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Malak Rizk, Marie Verriele, Sébastien Dusanter, Coralie Schoemaecker,

Stéphane Le Calvé, Nadine Locoge

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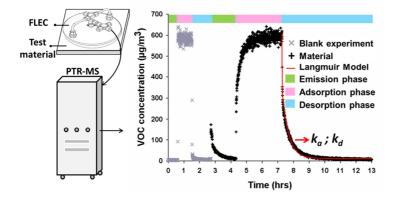
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Graphical abstract



Fast sorption measurements of volatile organic compounds on building materials: Part 1 - Methodology developed for field applications

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M. RIZK^{1,2,4*}, M. VERRIELE^{1,2}, S. DUSANTER^{1,2}, C. SCHOEMAECKER³, S. LE CALVE⁴, N.
LOCOGE^{1,2}

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⁸ ¹Mines Douai, SAGE, F-59508 Douai, France

9 ²Université de Lille, F-59000, Lille, France

³Université de Lille 1, Laboratoire de Physico-chimie des Processus de Combustion et de

11 l'Atmosphère, Villeneuve d'Ascq, France

⁴Université de Strasbourg/CNRS. Institut de Chimie et Procédés pour l'Energie,
 l'Environnement et la Santé (ICPEES), UMR 7515, F-67087, Strasbourg.

^{*}Corresponding author present address: Mines Douai, 941 Rue Charles Bourseul, CS 10838,

15 59508 Douai Cedex France ; Phone : +33 27 71 26 33 ; e-mail : malak.rizk@mines-douai.fr

16 Abstract

Several physicochemical processes occurring within buildings are key drivers of indoor 17 18 concentrations of Volatile Organic compounds VOCs. Many models and experimental studies have been proposed to predict VOCs concentration indoors given these processes. However, 19 there is a lack of representative data in literature to present gas-surface interaction in order to 20 validate mathematical models. This work is divided in two parts and aims to develop and 21 22 validate a method to perform fast measurements of VOC sorption parameters on the field by coupling a Field and Laboratory Emission Cell (FLEC) to a Proton Transfer Reaction-Mass 23 Spectrometer (PTR-MS). In the part 1 of the work, sorption coefficients of aromatic 24 compounds on a gypsum board and vinyl flooring were investigated at ppb levels to test and 25 evaluate the proposed methodology. Sorption coefficients in the range of 0.03-1.88 m.h⁻¹ for 26 27 k_a and 2.04-17.32 h⁻¹ for k_d were successfully measured within a (0.5-8 hours) for the two materials. Robustness tests highlight that the determination of sorption coefficients does not 28 depend on operating conditions. While sorption coefficients for the gypsum board were 29 measured with a PTR-MS time resolution of 20 seconds, the vinyl flooring material required 30 measurements at a higher time resolution of 2 seconds due to its lower sorption properties. 31 Limits of applicability assessed for this method indicate that sets of sorption parameters (k_a, k_b) 32 k_d) of (0.01 m.h⁻¹; 0.01 h⁻¹) and (0.09 m.h⁻¹; 0.09 h⁻¹) can be measured with an accuracy better 33

than 10% at time resolutions of 2 and 20 seconds respectively.

35 <u>Keywords</u>

36 Field and laboratory emission cell (FLEC), Proton transfer reaction-mass spectrometer (PTR-

37 MS), Sorption, VOCs, Building materials.

38 1. Introduction

Volatile organic compounds VOCs are the main pollutants in indoor environment, which 39 present a strong impact on human health, comfort and productivity [1-3]. Several 40 physicochemical processes occurring within buildings are key drivers of indoor 41 concentrations of VOCs [4]. These processes include heterogeneous and gas-phase chemical 42 reactions, air exchange with outdoor and gas-surface interactions. A good understanding of 43 these processes is important to develop efficient strategies to reduce human exposure to 44 45 indoor air pollution. The available methods developed in literature to study the concentrations of VOCs indoors, given the above-mentioned processes fall into two categories, modeling 46 approaches and experimental investigation under well-controlled environments. 47

Under the first category, several models have been developed to simulate the VOC 48 emission/sorption by indoor surfaces. As far as the sorption process is concerned, some 49 models considered the adsorption (k_a) and desorption (k_d) rates [5-7] while, other accounted 50 for the diffusion coefficient (D_m) in the building material and represents the sorption with a 51 partitioning coefficient (K) between the air and the material through a diffusion-controlled 52 mass transfer model proposed by Little [8]. Later Deng [9] proposed an improved model that 53 considers for the convective mass transfer coefficient (h_m) through the boundary layer present 54 on the surface of a material as well as the diffusion and the partitioning coefficients. For the 55 emission process, the diffusion-controlled mass transfer model proposed by Little [8] 56 promoted the development of the emissions mass transfer model such as the model of Xu [10] 57 applied for single-layer building material, the model of Lee [11] applied for porous materials 58 59 and the model of [12, 13] applied for multilayer building materials. A general model was developed by Xiong [14] to characterize both emission and sorption process in ventilated and 60 airtight chambers taking into account the convective mass transfer coefficient, the diffusion 61 coefficient (D_m) and the partitioning coefficient (K). All these models are presented in the 62 reviews of Liu [13] and a comparison between some of the typical models is given elsewhere 63 64 [15]. Nevertheless, all the mentioned-above models consider only the gas-surface interactions and neglect the chemical reactions that can take place indoors in both homogenous and 65 heterogeneous phases. Therefore, some studies [16, 17] proposed indoor air quality models 66 which accounts for the effect of ventilation, deposition of inorganic species on surfaces, 67 68 emission and photochemistry reactions with a consideration for a perfect mixing of the air inside simulated room. However, these photochemistry models neglects the sink behavior of 69 surfaces. 70

