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1           What are the limitations for the use of Carbopack X as passive or active  
2           sampling adsorbent for determination of 1,3-butadiene in ambient  
3           environment?

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11  
12           **Key Words:** 1,3-butadiene, diffusive sampling, active sampling, Carbopack X, environmental  
13           monitoring

14  
15           **Abstract**

16           Two widely used sampling methods for measurement of 1,3 butadiene in ambient air include active  
17           sampling and radial passive sampling techniques using sorbent tubes filled with Carbopack X  
18           adsorbent. The laboratory study was designed to evaluate the suitability of these sampling methods  
19           for long-term monitoring of 1,3-butadiene in ambient air. The results point against the use of passive  
20           radial diffusive sampling for determination of 1,3-butadiene due to the dependence of its uptake rate  
21           on experimental conditions. Inability to correctly reflect the occurrence of episodes of high  
22           concentration levels using radial diffusive passive sampling was proven experimentally. As for active  
23           sampling technique, caution must be taken as to not overreach the safe sampling limit which  
24           considerably decreases as a function of temperature and relative humidity. At 10 ml min<sup>-1</sup> flow-rate,  
25           the breakthrough volume per gram of Carbopack X material is established at 81.6-84.0 L at 50% RH,  
26           20 °C; 61.2-64.8 L at 80% RH, 20 °C; and 24.0-28.8 L at 80% RH, 30 °C. Relatively low sampling times  
27           associated with these sampling volumes point to the need to develop more adequate supports for  
28           active sampling to enable long-term ambient monitoring.

29

## 30 1. Introduction

31 1,3-butadiene is a volatile hazardous pollutant which is used as an intermediate in the manufacturing  
32 of adhesives, synthetic rubber, polymers, organic fiber, plastics, resin, paints, coatings, lubricants,  
33 and automotive care products [1]. Along with vicinity of the production sites of the above-mentioned  
34 products, its major environmental sources are linked to automobile exhaust and wood smoke [2], [3],  
35 [4]. The highest exposure to butadiene occurs in occupational settings with exposure levels of up to 2  
36 mg m<sup>-3</sup> reported for US and EU [4]. For non-occupational exposure, 1,3-butadiene is detected at  
37 lower levels. Mean indoor air concentrations of 1,3-butadiene measured inside of residential homes  
38 range from 0.1 to 2.5 µg m<sup>-3</sup> [5]. Ambient levels of 1,3-butadiene show high variability and range  
39 from a few ng m<sup>-3</sup> in rural areas to hundreds of µg m<sup>-3</sup> in the direct vicinity of industrial sources [6],  
40 [7], [8].

41 1,3-butadiene is a colorless gas characterized by high reactivity and short lifetime [9]. Its major fate  
42 in the atmosphere is removal by hydroxyl radicals, with lifetimes estimated at 4.2 and 21 hours in  
43 summer and winter respectfully (rate coefficient for the reaction of 1,3-butadiene with OH at 298 K is  
44 equal to  $6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [9]. Due to the short lifetime, the potential for long-range  
45 transport of this compound is limited [10].

46 1,3-butadiene is classified as a Group 1 carcinogen by International Agency for Research on Cancer  
47 (IARC) which puts it on the list of compounds that require adequate monitoring [4]. European  
48 chemical agency (ECHA) classifies 1,3-butadiene as Class 1A carcinogen and 1B mutagen [11]. Based  
49 on modelled animal data, ovarian atrophy presents the highest risk linked to exposure to 1,3-  
50 butadiene [12]. Benchmark concentration associated with 10% benchmark response due to 50-year  
51 exposure (birth to menopause) was established at just 0.9 ppb (2.0 µg m<sup>-3</sup>) [12]. The highest  
52 carcinogenic risk for general population was associated with a specific type of leukemia, called  
53 lymphoid neoplasm [13]. More specifically, by the age of 70 an excess risk of 1/100,000 was  
54 established at environmental concentration of 0.06 ppm (135 µg m<sup>-3</sup>) [13]. As for occupational  
55 exposure, by the age of 70, a risk of 1/100,000 for 45-year exposure (from 20 years) was linked to  
56 0.273 ppm (614 µg m<sup>-3</sup>) concentration of 1,3-butadiene [13]. According to the French Agency for  
57 Food, Environmental and Occupational Health & Safety (ANSES) a 45-year occupational exposure to 8  
58 µg m<sup>-3</sup> (3.6 ppb) for 8 h a day, 240 days a year (from 25 to 70 years) leads to an increased mortality  
59 risk of 1/100,000 associated with leukemia [14]. Currently, based on summary reports by  
60 internationally recognized organizations (US EPA, 2002; JRC, 2002; AFSSET, 2010; INERIS, 2019;  
61 ANSES, 2019) a toxicity reference value of 2.0 µg m<sup>-3</sup> is established by ANSES for chronic exposure by  
62 respiratory route [15]. In addition, the products of 1,3-butadiene reaction with hydroxyl radicals and  
63 ozone in ambient air include acrolein and formaldehyde that are likewise considered to be toxic [16].

64 For 1,3-butadiene two types of monitoring can be distinguished: short-time occupational monitoring  
65 at concentrations in the order of mg m<sup>-3</sup> and long-time ambient air monitoring with concentrations in  
66 the order of µg m<sup>-3</sup>. Of the two, environmental monitoring presents additional challenges due to the  
67 fact that ambient air is a dynamic system and thus high fluctuations of temperature and humidity,  
68 changes in wind speed and direction, and possibility of transient episodes are expected. Personal  
69 exposure and lifetime cancer risk estimation due to 1,3-butadiene in various environments is an area  
70 of active research [17], [5]. This article specifically addresses the challenges of 1,3-butadiene ambient  
71 air monitoring where the optimum method is expected to have the following characteristics: is  
72 sensitive to low concentrations of 1,3-butadiene; has a sufficiently wide response range to include  
73 transient episodes of high concentrations; applicable to long-term monitoring (in order to provide  
74 the most accurate information on the average yearly exposure levels by employing the least number  
75 of measurements); compliant with real levels of environmental parameters such as temperature,

76 humidity and wind speed; resistant to variations of temperature and humidity; specific to 1,3-  
77 butadiene in the presence of other compounds; is cost-effective to enable long-term monitoring at  
78 multiple locations; and last, but not least, is straightforward to use. Based on these criteria, direct  
79 automated methods for determination of 1,3-butadiene, such as online GC-MS, PTR-MS or SIFT-MS  
80 monitoring, even though operating in real time, robust, and exhibiting detection limits as low as 50  
81 ppt, are judged to be too expensive for routine monitoring at multiple location sites and will not be  
82 further discussed [18], [19]. Instead, we will focus on passive and active sampling using adsorbent  
83 materials.

