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1 Indoor use of essential oils: *Emission rates,*
2 *exposure time and impact on air quality*
3

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14 **Abstract**

15 Essential-oils have attracted increasing interest due to their performance as inhibitors of
16 the metabolic functions of microorganisms. They are widely promoted as easy-to-use compounds
17 to improve indoor air quality and are associated with purifying actions. This study aims to assess
18 the emissions of molecules contained in essential-oils in confined environments by employing
19 different diffusion mechanisms under realistic conditions. Terpenes and carbonyl compounds are
20 the typical identified and quantified compounds emitted from the tea tree essential-oil.
21 Contrasted concentration levels and kinetic parameters are evidenced depending on the
22 mechanism of diffusion, and the concentration levels can exceed the recommended critical
23 exposure level by one order of magnitude. Additionally, the relative contributions of individual
24 terpenes in the gas phase vary throughout the diffusion process for all the investigated diffusers.
25 To assess the duration of the impact of essential-oil diffusion on indoor air quality, the mass
26 emission rates of individual terpenes are estimated. This study shows that, depending on the
27 diffusion mechanism, the impact of essential-oil diffusion in confined environments varies from
28 5 hours to 60 days. The proposed experimental approach and the results provided offer the first
29 insights into the definition of risk scenarios and human exposure to essential-oils in indoor
30 environments.

31

32 **Keywords:** Essential oils; Indoor air; Indoor diffusion; Emission; Terpenes

33 **Abbreviations**

34 **TerVOCs** Terpenic volatile organic compounds

35 **AER** Air exchange rate

36 **CEL** Critical exposure limits

37 **1. Introduction**

38

39 The efforts of the scientific community to address indoor air quality challenges have
40 increased considerably in the last decade, and society has become aware of the health risks
41 related to human contact with hazardous substances in confined environments. Promoted as air
42 “*cleaners*” and “*purifiers*” due to their acknowledged antibacterial, antifungal, antiviral and
43 sedative properties, essential oils have experienced an upsurge as easy-to-implement products to
44 improve indoor air quality. However, their widespread use and positive perception do not rule
45 out any consequences on indoor gas pollutant levels. Therefore, detailed evaluations of the
46 corresponding emissions under realistic conditions must be undertaken. [1]–[3]

47

48 Essential oils are extracted from plants by water vapor distillation, dry distillation or
49 mechanical extraction methods that do not involve temperature changes. [4] These oils usually
50 contain more than 100 different chemical substances; most of these substances are odorants and
51 mainly belong to the terpene chemical family, such as monoterpenes, sesquiterpenes, terpene
52 alcohols and terpenoids – hereinafter referred to as *TerVOCs*. [5], [6] An essential oil is
53 generally characterized by major compounds with specific relative abundances that provide its
54 typical odor. [7] Nonetheless, the proportions of *TerVOCs* in essential oils might vary slightly
55 depending on (i) the species of the plant, (ii) the place of growth, (iii) the environmental
56 conditions along the growth process and (iv) parameters set during the extraction process such as
57 pressure. [5], [6], [8]

58

59 Depending on their composition, essential oils can inhibit the metabolic functions of
60 microorganisms. Indeed, Inouye et al. [9]–[11] exhibited the antimicrobial action of essential oils

61 by gaseous contact. The results suggest that vapor levels of 0.1 – 0.9 mg/L in air may suppress
62 the growth of the bacterial pathogens of respiratory infection. Cinnamon bark, lemongrass and
63 thyme oils are evidenced as the most effective for this purpose. Likewise, tea tree oil (*Melaleuca*
64 *alternifolia*) has been widely investigated for its acknowledged antimicrobial, anti-inflammatory
65 and antiseptic properties. [12]–[15] Usachev et al. [16] reported a strong antiviral efficiency of
66 the vapors of tea tree and eucalyptus oils against two different viruses, highlighting the use of
67 essential oils as natural disinfectants for the further development of air treatment technologies
68 and indoor air quality improvement [17]. Tea tree oil is also commonly incorporated into
69 household products, but to our knowledge, no scientific data have shown that this oil has air
70 sanitation properties related to the improvement of indoor air quality from a chemical point of
71 view.

72 Terpene hydrocarbons, presenting low molecular weights and high pressure vapors, are
73 highly volatile molecules that have boiling points ranging from 150 to 260 °C. [6] Monoterpenes
74 result from the condensation of a penta-carbonate unit with two unsaturated bonds, isoprene (2-
75 methyl-1, 3-butadiene). They are composed of 10 carbon atoms and 16 hydrogen atoms that can
76 be linearly or cyclically arranged according to different isomers. These species might have
77 various degrees of unsaturation, leading to highly reactive sites in their structures. [6], [18], [19]
78 In that regard, terpenes are highly reactive towards major oxidants such as ozone, hydroxyl
79 radicals (HO°) and nitrate radicals and are the most common initiators for gas phase oxidation
80 reactions in indoor and outdoor environments. [20] Consequently, the use of essential oil
81 diffusers in confined environments may contribute to worsening indoor air quality related to the
82 emissions of primary VOCs and the potential formation of secondary products, i.e., gas and

83 particulate byproducts. In indoor environments, primary VOC emissions must be addressed first
84 to determine the contribution of these sources to indoor air quality.

85 Although these diverse biological benefits have been recognized related to the use of
86 essential oils, several risks associated with their use in indoor environments are still questioned.

87 ***Can essential oils be considered a healthy remediation practice for facing current indoor air***
88 ***problems?*** The lack of baseline information about the release of hazardous fragrance molecules
89 during the dissemination of essential oils in confined environments motivates the present work.
90 To that end, the emission dynamics of TerVOCs related to tea tree oil diffusion were investigated
91 using three different and widespread diffusers. Then, the effects of essential oil diffusion on
92 indoor air quality are discussed in terms of diffusion mechanisms, emission rates and duration of
93 impact on indoor air.

94

95 **2. Materials and methods**

96

97 ***2.1. Selection of an essential oil and diffusers of interest***

98

99 ***2.1.1. Essential oil***

100

101 Based on the detailed literature review recently proposed by Angulo Milhem et al. [21], a
102 benchmark analysis was performed regarding the most widespread essential oils for indoor
103 diffusion. A total of 38 essential oils claiming the ability to clean the air and/or neutralize toxins
104 were identified. Among them, tea tree oil is selected not only for its reported sanitation
105 properties but also for its extensive use and chemical composition. Interestingly, the predominant
106 terpenes contained in this tea tree essential oil are highly reactive towards indoor oxidants.

107

108 2.1.2. *Diffusers*

109

110 Along the benchmark investigation, three different and major diffusion mechanisms have
111 been identified. As a consequence, three representative diffusion devices are selected for this
112 study:

113

114 Nebulizing diffuser / This diffuser consists of a waterless diffusion device where essential oil is
115 diffused through an aerosol. Hence, an air flow is forced through a small tube, thus increasing its
116 velocity while the pressure at the exit point is reduced. This difference in pressure induces a
117 suction, causing the essential oil to rise upwards in a separate glass tube. Subsequently, a stream
118 of pressurized air contacts the oil surface and creates micro-droplets that easily evaporate.
119 Experiments conducted using this diffusion device are performed at medium nebulization
120 intensity.

121

122 Ceramic heat diffuser / This diffuser evaporates essential oil through a soft heat gain. Heating
123 resistance is maintained in a small ceramic receptacle at a constant and single temperature. In
124 this study, the selected device heats the oil to 68 ± 2 °C. The steady-state temperature is reached
125 within 30 minutes after the equipment is turned on. Moderate heating has been shown to allow
126 the evaporation of oil without impacting its chemical composition.

127

128 Capillarity diffuser / This diffuser consists of a wick-based system that combines the actions of
129 wicking and evaporating. In this diffuser, a beech wood stick is directly screwed on the essential

130 oil flask, and the top of this porous stick is exposed to the air so that the volatile liquid slowly
131 diffuses from the liquid-air interphase. The dimensions of the stick are L: 6.5 cm x D: 4 cm.

132

133 The 3 selected diffusers were purchased from environmentally friendly retail stores. Note
134 that each diffuser was operated a technical recommendations indicated on the device. The
135 selection of the presented diffuser is based on the different physical processes of these devices as
136 a representative selection of the most extensively used diffusers by consumers. Figure 1 present a
137 description schema of the selected diffusers.

138



(a)



(b)



(c)

139 **Figure 1.** Pictures of the selected diffusers: (a) nebulizing diffuser, (b) ceramic electric heat
140 diffuser, (c) capillary diffuser

141

142 **2.2. Characterization of the chemical composition of tea tree essential oil**

143

144 For the composition analysis of tea tree essential oil, three samples were diluted in
145 methanol at a concentration of 0.7 mg/mL. Then, 1 μ L of each sample was directly introduced
146 into the split/splitless injector using a 1/10 split ratio. The analysis is performed using a 7890A-
147 type instrument from Agilent Technologies equipped with a Restek Rtx®-1 (Crossbond® 100%
148 dimethyl polysiloxane) chromatographic column (105 m x 530 μ m, 3 μ m film thickness)

149 connected to two different detectors: (i) a flame ionization detector (FID) used for quantification
150 and (ii) mass spectrometry (MS), in the SCAN mode, used for identification from Agilent
151 Technologies 5975C inert MSD. Additionally, 27 high-purity standards of terpenes from Sigma-
152 Aldrich® diluted in methanol and separated into 3 distinct mixtures are used for analytical
153 development (identifying and quantitating the compounds). The typical detection limit of this
154 instrument for hydrocarbon VOCs with the abovementioned sampling conditions is 0.01 mg/mL.
155 Note that the detection limit is determined as three time the signal over noise (S/N) ratio using a
156 sample close to the detection limit of the instrument. The same method is applied to any
157 determination of the limit of detection throughout the paper.

