Outdoor air 1,3-butadiene monitoring: comparison of performance of Radiello® passive samplers and active multi-sorbent bed tubes

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Abstract

A comparison was made between the relative performance of active and passive sampling methods for the analysis of 1,3-butadiene in outdoor air. Active and passive sampling was conducted using multi-sorbent bed tubes (Carbotrap, Carbopack X, Carboxen 569) and RAD141 Radiello® diffusive samplers (filled with Carbopack X), respectively. Daily duplicate samples of multi-sorbent bed tubes were taken over a period of 14 days (9 + 5 days) at El Morell (Tarragona, Spain), near the petrochemical area. As 1,3-butadiene is a reactive pollutant and can be rapidly oxidized, half of the samplers were equipped with ozone scrubbers. Samples consisted in two tubes connected in series (front and back) to allow determination of breakthrough. Quadruplicate samples of Radiello® tubes were taken over a period of 14 days (9days and 5 days), too. During those days, ozone concentration was measured using RAD172 Radiello® samplers. In addition to this, daily duplicate samples of multi-sorbent bed tubes were taken in the city of Barcelona over a period of 8 days. Simultaneously, 4 samples of Radiello® tubes were exposed to outdoor air. Sampling was done throughout June and July 2017. Analysis was performed by thermal desorption coupled with gas chromatography/mass spectrometry. Analytical performance of the two sampling methods was evaluated by describing several quality assurance parameters, with results showing that performances are quite similar. They display low detection limits, good precision, linearity and desorption efficiency, low levels of blank values, and low breakthrough for multi-sorbent bed tubes. However, Radiello® samplers were not able to uptake episodic 1,3-butadiene high concentrations, leading to underestimation of real values. Hence, we can conclude that Radiello® samplers can be used for baseline 1,3-butadiene levels whereas multi-sorbent bed tubes would be advisable when relevant episodes are expected.

Keywords: 1,3-butadiene, TD-GC/MS, outdoor air quality, passive sampling, active sampling

1. Introduction

1,3-butadiene is an ubiquitous pollutant in the atmosphere which is emitted from several sources such as combustion of organic matter, residential heating, traffic or fuel distribution (Arayasiri et al., 2010; Aurell et al., 2017; Curren et al., 2006; Delgado-Saborit et al., 2011; Nagpure et al., 2016; Özkaynak et al., 2008; Sapkota and Buckley, 2003). Petrochemical industry processes, especially those occurring at manufacturing plants using or producing this compound (Axelsson et al., 2010; Bari and Kindzierski, 2017; European Communities, 2002; Liang et al., 2017; Mo et al., 2015; Myers et al., 2015) may result in significant fugitive and episodic emissions (Czader and Rappenglück, 2015; Gallego et al., 2018; Grant et al., 2007) that can be difficult to evaluate due to their intermittent nature (Chen et al., 2015). 1,3-butadiene is carcinogenic to humans (Group 1) according to IARC (IARC, 2012, Simpson et al., 2013), can cause DNA damage (Ruchirawat et al., 2010), affects the hematopoietic system (Arayasiri et al., 2010), has been related to central nervous system primitive neuroectodermal tumours in children (PNET) (von Ehrenstein et al., 2016), and has been found to significantly contribute to estimated inhalation cancer risk worldwide (de Blas et al., 2012; Dhaini et al., 2017; Huy et al., 2018; Zhou et al., 2011). Additionally, 1,3-butadiene can contribute to high ozone concentration events as it is an important ozone precursor in the presence of NO_x and solar radiation (Liang et al., 2017; Simpson et al., 2013).That is why air quality long-term evaluation (Gallego et al., 2018) must take this compound into account, especially because of its toxic properties (Mo et al., 2015).

