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1	Assessment of gas-phase concentrations of organophosphate flame
2	retardants at the material surface using a midget emission cell
3	coupled to solid-phase microextraction

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#### 13 ABSTRACT

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Actual methods for on-site measurement of gaseous concentrations of Semi-Volatile Organic 14 Compounds (SVOCs) at the material surface  $(y^0)$  are not yet sufficiently developed mainly 15 due to sampling difficulties. These concentrations are the key data to improve knowledge 16 about indoor sources and human exposure to SVOCs. To the end, a specific emission cell 17 coupled to solid-phase microextraction (SPME) was developed. The main challenge with this 18 method is calibration because of very low volatility of SVOCs and static sampling mode. In 19 20 this study, a generating system of organophosphate flame retardants (OFRs) using polyurethane foam as source combined with an active sampling method with Tenax tubes was 21 proposed as a novel calibration device for SPME-based method. The generating system 22 delivered stable OFR concentrations after 190 hours of operation with a variation not 23 exceeding  $\pm 5\%$ . It allowed to obtain robust calibrations for tris-(2-chloropropyl)-phosphate 24 (TCPP) and tri-butyl-phosphate (TBP) measured with the emission cell coupled to SPME-25 based method, define the optimal sampling requirements and achieve reproducible and 26 accurate measurements of  $y^0$  at  $\mu g.m^{-3}$  level. 27 28

TCPP and TBP gas-phase concentrations at the polyurethane foam surface (y<sup>0</sup>) were followed up over more 228 days under controlled temperature conditions. A high stability of these concentrations was observed showing that polyurethane foam acts as a stable and continuous source of organophosphate flame retardants indoors. This novel method should be useful for assessing the dynamic of emissions from indoor sources and potential exposure to SVOCs in indoor environments.

#### 35 **KEYWORDS**

Indoor air quality, Organophosphate flame retardants, Material emission, Polyurethane foams,
Gas-phase SVOCs generation system.

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#### 39 1. Introduction

A large number of building materials and household products contain Semi-Volatile Organic 40 Compounds (SVOCs) which are used as plasticizers, flame retardants, preservatives, 41 repellents, combustion products, pesticides, surfactants and personal care products [1-3]. In 42 many materials, SVOCs account for a mass fraction from 1 to 30% [1,4]. Despite their low 43 saturated vapor pressures ranging from 10<sup>-2</sup> to 10<sup>-8</sup> kPa at 298 K, SVOCs can vaporize from 44 the surfaces of products containing them [5]. They are partitioned partly as gaseous chemicals 45 46 and partly as chemicals sorbed on indoor surfaces and onto airborne and settled particles [6]. 47 People are exposed to SVOCs via multiple pathways (inhalation, ingestion and dermal contact) [7-8]. Human exposure to many SVOCs has been associated with severe health 48 impacts as including asthma, allergies, endocrine disruption, reproductive disorders and 49 cancer [9-12]. As shown by Little et al. [13], the SVOCs gas-phase concentration adjacent to 50 the source material  $(y^0, \mu g.m^{-3})$  is a key parameter to describe the behavior of these 51 52 compounds indoors.

53 Many methods have been developed to measure  $y^0$  [14]. There are two main experimental 54 approaches: (1) the ventilated emission chambers (or cell) with active air sampling like 55 CLIMPAQ [15], FLEC [16], microchamber [17], sandwich-like chamber [18], Early stage C-56 history method [19] and varied ventilation rate (VVR) method [20] and (2) the 57 closed emission chambers (or cell) with passive sampling like the passive flux sampler (PFS) 58 [21], thermal desorption tube [22] and SPME-based method [23]. Gong and Poppendieck [24] 59 discussed the main features, advantages and disadvantages of these methods.

Normally, the closed systems with passive sampling methods require shorter experimental
time (from one to several days) than ventilated devices (from a few days to many months) and
are the only devices that can be used for on-site measurement of SVOCs indoors [24].

