. 2 shows the correlation between the total terpene mass concentrations in the liquid  
 350 phase of the selected products ( $\mu\text{g/g}$  of product) and the total gas-transferred concentrations of  
 351 TerVOCs ( $\mu\text{g}/\text{m}^3$ ) for the same products. For the multiuse cleaners (MC – 1 and MC – 2), the  
 352 volatile concentrations reached equivalent levels of  $27\ 000\ \mu\text{g}/\text{m}^3$ , but their total terpene mass  
 353 concentrations in the liquid phase differed by a concentration ratio of 2:1. The pattern between  
 354 the surface cleaner SC – 1 and the kitchen cleaner KC – 2 was similar, with gas-transferred  
 355 concentrations that both reached approximately  $80\ 000\ \mu\text{g}/\text{m}^3$ , considering the standard  
 356 deviation, but a terpene content of the surface cleaner SC – 1 that was half that of the kitchen  
 357 cleaner KC – 2 ( $3200 \pm 270\ \mu\text{g/g}$ ). In contrast, the two household products SC – 1 and MC – 1  
 358 had equivalent terpene mass contents but gas-transferred concentrations that differed by a factor  
 359 of 3. Consequently, no direct correlation was evidenced between the total terpene mass content  
 360 and the total gas-transferred concentration among the six selected products. Therefore, the  
 361 amount of terpenes emitted by a given product cannot be estimated from its liquid terpene  
 362 content, and emission tests are required.



363 **Fig. 2.** Total TerVOC gas-transferred concentration from micro-chamber testing ( $\mu\text{g}/\text{m}^3$ ) as a  
 364 function of the total terpene mass concentration in the liquid form ( $\mu\text{g}/\text{g}$ ) for the six selected  
 365 cleaning products ( $T = 40\text{ }^\circ\text{C}$ , dry air flow = 50 mL/min, micro-chamber volume = 44 mL).

366

### 367 3.2.2 Individual gas-transferred concentrations

368 Only 19 terpene molecules from the 27 TerVOCs contained in the cleaning products were  
 369 identified in the gas phase during the micro-chamber evaluation, and the number of emitted  
 370 terpenes varied from 1 to 14 per cleaning product. Table 5 lists the (i) volatile/liquid fraction  
 371 concentration ratio (V/L) of each cleaning product and (ii) various physical and chemical  
 372 properties of the individual terpene molecules. For discussion purposes, in this paper, the V/L  
 373 concentration ratio is defined as the ratio of an individual gas-transferred concentration to its  
 374 mass fraction in the liquid phase for each identified terpene. Higher is the V/L value, greater is  
 375 the ability of the considered molecule to be transferred from the liquid to the gas phase.

376

377 **Table 5.** Comparison of the total TerVOC gas-transferred concentrations ( $T = 40\text{ }^\circ\text{C}$ , dry air  
 378 flow = 50 mL/min, micro-chamber volume = 44 mL) with the total TerVOC mass fractions in  
 379 the liquid form for each cleaning product, individually. NB: The physical and chemical  
 380 properties of identified terpenes (VP, boiling point and molar mass) from the literature are  
 381 detailed.

TERPENES	<i>RATIO</i> – Gas-transferred concentration/Mass fraction (V/L) - (this work)						Vapor pressure (VP) from the literature (Pa)*	Boiling point ( $^\circ\text{C}$ )
	MC - 1	MC - 2	SC - 1	GC - 1	KC - 1	KC - 2		
$\alpha$ -Pinene	1.15	1.39	-	-	-	1.27	529- 599,	156
Limonene	1.15	1.02	0.68	-	3.99	1.51	189- 213	176

Linalool	-	0.47	0.97	-	-	1.17	20-27	198
Eucalyptol	1.27	-	1.13	2.17	-	0.80	230- 260	176
Cymene	0.58	0.99	-	-	-	1.73	192-195	177
Bergamol	-	-	1.15	-	-	-	NS	220
Camphor	-	-	1.25	-	-	1.02	28	209
$\beta$ -Pinene	0.49	1.02	0.53	-	2.83	1.12	391-400	166
$\gamma$ -Terpinene	0.17	1.19	0.64	-	-	1.99	103-145	183
$\alpha$ -Terpineol	-	-	1.31	-	-	-	**	175
Menthol	-	-	-	-	-	1.49	11-18	212

382 NS: Not specified in the literature; \*: (Harb et al., 2016; ISO 16000-9, 2006; López and Gómez, 2000; Lucas et al.,  
383 2009; Rastogi et al., 2001; Teixeira et al., 2013 ; Espinoza et al., 1999; Hoskovec et al., 2005; Štejfa et al., 2014);  
384 \*\*Vapor pressure near 0 Pa

385 Among the physical and chemical properties of TerVOCs, the saturation vapor pressure  
386 (VP) of a pure molecule (expressed in Pa) is an inherent property required for the investigation  
387 of vapor-liquid equilibrium and a key parameter for emission assessment. It is defined as the  
388 pressure exerted by a vapor in equilibrium with its pure condensed phase at a given temperature  
389 in a closed system. VPs have been experimentally determined in the literature for most  
390 TerVOCs, and the corresponding values are given in Table 5. The reported VPs of terpenes are  
391 highly varied, ranging from 0.3 Pa for  $\alpha$ -terpineol to 599 Pa for  $\alpha$ -pinene.

392 As shown in Table 5,  $\alpha$ -pinene had a V/L ratio higher than 1, ranging from 1.15 to 1.39  
393 among the cleaning products in which this molecule was detected. This suggests a significant  
394 ability of  $\alpha$ -pinene to be transferred to the gas phase independent of the solvent matrix  
395 composition and could be related to its high VP of 599 Pa, the highest among all identified  
396 terpenes. In contrast, for the other compounds, the relation between the VP and V/L ratio was not  
397 predictable. Unique behaviors were observed for different terpenes: (i) the V/L ratio of linalool,  
398 with low volatility (VP values below 30 Pa), differed greatly depending on the cleaning product,

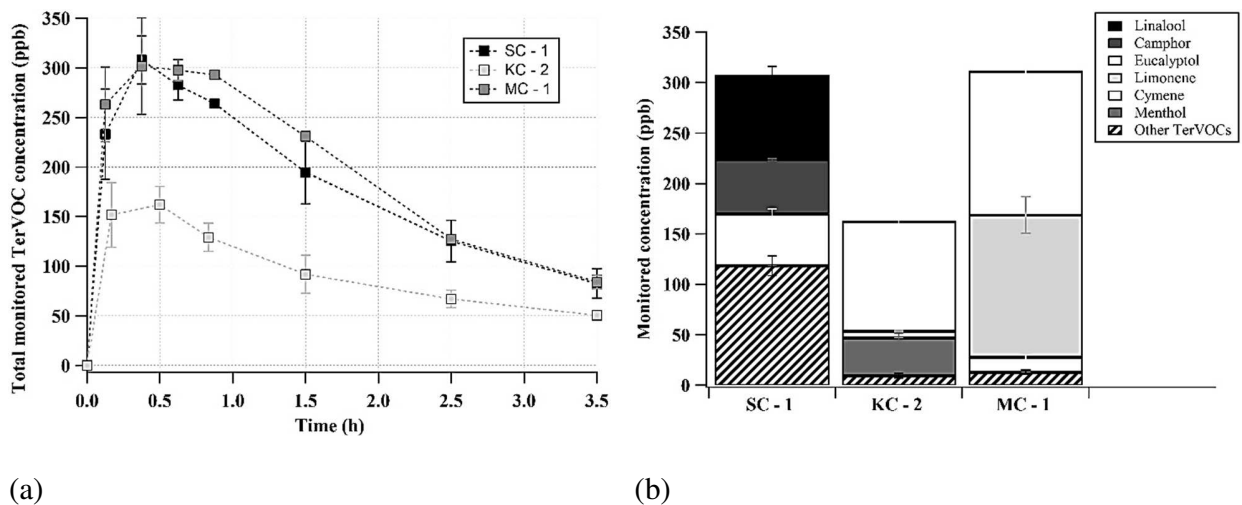
399 ranging from 0.47 for MC – 2 to 1.17 for KC – 2, while (ii) V/L ratio of  $\beta$ -pinene, with chemical  
400 and physical properties analogous to those of  $\alpha$ -pinene, widely varied from 0.49 for MC – 1 and  
401 2.83 for KC – 1. Thus, for most terpene species, the transfer to the gas phase is not exclusively  
402 driven by the intrinsic properties of the pure molecule but more by the solvent properties. The  
403 proportion of organic solvent and the presence of texturing agents in the aqueous media of a  
404 cleaning product play key roles in flavor release (Jouquand et al., 2008). Interactions between  
405 flavor compounds and a matrix have been extensively studied in the field of food sciences  
406 (Guichard, 2002). The determination of the gas-liquid partition coefficient under equilibrated  
407 conditions specific to each VOC/matrix pair could be used to explain the various observed  
408 behaviors (Ettre et al., 1993).