In recent years, passive and active sampling methods have been used to determine 1,3-butadiene levels in outdoor air (Gallego et al., 2018; Oliver et al., 2017; Sakurai et al., 2013;Strandberg et al., 2014; US EPA 2015a, 2015b; Vallencillos et al., 2018). Passive samplers are easy to operate, are generally low cost and do not need electricity supply. They provide average pollutant concentrations based on uptake rates (Gallego et al., 2009a; 2011). In this line, EPA 325A/B methods (US EPA 2015a; 2015b) have been established to monitor fenceline fugitive and area source VOC emissions using passive samplers coupled with TD-GC/MS analysis to define regional emission inventories (Eisele et al., 2016; Oliver et al., 2017). Additionally, the Regulations Respecting Reduction in the Release of Volatile Organic Compounds (Petroleum Sector) came into force in Canada on 1 January 2018. These Regulations also propose fenceline monitoring of benzene, 1,3-butadiene and all retainable VOC using passive samplers in petroleum and petrochemical facilities (Government of Canada, 2017). However, the effectiveness of passive samplers in displaying environmental pollutant concentrations is limited because their way of operating can underestimate episodic high peak concentratios. By contrast, even though active samplers need power supply, they enable short-term sampling, from a few minutes to several hours (Gallego et al., 2009a), to assess concentration peak profiles (Dettmer and Engewald, 2003, Strandberg et al., 2014). This must be taken into account when establishing monitoring strategies such as those proposed in Canada and USA. Thus, it can be concluded that the two sampling approaches are valid depending on the information required. However, in order to evaluate the performance of Radiello® passive samplers, mainly related to their capacity to display episodic 1,3-butadiene high concentrations accurately, a widely used active sampling methodology based on multi-sorbent bed tubes (Carbotrap, Carbopack X and

Carboxen 569) and Radiello® passive samplers (Carbopack X) specific for analysis of 1,3-butadiene were compared.

Concentrations of 1,3-butadiene in outdoor air were measured in two Catalan locations, namely El Morell, near a 1,3-butadiene manufacturing plant with an annual production of 202,000 t located at 41º11'26.8" N and 1º13'13.9" E in the Tarragona petrochemical complex, and the city of Barcelona. 1,3-butadiene is a highly volatile and reactive compound (Martin et al., 2005), and so special attention must be paid to the sampling and analytical methodologies used for its evaluation. This compound can be transformed into a variety of products in the atmosphere through oxidation by ozone (Kramp and Paulson, 2000; Martin et al., 2005; Sakurai et al, 2013) and its collection in several samplers can be altered by ozone interferences (Sakurai et al., 2013). Therefore, ozone scrubbers were attached to several active samplers to evaluate the possible effects of outdoor ozone concentrations on 1,3-butadiene sampling.

Analysis of 1,3-butadiene was performed by automatic thermal desorption coupled with capillary gas chromatography/mass spectrometry (TD-GC/MS). TD-GC/MS has been widely used in VOC and 1,3-butadiene analysis (Gallego et al., 2009a, 2012, 2016, 2017, 2018). This selective methodology allows good chromatographic separation, and identification and quantification of target analytes through their characteristic mass spectrum and quantification ion, respectively (Ribes et al., 2007). The performance of the two sampling methodologies was evaluated by describing several quality assurance parameters, i.e. detection limit, linearity range, precision, desorption efficiency, blank values, and breakthrough values for active samplers. Additionally, outdoor ozone concentrations were determined using Radiello® ozone passive samplers and analyzed by spectrophotometry.

2. Materials and methods

2.1 Chemicals and materials

1,3-butadiene solution (20% wt in toluene), 3-methyl-2-benzothiazolinone hydrazine hydrochloride (MBTH), 4-pyridylaldehyde, potassium iodide ozone scrubbers of 1.5 g, and RAD141 and RAD172 Radiello® passive sampling tubes were obtained from Sigma-Aldrich Chemie (Steinheim, Germany). Toluene for gas chromatography (SupraSolv®) with a purity ≥ 99.8% was obtained from Merck (Darmstadt, Germany). Concentrated sulphuric acid (96%) was obtained from Panreac (Montcada i Reixac, Spain). Perkin Elmer glass tubes (Pyrex, 6 mm external diameter, 90 mm long), unsilanized wool, and Carbotrap (20/40 mesh), Carbopack X (40/60 mesh) and Carboxen 569 (20/45 mesh) adsorbents were purchased from Supelco (Bellefonte, PA, USA).

