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1 **The indoor fate of terpenes: quantification of the limonene uptake by materials**

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23 **Abstract**

24 Beyond their indoor emission by various sources, another aspect of the presence of VOCs in
25 confined environments involves their indoor fate. Terpenes, because of their ubiquity, source
26 variety and reactivity, are VOCs whose contributions to the indoor air quality may largely
27 exceed primary emissions because of possible secondary processes such uptake and secondary
28 emissions. Limonene is flagged as a species typifying the behavior of terpenes, and a selection of
29 representative indoor materials is proposed. Limonene uptake characterization of selected
30 surfaces is performed under typical indoor conditions using a FLEC-based experimental setup
31 allowing (i) limonene partitioning coefficient determination and (ii) quantification of the
32 reversible nature of this interaction. Interestingly, the materials of interest exhibit highly
33 differentiated affinities for limonene, evidencing the contrast in their surface contributions to
34 terpene loss. Glazing is confirmed as a non-significant sink, while cotton fabric and gypsum
35 board are major contributors to limonene surface loss and exhibit high surface uptake capacities.
36 This work allows a quantitative ranking of the selected materials from minor to major limonene
37 sinks. Reversibility quantification of the uptake process provides key insights into further
38 secondary limonene emissions. The major sink materials are highlighted such as inducing
39 irreversible limonene uptake, thus creating indoor surface pools of reactive organics possibly
40 available for further oxidation processes.

41

42 **Keywords:** terpenes; uptake; sorption; partitioning coefficient; indoor air quality; VOC

43

44 **1 Introduction**

45 The indoor concentrations of volatile organic compounds (VOCs) result from various
46 contributions, mainly involving the (i) air renewal rate, (ii) emissions from materials and
47 activities in the indoor environment, (iii) reactive processes, either homogeneous or
48 heterogeneous, inducing the conversion of primary VOCs into secondary ones, and (iv) VOC
49 exchange with indoor surfaces [1]. Among these phenomena, the interactions between VOCs and
50 materials, such as emission and uptake processes, have been demonstrated as being drivers of the
51 temporal dynamics of the VOC concentration in indoor environments [2]. If indoor materials
52 have first been addressed as sources to be controlled [3-5], they can also be regarded as sinks [6-
53 8]. However, the contribution of heterogeneous VOC losses has neither quantitatively nor
54 temporally been assessed, while it has been identified by several authors as a key driver. Indeed,
55 Weschler [9] in 2011 suggested that the interactions between VOCs and the surfaces of indoor
56 materials impose a more notable impact than the gas-phase reactivity on indoor VOC
57 concentrations. However, the diversity of materials present in indoor environments should be
58 considered and addressed. As a first insight, Gunschera et al. [10] conducted a comprehensive
59 study of the sorption-desorption processes of VOCs on building materials. The physical and
60 chemical properties of surfaces as well as the morphology of the materials considerably impact
61 their heterogeneous behaviors towards the uptake of VOCs.

62 The description of the exchange processes between VOCs and materials requires the
63 preliminary definition of the relevant physical and chemical concepts. Three processes contribute
64 to the VOC-material interactions [11]: (i) the transport of VOCs in the boundary layer formed in
65 the vicinity of the surface of the materials, (ii) the adsorption and/or desorption of VOCs onto the
66 surface of the materials, and (iii) the diffusion of VOCs into the bulk structure of the materials.

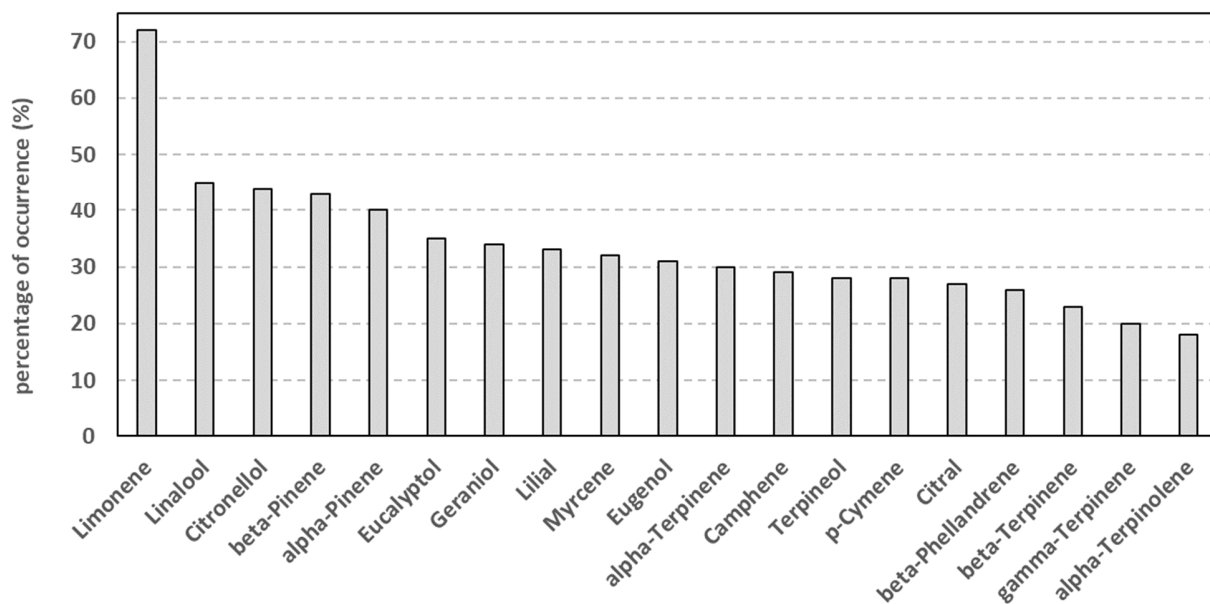
67 Adsorption and desorption are defined by the orientation of the concentration gradient of the
68 VOCs in the boundary layer. The concept of sorption encompasses multiple interactions between
69 VOCs and surfaces. Physisorption refers to weak electrostatic interactions between sorbent and
70 sorbate molecules. Thus, the physisorbed fraction is mostly reversibly adsorbed at ambient
71 temperature. Hence, a slight variation in the VOC concentration gradient in the boundary layer or
72 a slight increase in temperature subsequently induces the desorption process. Chemisorption
73 corresponds to stronger VOC/material interactions, such as covalent bonds with the surface.
74 Chemisorption generally leads to an irreversible sorptive process. This may also result in the
75 modification of the adsorbed VOC structure. Uptake is not a permanent state, indeed the
76 adsorbate can return to the gas phase, depending on the environmental conditions. Therefore, it
77 may contribute to the gas phase dynamic of pollutants again. These aspects refer to the reversible
78 or irreversible nature of the uptake. Indeed, if a material acts as a sink, to what extent is it a long-
79 lasting sink? Should it be considered as a secondary source later on? As a complement to the
80 concept of sorption, diffusion corresponds to the migration of a species in the bulk structure of
81 the material. This phenomenon becomes all the more significant at a large material thickness,
82 and the considered species are characterized by high diffusion coefficients (K_d) in the material.
83 The review conducted by Haghghat et al. [12] in 2002 on the VOC diffusion coefficient in
84 typical building materials points to the fact that diffusion coefficients vary considerably
85 according to the considered material-VOC system. Nonetheless, gypsum board and highly
86 porous concrete characteristically exhibit the highest diffusion coefficients with any VOC.
87 Similarly, Meininghaus et al. [13] and Blondeau et al. [14] in 2003 reported VOC diffusion
88 coefficients of gypsum boards that were higher than those of other indoor materials.

