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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**

4  
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12

13 **ABSTRACT**

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

28 TCPP and TBP gas-phase concentrations at the polyurethane foam surface ( $y^0$ ) were followed  
29 up over more 228 days under controlled temperature conditions. A high stability of these  
30 concentrations was observed showing that polyurethane foam acts as a stable and continuous  
31 source of organophosphate flame retardants indoors. This novel method should be useful for  
32 assessing the dynamic of emissions from indoor sources and potential exposure to SVOCs in  
33 indoor environments.  
34

35 **KEYWORDS**

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

38

39 **1. Introduction**

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

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

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

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

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  
78 SVOCs because of their very low volatility. Furthermore, SVOCs can be partially sorbed or  
79 deposited onto all inner surfaces of the generation device and tubing [2].  
80

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

93 This work was part of development on an emission cell (MOSEC) coupled to SPME-based  
94 method intended to on-site measurement of SVOCs gas-phase concentration at the material  
95 surface already described in a previous paper [25]. It focused on the measurement of tris-(2-  
96 chloropropyl)-phosphate (TCPP) and tri-butyl-phosphate (TBP), flame retardants emitted  
97 from polyurethane (PU) foam. The objectives were: (1) to test and validate a calibration  
98 procedure based on a new experimental device to generate gas-phase TCPP and TBP from PU  
99 foam, (2) to define the optimal sampling conditions (steady state condition and extraction  
100 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.

101

## 102 **2. Materials and Methods**

103  
104

### 104 **2.1. Passive sampling method**

105

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

127

128

### 128 **2.2. Material samples and target SVOC**

129

130

131 The test material used as the SVOC emission source was a soft polyurethane (PU) foam. It  
132 was part of a series of polyurethane foam models manufactured in an earlier study to assess  
133 the migration and potential risks of phosphorus flame retardants from fireproofing of  
134 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

135 given in detail by Ghislain *et al.* [34]. It was obtained by polymerization of polyol mixture  
136 with isocyanate following a commonly used procedure. Phosphorus flame retardants were  
137 directly incorporated in the reactant mixture during foam polymerization. The test material  
138 initially contained TCPP and TBP in mass fractions of 7.6 %. Polyurethane foam samples  
139 were 41 × 24 cm panels with a thickness of 1 cm and a density of 200 kg.m<sup>-3</sup>. Each material  
140 sample was wrapped in aluminum foil and stored at room temperature prior to the tests.  
141 TCPP and TBP were the target compounds chosen for these tests. TBP is an alkylphosphate  
142 and its vapor pressure is to 4.65 × 10<sup>-1</sup> Pa at 298 K. TCPP is a chlorinated organophosphate  
143 less volatile than TBP with a vapor pressure of 7.52 × 10<sup>-3</sup> Pa at 298 K. They are in a class of  
144 organophosphate esters commonly used as flame retardants, plasticizers and anti-foaming  
145 agents in a wide variety of consumer products like foams, textiles, resins and vinyl polymers  
146 [35,36].  
147

### 148 **2.3. Implemented experimental device for calibration**

149  
150 A new experimental device was especially developed to generate gas-phase TCPP and TBP  
151 from PU foam. It consisted of three 89 mm long and 6.35 mm diameter stainless steel tubes  
152 filled each one with 0.35 g of PU foam and connected in series to the MOSEC cell (Fig.2a).  
153 These tubes were flowed by humidified clean air at the stable conditions of relative humidity  
154 and temperature (HR=50 ± 3% at T=23 ± 2°C) produced by a dry zero air generator (Claind,  
155 Marcq-en-Baroeul, France) and a humidifier made of a water bubbler and regulated by mass  
156 flow controllers (Bronkhorst, Montigny-les-Cormeilles, France). The airflow rate was  
157 maintained at 60 mL.min<sup>-1</sup> for all the duration of test. The air flow was transferred from the  
158 tubes to MOSEC cell via a needle introduced in two septa (the one placed in the nut of the last  
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  
161 favouring a fast transfer of SVOC from the source to the cell. The sealed closing of the cell  
162 was provided by an o-ring placed in the screw cap. The air leakage rate in this generation  
163 device of SVOC was assessed at less than 5% and checked systematically after each sampling  
164 throughout the test using a soap film flowmeter (Model M-30, AP BUCK, USA).  
165 First, the emission cell was continuously crossed by air coming from the tubes containing the  
166 source material until the gas-phase SVOC concentrations became stable (Fig.2a). The SPME-  
167 based method described in section 2.1 was used to describe the increase in gaseous SVOC  
168 concentrations in the cell. To this end, the MOSEC cell was temporally isolated for sampling