2.2 1,3-butadiene sampling tubes

Multi-sorbent bed tubes used for 1,3-butadiene sampling were custom packed and composed of Carbotrap (activated graphitized black carbon, weak sorption strength, 70 mg), Carbopack X (activated graphitized black carbon, medium sorption strength, 100 mg) and Carboxen 569 (spherical carbon molecular sieve, high sorption strength, 90 mg) (Figure 1). They were evaluated in an earlier study and found to be highly versatile regarding polarity and volatility of a wide range of target VOCs (Ribes et al., 2007), and were used for analysis of 1,3-butadiene in outdoor air (Gallego et al., 2018). 1,3-butadiene in outdoor air was actively sampled with multi-sorbent bed tubes for 24 h by connecting the self-packed glass multi-sorbent cartridge tubes to air collector pump samplers specially designed in the LCMA-UPC laboratory (Roca et al., 2003). The flow sampling rate was set at 70 ml min^{-1}. The sorbents are hydrophobic enough to avoid interferences derived from the humidity in the air sampled (Ribes et al., 2007). As an

148 additional measure, tubes are purged at ambient temperature for 2 min with a helium
149 flow rate of 50 ml min^{-1} prior to TD-GC/MS.
150 RAD141 Radiello® tubes specially designed to evaluate 1,3-butadiene passively were
151 filled with Carbopack X by the manufacturer (Figure 1).
152 Both sampling tubes were conditioned before use at 400ºC, sealed with Swagelock end
153 caps fitted with PTFE ferrules and stored at 4ºC for 1 week at most before use. Once
154 sampled, tubes were injected into a TD-GC/MS system with a maximum storage time
155 before injection of 1 week (clean refrigerator at 4ºC).
156 *2.3 1,3-butadiene analytical instrumentation*
157 Analysis of 1,3-butadiene for multi-sorbent and Radiello® tubes was performed by TD-
158 GC/MS using a Markes Unity Series 2 (Markes International Ltd., Lantrisant, UK) via
159 Thermo Scientific Focus GC fitted with a Thermo Scientific DSQII MSD (Thermo
160 Fisher Scientific, Austin, Texas, USA).
161 The methodology is described in the literature (Ribes et al., 2007; Gallego et al.,
162 2009b). Primary thermal desorption of the sampling tubes was carried out at 300ºC with
163 a helium flow rate of 55 ml min^{-1} for 10 min. A double split was applied to the TD
164 system (cold trap inlet and outlet splits of 11 ml min^{-1}). The cold trap (U-T15ATA: TO-
165 15/TO-17 Air Toxics trap, Markes) was maintained at -30ºC. After primary desorption,
166 the cold trap was rapidly heated from -30ºC to 300ºC (secondary desorption) and
167 maintained at this temperature for 10 min. Analytes were then injected into the capillary
168 column (DB-624, 60 m x 0.32 mm x 1.8 µm, inert for active compounds) via a transfer
169 line heated at 200˚C. The column oven temperature started at 40˚C for 1 min, increased
170 to 230˚C at a rate of 6˚C min^{-1} and was then maintained at 230˚C for 5 min. Helium
171 (99.999%) carrier gas flow in the analytical column was approximately 1.8 ml min^{-1}
172 (1.4 bar). The chromatographic parameters allow the determination of 1,3-butadiene,

173 together with a wide range of VOC families present in outdoor air (alkanes, aromatic
174 hydrocarbons, alcohols, ketones, aldehydes, ethers, esters, halocarbons, terpenoids,
175 carboxylic acids, organonitrogenated and organosulfur compounds and glycols), in a
176 single sample and a single analysis (Gallego et al., 2018).
177 The electron impact source was obtained at an electron energy of 70 eV. Mass spectral
178 data were acquired over a mass range of 20-300 amu. *m/z*=54 was used as 1,3-butadiene
179 quantification ion. Samples were quantified by the external standard method, according
180 to Ribes et al., 2007. Calibration curves of 1,3-butadiene were freshly prepared and
181 clean tubes were spiked and injected into the TD-GC/MS system daily.
182 *2.4 Ozone analytical instrumentation*
183 In order to determine ozone levels at El Morell, Tarragona, RAD172 Radiello® tubes
184 were desorbed with 5 ml of MBTH solution (5g MBTH in one litre of water with
185 addition of 5 ml of concentrated sulphuric acid)for 1 h stirring occasionally. Samples
186 were analyzed with a spectrophotometer at 430nm. Ozone was quantified with 4-
187 pyridylaldehyde, where 1 µg of 4-pyridylaldehyde is equal to 0.224 µg of ozone.
188 Ozone levels in the city of Barcelona were obtained from a node of the Air Quality
189 Network of the Departament de Territori i Sostenibilitat of the Generalitat de Catalunya,
190 located approximately 500 meters from the 1,3-butadiene sampling point. These levels
191 are presented on an hourly basis.
192 *2.5 Sampling strategy*
193 Daily duplicate 24-h samples of multi-sorbent (Carbotrap, Carbopack X and Carboxen
194 569) bed tubes (half of them equipped with ozone scrubbers containing potassium
195 iodide) were taken over a period of 14 days. Quadruplicate samples of RAD141
196 Radiello® tubes (Carbopack X) were exposed to outdoor air for the same period of time
197 (9+5 days) in El Morell, Tarragona. That number of sampling days was chosen to avoid