158

159 ***2.3. Experimental chamber: simulation of a real case scenario***

160

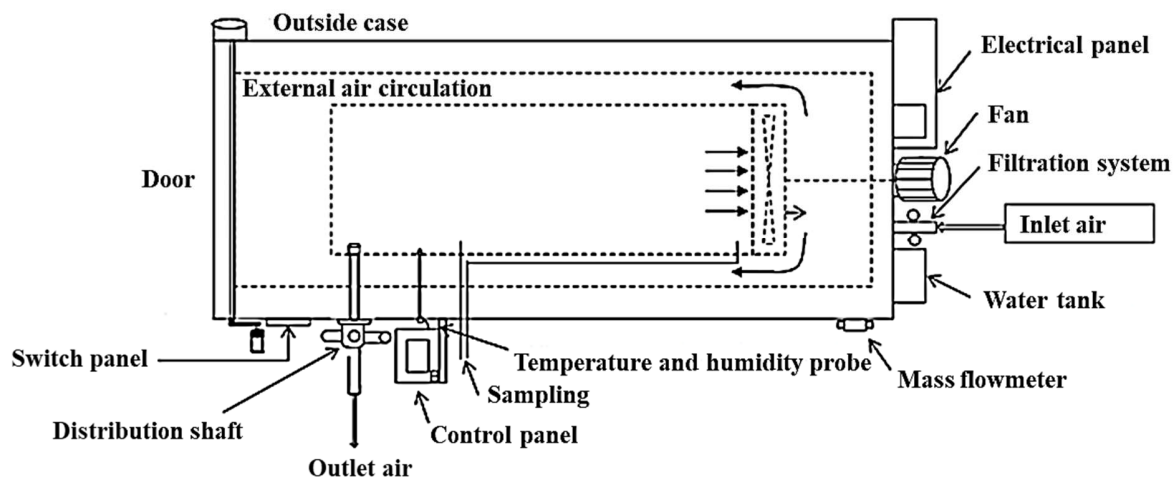
161 ***2.3.1. Emission chamber parameters***

162

163 The experiments reported in this paper are conducted in a 1 m³ experimental chamber
164 (Vötsch VCE1000 Classic) that complies with the ISO 16000-9 standards. [22] The chamber is
165 operated under a controlled temperature, humidity and air exchange rate (AER). These values are
166 set at 23 ± 1 °C, 50 ± 5 % and $0.3 \text{ h}^{-1} \pm 0.05$, respectively. The values for humidity and
167 temperature are established according to ISO 16000-9. The established AER corresponds to the
168 25th percentile reported in French dwellings by the Indoor Air Quality Observatory (OQAI). [23],
169 [24] Detailed characteristics of the experimental chamber are presented in Figure 2. Before
170 loading the test chamber with the selected product, blank measurements are performed to
171 determine background levels of TerVOCs and carbonyl compounds. Note that the mean

172 concentration level of blank measurements in the experimental chamber did not exceed
173 standardized values for background concentrations of individual VOCs.

174



175

176 **Figure 2.** General scheme of the Vötsch VCE1000 Classic experimental chamber (adapted from
177 Manoukian, 2012).

178

179 For each diffuser, a set of three experiments is performed to guarantee the repeatability of
180 the experimental protocol. Essential oil diffusers are introduced and placed in the center of the
181 chamber, and 20 drops of tree tea oil are applied according to the manufacturer's instructions for
182 each diffusion device to simulate realistic usage. Time zero of the experiment corresponds to the
183 time when (i) the nebulizing and electric diffusers are switched on and off from outside the
184 experimental chamber, which remains closed during the measurements (ii) or for a capillarity
185 diffuser, when the bottle with the diffusing stick is introduced in the center of the chamber.
186 Detailed experimental protocol parameters are described and presented in Table 1.

187

188 2.3.2. Sampling and analytical parameters

189

190 Regarding the analytical methodology, the temporal dynamics of TerVOC concentrations
 191 at the outlet of the experimental chamber are determined by offline and online samplings with
 192 different temporal resolutions. Details concerning the sampling parameter optimized for essential
 193 oil diffusion tested are gathered in Table 1.

194

195 **Table 1.** Experimental protocol and sampling parameters.

<i>Experimental Protocol</i>			
	<i>ELECTRIC DIFFUSER</i>	<i>NEBULIZING DIFFUSER</i>	<i>CAPILLARITY DIFFUSER</i>
Duration of experiment	18 h		65 h
Applied / used mass (average ± standard deviation) N=3	0.79 ± 0.02 g	0.82 ± 0.01 g	0.55 g
<i>Sampling parameters</i>			
	<i>Offline</i>		<i>Online</i>
	<i>Tenax TA® for TerVOCs</i>	<i>DNPH Cartridges for OVOCs</i>	
Sampling Flow	0.040 L/min	0.800 L/min	0.025 L/min
Sampling duration (min) and time intervals (h)	Electric and nebulizing diffusers: 0 – 2 h : 10 min sampling every 30 min 2h – 6h : 10 min sampling every hour 0 – 1 h : continuous sampling every 15 min 1 – 5 h : continuous sampling every hour 8 – 60 h : 1 hour sampling with intervals of 6, 8, and 12 hours		4 min every 15 min

196

197

198 **Offline measurements** are performed with Tenax TA® cartridges and 2, 4-
 199 dinitrophenylhydrazine (DNPH)-impregnated silica Supelco cartridges according to ISO 16000-3
 200 and 16000-6. [25], [26] Samplings are controlled by a pump connected to a mass flow controller

201 under specific flow rates and duration times specifically optimized for each type of diffuser
202 tested, as described in Table 1. Note that preliminary experiments allowed optimizing the
203 sampling flow and sampling time to avoid any breakthrough of the analytes on the cartridges.
204 The offline sampling with the two types of cartridges were performed with parallel connections
205 using separated sampling lines. These sampling lines were controlled by one pump but two
206 distinct flow controllers.

207 The sampled Tenax TA[®] cartridges are desorbed using a PerkinElmer[®] thermal
208 desorption (TD) instrument (Model: Turbo Matrix 350) coupled to a 7890A instrument from
209 Agilent Technologies. Desorbed compounds are thermally transferred under helium and
210 refocused on a Carbotrap B/C trap at 5 °C. The gas chromatographic analysis was performed
211 using a Restek Rtx[®]-1 (Crossbond[®] 100% dimethyl polysiloxane) chromatographic column (60
212 m x 320 µm, 1 µm film thickness) connected to two different detectors (i) an FID for
213 quantification and (ii) MS (Agilent Technologies 5975B inert MSD) for the identification of
214 compounds (SCAN mode). The typical detection limit of this instrument (TD-GC-FID/MS) for
215 VOCs with the abovementioned sampling conditions is 0.1 ppb. Calibration is achieved by
216 sorbent tube spiking with homemade diluted mixtures of 27 TerVOCs, individually provided by
217 Sigma-Aldrich[®].

218 Carbonyl compounds were extracted from DNPH cartridges with 3 mL acetonitrile and
219 analyzed with a Thermo Dionex Ultimate U3000. Compounds are eluted on an Acclaim RSLC
220 carbonyl column (2.1 x 150 mm) and detected by RS variable wavelength UV absorption.
221 Calibration of the carbonyls is achieved using high-purity certified standard solutions
222 (aldehyde/ketone-DNPH stock standard-13). Considering these conditions, the typical detection
223 limit for carbonyl compounds is 0.01 ppb.

224

225 **Online measurements** were performed with a compact gas chromatography system (C-
226 GC/FID) (Model: Global Analyzer Solutions CGC4) with a Restek-VMS (proprietary
227 Crossbond® phase) column (15 m x 0.32 mm ID, 1.8 µm film thickness). This system is coupled
228 to an FID for compound quantification. Additionally, this online device is equipped with an
229 automated sampling system that samples air at a flow rate of 0.025 L.min⁻¹ for 4 min every 15
230 minutes. Subsequently, analytes are refocused on a multilayer sorbent (Model: General Purpose
231 Hydrophobic from Markers Internationals®) and transferred to the column under helium at 280
232 °C. Several C-GC/FID parameters were preliminarily optimized by the injection of individual
233 TerVOCs vaporized in a 6 L canister (Model: Silonite® from Entech). The typical detection
234 limits of this instrument for TerVOCs with the abovementioned sampling conditions are 0.1 ppb.

235

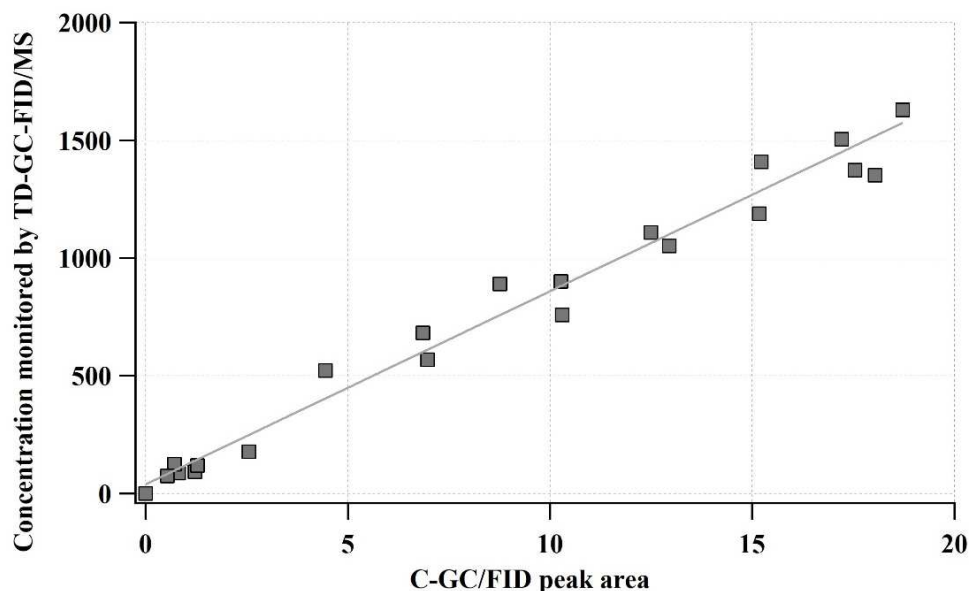
236 2.3.3. *Inter-comparison of monitoring methods*

237

238 Since no gaseous standards are available for the calibration of the considered TerVOCs
239 using C-GC/FID, a specific calibration methodology was developed. This method relies on the
240 cross-calibration of C-GC/FID with TD-GC-FID/MS. TD-GC-FID/MS is preliminarily
241 calibrated offline through Tenax TA® sorbent cartridges doped with liquid TerVOC standard
242 solutions. TerVOCs are identified using the MS detector and quantified using the FID detector.
243 A correlation between the C-GC/FID signal and the TD-GC-FID/MS quantitative response is
244 achieved through simultaneous samplings of the diffusion of terpenes in the experimental
245 chamber. For each TerVOC, the concentration monitored by the quantitative offline system is
246 plotted as a function of the peak area of the C-GC/FID signal, as reported in Figure 3. For all
247 detected TerVOCs, a linear trend is observed with correlation coefficients ranging from 21 to

248 124. The slopes of the linear regression are used for the quantitative analysis of TerVOCs by C-
249 GC/FID.

250



251

252 **Figure 3.** Evolution of the α -pinene concentration measured by offline TD-CG-FID/MS as a
253 function of the online C-GC/FID peak area of α -pinene (equation of the linear regression: $y = 85$
254 x).

255 Offline sampling is considered as the reference measurement method; however, the
256 characterization of the emission process of essential oil requires a higher temporal resolution
257 than that given by the reference method. For this reason, in the context of this paper, C-GC/FID
258 is preferred over other methods since it allows a complete quantitative screening of all TerVOCs
259 of interest every 15 minutes.

260 3. Results and discussion

261

262 3.1. Chemical composition of liquid tea tree oil

263

264 The chemical composition determined for the selected tea tree oil is reported in Table 3.
265 The detected TerVOCs are listed by decreasing molar masses, and major compounds are written
266 in bold. Note that the results show that the total mass concentration of the quantified terpene
267 molecules represents 98.8 % w/w of the injected mass. This point ensures that the developed
268 methodology allows an exhaustive quantitative and qualitative analysis of TerVOCs present in
269 tea tree oil.