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

178  
179

#### 2.4. Tenax cartridge analysis

180  
181 Analysis of Tenax tubes was carried out with a TurboMatrix 650 ATD thermal desorption  
182 system (PerkinElmer, Waltham, MA, USA). The Tenax tubes were heated at 330 °C for 15  
183 min, using a helium flow rate of 100 mL.min<sup>-1</sup> without inlet split to desorb the analytes and  
184 focus them into a cold trap kept at 1 °C. Desorption trap was ramped at 99 °C.s<sup>-1</sup> to 350 °C,  
185 held for 10 min, with an outlet split of 5 mL.min<sup>-1</sup>. The transfer line to the GC and the valve  
186 were maintained at 250 °C. Separation and detection were performed with a PerkinElmer  
187 Clarus 680 gas chromatograph. The carrier gas was helium with a flow rate of 1.3 mL.min<sup>-1</sup>.  
188 A 5% phenyl Elite-5 capillary column (PerkinElmer, Waltham, MA, USA) of 60 m, 0.25 mm  
189 i.d. and 0.25 µm film thickness was used. The oven temperature was maintained 2 min at 50  
190 °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  
191 °C, held for 14 min. The gas chromatograph was equipped with dual MS/FID detection. MS is  
192 a PerkinElmer Clarus SQ 8T. Acquisition was operated in full scan (50 to 470 amu) using  
193 electron impact mode (70 eV). MS data were used to identify target SVOCs and check there  
194 was no co-elution with other compounds. Quantitative analysis was performed by FID and  
195 based on an external calibration. To this end, Tenax tubes were loaded with 2 µL of standard  
196 mixtures of the analytes in methanol using a GC syringe and then purged for 5 min with a  
197 helium flow of 50 mL.min<sup>-1</sup> to remove the solvent. The calibration ranges were from 0.1 to  
198 1.6 µg for TCPP and from 0.8 to 4.6 µg for TBP according to the sampling conditions and  
199 concentrations produced by the SVOC generation system. The calibration curves with six  
200 standard levels obtained showed higher correlation  $R^2 > 0.99$  for the two compounds (as  
201 shown in Fig. S1 in the Supplementary materials).

202

203

## 2.5. SPME analysis

204

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

223

## 3. Results and discussions

224

225

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

226

227

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

231

232 The concentrations increase in the first tens of hours to reach the maxima of 382 µg.m<sup>-3</sup> for  
233 TBP and 35 µg.m<sup>-3</sup> for TCPP around 70 hours. Large fluctuations are observed in  
234 concentrations around the maximum values. Then, the concentrations slightly decrease by 20  
235 % reaching a stable level of 298 µg.m<sup>-3</sup> for TBP and 27 µg.m<sup>-3</sup> for TCPP after 190 h (mean  
236 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



237 h are 1.3 % for TBP and 3.0 % for TCPP. This experimental device provides a technical  
238 solution for calibration of organophosphate flame retardants measurement methods. Its  
239 characteristics in terms of time to reach a stable generating state and concentration stability  
240 are comparable to those of the most advanced techniques using the solid materials to generate  
241 gas-phase SVOCs [18,28].

242 Fig. 4 shows the calibrations obtained on a wide range of exposure dose extending up to 400  
243  $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{min}$  for TCPP and 4400  $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{min}$  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  $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{min}$  for TCPP and 4400  $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{min}$  for TBP. When  
252 the sampling time is increased, this SPME method is sensitive enough to measure  
253 concentrations in the  $\mu\text{g}\cdot\text{m}^{-3}$  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  $\text{ng}\cdot(\mu\text{g}\cdot\text{m}^{-3}\cdot\text{min})^{-1}$ , 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.

260

261

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

262

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

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

278 Considering the beginning of increase in concentration in Fig.5, the initial emission rates in  
 279 the cell can be evaluated to  $0.66 \text{ ng}\cdot\text{min}^{-1}$  for TBP and  $0.0014 \text{ ng}\cdot\text{min}^{-1}$  for TCPP.

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

286  
 287

### 3.3. Method performance

288

289 The limits of detection (LoD) and quantification (LoQ) were calculated as three times and ten  
 290 times the standard deviation of the blank for both compounds. Blank test consisted in placing  
 291 the cell on a glass plate and performing a SPME measurement. Low detectable quantities of  
 292 0.05 and 0.04 ng were obtained for TCPP and TBP in the blank analysis. Consequently, all  
 293 the measurements by SPME sampling method were systematically subtracted from the  
 294 average of blanks. As shown in Table 1, the sampling time should be close to 11 min in order  
 295 to accurately measure concentrations of a few  $\mu\text{g}\cdot\text{m}^{-3}$ .