198 possible back diffusion from the passive samplers and to avoid as much as possible
199 divergence from the adopted uptake rates (Strandberg et al., 2005). Simultaneously,
200 quadruplicate RAD172 Radiello® tubes for ozone analysis were exposed to outdoor air
201 for 4+4+3+3 days.
202 Additionally, 24-h multi-sorbent bed samples were taken over a period of 8 consecutive
203 days in the city of Barcelona. Quadruplicate samples of Radiello® were exposed to
204 outdoor air for the same period of time (Figures S1 and S2). Sampling was done
205 throughout June and July 2017.
206 Uptake rates for RAD141 Radiello® tubes were extracted from Strandberg et al. (2005),
207 as recommended by Fondazione Salvatore Maugeri-IRCCS (2009).
208 *2.6 Quality assurance parameters*
209 Extreme precautions must be taken to ensure reproducible quality results. The mass
210 spectrometer was manually tuned at *m/z*=69, 131, 264 and 502 every day and air leaks
211 (*m/z*= 4, 18 and 28) were controlled. To avoid artefact formation, both TD trap and
212 sampling tubes were properly conditioned at 325 and 400ºC, respectively. Analytical
213 blank samples, i.e. two clean tubes, were analyzed daily before injection of samples and
214 standards.
215 Method detection limit (MDL), linearity range, precision, desorption efficiency, blank
216 values, and breakthrough values for multi-sorbent bed and Radiello® tubes were
217 evaluated. MDL was calculated by analyzing 7 replicates of the lowest concentrated
218 standard, which had a signal-to-noise factor between 2.5 and 10. The obtained standard
219 deviation (SD) for the replicate concentration was multiplied by 3.14 (Student's *t* value
220 at the 99% confidence interval), according to the US EPA (Part 136-Guidelines
221 establishing test procedures for the analysis of pollutants, Appendix B). Linearity was
222 evaluated within a range from 0.01-6500 ng per tube. It was considered acceptable

when $r^2 \geq 0.999$, signal-to-noise ratios > 10, and peaks had a Gaussian shape. Precision was calculated by consecutive analysis of seven tubes spiked with the same amount of a standard solution of 1,3-butadiene. Desorption efficiency was estimated re-analyzing the sorbent tubes at a higher temperature (350ºC) to remove any remaining analytes from the tubes (n=6). Blank values were evaluated for freshly conditioned tubes and for tubes stored in a clean refrigerator (4ºC) for 1 week. Finally, maximum volume of air of a specific pollutant concentration that can be actively sampled without loss of adsorbent had to be estimated. Otherwise, in the event of breakthrough, the obtained sample would not be representative. Breakthrough, i.e. the volume of air passing through an adsorbent that causes adsorbate molecules to migrate from the front to the back of the adsorbent bed (Gallego et al., 2009a), is generally expressed as the percentage of analyte in the back tube of the total amount of analyte in two tubes connected in series. In our study, breakthrough for real outdoor air samples of 81-101 litres was evaluated for the multi-sorbent bed tubes.

2.7 Data analysis

Data was treated using MicrosoftExcel™ 2010.