84 Diffusive sampling technique is widely used in ambient monitoring of hazardous volatile compounds  
85 due to its ease of use, low cost and ability to survey simultaneously large areas at multiple location  
86 sites. The technique is currently employed by US EPA at petroleum refineries for fenceline  
87 monitoring of a number of volatile organic compounds (VOCs), such as benzene, toluene and xylene  
88 with a recommended sampling period of 2 weeks using industry standard inert-coated stainless steel  
89 tubes packed with Carbograph 1, Carbopack B, Carbopack X or another equivalent sorbent [20],  
90 [21], [22]. For environmental sampling of 1,3-butadiene using Carbopack X or Carbograph 5 one-  
91 week long sampling is recommended [23]. Diffusive sampling is relatively cheap, requires no energy  
92 supply and is easy to operate. Nevertheless, evaluating analyte concentration using diffusive  
93 sampling technique heavily relies on correct values of analyte's uptake rate, which is linked to  
94 environmental conditions (humidity, temperature, pollutant concentration, change in wind speed)  
95 and experimental parameters (sampling time, presence of co-pollutants, variability of concentration).  
96 Diffusive samplers include badge-type samplers and tube-type samplers, that can be further  
97 classified as axial (diffusion path is parallel to the axis of the sorbent cartridge) and radial (diffusion  
98 path is parallel to the radius of the sorbent cartridge). Radial diffusive samplers, such as Radiello  
99 samplers have a higher diffusive surface than axial samplers and thus allow higher sampling rates.  
100 Based on the data obtained using Radiello diffusive samplers that consist of cylindrical cartridge (60  
101 mm long, 100 mesh hole size) filled with 350 mg of Carbopack X adsorbent housed in a cylindrical  
102 diffusive body made of polycarbonate and microporous polyethylene (50 mm long, 16 mm diameter)  
103 and exposed to standard atmospheres of 1,3-butadiene and benzene in experimental chamber (20°C  
104 et 1013 hPa), Strandberg et al. calculated the uptake rate for  $2.26 \mu\text{g m}^{-3}$  of 1,3-butadiene to be  
105  $5.1 \pm 0.31 \text{ ml min}^{-1}$  if sampled for a one-week period and  $22.6 \pm 0.23 \text{ ml min}^{-1}$  if sampled for a 24 h.  
106 Thus, it is highlighted that for 1,3-butadiene time of sampling affects significantly the uptake rates  
107 [23]. It was suggested that sampling rates should be validated for different time periods [23].

108 In the current work radial diffusive sampling of 1,3-butadiene is evaluated by studying the  
109 dependency of its uptake rates on changes in ambient conditions. To this end, 1,3-butadiene uptake  
110 rates for RAD 141 Radiello diffusive samplers filled with Carbopack X (40/60 mesh) are obtained for  
111 one-week exposure at various experimental conditions, such as humidity, temperature, constant and  
112 changing concentration levels. Carbopack X is a hydrophobic graphitized carbon adsorbent able to  
113 withstand high bake-out temperatures and is commonly used for determination of 1,3-butadiene [24],  
114 [23], [25], [26], [27]. Carbopack X adsorbent is preferred to traditionally used molecular sieves mostly  
115 due to the fact that this support is less affected by the excess of water and demonstrates higher  
116 storage stability [28], [23], [24]. Having said that, a 30% decrease in uptake rates for  $3.4 \mu\text{g m}^{-3}$  of 1,3-  
117 butadiene was observed at 80% humidity while sampling with Radiello samplers [23]. In the present  
118 study similar uptake rates under various conditions would be a good indication for robust reliable  
119 sampling while variable uptake rates and their dependency on environmental parameters could  
120 signal a problem, as clearly outdoor conditions are prone to change.

121 An alternative to diffusive sampling is active sampling where air is actively pumped through the  
122 sampler containing one or more adsorbents. It is costlier since it requires a pump and a power  
123 supply. On the other side, active sampling does not depend on the diffusion rates and the calculated  
124 concentration is only a function of sampled volume (till reaching maximum sorbent adsorption  
125 capacity). The volume of sampled atmosphere required for adsorbent to get saturated, so-called  
126 breakthrough volume, can be experimentally determined. This volume depends on the species being  
127 sampled along with environmental parameters, such as humidity and temperature [29]. Seventy  
128 percent of the breakthrough volume is a value accepted as a safe sampling volume [24]. For the  
129 concentration of  $0.60 \pm 0.03$  ppb ( $1.35 \pm 0.07 \mu\text{g m}^{-3}$ ) of 1,3-butadiene, safe sampling volume was  
130 determined at 82 L per gram of Carbopack X material (40/60 mesh) at 20°C, 50% RH [24]. Thus,  
131 sampling 1,3-butadiene at  $5 \text{ mL min}^{-1}$  using an active sampling tube filled with 300 mg of Carbopack X  
132 material will allow 82 hr sampling which is roughly 3.4 days, a half of the recommended one-week  
133 sampling time for diffusive sampling. While this value is validated for a defined set of conditions, the  
134 question is whether the breakthrough volume is further affected by change in temperature, humidity  
135 and presence of others pollutants. In the current work the dependence of breakthrough volume on  
136 temperature, RH and presence of co-pollutants will be investigated to better evaluate possible  
137 sampling time determination of atmospherically relevant concentrations of 1,3-butadiene, keeping in  
138 mind that longer sampling time is cost-effective for environmental sampling. Due to its common use  
139 for determination of 1,3-butadiene, Carbopack X (40/60 mesh) is once again chosen as an adsorption  
140 medium.  $1 \mu\text{g m}^{-3}$  is chosen as a relevant concentration of 1,3-butadiene [15], [5], [17].

141 To sum up, practical use of two sampling methods is evaluated by investigating the shortcomings of  
142 each technique: radial diffusive sampling is evaluated as a function of stability of its uptake rate,  
143 while active sampling is evaluated as a function of its safe sampling volume and thus conceivable  
144 sampling time. Whatever is the sampling technique, it is most often followed by gas chromatography  
145 coupled to flame ionization or mass spectrometry analysis for quantitative separation and  
146 identification of both 1,3-butadiene and its numerous degradation products [26].