409         Consequently, terpene emissions from essential oil-based household cleaning products  
410 cannot be directly predicted from the liquid composition of the product. Instead, the  
411 concentrations of TerVOC species released from such products could be governed by three main  
412 factors: (i) the inherent volatility of the TerVOCs, (ii) the chemical affinities between the  
413 TerVOCs and other compounds in the formulations and (iii) the mass concentrations of terpenes  
414 in the liquid phase. In the micro-chamber tests, the major compounds emitted and transferred to  
415 the gas phase were identified, but this experimental approach is not a substitute for emission  
416 testing using experimental chambers of conventional size. Moreover, micro-chamber tests are  
417 not conducted under realistic conditions of temperature, humidity and air velocity, but under  
418 conditions which potentially enhance the transfer from the product to the gas phase. Next,  
419 primary emissions were investigated from a representative cleaning product for each of the three  
420 product categories of the six selected products.

421

422 **3.3 Emission of TerVOCs under realistic application conditions: 1 m<sup>3</sup> emission test chamber**

423 To assess the primary emissions associated with the application of essential oil-based products,  
424 one representative product from each category was selected. This selection was based on the  
425 previously discussed results regarding the correlation between the gas-transferred concentration  
426 and the liquid content of TerVOCs. The cleaning product in each category attesting the highest  
427 ratio between its gas-transferred and liquid concentrations (V/L) was selected: (i) the surface  
428 cleaner SC – 1, (ii) the multiuse cleaner MC – 1, and (iii) the kitchen cleaner KC – 2. Regarding  
429 the diversity of the species emitted, 19 out of the 23 TerVOCs contained in the three liquid  
430 cleaners were identified in the gas phase. Fig. 3b shows the contributions of the top three emitted  
431 terpenes to the total TerVOC concentration after the separate application of the selected cleaners.  
432



433 **Fig. 3.** (a) Temporal evolution of the total TerVOC concentration during cleaning with SC – 1  
434 (black symbols), MC – 2 (dark gray symbols) and KC – 2 (light gray symbols) ( $T = 23\text{ }^{\circ}\text{C}$ ,  $\text{RH} =$   
435  $50\%$ , air renewal rate =  $0.3\text{ h}^{-1}$ , chamber volume =  $1\text{ m}^3$ ). (b) Peak concentration of total  
436 TerVOCs and the contributions of the 3 predominant terpenes after the application of SC – 1,  
437 MC – 1 and KC – 2.



438

### 439 3.3.1 Emission Profile of total TerVOCs

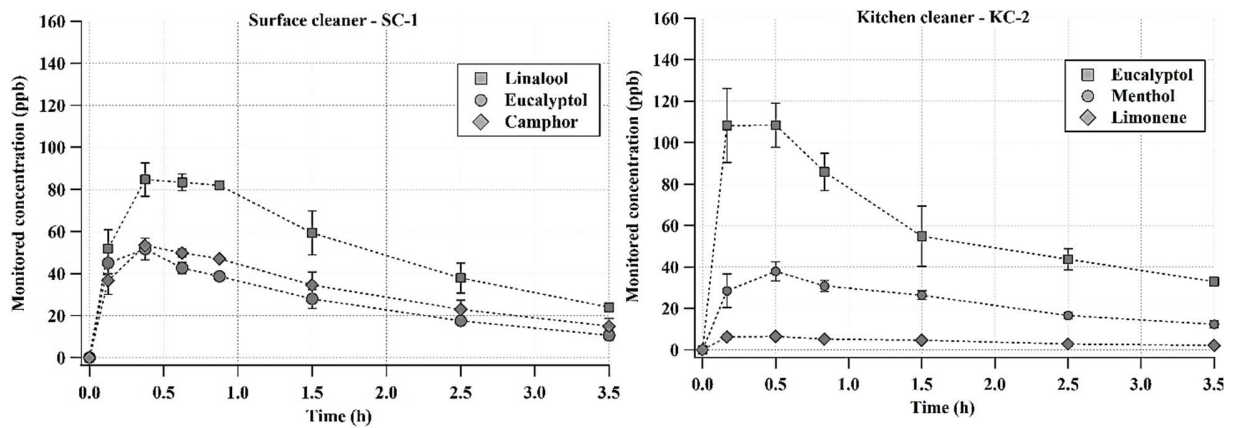
440 The temporal profiles of the total TerVOC concentrations in SC – 1, KC – 2 and MC – 1,  
441 reported in Fig. 3a, are characterized by the three typical phases of transient emission: (i) a  
442 sudden increase in the total TerVOC concentration, reflecting the rapid transfer of terpenes from  
443 the applied cleaning product layer to the gas phase until a peak concentration is reached (< 30  
444 minutes); (ii) a long decrease, corresponding to the gradual depletion of the VOC source and  
445 removal of VOCs from the experimental chamber; and (iii) a final decrease exclusively  
446 associated with the evacuation of the gas phase terpenes by air exchange and possible deposition  
447 on the inner walls of the experimental chamber. Note that in any of the three phases, possible  
448 losses of terpenes from deposition on the chamber walls must be considered. As observed in Fig.  
449 3a, SC – 1 and MC – 1 had similar, considering their respective standard deviations, peak total  
450 TerVOC concentrations of approximately 300 ppb within a half-hour after application. The  
451 maximum emitted concentration of TerVOCs KC–2 (160 ppb) was lower than those of the other  
452 two cleaning products but was reached at an analogous time. However, considering the total  
453 terpene composition in the liquid phase (section 2.1), KC – 2 was characterized by the highest  
454 mass concentration of TerVOCs ( $3200 \pm 200 \mu\text{g/g}$ ) among the three cleaners. These results  
455 confirm the absence of correlation between the liquid content of terpenes and the resulting  
456 concentrations of terpenes in the  $1 \text{ m}^3$  emission test chamber. Based on the investigated products,  
457 the temporal emission dynamics of essential oil-based cleaning products cannot be directly  
458 predicted from their liquid composition.

459 In comparison with other indoor terpene sources, primary emissions from a wood-based  
460 building product evaluated by Harb et al. (2018) produced a peak concentration of total

461 TerVOCs of 31 ppb under realistic conditions. Brown (1999) identified similar emitted  
 462 concentrations from a 16-mm pine softwood particleboard. Thus, the contribution to the indoor  
 463 total concentration of TerVOCs made by cleaning activities may transiently exceed that made by  
 464 wood-based materials. However, emissions from cleaning products are characterized by temporal  
 465 dynamics different from those of indoor material emissions; the former emissions mostly act as  
 466 punctual or transient sources of pollutants. Thus, the cumulative exposure to TerVOCs from  
 467 cleaning products is directly related to cleaning frequency and human factors. This behavior  
 468 contrasts with wood-based materials, which mostly act as long-term and continuous emission  
 469 sources.

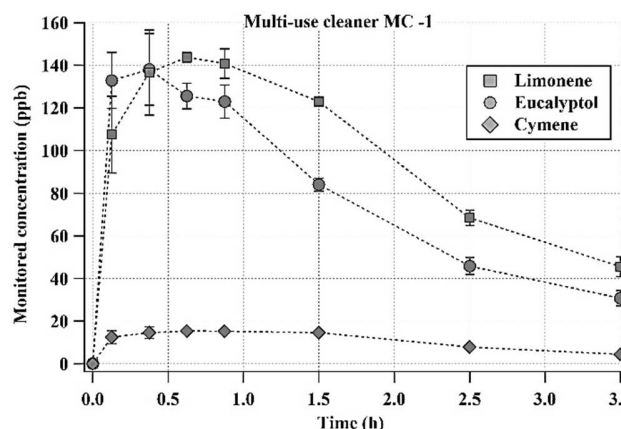
470 *3.3.2 Individual emission profiles of TerVOC*

471



(a)

(b)



**Fig. 4.** Temporal evolution of the concentrations of major terpenes identified during the use of three cleaning products: (a) surface cleaner (SC - 1), (b) kitchen cleaner (KC - 1), and (c) multiuse cleaner (MC - 1) ( $T = 23\text{ }^{\circ}\text{C}$ ,  $\text{RH} = 50\%$ , air renewal rate =  $0.3\text{ h}^{-1}$ , chamber volume =  $1\text{ m}^3$ ).

(c)

472 The individual emissions of 9 monoterpenes, 7 terpene alcohols, 1 oxygenated terpene,  
 473 and 1 sesquiterpene were quantified. SC - 1 was characterized by the largest diversity of  
 474 terpenes, since it emitted a total of 16 different terpene molecules. Fig. 4 shows the individual  
 475 profiles of the predominantly emitted terpene species. The individual profiles were characterized  
 476 by the same three phases observed in the emission profiles of the total TerVOCs (Fig. 3a).  
 477 Nonetheless, some differences can be observed among the tested products.

478 The predominant terpenes released from *surface cleaner SC - 1* were linalool, eucalyptol  
 479 and cymene, which had peak concentrations of  $85 \pm 10\text{ ppb}$ ,  $50 \pm 5\text{ ppb}$  and  $55 \pm 5\text{ ppb}$ ,  
 480 respectively. Their cumulative concentration accounted for 47.6 % of the peak total TerVOC  
 481 concentration. Interestingly, regarding the emission kinetics, despite these compounds showing  
 482 contrasting physical and chemical properties (Table 5), their peak concentrations were reached at  
 483 equivalent emission times, i.e., nearly 25 minutes after the cleaning activity was completed (Fig.  
 484 4a). This observation suggests that determinants other than the physical and chemical properties  
 485 of individual TerVOCs are involved in the emission of TerVOCs during cleaning. For instance,  
 486 in the liquid composition of SC - 1, a significant concentration of ethanol of 70 % w/w was

487 detected. In general, in their formulations, surface cleaners contain water and various water-  
488 miscible solvents, i.e., alcohols and glycols, which are included to (i) enhance the “fast-dry  
489 effect” and (ii) dissolve grease on the surface being cleaned (Magnano et al., 2009; Missia et al.,  
490 2012; Steinemann et al., 2011; Wolkoff et al., 1998). The ethanol in surface cleaner SC – 1 was  
491 probably included for those purposes and may have accelerated the emission kinetics of  
492 TerVOCs due to the fast drying rate.