89 Nevertheless, diffusion coefficients can greatly vary from one VOC to another since they are
90 dependent on their chemical structures [12].

91 When uptake is mostly attributed to physisorption interactions, the Langmuir model can
92 be applied to typify the interactions between VOCs and materials. The Langmuir isotherm
93 describes the evolution of the amount of VOCs taken up by the material as a function of the gas-
94 phase concentration. The typical profiles of this isotherm can be described by two regimes. At
95 the lowest concentrations, typically in the ppb range, the taken-up quantity linearly increases
96 with increasing gas-phase concentration. This behavior was confirmed by Thevenet et al. [8] in
97 2018 under typical indoor conditions for toluene and formaldehyde onto various types of gypsum
98 boards. At higher concentrations, the isotherm is characterized by a saturation regime. However,
99 typical indoor conditions are not associated with ppm-level concentration ranges, and only the
100 linear section of the isotherm needs to be determined [15]. The corresponding slope of the
101 isotherm within the ppb range is named the partitioning coefficient K , expressed in m . It
102 describes the uptake capacity of a given material for a specific VOC. The concept of uptake
103 represented by the partitioning coefficient encompasses both sorption and diffusion phenomena,
104 and it characterizes the loss of a given VOC to a certain material under specific temperature (T)
105 and relative humidity (RH) conditions.

106 Among the various indoor sources of pollutants, the activities of building occupants such
107 as interior renovation or decoration, smoking, cooking, and intense cleaning activities constitute
108 major sources of contaminants [16]. Cleaning is commonly performed by occupants to increase
109 hygiene, improve esthetics, and preserve materials [17]. Many available cleaning products are
110 scented" because a pleasant odor provides the perception of a clean environment. Despite all the
111 benefits provided by cleaning activities, cleaning product use presents many associated risks.

112 Terpenoid VOCs are widely adopted as natural fragrances in household cleaning products and air
113 fresheners marketed as green and healthy. Therefore, natural essential oils or synthetic terpenes
114 are widespread, these VOCs commonly occur indoors. A review on the ubiquity of terpenes in
115 indoor environments was performed by Angulo Milhem et al. [18] in 2020. They addressed the
116 current issues related to terpenes and air quality in confined spaces. Adapted from the work of
117 Angulo Milhem et al. [18], Figure 1 shows the occurrence percentages of the 19 main terpenes
118 identified in the liquid composition of 450 household cleaning products. Aggregated data are
119 retrieved from 14 different references published between 2001 and 2015, i.e., [19-32]. Each of
120 these works highlights the significance and recurrence of household cleaning products as indoor
121 sources of terpenes. The occurrence percentages of the main individual terpenes range from 18%
122 for α -terpinolene to 72% for limonene (Figure 1). The occurrence of limonene as a fragrance
123 compound in household cleaning products clearly exceeds that of any other terpene (Figure 1).
124 Moreover, the application of select household cleaning products under realistic scenarios in
125 large-scale experimental setups demonstrated that the indoor limonene concentration may even
126 exceed 250 $\mu\text{g}/\text{m}^3$. Similar concentration ranges were reported by Missia et al. [33] and Krol et
127 al. [34], thus identifying limonene as a representative terpene of indoor environments.



128

129 **Figure 1.** Occurrence percentages of the 19 major terpenes identified in the liquid composition
 130 of 450 household products (adapted from the review article of Angulo Milhem et al. [18])

131

132 Beyond the monitoring of the terpene concentrations in indoor air, the fate of these VOCs
 133 in indoor environments is assessed in two aspects: (i) their gas-phase reactivity and (ii) their
 134 deposition on surfaces. Long et al. [35], Sarwar et al. [36] and Langer et al. [37], reported the
 135 formation of ultrafine particles from terpenes in the presence of ozone under indoor conditions.
 136 More specifically, the use of - detergent containing limonene in schools is reported as a source of
 137 secondary organic aerosols (SOAs) by Morawska et al. [38]. This observation is confirmed by
 138 Rossignol et al. [39]. In addition to this gas phase reactivity, Waring et al. [40] showed that
 139 limonene sorbed onto various surfaces highly contributes to the generation of SOAs as well. This
 140 finding suggests that the impact of limonene as a heterogeneous source of secondary pollutants
 141 may largely exceed its emission time span from household products.

142 Limonene adsorbed onto the surface of materials may represent a pool of reactive
143 contaminants that could subsequently impact the indoor air quality. This aspect was emphasized
144 by Destailats et al. [41], who suggested that the consumption of ozone by the adsorbed terpenes
145 may exceed the removal of ozone by ventilation systems. This point was supported by Springs et
146 al. [42], who showed that the reaction rates of 3-carene and limonene adsorbed onto glass and
147 polyvinylchloride (PVC) are 10 to 100 times higher than the reaction kinetics in the gas phase. In
148 addition, Shu and Morrison determined the surface reaction rate of α -terpineol on 3 typical
149 indoor surfaces: (i) glass, (ii) PVC and (iii) paint. For all evaluated surfaces, the heterogeneous
150 reaction kinetics were higher than those in the gas phase by a factor of 25 [43]. Consequently,
151 the main sinks of terpenes in indoor environment have to be identified first. These materials may
152 potentially represent emission sources of secondary products from the heterogeneous oxidation
153 of terpenes.

154

155 The objective of this study is to characterize the uptake of limonene, as a model terpene,
156 onto ten representative indoor materials. This investigation aims to address the uptake behavior
157 of limonene under realistic indoor conditions and materials to provide an overview of the
158 corresponding partitioning coefficients and identify the main indoor sinks of terpenes. Beyond
159 these two main tasks, this work aims to provide a more precise understanding of the reversible or
160 irreversible nature of the limonene uptake process to identify materials representing long-term
161 pools of adsorbed terpenes in indoor environments.

162

163 **2 Materials and methods**

164

165 **2.1 Selection and characterizations of the indoor materials**

166 To address the variety of building products in indoor environments, materials from five main
167 categories were selected, including glazing materials, construction materials, textiles, paints, and
168 wood-based materials. Table 1 lists the ten materials selected with their characteristics. Despite
169 the interest of this study in the uptake process, materials recognized as potential sources of VOCs
170 have been selected, such as paints or wood-based materials, and this point is further addressed
171 below.

172 The specific surface areas (m^2/g) of the selected materials were determined using a
173 sorption analyzer relying on the nitrogen Brunauer-Emmett-Teller (BET) isotherm (Table 1).
174 This experimental approach is successfully performed on glass, construction materials, paints
175 and textiles. To avoid inducing any modification of the composition and morphology of the
176 investigated materials, no thermal treatment was applied to the samples prior to N_2 adsorption.
177 This technical specificity may lead to a moderate underestimation of the specific surface area.
178 However, this approach is required since the specific surface area of materials such as gypsum
179 and fabrics is known to be highly impacted by the slightest thermal treatment. Note that the
180 structure of the wood-based materials did not allow the determination of their specific surfaces.