Concerning the experimental investigations, only laboratory studies have provided adsorption 71 (k_a) and desorption (k_d) rate coefficients for VOCs on surfaces, to describe the role of these 72 interactions on VOCs indoors concentrations. The experimental procedure is based on the 73 74 exposure of sample materials, inside an emission test chamber, to artificially polluted atmospheres containing several ppm of VOCs [7, 18-20]. The mixing ratios of VOCs used in 75 these experiments are several orders of magnitude higher than those observed in indoor 76 77 environments at ppb levels [21] and are then not representative. These works were conducted 78 considering either a single organic compound and a single material [7, 18, 22, 23] or mixtures of VOCs and combinations of materials [5, 24, 25]. To extract the parameters of interest, 79

experimental concentration profiles, usually measured by gas chromatography techniques, are
fitted by a relevant model, more or less complex as already presented above, depending on the
processes considered (sorption processes, diffusion into the material, and diffusion through
the boundary layer formed above the material surface) and the type of material (homogenous
or porous media).

However, when sorption coefficients derived from chamber experiments was incorporated in 85 indoor air quality (IAO) models, a significant differences as high as a factor of 9 [6] was 86 87 shown between modeled concentrations and ambient observations made in test houses. This disagreement may be due to sorption coefficients for real indoor surfaces that are different 88 than those measured during laboratory experiments [6] because the implementation of a 89 material in a real environment and its aging due to varying environmental conditions can 90 affect its sorption properties compared to those observed in laboratory chambers. In addition, 91 92 the use of inappropriate models to describe real situations can leads to this disagreement as already highlighted by Xu [10]. 93

94 Given the studies mentioned above, there is actually a need to:

- Develop a model that account for all physical and chemical processes occurring indoors
 such as emission, outdoor input, chemical reactivity and also sorption on the surface of
 building materials and,
- Validate proposed models using more representative experimental data from real environment to determine the influence of each process on the VOCs concentration indoors.

101 Consequently, a research project called MERMAID (Mesures Expérimentales Représentatives 102 et Modélisation Air Intérieur Détaillée / Representative Experimental Measurement-Indoor Air Detailed Model) was designed to address the leaks found in literature as already 103 mentioned above [26]. The originality of the MERMAID project is the combination between 104 an experimental approach based on several types of measurements for VOCs, inorganic gases, 105 particulate matter and reactive species to a modeling approach based on a detailed indoor air 106 quality model called INCA-Indoor, including the physical and chemical processes. 107 Concerning the sorption processes, the INCA-indoor model proposed by Mendez [27] treats 108 the sorption of VOCs on the surface of building materials through the adsorption (k_a) and 109 desorption (k_d) coefficients represented as a function of the mass transfer coefficient (h_m) in 110 the boundary layer. However, the INCA-Indoor model neglects the diffusion or the mass 111 transfer in the inner of the material since several inputs parameters are needed which is 112 difficult to determine on the field (effective diffusion coefficients, initial concentration in the 113 materials...etc) and which also requires computational efforts to solve diffusion equations. 114 Nevertheless, the emission rate coefficient is taken into account to represent the mass transfer 115 in the inner of the material. To meet the objective of the MERMAID project, this study aims 116 to develop a methodology suitable to perform in-situ fast measurements of VOC sorption 117 coefficients in indoor environments and under real conditions. Derived experimental 118 119 parameters will be useful as data inputs to INCA-indoor air quality model.

- 120 This work aims to develop a method to determine in a fast and simple way the sorption 121 parameters on the surface of a material present in indoor environment. Therefore this work is 122 divided in three steps:
- (1) Develop a new device based on a field and laboratory emission cell (FLEC) coupled to aproton transfer reaction mass spectrometer (PTRMS);
- (2) Validate the proposed methodology during laboratory experiments to assess the feasibilityof fast in-situ measurements and the limitations of the method applicability; and
- (3) Compare this method to the traditional emission test chamber method used usually inliterature to perform sorption measurements.

Only the findings of the first two steps are presented in this part of the study and the 129 comparison with the traditional method is presented in the part 2 which includes a discussion 130 on the usage of the experimental data in the INCA-Indoor model. Therefore, in this first part 131 of the work the sorption properties of a mixture of aromatic VOCs at ppb levels were 132 investigated on an unpainted gypsum board and vinyl flooring presenting contrasting sorption 133 behavior [18]. These VOCs are considered as ubiquitous compounds in indoor environments 134 and presents a large fraction of total VOC concentrations [21, 28-30]. Moreover, BTEX were 135 chosen to test the proposed methodology, because they can be easily purchased in certified 136 137 cylinders and are not prone to memory effects on sampling materials.

138 2. <u>Materials and Methods</u>

139 **2.1.** Chemicals

For all the experiments, the BTEX mixture was provided by Air products and contained the following VOC in the mixing ratio of 2 for benzene, 6 for toluene, 1 for ethyl benzene, 2 for p-xylene and 1 for o-xylene.

143 2.2. Test materials

An unpainted 12.5-mm thick gypsum board and a 2.4-mm thick piece of vinyl flooring were used. Several samples of each material were stored at 4°C for three months before the experiments to ensure that replicate measurements are performed on samples having the same aging history.