## 147 2. Materials and methods

### 148 2.1. Gases

149 Certified gas cylinders are used as a source of 1,3-butadiene. For calibration purposes NPL Primary  
150 Reference material (Cylinder # D600109, National physical laboratory, Teddington Middlesex, UK)  
151 consisting of a mixture of 34 components at around 4 ppb, including 1,3-butadiene at  $4.29 \pm 0.09$  ppb  
152 is used without dilution. To generate a single-component atmosphere a 1,3-butadiene cylinder of  
153 1.05 ppm in air provided by Messer, France is used. To generate multi-component atmosphere, a  
154 cylinder containing a 51-component mixture (hydrocarbons and aromatics ranging from C2 to C10) at  
155 around 1 ppm each in nitrogen including 1,3-butadiene was purchased from Air Products, Belgium. In  
156 both single-component and multi-component atmosphere the targeted concentration of 1,3-  
157 butadiene after dilution is  $1 \mu\text{g m}^{-3}$ . Experiments are carried out using zero air; it is generated by a  
158 classical air compressor, and then passed through a catalytic zero air generator (Claind ZeroAir 2020,  
159 Lenno, Italy) coupled to a swing adsorption (PSA) device. The remaining impurity levels in the air  
160 stream before entering the reactor are lower than the analytical system detection limits: VOCs < 0.1  
161 ppb,  $\text{CO}_2$  < 10 ppb, and CO < 80 ppb. Moisture level is ca. 2 ppm. A second flow of zero air going  
162 through a bubbler of ultrapure water (milli-Q, resistivity  $18.2 \text{ M}\Omega \text{ cm}$ ) is mixed with the dry air flow,  
163 in proportions necessary to reach the relative humidity targeted.

## 164 2.2. Sampling tubes

### 165 2.2.1 Passive sampling

166 Radiello diffusive samplers filled with Carbopack X were used for passive sampling. Diffusive  
167 samplers, each consisting of an adsorbing cartridge, diffusive body and a support plate, were  
168 purchased from Sigma-Aldrich, France. Adsorbing RAD141 cartridges consist of a stainless-steel net  
169 cylinder with 3x8  $\mu\text{m}$  mesh grid opening and 4.8 mm diameter, packed with approximately 480 mg of  
170 graphitized carbon Carbopack X material (particle size 40/60 mesh). A graphitic solid adsorbent  
171 Carbopack X has 40-60 mesh particle size and a specific surface area of  $240 \text{ m}^2 \text{ g}^{-1}$  [30]. Adsorbing  
172 cartridge is placed in a Radiello yellow diffusive body (RAD1202) made of microporous 5 mm thick  
173 polyethylene with average porosity  $10 \pm 2 \mu\text{m}$  that ensures diffusive path length of approximately 150  
174 mm. Before use, cartridges are placed in empty inox tubes and are conditioned with nitrogen at the  
175 flow rate of  $30 \text{ mL min}^{-1}$  at  $250 \text{ }^\circ\text{C}$  for 12 h using RTA tube conditioner, Tera, France. After exposure,  
176 the tubes are placed in empty inox tubes, closed with caps and analyzed immediately using GC-MS.  
177 Blanks levels were evaluated for freshly conditioned tubes and concentration of 1,3-butadiene was  
178 below the limit of detection.

### 179 2.2.2 Active sampling

180 For active sampling CX 500 tubes (8.9-cm  $\times$  5-mm i.d.  $\times$  6.3-mm o.d) filled with 500 mg of graphitized  
181 carbon Carbopack X material (particle size 40/60 mesh) were purchased from Tera, France. These  
182 tubes served for online determination of the breakthrough volumes and do not require post analysis.  
183 Before and after use tubes are conditioned with nitrogen at the flow rate of  $30 \text{ mL min}^{-1}$  at  $250 \text{ }^\circ\text{C}$  for  
184 12 h. Concentration of 1,3-butadiene in the blanks was below the detection level.

## 185 2.3. Instrumentation and chromatographic conditions

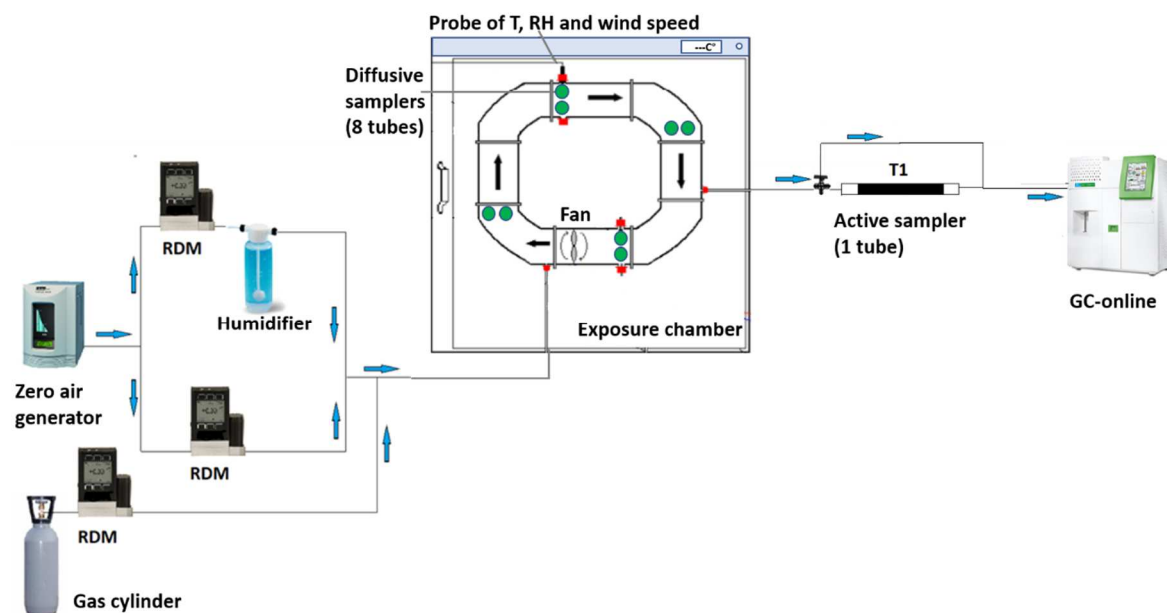
186 Continuous gas-phase monitoring of the exposition chamber where the diffusive Radiello samplers  
187 were placed as well as investigation of the breakthrough volumes during active sampling was  
188 achieved by using Perkin Elmer Thermal Desorber (TD) coupled with Perkin Elmer GC CLARUS 580 gas  
189 chromatograph and FID detector. TD conditions: sampling flow at  $10 \text{ mL min}^{-1}$  for 30 min; trap  
190 adsorbent consisting of 100 mg of Carbosieve SIII and 20 mg of Carbopack B; trap low:  $-30^\circ\text{C}$ ; trap  
191 high:  $350 \text{ }^\circ\text{C}$  for 15 min; inlet split none; outlet split at  $4 \text{ mL min}^{-1}$ ; valve at  $210 \text{ }^\circ\text{C}$ ; transfer line at  $210$   
192  $^\circ\text{C}$ . GC/FID conditions: dual columns (i) CP SIL 5CB 50 m capillary column (100% dimethylpolysiloxane  
193 (PDMS) phase) and (ii)  $\text{Al}_2\text{O}_3 / \text{Na}_2\text{SO}_4$  50 m; carrier gas helium=41 psi; oven  $45 \text{ }^\circ\text{C}$  (12 min) to  $200^\circ\text{C}$   
194 (8min) at  $6 \text{ }^\circ\text{C min}^{-1}$ ; FID detector at  $225^\circ\text{C}$ .