3. Results and discussion

3.1 Comparison of quality assurance parameters

Sampling using multi-sorbent bed tubes and TD-GC/MS analysis was chosen as a reference methodology as it had been used for analysis of 1,3-butadiene and a wide range of VOCs in ambient air in previous studies (Gallego et al., 2016; 2017; 2018) and had given solid results for selectivity, sensitivity, linearity, precision, desorption efficiency, artifact formation, breakthrough and stability during storage (Ribes et al., 2007; Gallego et al., 2010; 2011). On the other hand, RAD141 Radiello® passive

248 sampling tubes are specially designed to determine 1,3-butadiene levels in the
249 workplace (Fondazione Salvatore Maugeri-IRCCS, 2009; Sacco, 2009) and outdoor air
250 (Martin et al., 2005; Strandberg et al., 2005; 2006).
251 Quality assurance parameters determined for multi-sorbent bed and Radiello® tubes are
252 presented in Table 1. MDL for both sampling methodologies is 0.2 ng of 1,3-butadiene
253 per sample. Linearity ranges for *m/z* 54 quantification ion are of four orders of
254 magnitude for both tube types. Precision, i.e. repeatability of 7 standards, was found to
255 be 1% and 2.7% for multi-sorbent bed and Radiello® tubes, respectively, < 25% in both
256 cases, thus meeting the EPA performance criteria (US EPA, 1999). Desorption
257 efficiency values for multi-sorbent bed and Radiello® tubes were 98±2 and 98±4,
258 respectively. Regarding blank values, 1,3-butadiene was not present in either of the
259 freshly conditioned sampling tubes. On the other hand, 1 ng of 1,3-butadiene was
260 observed in the Radiello® tubes after 1 week storage in a clean refrigerator at 4ºC.
261 Breakthrough for multi-sorbent bed tubes was 1.3±1.9% (*n*=13) on average for samples
262 without ozone scrubber and 1.1±2.2% (*n*=14) for samples with ozone scrubber in the
263 second tube relative to the total mass in two tubes connected in series for 81-101 l
264 samples with sampling rates of 70ml min^{-1} approximately. The results meet the US EPA
265 criteria of < 5% (US EPA, 1999). Figure 2 presents breakthrough values for 1,3-
266 butadiene concentrations in outdoor air. As can be seen, two samples have breakthrough
267 values slightly higher than 5%. In these cases, 1,3-butadiene concentrations in outdoor
268 air were ≤ 0.2 μg m^{-3}. Since breakthrough is calculated as a percentage, this aspect
269 could be related to low 1,3-butadiene concentrations in the front tubes and a minor
270 presence of the target compound in the back tubes due to slight contamination during
271 storage. No breakthrough was observed for higher 1,3-butadiene concentrations.

The two sampling methodologies have quite similar analytical performances, as they both show low detection limits, good precision and desorption efficiency. Additionally, multi-sorbent bed tubes exhibit very low breakthrough values.

3.2 Comparison of multi-sorbent bed (Carbotrap, Carbopack X, Carboxen 569) and Radiello® (Carbopack X) tube concentrations

The performance of the two sampling methodologies was evaluated in two different scenarios. The first was the Tarragona petrochemical area, where 1,3-butadiene concentrations were expected to be higher than in a typical urban area due to its nearness to the sampling point of a 1,3-butadiene plant. Additionally, important 1,3-butadiene episodic emissions in this sector had been reported in a previous study (Gallego et al., 2018). The second scenario was the city of Barcelona, where 1,3-butadiene concentrations were expected to come mainly from traffic (Gallego et al., 2018).

3.2.1 Tarragona petrochemical area

In this area, half of the samples were taken with ozone scrubber to determine whether tropospheric ozone could affect the sampling process negatively, as suspected by several authors (Kim et al., 1999; Martin et al., 2005; Palluau et al., 2007) and reported by others in previous works (Sakurai et al., 2013, Vallecillos et al. 2018). Table 2 and Figure 3 show 24-h 1,3-butadiene concentrations for samples taken with and without ozone scrubber at El Morell, Tarragona. Table 2 also presents ozone concentrations at the sampling point, with average values from 42 to 66 μg m^{-3}. As can also be observed in Figure S3, samples without ozone scrubber have higher concentrations. Apparently, the scrubber affects target compound collection negatively, as 1,3-butadiene seems to be adsorbed in the scrubber, contrary to what was observed by Sakurai et al. (2013).