296

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

299

	Sampling time		
	1 min	7 min	11 min
<b>TCPP:</b>			
LoD ( $\mu\text{g}\cdot\text{m}^{-3}$ )	8.5	1.2	0.8
LoQ ( $\mu\text{g}\cdot\text{m}^{-3}$ )	28	4.1	2.6
<b>TBP:</b>			
LoD ( $\mu\text{g}\cdot\text{m}^{-3}$ )	11	1.6	1.0
	38	5.4	3.4

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

300  
301 Reproducibility was evaluated from a series of ten replicate measurements performed on the  
302 selected PU foam using three different SPME fibers for different days (Table 2). The  
303 sampling times were from 7 to 11 min and these tests were carried out in a room where  
304 temperature was kept at  $23 \pm 3$  °C. A satisfying level of reproducibility was achieved with a  
305 relative standard deviation (RSD) of 3.6% for TBP and 9.3% for TCPP. The RSD values are  
306 higher than those obtained in the cell of the generation system after stabilization of  
307 concentrations (RSD of 1.3% for TBP and 3.0% for TCPP). The difference in RSD suggests  
308 that the variability in emission of a same material surface is the main source of uncertainty in  
309 measurement for this method.

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

318  
319 Table 2. Reproducibility (RSD) obtained from replicate measurements performed on the  
320 selected PU foam surface with the emission cell coupled to SPME-based method.  
321

	Number of replicate measurements	$y^0$ ( $\mu\text{g}\cdot\text{m}^{-3}$ ) mean $\pm$ standard deviation	RSD (%)
<b>TCPP</b>	10	29.6 $\pm$ 2.7	9.3
<b>TBP</b>	10	472 $\pm$ 17	3.6

322  
323  
324  
325 **3.4. Time variation of TCPP and TBP gas-phase concentrations at the polyurethane  
foam surface**

326  
327 The  $y^0$  changes over time of selected polyurethane foam for TCPP and TBP was followed  
328 from November 8, 2019 to June 23, 2020 (228 days in total). For this experiment, the material  
329 was placed in a laboratory room where temperature was kept at  $23 \pm 3$  °C.  $y^0$  was measured  
330 eight times during the experiment period using the method developed in this study. The  
331 sampling time was 7 min. As shown in Fig.6, no trend was observed in the  $y^0$  variation

332 compared to the value measured on the 1<sup>st</sup> day (designated as initial value). These  $y^0$  values  
333 do not differ by more than 20% for TCPP and 10% for TBP from its initial value. The release  
334 of TCPP and TBP from soft polyurethane foam appears as very stable for more than 200 days  
335 compared to emission kinetics that usually have a decay phase observable over several  
336 months [41,42]. Pei *et al.* [43] also found no decrease in  $y^0$  after 60 days for TCPP emitted  
337 from a PU foam.

338 The tests for assessing the time to reach the steady state shown in section 3.2 were performed  
339 with the selected PU foam in October 2015, i.e. 4 years before the start of temporal follow-up  
340 of  $y^0$  for this same material and shown in Fig.6.  $y^0$  for 228 days in Nov. 2019/June 2020 (460  
341 and 29.5  $\mu\text{g.m}^{-3}$  for TBP and TCPP, respectively) were lower than  $y^0$  measured in October  
342 2015 (1150  $\mu\text{g.m}^{-3}$  for TBP and 37  $\mu\text{g.m}^{-3}$  for TCPP) for the same piece of PU foam. This  
343 indicates that  $y^0$  decreased 60% for TBP and 20% for TCPP after about 4 years. Although the  
344 medium-term trend (over many months) showed no decrease in  $y^0$ , there seems that a slow  
345 decay occurred over the longer term (over many years).

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.

#### 349 350 **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  $y^0$  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  $\mu\text{g.m}^{-3}.\text{min}$  for TCPP and 4400  $\mu\text{g.m}^{-3}.\text{min}$  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  $\mu\text{g.m}^{-3}$  for TCPP and 1 $\mu\text{g.m}^{-3}$  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  $\mu\text{m}$  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 ( $\text{HR}=50 \pm 3\%$  and  $T=23 \pm 2^\circ\text{C}$ ).