493         The major terpenes emitted from *kitchen cleaner KC – 2* were eucalyptol, menthol, and  
494 limonene, as reported in Fig. 4b. Their respective peak concentrations were  $110 \pm 10$  ppb,  $38 \pm 5$   
495 ppb, and  $7 \pm 1$  ppb, contributing to 96 % w/w of the total TerVOC peak concentration.  
496 Analogous times (15 minutes) were observed for the peak concentrations of eucalyptol and  
497 limonene (Fig. 4b). Noticeably, the emission profile of eucalyptol was characterized by a sharp  
498 increase in its concentration and a subsequent clearly identifiable maximum concentration ca. 15  
499 minutes. The emission kinetics of eucalyptol contrasts with those of menthol, which had a peak  
500 concentration at 30 minutes after the cleaning product was applied. The lower VP of menthol of  
501 approximately 18 Pa may explain this different behavior.

502         In the case of the *multiuse cleaner MC – 1*, limonene, eucalyptol and cymene were the  
503 main terpenes identified in the gas phase. As shown in Fig. 4c, limonene and eucalyptol had peak  
504 concentrations of approximately 145 ppb. However, despite their similar VPs, several differences  
505 can be noted in the emission profiles of these terpenes. Limonene and eucalyptol were  
506 characterized by a sharp increase up to their peak concentrations within 8 minutes, and 90  
507 minutes after the cleaning activity was completed, their gas phase concentrations still accounted  
508 for more than 60 % of their peak concentrations. This behavior suggests that after the intense  
509 emission within the first minutes post cleaning, their emissions may continue over a long time

510 scale. This phenomenon can be evaluated through the determination of individual TerVOC  
511 emission rates as a function of time. In contrast, cymene presents a concentration profile  
512 characterized by a broad emission peak corresponding to a low peak concentration but possibly  
513 emission over a longer time scale.

514 Comparing the emission dynamics of eucalyptol (commonly released from all cleaners),  
515 rapid emission kinetics were observed for MC – 1, from which the maximum emitted  
516 concentration of eucalyptol was reached within the first 8 minutes after its application. The peak  
517 eucalyptol concentration (140 ppb) emitted from this product (MC – 1) was higher than that from  
518 the other tested products; however, the liquid form contained only 424  $\mu\text{g/g}$  eucalyptol. In  
519 contrast, slower eucalyptol emission dynamics were observed from KC – 2, with the peak  
520 concentration occurring nearly 23 minutes after the application of the kitchen cleaner. KC – 2  
521 contained the highest concentration (2230  $\mu\text{g/g}$ ) of eucalyptol in its liquid phase, but its  
522 maximum emitted eucalyptol concentration was only 110 ppb. These observations suggest that  
523 the liquid concentration of individual terpene molecules is not the only key factor driving the  
524 transfer from the liquid to the gas phase. To assess the emission of individual TerVOCs from  
525 each cleaner, the mass emission rate was calculated from the concentration profiles and assessed  
526 in the next section.

527

### 528 ***3.4 Estimation of TerVOC mass emission rates from monitored concentration profiles***

529 In this study, the emission rate of a cleaning product is defined as the mass of volatile compound  
530 emitted per gram of applied product per unit time for a given duration  $t$  from the beginning of the  
531 emission. The estimated mass emission rate from a source is of major importance since (i) it  
532 provides key information to understand and describe the emission from an indoor source of

533 pollutants; (ii) it is a representative parameter that can be extrapolated to realistic cases, allowing  
 534 the prediction of pollutant emissions in other scenarios; and (iii) it is required for the evaluation  
 535 of human exposure and indoor quality control technologies.

536 Indoor pollutant concentrations are governed by various processes, including ventilation,  
 537 pollutant emission, and pollutant transformation, such as uptake or chemical interaction. The  
 538 same phenomena could be observed in an emission test chamber. Therefore, it is necessary to  
 539 address the fate of pollutants considering the contribution of each process separately. In a typical  
 540 indoor environment, the variation in the concentration of an individual VOC is driven by the  
 541 mass conservation equation shown in *Eq. 1*.

$$\begin{array}{c} \frac{d[X]}{dt} \\ \text{Concentration} \\ \text{profile} \end{array} = - \begin{array}{c} \frac{d[X]_{Out}}{dt} \\ \text{Air Exchange} \end{array} + \begin{array}{c} \frac{d[X]_E}{dt} \\ \text{Pollutant} \\ \text{source} \end{array} - \begin{array}{c} \frac{d[X]_{Dep}}{dt} \\ \text{Deposition on} \\ \text{surfaces} \end{array} + \begin{array}{c} \frac{d[X]_{Des}}{dt} \\ \text{Desorption} \\ \text{from surfaces} \end{array} + \begin{array}{c} \frac{d[X]_{Hom}}{dt} \\ \text{Homogeneous} \\ \text{reactivity} \end{array} + \begin{array}{c} \frac{d[X]_{Het}}{dt} \\ \text{Heterogeneous} \\ \text{reactivity} \end{array} \quad \text{Eq. 1}$$

543 In controlled environments, such as the emission chamber used for our experiments,  
 544 several processes included in *Eq. 1* can be ruled out because of the design and operation of the  
 545 chamber. First, the concentration of one of the main oxidants in the experimental chamber was  
 546 continuously monitored during experiments; the ozone level remained lower than the detection  
 547 limit of the ozone analyzer (0.4 ppb) during all experiments, suggesting that the contribution of  
 548 ozone-induced homogeneous and heterogeneous reactions can be neglected. Harb et al. (2016)  
 549 and Haghghat and De Bellis (1998) evidenced that stainless steel is the most common chamber  
 550 material in reviewed publications due to its inert properties. The use of stainless steel prevents  
 551 the reaction of deposited TerVOCs with the inner material surface of the chamber. This is  
 552 supported by the fact that no terpenes other than those monitored in the liquid composition and  
 553 no carbonyls other than those reported in the literature were detected in the gas phase in the

554 experimental chamber. Therefore, surface reactivity on stainless steel was disregarded.  
 555 Additionally, desorption is endothermic. Moreover, in a temperature-controlled environment, the  
 556 sorption of TerVOCs is suggested to be irreversible, and desorption is considered negligible.

557 Thus, in the emission experiments with the cleaning products, the TerVOC  
 558 concentrations in the emission test chamber were predominantly controlled by (i) the air  
 559 exchange, (ii) the emission rate from the TerVOC sources, and (iii) the loss due to sorption to the  
 560 inner walls of the chamber ( $k_D$ ). Therefore, *Eq. 2* describes the resulting pollutant concentration  
 561  $[X]$  in the experimental chamber. Determining the TerVOC emission rates from their monitored  
 562 concentration profiles requires knowledge of the contributions of their respective AERs and  
 563 deposition rates.

$$\frac{d[X]}{dt} = -\frac{d[X]_{Out}}{dt} + \frac{d[X]_E}{dt} - \frac{d[X]_{Dep}}{dt}$$

Concentration profile
Air Exchange
Pollutant source
Deposition on surfaces

*Eq. 2*

### 566 3.4.1 Air exchange

567 Air exchange removes species  $X$  via the air renewal system of the emission test chamber and is  
 568 characterized by  $k_{AER}$ , expressed in  $h^{-1}$ . The air exchange can be calculated considering the  
 569 ventilation flow and the volume of the chamber or experimentally determined using a relevant  
 570 tracer gas. Based on the inlet ventilation flow of our emission test chamber,  $k_{AER}$  was fixed at 0.3  
 571  $h^{-1}$  in all sets of experiments.

$$-\frac{d[X]_{Out}}{dt} = -k_{AER} \times [X]$$

Air Exchange

*Eq. 3*

574 3.4.2 Emission rate

575 The emission rate of species  $X$  is determined from its release from the mass of applied product  
576 per unit of time. For cleaning products, the mass emission rate is determined using *Eq. 4*, where  
577  $m_p$  is the mass of cleaner applied over the surface depending on the cleaning purpose, i.e., floor  
578 or surface cleaning, and  $V_{chamber}$  corresponds to the volume of the experimental chamber.

579 
$$\boxed{\frac{d[X]_E}{dt}} = \frac{\tau(t) \times V_{chamber}}{m_p}$$
 *Eq. 4*

Pollutant source

580 3.4.3 Deposition on the inner surfaces of the emission test chamber

581 This phenomenon corresponds to the sorption of gas-phase TerVOCs to the surface of the  
582 stainless steel chamber. The nonreactive sorption of TerVOCs on indoor materials can be  
583 characterized by the deposition rate  $k_D$  expressed in  $h^{-1}$  and is driven by the concentration of the  
584 gas-phase species  $X$ , as reported in *Eq. 5*. Note that  $k_D$  depends on the nature of the material and  
585 the VOC and was assessed for each set of experiments to provide a comprehensive evaluation of  
586 the fate of emitted TerVOCs and its impact on the resulting TerVOC concentrations in the gas  
587 phase.