In the case of the SPME-based method,  $y^0$  can be measured directly inside the closed device containing the source material after that the steady state is reached [23,25]. Indeed, when the gaseous concentration becomes stable inside the closed device, there is no more mass transfer of compound between the gas phase and the inner surfaces (source material and inner walls of

device). In consequence, the steady state SVOC concentration can be assimilated to  $y^0$ 67 [23,25]. The main difficulties of the SPME-based method for measuring  $y^0$  concern the 68 calibration and setting of sampling parameters including air/material equilibrium time and 69 sampling time [24]. The SPME sampling is based on the molecular diffusion process of the 70 71 compound in air to a sorbent according to the Fick's first law [26]. In non-equilibrium conditions (linear sorption), the mass of SVOC sorbed onto the fiber (m) and the product of 72 its concentration in air and the exposure time  $(y^0 \times t)$  are linearly related [26-27]. To establish 73 this linear relationship  $m=k\times(y^0\times t)$  with k constant, a calibration related to a traditional active 74 sampling method and the use of a generation of gas atmospheres are required. 75

76 . However, the conventional means used for the continuous production of gas atmospheres, 77 such as permeation tube, syringe pump or compressed gas cylinder, cannot be used for SVOCs because of their very low volatility. Furthermore, SVOCs can be partially sorbed or 78 79 80 deposited onto all inner surfaces of the generation device and tubing [2].

In the literature, a few methods are available to generate gas-phase SVOCs with stable and 81 controlled concentrations. They most often require very long times (several days or even 82 several months) to reach stable concentrations [28]. The favored approach is gaseous release 83 from solid or liquid phase materials containing SVOCs [29,30]. As shown by Clausen et al. 84 [15], the DEHP generation from PVC placed in a FLEC cell was stable after 240 days, while 85 in a CLIMPAQ chamber, the stable concentration was not reached for the entire duration of 86 the experiment (450 days). Extended to phthalates from building materials, a special stainless-87 steel chamber designed by Xu et al. [31] and its improved version [18] allowed to short the 88 times to reach stable generating states to 20 days and 1-2 days, respectively. More recently, 89 Chen et al. [28] used impregnated porous media (Carbon sponges and honeycomb ceramics) 90 to generate constant gas-phase concentrations of phthalates after 4.5, 18.5 and 89.5 hours 91 according the compounds. 92

This work was part of development on an emission cell (MOSEC) coupled to SPME-based 93 method intended to on-site measurement of SVOCs gas-phase concentration at the material 94 surface already described in a previous paper [25]. It focused on the measurement of tris-(2-95 chloropropyl)-phosphate (TCPP) and tri-butyl-phosphate (TBP), flame retardants emitted 96 from polyurethane (PU) foam. The objectives were: (1) to test and validate a calibration 97 procedure based on a new experimental device to generate gas-phase TCPP and TBP from PU 98 foam, (2) to define the optimal sampling conditions (steady state condition and extraction 99 time) and provide method performance characteristics, (3) to provide information on time variation of TCPP and TBP gas-phase concentrations at the polyurethane foam surface.

#### 102 2. Materials and Methods

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#### 2.1. Passive sampling method

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The passive sampling device used for the determination of gaseous SVOC 106 concentrations at the material surface was already described in a previous article [25]. 107 It consists of a home-made emission glass cell (named MOSEC) of 60 mL covering a 108 sampling area of 17 cm<sup>2</sup>. The top of the cell has a cap with a septum for SPME fiber 109 introduction. The bottom was fitted with a thread for hermetically sealing the cell with 110 111 a silonite coated stainless steel screw cap equipped with a vacuum valve. This airtight cell configuration is used in the cleaning procedure and in the experimental device for 112 113 calibration, as described below. First of all, the emission cell is placed directly on the material surface (Fig.1a). SVOCs released from the material, diffuse inside the air 114 115 volume of the cell, and are partially sorbed onto the cell walls. When the gaseous concentration is stable in the cell, the mass transfers from the source material to air and 116 from air to the cell walls become zero. At this steady state, the gaseous concentration is 117 measured using a 100 µm PDMS SPME fiber in the linear sorption conditions (Fig.1b). 118 A previous study [25] showed that there is no significant difference in the steady state 119 SVOC concentration measured in the 60 mL and 120 mL cells. This confirmed that 120 this gaseous concentration can be assimilated to  $y^0$ , since its value does not depend on 121 the amount sorbed onto the cell walls before reaching the steady state. 122 123