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

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

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

388

### 389 **Acknowledgement**

390

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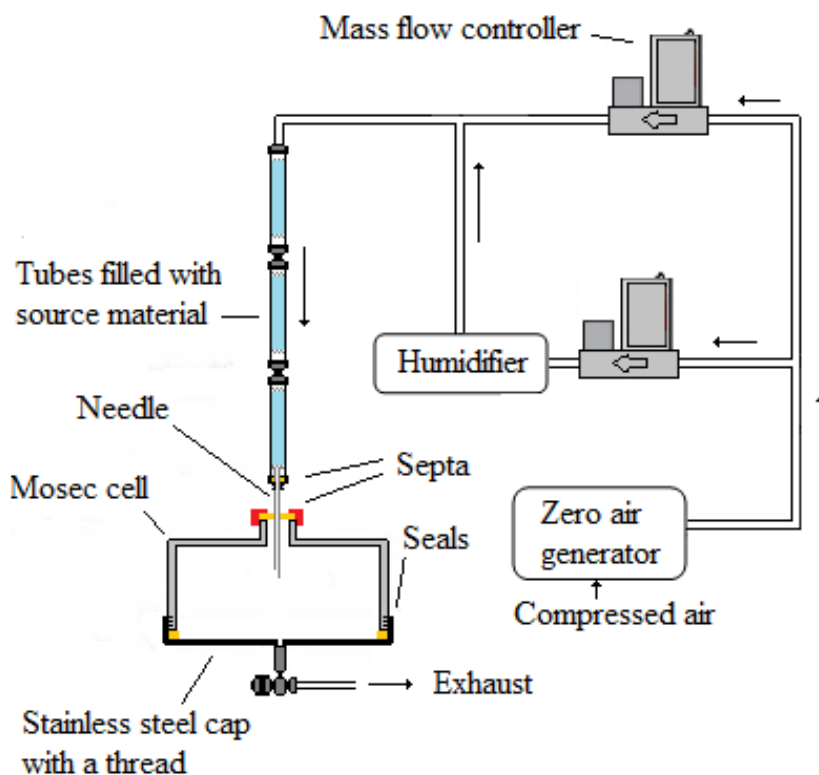
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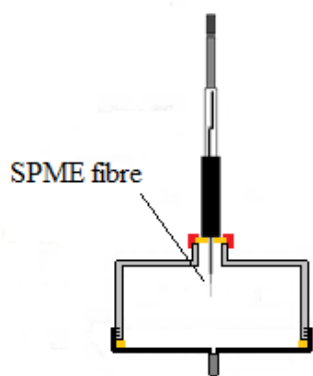
Figure 1. Pictures showing the emission cell placed on the material surface before sampling (a) and SVOCs sampling by SPME in the cell (b).

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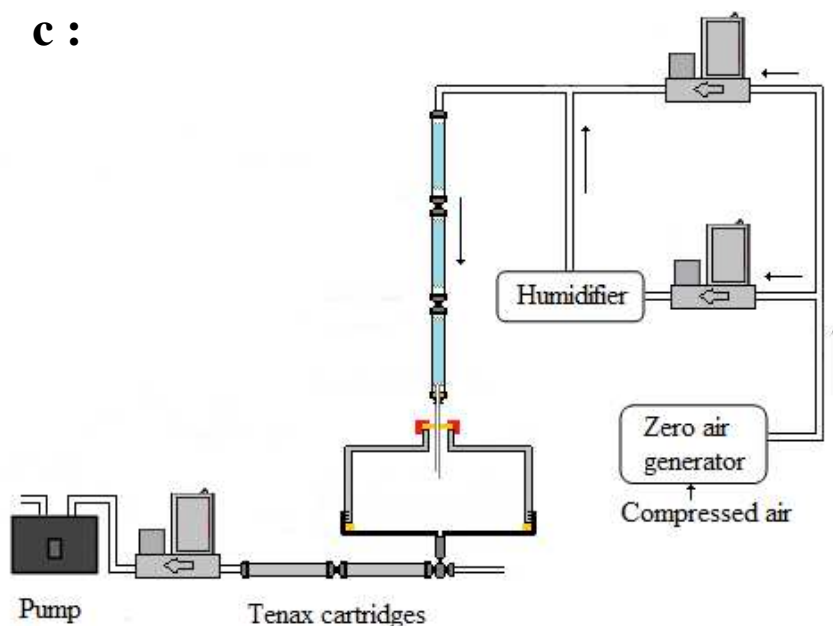
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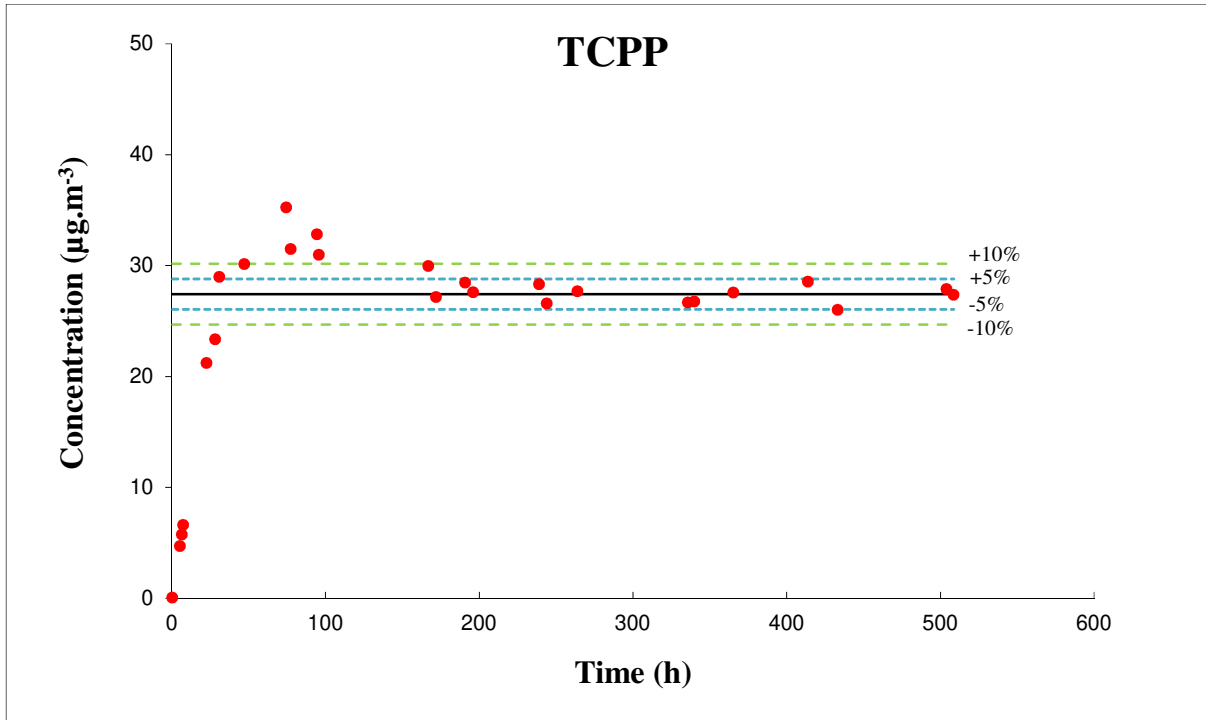