181

182

Category	Material	Characteristics	Specific surface area (m^2/g)
glazing materials	1 glass	house glazing, no specific surface treatment	n.d.
construction materials	2 classical gypsum board	13 mm thick, no specific additive	3 ± 0.5
	3 modified gypsum board	13 mm thick, gypsum combined with physical sorbent	40 ± 3

fabrics	4	cotton fabric	<i>beige color, natural cloth, 100% organic cotton</i>	63 ± 2
	5	polyester fabric	<i>white color, synthetic cloth, 100% polyester</i>	3.5 ± 0.5
paints	6	acrylic paint	<i>indoor wall paint, white color, soluble in water, belongs to the A+ class regarding its VOC emissions according to French laws [44]</i>	< 0.1
	7	glycerophthalic paint	<i>indoor wall pain, white color, soluble in solvents, belongs to the A+ class regarding its VOC emissions according to French laws [44]</i>	< 0.1
wood-based materials	8	particle board	<i>fine particles (mm range) of wood, compacted with urea formaldehyde-based resin, 2.5 cm thick</i>	<i>n.d.</i>
	9	oriented strand board	<i>large particles (cm range) of wood, compacted with phenolic resin, 2.5 cm thick</i>	<i>n.d.</i>
	10	natural pine board	<i>raw pine tree used for wooden floors, 1.5 cm thick</i>	<i>n.d.</i>

183 **Table 1.** Categorized list of the selected indoor materials with their respective characteristics and
184 experimentally determined specific surface areas (n.d. = not determined; < l.d. = below the limit
185 of detection)

186

187 *2.2 Emissive behavior of the selected materials*

188

189 Since the sorptive behavior of a given VOC is driven by its concentration gradient at the gas-
190 material interface, the gas-phase concentration of the VOC is not the single driver. Indeed, the
191 gradient can also be impacted by the possible emission of the considered VOC from the material.
192 Therefore, the investigation of the limonene uptake process can be impacted by the VOC
193 emissions from the material itself. As such, the emissive behavior of the material is first
194 characterized, chiefly regarding its limonene emissions but also concerning the major VOCs
195 emitted by each material.

196

197 *Glazing and gypsum-based* construction materials are known to be characterized by the
198 absence of any primary VOC emissions because of their fully inorganic composition. The only
199 emissions reported for these types of materials result from the desorption of preliminarily
200 adsorbed organics but not from their intrinsic constituents. For instance, the desorption of α -
201 pinene from glass reported by Goss in a real-scale experimental chamber is attributed to the
202 preliminary contamination of the glazing surface by the terpenes occurring in the investigated
203 indoor environment [45]. Nonetheless, to evaluate the potential emission of preliminarily
204 adsorbed terpenes prior to any uptake experiment, samples of glass and gypsum are individually
205 placed in the FLEC under zero-air flow, at 23 ± 1 °C and $\text{RH} = 50\% \pm 2\%$. With individual
206 limits of detection lower than 2 ppb using SIFT-MS, no terpenes were detected in the FLEC,
207 implying the nonemissive nature of these materials. The same experiments are repeated using
208 *cotton* and *polyester fabrics*. No limonene or terpenes are recorded, confirming that these
209 materials are not intrinsic sources of terpenes and have not been contaminated prior to the uptake
210 experiments.

211
212 *Paints* are coating materials with potentially intense but transient emissions. The major
213 VOCs emitted are driven by the given paint composition [46-48]. The uptake experiments can be
214 potentially impacted by the emissions of fresh paints. Therefore, to determine the emission
215 exhaust time of each selected paint, glycerophthalic and acrylic paints are applied on glass plates
216 and individually placed in the FLEC. To characterize the VOCs emitted from these materials,
217 two sets of complementary samplings and analyses are specifically performed:

- 218 (i) *Hydrocarbon VOC* sampling is performed with Carbotrap 202 cartridges for 30
219 min using an automated Across sampling system at a flow rate of $0.20 \text{ L}\cdot\text{min}^{-1}$.

220 The sampled cartridges are desorbed using a Gerstel thermal desorber. Gas
221 chromatography analysis is performed using a 7890A instrument from Agilent
222 Technologies equipped with a DB-5 MS chromatographic column connected to
223 (i) a flame ionization detector (FID) and (ii) a mass spectrometry (MS)
224 instrument. The typical detection limit of this instrument for hydrocarbon VOCs
225 under the abovementioned sampling conditions is 0.1 ppb. Calibration of the
226 VOC concentration is achieved with certified gas cylinders.

227 (ii) *Carbonyl VOCs* (OVOCs) are derivatized on 2,4-dinitrophenylhydrazine
228 (DNPH)-impregnated silica Supelco cartridges for 30 min at a flow rate of 2
229 L.min⁻¹. Hydrazones are extracted from the DNPH cartridges with 3 mL
230 acetonitrile and analyzed with a Water 2487 high-performance liquid
231 chromatography (HPLC) instrument. The compounds are eluted on a C18
232 column and detected via tunable wavelength UV absorption (Water 2695).
233 Under these conditions, the typical detection limit for carbonyl compounds is
234 0.01 ppb. Calibration of the carbonyl compounds is achieved using certified
235 standard solutions.

236 Both protocols are performed at the FLEC outlet every 12 h over 10 days. In accordance
237 with the formulation of the paints, glycerophthalic paint exhibits the highest emissions.
238 Carboxylic acids from C₂ to C₆ are observed over time along with linear alkanes from C₆ to C₁₁.
239 Linear carbonyl compounds from C₁ (formaldehyde) to C₆ (hexanal) are encountered in addition
240 to isopentanal and acetone. No limonene or other terpenes are recorded in any sampling.
241 Maximum concentrations are observed in the first and second samplings. Within 72 h after the
242 application of the glycerophthalic paint, all concentrations at the FLEC outlet are lower than 1

243 ppb, confirming the transient nature of the VOC emissions from this material. Regarding the
244 acrylic paint, the diversity of the transiently emitted VOCs is similar to that of the glycerophthalic
245 paint, but the resulting concentrations are lower by more than one order of magnitude. Similarly,
246 no limonene or any terpene is observed in the samplings. The emission process from the acrylic
247 paint can be considered to be exhausted within 50 h. The limonene uptake experiments are
248 performed 14 days, i.e., 336 h, after the application of the paints. As a consequence, since the
249 emission of the VOCs used as solvents has stopped and no limonene emissions are observed, no
250 emission impact occurs on the investigation of the limonene uptake by these materials.