270 **Table 3.** Liquid composition of the selected tea tree essential oil and physical and chemical properties of identified terpenes (vapor
 271 pressure, boiling point and molar mass), and a comparison with the literature. NB: the three predominant TerVOCs of tea tree oil are
 272 written in bold.

	Mass of individual TerVOCs (this work) Mass ± SD (mg/g)	Mass percentages per TerVOCs (this work) (% w/w)	Mass percentages from the literature [27]–[30] (% w/w)	Vapor pressure from the literature at ambient temperature (23 °C – 25 °C) [Reference] (Pa)	Boiling point (° C)	Molar mass (g / mol)
<i>Monoterpenes</i>						
α - thujene	12.0 ± 0.1	1.21	NS	NS	151	136.24
β - myrcene	11.7 ± 0.1	1.18	NS	220, 251, 268 [31]	167	136.24
α - pinene	26.9 ± 0.1	2.72	2.0 – 2.6	589, 599, 529 [32], [33]	156	136.24
α -terpinene	127.0 ± 0.3	12.85	6.0 – 10.4	222 [34]	175	136.24
β - pinene	7.1 ± 0.1	0.72	NS	400, 391 [34]–[36]	166	136.24
α – phellandrene	5.1 ± 0.2	0.52	NS	195, 220 [35]	172	136.24
limonene	10.7 ± 0.2	1.09	1.0	189, 192, 213 [35], [37]	176	136.24
γ - terpinene	226.0 ± 1.5	22.88	20.0 – 25.0	103, 145 [32]	183	136.24

α - terpinolene	34.5 ± 0.2	3.49	1.5 – 5	90, 99 [32], [35]	187	136.24
<i>Terpene alcohols</i>						
4 -terpineol	419.3 ± 1.9	42.45	40.1 – 41.0	37, 20 [35]	209	154.25
α -terpineol	31.7 ± 0.2	3.21	2.4 – 4.0	*	175	154.25
eucalyptol	36.5 ± 0.2	3.70	0 – 5.6	230, 260, 254 [37]	176	154.25
<i>Sesquiterpenes</i>						
aromadendrene	15.9 ± 0.1	1.61	NS	NS	NS	204.36
varidiflorene	12.2 ± 0.3	1.23	NS	2 [38]	NS	204.36
δ - cadinene	11.3 ± 0.2	1.14	NS	NS	NS	204.36

273 NS: Not specified in the literature; *: Vapour pressure of nearly 0 Pa;

274 Regarding the diversity of TerVOCs, the tea tree oil is mainly composed of 9
275 monoterpenes, 3 terpene alcohols, and 3 sesquiterpenes. The predominant compounds in tea tree
276 oil are 4-terpineol, γ -terpinene, α -terpinene, eucalyptol and α -terpineol, with respective mass
277 concentrations of 42.5, 22.8, 12.8, 3.70 and 3.21 % w/w. These five molecules account for 85.1
278 % w/w of the total mass concentration. Seven other TerVOCs are detected at trace
279 concentrations below 1.5 % w/w of the total mass concentration, namely, α -thujene, β -myrcene,
280 β -pinene, α -phellandrene, d-limonene, varidiflorene, and δ -cadinene. The results obtained for the
281 chemical composition of tea tree oil are in agreement with the range of mass concentrations of
282 the typical terpenes reported in the literature, as reported in Table 3. As an example, Chiu et al.
283 [28] reported the chemical composition of a commercial oil, in which 4-terpineol, γ -terpinene, α -
284 terpinene, eucalyptol and α -terpineol represent 87 % w/w of the total mass concentration (i.e.,
285 43, 19, 7, 6, and 5 % w/w, respectively). Possible variations between tea tree oil mass
286 concentrations can be related to the origin, extraction procedure and intrinsic properties of the
287 plant.

288 Among the physical and chemical properties of TerVOCs, the saturation vapor pressure
289 of pure molecules is one of the key drivers governing emissions. The volatility of an essential oil
290 is directly driven by the abilities of the respective terpenes to transfer from the liquid phase to the
291 gas phase since no solvent matrix is present in the chemical composition. The vapor pressures
292 have been experimentally determined for most TerVOCs, and the corresponding values are
293 displayed in Table 3. Highly different vapor pressures for monoterpenes have been reported,
294 with values ranging from 90 to 599 Pa. Nevertheless, concerning the predominant compound in
295 tea tree oil (4-terpineol), its vapor pressure value is among the lowest compared to that of other
296 TerVOCs, such as β -pinene and α -pinene, with respective vapor pressures of 572 and 396 Pa.

297 After the evaluation of the content of the selected essential oil, this work addressed the
298 impact of its dissemination in indoor environments through the use of the above-described
299 diffusers. Depending on the devices and the amount of essential oil in the diffuser, the temporal
300 emission dynamics might be highly different. Therefore, in this paper, the evaluated diffusers are
301 classified as (i) transient diffusers or (ii) continuous diffusers. Transient diffusers are devices in
302 which a limited mass of oil is introduced, typically from one to tens of droplets of oil. As a
303 consequence, these diffusers mostly act as a finite, short-term emission source. In contrast,
304 diffusers involving the whole flask of essential oil, which is typically several milliliters in
305 volume, are classified as continuous diffusers; they represent finite but long-term sources. For
306 clarity, the temporal dynamics of the selected diffusers are separately assessed according to this
307 classification.

308

309 **3.2. *Transient diffusers: TerVOC emissions from electric and nebulizing devices***

310

311 The temporal dynamics of the total TerVOC concentrations from the two transient
312 diffusers evaluated (electric and nebulizing devices) are presented in Figure 4. Among the 15
313 compounds identified and quantified in the liquid chemical composition of tea tree oil, only 12
314 are detected in the gas phase in the emissions by both transient diffusers. The three constituents
315 which are not detected in the gas phase are: aromadendrene, varidiflorene and δ – cadinene. It is
316 suggested that these molecules (sesquiterpenes) remain in the liquid phase, since their physical
317 and chemical properties may hinder the mass transfer of sesquiterpenes from the liquid to the gas
318 phase.

319 The detailed temporal dynamics of the four predominant TerVOCs monitored in the gas
320 phase are displayed in Figure 4, and the results of the complete gas phase composition are

321 provided in Table 4. The results presented are obtained from a set of three distinct experiments to
322 evaluate the repeatability of the experimental protocol for each diffuser. The variation
323 coefficients for the various sets of experiments range from 4.1 % to 16.5 %.

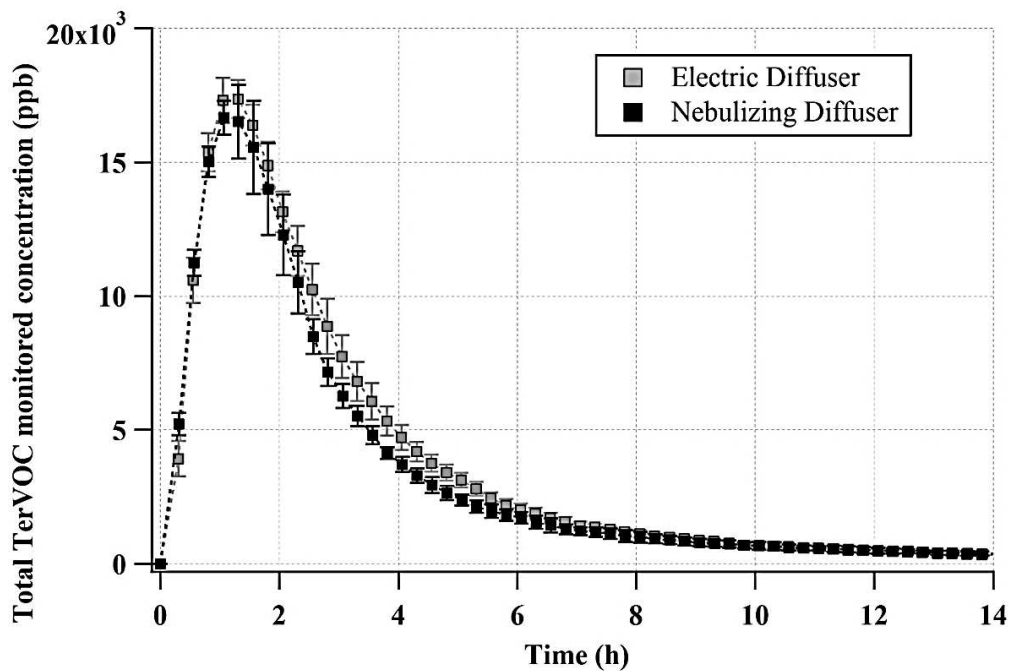
324

325 *3.2.1. Profiles of total TerVOCs*

326

327 Although electric and nebulizing diffusers are characterized by different emission
328 mechanisms, both transient devices showed analogous temporal emission dynamics regarding
329 the total released TerVOCs. The corresponding profiles are shown in Figure 4, and they are both
330 characterized by three main phases associated with the diffusion process: (i) a sudden increase in
331 the total TerVOC concentrations, confirming the rapid vaporization of terpenes from tea tree oil
332 until peak concentrations are reached, (ii) a primary decreasing trend associated with the gradual
333 exhaust of the VOC source and the removal of VOCs from the experimental chamber, and (iii) a
334 final decreasing stage associated with the evacuation of emitted terpenes by the air exchange and
335 the possible loss of these compounds on the walls.

336



337

338 **Figure 4.** Evolution of total TerVOC concentrations emitted from electric and nebulizing
 339 diffusers as a function of time ($T = 23 \text{ }^{\circ}\text{C}$, $\text{RH} = 50 \%$, air renewal rate = 0.3 h^{-1} , chamber
 340 volume = 1 m^3 , online monitoring using C-GC-FID is used for analysis).

341 Regarding the emission levels, the peak concentrations of the total TerVOCs reached
 342 $17\,350 \pm 710 \text{ ppb}$ and $16\,660 \pm 630 \text{ ppb}$ for electric and nebulizing diffusers, respectively.
 343 Considering the standard deviation values, both diffusers are characterized by equivalent
 344 maximum concentrations. Additionally, maximum concentrations are reached at approximately
 345 90 minutes after the diffusers are turned on. Interestingly, the maximum total TerVOC
 346 concentrations are higher than (i) the usual VOC concentrations in indoor air by 3 orders of
 347 magnitude and (ii) the long-term exposure limit value proposed in by the project INDEX by 2
 348 orders of magnitude. [19], [23] The total concentration of TerVOCs emitted by electric or
 349 nebulizing diffusers of essential oils is much greater than that of other indoor sources of VOCs.
 350 Transient diffusers of essential oils may appear as intense sources of VOCs in indoor
 351 environments.