195 Post-analysis of Radiello sampling tubes was performed by TD-GC/MS using Perkin Elmer Turbo  
196 Matrix 650 thermal desorber coupled with Perkin Elmer CLARUS 680 gas chromatograph and Perkin  
197 Elmer Clarus SQ8T mass spectrometer detector. Optimized TD conditions: trap adsorbent 100 mg  
198 Carbopack B; tube purge: 1min; tube desorb:  $25 \text{ mL min}^{-1}$  at  $280 \text{ }^\circ\text{C}$  for 5 min; trap low:  $-30^\circ\text{C}$ ; trap  
199 high:  $300 \text{ }^\circ\text{C}$  for 15 min; inlet split none; outlet split at  $4 \text{ mL min}^{-1}$ ; valve at  $210 \text{ }^\circ\text{C}$ ; transfer line at  $210$   
200  $^\circ\text{C}$ . GC conditions: Agilent CP 8780 column (CP Sil 5C B 60 m 0.25 mm  $1 \mu\text{m}$  capillary column with  
201 100% dimethylpolysiloxane (PDMS) phase); carrier gas helium=5 psi; oven  $30 \text{ }^\circ\text{C}$  (10 min) to  $250^\circ\text{C}$   
202 (2.5 min) at  $8 \text{ }^\circ\text{C min}^{-1}$ . MS conditions: mass range: 25 to 250 Da,  $m/z=54$  was used as 1,3-butadiene  
203 quantification ion, source temperature:  $250^\circ\text{C}$ , transfer line at  $250^\circ\text{C}$ ; photomultiplier at around 2000  
204 Volts.

## 205 2.4. Experimental procedure

206 Throughout the experimental work, concentration of 1,3-butadiene generated in the experimental  
207 chamber is monitored using online gas chromatography system that was calibrated by means of  
208 undiluted NPL Reference Standard. During experimental sampling diffusive samplers are placed

209 inside of the chamber. Tubes for active sampling are incorporated one at a time in the exit line  
210 leading from the exposure chamber to the TD-GC. Check point is incorporated into the setup  
211 between the chamber output and the active sampler and the supplied concentration is verified daily.  
212 The detailed setup is shown in Figure 1.



213  
214 *Figure 1 : Schematic representation of a setup used for passive and active sampling of 1,3-butadiene used in this study.*

#### 215 2.4.1 Experimental chamber

216 Experiments are conducted in an exposure chamber, which allows control of supplied gas  
217 concentrations, temperature, humidity and air velocity. It consists of a ring tube made of thick glass  
218 placed in a 1500 L thermostatic enclosure (Aralab Climatic Chamber, FITOCLIMA 1500 EC20). The  
219 glass ring has a size of 74 cm by 88 cm, 15 cm inner diameter and a total capacity of 51 L. The  
220 chamber contains either a single-component or a multi-component atmosphere. Standard  
221 atmospheres containing 1,3-butadiene are generated by diluting one of the 1,3-butadiene standard  
222 gas cylinders (1,3-butadiene only or multi-component) in a desired proportion of dry and humidified  
223 air. The air and gas flows are regulated by using OMNICON mass flow controllers. Exposure  
224 chamber is supplied with the standard atmosphere at the rate of 10 L min<sup>-1</sup>. An inductive fan (Papst  
225 P/N 5112N) is set up to regulate the air velocity inside the chamber. The diffusive samplers are  
226 placed perpendicularly to the dynamic airflow. Controlled parameters include: concentration of 1,3-  
227 butadiene ranging from 1 to 14 µg m<sup>-3</sup>, relative humidity (RH) of 50 and 80%, temperature of 20 and  
228 30 °C and wind speed at 1.0 m s<sup>-1</sup>.

#### 229 2.4.2 Passive sampling

230 Once the test atmosphere in the chamber reaches a stable level, a diffusive Radiello adsorbing  
231 cartridge is opened, inserted inside of the yellow diffusive body and screwed to the support. The  
232 sampler is then placed inside of the chamber for a period of one-week at either constant or variable  
233 conditions as described below. During each exposition six to eight replicate samples are obtained by  
234 placing in the experimental chamber six to eight diffusive samplers. Three replicate trials for each of  
235 the constant exposure conditions are conducted in order to evaluate repeatability of the  
236 measurements. Note, that experiments were specifically designed so that each tube is subjected to a  
237 very similar average concentration of 1,3-butadiene within the 7-day exposure. Three sets of  
238 conditions were investigated at constant concentration of 1 µg m<sup>-3</sup> 1,3-butadiene: (i) T=20°C,

239 RH=50%, (ii) T=20°C, RH=80%, (iii) T=30°C, RH=80%. In addition, at the conditions of 20°C and 50%  
240 RH three expositions to transient concentrations were performed in the following way: (i) 7 day  
241 experiment while alternating 12 hour exposure to clean air and 12 hour exposure at 2 µg m<sup>-3</sup>, (ii) 7  
242 day exposure starting with 12 hours of clean air followed by 12 hours of exposure to 1,3-butadiene at  
243 14 µg m<sup>-3</sup> and finishing with 6 days of clean air, (iii) 7 day exposure starting with 6 days of clean air  
244 followed by 22 hours of exposure to 1,3-butadiene at 6 µg m<sup>-3</sup>. Note, that in the last scenario the  
245 tubes were subjected to smaller average concentration of 1,3-butadiene equivalent to 0.8 µg m<sup>-3</sup> as  
246 opposed to 1.0 µg m<sup>-3</sup> in the scenarios (i) and (ii). At the end of each exposure period the diffusive  
247 samplers are removed, adsorbing cartridges are placed in empty inox tubes and the tubes are  
248 analyzed immediately. Analysis is performed using thermal desorption coupled with ion specific MS  
249 detection.

### 250 2.4.3 Active sampling

251 Experiments aimed to investigate the breakthrough volume of 1,3-butadiene 1 µg m<sup>-3</sup> alone or in the  
252 presence of other species are conducted concurrently with passive sampling experiments using the  
253 testing atmosphere generated in the experimental chamber at (i) T=20°C, RH=50%, (ii) T=20°C,  
254 RH=80%, (iii) T=30°C, RH=80%. An active sampling tube is connected to the line leading from the  
255 experimental chamber to the thermal desorber. By switching the valve, one can direct the air from  
256 the chamber either through a sampling tube or straight to the TD at 10 ml min<sup>-1</sup> as shown in Figure 1.  
257 Only one active tube can be used at a time and two essays are done to ensure reproducibility of the  
258 results. A breakthrough profile is constructed by first bypassing the sampling tube and thus obtaining  
259 the concentration of 1,3-butadiene in the chamber, then switching the flow so that it goes through  
260 the tube leading to the adsorption of 1,3-butadiene in the tube and registering concentration by the  
261 GC-online. With time, capacity of the active sampler filled with Carbopack X to adsorb 1,3-butadiene  
262 diminishes and the molecules of 1,3-butadiene start to emerge from the tube, leading to increase in  
263 the concentration of 1,3-butadiene registered by GC-online. The breakthrough time is established  
264 when the level of concentration in the air emerging from the active tube reaches 10% of the  
265 concentration that is supplied to the tube.