588 
$$\boxed{-\frac{d[X]_{Dep}}{dt}} = -k_D \times [X]$$
 *Eq. 5*

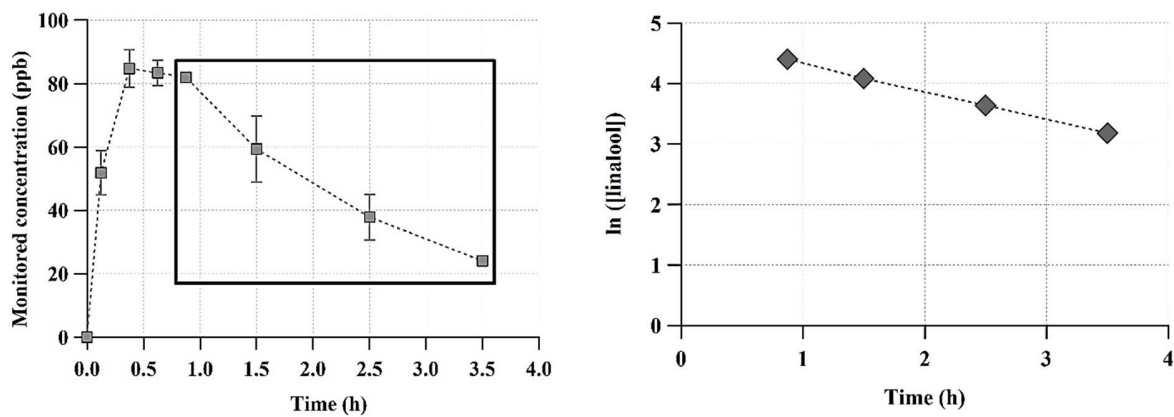
Deposition on surfaces

589 As finite sources of TerVOCs, fragrance molecules in cleaning products may become  
590 depleted. Thereafter, the drivers of the TerVOC concentrations in the experimental chamber are  
591 only (i) the air renewal at a known decay rate ( $k_{AER}$ ) and (ii) the deposition on walls at a decay  
592 rate ( $k_D$ ). This situation is described in *Eq. 6*, the linearized form of *Eq. 2*. The air renewal rate  
593 was set to  $0.3 h^{-1}$  in our emission test chamber and was therefore easy to account for. The method



594 to determine  $k_D$  is illustrated with the temporal profile of linalool emitted from the surface  
 595 cleaner SC – 1 in Fig. 5a. After 1 hour of emission, the peak in linalool emission has past, and  
 596 the experimental data inside the box (Fig. 5a) correspond to a decaying linalool concentration  
 597 due to air exchange and possible sorption on the emission chamber walls. Based on Eq. 6, this  
 598 portion of the data series is plotted in Fig. 5b as  $\ln([linalool])$  as a function of time (h). The  
 599 linear relationship indicates pseudo-first-order decay. The slope of the straight line in Fig. 5b is  
 600 the sum of  $k_{AER}$  and  $k_D$ . Since  $k_{AER}$  is a known experimental constant, the deposition rate of  
 601 linalool under our experimental conditions can be determined as  $k_D(linalool) = 0.16 \text{ h}^{-1}$ .

602  $\ln(X(t)) = -(k_{AER} + k_D) \times t + A \quad (A = \text{constant}) \quad \text{Eq. 6}$



(a) (b)

603 **Fig. 5.** (a) Temporal evolution of the linalool concentration (ppb) during cleaning using the  
 604 surface cleaner SC – 1 ( $T = 23 \text{ }^\circ\text{C}$ ,  $\text{RH} = 50 \%$ , air renewal rate =  $0.3 \text{ h}^{-1}$ , chamber volume =  $1$   
 605  $\text{m}^3$ ); the data series in the box corresponds to linalool decay after depletion of its source. (b) Plot  
 606 of  $\ln([linalool])$  as a function of time (h); NB: in b), only the data series within the box in (a) is  
 607 plotted.

608 The deposition rates ( $k_D$ ) of the 6 predominant released TerVOCs were experimentally  
 609 determined during the application of the surface cleaner SC – 1, the kitchen cleaner KC – 2, and

610 the multiuse cleaner MC – 2 (Table 6) and ranged from 0.12 to 0.52 h<sup>-1</sup>. These values clearly  
 611 show that the deposition rates of TerVOCs on the chamber walls have to be determined to  
 612 interpret the concentration profiles since they impact the resulting concentrations by the same  
 613 order of magnitude as the AER (0.3 h<sup>-1</sup>).

614  
 615 **Table 6.** Comparison of the deposition rate coefficient  $k_D$  (h<sup>-1</sup>) of the predominant terpenes from  
 616 the three selected cleaning products: (i) the surface cleaner SC – 1, (ii) the kitchen cleaner KC –  
 617 2, and (iii) the multiuse cleaner MC – 1.

<i>Deposition rate <math>k_D</math> (h<sup>-1</sup>)</i>			
<b>TERPENE</b>	<b>Cleaning Product</b>		
	<b>SC – 1</b>	<b>KC – 2</b>	<b>MC – 1</b>
$\alpha$ -Pinene	0.52	0.46	0.26
Limonene	0.12	0.11	0.24
Linalool	0.16	ND	ND
Eucalyptol	0.19	0.38	0.30
Cymene	Ø	0.22	0.31
Bergamol	0.12	Ø	Ø
Camphor	0.12	ND	Ø
Menthol	Ø	0.08	Ø

618 Ø = This terpene was not identified in a cleaning product in its liquid form.

619 ND: This terpene was not a predominantly emitted terpene from a cleaning product; therefore, it was not detected in  
 620 the gas phase.

621 According to Table 6, the  $k_D$  values for the same species may differ from one applied  
 622 product to another. For instance, the  $k_D$  of  $\alpha$ -pinene was 0.52, 0.46, and 0.26 h<sup>-1</sup> for SC – 1, KC –  
 623 2, and MC – 1, respectively. These differences are suggested to be associated with the cleaning  
 624 product formulations. Among cleaning product constituents, water can be present in formulations  
 625 at mass percentages ranging from 95 % and 50 %. Subsequently, during cleaning, the RH of the

626 confined environment increases. Springs et al. (2011) evidenced that the number of moles of  
 627 terpenes taken up per unit of surface area tends to decrease with increasing RH, suggesting  
 628 competitive interactions with water molecules for uptake surfaces. Consequently, the deposition  
 629 rate ( $k_D$ ) of fragrance molecules on indoor materials could be impacted by two main factors: (i)  
 630 competition for uptake among terpenes and cleaning constituents and (ii) the increase in RH  
 631 related to the water content of the cleaner. Consequently, the  $k_D$  value for a given terpene might  
 632 differ depending on the cleaning product formulation.

633

#### 634 3.4.4 Determination of the mass emission profiles from the concentration profiles

635 The mass conservation equation under our experimental conditions during cleaning is described  
 636 by Eq. 7, where  $[X]$  is the concentration of species X,  $m_p$  is the mass of applied cleaning product,  
 637  $V_{chamber}$  corresponds to the volume of the chamber ( $m^3$ ), and  $k_{AER}$  and  $k_D$  are the decay rates ( $h^{-1}$ )  
 638 of species X related to air renewal and deposition.

639

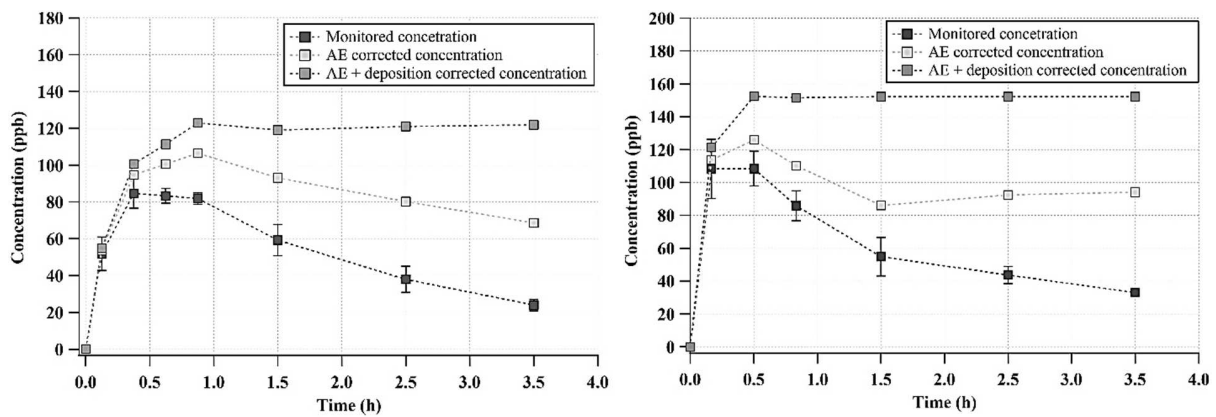
$$\underbrace{\frac{d[X]}{dt}}_{\text{Concentration profile}} = \underbrace{\frac{\tau(t) \times V_{chamber}}{m_p}}_{\text{Pollutant source}} - \underbrace{(k_D + k_{AER}) \times [X]}_{\text{Concentration of X removed by air exchange and deposition}}$$