352 Su et al. [18] investigated the effects of evaporating three of the best-selling essential oils,
 353 including tea tree oil, in two different indoor settings characterized by equivalent volumes of
 354 21.6 m³. In that study, environmental parameters, such as temperature and humidity, were not
 355 controlled and were not specified. The experimental procedure was based on the diffusion of 300
 356 μL of essential oils diluted in 50 mL of water using a candle diffuser. Note that the mass of tea
 357 tree oil evaporated in the study by Su et al. [18] was 3 orders of magnitude lower than the mass
 358 used in this work, and the oil was diluted in aqueous media. Studying the evaporation of tea tree
 359 oil, the authors observed a peak concentration of total TerVOCs of approximately 1400 ppb.
 360 Likewise, terpene emissions during the evaporation process mostly occurred during the first 20
 361 minutes for eucalyptus and tea tree oils, and peak concentrations were achieved after the same
 362 time span. The differences in terms of temporal profiles (levels of emitted TerVOCs and the
 363 positions of emission peaks) from one study to another may be directly related to (i) the air
 364 exchange rate and chamber volume, (ii) the mechanism of diffusion, and (iii) the quantity of
 365 diffused essential oils. Therefore, relevant comparisons between studies are allowed if the typical
 366 emission scenarios are defined. Nonetheless, irrespective of the variability of the emission
 367 protocols, the resulting total concentrations of TerVOCs largely exceed ppm levels.

368
 369 **Table 4.** Emission characteristics of the 6 major terpenes emitted by electric and nebulizing
 370 diffusion of tea tree oil (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h⁻¹, chamber volume = 1
 371 m³).

Tea tree oil <i>Transient diffusers</i>		
Maximum concentration (ppb) ± SD	Time of maximum concentration (h)	k_D Deposition rate (h⁻¹)

MAJOR TERPENES	ELECTRIC / NEBULIZING	CONCENTRATION RATIO ELECTRIC / NEBULIZING	ELECTRIC / NEBULIZING	ELECTRIC / NEBULIZING
γ -terpinene	5900 \pm 125 / 5520 \pm 330	1.07	1.31 / 1.31	0.31 / 0.31
α -terpinene	5090 \pm 200 / 4900 \pm 145	1.04	1.06 / 1.06	0.34 / 0.35
α -pinene	1600 \pm 80 / 1600 \pm 85	1.00	0.56 / 0.56	0.38 / 0.38
α -terpinolene	1530 \pm 30 / 1400 \pm 100	1.09	1.56 / 1.56	0.26 / 0.23
eucalyptol	1490 \pm 120 / 1340 \pm 150	1.11	1.31 / 1.31	0.31 / 0.31
4-terpineol	1100 \pm 20 / 800 \pm 45	1.38	5.06 / 4.82	N.D

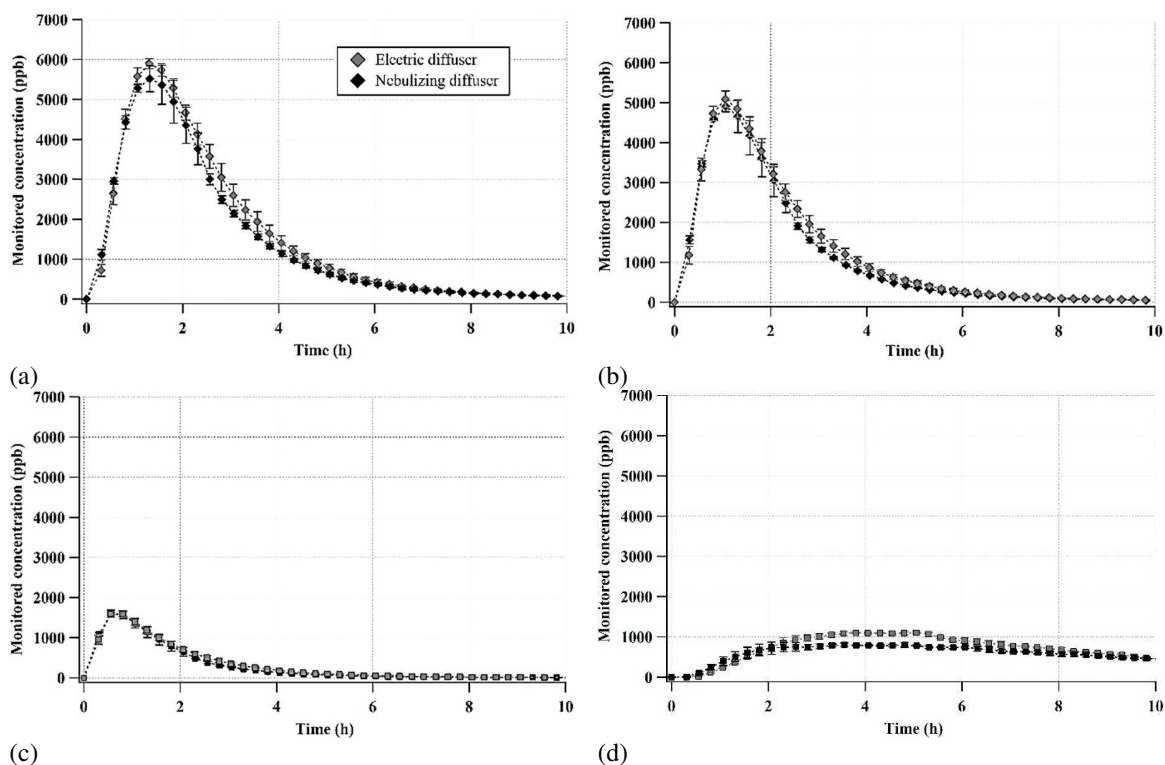
372 N.D.: Not determined

373

374 *3.2.2. Individual profiles of TerVOCs*

375

376 Beyond the global profile addressed through total TerVOC concentrations, the individual
377 emissions of 9 monoterpenes and 2 terpene alcohols were identified and quantified in the gas
378 phase. The main three predominant TerVOCs detected along the electric diffusion of tea tree oil
379 are γ -terpinene, α -terpinene, and α -pinene. Their individual temporal profiles are reported in
380 Figure 5. They are characterized by the same three phases as shown by the total TerVOC
381 concentration profile (Figure 4). Therefore, maximum concentrations can be determined for
382 electric diffusion as 5900 \pm 125 ppb for γ -terpinene, 5090 \pm 200 ppb for α -terpinene and 1600 \pm
383 80 ppb for α -pinene. The corresponding data are reported in Table 4. In the case of the
384 nebulizing diffuser, γ -terpinene, α -terpinene, and α -pinene are the major TerVOCs with typical
385 transient temporal profiles. Their maximum concentrations are within the same concentration
386 range as those with the electric diffuser, as confirmed by the concentration ratios reported in
387 Table 4.



389 **Figure 5.** Evolution of (a) γ -terpinene, (b) α -terpinene, (c) α -pinene and (d) 4-terpineol
 390 concentrations as a function of time during the diffusion of tea tree oil using an electric diffuser
 391 (grey symbols) and a nebulizing diffuser (black symbol) ($T = 23\text{ }^{\circ}\text{C}$, $\text{RH} = 50\%$, air renewal rate
 392 $= 0.3\text{ h}^{-1}$, chamber volume $= 1\text{ m}^3$, online monitoring using C-GC-FID is used for analysis).

393 Highly different emission dynamics are evidenced among individual terpenes. Comparing
 394 two molecules with distinct chemical and physical properties, such as α -pinene (Figure 5c) and
 395 4-terpineol (Figure 5d), their concentration profiles are highly different. The concentration of α -
 396 pinene is characterized by a sharp increase with a subsequent clearly marked maximum
 397 concentration at only 0.56 h, whereas the concentration of 4-terpineol remains negligible within
 398 the first minutes of diffusion and is characterized by a broad emission peak, leading to a weakly
 399 marked maximum concentration after approximately 5 h of diffusion. Additionally, for both
 400 diffusion devices, 10 hours after the emission started, the gas phase concentration of 4-terpineol

401 still represents nearly 40 % of the peak concentration, while the gas phase concentration of α -
402 pinene is completely evacuated beyond 4 hours. Consequently, 4-terpineol has particularly slow
403 emission kinetics compared to the other predominant molecules. For other major TerVOCs,
404 namely γ -terpinene, α -terpinene and α -terpinolene, analogous concentration dynamics with α -
405 pinene are evidenced. The investigation of the individual concentration profiles suggests that the
406 dynamic of the liquid-to-gas transfer is driven by (i) the intrinsic physical and chemical
407 properties of individual TerVOCs and (ii) the abundance of individual TerVOCs in the pure
408 essential oil.

409 As can be observed in Figure 5, although TerVOCs exhibit different emission profiles,
410 this is only related to the TerVOC itself and not to the diffusion mechanism. Indeed, for each
411 VOC, profiles observed for electric and nebulizing diffusers overlap. However, a slight
412 difference can be noted for the less volatile terpenes, such as 4-terpineol (Figure 5d). It appears
413 that the electric diffuser promotes the maximum concentration of low-volatility TerVOCs by 30
414 % (Table 4). This phenomenon can be associated with the possible effect of distinct temperatures
415 on terpenes with a comparatively high molar mass and low volatility.

416 In the frame of the European project Emissions, Exposure Patterns and Health Effects of
417 Consumer Products in the EU (EPHEC) [7], [39], [40], a health risk assessment methodology
418 was developed for limonene and α -pinene for the estimation of their critical exposure levels
419 (CELs) regarding short- and long-term exposures. In the EPHEC project, these values were
420 established at 810 ppb and 1620 ppb for α -pinene and limonene, respectively. Indeed, the results
421 presented in this section confirmed that the diffusion of tea tree oil through transient devices
422 might induce indoor concentration levels to become one order of magnitude higher than the
423 CEL, considering α -pinene as the reference compound.