## 266 3. Results and discussion

### 267 3.1. Passive sampling

268 Having obtained the mass of 1,3-butadiene in the tubes and knowing its concentration in the  
269 chamber uptake rates were calculated for each set of conditions.

270 Fick's First Law of Diffusion is used to calculate the uptake of 1,3-butadiene and is given by Equation  
271 1:

272 *Equation 1*

$$273 \quad C = \frac{m}{U_p t}$$

274 where  $C$  is concentration in ppm,  $U_p$  is uptake rate in ng ppm<sup>-1</sup> min<sup>-1</sup>,  $m$  is mass in ng and  $t$  is time in  
275 min. Knowing the generated concentration we can calculate uptake rate:

276 *Equation 2*

$$277 \quad U_p = \frac{m}{C \times t}$$

278



279 Uptake rate can be conveniently expressed in mL min<sup>-1</sup> by converting the concentration C commonly  
 280 expressed in ppm to that expressed in ng mL<sup>-1</sup> by using the Equation 3:

281 Equation 3

$$282 \quad C_{(ng\ mL^{-1})} = \frac{C_{(ppm)} \times M}{V_m} \times 10^6$$

283 where C is concentration expressed either in ng mL<sup>-1</sup> or in ppm, M is molar mass in g mol<sup>-1</sup> and V<sub>m</sub> is  
 284 standard molar volume of the ideal gas at 20 °C equal to 24.0 L mol<sup>-1</sup>. Thus, 1 ppm (v/v) of 1,3-  
 285 butadiene is equal to 2.25 ng mL<sup>-1</sup> (1 ppb=2.25 µg m<sup>-3</sup>).

286 Using Equation 2 uptake rates of 1,3-butadiene in various conditions were calculated (Table 1, Table  
 287 2). The average standard deviation for experiments consisting of multiple runs ranged from 5.6 to  
 288 40.1%. An average %RSD of multiple runs was calculated at 18.1% and a rounded value of 20% was  
 289 used as a method reproducibility. From Table 1 and Figure 2 the uptake rates are within the method  
 290 reproducibility for single and multi-component atmosphere and so we can consider that the uptake  
 291 rates of 1,3-butadiene are not significantly affected by the competition with other components for  
 292 the adsorption sites.

293 The value of 4.95±0.70 ml min<sup>-1</sup> obtained at 50% RH and 20 °C (Table 1) corresponds well to 4.9±0.37  
 294 ml min<sup>-1</sup> measured by Strandberg et al. for one week exposure using the same type of diffusive  
 295 sampler at the concentrations of 1,3-butadiene between 0.23 µg m<sup>-3</sup> and 2,26 µg m<sup>-3</sup> [23]. Note, that

Conditions	Single-component atmosphere						Multi-component atmosphere					
	Run #	# Tubes	Average uptake rate mL min <sup>-1</sup>	%RSD	Average uptake rate mL min <sup>-1</sup>	%RSD	Run #	# Tubes	Average uptake rate mL min <sup>-1</sup>	%RSD	Average uptake rate mL min <sup>-1</sup>	%RSD
T=20°C RH=50%	1	8	5.08±0.52	9.6	4.95±0.70	14.2	1	8	3.00±0.17	5.04	3.36±0.66	19.6
	2	8	4.20±0.28	6.2			2	8	2.98±0.32	10.23		
	3	8	5.58±0.27	4.6			3	8	4.13±0.49	11.16		
T=20°C RH=80%	1	8	2.41±0.24	9.5	2.65±0.25	9.3	1	7	2.56±0.10	4.49	2.45±0.14	5.6
	2	8	2.89±0.15	4.8			2	8	2.50±0.23	9.47		
	3	7	2.58±0.24	8.5			3	6	2.30±0.23	10.57		
T=30°C RH=80%	1	7	1.03±0.08	7.0	1.74±0.71	40.1	1	8	1.69±0.35	20.19	1.94±0.41	21.1
	2	8	2.45±0.33	12.6			2	8	1.71±0.51	29.38		
	3	8	1.83±0.16	8.3			3	8	2.41±0.38	16.25		

296 for the exposure shorter than 24 h, a higher rate of 22.00±0.44 ml min<sup>-1</sup> was obtained [23].

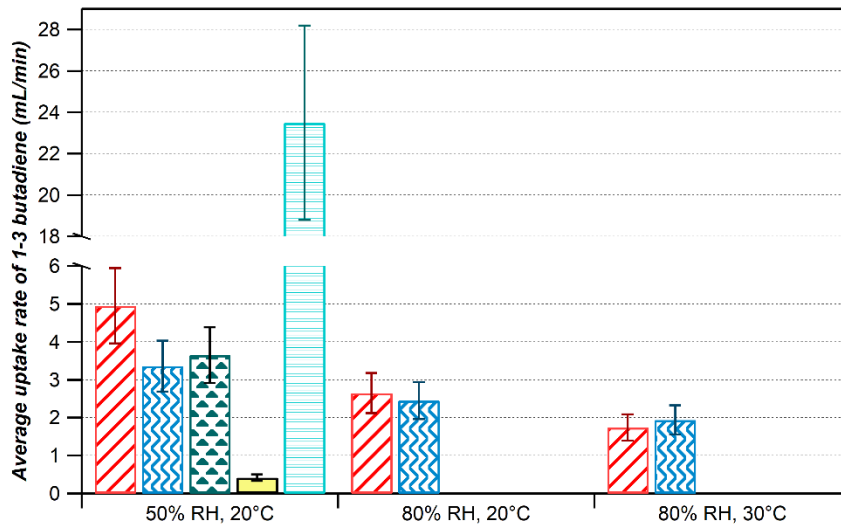
297 Table 1 : Uptake rates for 1,3-butadiene at constant concentration of 1 µg m<sup>-3</sup>: (i) T=20°C, RH=50%, (ii) T=20°C, RH=80%, (iii)  
 298 T=30°C, RH=80%.