148 2.3. Experimental setup

The setup used in this study is based on coupling a FLEC (Chematec) and a high resolution 149 PTR-MS (PTR-ToFMS, Kore technology) and presented in Figure 1. The FLEC inlet is 150 connected to two gas generation systems using a three-way valve. The first generation system 151 152 is composed of a dry zero air generator (Claind) and a humidificator made of a water bubbler and mass flow controllers (MKS). This system is used to supply the FLEC with humid clean 153 air at constant flow rate (200-500 ml.min⁻¹) and stable relative humidity (50 ± 5 % at 23 ± 2 °C). 154 The second generation system is made of a VOC cylinder connected to a dilution system (Gas 155 Calibration Units - Ionicon Analytik), which is used to dilute the VOC mixture at a constant 156

- relative humidity of 50%. The FLEC's outlet is connected to the PTR-MS to quantify VOC
- 158 concentrations exiting the cell. An exhaust is left at atmospheric pressure to prevent a pressure
- 159 build-up in the FLEC apparatus.

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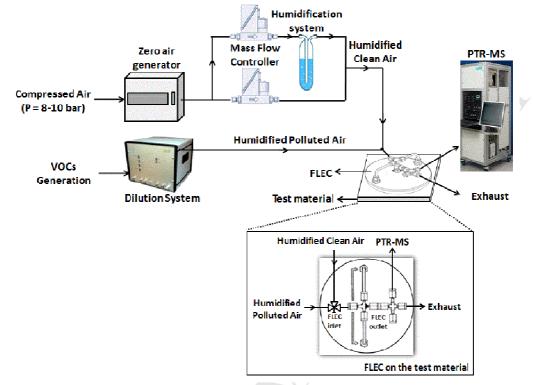


Figure 1. Experimental setup for measuring adsorption and desorption coefficients of VOCs on
 building materials.

The FLEC can be easily handled and fixed on surfaces and the PTR-MS instrument was designed for easy and safe transportation. In fact, the deployment of PTRMS instruments has been demonstrated during field campaigns in ambient air [31] and for indoor studies [32]. This setup exhibits reasonable dimensions to be used during intensive field campaigns for research purposes in buildings but is not proposed as a tool for quick indoor air diagnostics due to its high price and high weight.

169 FLEC. The FLEC[®] is a portable tool commercialized by CHEMATEC, which can be 170 exposed on flat and non-porous surfaces to investigate gas-surface interactions. Technical 171 details have been provided elsewhere [33]. When the cell is exposed on a flat material, it 172 covers a surface area of 177 cm², leading to a loading factor of 506 m².m⁻³. It has a small 173 internal volume (35 mL), which allows conducting fast sorption experiments (a few hours) 174 compared to laboratory emission test chambers of several liters (a few days).

175 *PTR-MS*. The PTR-MS was chosen as a fast analytical tool to accurately monitor the 176 fast variations of VOC concentrations at the sub ppb level [34] with time resolutions in the 177 range of 2-20 seconds. As shown in the result section, the measurement time resolution is a 178 critical parameter to correctly describe fast sorption processes taking place at the material 179 surface inside the FLEC apparatus. The PTR-MS technique has been described in detail 180 elsewhere [34]. As proposed by De Gouw [34], signals of protonated VOCs are normalized to 181 H_3O^+ and $H_3O^+(H_2O)$ to correct for a small humidity dependence of the PTR-MS response.

 $H_3O^+(H_2O)$ is an ionic cluster that is formed when humid samples are analyzed. Detected 182 VOC signals are then converted to concentrations $(\mu g.m^{-3})$ using calibration coefficients 183 determined experimentally for each targeted species. In the following, ethylbenzene and o/p-184 xylene are referred as C8-aromatics due to their detection as a sum of isobaric compounds 185 with the PTR-MS. Calibration coefficients were measured before each experiment using zero 186 air and a standard mixture of VOCs provided by IONICON. Response factors measured over 187 188 a period of 3 months indicate a good stability of the PTR-MS instrument with a relative standard deviation for each species in the range 9-10%. In addition, the stability of the PTR-189 MS response over the time of a sorption experiment (only a few hours) is estimated to be 190 better than 3% from differences observed between subsequent calibrations performed every 2-191 3 days. VOCs background signals measured using zero air were used to estimate detection 192 limits (LOD) as three times the standard deviation on the zero measurements. Measured 193 LODs are less than 3.4, 4.7 and 11 μ g m⁻³ for a time resolution of 20, 10 and 2 seconds 194 respectively and which is low enough to measure accurately the concentrations used in this 195 196 study (See Table 1- [15]).

197 2.4. Experimental protocols

First of all, a blank experiment is carried out on a Pyrex glass before each sorption experiment 198 on a tested material and using the same procedure. This experiment, referred as "No sink" in 199 the following, allows evaluating sorption processes on internal surfaces of the FLEC 200 apparatus and the Teflon tubing. A sorption experiment involves a 3-step procedure as 201 described in the following. The FLEC is first exposed on a material and supplied with 202 humidified zero air. When concentrations reach relatively steady state, the FLEC is supplied 203 with humid air containing targeted VOCs. This second phase is named "adsorption phase" as 204 illustrated in Figure 2. During this step, VOCs concentrations increase until an equilibrium is 205 reached where the concentrations are equal to those registered for the adsorption phase 206 already performed on the Pyrex glass. Once the VOCs concentrations are stable (Figure 2: 207 t_{eq}), humidified zero air is provided to the cell instead of the VOCs mixture. This third phase 208 is named "desorption phase". During this step, VOC concentrations decrease until steady 209 concentrations similar to those reached in the end of the first phase, are observed (Figure 2). 210 Standard operating conditions were defined as an air temperature of $23 \pm 2^{\circ}C$ and a relative 211 212 humidity of 50 ± 5 % for all experiments described in this study.