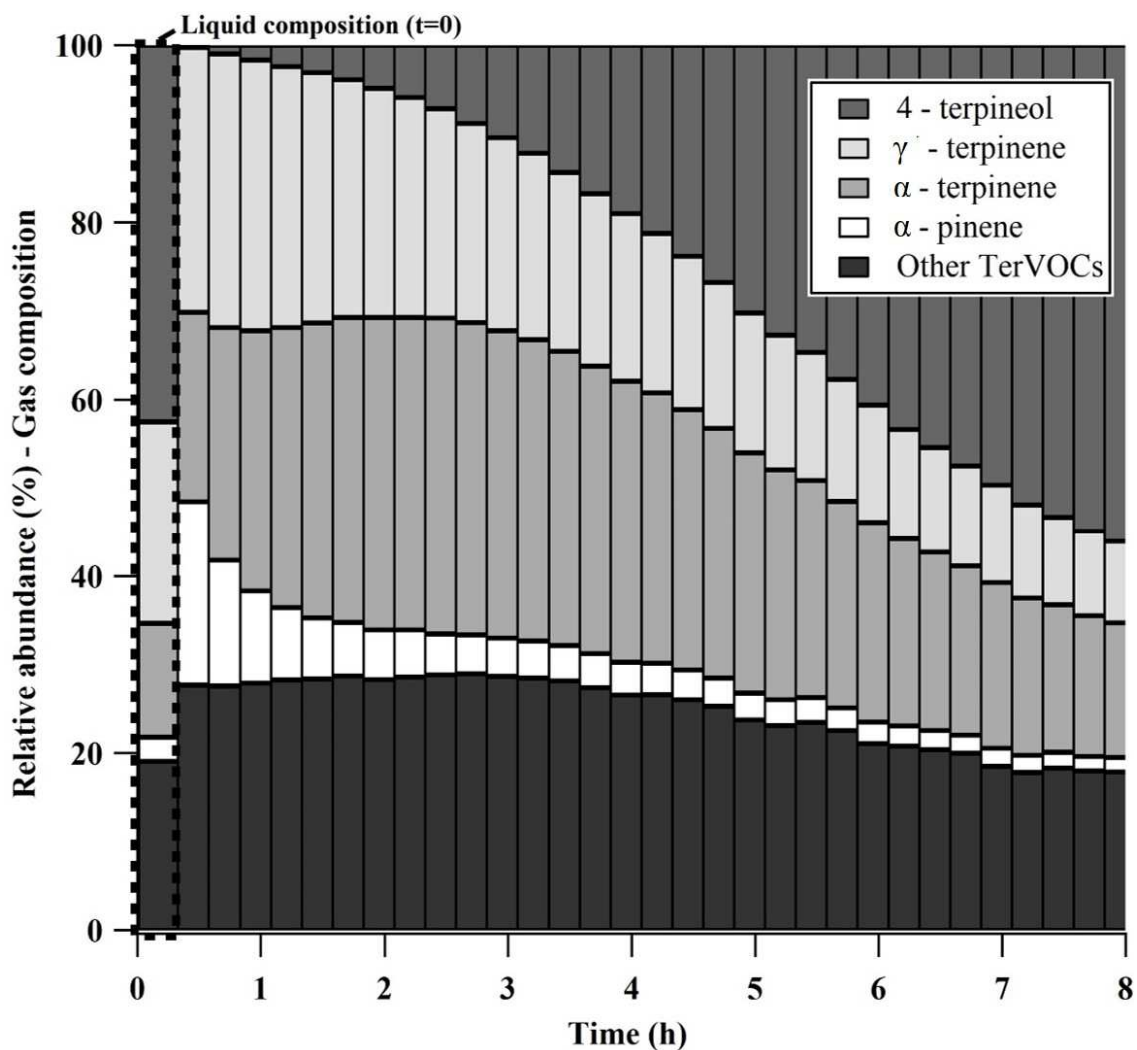
424

425 3.2.3. *Quantitative fingerprint of tea tree essential oil as it diffuses*

426

427 In this work, the fingerprint of an essential oil is defined as the contribution of each
428 terpene molecule to the TerVOC gas concentration at a specific time t . Considering that the
429 temporal profiles of individual TerVOCs are analogous for both electric and nebulizing diffusers,
430 the analysis of the fingerprint is illustrated with the results obtained only from the nebulizing
431 diffuser.

432 The diffusion through the nebulizing device initiates at $t = 0$. At this time, all individual
433 terpenes are in the liquid phase, as reported on the left side of Figure 6. In the liquid composition
434 of the tea tree oil, α -pinene is one of the minor compounds, present at 2.78 % w/w, and 4-
435 terpineol is the major compound, present at 42.5 % w/w. Nonetheless, nearly 30 minutes after
436 the diffusion process starts, the concentration of α -pinene contributes up to 20 % of the total
437 TerVOCs emitted in the gas phase (Figure 6). At the same time, 4-terpineol, characterized by a
438 lower saturation partial pressure than that of α -pinene, is still present in the liquid phase and is
439 not transferred to the gas phase. After 4 hours of diffusion, 4-terpineol contributes up to 16.7 %
440 to the TerVOCs transferred to the gas phase, while α -pinene only accounts for 3.8 % of the total
441 gas phase terpenes.



442
 443 **Figure 6.** Temporal evolutions of the relative abundances of major TerVOCs transferred to the
 444 gas phase during the diffusion of tea tree essential oil using the nebulization device. NB: the
 445 relative abundances of major TerVOCs in the liquid phase are reported at $t = 0$ ($T = 23$ °C, $RH =$
 446 50 %, air renewal rate = 0.3 h^{-1} , chamber volume = 1 m^3).

447
 448 Indeed, at $t = 4$ h, α -pinene is almost exhausted from the tea tree oil and has gradually
 449 escaped from the experimental chamber due to air renewal or deposition on inner surfaces. As a
 450 consequence, the different emission dynamics of individual TerVOCs emitted from tea tree oil

451 induce a considerable variation in the gas phase terpene composition within the diffusion time
452 span. The fingerprint of the essential oil in the gas phase varies with the emission process, as
453 evidenced in Figure 6. This phenomenon has a direct impact on (i) odor perception and (ii) the
454 exposure of individuals to terpenes while diffusing essential oils in an indoor environment.

455

456 *3.2.4. Individual profiles of oxygenated VOCs (OVOCs)*

457

458 Additionally, carbonyl compounds are monitored during every diffusion experiment.
459 Acetone, methylglyoxal, o-tolualdehyde, p-tolualdehyde, glyoxal and 2,5-dimethyl benzaldehyde
460 are identified and quantified along the diffusion of tea tree oil using an electric diffuser and a
461 nebulizing diffuser. Concerning the electric diffuser, the three predominant carbonyls monitored
462 in the gas phase are acetone, methylglyoxal, and o-tolualdehyde. Their respective maximum
463 concentrations are 840 ± 55 , 600 ± 85 , and 175 ± 10 ppb; they are observed at 1.1 h for acetone
464 and 0.6 h for methylglyoxal and o-tolualdehyde. The nebulizing device is characterized by the
465 emission of the same major carbonyls with maximum concentrations at analogous times. The
466 maximum concentration levels are on the same order of magnitude, confirming that the emission
467 characteristics of electric and nebulizing diffusers are equivalent. In the literature, Chiang et al.
468 [41] indicated that the distillation of aromatic plants could induce the generation of
469 decomposition products such as acetone, methyl alcohol, low-molecular-weight fatty acids, and
470 phenols. Likewise, the monitored aldehydes and ketones might originate from the extraction
471 process. Due to the heating system used in the electric diffuser, some OVOCs may originate
472 from a possible thermal degradation of terpenes. However, equivalent emission profiles of
473 aldehydes and ketone are evidenced irrespective of the diffusion mechanism; for example, with
474 heating (electric diffuser) or without heating (nebulization diffuser), the formation of OVOCs

475 cannot be attributed to any thermal decomposition by an electric device. Interestingly, it has been
476 evidenced in the literature that among 5 investigated essential oils, the sequence of carbonyl
477 VOC content is tea tree > lavender > rosemary > lemon = rose. [10], [11], [42]

478

479 **3.3. Determination of TerVOC emission rates from tea tree essential oil using transient** 480 **diffusers**

481

482 **3.3.1. Mass conservation equation**

483

484 According to the international standards ISO 16000-9, the emission rate of a source is
485 defined as the “*product specific rate describing the mass of volatile organic compound emitted*
486 *from a product per time at a given time from the start of the emission*”. [21] It must be
487 highlighted that determining the source emission rate is important since (i) it provides key
488 information to understand and characterize the emission process of an indoor source of a
489 pollutant, (ii) it is a representative parameter that can be extrapolated to real cases, thus allowing
490 the prediction of pollutant emissions in other scenarios, and (iii) it is required for the evaluation
491 of human exposure and indoor quality control technologies. Indoor pollutant concentrations are
492 governed by various processes, including ventilation, emission sources, and pollutant
493 transformation, such as uptake rates or chemical interactions. Therefore, the fate of pollutants
494 must be understood considering the contribution of each process distinctively. In a typical indoor
495 environment, the concentration variation of an individual VOC is driven by the mass
496 conservation equation reported in *Eq. 1*.

497

498

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

Concentration variation
Air Exchange
Pollutant source
Deposition on surfaces
Desorption from surfaces
Homogeneous reactivity
Heterogeneous reactivity

Eq. 1

499

500

501

502

503

504

In controlled environments, such as the experimental chamber used for our experiments, several processes encompassed in *Eq. 1* can be ruled out. First, the concentration of one of the main oxidants in the experimental chamber is continuously monitored during the experiments; the ozone level remains lower than the detection limit of the ozone analyzer (0.4 ppb) for all experiments, suggesting that the contribution of ozone-induced homogeneous and heterogeneous reactivities can be neglected.

505

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513

Harb et al. [43] and Haghghat and De Bellis [44] evidenced that stainless steel is the most widely used chamber material in the reviewed publications due to its inert properties. Indeed, the use of stainless steel avoids a surface reaction of deposited TerVOCs with the inner material of the chamber. This is supported by the fact that no other terpenes than those monitored in the liquid composition and no other carbonyls than that reported in the literature were detected in the gas phase of the experimental chamber. Therefore, surface reactivity on stainless steel is disregarded. Additionally, desorption phenomena are endothermic processes. Then, in a temperature-controlled environment, the sorption processes of TerVOCs are suggested to be irreversible, and desorption is considered negligible.

514

515

516

517

518

Finally, in our essential oil diffusion experiments, the resulting TerVOC concentrations in the experimental chamber are predominantly a result of (i) the air exchange, (ii) the emission rate of the pollutant sources, and (iii) the loss of pollutants on the inner walls of the chamber (k_D). Therefore, *Eq. 2* can be considered to describe the resulting pollutant concentration $[X]$ in the experimental chamber. The determination of the TerVOC emission rates from their monitored

519 concentration profiles requires separating the contribution of their respective air exchange rates
 520 and deposition rates.

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

Concentration variation
Air Exchange
Pollutant source
Deposition on surfaces

521 *Eq. 2*

522

523 Air exchange / Air exchange induces the removal of species X by the ventilation system of the
 524 chamber. It is characterized by the air exchange rate k_{AER} expressed in h^{-1} and can be calculated
 525 considering the ventilation flow and the volume of the chamber or experimentally determined
 526 using a relevant tracer gas. Based on the inlet ventilation flow of our experimental chamber, k_{AER}
 527 is set to $0.3 h^{-1}$ for all experiments.