251

252 *Wood-based materials*, extensively applied as construction or furniture materials, are
253 responsible for the occurrence of hexaldehyde, α -pinene and limonene in indoor environments
254 [49]. As reported by Harb et al. [50], wood-based materials are indoor sources of (i) terpenoid
255 VOCs (α -pinene, camphene, β -pinene, 3-carene, d-limonene and β -phellandrene) and (ii)
256 oxygenated VOCS (formaldehyde, acetaldehyde, acetone, propanal, pentanal, hexanal and
257 dimethylbenzaldehyde). The contribution of oxygenated VOCs is considerably enhanced in the
258 case of oriented strand board (OSB) and particle board since these materials contain synthetic
259 resins and glues. The diversity and respective ratios of the emitted terpenes are dependent on the
260 nature of the wood, as pointed out by Pohleven et al. [51] in 2019 in their review. The wood-
261 based materials considered in our study have been formerly adopted and characterized in the
262 work of Harb et al. [50] in 2018. After having been studied by Harb et al. [50], samples were
263 kept in a ventilated storage room for 18 months at temperatures ranging from 15 to 25 °C and an
264 RH ranging from 40% to 60%. Interestingly, through 500 h-long experiments, Harb et al. [50]
265 determined not only the diversity of the VOCs emitted from fresh wood-based samples but also

266 their individual depletion rates when stored in a real-scale room. Based on the depletion rates of
267 the individual VOCs of the considered wood-based samples, it can be assumed that oxygenated
268 VOCs and terpenes are no longer emitted beyond 5 and 8 months, respectively, from any
269 selected wood-based materials. The nonemissive behaviors of the samples after 18 months of
270 storage are confirmed by preliminary experiments. The wood-based samples are individually
271 placed in the FLEC under a zero-air flow, at 23 ± 1 °C and $RH = 50\% \pm 2\%$. With an individual
272 limit of detection ranging from 1 to 4 ppb using SIFT-MS, no typical VOCs, as previously
273 reported by Harb et al. [50], are observed, indicating the absence of major emissions from the
274 wood-based samples used in this study.

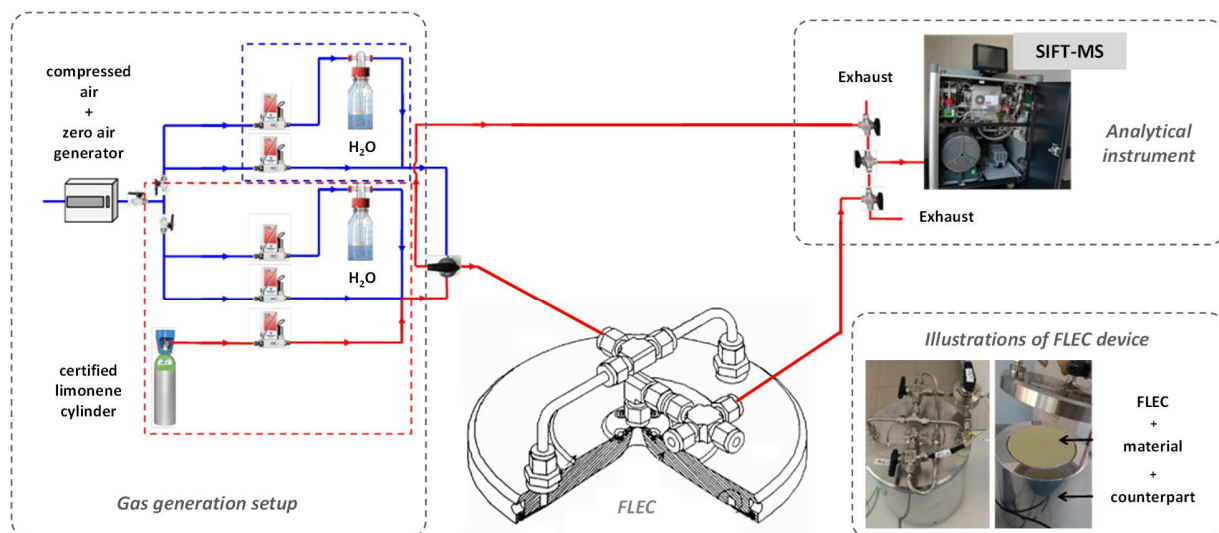
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276 **Wrap-up / The characterization of the emissive behavior of the selected materials indicates**
277 **that, as the limonene uptake experiments are performed, no major emissions are observed**
278 **from any selected material, either because they are confirmed to be intrinsically**
279 **nonemissive or because emissions have ceased. Subsequently, the concentration gradients**
280 **in the limonene uptake experiments are not impacted by any emissions, and the**
281 **partitioning coefficients determined in this study are intrinsic parameters characterizing**
282 **the long-term behavior of each considered material.**

283

284 *2.3 Experimental setup and measurement apparatus.*

285 The experimental setup designed to investigate the interactions between limonene and the
286 selected indoor materials consists of three complementary parts: (i) the gas-phase preparation
287 system, (ii) the Field and Laboratory Emission Cell (FLEC) holding each material, and (iii) the
288 analytical device used to monitor the limonene concentration (Figure 2).



289
 290 **Figure 2.** General scheme of the experimental setup designed to investigate the interactions
 291 between VOCs and the selected materials: gas generation, Field and Laboratory Emission Cell
 292 (FLEC) and analytical device.

293
 294 *Gas phase preparation* / Limonene is generated from a certified cylinder provided by *Praxair* at
 295 a nominal concentration of 25 ppm in nitrogen. A regulated flow of dry limonene is diluted with
 296 zero air produced by a catalytic zero-air generator (*Claind*, Lenno, Italy) ensuring a residual
 297 VOC concentration lower than 100 ppt. The limonene concentration is set by adjusting the ratio
 298 between the limonene and zero-air flows. In parallel, an equivalent flow of zero air is saturated
 299 with water vapor. The mixing of both gas lines provides a flow of limonene with the targeted
 300 concentration diluted with zero air at an RH of $50\% \pm 2\%$. This setup allows varying the
 301 limonene concentration from 50 to 900 ppb.

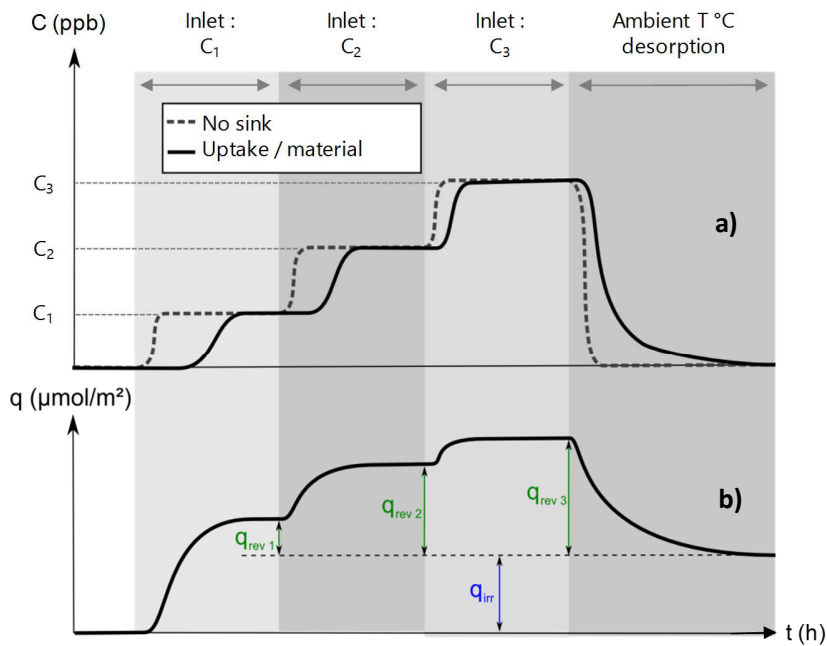
302
 303 *FLEC* / The setup includes a FLEC (*CHEMATEC*, Denmark) combined with its stainless steel
 304 counterpart. Samples of the investigated materials are cut and placed in the counterpart. The tight

305 arrangement of the FLEC and counterpart prevents any loss of limonene that may occur by
306 diffusion across the investigated materials. The injection and exhaust of the humidified limonene
307 or zero-air flow are accomplished through the FLEC inlet and outlet ports, respectively, thus
308 exposing the surface of the material to the targeted gas mixture under a constant RH of 50%.