The feasibility of measuring sorption parameters with the FLEC/PTR-MS coupling was first 213 investigated by repeating the same experiment on a gypsum board and a piece of vinyl 214 flooring (FLEC inlet flow rate = 400 mL.min^{-1} ; PTR-MS time resolution = 20 s). The VOCs 215 concentrations used for the adsorption phase were closed to 565 μ g.m⁻³ for toluene, 434 μ g.m⁻ 216 3 for C8 aromatics, and 160 µg.m⁻³ for benzene. The VOC steady-state-concentrations 217 measured before the sorption experiment by exposing the material to humidify zero air, are 218 negligible and represent less than 3% of Ce. A second set of experiments was carried out on 219 the gypsum board to test the robustness of this method. It consisted in assessing (1) the 220 221 repeatability on 5 different samples (of the same board); (2) the repeatability of 4 tests performed consecutively on the same sample; (3) the influence of VOCs concentrations 222

223 (threefold variation); and (4) the influence of different inlet flow rates (threefold variation)

keeping VOCs concentrations unchanged. Experimental conditions are listed in Table 1.

					Air exchange		Specific flow		Concentration (µg.m ⁻³)			
Test Flow rate (mL.min ⁻¹)		rate (h ⁻¹)		rate per unit of surface [m ³ /(h.m ²)]		Benzene	C8 aromatics	Toluene				
R (n=5)	300			514		1.0			106	289	377	
M (n=4)	300		514		1.4		106	289	377			
F (n=3)	300	400	500	514	686	857	1.0	1.4	1.7	106	289	377
C (n=3)		400			686			1.4		479 319	868 434	1131 565
									·	106	289	377

Table 1. Experimental conditions used to perform tests of robustness on an unpainted gypsum
 board at a PTR-MS time resolution of 20sec.

227n: number of experiments; R= Repeatability tests performed on different samples of the same board; M=228Multiple successive measurements (replicates on the same sample); F= Inlet flow rate tests performed using229three different air flow and C = Concentrations tests performed using three different concentrations.

230 **3.** <u>Theory and data treatment</u>

The data analysis yields values for C_{se} the mass of VOCs in the sink per unit area of the material at equilibrium ($\mu g.m^{-2}$), k_a the adsorption rate constant ($m.h^{-1}$), k_d the desorption rate constant (h^{-1}) and K_e (k_a/k_d) the equilibrium constant (m) described in the following.

234 3.1. Determination of C_s

Based on the experimental procedure described above, the mass of VOCs adsorbed on the material is in steady state at time t_{eq} . The total mass adsorbed or desorbed by a material corresponds to the area between the sorption curves (FLEC exposed on a material) and the "no sink" curve (FLEC exposed on pyrex), for the adsorption and the desorption phases respectively (Figure 2).

Equations (1) and (2) were used to calculate the absorbed and the desorbed mass of VOCrespectively.

242
$$C_{se} = \int_{t_0}^{t_{eq}} \frac{C_s \times F}{A} dt$$
 (1)

243
$$C_{se} = \int_{t_{eq}}^{t_f} \frac{C_g \times F}{A} dt$$

where, *F* is the flow rate at the FLEC's inlet $(m^3.h^{-1})$, *A* the surface area of the material covered by the cell $(177 \times 10^{-4} m^2)$, and *t* the exposure time to the VOCs mixture (h).

246 3.2. Determination of k_a and k_d

(2)

The model used to derive sorption parameters from experimental data is the Tichenor model 247 based on the Langmuir theory [7]. This model is based on the assumption that the 248 concentration of a species in bulk air is homogeneous and proportional to the surface 249 concentration. However, this model neglects the diffusion (D_m) inside the material and the 250 mass transfer coefficient (h_m) between the surface of the material and the bulk air. Despite 251 these limits, this model is suitable for this work to determine k_a and k_d coefficients, for the 252 253 reasons detailed below. Zhang [35] studied the flow filed in the FLEC cavity and calculated the local Sherwood number Sh_L for the different flow rates (186 to 509 mL.min⁻¹). According 254 to this work, the mass transfer coefficient was calculated in the FLEC cavity for the different 255 flow rates used in Table 1 (See Figure 1 in [36]). The flow field in the FLEC is laminar 256 257 because the Reynolds number Re varies between 1.4 and 2.3 for.316 mL/min and 509 mL/min respectively (Re<2000 for laminar flow). The mass transfer coefficient is very high on the 258 FLEC periphery and decreases in the center to reach a value varying between 1.4 and 2.3 259 $m.h^{-1}$. The mass transfer coefficient h_m , is always higher than the specific flow rate per unit of 260 261 surface (Table 1) which means that the that any substance present on the surface of the material is immediately diffused in the transverse direction of the flow by molecular diffusion 262 as already highlighted by Zhu [37]. Therefore, the effect of the mass transfer coefficient is not 263 significant on the concentrations in the FLEC cavity and the concentration measured in the 264 FLEC is considered uniform in the entire cavity (C_g) as Zhang [35] confirmed previously by 265 conducting experimental and numerical studies of the fluid flow and the convective mass 266 transfer coefficients in a FLEC. They concluded that the air becomes nearly saturated shortly 267 after it begins to flow on the emission surface, due to the small spacing between the cap and 268 the bottom surface. Concerning the diffusion in the inner of the material, this parameter is 269 270 neglected in this work and supposed to be slower than the instantaneous adsorption on the surface of the material, since the FLEC-PTRMS method is dedicated to fast in-situ 271 measurements and the INCA-indoor model neglects the diffusion in the inner of the material. 272 It worth to note that further works will use a model that considers the diffusion coefficient in 273 274 the inner of the material to determine the diffusion coefficient and this point will be discussed later in this paper. 275