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

Air Exchange

528 *Eq. 3*

529

530 Emission rate / The emission rate of species X is determined by its release from an emissive item
 531 per unit of time, it is describe in the Eq. 4 as $\tau(t)$. In the case of essential oil diffusion, the mass
 532 emission rate is determined using *Eq. 4*, where m_p is the mass of tea tree oil used in the diffuser
 533 expressed in g and $V_{chamber}$ corresponds to the volume of the experimental chamber in m^3 :

$$\frac{d[X]_E}{dt} = \frac{\tau(t) \times V_{chamber}}{m_p}$$

Pollutant source

534 *Eq. 4*

535

536

537 Deposition on inner surfaces of the chamber / This phenomenon corresponds to the uptake of gas
538 phase TerVOCs on the surface of the stainless steel chamber. The nonreactive uptake of
539 TerVOCs on indoor materials can be characterized by the deposition rate k_D expressed in h^{-1} . The
540 uptake is also driven by the concentration of the gas phase species X, as reported in *Eq. 5*. Note
541 that k_D depends on the nature of the material and on the VOC; it was assessed for each set of
542 experiments to provide a comprehensive evaluation of the process in the fate of emitted
543 TerVOCs and its impact on the resulting TerVOC concentrations in the gas phase.

$$\boxed{-\frac{d[X]_{Dep}}{dt} = -k_D \times [X]}$$

Deposition on
surfaces

544 *Eq. 5*

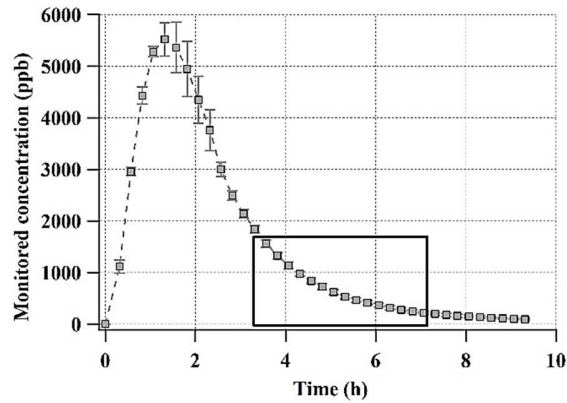
545 As finite sources of TerVOCs, transient diffusers of essential oils may become depleted.
546 Thereafter, the drivers of the TerVOC concentrations in the experimental chamber are (i) the air
547 renewal at a known decay rate (k_{AER}) and (ii) the deposition on walls at a decay rate (k_D), which
548 need to be calculated. The corresponding situation is described in *Eq. 6* by the linearized and
549 simplified form of *Eq. 2*. The air renewal rate is set to $0.3 h^{-1}$ in our experimental chamber;
550 therefore, it can be taken into account. The methodology to determine k_D can be illustrated
551 using the temporal profile of γ -terpinene emitted by the nebulization diffuser shown in Figure 7a.
552 After 3 hours of diffusion, the profile of γ -terpinene reveals that the emission peak is overcome
553 and the experimental data inside the square frame (Figure 7a) correspond to the decay of the γ -
554 terpinene concentration due to air exchange and loss on the chamber walls. Based on *Eq. 6*, this
555 reduced data series is plotted in Figure 7b as $\ln([\gamma\text{-terpinene}])$ as a function of time (h). The
556 linear form attests of the pseudo-first order decay process. The slope of the straight line
557 displayed in Figure 7b is contributed by the sum of k_{AER} and k_D . Since k_{AER} is a known

558 experimental constant, the deposition rate of γ -terpinene under our experimental conditions can
559 be determined as $k_D(\gamma\text{-terpinene}) = 0.25 \text{ h}^{-1}$.

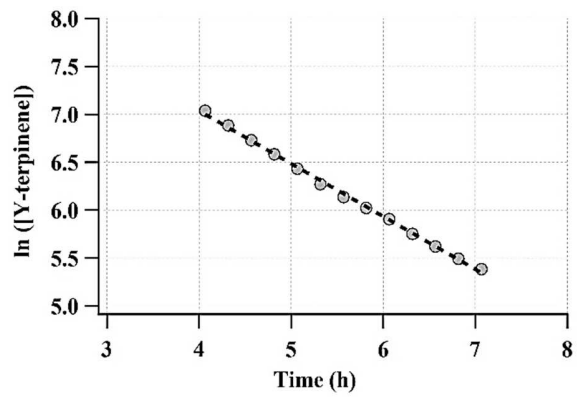
$$560 \ln(X(t)) = -(k_{AER} + k_D) \times t + A \quad (A = \text{constant}) \quad \text{Eq. 6}$$

561

562 The deposition rate k_D of the 5 major emitted TerVOCs was experimentally determined
563 with the electric diffusion and nebulizing diffusion of tea tree oil. The results are reported in
564 Table 4 for both diffusers. First, for a given terpene, the type of transient diffuser has no impact
565 on the TerVOC deposition rate. This process relies only on the VOC characteristics and on the
566 nature of the chamber walls. From one terpene to another, the deposition rates range from 0.23 to
567 0.38 h^{-1} . These values clearly support the fact that the deposition rates of TerVOCs on the
568 chamber walls must be determined to interpret the concentration profiles since they impact the
569 resulting concentrations by the same order of magnitude than the air exchange rate (0.3 h^{-1}).
570 Based on Table 4, it can be pointed out that α -pinene has the highest affinity for the chamber
571 walls. Several studies have been carried out to evaluate the interactions of terpenes with indoor
572 materials. These investigations evidenced that the intensity of the uptake process can vary
573 depending on (i) the molecular structure of the considered species, (ii) the physical and chemical
574 properties of the solid substrate and (iii) the environmental conditions, mainly temperature and
575 humidity. [45]–[49] For instance, Springs et al. [50] showed that the number of moles of terpenes
576 taken up per unit of surface area tends to decrease with relative humidity (RH), suggesting
577 competitive interactions with water molecules for uptake sites.



(a)



(b)

578 **Figure 7.** a) Evolution of γ -terpinene concentration (ppb) as a function of time during the
 579 diffusion of tea tree oil using the nebulizing diffuser ($T = 23\text{ }^{\circ}\text{C}$, $\text{RH} = 50\%$, air renewal rate =
 580 0.3 h^{-1} , chamber volume = 1 m^3 , online monitoring using C-GC-FID is used for analysis); the
 581 data series in the square frame corresponds to γ -terpinene decay beyond the depletion of its
 582 source. b) Evolution of $\ln([\gamma\text{-terpinene}])$ as a function of time (h); NB: only the data series from
 583 the square frame is plotted.

584

585 From concentration profiles to emission profiles / Finally, the mass conservation equation under
 586 our experimental conditions during essential oil emission using transient diffusers is described by
 587 Eq. 7, where $[X]$ is the concentration of species X, m_p is the applied mass of tea tree oil, V_{chamber}
 588 corresponds to the volume of the chamber (m^3), and k_D and k_{AER} are the decay rates (h^{-1}) of the
 589 species X related to air renewal and deposition, respectively.

$$\begin{array}{c}
 \boxed{\frac{d[X]}{dt}} \\
 \text{Concentration} \\
 \text{variation}
 \end{array}
 =
 \begin{array}{c}
 \boxed{\frac{\tau(t) \times V_{\text{chamber}}}{m_p}} \\
 \text{Pollutant source}
 \end{array}
 -
 \begin{array}{c}
 \boxed{(k_D + k_{AER}) \times [X]} \\
 \text{Concentration of X removed by} \\
 \text{air exchange and deposition}
 \end{array}$$

590

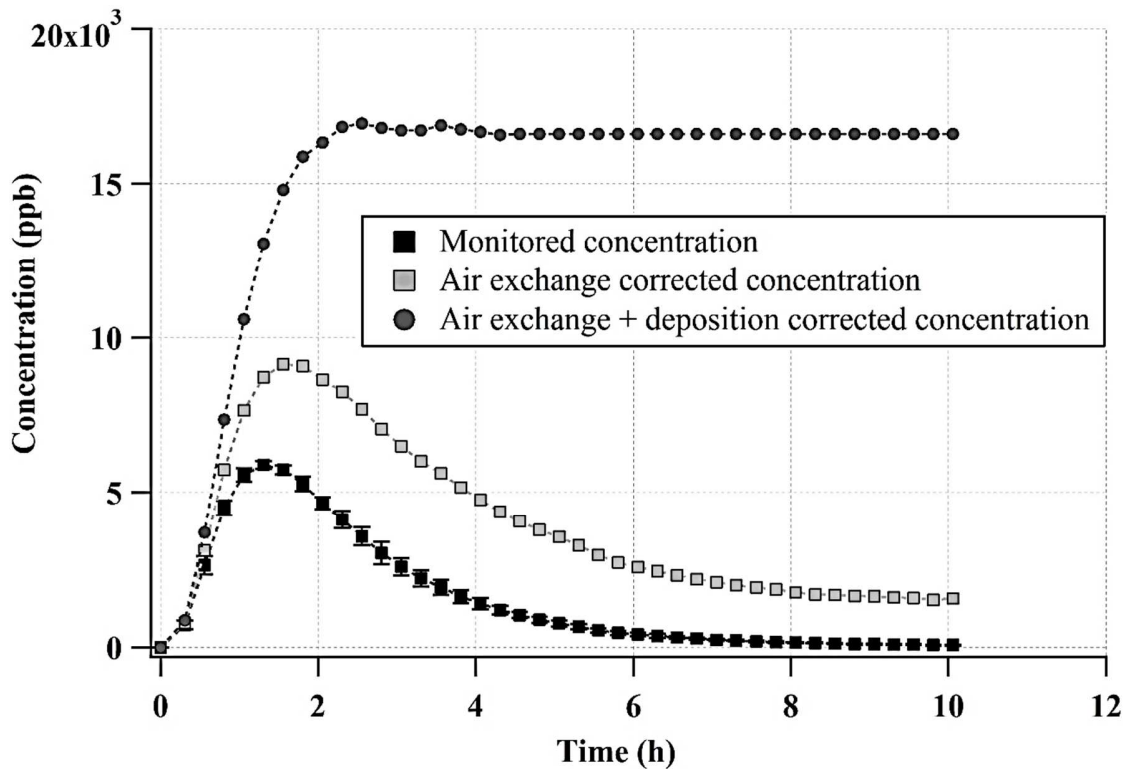
Eq. 7

591

592 Based on *Eq. 7*, the emission rate of a given TerVOC is obtained from its concentration
593 profile corrected by the air renewal rate and by the depletion rate. Figure 8 shows the temporal
594 evolution of γ -terpinene emitted from tea tree essential oil using the nebulizing diffuser. The
595 concentration of γ -terpinene directly monitored in the experimental chamber is reported using
596 black squares in Figure 8. First, this raw profile is corrected by the air renewal rate. This leads to
597 the γ -terpinene profile that would have been monitored if no VOCs were extracted by ventilation
598 from the chamber (light grey squares in Figure 8). Second, the latter profile is corrected by the
599 deposition rate of γ -terpinene. This final profile corresponds to the concentration profile of γ -
600 terpinene if no γ -terpinene were lost on the chamber walls and by air exchange (dark grey circles
601 in Figure 8). As a consequence, the resulting profile is based solely on γ -terpinene emission.
602 Therefore, the time when γ -terpinene reaches a steady state indicates the end of γ -terpinene
603 emission from the diffused oil. Moreover, this final profile can be used to calculate the emission
604 rate of γ -terpinene according to *Eq. 8*.

$$605 \tau(t) = \frac{V_{chamber}}{m_p} \times \frac{(C_{i+1} - C_i)}{(t_{i+1} - t_i)} \quad Eq. 8$$