Eq. 7

640 Based on Eq. 7, the emission rate of a given TerVOC can be retrieved from its  
 641 concentration profile corrected by the air renewal rate and by the depletion rate. Fig. 6 shows the  
 642 temporal evolution (a) of linalool emitted during cleaning using the surface cleaner SC – 1 and  
 643 (b) of eucalyptol released during cleaning using the kitchen cleaner KC – 2. The concentrations  
 644 of linalool and eucalyptol directly monitored in the 1  $m^3$  emission test chamber are plotted as  
 645 black squares in Fig. 6a and b. First, the raw profile was corrected by the air renewal rate,  
 646 resulting in linalool and eucalyptol concentration profiles that would have been recorded if no air

647 exchange occurred in the emission test chamber (light gray squares in Fig. 6). Then, these  
 648 profiles were corrected by the specific deposition rate of each terpene, producing final profiles  
 649 that correspond to the concentrations if no linalool and eucalyptol had been removed from the  
 650 gas phase in the chamber, neither by sorption on the chamber walls nor by air exchange (dark  
 651 gray circles in Fig. 6). The resulting profiles reflect only the linalool and eucalyptol emissions  
 652 from SC – 1 and KC – 2, respectively. Therefore, the times when these terpenes reach steady  
 653 state indicates the end of their emission from their respective cleaners. Moreover, this final  
 654 profile can be used to calculate the emission rate of linalool and eucalyptol according to *Eq. 8*.  
 655 The same calculations were performed for all terpenes detected in the gas phase during the use of  
 656 the three cleaners.

$$657 \quad \tau(t) = \frac{V_{chambre}}{m_{produit}} \times \frac{(C_{i+1} - C_i)}{(t_{i+1} - t_i)} \quad Eq. 8$$



(a) (b)

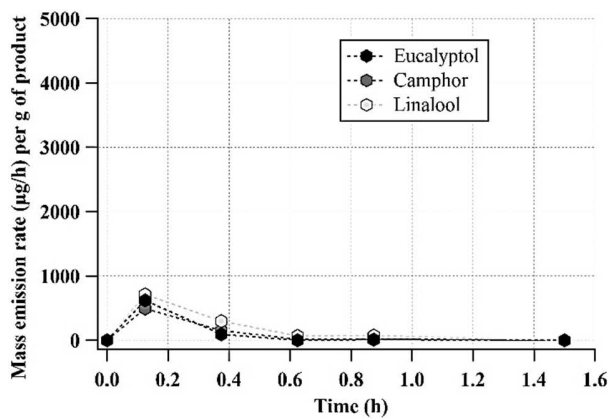
658 **Fig. 6.** (a) Temporal evolution of the (i) monitored concentration (ppb), (ii) air exchange-  
 659 corrected concentration (ppb), and (iii) air exchange + deposition-corrected concentration (ppb)  
 660 of linalool during cleaning using the surface cleaner SC – 1. (b) Temporal evolution of the (i)  
 661 monitored concentration (ppb), (ii) air exchange-corrected concentration (ppb), and (iii) air  
 662 exchange + deposition-corrected concentration (ppb) of eucalyptol during cleaning using the

663 kitchen cleaner KC – 2 ( $T = 23\text{ }^{\circ}\text{C}$ ,  $\text{RH} = 50\%$ , air renewal rate =  $0.3\text{ h}^{-1}$ , chamber volume = 1  
664  $\text{m}^3$ ).

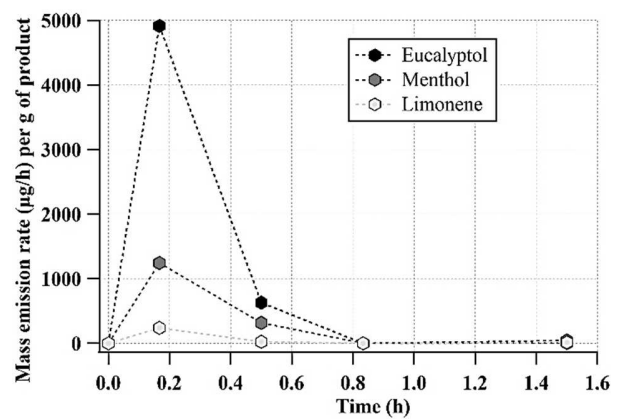
665

### 666 3.4.5 Emission rate profiles of individual TerVOCs

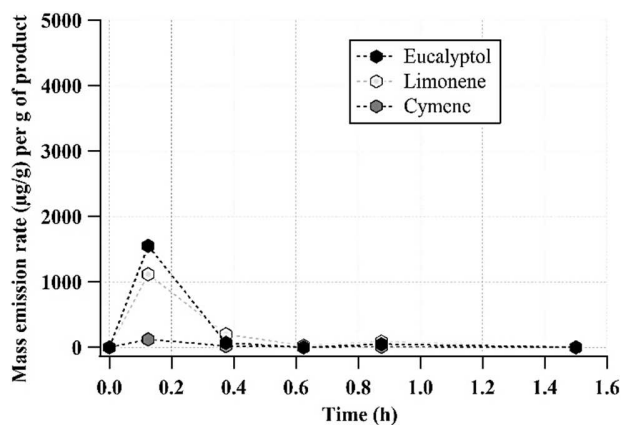
667 Based on Eq. 8, the temporal evolution of the mass emission rate was calculated for each cleaner  
668 and for each TerVOC emitted. Fig. 7 presents the temporal evolution of the mass emission rates  
669 of the three predominant TerVOCs monitored during the use of (a) SC – 1, (b) KC – 2 and (c)  
670 MC – 1. The temporal profiles of the emission rates allow the determination of (i) the time  
671 required to reach the maximum emission rate, (ii) the value of the maximum emission rate, and  
672 (iii) the time at which the emission source is depleted.



a)



b)



**Fig. 7.** Temporal evolution of the mass emission rates of the three predominant terpenes detected in the gas phase during the use of (a) the surface cleaner SC – 1, (b) the kitchen cleaner KC – 2 and (c) the multiuse cleaner MC – 1 applied in the 1 m<sup>3</sup> emission test chamber (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h<sup>-1</sup>, chamber volume = 1 m<sup>3</sup>).

c)

673 Based on Fig. 7, irrespective of the cleaning product, the time required for a given  
 674 terpene to reach the maximum emission rate was similar for all monitored terpenes: within 8  
 675 minutes after cleaning was completed. However, the magnitude of the peak emission rate of the  
 676 predominant terpene released clearly differed from one cleaning product to another: (i) 710 ± 15  
 677 µg/h linalool from SC – 1, (ii) 1550 ± 90 µg/h eucalyptol from MC – 1, and (iii) 5 000 ± 120  
 678 µg/h eucalyptol from KC – 2.

679 Noticeably, the emission of eucalyptol and menthol from KC – 2 was exhausted within  
 680 50 minutes and after 30 minutes for limonene. Of the three selected categories, this product  
 681 category had the highest emission rates. However, SC – 1 and MC – 1 showed shorter emission  
 682 durations than KC – 2. Their total TerVOC emissions were exhausted within only 24 minutes, as  
 683 shown in Fig. 7a and b.

684 Regarding the emission of individual terpenes, eucalyptol was only terpene emitted from  
 685 all three tested cleaners. However, its peak emission rate varied widely, reaching 620 ± 20 µg/h,  
 686 4 900 ± 110 µg/h and 1460 ± 30 µg/h for the surface cleaner (SC – 1), the kitchen cleaner (KC –

687 2) and the multiuse cleaner (MC – 1), respectively. Similar emission rate variability was  
688 observed for the limonene emitted from two products:  $240 \pm 30 \mu\text{g/h}$  and  $1100 \pm 80 \mu\text{g/h}$  for KC  
689 – 2 and MC – 1, respectively.

690 The assessment of the emission rates confirms that in addition to the liquid TerVOC  
691 content in the cleaner, the emission dynamics are also driven by (i) the solvent matrix in which  
692 the fragrance molecules are contained due to chemical affinities that might be generated among  
693 species, delaying the emission kinetics, and (ii) the volatility of individual terpene molecules.

694

### 695 ***3.5 Emission of OVOCs from natural cleaning products under realistic application conditions:***

#### 696 ***1 m<sup>3</sup> emission test chamber***

697 Carbonyl compounds were monitored during each set of emission experiments. Three targeted  
698 oxygenated VOCs emitted from the application of SC – 1, KC – 2 and MC – 1 were identified  
699 and quantified: formaldehyde, acetaldehyde and acetone. Their individual maximum emitted  
700 concentrations varied from one cleaning product to another, ranging from (i)  $6 \pm 1$  to  $18 \pm 3$  ppb  
701 formaldehyde, (ii)  $22 \pm 3$  to  $210 \pm 20$  ppb acetaldehyde, and (iii)  $18 \pm 4$  to  $108 \pm 15$  ppb acetone.  
702 Among the identified OVOCs, formaldehyde was classified in 2016 by the European  
703 Commission as carcinogenic (Group 1) and genotoxic (International Agency for Research on  
704 Cancer, 1979). Additionally, the long-term exposure limit was established at 9 ppb by the World  
705 Health Organisation (2010). Thus, in the framework of this study, formaldehyde is of particular  
706 interest because of its toxicity.