Giving the reasons above, the concentration variations (dCg/dt and dCs/dt) observed in a 276 chamber depends on the adsorption (k_a) and desorption (k_d) coefficients, as shown in the 277 following equations: 278

dt

279
$$\frac{dC_g}{dt} = NC_{in} - NC_g - k_a C_g L + k_d C_s L$$
(3)
280
$$\frac{dC_s}{dt} = k_a C_g - k_d C_s$$
(4)

where, N is the air exchange rate (h^{-1}), C_{in} the VOC concentration at the chamber inlet 281 performed (μ g.m⁻³), C_g the gas-phase VOC concentration inside the chamber (μ g.m⁻³), k_a the 282 adsorption rate constant (m.h⁻¹), k_d the desorption rate constant (h⁻¹), C_s the surface 283 concentration (μ g.m⁻²), and *L* the loading factor (m².m⁻³). 284

The model used to fit the experimental observations is characterized by equations (3) and (4). Analytical solutions given in equations (5) and (6) can be derived for the desorption phase using the following initial conditions at t_{ac} : t = 0: $C_{a}(0) = C_{a}$ and $C_{a}(0) = C_{ac} = C_{a}(k_{a}/k_{d})$

using the following initial conditions at
$$t_{eq}$$
: $t = 0$; $C_g(0) = C_e$ and $C_s(0) = C_{se} = C_e(k_a/k_d)$

288
$$C_{g}(t) = \frac{C_{e}[(N-r_{2})e^{-r_{1}t} - (N-r_{1})e^{-r_{2}t}]}{r_{1} - r_{2}}$$
(5)

289
$$C_s(t) = \frac{C_e k_a [r_1 e^{-r_2 t} - r_2 - r_2]}{k_d (r_1 - r_2)}$$

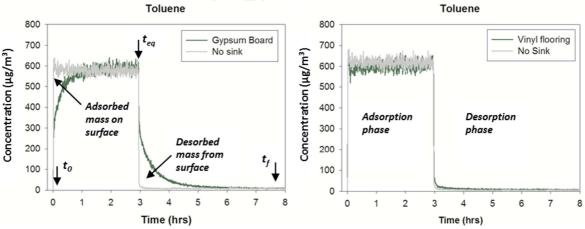
290 where,
$$r_{1,2} = \frac{(N + k_a L + k_d) \pm [(N + k_a L + k_d)^2 - 4Nk_d]^{1/2}}{2}$$

To determine k_a and k_d , the concentration time profiles $C_g(t)$ measured from t_{eq} to the end of the test (desorption phase) is fitted using equation (5) and a non-linear least square regression procedure in SigmaPlotTM. C_e is the average concentration observed in the gas-phase at the end of the adsorption phase. N, L and C_e are experimental parameters so that they are constrained during the fit.

296 **4.** <u>Results</u>

297 4.1. Technical feasibility

Time-resolved concentration profiles obtained for toluene are shown in Figure 2 for two experiments performed on a gypsum board and a piece of vinyl flooring. Concentration profiles of other compounds are given elsewhere (see Figure 2 in [15]) and exhibit the same behavior.



302Time (hrs)Time (hrs)303Figure 2. Concentration profiles measured during sorption experiments on a gypsum board and a304piece of vinyl flooring for benzene, C8 aromatics and toluene. The "no sink" plot is also shown for305comparison.

The concentration profiles indicate that the duration of a sorption experiment is about (0.5-8 hours), which is faster than that observed for regular chamber experiments, usually few days [7, 18]. The experimental no sink profile obtained using Pyrex glass indicate that VOC sorption on the FLEC internal walls is negligible since no difference can be observed with the

)

(6)

theoretical no sink profile obtained according to the equation $C_g(t) = C_e e^{-Nt}$. In addition, these results figure out different sorption behaviors for the 2 materials as seen from the total mass adsorbed on the material at equilibrium and the time needed to reach this equilibrium.

Similar concentration profiles are observed for vinyl flooring and pyrex, suggesting low 313 sorption properties for this material. As a consequence, experiments discussed below to 314 characterize the proposed methodology were only performed using the gypsum board, which 315 exhibit significant sorption properties. Values of k_a and k_d were evaluated for the gypsum 316 board by fitting Equation (4) to concentration profiles acquired during the desorption phase as 317 described in the theory and data treatment section. Obtained values for ka and kd are 318 respectively $(3.2 \text{ m.h}^{-1}-24 \text{ h}^{-1})$ for benzene, $(1.3 \text{ m.h}^{-1}-1.6 \text{ h}^{-1})$ for C8 aromatics and $(1.7 \text{ m.h}^{-1}-1.6 \text{ h}^{-1})$ 319 5.5 h^{-1}) for toluene. The modeled curves shown in Figure 3 are in good agreement with 320 experimental observations because the correlation coefficient R^2 is very close to 1 (0.96 for 321 benzene, 0.97 for C8 aromatics and 0.97 for toluene). This good agreement is also observed 322 for the first minutes of the experiments (Figure 3 (d)) contrary to some previous studies made 323 using emission chambers [7, 38]. 324