296 Table 3 shows average concentrations of 1,3-butadiene calculated by the three different
297 sampling methodologies (active multi-sorbent bed with ozone scrubber, active multi-
298 sorbent bed without ozone scrubber and Radiello® passive tubes). During the first
299 sampling period (21-30/6/2017), an important 1,3-butadiene episodic event generated in
300 the petrochemical area (NE to SE wind direction) of 3 days with 24h average 1,3-
301 butadiene concentrations of 8.7, 39 and 7.5 μg m^{-3}, respectively, was reported (Figure3).
302 The average active concentration of the 9 days was 6.6 ± 12.5 μg m^{-3} when no ozone
303 scrubber was used, with concentrations ranging from 0.1 to 39 μg m^{-3}. On the other
304 hand, the Radiello® passive samplers recorded an average value of 0.9 ± 0.2 μg m^{-3} for
305 the 9 days. As an overall value, multi–sorbent bed tubes represented 772% of the
306 Radiello® results. This shows that the Radiello® passive samplers are unable to uptake
307 high 1,3-butadiene episodic concentrations, leading to underestimation of real values.
308 Reverse diffusion can occur in passive samplers when the concentration differential
309 between the surface of the adsorbing medium and the surrounding atmosphere is
310 negative. Analytes can be diffused from the sampler to ambient air, leading to biased
311 calculations and, in turn, to underestimation of values. Generally, this occurs when
312 episodic high concentration events take place at the beginning of the sampling period
313 (Strandberg et al., 2005). However, for our study, high concentrations of 1,3-butadiene
314 in outdoor air were recorded during the second half of the sampling period, suggesting
315 that the passive sampler was unable to adsorb the high concentrations of 1,3-butadiene
316 in outdoor air. Accidental/sporadic emissions of 1,3-butadiene can occur at
317 petrochemical facilities and chemical plants. In these cases, episodic concentrations can
318 be very high (Chen et al., 2015), e.g. at Milby Park (Houston, USA) fugitive emissions
319 are much more important than flare emissions, in the order of hundreds to thousands of
320 μg m^{-3} (Czader and Rappenglück, 2015). Additionally, Czader and Rappenglück (2015)

observed that the Community Multiscale Air Quality (CMAQ) model often underpredicted 1,3-butadiene concentrations when sporadic releases of this compound occurred, and that some source emissions were not properly accounted for in the emission inventory. Similarly, high punctual/episodic emissions do not seem to be collected by passive samplers, either. In this case, 24-hour active sampling would be the most appropriate 1,3-butadiene collection methodology when relevant episodes are expected, as is the case of the Tarragona petrochemical area.

During the second sampling period (1-4/7/2017), no episodic 1,3-butadiene events were recorded with multi-sorbent bed tubes (Table 3, Figure 3). The average active concentration obtained without the use of ozone scrubbers was 0.4 ± 0.1µg m^{-3}, with values ranging from 0.3 to 0.5µg m^{-3}. In this case, multi-sorbent bed tubes accounted for 70% of concentrations obtained by the Radiello® tubes (0.5 ± 0.1 µg m^{-3}). Passive samplers showed slightly higher concentrations, but both values were much closer than during the episodic period.

The performance of a Radiello® tube for VOC analysis with thermal desorption (RAD145, Carbograph 4) was evaluated in a previous study (Gallego et al., 2011). In that case, Radiello® tubes also exhibited higher values than multi-sorbent bed tubes. As passive sampling depends on the uptake rates determined by the manufacturer, the used values would be crucial. In most cases, uptake rates are calculated experimentally in exposure chambers, with only the target compounds present in the air samples (Gallego et al., 2011; Ramos et al., 2018). The uptake rates used in our study were taken from Stranberg et al. (2005). They had been calculated in a standard atmosphere containing only 1,3-butadiene and benzene for two 1,3-butadiene concentrations: 0.23 and 2.26 µg m^{-3}. Hence, the application of the manufacturer or laboratory calculated uptake rates in passive sampling can sometimes lead to concentration values slightly different from real