Conditions	Single-component atmosphere					
	Run #	# Tubes	Average uptake rate mL min <sup>-1</sup>	%RSD	Average uptake mL min <sup>-1</sup>	%RSD
T=20°C; RH=50% Alternating for 7 days: 12 hours of clean air and 12 hours of 1,3-butadiene at 2 µg m <sup>-3</sup>	1	8	4.08±0.45	10.4	3.65±0.61	16.7
	2	8	3.22±0.19	5.5		
T=20°C; RH=50% (i) 12 hours of clean air, (ii) 12 hours of exposure to 1,3-butadiene at 14 µg m <sup>-3</sup> (iii) 6 days of clean air	1	8	0.42±0.14	31.7	-	-
T=20°C; RH=50%	1	5	23.48±0.41	1.6	-	-

(i) 6 days of clean air, (ii) 22 hours of exposure to 1,3-butadiene at  $6 \mu\text{g m}^{-3}$

299 Table 2 : Uptake rates for 1,3-butadiene at variable concentration conditions: (i) 7 day experiment while alternating 12 hour  
 300 exposure to clean air and 12 hour exposure at  $2 \mu\text{g m}^{-3}$ , (ii) 7 day exposure starting with 12 hours of clean air followed by 12  
 301 hours of exposure to 1,3-butadiene at  $14 \mu\text{g m}^{-3}$  and finishing with 6 days of clean air, (iii) 7 day exposure starting with 6  
 302 days of clean air followed by 22 hours of exposure to 1,3-butadiene at  $6 \mu\text{g m}^{-3}$ .

303



304

305 Figure 2: Uptake rates for 1,3-butadiene at constant and variable conditions. Method reproducibility is estimated at 20 %.  
 306 (A) Red bars with diagonal lines represent an average of three trials obtained using seven to eight tubes each and refer to  
 307 constant exposure to single component atmosphere at 1,3-butadiene concentration of  $1 \mu\text{g m}^{-3}$ . (B) Blue bars with waves  
 308 represent an average of three trials obtained using six to eight tubes each and refer to constant exposure to  
 309 multicomponent atmosphere at 1,3-butadiene concentration of  $1 \mu\text{g m}^{-3}$ . (C) Dark green bar with triangles represents an  
 310 average of two trials obtained using eight tubes each and refer to variable exposure to single component atmosphere at 1,3-  
 311 butadiene concentration of  $1 \mu\text{g m}^{-3}$ : 7-day experiment while alternating 12-hour exposure to clean air and 12-hour  
 312 exposure at  $2 \mu\text{g m}^{-3}$ . (D) Yellow solid bar represents one trial obtained using eight tubes and refer to variable exposure to  
 313 single atmosphere at 1,3-butadiene concentration of  $1 \mu\text{g m}^{-3}$ : 7-day exposure starting with 12 hours of clean air followed by  
 314 12 hours of exposure to 1,3-butadiene at  $14 \mu\text{g m}^{-3}$  and finishing with 6 days of clean air. (E) Blue bar with horizontal lines  
 315 represents one trial obtained using five tubes and refer to variable exposure to single atmosphere at 1,3-butadiene  
 316 concentration of  $1 \mu\text{g m}^{-3}$ : 7-day exposure starting with 6 days of clean air followed by 22 hours of exposure to 1,3-  
 317 butadiene at  $6 \mu\text{g m}^{-3}$ .

318 Figure 2 shows that the uptake rates depend to a great extent on experimental conditions. This is  
 319 especially true for variable exposure to 1,3-butadiene, with high concentrations either at the  
 320 beginning or at the end of the experiment. Thus, for 50% RH and  $20^\circ\text{C}$  exposure of the tubes to  $14 \mu\text{g m}^{-3}$   
 321 of 1,3-butadiene at the beginning of the experiment followed by 6-day exposure at zero air led  
 322 to the uptake rates almost 10 times lower than when tubes were exposed at a steady 1,3-butadiene  
 323 concentration at  $1 \mu\text{g m}^{-3}$ . On the other hand, when tubes were exposed to  $6 \mu\text{g m}^{-3}$  of 1,3-butadiene  
 324 at the end of the experiment a significant 5 times increase in uptake rates was observed (compared  
 325 with standard constant conditions of 50% RH and  $20^\circ\text{C}$ ). Remember that the 7-day experiment,  
 326 where 6 days of clean air is followed by 22 h at  $6 \mu\text{g m}^{-3}$ , corresponds to the average concentration of  
 327 roughly  $0.8 \mu\text{g m}^{-3}$ , while in all other cases the average concentration is  $1 \mu\text{g m}^{-3}$ . For a 7-day  
 328 experiment starting with 6 days of clean air and following with 24 h at  $7 \mu\text{g m}^{-3}$  (and thus  
 329 corresponding to the average concentration of  $1 \mu\text{g m}^{-3}$ ) the uptake of butadiene is expected to be  
 330 even higher. In the case where  $2 \mu\text{g m}^{-3}$  of 1,3-butadiene was alternated with clean air every 2 hours  
 331 the results are consistent with exposure at constant concentration. Remember, that tubes were  
 332 exposed to a similar amount of pollutant, but differently distributed in time. This type of variability

333 reflects back diffusion of the species on the adsorbent and signals a problem in applying passive  
334 sampling to environmental sampling where changing levels of pollutant concentration are expected,  
335 as it is likely to either underevaluate or overevaluate the measurements.

336 Variability of uptake rates of 1,3-butadiene was addressed in previous publications. Strandberg et al.  
337 witnessed a considerable drop in the 1,3-butadiene uptake rate on Radiello sampler filled with  
338 Carbopack X as a function of exposure time and suggested validating sampling rates over the desired  
339 time period before field sampling [23]. Similarly, Martin et al. noticed a significant fall-off in uptake  
340 rates as a function of time when Radiello samplers were exposed to 5 ppb of 1,3-butadiene for 4  
341 hours versus 4 days and suggested that back diffusion or sorbent saturation is responsible for the  
342 decline [24]. In our case sorbent saturation is an unlikely explanation as the diffusive tubes are  
343 subjected to a similar average 1,3-butadiene concentration. The reason behind the phenomenon is  
344 most probably back diffusion of 1,3-butadiene and inability of Radiello diffusive samplers to durably  
345 retain the compound. In addition, comparing 1,3-butadiene concentrations measured in the vicinity  
346 of the industrial plant near Barcelona producing 1,3-butadiene using diffusive Radiello samplers with  
347 concentrations measured at the same time and location but using multi-sorbent bed tubes (active  
348 sampling) Gallego et al. reported that Radiello diffusive samplers are unable to uptake high amounts  
349 of 1,3-butadiene concentrations leading to underestimation of real values [25]. They suggested that  
350 back diffusion occurs when the concentration differential between the surface of the adsorbing  
351 medium and the sampling atmosphere is negative [25]. Similarly, Strandberg et al. observed 56 %  
352 decline in the percent recovery of 1,3-butadiene on Radiello Carbopack X samplers when the sampler  
353 previously exposed to a given concentration was subjected to clean air [23]. Thus, it seems that  
354 uptake rates of 1,3-butadiene are a function of both time and change in concentration, making its  
355 quantification prone to errors. It's important to keep in mind, that determination of many other  
356 compounds, such as benzene, do not suffer from back diffusion nor the drop in uptake rates as a  
357 function of time during typical sampling procedure [23].