Prior to sampling, the fiber was conditioned in the injection port at 300 °C. Before use, the cell was soaked in water, rinsed with methanol and then dried in an oven at 100 °C. Some vacuum/clean air filling cycles complemented the procedure of cleaning, in order to achieve acceptable blank levels [25].

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#### 2.2. Material samples and target SVOC

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The test material used as the SVOC emission source was a soft polyurethane (PU) foam. It was part of a series of polyurethane foam models manufactured in an earlier study to assess the migration and potential risks of phosphorus flame retardants from fireproofing of domestic upholstered furniture [32]. Upholstered furniture is one of the main known sources of phosphorus flame retardants indoors [33]. The manufacturing method of material test was given in detail by Ghislain *et al.* [34]. It was obtained by polymerization of polyol mixture with isocyanate following a commonly used procedure. Phosphorus flame retardants were directly incorporated in the reactant mixture during foam polymerization. The test material initially contained TCPP and TBP in mass fractions of 7.6 %. Polyurethane foam samples were  $41 \times 24$  cm panels with a thickness of 1 cm and a density of 200 kg.m<sup>-3</sup>. Each material sample was wrapped in aluminum foil and stored at room temperature prior to the tests.

TCPP and TBP were the target compounds chosen for these tests. TBP is an alkylphosphate and its vapor pressure is to  $4.65 \times 10^{-1}$  Pa at 298 K. TCPP is a chlorinated organophosphate less volatile than TBP with a vapor pressure of  $7.52 \times 10^{-3}$  Pa at 298 K. They are in a class of organophosphate esters commonly used as flame retardants, plasticizers and anti-foaming agents in a wide variety of consumer products like foams, textiles, resins and vinyl polymers [35,36].

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#### 2.3. Implemented experimental device for calibration

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A new experimental device was especially developed to generate gas-phase TCPP and TBP 150 151 from PU foam. It consisted of three 89 mm long and 6.35 mm diameter stainless steel tubes filled each one with 0.35 g of PU foam and connected in series to the MOSEC cell (Fig.2a). 152 These tubes were flowed by humidified clean air at the stable conditions of relative humidity 153 and temperature (HR=50  $\pm$  3% at T=23  $\pm$  2°C) produced by a dry zero air generator (Claind, 154 Marcq-en-Baroeul, France) and a humidifier made of a water bubbler and regulated by mass 155 flow controllers (Bronkhorst, Montigny-les-Cormeilles, France). The airflow rate was 156 maintained at 60 mL.min<sup>-1</sup> for all the duration of test. The air flow was transferred from the 157 tubes to MOSEC cell via a needle introduced in two septa (the one placed in the nut of the last 158 159 tube and the other one at the cap of MOSEC cell). This connection and the source material set 160 in thin tubes had the advantage of reducing the air volume upstream from the MOSEC cell favouring a fast transfer of SVOC from the source to the cell. The sealed closing of the cell 161 162 was provided by an o-ring placed in the screw cap. The air leakage rate in this generation device of SVOC was assessed at less than 5% and checked systematically after each sampling 163 throughout the test using a soap film flowmeter (Model M-30, AP BUCK, USA). 164