707

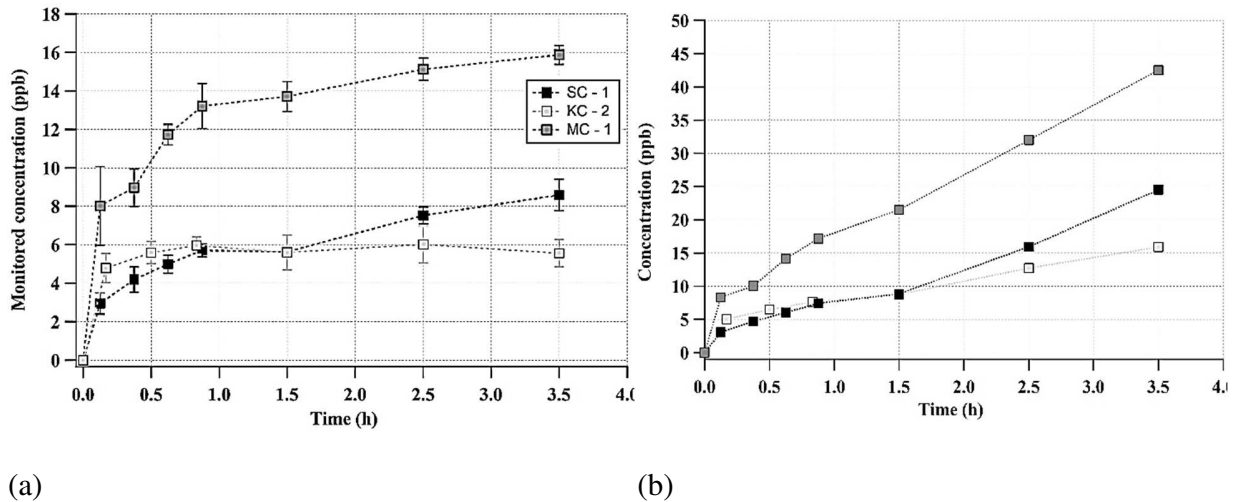
#### 708 ***3.5.1 Formaldehyde emission profiles from the use of natural cleaning products***

709 Fig. 8a presents the temporal evolution of the concentration of formaldehyde emitted by cleaning  
710 with SC – 1, KC – 2 and MC – 1. Unlike the terpene emission profiles, the temporal evolution of  
711 the formaldehyde concentration in Fig. 8 is characterized by two phases: (i) a marked increase  
712 confirming the rapid transfer of formaldehyde from the product to the gas phase during the first  
713 50 minutes of emission and (ii) either a slow increase for SC – 1 and MC – 1 or steady state for  
714 KC – 2. In contrast to the terpene concentration profiles, the emission profiles of formaldehyde  
715 do not follow a typical transient emission process. As observed in Fig. 8a, the maximum emitted  
716 concentration of formaldehyde was 9 and 16 ppb for the surface cleaner (SC – 1) and for the  
717 multiuse cleaner (MC – 1), respectively. These values were observed 3.5 hours after the cleaning  
718 was finished. For the kitchen cleaner KC – 2, the concentration of formaldehyde reached 6 ppb at  
719 0.8 hours and then remained constant for at least 3.5 hours after the product application. These  
720 observations suggest that even after 3.5 h, the emission source of formaldehyde was not  
721 exhausted, reflecting delayed emission kinetics that may not solely be related to a primary  
722 release from the cleaning product itself. In agreement with our findings, (CSTB, 2006); Solal et  
723 al. (2014) assessed the emissions of formaldehyde from 35 consumer products in different  
724 categories applied under realistic conditions in the experimental house MARIA. Among the  
725 evaluated products, the uses of (i) 2 vacuum fresheners, (ii) 2 carpet cleaners, (iii) 3 toilet  
726 cleaners, (iv) 4 glass cleaners and (v) 2 furniture polishes were associated with increases in the  
727 formaldehyde concentration in the experimental house. The observed concentrations were  
728 described by the same two phases shown in Fig. 8a: (i) a sharp increase in the HCHO  
729 concentration confirming the rapid transfer of formaldehyde from the product to the gas phase  
730 and (ii) a slower increase or steady state. The maximum concentrations that arise from the



731 emission were 6 to 16 ppb, depending on the category of product applied. These values were  
732 observed at 120 minutes after the cleaning was completed.

733



734 **Fig. 8.** (a) Temporal evolution of the concentration of formaldehyde (ppb) from the use of three  
735 cleaning products: (i) surface cleaner (SC-1), (ii) kitchen cleaner (KC-1) and (iii) multiuse  
736 cleaner (MC-1) ( $T = 23\text{ }^{\circ}\text{C}$ ,  $\text{RH} = 50\%$ ,  $\text{AER} = 0.3\text{ h}^{-1}$ ). (b) Temporal evolution of the *air*  
737 *exchange-corrected* concentration of formaldehyde (ppb) as a function of time during cleaning  
738 with the three cleaners: (i) SC - 1, (ii) KC - 2, and (iii) MC - 1 ( $T = 23\text{ }^{\circ}\text{C}$ ,  $\text{RH} = 50\%$ ,  $\text{AER} =$   
739  $0.3\text{ h}^{-1}$ ).

740

741 To confirm these observations, the emission profile was corrected by the air exchange in  
742 the experimental chamber, i.e.,  $k_{\text{AER}}$  of  $0.3\text{ h}^{-1}$ . The corrected profile is presented in Fig. 8b,  
743 which depicts the temporal evolution of the concentration of formaldehyde that would have been  
744 monitored if no air exchange occurred in the emission test chamber. The concentration variation  
745 resulted from only the transfer of formaldehyde to the gas phase and the possible sorption on the  
746 inner walls of the experimental chamber. However, the mass emission rate of formaldehyde

747 cannot be calculated by the estimation method in section 3.4 since the emission source could not  
748 be assumed to be exhausted and the deposition rate ( $k_D$ ) could not be determined. As shown in  
749 Fig. 8b, the corrected profile of formaldehyde emission from SC – 1, MC – 1 and KC – 2 was  
750 characterized by two main phases: (i) a primary increase in the concentration, suggesting a  
751 release linked to a primary emission of formaldehyde potentially contained in the cleaning  
752 product, and (ii) a linear increase in the concentration of formaldehyde. The slope of the linear  
753 relationship of the corrected formaldehyde concentration varied depending on the cleaning  
754 product. Therefore, the temporal evolution of the corrected formaldehyde concentration,  
755 presented in Fig. 8b, did not correspond to a transient emission profile but suggested the  
756 presence of formaldehyde releasers in the cleaning product formulation, in which case, the  
757 concentration of formaldehyde might be associated with secondary emission sources.

758         The specific concentration dynamics associated with the emission of formaldehyde are  
759 suggested to be related to two mechanisms: (i) direct (or primary) emission of formaldehyde  
760 contained in the cleaning product and (ii) emission of formaldehyde from formaldehyde-  
761 releasing molecules present in the cleaning product formulations (Pastor-Nieto et al., 2017).  
762 Formaldehyde releasers are defined as chemical compounds that decompose to release  
763 formaldehyde when dissolved in aqueous solvents (De Groot et al., 2009; Flyvholm and  
764 Andersen, 1993; Kajimura et al., 2008). This process is characterized by an in situ degradation of  
765 non-formaldehyde-containing components, i.e., the self-oxidation of ethoxylated alcohols.  
766 Generally, these chemicals are used in consumer products as preservatives, antiseptics, and/or for  
767 enhancing their disinfectant performance. The concentration of formaldehyde or formaldehyde-  
768 releasing compounds added in product formulations might depend on their use purpose and  
769 manufacturer preferences. According to the National Database for Products and Compositions in

770 France (BNPC), formaldehyde releasers are included in the formulations of 78 % of household  
771 products as preservative agents, corresponding to a mass concentration ranging from 0.2 % to 0.3  
772 % w/w (Affset, 2009).

773 De Groot et al. (2009) assessed formaldehyde and formaldehyde releasers contained in  
774 consumer products in various categories by reviewing the Danish Product Register Database  
775 (*PROBAS*). His findings reveal that the most important product categories containing  
776 formaldehyde or formaldehyde releaser are (i) biocides or pesticides; (ii) paints, lacquers and  
777 varnishes; and (iii) cleaning and washing agents. In the cleaning and washing agents, 9 different  
778 formaldehyde-releasing compounds were identified. Among these chemicals, Bronopol<sup>®</sup> (2-  
779 *brono-2-nitropropane-1,3-diol*) was the most frequently used formaldehyde releaser, being  
780 detected in 124 out of 275 cleaning products or washing agents. However, the authors indicated  
781 that a total of 19 out of the 42 detected formaldehyde-releasing compounds were not found in  
782 *PROBAS*. Similarly, the BNPC in France reported the presence of formaldehyde releasers in 236  
783 out of 692 cleaning products on the European market (Affset, 2009). Additionally, the BNPC  
784 published and identified a list of 24 compounds confirmed as formaldehyde releasers, including  
785 Bronopol<sup>®</sup> and Methenamine as the most frequently used among household products. Kajimura  
786 et al. (2008) investigated the formation of HCHO from a common formaldehyde-releasing  
787 compound known as Bronopol<sup>®</sup> from a homemade cosmetic product prepared with 0.1 % w/v of  
788 this molecule. This study aimed to correlate the presence of Bronopol<sup>®</sup> and the respective  
789 formation of formaldehyde by headspace analysis. Their results verified an increase in  
790 formaldehyde concentration over time, reaching 20 ppm after 10 days, and this level was  
791 observed to be constant over 50 days. Note that this concentration cannot be compared to our  
792 results because of differences in the experimental protocol and approach.