358 In addition, high air humidity can adversely affect the adsorption capacity of a sampler. Carbopack X  
359 belongs to a group of Graphitized Carbon Black adsorbents that are hydrophobic in nature,  
360 nevertheless, considerable water sorption can occur on this material at higher RH values as water  
361 condenses inside of the micropores, thus changing adsorption capacity of the sampler [28]. From  
362 Table 1, humidity has a negative impact on the uptake rate of 1,3-butadiene. For the same  
363 temperature, measured uptake rates for 1,3-butadiene at 50% RH are 40% higher than the rates  
364 measured at 80% RH. In line with the results of this study, Strandberg et al. reported a constant  
365 uptake rate for humidities between 30% and 65 %, but noticed a decrease in uptake rates at  
366 humidities higher than 65% [23]. Minimizing the effect of humidity on the adsorption of 1,3-  
367 butadiene for diffusive sampling was successfully attempted by Sakura et al. by developing a  
368 dehumidification system employing magnesium perchlorate as a dehumidifying agent [31]. Even  
369 though a dehumidification system can work to ensure constant sampling rate at the conditions of  
370 various RH the problem of back diffusion remains unsolved.

371 During a field study Strandberg et al. noticed minor effect of temperature on the uptake of 1,3-  
372 butadiene on Carbopack X Radiello tubes with a decrease in calculated uptakes when going from cold  
373 to warm temperatures, especially for longer sampling times of one week [3]. This trend can be  
374 explained by the fact that back diffusion for compounds with weak affinity for the sorbent increases  
375 with temperature [22], [3]. In addition, adsorption efficiency of an analyte may decrease with  
376 increase of temperature [32]. In the current study the decreasing trends in average uptake of 1,3-  
377 butadiene with increase in temperature cannot be confirmed as the values fall within method

378 reproducibility (Figure 2). In addition to studying the effect of temperature and humidity individually,  
379 it would be of interest to investigate the effect of absolute humidity on the uptake rates.

380 If one compares the effects of humidity, temperature and variability in concentration of 1,3-  
381 butadiene within a single experiment on the uptake rates, it is clear that the latter plays a major role.  
382 Taking into account the inconsistency in uptake rates as a function of variability of concentration  
383 (Table 1, Figure 2), radial diffusive sampling using Carbopack X as a sorbent is not a reliable sampling  
384 technique for determination of 1,3-butadiene mostly due to the fact that it does not reflect changing  
385 concentration levels in ambient environment.

### 386 3.2. Active sampling

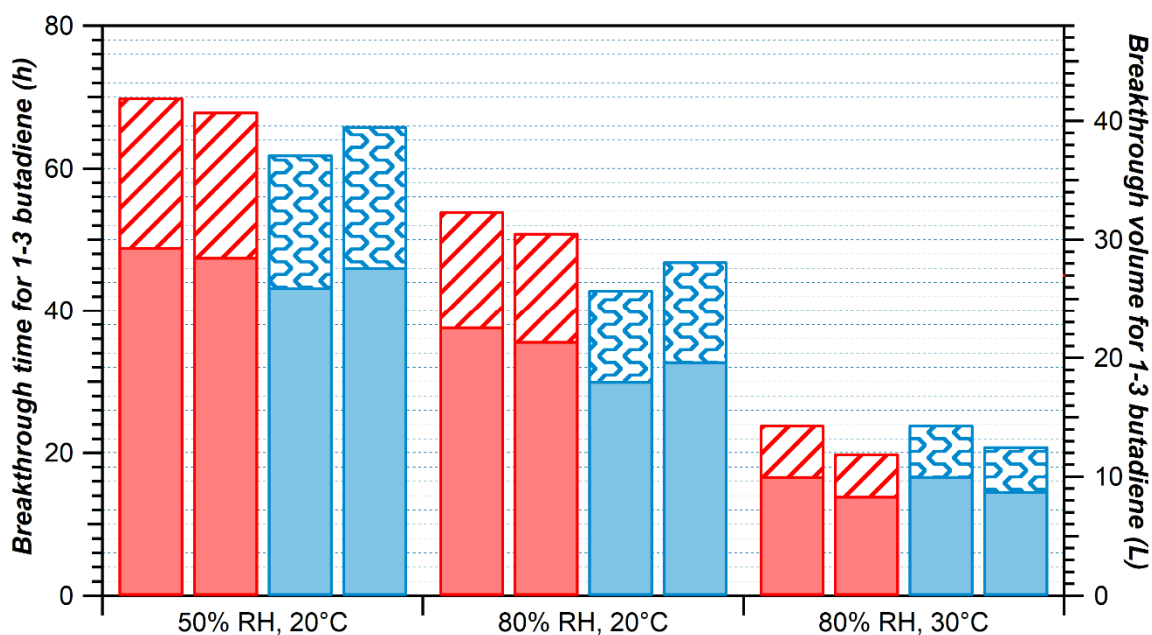
387 Calculation of the concentration using active sampling is very straightforward:

388 *Equation 4*

$$389 \quad C = \frac{m}{v \times t} \times 10^6$$

390 where  $C$  is concentration in  $\mu\text{g m}^{-3}$ ,  $m$  is mass in  $\mu\text{g}$ ,  $v$  is sampling flow rate in  $\text{mL min}^{-1}$ , and  $t$  is time  
391 in min. This formula can be used as long as the mass measured on the sampling tube is proportional  
392 to the sampled volume  $V$  ( $V = v \times t$ ). As time increases at some point a tube is no longer capable to  
393 adsorb all the analyte molecules passing through it and the unretained molecules emerge from the  
394 tube. The time/volume it takes to observe 10% of the inlet concentration at the exit of the sampling  
395 tube is defined as a breakthrough time/volume. Similar to the chromatographic elution,  
396 breakthrough time and volume (time necessary for the molecule to pass through the tube) are  
397 independent of the concentration of the species, but are dependent on the type of the molecule  
398 being sampled, sampling rate, temperature and humidity of the matrix gas [29].

399 In this work breakthrough time was evaluated by directly measuring the exit concentration of 1,3-  
400 butadiene using online GC system and comparing it to the  $1 \mu\text{g m}^{-3}$  generated in the experimental  
401 chamber that serves as a gas source. The moment when 10% of the initial concentration is reached a  
402 breakthrough time is established and a breakthrough volume is calculated.