309
310 *Analytical device* / A fraction of the outlet flow of the FLEC is sampled with a selected ion flow
311 tube mass spectrometry (SIFT-MS) (*SYFT Technology*, Christchurch, New-Zealand) to monitor
312 the downstream VOC concentration. This analytical device allows the real-time monitoring of
313 the VOC concentration at a temporal resolution lower than 10 s under our experimental
314 conditions. It relies on soft chemical ionization of the analytes by H_3O^+ , NO^+ and O_2^+ . Ions are
315 generated by the application of radiofrequency discharge to the humidified air and selected by
316 the first quadrupole. After the reactions of the ions with the analytes in the flow tube, the formed
317 charged species are detected with the second quadrupole. The SIFT-MS signals are measured
318 with preliminary calibrations using certified gas cylinders under relevant RH conditions. The
319 detection limit of limonene was determined to be 10 ppb under our experimental conditions, i.e.,
320 23 ± 1 °C, and $\text{RH} = 50\% \pm 2\%$.

321

322 ***2.4 Experimental protocol and data processing***



323 **Figure 3.** (a) Theoretical temporal concentration profiles of limonene monitored at the outlet of
 324 the FLEC system adopted as a breakthrough reactor in the absence (dashed line) and presence
 325 (full line) of the selected material; (b) theoretical temporal profile of the limonene quantity q
 326 ($\mu\text{mol}/\text{m}^2$) taken up by a given material at the consecutive steps of the experimental protocol.

327

328 The capacity of the various typical indoor materials to uptake limonene is determined with the
 329 experimental protocol shown in Figure 3. This protocol relies on the operation of the FLEC as a
 330 breakthrough reactor to expose each selected material to limonene under typical indoor air
 331 conditions. The protocol is divided into three consecutive phases.

332

333 2.4.1 Determination of the mixing curves

334 First, it is necessary to determine the concentration profile of limonene at the outlet of the FLEC
 335 in the absence of any materials, i.e., no sink. This step allows us to consider the impact of the gas

336 flow and potential sorptive effects on the walls of the experimental setup. To that end, a
337 concentration C_1 of limonene is set at the inlet of the empty FLEC, while the limonene
338 concentration is monitored at the outlet. The corresponding profile is shown in Figure 3a as a
339 dashed line. It can be observed that the limonene concentration rapidly increases at the outlet of
340 the FLEC until the value set at the inlet is reached. The same procedure is applied with inlet
341 concentrations C_2 and C_3 such that $C_1 < C_2 < C_3$ (Figure 3a, dashed line).

342

343 *2.4.2 Determination of the breakthrough curves*

344 After the determination of the mixing curves, one material of interest is placed in the FLEC
345 system, and the selected material is first exposed to concentration C_1 . The outlet limonene
346 concentration is monitored as a function of time, and the corresponding profile is displayed in
347 Figure 3a as a solid line. As limonene is taken up by the investigated material, a temporal delay
348 is observed between the mixing and breakthrough curves, both obtained at C_1 . After a certain
349 time, depending on the capacity of the material to uptake the VOC, the set inlet limonene
350 concentration is encountered at the outlet. In that case, uptake equilibrium has been achieved
351 between the gas-phase limonene and the limonene taken up by the material for the given inlet
352 concentration. The uptake equilibrium at a given inlet concentration is considered to have been
353 reached when the difference between the concentration at the FLEC outlet and the inlet
354 concentration is smaller than the standard deviation of the analytical instrument for longer than
355 15 min. The full temporal integration between the mixing and breakthrough curves allows the
356 determination of the limonene amount taken up by the selected material for the given inlet
357 concentration C_1 . Similarly, from the introduction of limonene until the uptake equilibrium is
358 reached, the current temporal integration between both sets of curves allows the determination of

359 the limonene quantity taken up by the material as a function of time. This temporal series is
360 shown in the lower part of Figure 3a. Based on Figure 3a, the limonene amount taken up by the
361 material increases to a maximum value q_1 , expressed in $\mu\text{mol}/\text{m}^2$, at concentration C_1 ($\mu\text{mol}/\text{m}^3$).
362 Then, multiple breakthroughs can be generated, i.e., the material is successively exposed to
363 increasing limonene concentrations ($C_2, C_3\dots$). Note that the increase from concentration step n
364 to $n+1$ is not performed prior to reaching the uptake equilibrium at step n .

365

366 *2.4.3 Determination of the partitioning coefficient K*

367 Based on the Langmuir isotherm, the affinity of a VOC for a given material can be assessed. The
368 maximal adsorbed quantities q_i ($\mu\text{mol}/\text{m}^2$) determined at each concentration step and the uptake
369 equilibrium can be plotted as a function of the inlet concentration C_i ($\mu\text{mol}/\text{m}^3$). At sub-ppm
370 VOC concentrations, this plot describes the linear regime of the Langmuir isotherm, and linear
371 regression allows the determination of the partitioning coefficient K (m). Note that the VOC
372 amount taken up is expressed as $\mu\text{mol}/\text{m}^2$, where m^2 does not refer to the specific surface area of
373 the material of interest but to its macroscopic surface area, i.e., its geometric area. This choice is
374 motivated by the applicability of the data.

375

376 *2.4.4 Ambient temperature flushing*

377 Once the final uptake equilibrium has been reached, the generation of limonene can be stopped,
378 and the FLEC system can be flushed with zero air while maintaining the total gas flow, RH and
379 constant temperature ($T_{\text{amb}} = 23 \pm 1$ °C). This ambient temperature flushing step provides
380 conditions that are equivalent to a decrease in the VOC concentration in an indoor environment.
381 Consequently, a decrease in limonene concentration is recorded at the FLEC outlet regardless of

382 whether it contains a material (Figure 3a). Similarly, a decrease in the limonene amount taken up
383 by the material can be observed (Figure 3b). The VOC amount desorbed at that step corresponds
384 to the weakly bonded fraction of limonene on the material, i.e., the reversibly adsorbed fraction.
385 Even if the limonene concentration at the FLEC system outlet decreases to zero, a fraction of the
386 initially taken up limonene molecules remain on the material, as shown in Figure 3b. This
387 fraction is considered the irreversibly adsorbed fraction. Thus, this protocol step allows the
388 assessment of the magnitude of the interactions between limonene and the materials and
389 subsequently indicates the propensity of the taken up VOCs to persist on the material surface or
390 to be released to the gas phase.