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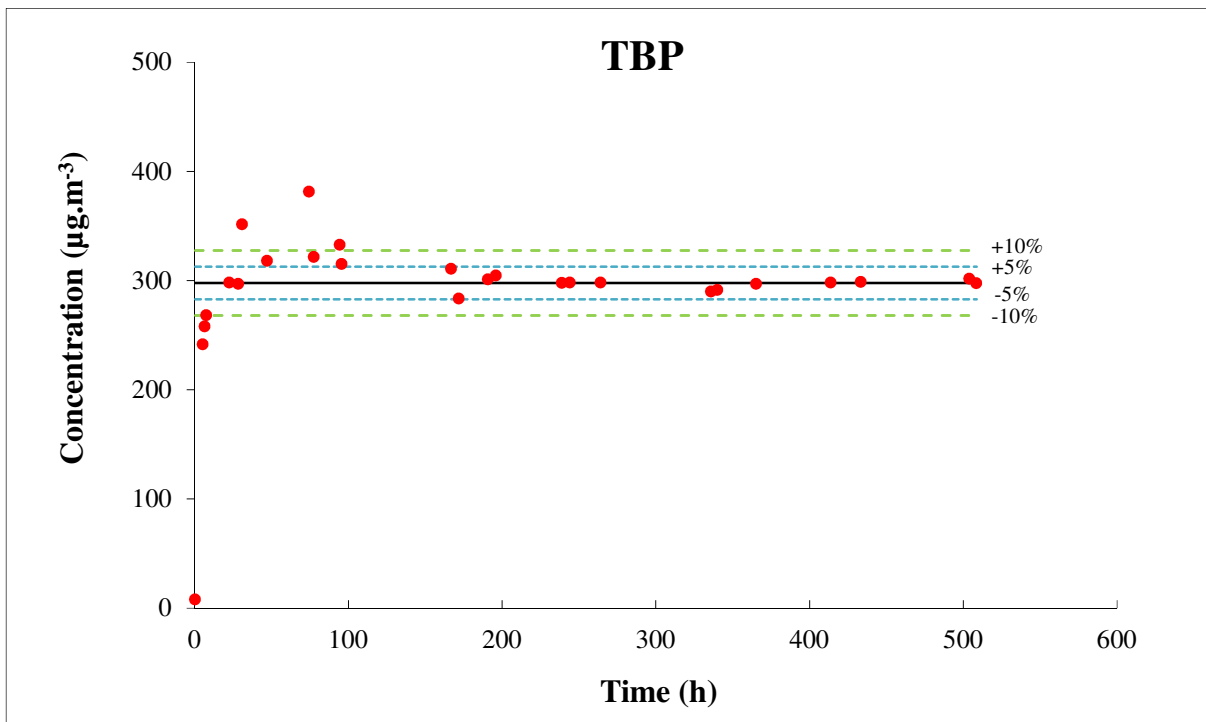
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626 Figure 2. Experimental device to generate gas-phase TCPP and TBP and steps for calibration  
627 of the SPME-based method: the emission cell is connected in series with the generation  
628 system to transfer SVOCs in the air of cell (a), the emission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