First, the emission cell was continuously crossed by air coming from the tubes containing the source material until the gas-phase SVOC concentrations became stable (Fig.2a). The SPMEbased method described in section 2.1 was used to describe the increase in gaseous SVOC concentrations in the cell. To this end, the MOSEC cell was temporally isolated for sampling

by SPME as shown in Fig.2b. Once the gaseous concentrations achieved stability, an active 169 sampling with Tenax tubes was performed at 40 mL.min<sup>-1</sup> for 6 hours (Fig.2c). This allowed 170 to assess the gaseous SVOC concentrations under the stable conditions of the generation 171 system. Then, a series of SPME measurements with variable extraction time from 1 to 10 172 minutes was carried out (in isolated cell) in order to plot the calibration curve between the 173 amount of compound adsorbed on the fiber and the product of its gaseous concentration 174 (assessed by active sampling method with Tenax tube) and the extraction time [27,37]. This 175 method of calibration was used to convert the compound amount sampled by SPME fiber into 176 177 the gaseous concentration.

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#### 2.4. Tenax cartridge analysis

Analysis of Tenax tubes was carried out with a TurboMatrix 650 ATD thermal desorption 181 system (PerkinElmer, Waltham, MA, USA). The Tenax tubes were heated at 330 °C for 15 182 min, using a helium flow rate of 100 mL.min<sup>-1</sup> without inlet split to desorb the analytes and 183 focus them into a cold trap kept at 1 °C. Desorption trap was ramped at 99 °C.s<sup>-1</sup> to 350 °C, 184 held for 10 min, with an outlet split of 5 mL.min<sup>-1</sup>. The transfer line to the GC and the valve 185 were maintained at 250 °C. Separation and detection were performed with a PerkinElmer 186 Clarus 680 gas chromatograph. The carrier gas was helium with a flow rate of 1.3 mL.min<sup>-1</sup>. 187 A 5% phenyl Elite-5 capillary column (PerkinElmer, Waltham, MA, USA) of 60 m, 0.25 mm 188 i.d. and 0.25 µm film thickness was used. The oven temperature was maintained 2 min at 50 189 °C, then ramped at 15 °C.min<sup>-1</sup> to 200 °C, held for 2 min, then ramped at 15 °C.min<sup>-1</sup> to 300 190 °C, held for 14 min. The gas chromatograph was equipped with dual MS/FID detection. MS is 191 192 a PerkinElmer Clarus SQ 8T. Acquisition was operated in full scan (50 to 470 amu) using electron impact mode (70 eV). MS data were used to identify target SVOCs and check there 193 was no co-elution with other compounds. Quantitative analysis was performed by FID and 194 based on an external calibration. To this end, Tenax tubes were loaded with 2 µL of standard 195 mixtures of the analytes in methanol using a GC syringe and then purged for 5 min with a 196 helium flow of 50 mL.min<sup>-1</sup> to remove the solvent. The calibration ranges were from 0.1 to 197 1.6 µg for TCPP and from 0.8 to 4.6 µg for TBP according to the sampling conditions and 198 concentrations produced by the SVOC generation system. The calibration curves with six 199 standard levels obtained showed higher correlation  $R^2 > 0.99$  for the two compounds (as 200 shown in Fig. S1 in the Supplementary materials). 201