403

404 *Figure 3: Breakthrough times and volumes for 1,3-butadiene on Carbopack X (500 mg) sampling tubes at varying values of*  
 405 *RH and temperature. Flow rate for all experiments is equal to 10 mL min<sup>-1</sup>. Each bar represents a separate experiment using*  
 406 *one active sampling tube. Red bars with diagonal lines: breakthrough time/volume for constant exposure to single*  
 407 *atmosphere at 1,3-butadiene concentration of 1 µg m<sup>-3</sup>. Red solid bars: safe breakthrough time/volume for constant*  
 408 *exposure to single atmosphere at 1,3-butadiene concentration of 1 µg m<sup>-3</sup>. Blue bars with waves: breakthrough time/volume*  
 409 *for constant exposure to multicomponent atmosphere at 1,3-butadiene concentration of 1 µg m<sup>-3</sup>. Blue solid bars: safe*  
 410 *breakthrough time/volume for constant exposure to multicomponent atmosphere at 1,3-butadiene concentration of 1 µg m<sup>-3</sup>.*  
 411

412 Figure 3 reflects the breakthrough times and volumes for 1,3-butadiene on Carbopack X at different  
 413 temperatures and humidities. It can be observed that the breakthrough time does not depend on the  
 414 presence of other VOCs in the air, as the breakthrough is virtually the same for single component and  
 415 51-component atmosphere. At 50% RH, 20 °C and at 10 ml min<sup>-1</sup>, the average breakthrough time of  
 416 68-70 h corresponds to 40.8-42.0 L per tube, and thus 81.6-84.0 L per gram of Carbopack X material.  
 417 The safe sampling volume being 70% of the breakthrough volume is thus established at 57.1-58.8 L g<sup>-1</sup>  
 418 <sup>1</sup>. This value is about 30% smaller than the value of 82 L g<sup>-1</sup> that Martin et al. established as a safe  
 419 sampling volume at 50 % RH for Carbopack X [24]. The reason for higher sampling volume  
 420 established by Martin et al. could be the slower flow rate of 5 mL min<sup>-1</sup> employed in the experiments  
 421 as opposed to 10 mL min<sup>-1</sup> employed in this work. The safe sampling volume is cut by 25% if relative  
 422 humidity is increased to 80% RH and by 68 % if both RH and temperature are positively affected (80%  
 423 RH and 30°C). Thus, for 80% RH and 30°C conditions safe sampling time falls to only 14.0-16.8 h and  
 424 represents 8.4-10.1 L per tube or 16.8-20.2 L per g of Carbopack X material. The 20 L volume was  
 425 estimated as acceptable volume by Carbopack X manufacturer Supelco, but the value was obtained  
 426 by doping and flushing the tubes with various volumes of nitrogen at 0% RH and at 50 ml min<sup>-1</sup> and is  
 427 hard to compare with values obtained at ambient 50% RH and low 10 ml min<sup>-1</sup> rate [33]. The  
 428 decrease in breakthrough volume with increase of humidity can be explained by increased  
 429 competition of 1,3-butadiene molecules with water molecules for the active sites of the adsorbent,  
 430 thus lowering the sorbent loading capacity causing 1,3-butadiene to elute earlier. Consequently,  
 431 long-term environmental measurements employing active sampling using Carbopack X presents a  
 432 challenge of switching a tube up to twice a day to obtain a long-term monitoring of average

433 concentrations. It might be possible to minimize the effect of humidity by using drying pre-tubes.  
434 Vallecillos et al. observed a three-time increase in 1,3-butadiene breakthrough volume (going from  
435 12 to 36 L) at RH between 56% and 68% when using a pre-tube filled with 0.5 g of calcium chloride  
436 (CaCl<sub>2</sub>) and 0.1 g of diatomaceous earth in addition to the triple-bed sampling tube containing  
437 Carbotrap B, Carbopack X and Carboxen 569 [8]. In the case of current study, increasing time of  
438 sampling three times will only provide 42.0-50.4 hr sampling under hot and humid conditions, which  
439 is far from the desired one-week period.

440 In conclusion, in comparison with passive sampling active sampling is definitely more reliable, but not  
441 practical for long-term monitoring as it requires deploying one or more tubes a day, which is time  
442 consuming and labor intensive. Thus, development of a different material for active sampling, the  
443 one that exhibits a higher capacity for 1,3-butadiene, is of vital importance. In this respect, using an  
444 active multi-sorbent bed is promising and needs to be thoroughly investigated for breakthrough  
445 volumes. To this end, breakthrough volumes for real outdoor air samples were evaluated by Gallego  
446 et al. at 81 to 101 L per tube using multi-sorbent tubes consisting of three materials: Carbotrap,  
447 Carbopack X and Carboxen 569 [25]. At 70 ml min<sup>-1</sup> these volumes translate to sampling  
448 breakthrough times of 19 to 24 h (safe breakthrough times of 13.3 and 16.8 h). Taking 70 % as a safe  
449 sampling volume, sampling at lower rate of 5 ml min<sup>-1</sup> will increase safe sampling time to 189 and  
450 235 h. Enabling sampling times on the order of a week would be a big step in facilitating active  
451 sampling protocol. To the best of our knowledge, the effect of humidity and temperature on the  
452 breakthrough time/volume at low rate sampling of 1,3-butadiene using multi-sorbent tubes has not  
453 yet been evaluated.

#### 454 4. Conclusions

455 In this study we evaluated the limitations for the use of Carbopack X as radial passive or active  
456 sampling adsorbent for determination of 1,3-butadiene in ambient environment. To this end uptake  
457 rates at a number of standard conditions were evaluated for 1,3-butadiene. Unlike other VOCs, 1,3-  
458 butadiene is not a good candidate for continuous passive monitoring using radial diffusive samplers  
459 due to the back diffusion and thus a potential for underestimation of real ambient concentrations of  
460 the pollutant. It is especially noticeable when perturbations in the form of isolated increase in  
461 concentration occur at the beginning of the exposure followed by the period of time when the air is  
462 free of 1,3-butadiene. Thus, roughly 10 times decrease in uptake rate is measured for the same mass  
463 of analyte when the mass is collected at the beginning of the experiment (12 hours of clean air  
464 followed by 12 hours of exposure to 1,3-butadiene at 14 µg m<sup>-3</sup> followed 6 days of clean air)  
465 compared to when it is evenly distributed throughout the experiment (7 days at 1 µg m<sup>-3</sup>). One can  
466 easily imagine a scenario where an emission peak for 1,3-butadiene is followed by a drop in  
467 concentration (caused, for example, by change in wind direction) leading to underestimation of 1,3-  
468 butadiene.

469 As for active sampling, current employment of Carbopack X has its limitation of a short sampling  
470 window of less than 1 day at high temperature and humidity. In practice it either means non-  
471 representative sampling (if a choice is made to test one day a week) or heavy and costly manpower  
472 employment in order to deal with changing tubes and analyzing results. Hence, in order to  
473 adequately address the need for monitoring of 1,3-butadiene a more adsorbing support is  
474 indispensable. Recently reviewed multi-sorbent bed tubes for active sampling show promising results  
475 and need to be further investigated for their use in active sampling.

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479

480

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**Breakthrough times and volumes in various environmental conditions, for  $1 \mu\text{g m}^{-3}$  1,3-butadiene using Carbopack X (500 mg) active sampling tubes at  $10 \text{ mL min}^{-1}$  sampling rate**