793           Regarding the three cleaning products evaluated in this study, the presence of Bronopol®  
794 was listed by manufacturers for only the multiuse cleaner MC – 1. Its presence may explain the  
795 unique formaldehyde emission profile observed for that product. However, according to  
796 European legislation for the cleaning product industry, numerous formaldehyde releasers are not  
797 required to be included in the product ingredient list. With this lack of information, the  
798 correlation between the formaldehyde emission profile observed for the tested cleaning products  
799 and the presence of formaldehyde releasers in their composition is suggested but has not been  
800 confirmed.

801           Therefore, the use of natural cleaning products might generate a continuously increasing  
802 indoor formaldehyde concentration, in which the maximum emitted levels might remain in the  
803 confined environment for several hours after the cleaning is completed. Additionally,  
804 formaldehyde releasers included in consumer products represent a hidden source of  
805 formaldehyde, of which consumers might not even be aware, extending its impact on IAQ by  
806 several tens of ppb for several hours after household activity is completed.

807

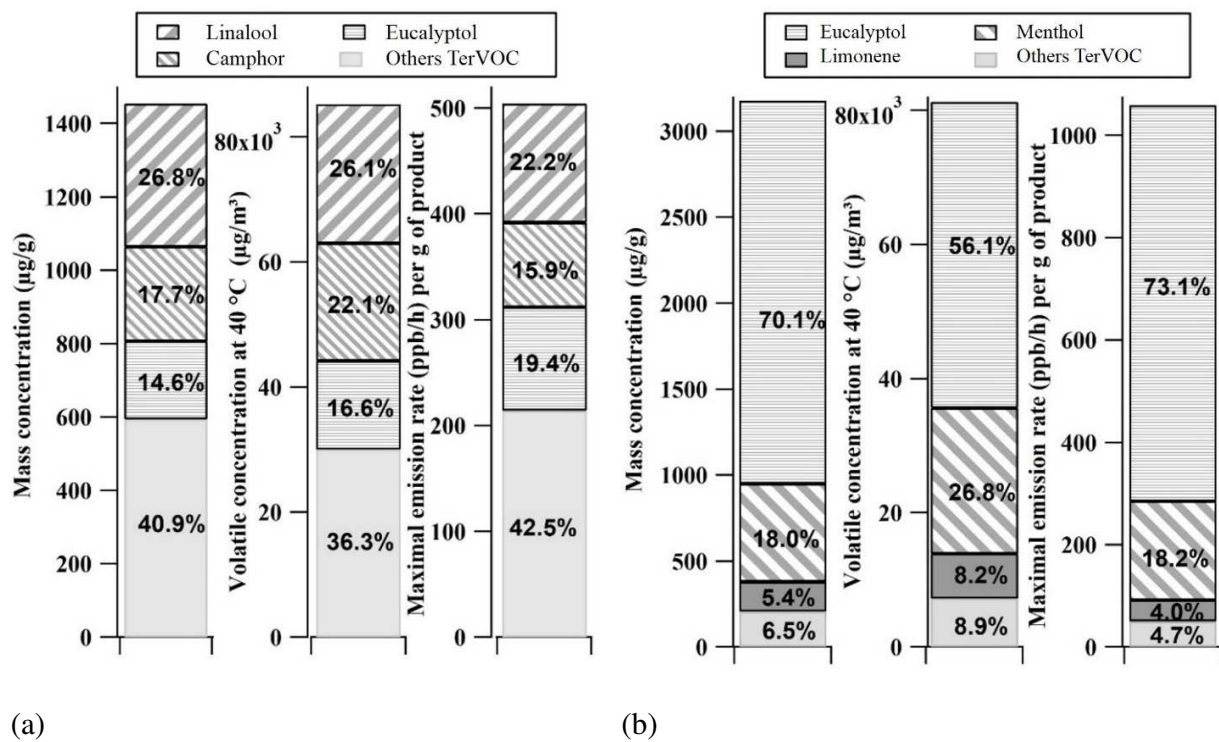
### 808 ***3.6 Wrap-up of the terpene emissions from cleaning products: from their liquid composition to*** 809 ***their mass emission rates***

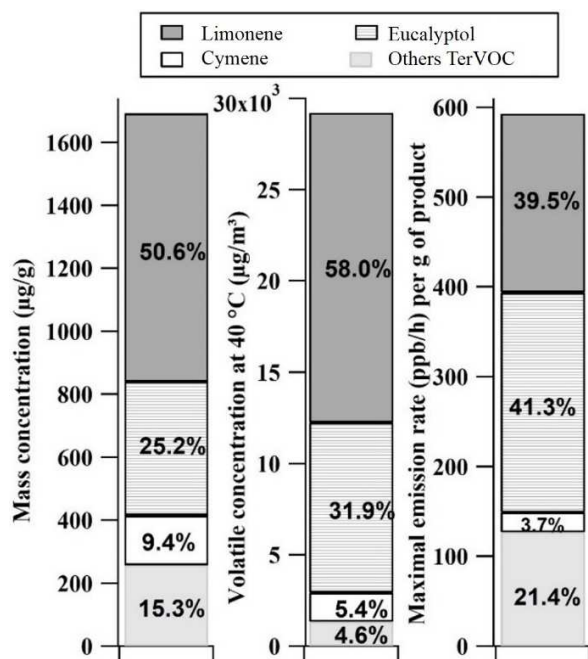
810 In this work, the TerVOC emissions from the use of 3 cleaners were investigated by comparing  
811 different scales, including their liquid composition, their gas-transferred concentration and their  
812 emission under realistic use patterns. This innovative methodology allowed the investigation of  
813 the emission of fragrance molecules at different scales to evaluate the impact on IAQ through an  
814 integrated approach, achieving an accurate assessment of the mass emission rates. These

815 estimated mass emission rates could be further implemented for the estimation of human  
 816 exposure to these chemicals and to the definition of risk scenarios.

817 Fig. 9 shows the relative abundances expressed as percentages of the predominant  
 818 TerVOCs and as their respective absolute scales for (i) the mass concentration detected in the  
 819 liquid form ( $\mu\text{g/g}$  of product), (ii) the volatile fraction (gas-transferred concentration) associated  
 820 with the micro-chamber testing ( $\mu\text{g/m}^3$ ), and (iii) the maximum emission rates per individual  
 821 terpene (ppb/h per g of product) associated with the use of (a) the surface cleaner SC – 1, (b) the  
 822 kitchen cleaner KC – 2, and (c) the multiuse cleaner MC – 1.

823





**Fig. 9.** Comparison of the relative abundances in the mass concentration ( $\mu\text{g/g}$ ) in the liquid phase, the volatile concentration ( $\mu\text{g/m}^3$ ) ( $T = 40\text{ }^\circ\text{C}$ , dry air flow = 50 mL/min, micro-chamber volume = 44 mL) and the maximum emission rate per gram of cleaning product ( $T = 23\text{ }^\circ\text{C}$ , RH = 50 %, air renewal rate =  $0.3\text{ h}^{-1}$ , chamber volume =  $1\text{ m}^3$ ) for (a) the surface cleaner SC – 1, (b) the kitchen cleaner KC – 2, and (c) the multiuse cleaner MC – 1.

(c)

824 In terms of the absolute values, written in bold in Fig. 9, no correlation was found  
 825 between them. As mentioned in section 3.2, the maximum emission rate of terpene molecules  
 826 from the use of essential-oil-based cleaning products cannot be directly predicted from their  
 827 content in the liquid form or from micro-chamber testing. Micro-chamber results can be used to  
 828 describe key general trends of the predominant emitted terpenes but should not be considered for  
 829 realistic emission assessment. Moreover, the relative distributions between terpenes for the liquid  
 830 content and for the maximum emission rate are much closer rather than one for the gas-  
 831 transferred concentration. That can be explained by the fact that micro-chamber experiments  
 832 were conducted at a temperature of  $40\text{ }^\circ\text{C}$ , enhancing the transfer from the liquid to the gas  
 833 phase.  
 834

835 In regard to the behavior of specific compounds, such as eucalyptol and limonene, two  
836 species with similar VPs (260 and 219 Pa, respectively), substantial differences were observed.  
837 In all the investigated cleaning products, eucalyptol evidence higher proportions in the maximum  
838 mass emission rate if compared to its relative abundance in the liquid form. This observation  
839 confirms the ability of eucalyptol to be transferred from the liquid to the gas phase, irrespective  
840 of the solvent matrix of the cleaner. In contrast, for a given cleaning product, limonene had (i) a  
841 lower relative abundance at the maximum mass emission rate than in the liquid phase and (ii) a  
842 higher relative abundance in the volatile fraction than in the liquid form. These observations  
843 suggest that the emission of limonene might be more impacted by the solvent matrix in the  
844 cleaning product than by its volatility (VP = 219 Pa), and therefore, its mass transfer might be  
845 delayed due to chemical affinities to other compounds.

846

#### 847 **4. CONCLUSIONS AND PERSPECTIVES**

848 This study has shown that the largest contributors of terpenes to indoor air are not only  
849 recognized, regulated and controlled sources, namely, building materials, but also “green”  
850 household products, which should be seriously considered as versatile and high-impact sources.  
851 These fragrance chemicals classified as allergens responsible for skin irritation, allergic rhinitis,  
852 and asthma are primarily associated with the use of cleaning products (Wolkoff and Nielsen,  
853 2017). Essential-oil-based household products might release concentrations of several tens to  
854 hundreds of ppb TerVOCs, exceeding the exposure limits established by the European Union and  
855 the United States (Dimitroulopoulou et al., 2015; Kirchner et al., 2001; World Health  
856 Organisation, 2010). Regarding formaldehyde emissions from the investigated cleaning products,  
857 this study has confirmed that these products could represent a hidden source of formaldehyde in

858 confined environments. Indeed, consumers might increase the formaldehyde concentration  
859 indoors by several ppb without being aware of it due to the presence of non-regulated  
860 formaldehyde-releasing compounds contained in these types of products.