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#### 2.5. SPME analysis

After sampling, the SPME fiber was directly desorbed in the injector port of a gas 205 chromatograph for analysis. An Agilent 7890B gas chromatograph (Agilent Technologies, 206 Les Ulis, France) equipped with dual MS/FID detection was used. The injection port was 207 equipped with a 0.75 mm i.d. liner and operated at 300 °C in splitless mode. The carrier gas 208 was helium with a flow rate of 2 mL.min<sup>-1</sup>. A 5% phenyl Elite-5 capillary column 209 210 (PerkinElmer, Waltham, MA, USA) of 60 m, 0.25 mm i.d. and 0.25 µm film thickness was used. The oven temperature was maintained at 60 °C for 2 min, then ramped at 30 °C.min<sup>-1</sup> to 211 200 °C, held for 2 min, then ramped at 15 °C. min<sup>-1</sup> to 310 °C, held for 22 min. MS is an 212 Agilent 5977B MSD. Acquisition was operated in full scan (50 to 400 amu) using the electron 213 impact mode (70 eV). Quantitative analysis was performed by FID basing on an external 214 calibration. The latter was used to express the result as the SVOC amount extracted by the 215 SPME fiber. It consisted in injecting and analyzing standard mixtures of TCPP and TBP in 216 methanol under the same chromatographic conditions than those for SPME desorption and 217 analysis. Due to volume expansion of standard solutions during the vaporization in the 218 injection port, a small volume (0.1 µL) compatible with the 0.75 mm I.D. liner was injected 219 [38]. Calibration curves used for the quantification of TCPP and TBP amounts sampled with 220 the SPME fiber are shown in Fig. S2 (Supplementary materials). 221 222

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#### 3. **Results and discussions**

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#### 3.1. Stability of SVOC generation system and calibration

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Fig. 3 shows the generated TBP and TCPP concentrations over a 500-h period obtained with the experimental device described in section 2.3. The results are expressed in gaseous concentrations using the calibration curves given below.

The concentrations increase in the first tens of hours to reach the maxima of 382  $\mu$ g.m<sup>-3</sup> for TBP and 35  $\mu$ g.m<sup>-3</sup> for TCPP around 70 hours. Large fluctuations are observed in concentrations around the maximum values. Then, the concentrations slightly decrease by 20 % reaching a stable level of 298  $\mu$ g.m<sup>-3</sup> for TBP and 27  $\mu$ g.m<sup>-3</sup> for TCPP after 190 h (mean concentrations after 190 h). High stability of concentrations was obtained between 190 and 500 h. In this time interval, the concentrations do not exceed the mean value by more than ±5 %. The coefficients of variation calculated from the last twelve measures performed after 190 h are 1.3 % for TBP and 3.0 % for TCPP. This experimental device provides a technical solution for calibration of organophosphate flame retardants measurement methods. Its characteristics in terms of time to reach a stable generating state and concentration stability are comparable to those of the most advanced techniques using the solid materials to generate gas-phase SVOCs [18,28].

Fig. 4 shows the calibrations obtained on a wide range of exposure dose extending up to 400 243 μg.m<sup>-3</sup>.min for TCPP and 4400 μg.m<sup>-3</sup>.min for TBP. The concentration determined by an 244 active sampling method with Tenax tubes was considered here as reference value. To check 245 linearity and robustness in calibration, several SPME measurements were performed by 246 changing exposure time (from 2 to 12 min) and three series with different samples of 247 polyurethane foam. These results confirm good linearity between the amount sampled by 248 SPME fiber and the product of gaseous concentration and the exposure time with a squared 249 correlation coefficient greater than 0.98. No significant deviation was observed between 250 points belonging to different calibration series. These results demonstrate that the linear 251 sorption domains extend up to 400 µg.m<sup>-3</sup>.min for TCPP and 4400 µg.m<sup>-3</sup>.min for TBP. When 252 the sampling time is increased, this SPME method is sensitive enough to measure 253 concentrations in the  $\mu$ g.m<sup>-3</sup> range. However, the SPME fiber extracts a SVOC amount at 254 each sampling. It may not exceed the SVOC amount in the gas phase of the cell. According to 255 the slopes of calibration curves given in Fig.4, the uptake rates of TCPP and TBP on the 256 SPME fiber are 0.0048 and 0.0051 ng.(µg.m<sup>-3</sup>.min)<sup>-1</sup>, respectively. Considering these uptake 257 rates and the cell volume (60 mL), the sampling time required to extract the total amount in 258 gas phase was determined to 12.5 min for TCPP and 11.8 min for TBP. Then, to respect this 259 sampling limit, the extraction time should be less than 11 min.