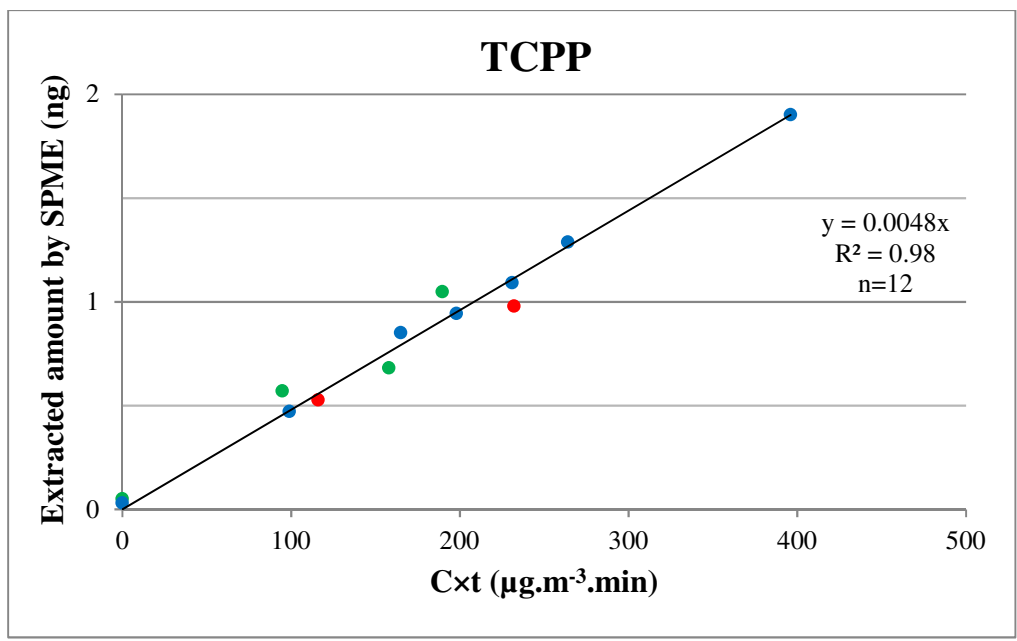


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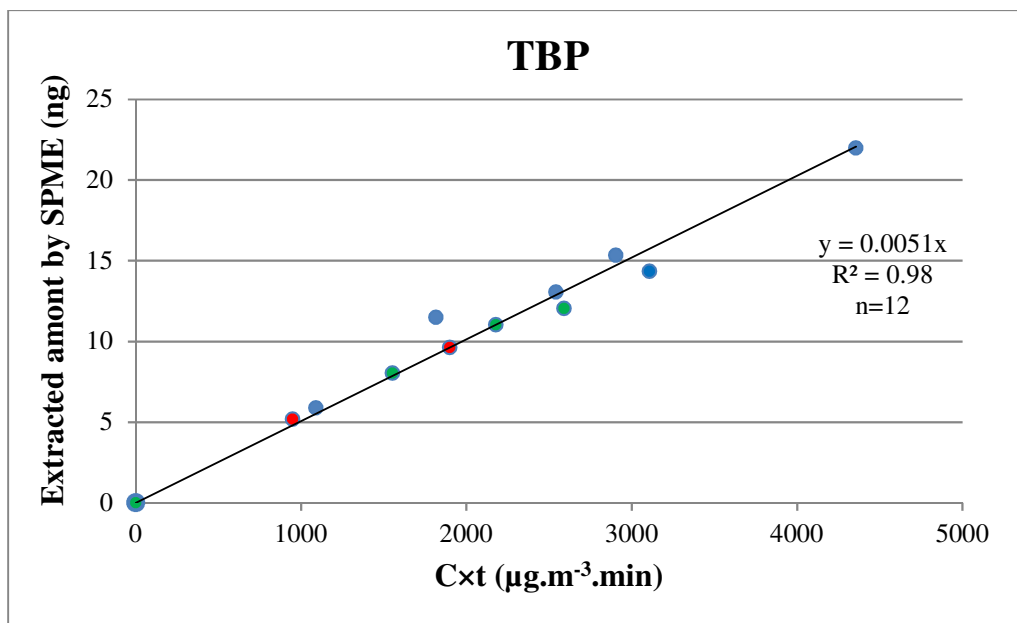