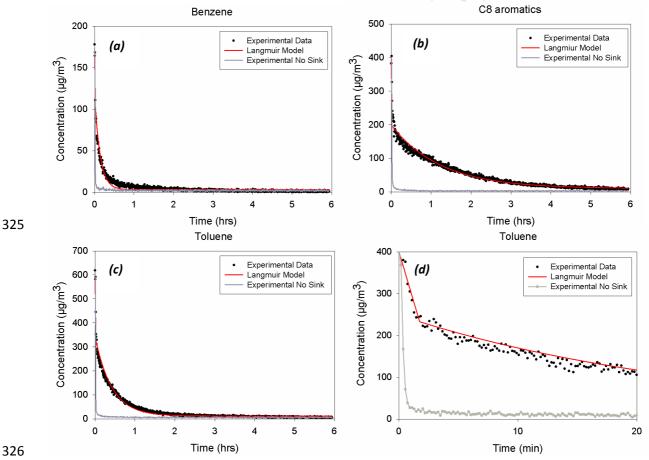
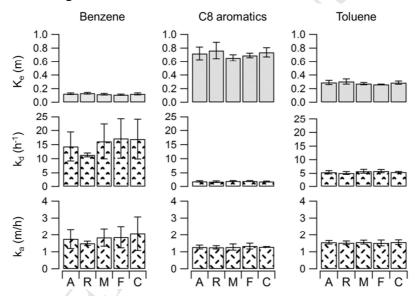


Figure 3. Analysis of the desorption phase for the gypsum board: Benzene (a), C8 aromatics (b),
 and toluene (c, d). The "no sink" curve is also shown in grey for comparison. The first minutes of
 the toluene decay are expended in panel (d) to evaluate the "best-fit" curve.



Figure 4 shows mean values of k_a, k_d and K_e measured for the targeted VOCs for the Gypsum 331 board and using experimental conditions described above in Table 1. The first set of 332 experiments made on different samples of the same gypsum board (R in Figure 4) indicates a 333 good repeatability for the 5 tests, with RSD (1 σ) values lower than 17% for k_a, k_d, and K_e. 334 Four adsorption/desorption cycles (M in Figure 4) made successively on the same sample also 335 336 show a good repeatability for Ke, ka, and kd, with RSD values lower than 12%, except for benzene for which the RSD reaches 38% for k_d . The high uncertainty seen on the 337 determination of benzene sorption parameters is due to the fact that the benzene profile is 338 close to that obtained on pyrex glass, having negligible sorption effect. The uncertainty on the 339 determination of low sorption values will be discussed later in this work. Tests performed at 340 341 different VOCs concentrations (C in Figure 4), as well as different inlet flow rates (F in Figure 4), give consistent results for sorption parameters with RSD values lower than 12% for 342 C8 aromatics and toluene but around 40% for benzene. These results highlight that the 343 determination of sorption coefficients does not depend on operating conditions such as the 344 345 VOCs concentration used, the inlet flow rate, and the number of measurements made previously on the investigated material. 346



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Figure 4. Average results for k_a , k_d and K_e measured on the gypsum board using a mixture of aromatic compounds (A=All experiments; R=Repeatability experiments; M = Multiples adsorptiondesorption experiments on the same piece of material; F = different air flow rates at the FLEC inlet; C = different concentrations of VOCs). Error bars correspond to 1 standard deviation.

- 352 **5.** <u>Discussion</u>
- 353 5.1. Method evaluation

Based on the results shown above, the FLEC/PTR-MS coupling appears as a promising setup to measure sorption coefficients of VOCs on building materials within a few hours (1-16 hours). Compared to common test chamber experiments usually conducted over 27-600 hours (i.e. over 1-24 days) [18-20, 38, 39], the experimental time is reduced by a factor of 54-75. This method exhibits also a good repeatability and the determination of sorption coefficients is independent on gas concentration or the number of tests investigated on the same sample.

In addition, derived parameters are independent on flow rates conditions, which validated the choice of the Langmuir model to extract sorption parameters from experiments performed using an enclosure where the gas-phase concentration above the material is homogenous under the conditions of this study.

The applicability of the Langmuir isotherm was verified by investigating the partitioning of 364 365 VOCs between the gas and adsorbed phases when the equilibrium is reached. The relationship between C_{se} (calculated from equations 1 and 2) and C_e (experimental measurements) for the 366 Gypsum board and target VOCs, shows a linear trend with a correlation coefficient of 0.92, 367 0.80 and 0.94 respectively for benzene, C8 aromatics and toluene (See Figure 3 in [15]). 368 According to the relation ($C_{se}=C_e \times K_e$), the slope of the regression line should be equal to K_e . 369 The slope determined for benzene (0.16), C8 aromatics (0.66) and toluene (0.29) is in 370 excellent agreement with the average Ke value derived from 15 measurements presented in 371 Figure 4. This linear relationship confirms that Langmuir equilibrium can be applied at the 372 concentrations used in this study (106-1131 μ g.m⁻³). 373

In order to test the robustness of the fitting procedure, multiple fits have been performed for several sorption experiments by varying the end-time of desorption phase (Table 2). All desorption phases were performed for 450 minutes and then were analyzed for three different

time durations of 450, 300, and 200 minutes.

Table 2. Comparison between k_a and k_d values derived from the fitting procedure applied to the gypsum board. All experimental measurements were made for duration of 450 minutes. Mathematical fits were performed using an end-time set at 450, 300, and 200 minutes of the desorption phase. Errors correspond to 1σ standard deviation. Number of replicates = 5.