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#### **3.2.** Time to reach the steady state concentration in the MOSEC cell

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To assess the time required to reach the steady state in the emission cell (stable gaseous 263 264 concentration), a series of tests was performed using selected polyurethane foam placed in a room where temperature was kept at  $23 \pm 3$  °C. To this end, the emission cell was placed on 265 266 the material surface for increasing periods before sampling. After each period, a SPME sampling was performed to measure the gaseous concentration in the cell. The results are 267 268 shown in Fig. 5 for both compounds. Steady state was reached after 3 hours for TBP and 3.5 hours for TCPP. These results confirm that the time to reach the steady state is shorter for a 269 closed cell (Fig.5) than for a ventilated device (Fig.3). This trend was already observed in 270

previous studies [23]. In the case of closed cell, this time is probably shortened due to the 271 small volume of the cell (60 mL). It depends on numerous characteristics of SVOC/material 272 couple like the diffusion of compound in the material, the material/air partition, the initial 273 274 emittable SVOC concentration in the material and the fraction sorbed on the inner walls of the cell [25,39,40]. Consequently, the pattern of gaseous concentration should vary according to 275 material and SVOC and it is necessary to check this time required to reach the steady state for 276 each compound and type of sampled material. 277

Considering the beginning of increase in concentration in Fig.5, the initial emission rates in 278 the cell can be evaluated to 0.66 ng.min<sup>-1</sup> for TBP and 0.0014 ng.min<sup>-1</sup> for TCPP. 279

Basing on the calibration data (section 3.1) and the steady state concentrations, the uptake 280 rates on the SPME fiber were 5.9 ng.min<sup>-1</sup> for TBP and 0.17 ng.min<sup>-1</sup> for TCPP, i.e. values 9 281 and 13 times higher than the initial emission rates given above. So, the extracted amount by 282 SPME during sampling mainly comes from the gas-phase. The emission rate is too slow for 283 that a significant part emitted by the material during the extraction phase contributes to the 284 285 amount sampled by the fiber.

- 286 287
- 3.3. Method performance
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#### The limits of detection (LoD) and quantification (LoQ) were calculated as three times and ten 289 times the standard deviation of the blank for both compounds. Blank test consisted in placing 290 the cell on a glass plate and performing a SPME measurement. Low detectable quantities of 291 0.05 and 0.04 ng were obtained for TCPP and TBP in the blank analysis. Consequently, all 292 the measurements by SPME sampling method were systematically subtracted from the 293 average of blanks. As shown in Table 1, the sampling time should be close to 11 min in order 294

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Table 1. Limits of detection (LoD) and quantification (LoQ) obtained from the analysis of 6 297 blanks. 298

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	Sampling time			
	1 min	7 min	11 min	
TCPP:				
LoD (µg.m <sup>-3</sup> )	8.5	1.2	0.8	
LoQ (µg.m <sup>-3</sup> )	28	4.1	2.6	
TBP:				
LoD (µg.m <sup>-3</sup> )	11	1.6	1.0	
	38	5.4	3.4	

to accurately measure concentrations of a few  $\mu$ g.m<sup>-3</sup>.

$LoQ(\mu g.m^{-3})$	

Reproducibility was evaluated from a series of ten replicate measurements performed on the 301 selected PU foam using three different SPME fibers for different days (Table 2). The 302 sampling times were from 7 to 11 min and these tests were carried out in a room where 303 temperature was kept at  $23 \pm 3$  °C. A satisfying level of reproducibility was achieved with a 304 relative standard deviation (RSD) of 3.6% for TBP and 9.3% for TCPP. The RSD values are 305 higher than those obtained in the cell of the generation system after stabilization of 306 concentrations (RSD of 1.3% for TBP and 3.0% for TCPP). The difference in RSD suggests 307 that the variability in emission of a same material surface is the main source of uncertainty in 308 309 measurement for this method.