861         Several key factors were confirmed to drive the mass transfer from the liquid to the gas  
862 phase of terpene molecules contained in essential-oil-based cleaning products: (i) the mass  
863 concentration of individual terpenes in the liquid phase, since a correlation between the major  
864 contained and the predominantly emitted terpenes was observed for all the tested cleaning  
865 products; (ii) the solvent matrix included in the cleaning formulation, which may generate  
866 chemical affinities between terpenes and the cleaner constituents, impacting the emission  
867 dynamics; and (iii) the volatility of the individual terpene molecules.

868         Micro-chamber testing cannot replace standard emission test chambers but is a  
869 complementary tool that allows evaluation of the gas-transferred concentrations and rapid  
870 screening of the potentially released TerVOCs from essential-oil-based household products prior  
871 to a detailed product emissions characterization. Micro-chamber experiments need to be  
872 accompanied by an evaluation of the effective emissions under realistic conditions in a test  
873 chamber to accurately estimate the human exposure to cleaning product constituents under  
874 recommend application scenarios.

875         While this study aimed to implement realistic scenarios, the 1 m<sup>3</sup> chamber imposes  
876 limitations regarding the application process. Due to space limitations, real consumer use  
877 patterns while performing a cleaning activity could not be completely reproduced. Without being  
878 wiped, trigger spray products were directly sprayed in the chamber and dispersed by droplets  
879 onto the surface, and liquid cleaning products were drizzled on the surface placed at the center of



880 the chamber. Therefore, further assessments of TerVOC emissions from essential-oil-based  
881 cleaning products under real consumer use patterns in a full-scale room are highly recommended.

882

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897

### 898 **DECLARATIONS OF INTEREST**

899 The authors declare that they have no conflicts of interest.

900

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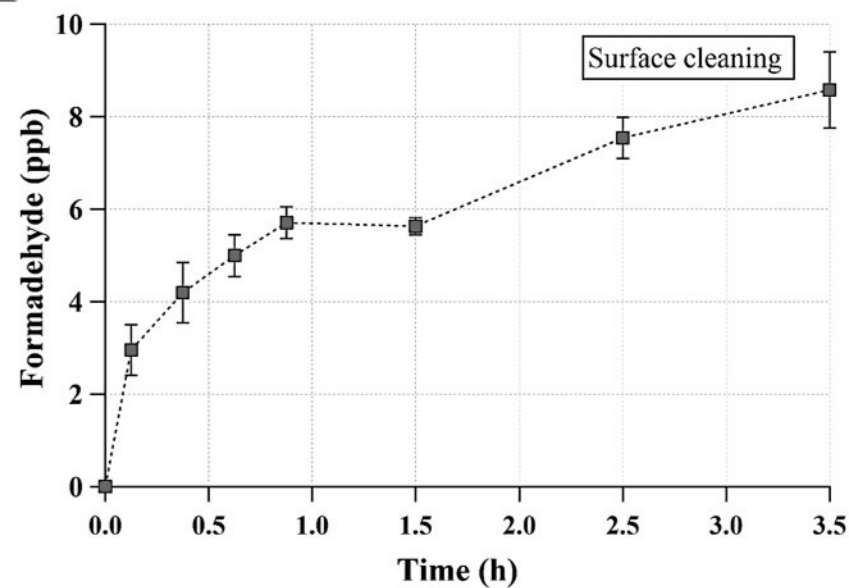
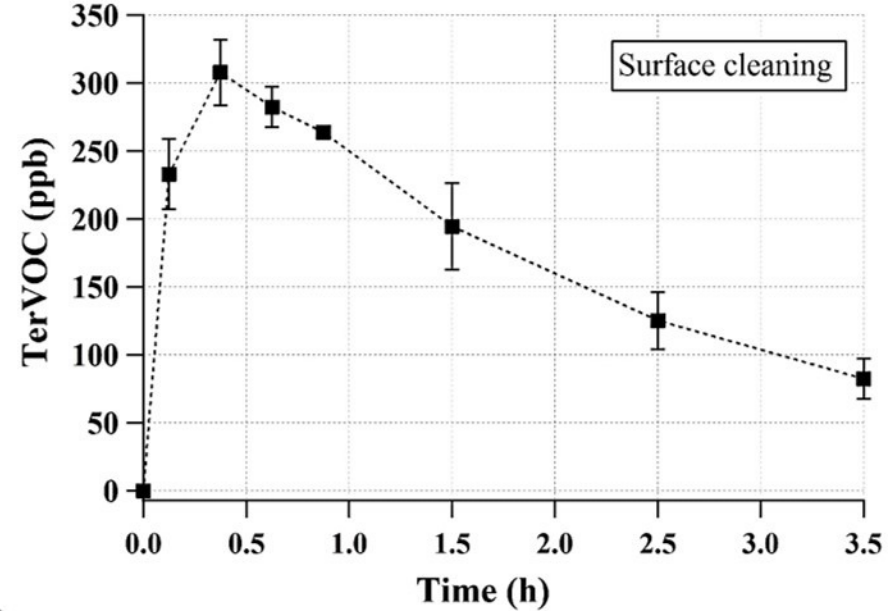
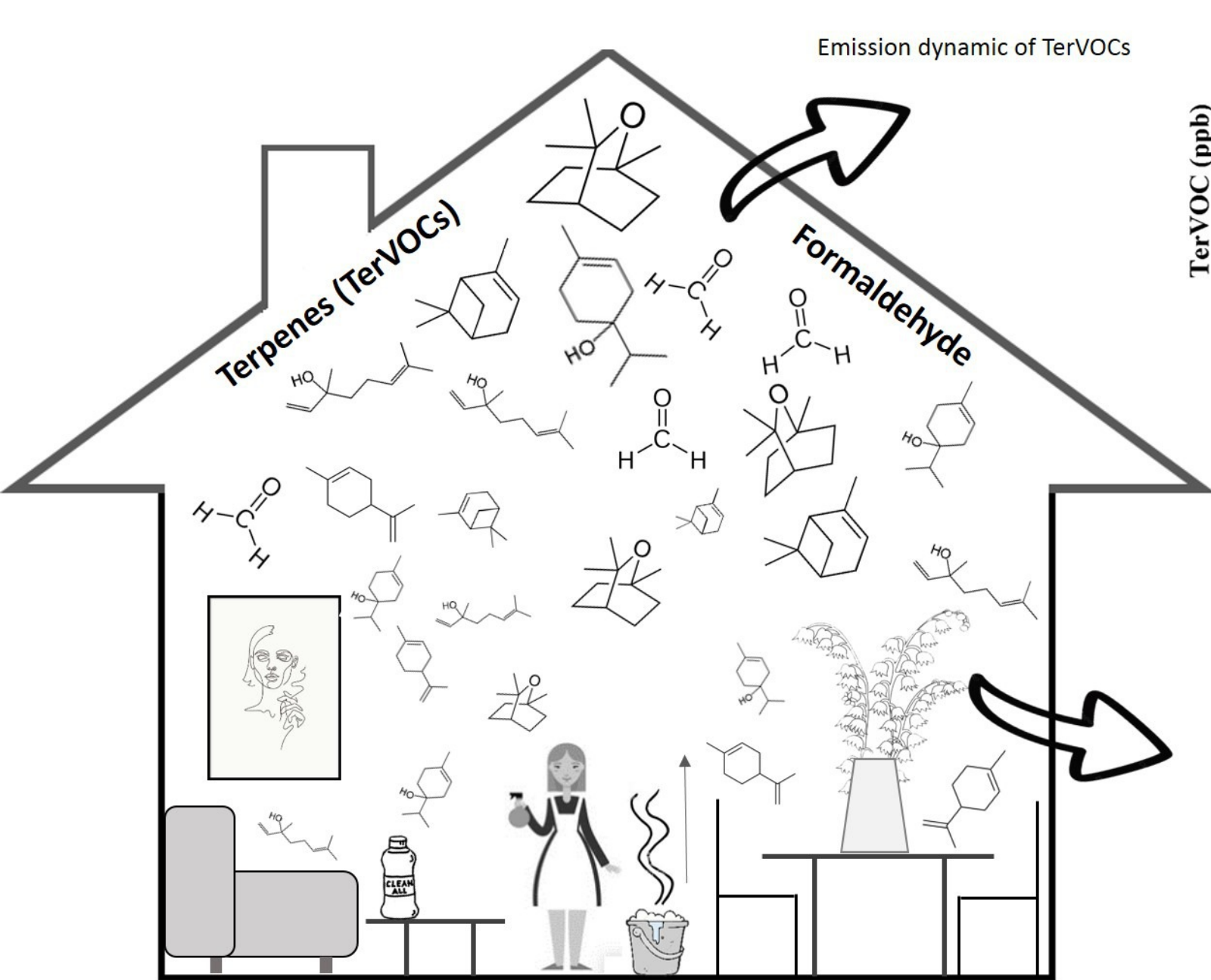
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**Emission dynamic of Formaldehyde**