Time of	Be	nzene	C8 :	aromatics	Toluene	
desorption phase (min)	$k_{a}\left(m.h^{-1}\right)$	$\mathbf{k}_{\mathbf{d}} (\mathbf{h}^{-1})$	$\mathbf{k}_{a} \left(\mathbf{m.h}^{-1} \right)$	$k_{d}\left(h^{\text{-}1}\right)$	$\mathbf{k}_{a}\left(\mathbf{m.h}^{-1}\right)$	$k_{d}\left(h^{\text{-1}}\right)$
450	1.8 ± 0.57	16±5.2	1.3±0.11	2,0±0.24	1.6±0.11	6.2±0.59
300	1.6 ± 0.16	12±1.1	1.3 ± 0.10	1.8 ± 0.32	1.6 ± 0.05	5.2 ± 0.35
200	1.7 ± 0.24	15±3.4	1.2±0.13	2.1±0.35	1.6 ± 0.04	5.8 ± 0.69

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This test indicates that determinations of k_a and k_d are robust for these 3 experimental durations. Deviations between individual calculated values and mean values (of all sorption experiments) are within the experimental RSD displayed in Figure 4 (10-17 %). This result also indicates that the time of a sorption experiment, including adsorption and desorption phases, can be adjusted to less than 7 hours for this type of material.

388 5.2. Limitations of applicability

While the setup described in this study is suitable for fast measurements of sorption coefficients in laboratory and indoor environments, this setup exhibits some drawbacks. On the first hand, it is important to avoid high leakage between the cell and the material. For homogenous and flat materials, the cell can be directly exposed on the surface. However, porous or rough surfaces cannot be sampled directly and need to be introduced in a sub unit (cylindrical container) made of aluminum, with the FLEC exposed on the top of the container. Even if this method is destructive in the case of porous materials, it still exhibits the

advantage of reducing the measurement time compared to test chambers. In addition, 396 measurements of sorption coefficients require a fast analytical tool such as the PTR-MS 397 instrument used in this study. In addition, PTR-MS instruments can only measure a limited 398 number of VOCs present in indoor environments and some species such as formaldehyde 399 cannot be measured due to a proton affinity that is only slightly higher than the water proton 400 affinity [34]. Further studies should focus on coupling the FLEC apparatus to other fast 401 402 analyzers, such as a formaldehyde analyzer to study interactions of this important indoor pollutant with indoor surfaces. Fast analytical tools that are currently under development in 403 several laboratories, designed to measure different compounds, may offer a more compact and 404 lighter alternative than the PTR-MS. 405

On the other hand, the Langmuir model used to extract sorption parameters neglects the 406 diffusion inside material which is an important key parameter for indoor air quality models. 407 Nevertheless, Jorgensen [40] used previously the Langmuir model and a diffusion model to 408 analyze sorption experiments performed in emission test chambers. They found that the 409 410 adsorption and desorption coefficients still unchanged between the two models even if the diffusion models determined a supplementary diffusion coefficients. Further works will be 411 conducted to analyze experimental data obtained by the FLEC-PTRMS method, using a 412 model that accounts for the diffusion in the inner of the material, to determine the VOCs 413 414 diffusion coefficient.

In order to determine the lower values of sorption parameters that could be measured with this method, measurements made on a piece of vinyl flooring exhibiting sorption properties close to that observed for a Pyrex glass, were investigated at different PTR-MS time resolutions. Indeed, an adsorption experiment made at a time resolution of 20 seconds showed that it was not possible to extract sorption coefficients from the desorption phase using equation (5) due to a fast decrease of VOCs concentrations (over a few minutes). Additional experiments were performed at resolution times of 10 and 2 seconds. These experiments showed that k_a and k_d

values could only be extracted from measurements performed at the fastest time resolution of2 seconds (Table 3).

424	Table 3. Average values of k_a , k_d , and K_e for a piece of vinyl flooring at a PTR-MS time resolution of
425	2 seconds. Number of replicates = 5.

	VOC	Toluene			C8	aromatic	S	Benzene		
ŀ	Sorption parameters	k _a (m.h ⁻¹)	k _d (h ⁻¹)	K _e (m)	k _a (m.h ⁻¹)	k _d (h ⁻¹)	K _e (m)	k _a (m.h ⁻¹)	k _d (h ⁻¹)	K _e (m)
	Average	0,06) 11	0,01	0,18	17	0,01	0,03	8,3	0,01
	Std	0,02	5,2	0,01	0,03	5,2	0,01	0,02	9,0	0,01
	RSD (%)	28	46	26	18	30	16	57	109	119

426 RSD values calculated from 5 replicates range from 15-110% and are higher than values 427 determined for the gypsum board due to higher noise levels on the PTR-MS measurements at 428 faster time resolutions (Table 3). These results highlight that large uncertainties are associated 429 to the determination of weak sink effects. However, materials exhibiting very weak sink 430 effects will have minor influences on the variation of VOCs concentrations in indoor 431 environments.

As mentioned above, faster measurements lead to higher noise levels on measured signals, 432 and thus lead to a degradation of the measurement precision. Therefore, the best conditions 433 correspond to a compromise between temporal resolution and noise levels. To determine the 434 best operating conditions of the proposed setup, a set of curves, characteristic of the 435 desorption phase, was simulated at 3 different time resolution (2, 10 and 20 seconds) using 436 equation (4), an air exchange rate of 514 h^{-1} and several values of adsorption (k_a) and 437 desorption (k_d) coefficients. To reduce the number of couples for k_a and k_d , the same value 438 was used for both parameters. The simulations were also performed using experimental values 439 measured for the vinyl flooring at a PTR-MS time resolution of 2 seconds. Equation (4) was 440 fitted on the simulated curves using Sigma Plot to check whether the mathematical fit is 441 capable of retrieving the values of k_a and k_d used to generate the curves. The accuracy of the 442 fit was calculated as the difference observed between values of k_a and k_d used to simulate the 443 curves and values determined by fitting the curve as shown in Table 4. 444