391

392

393

394 **3 Results and discussion**

395 The interactions of limonene with the ten selected indoor surfaces is experimentally addressed.
396 To provide a first detailed insight into the uptake results, the behavior of the *limonene + natural*
397 *pine-wood* system is primarily described and examined. Thereafter, the partitioning coefficients
398 K for the various materials are presented and assessed. Finally, the reversible nature of the
399 uptake process is reported and evaluated in terms of the impacts on the indoor air quality.

400

401 ***3.1 First uptake insights: limonene by natural pine-wood samples***

402 A complete set of results related to the limonene uptake by natural pine-wood board material is
403 gathered, as shown in Figure 4. First, Figure 4a shows the temporal limonene concentration
404 taken up by the sample as it is successively exposed to 300, 500 and 700 ppb. The limonene

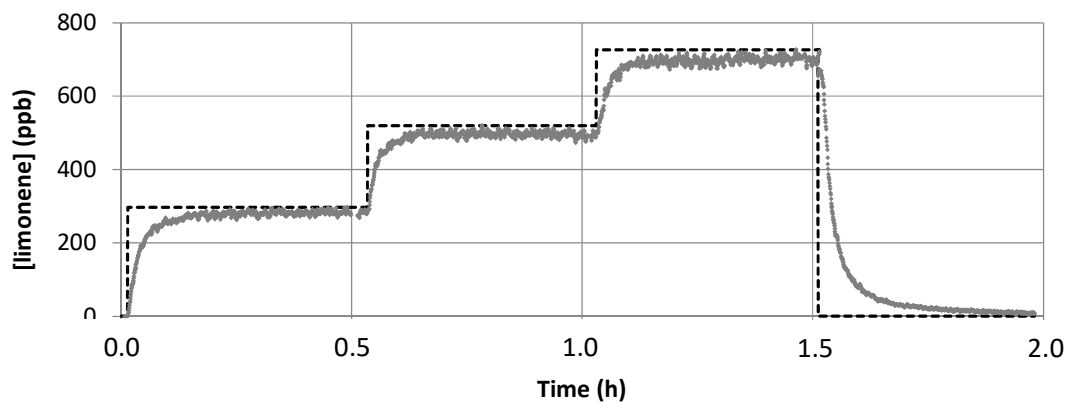
405 breakthrough curve is overlaid on Figure 4a with the corresponding mixing curve. In particular,
406 both temporal series are delayed, thus indicating the limonene uptake by natural wood at each
407 concentration step. Beyond the transient delays, the uptake equilibria are reached for each set
408 inlet concentration. The equilibrium gradually moves as the inlet concentration increases.
409 Interestingly, this material considered a long-term source of terpenes, especially limonene in
410 indoor environments, is demonstrated to potentially act as a limonene sink.

411

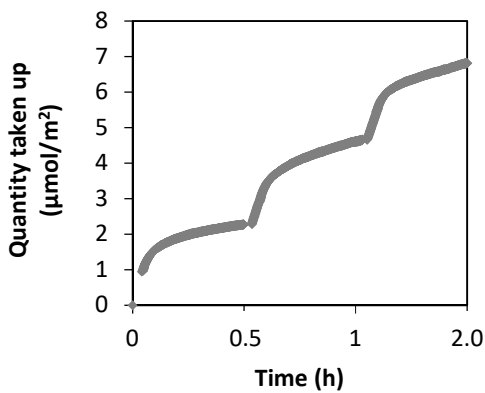
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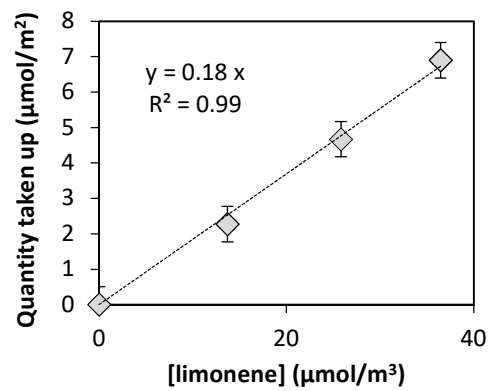
414



a/



b/



c/

415 **Figure 4.** Characterization of the limonene uptake by the natural pine-wood sample under typical
416 indoor air conditions: $T = 23 \pm 1$ °C, $RH = 50\% \pm 2\%$, and ppb-level limonene concentrations;
417 a/temporal profile of the limonene concentration (ppb) taken up at the three concentrations steps
418 of 300, 500 and 700 ppb; b/temporal evolution of the limonene quantity ($\mu\text{mol}/\text{m}^2$) taken up for
419 the various inlet limonene concentrations of 300, 500 and 700 ppb; c/quantity of the limonene
420 ($\mu\text{mol}/\text{m}^2$) taken up at the uptake equilibrium as a function of the limonene concentration.

421

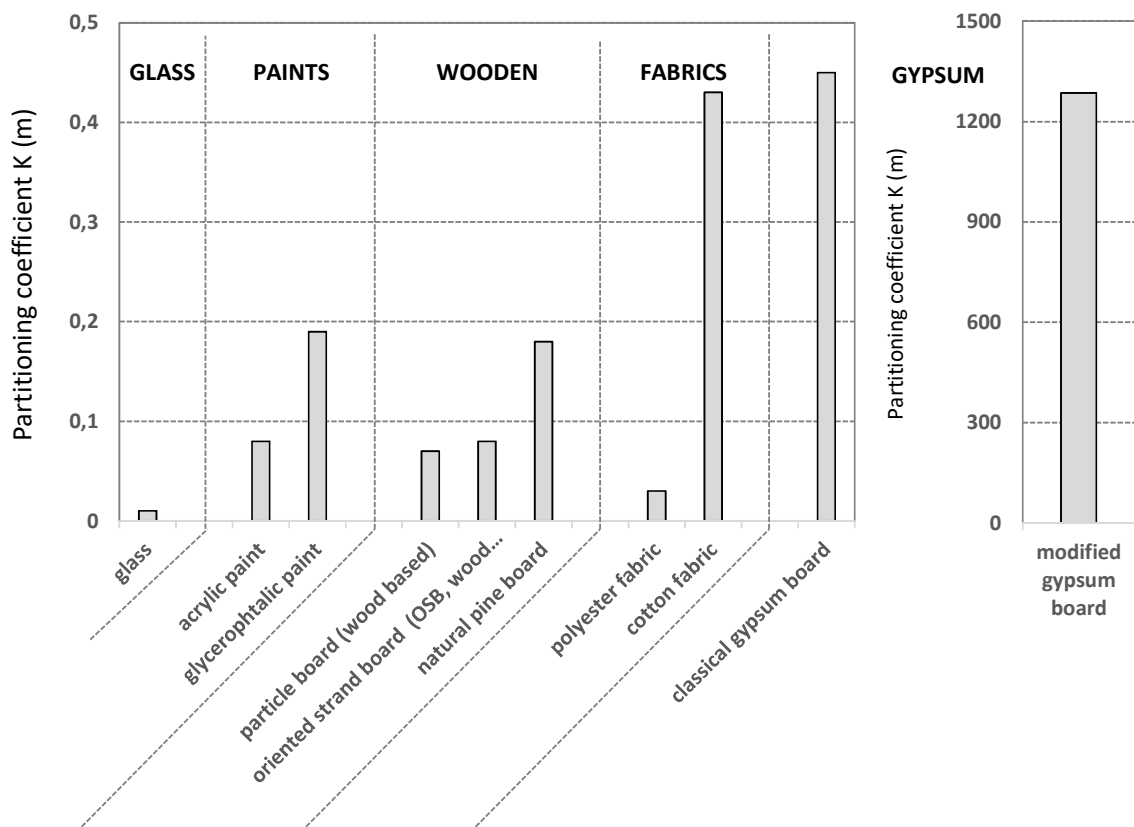
422 The temporal integration of the delays between the mixing and breakthrough curves
423 across the three concentration steps allows the determination of the limonene amounts taken up
424 by natural pine wood. Corresponding temporal data are shown in Figure 4b. At each equilibrium
425 reached, it is possible to plot the limonene quantity taken up by the natural pine-wood sample as
426 a function of the inlet limonene concentration. This plot is shown in Figure 4c, where a linear
427 relationship is observed confirming the linear Langmuir isotherm regime within the investigated
428 ppb concentration range. It has to be mentioned that R^2 values of all the selected materials are
429 higher than 0.99. Note that the data point at the origin of this graph is retrieved from the
430 nonemissive behavior of the material as the limonene uptake experiment is initiated. The value
431 of the partitioning coefficient of limonene by natural pine-wood board is thus determined as $K =$
432 0.18 m. Former studies dedicated to the determination of the partitioning coefficients of typical
433 indoor materials mostly considered linear and aromatic C1 to C10 hydrocarbons as model VOCs
434 rather than terpenes. As a consequence, no literature data are available for the limonene
435 partitioning coefficient so far. Moreover, construction materials were primarily investigated, and
436 wood-based materials have not yet been addressed. To provide a valuable overview of the
437 obtained experimental limonene data, in the next section, the material in question is compared to