Note also that the high TBP gaseous concentration at the polyurethane foam surface ( $y^0 = 472$ ) 310 µg.m<sup>-3</sup>) tends to reduce RSD%. These results confirm those previously obtained by Ghislain 311 et al. [25] giving RSD values from 2 to 10% for the measurements of three organophosphate 312 esters with this same method. Reproducibility was also assessed by performing an additional 313 series of measurements at the surface of a cushion consisted of a PU foam containing TCPP at 314 2% by mass covered with a fabric. A RSD of 10.8 % for a TCPP concentration (y<sup>0</sup>) of 3.4 315 µg.m<sup>-3</sup> was obtained from six replicate samplings at the cushion surface under laboratory 316 conditions. Despite a low concentration close to LoQ, RSD value remains acceptable. 317

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Table 2. Reproducibility (RSD) obtained from replicate measurements performed on the
selected PU foam surface with the emission cell coupled to SPME-based method.

	Number of replicate measurements	$y^0$ (µg.m <sup>-3</sup> ) mean ± standard deviation	RSD (%)
ТСРР	10	$29.6 \pm 2.7$	9.3
ТВР	10	472 ± 17	3.6

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## 3.4. Time variation of TCPP and TBP gas-phase concentrations at the polyurethane foam surface

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The y<sup>0</sup> changes over time of selected polyurethane foam for TCPP and TBP was followed from November 8, 2019 to June 23, 2020 (228 days in total). For this experiment, the material was placed in a laboratory room where temperature was kept at  $23 \pm 3$  °C. y<sup>0</sup> was measured eight times during the experiment period using the method developed in this study. The sampling time was 7 min. As shown in Fig.6, no trend was observed in the y<sup>0</sup> variation

- compared to the value measured on the 1<sup>st</sup> day (designated as initial value). These  $y^0$  values do not differ by more than 20% for TCPP and 10% for TBP from its initial value. The release of TCPP and TBP from soft polyurethane foam appears as very stable for more than 200 days compared to emission kinetics that usually have a decay phase observable over several months [41,42]. Pei *et al.* [43] also found no decrease in  $y^0$  after 60 days for TCPP emitted from a PU foam.
- The tests for assessing the time to reach the steady state shown in section 3.2 were performed 338 with the selected PU foam in October 2015, i.e. 4 years before the start of temporal follow-up 339 of y<sup>0</sup> for this same material and shown in Fig.6. y<sup>0</sup> for 228 days in Nov. 2019/June 2020 (460 340 and 29.5 µg.m<sup>-3</sup> for TBP and TCPP, respectively) were lower than y<sup>0</sup> measured in October 341 2015 (1150 µg.m<sup>-3</sup> for TBP and 37 µg.m<sup>-3</sup> for TCPP) for the same piece of PU foam. This 342 indicates that y<sup>0</sup> decreased 60% for TBP and 20% for TCPP after about 4 years. Although the 343 medium-term trend (over many months) showed no decrease in  $y^0$ , there seems that a slow 344 decay occurred over the longer term (over many years). 345
- 346 In a context of using the PU foam in upholstered furniture, this stable character of  $y^0$  is a 347 factor favoring the persistence of SVOC indoors and contributing to long-term exposure of 348 people to these contaminants.
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#### 4. Conclusions and perspectives