606

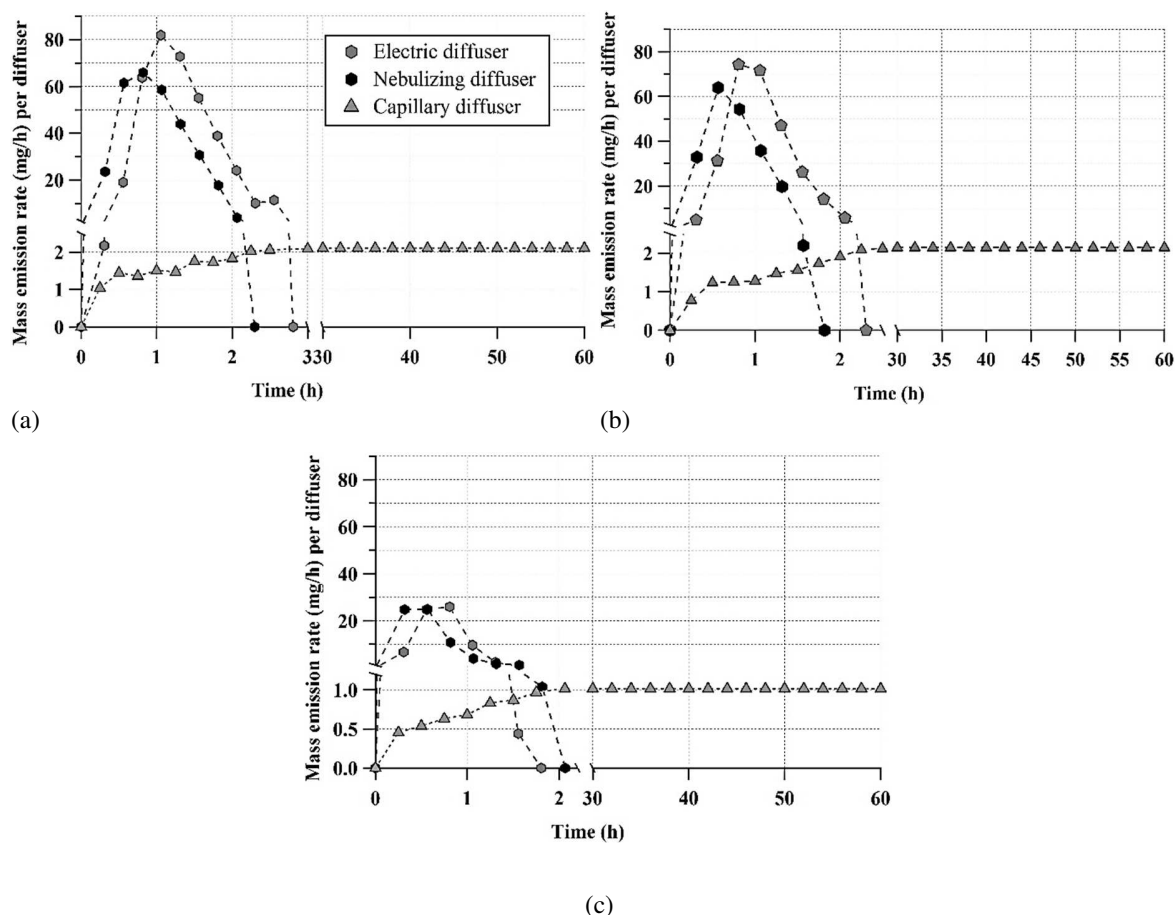


607
 608 **Figure 8.** Evolution of the γ -terpinene monitored concentration (ppb), air exchange corrected
 609 concentration (ppb) and air exchange + deposition corrected concentration (ppb) as a function of
 610 time (h) during the diffusion of tea tree oil using a nebulizing device. ($T = 23\text{ }^{\circ}\text{C}$, $\text{RH} = 50\%$, air
 611 renewal rate = 0.3 h^{-1} , chamber volume = 1 m^3).

612
 613 *3.3.2. Emission rate profiles using transient diffusers*
 614

615 Based on *Eq. 8*, the temporal evolution of the mass emission rates is calculated for each
 616 evaporation device and for each TerVOC emitted. The temporal evolution of the mass emission
 617 rates of the three major TerVOCs (γ -terpinene, α -terpinene and α -pinene) is presented in Figure
 618 9. As reported in Figure 9, transient diffusers show equivalent temporal emission rate profiles.
 619 The temporal profiles of the emission rates allow the determination of (i) the time required to
 620 reach the maximum emission rate (ranging from 0.3 to 0.8 for α -pinene, α -terpinene and γ -

621 terpene), (ii) the value of the maximum emission rate (ranging from approximately 17 to
 622 approximately 82 for α -pinene, α -terpinene and γ -terpinene), and (iii) the time the emission
 623 source is exhausted (ranging from 1.3 to 2.8 hours for α -pinene, α -terpinene and γ -terpinene).
 624



625
 626 **Figure 9.** Evolution of the mass emission rates of (a) γ -terpinene, (b) α -terpinene and (c) α -
 627 pinene as a function of time during the diffusion of tea tree oil by electric, nebulizing and
 628 capillarity diffusers ($T = 23\text{ }^{\circ}\text{C}$, $\text{RH} = 50\%$, air renewal rate = 0.3 h^{-1} , chamber volume = 1 m^3).
 629

630 Noticeably, in the case of α -pinene, the emission process is exhausted 2.2 times faster
 631 than that for γ -terpinene using the same nebulizing diffuser. These observations confirm that a

632 faster emission dynamic process characterizes monoterpenes with a comparatively higher vapor
 633 pressure and lower molar weight. Nonetheless, regardless of the transient diffuser, for a given
 634 VOC, the emission rate profile is analogous to the other profiles. Additionally, Table 5 displays
 635 the experimentally determined maximum emission rates for the 5 major released terpenes. The
 636 first two data series refer to electric and nebulizing devices, respectively. Note that the
 637 predominantly emitted molecule for each device is written in bold.

638 **Table 5.** Comparison of mass emission rates (mg/h) per gram of tea tree oil diffused through (i)
 639 an electric diffuser, (ii) a nebulizing diffuser, and (iii) a capillarity diffuser.

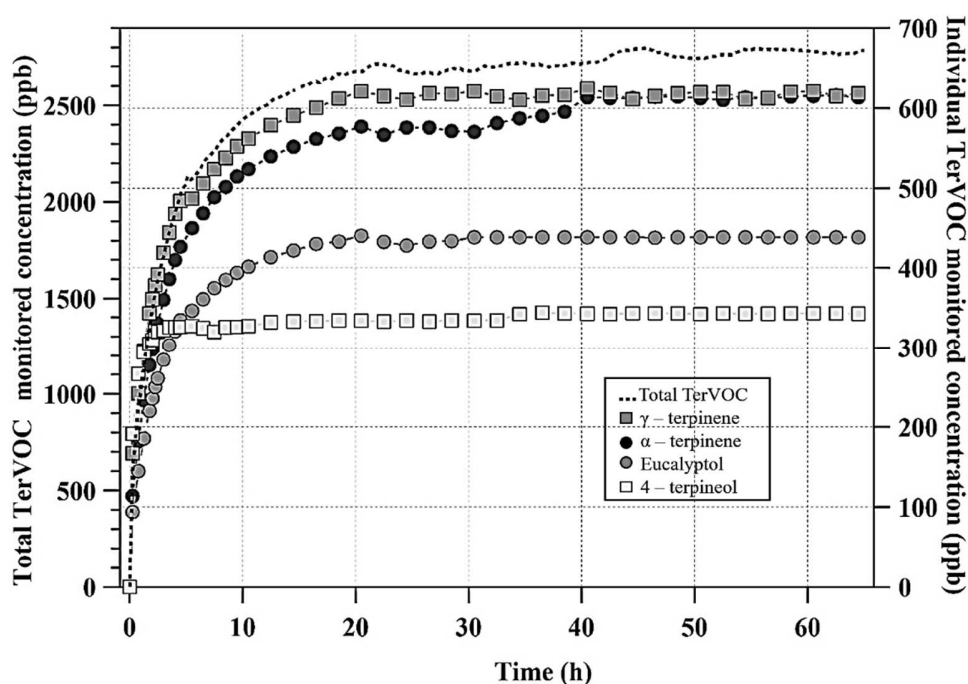
Tea tree oil - Tested diffusion devices			
Maximum mass emission rate (mg/h) per g of product			
COMPOUND	ELECTRIC DIFFUSER	NEBULIZING DIFFUSER	CAPILLARITY DIFFUSER
γ -Terpinene	81.8	66.0	3.8
α -Terpinene	74.3	64.0	3.9
α -Pinene	26.0	25.0	1.8
α -Terpinolene	19.0	16.4	3.1
Eucalyptol	20.7	17.3	1.0

640
 641 In the discussion, a complete assessment of the diffusion of tea tree oil by transient
 642 diffusers in a confined environment is accomplished including (i) the experimentally measured
 643 concentration profiles for the detected species, (ii) the calculation methodology for the
 644 evaluation of their mass emission rates and (ii) the quantitative fingerprint evolution of the gas
 645 phase during the diffusion of tea tree oil. In the next section, the same analysis is conducted in
 646 relation to the diffusion of essential oil by a long-term diffusion device.

647 3.4. Continuous diffuser: capillarity devices

648

649 Using a capillarity diffuser with tea tree oil in the experimental chamber, the same 12
650 terpenes (9 monoterpenes and 3 terpene alcohols) are detected. Figure 10 displays the total
651 TerVOC concentration profile as well as the concentration profiles of the four predominant
652 individual TerVOCs, namely, γ -terpinene, α -terpinene, 4-terpineol and α -pinene. Using the
653 capillary diffuser, all emission profiles, the total TerVOCs and individual TerVOCs, are
654 characterized by two main phases: (i) an increase in the gas concentration of TerVOCs and (ii) a
655 steady-state concentration regime of gas phase TerVOCs inside the experimental chamber. The
656 steady-state regimes confirm that an equilibrium is reached among (i) the emissions from the
657 diffusion device, (ii) the removal of diffused terpenes by air renewal and (iii) possible losses on
658 the inner walls of the experimental chamber.



659

660 **Figure 10.** Evolution of γ -terpinene, α -terpinene, eucalyptol, and 4-terpineol and total TerVOC
661 concentrations as a function of time during the diffusion of tea tree oil using a capillarity
662 diffuser. ($T = 23\text{ }^{\circ}\text{C}$, $\text{RH} = 50\%$, air renewal rate = 0.3 h^{-1} , chamber volume = 1 m^3).

663 For the continuous diffuser, unlike transient diffusers, no peak concentration is observed,
664 but maximum concentrations can be defined from the steady-state regimes (Figure 10).
665 Noticeably, one order of magnitude difference is observed between the maximum concentrations
666 reported for transient diffusers and the steady-state concentrations observed using the continuous
667 diffuser. Another feature of the TerVOC profiles using the continuous diffuser (Figure 10) is that
668 the mean time to achieve the steady-state regime can exceed 20 hours, while for transient
669 diffusers, the maximum concentrations are reached within only 1 to 4 hours, depending on the
670 terpene molecule.