438 other selected materials using the same experimental protocol, and the experimental data are
439 compared to data retrieved from the literature.

440

441 **3.2 Partitioning coefficients (K) of limonene for the typical indoor materials**

442 The experimental protocol detailed in section 3.1. has been implemented to determine the K
443 values of limonene for each selected material. Limonene uptake is observed for every material
444 with highly different values. The partitioning coefficients K of limonene of the materials of
445 interest are shown in Figure 5. This figure clearly highlights the differentiated interactions since
446 the most extreme behaviors differ by 5 orders of magnitude: the partitioning coefficients range
447 from 0.010 ± 0.001 m for glass to 1000 ± 50 m for the modified gypsum board.



448

449 **Figure 5.** Partitioning coefficients K (expressed in m) of limonene for the selected indoor
450 materials; the materials are classified by the main categories ($T = 23 \pm 1$ °C, $RH = 50\% \pm 2\%$,
451 ppb-level limonene concentrations)

452

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460 **Table 2.** Partitioning coefficient K of the most investigated VOCs for classical gypsum board

461

Reference	VOC	K (m)
	Benzene	0.12
Rizk et al. [53]	Toluene	0.29
	C8 aromatics	0.72
Xu et al. [54]	Ethylbenzene	0.90
	n-Decane	1.27
Liu et al. [55]	Formaldehyde	6.02
	1-Butanol	6.67
	Toluene	0.12
	Perchloroethylene	0.20
Won et al. [56]	Ethylbenzene	0.24
	Methyl tert-butyl ether (MTBE)	0.35
	Isopropanol	7.20
Tichenor et al. [6]	Ethylbenzene	0.30

Thevenet et al. [8]	Toluene	0.30
	Formaldehyde	40

462

463

464 In the literature, data related to the partitioning coefficients of VOCs for various materials
465 are available. It is noted that gypsum boards are among the most investigated materials. A
466 selection of K values reported for the uptake of the most investigated VOCs by classical gypsum
467 is provided in Table 2 to compare the orders of magnitudes. It appears that the widespread use of
468 aromatics (substituted or not) and oxygenated VOCs (formaldehyde and short-chain alcohols) as
469 model VOCs is motivated by their occurrence and/or toxicity in indoor environments.
470 Interestingly, the literature data summarized in Table 2 indicate that unsaturated hydrocarbons
471 are characterized by K values ranging from 0.1 to 1 m. Only saturated hydrocarbons and
472 particularly oxygenated VOCs are characterized by K values exceeding 1 m because of their
473 affinity for the hydrophilic gypsum surface [8,52]. These data support the fact that K values are
474 mostly driven by the physical and chemical affinities between the VOC and material.

475

476 Based on the experimentally determined K values, it is proposed to classify the 10
477 investigated materials into three groups:

478

479 *Minor sinks* / The materials with a limited limonene uptake capacity, characterized by a
480 partitioning coefficient lower than 0.1 m include glass, acrylic paint, particle board, OSB and
481 polyester. Noticeably, glass, acrylic paint and polyester are the three materials with the lowest
482 specific surfaces. This characteristic results in the limited limonene amount taken up by the
483 material. The presence of polyester fabric and OSB in the low-contribution group to limonene

484 uptake may be related to the surface chemistry of these materials. Another hypothesis relies on
485 the fact that polymeric materials such as nylon and phenolic resin hinder limonene diffusion in
486 the bulk of these materials. In any case, it can be assumed that this group of materials imposes a
487 modest impact on the heterogeneous fate of terpenoid VOCs in indoor environments, and they
488 are minor sinks.

489
490 *Moderate sinks* / The materials with a moderate limonene uptake capacity, characterized by a
491 partitioning coefficient ranging from 0.1 to 0.5 m, include the glycerophthalic paint, natural pine
492 board, cotton and classical gypsum board. Interestingly, classical gypsum board and cotton
493 fabrics exhibit the highest K values of this group and the highest specific surface areas. Table 2
494 indicates that the partitioning coefficient of toluene for classical gypsum board at an RH of 50%
495 is within the corresponding range, namely, at 0.3 m. In their study, the authors revealed that the
496 impact of this kind of material on the concentration of the VOC of interest in a 40-m³ room is
497 moderate, and depending on the material load in the room, less than a few hours are required to
498 reach the uptake equilibrium. Therefore, this group of materials is assumed to moderately or
499 temporarily impact the terpene concentration and can be regarded as moderate sinks.
500 Nonetheless, their impacts are considerably enhanced by their respective loading factors in a
501 given indoor environment.

502
503 *Major sink* / One material is characterized by a high limonene uptake capacity with a partitioning
504 coefficient of 1000 ± 50 , namely, the modified gypsum board. It clearly behaves as a major sink
505 among the 9 materials with a partitioning coefficient that is higher by more than 4 orders of
506 magnitude. This material supports the supposition that the specific surface area is not the only

507 driver of the K value. Indeed, with the same inorganic matrix and a specific surface only 14
508 times higher, the K value of the modified gypsum board exceeds that of the classical gypsum
509 board by a factor of 2000. A similar impact has been reported by Thevenet et al. [8] for
510 formaldehyde, whose partitioning coefficient increased by 2 orders of magnitude as a physical
511 sorbent was introduced in a gypsum-based matrix. This kind of material can be considered a
512 major terpenoid sink in indoor environments.