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Figure 3. Time variation of TBP and TCPP concentrations produced by the generation system over a 500-h period. The solid line corresponds to the mean concentration during stable generating state ( $t > 190$  h). The solid line corresponds to this mean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



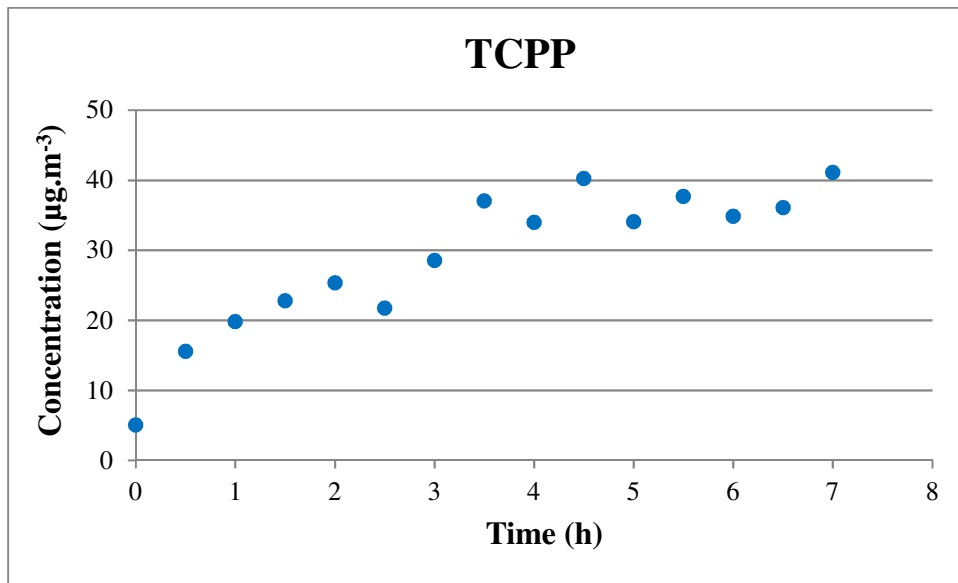
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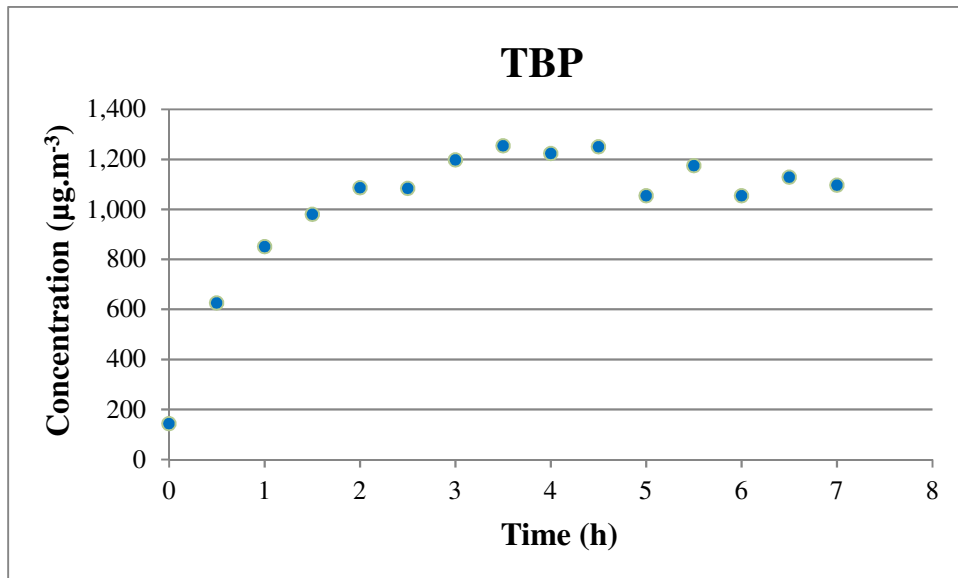
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Figure 4. Calibration curves obtained for TCPP and TBP. Extracted mass by SPME versus the product of sampling time (t) and gas-phase SVOC concentration in the air (C) by combining the data of three calibration series (blue, green and red circles).