351 352 One of the main challenges in the use of the SPME-based method for accurately measuring  $y^0$ 353 concern the calibration. In this study, an atmosphere generation system coupled with an active 354 sampling with Tenax tubes was developed as a means to set up an external calibration of the 355 SPME-based method suitable for y<sup>0</sup> measurements of TCPP and TBP. Using a PU foam as 356 source of organophosphate flame retardants, the generating system delivered stable 357 concentrations after 190h of operation with variation not exceeding  $\pm 5\%$ . This experimental 358 set-up allowed to make calibration curves for the SPME-based method on a wide range of 359 exposure dose extending up to 400 µg.m<sup>-3</sup>.min for TCPP and 4400 µg.m<sup>-3</sup>.min for TBP. This 360 new calibration mode improves the accuracy of  $y^0$  measurements using a conversion 361 relationship with an active sampling method. Emission cell (MOSEC) coupled to the SPME-362 based method achieves low detection limits of 0.8 µg.m<sup>-3</sup> for TCPP and 1µg.m<sup>-3</sup> for TBP and 363 satisfying reproducibility expressed in RSD of 3.6% for TBP and 9.3% for TCPP. Limitations 364 in the sampling conditions were identified as the time of at least 3.5 hours required to reach 365 the steady state in the emission cell before the extraction step and a maximum extraction time

366 of 11 min for a 100 µm PDMS fiber. To complete the evaluation of the method, additional 367 tests will be carried out to investigate temperature and humidity influences on SPME 368 sampling. The influences of these factors can not be directly assessed from tests performed in 369 static sampling mode with the emission cell placed on the material surface because the 370 material emission also varies with temperature and humidity. In the device of generation and 371 control of gas atmospheres containing SVOC, the emission cell is isolated from material 372 during SPME sampling and the gas concentration in the emission cell is measured with an 373 active sampling method independent from that of SPME-based method. It would therefore be 374 possible to investigate temperature and humidity influences on SPME sampling only, 375 regardless of material emission changes. These additional tests provide to extend the field of 376 application of this method to other environmental conditions than the standard indoor 377 conditions examined in this study (HR=50  $\pm$  3% and T=23  $\pm$  2°C). 378

This method was applied to determine gas-phase concentrations of TCPP and TBP at the polyurethane foam surface  $(y^0)$  over more 228 days under controlled temperature conditions.

A stability of concentrations was observed over this period confirming that the impact of emissions of organophosphate flame retardants from PU foam on indoor air quality can persist in the long term after introduction of material indoors. PU foam acts as a stable and continuous source of organophosphate flame retardants for at least several months.

Further studies will be conducted to extend this method to other SVOCs and source materials and carry out field measurement campaigns to locate the sources in indoor environments, examine the variation of source term in real conditions and provide the input data for modelling SVOCs behaviour indoors.

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**a** :



Figure 1. Pictures showing the emission cell placed on the material surface before sampling (a) and SVOCs sampling by SPME in the cell (b).



<sup>625</sup> 

Figure 2. Experimental device to generate gas-phase TCPP and TBP and steps for calibration of the SPME-based method: the emission cell is connected in series with the generation system to transfer SVOCs in the air of cell (a), the emission cell is isolated and SPME fiber is introduced in the cell for sampling (b) and (c), an active sampling with Tenax tubes was performed when the concentrations are stabilized.



Figure 3. Time variation of TBP and TCPP concentrations produced by the generation system over a 500-h period. The solid line corresponds to the mean concentration during stable generating state (t > 190 h). The solid line corresponds to this mean concentration. The dotted lines represent the intervals of  $\pm 5\%$  and  $\pm 10\%$  around this mean concentration. 



Figure 4. Calibration curves obtained for TCPP and TBP. Extracted mass by SPME versus the product of sampling time (t) and gas-phase SVOC concentration in the air (C) by combining the data of three calibration series (blue, green and red circles). 



Figure 5. Gas-phase concentration of TCPP and TBP versus time during which the emissioncell is placed on the polyurethane foam before sampling by SPME.



Figure 6. Time variation of TCPP and TBP gas-phase concentration at the polyurethane foam surface  $(y^0)$  for the period of 228 days. The solid line corresponds to the concentration measured on the 1<sup>st</sup> day (designated as initial value). The dotted lines represent the intervals of ±10% and ±20% around the initial value.