446	resolutions.						
	Temporal resolution (sec)	$\mathbf{k}_{a} (\mathbf{m} \mathbf{h}^{-1})$	$\mathbf{k}_{\mathbf{d}} (\mathbf{h}^{-1})$	Accuracy k _a (%)	Accuracy k _d (%)		
		0.01	0.01	9.89	10.00		
		0.02	0.02	4.71	5.00		
	2	0.10	0.10	0.10	0.10		
	2	0.01	0.10	0.001	0.60		
		0.10	0.01	1.20	1.00		
		0.03	17.00	0.33	0.24		
		0.07	0.07	6.22	8.71		
	10	0.09	0.09	2.51	4.33		
		0.10	0.10	1.63	3.00		
		0.09	0.09	5.39	10.11		
	20	0.10	0.1	3.63	7.30		
		0.20	0.20	0.02	0.95		

445 Table 4. Accuracy determined by simulation for low values of k_a and k_d for three PTR-MS temporal 446 resolutions.

An accuracy lower than 10% is considered as satisfactory to accurately determine k_a and k_d. A 447 close inspection of Table 4 indicates that temporal resolutions of 20 and 10 seconds are fast 448 enough to accurately measure adsorption and desorption parameters (k_a; k_d) as low as 449 (0.09m.h⁻¹; 0.09h⁻¹) and (0.07m.h⁻¹; 0.07h⁻¹), respectively. Faster measurements (2 seconds 450 time resolution) are needed to determine lower values down to $k_a=0.01$ m.h⁻¹ and $k_d=0.01$ h⁻¹. It 451 is important to note that these results only provide an estimation of the lower values of k_a and 452 k_d that can be measured at a specific time resolution with the FLEC-PTRMS coupling since 453 combinations of different values of k_a and k_d are usually observed. Experimental values 454 derived for the vinyl flooring were also tested and they prove that more resolute 455 measurements are necessary to accurately determine sorption coefficients in this range. In 456 addition, these simulations indicated that the determination of low values of k_a is more 457 impacted by the temporal resolution than k_d because the value of k_a is mainly determined by 458 459 using the first minutes of the experimental measurements.

460 5.3. Literature comparison

461 Won [6] measured sorption coefficients for a gypsum board exposed to toluene and 462 ethylbenzene. Tichenor et al. [7] also report sorption coefficients of toluene for the same type

of material. To the best of our knowledge, there is no measurement of sorption coefficients for 463 benzene available in the literature. Sorption coefficients measured in this study are in the 464 same order of magnitude of previous studies and show a difference by a factor of 2-3 times 465 for K_e parameter (Table 5). However, a difference is also reported between previous works for 466 the same type of material with ethylbenzene. For the vinyl flooring the difference is more 467 468 important. This difference can be due to the composition of the tested material as reported by Won [41]. The aging of the surface, or its physicochemical properties may also introduce 469 some variability in the results as observed by Meininghaus [42]. From the other hand, this 470 difference can be due to the inappropriate use of the Tichenor model for emission test 471 chambers used for sorption experiments. The effect of the mass transfer due to the presence of 472 a boundary layer on the surface of the tested material can have an important effect on the 473 determination of sorption parameters. The companion paper (part 2 of this work), will present 474 a comparison using an emission test chamber and the same type of material and the same 475 VOCs mixture. Therefore, different type of models will be used to determine sorption 476 477 parameters with a consideration for the effect of the mass transfer coefficient and the effect of the boundary layer. 478

479Table 5. Comparison of literature values of K_e for a gypsum board with results from this480study.

VOCs	$\mathbf{k}_{a} \left(\mathbf{m} \cdot \mathbf{h}^{-1} \right)$	\mathbf{k}_{d} (h ⁻¹)	K _e (m)	References
Benzene	1.8 ± 0.57	14 ± 5.2	0.12 ± 0.01	This work
Talmana	0.21	1.7	0.12	[6]
Toluene	1.6 ± 0.11	5.4 ± 0.59	0.29 ± 0.03	This work
E4blb or going	0.21	0.87	0.24	[6]
Ethylbenzene	0.45	1.50	0.30	[7]
C8 aromatics	1.3 ± 0.11	1.8 ± 0.24	0.72 ± 0.09	This work

481 6. <u>Conclusions</u>

The proposed experimental approach, based on a FLEC-PTRMS coupling, has been used 482 successfully to measure sorption coefficients of aromatic compounds on different types of 483 materials. This method presents the advantage to be transportable and non-destructive method 484 485 for flat and homogeneous material to perform fast measurements in real environments and under indoor conditions. Moreover, this new setup exhibits the advantage of reducing the 486 measurement time to 0.5-8 hours compared to emission test chambers that require several 487 days of measurements and allows measuring low sorption values. The FLEC/PTR-MS 488 coupling allows measuring low sorption values and will be used for in-situ measurements in 489 energy efficient buildings. Sorption coefficients determined on the field will be then used as 490 inputs for a new indoor air quality model (INCA-indoor) that takes into account the boundary 491 layer effect and the mass transfer coefficient, to predict VOCs concentrations in indoor 492 environments (see companion paper). The FLEC-PTRMS method will be compared in the 493 494 part 2 of this work, to the traditional emission test chamber method used previously in literature to measure sorption parameters only on the laboratory scale. Further works, will use 495 a more complex model to take into account for the diffusion inside building materials. 496

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<u>Highlights</u>

- Development of a new methodology to measure *in-situ* VOCs sorption on building materials
- Evaluation of sorption parameters under real conditions within few hours
- Measurement of low sorption properties with 10% of accuracy
- Sorption parameters are useful to IAQ models to predict VOCs concentration indoors