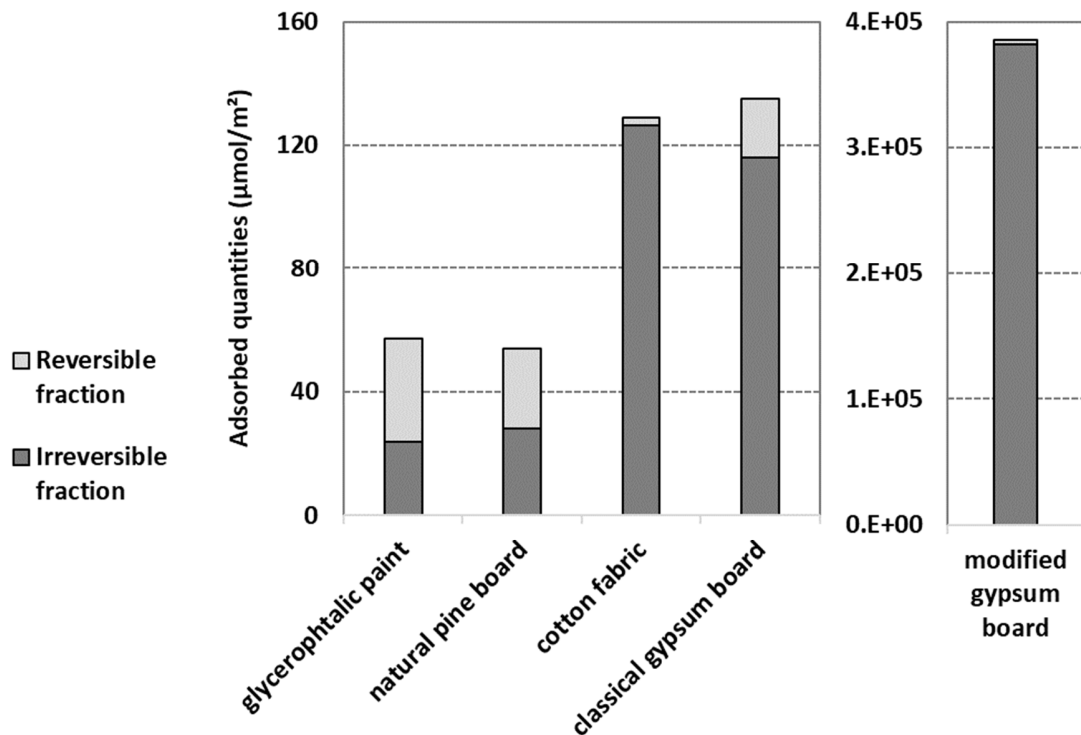
513

514 The selected materials exhibit highly differentiated uptake behaviors, and modified
515 gypsum board is identified as the predominant limonene sink in indoor environments. Beyond
516 the partitioning coefficient, the reversible or irreversible nature of the VOC uptake process is the
517 second main descriptor of indoor VOC sinks.

518

519 ***3.3 Reversibility and irreversibility of the limonene uptake process***

520 In this section, the five most sorptive materials, categorized as moderate and major sinks, are
521 investigated as they potentially affect the indoor fate of limonene. Figure 6 shows the
522 contributions of the reversibly and irreversibly adsorbed fractions of limonene under typical
523 indoor conditions, at an RH of 50% and 23 ± 1 °C.



524 **Figure 6.** Reversible and irreversible fractions of limonene taken up by the 5 most sorptive
 525 materials expressed as the adsorbed quantities of limonene in $\mu\text{mol}/\text{m}^2$, at 50% RH and 23 ± 1
 526 $^{\circ}\text{C}$.

527 As is shown in Figure 6, cotton fabric and gypsum boards are not only characterized by
 528 the highest adsorbed quantities, corresponding to the highest K values, under representative
 529 indoor conditions, but more than 85% of the taken-up limonene molecules also remains on the
 530 surfaces of these materials as the limonene concentration decreases to zero. By comparing the
 531 classical and modified gypsum board samples, it is evident that the presence of a physical
 532 sorbent in the modified gypsum board sample not only increases the adsorbed limonene quantity
 533 by three orders of magnitude (Figure 6) but also enhances the strength of interactions, thus
 534 increasing the irreversible fraction of limonene from 85% to 99%. Similarly, cotton fabric

535 provides limonene with a highly stable uptake surface since almost 98% of the terpenes remain
536 adsorbed under the zero-air flow. The markedly irreversible nature of the limonene uptake
537 process on the cotton fabric and gypsum board samples clearly classifies these materials as long-
538 term indoor pools of limonene and potential contenders for further heterogeneous reactions with
539 indoor oxidants.

540 In contrast, 48% and 58% of limonene was reversibly taken up by natural pine board and
541 glycerophthalic paint, respectively (Figure 6). On the one hand, this result highlights the fact that
542 both materials may act as transient secondary sources via the desorption of limonene from their
543 surfaces, which may subsequently cause a transient limonene pollution event. On the other hand,
544 their ability to release limonene to the gas phase decreases the surface concentration of this
545 terpene. Indoor materials typified by a behavior similar to that of natural pine board and
546 glycerophthalic paint can be considered buffers of gaseous terpenes. Indeed, their mixed source
547 and sink behaviors may induce a more stable terpene concentration. This specific behavior
548 should be further addressed from a real-scale experimental as well as modeling perspective
549 because these materials may alternatively act as sources or sinks depending on the temporal
550 dynamics of the VOC concentration.

551

552

553

554 **4 Conclusion**

555 The determination of the partitioning coefficient of limonene for a selection of representative
556 indoor materials allows an effective and quantitative ranking of the main sinks of terpenes in
557 indoor environments. Even though all materials exhibit linear relations of the limonene uptake

558 amount within the investigated indoor concentration range, the results reveal different
559 contributions of the selected materials in terms of the limonene uptake amount. Indeed, the
560 partitioning coefficients range from 0.010 ± 0.001 m for glass to 1000 ± 50 m for the modified
561 gypsum board. In terms of the applicability of the results, the partitioning coefficients are
562 calculated based on 1 m^2 of the considered material. The glass and polyester fabric samples are
563 categorized as minor sinks, while the others, such as the cotton fabric and gypsum board
564 samples, are clearly identified as major sinks, potentially affecting the gas-phase concentration of
565 limonene. In addition, the investigation of the reversibility of the taken-up fraction provides
566 insights into the processes subsequent to sorption. Interestingly, the materials classified as
567 moderate sinks exhibit mixed sink and source behaviors depending on the gas-phase
568 concentration. It is suggested that these materials may act as buffers of the terpene concentration.
569 The major limonene sinks are shown to be largely irreversible sinks, implying that they
570 constitute surface pools of terpenes in indoor environments, possibly available for further surface
571 reactions. This study highlights the fact that beyond emission sources, an accurate description
572 and modeling of the indoor VOC concentration must encompass uptake, secondary emission and
573 possible subsequent reactions. In this regard, this work provides quantitative data to improve the
574 description of the heterogeneous behavior of indoor surfaces, which is aimed at their integration
575 into indoor physics and chemistry models to improve the model representativeness and our
576 understanding of the indoor fate of VOCs.

577

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603

604 **Declarations of Interest Statement**

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

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Graphical Abstract