671 Once the steady-state diffusion regime is reached, the 4 major emitted TerVOCs are γ -
672 terpinene, α -terpinene, eucalyptol and 4-terpineol. Their respective concentrations are 610 ± 5 ,
673 600 ± 20 , 340 ± 5 and 270 ± 10 ppb. At steady state, these concentration levels account for 23,
674 21, 16 and 12 % of the total emitted concentration for γ -terpinene, α -terpinene, and eucalyptol,
675 respectively. Indeed, at stable concentrations, these four predominant molecules account for 72
676 % of the total terpene concentration. Finally, irrespective of the diffuser, it can be observed that
677 the same two predominant terpenes are detected in the gas concentration, i.e., γ -terpinene and α -
678 terpinene. The predominance of γ -terpinene, α -terpinene, and eucalyptol can be explained by
679 three key factors: (i) their significant mass contribution in the composition of the liquid tea tree
680 oil, (ii) their volatility and (iii) their affinity to the diffuser stick. Nevertheless, a specific
681 behavior is observed for 4-terpineol. The selected tea tree oil primarily contains 4-terpineol at

682 42.6 % w/w; however, its steady-state concentration only accounts for 12 % of the total emitted
683 TerVOC concentration at the stabilization time.

684 The individual behavior of TerVOCs diffused by capillarity shows that the time to reach
685 the steady-state concentration strongly varies from one molecule to another. Indeed, the
686 stabilization times range from 4 hours for 4-terpineol to 27 hours for eucalyptol. For 4-terpineol,
687 this observation contrasts with its behavior when diffused by transient diffusers because it was
688 characterized by a delayed emission relative to that of the other TerVOCs. For the capillarity
689 diffuser, the first step of the emission process relies on the capillarity diffusion of liquid
690 TerVOCs in the fibrous beech wood stick. The specific behavior of 4-terpineol may be
691 associated with its capillarity diffusion ability in the fibrous stick. Once again, the individual
692 physical and chemical properties of TerVOCs directly impact their diffusion and the resulting
693 gas phase concentrations depending on the diffusion mechanisms involved.

694

695 3.4.1. Emission rates

696

697 Based on the individual concentration profiles, the emission rate of each TerVOC is
698 determined for the capillarity diffuser according to the methodology presented in section 2.3.
699 The emission process associated with the use of the continuous diffuser in the experimental
700 chamber is described by the mass conservation equation in *Eq. 8*, and the emission rates are
701 calculated using previously determined parameters.

702 As reported in Figure 9, for the capillary diffuser, the emission rates achieve a steady
703 state after 3, 2.5, and 1.7 hours of diffusion for γ -terpinene, α -terpinene and α -pinene,
704 respectively. Moreover, in the steady-state regime, the emission rates reached an equivalent
705 value of 4 mg/h for γ -terpinene and α -terpinene and approximately 2 mg/h for α -pinene.

706 Additionally, long-term diffusion devices maintain a constant emission rate for several days.
 707 Indeed, the emission process might be solely limited by the liquid essential oil source itself.
 708 Thus, it can be assumed that constant emission rates for capillarity diffusers could be observed
 709 on time scales up to several days or weeks under stable environmental conditions, i.e.,
 710 temperature and humidity, and until the source is exhausted.

711 To assess the duration of impact on indoor air quality from the diffusion of tea tree oil by
 712 a capillarity diffuser, several calculations were performed to extrapolate the time span of the
 713 emission process until the source is exhausted. Based on *Eq. 9*, the emitted mass E_{mass} in grams
 714 can be calculated by employing the determined emission rates (ERs) at the steady-state regime
 715 per individual terpene X (section 2.3) in grams per day and the time t in days.

$$716 \quad E_{\text{mass}_X} = ER_X \times t \quad \text{Eq. 9}$$

717 The total mass contained in the essential oil bottle is determined to establish the total
 718 boundary mass corresponding to the emission exhaust. This value is represented in Figure 11 by
 719 a dashed line. Subsequently, considering the chemical composition determined in section 2.1,
 720 this same boundary mass is now identified per individual terpene. These values are shown in
 721 Table 6. Note that when the source exhaust time is reached, the total emitted mass equals the
 722 sum of the individual boundary masses.

723 **Table 6.** The calculated mass boundary for individual and total TerVOCs contained in the tea
 724 tree oil bottle.

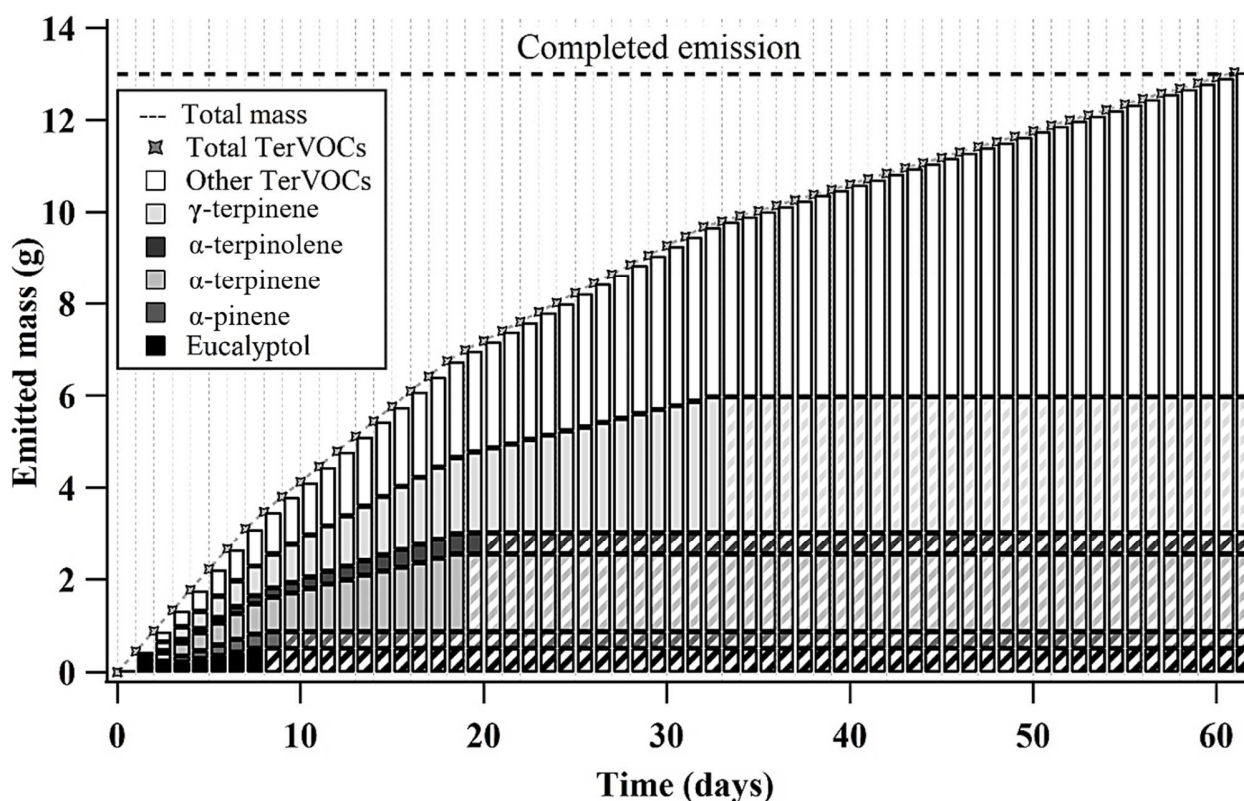
Compound	Individual boundary mass (g)	Emission rate at steady state (g/day)	Source exhaust time (days)
γ -terpinene	2.98	0.09	32
α -terpinene	1.67	0.09	18

α -pinene	0.35	0.04	8
α -terpinolene	0.45	0.02	19
eucalyptol	0.48	0.07	7
other TerVOCs	7.07	0.12	61
TOTAL MASS IN THE TEA TREE OIL BOTTLE	13.01	-	-

725

726 The mass of individual terpenes emitted from the capillarity diffuser (E_{massX}) is calculated
727 per day by employing *Eq. 9* until the cumulative emitted masses reach the boundary mass
728 previously established from the liquid content of the essential oil bottle. The bar series in the
729 histogram of Figure 11 shows the emitted mass of individual TerVOCs per day. Note that when
730 the bar series in Fig. 11 turns from a solid color to stripes, the source of individual terpenes is
731 considered to be exhausted.

732



733
 734 **Figure 11.** The temporal evolution of the emitted mass per day during capillarity diffusion from
 735 $t=0$ until the mass content is depleted in the bottle of tea tree oil.

736 As observed in Figure 11, the contribution of individual TerVOCs to the total emitted
 737 mass per day might vary throughout the entire emission process. Indeed, α -pinene and eucalyptol
 738 have higher emission rates than the other detected terpenes. Therefore, these molecules are
 739 entirely emitted after only 8 and 9 days of diffusion, respectively. This observation is explained
 740 by the acute volatility that characterizes these species, which is associated with the high vapor
 741 pressures of 599 and 260 Pa for α -pinene and eucalyptol, respectively. In contrast, the other
 742 terpene molecules characterized by lower volatilities, such as γ -terpinene, are completely
 743 transferred to the gas phase 30 days after the capillarity diffusion is initiated. Note that at this
 744 same time of diffusion (30 days), the emissions of 4 out of 6 terpenes (α -pinene, eucalyptol, α -
 745 terpinene and α -terpinolene) presented in Figure 11 are no longer detected. Therefore, after 30

746 days of capillarity diffusion of tea tree oil, the gas phase composition is contributed only by
747 terpene molecules that have the lowest vapor pressures, predominantly 4-terpineol. Finally, the
748 total mass contained in the tea tree oil bottle is evidenced to be completely transferred to the gas
749 phase after 62 days. Beyond this time period, concentration levels are evacuated from the room.
750 Therefore, when diffusing essential oils in indoor environments through a capillary device,
751 occupants might be exposed to terpene molecules at concentration levels reaching the ppm range
752 and on a time span from several days to weeks.

753 **4. Conclusions and perspectives**

754

755 This study indicates that the use of essential oil diffusers in confined environments
756 represents a substantial source of indoor terpene VOCs. The emitted concentration levels
757 associated with essential oil diffusion potentially impact indoor air quality over a time span
758 ranging from 5 hours to 60 days for transient and continuous devices, respectively. On the one
759 hand, regarding the exposure of consumers during the evaporation of essential oils in an indoor
760 environment, transient diffusers are associated with high emission rates, i.e., 100 mg/h per gram
761 of product, during a short period, typically in the hour range. Instead, continuous diffusion
762 releases a moderate concentration of terpenes, nearly 5 mg/h per gram of emitted product, but on
763 much longer time spans, exceeding tens of days. Therefore, transient diffusers can be associated
764 with acute exposures, while capillarity diffusers result in chronic exposure.

765 The results provided in this work provide the first quantitative insights into the
766 assessment of human exposure associated with the use of essential oils in indoor environments.
767 Further studies are required to (i) define risk scenarios, (ii) address human exposure to diffused
768 essential oils and (ii) assess the representativeness of the results in the context of this work

769 compared to experiments conducted in a real size room under equivalent controlled conditions.
770 Furthermore, essential oil diffusion, as a source of indoor contaminants, deserves more attention
771 because of its potential formation of formaldehyde and secondary organic aerosols as a
772 consequence of their high reactivity with indoor oxidants.

773 **5. Conflict of interest**

774 The authors declare that they have no conflict of interest

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783 **7. References**

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Emission dynamics of TerVOCs depends on the diffusion mechanisms