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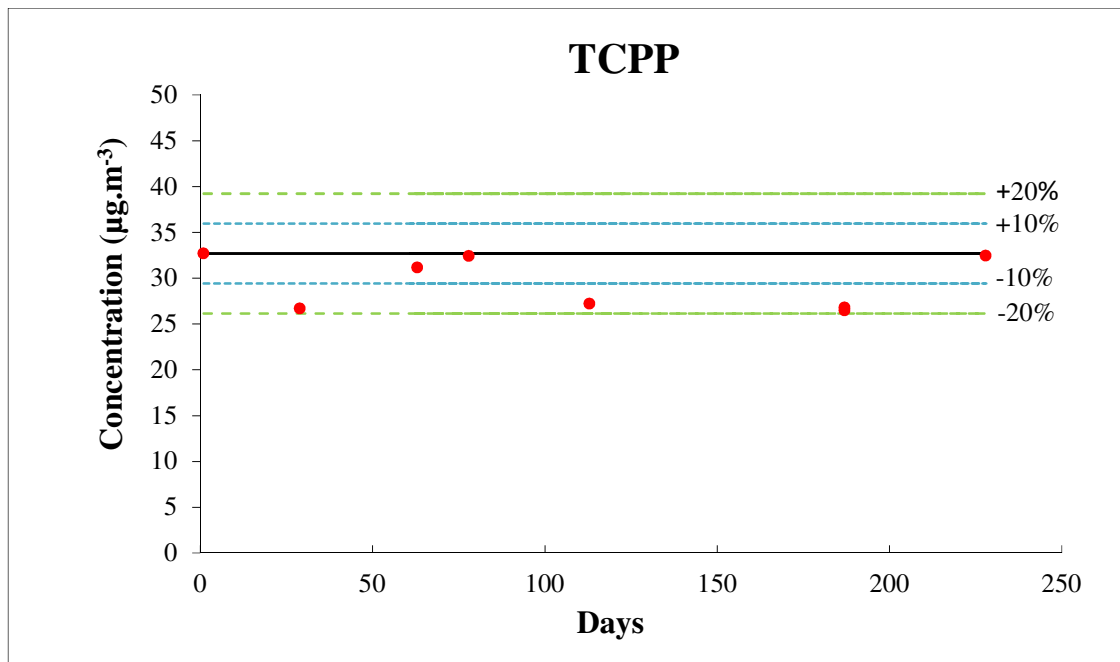


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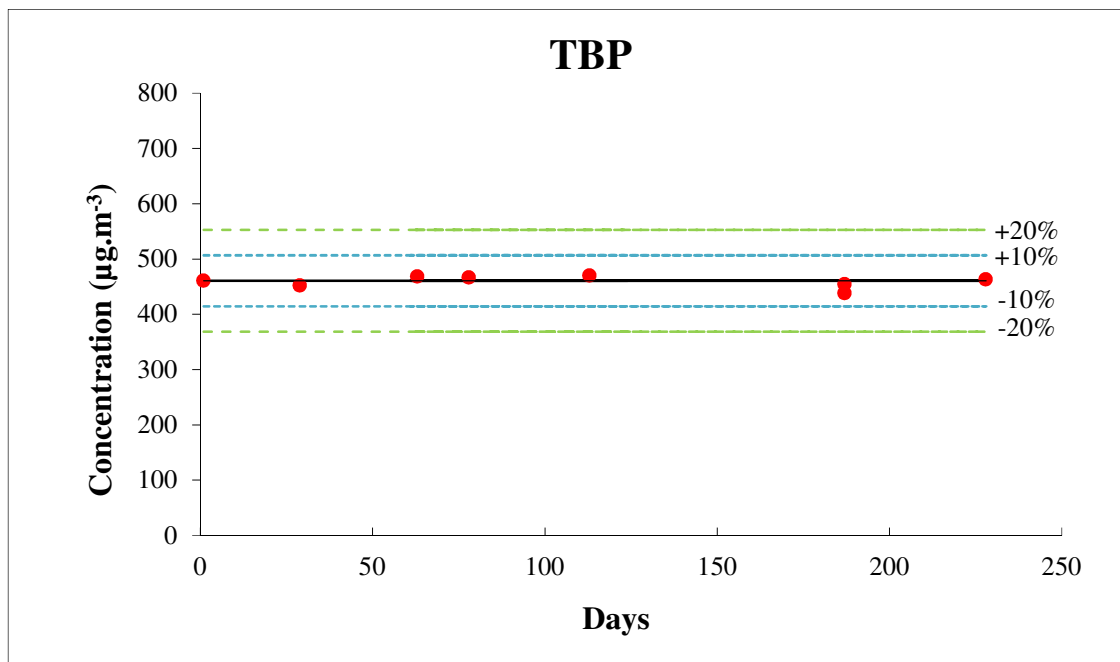


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Figure 5. Gas-phase concentration of TCPP and TBP versus time during which the emission cell is placed on the polyurethane foam before sampling by SPME.



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