346 values in complex field scenarios (Barro et al., 2009; Gallego et al., 2009a; 2011;
347 Walgraeve et al., 2011).
348 1,3-butadiene emission profiles from different petrochemical facilities are process-
349 dependent and region-specific (Mo et al., 2015). Hence, reliable monitoring strategies
350 are needed by policymakers to establish control approaches to emissions ─mainly
351 diffuse and/or fugitive emanations─ of this compound to the atmosphere. In this line,
352 both USA and Canada have established passive fenceline control of fugitive VOC
353 releases, specifically 1,3-butadiene, in petroleum sector facilities (Government of
354 Canada, 2017; US EPA 2015a,b). This kind of regulation procedures are expected to be
355 put into effect worldwide in the near future. Thus, the reliability of the proposed passive
356 monitoring strategy must be evaluated thoroughly to identify possible flaws in the
357 procedure. In our study, it was observed that Radiello® passive samplers are incapable
358 of incorporating high episodic 1,3-butadiene concentrations to the average values that
359 they display, leading to underestimation of real concentration values of this compound
360 in ambient air. This aspect must be taken into consideration when applying this
361 methodology to petrochemical industry monitoring. Moreover, it would be advisable to
362 complement the sampling strategy with active samples in locations where significant
363 diffuse emissions could be expected.
364 *3.2.2 City of Barcelona*
365 1,3-butadiene concentrations from multi-sorbent bed and Radiello® tubes in the city of
366 Barcelona are shown in Table 4. All samples were taken without ozone scrubber in view
367 of the negative effects observed at El Morell, where less concentrated samples were
368 obtained when using the scrubber.
369 As can be seen, Radiello® concentrations in the city of Barcelona are slightly higher
370 than those from obtained by multi-sorbent bed tubes, as observed during the second

371 sampling period (1-4/7/2017) in the Tarragona petrochemical area, where no 1,3-
372 butadiene episodes were recorded by active sampling. However, both concentrations are
373 of the same order of magnitude, with multi-sorbent bed tubes (0.3 ± 0.1 μg m^{-3}, ranging
374 from 0.13 to 0.56 μg m^{-3}) accounting for 60% of the Radiello® concentrations (0.5 ± 0.1
375 μg m^{-3}). As said before, the application of manufacturer sampling rates can lead to slight
376 overestimation of results (Barro et al., 2009; Gallego et al., 2009a, 2011). Hence, we can
377 conclude that, for baseline 1,3-butadiene levels, Radiello® samplers could be employed
378 taking into account this minor limitation. In this line, it would be advisable to calculate
379 uptake rate values in outdoor air scenarios prior to their use to ensure better approaches
380 to 1,3-butadiene concentrations (Gallego et al., 2011).

381 *3.3 O_3 effect on sampling performance*

382 Even though negative effects of tropospheric ozone levels on 1,3-butadiene sampling
383 have been observed by several authors (Sakurai et al., 2013; Vallecillos et al., 2018), in
384 our study, no correlation was found between 1,3-butadiene and ozone concentrations, as
385 suggested by other authors (Kim et al., 1999; Martin et al., 2005; Palluau et al., 2007).
386 Furthermore, samples obtained using ozone scrubbers showed lower ng of 1,3-
387 butadiene than those obtained without using ozone scrubbers. These accessories,
388 therefore, seem to retain 1,3-butadiene, leading to underestimation of ambient air
389 concentration levels. Figure 4 plots 1,3-butadiene concentrations against ozone
390 concentrations during all the two sampling periods. A decreasing tendency in 1,3-
391 butadiene levels is observed at El Morell when ozone levels increase in outdoor air.
392 However, although 1,3-butadiene concentrations are lower when ozone levels are
393 higher, the highest 1,3-butadiene concentrations were derived from an episodic event,
394 coinciding with the lowest ozone levels recorded. On the other hand, a decrease in 1,3-
395 butadiene is observed in the city of Barcelona when ozone concentrations are above 70

396 µg m^{-3}. However, similar values can be observed when these levels are around 45 µg m^{-3}
397 (Figure 4). Thus, no correlation is evident between 1,3-butadiene and ozone
398 concentrations, although further research would be required to know more about the
399 possible negative effects of tropospheric ozone levels on the 1,3-butadiene sampling
400 process (Vallecillos et al., 2018).

401 *3.4 Effects of meteorological conditions on sampling performance*

402 The performance of the two sampling methodologies was evaluated outdoors to test
403 them under real environmental conditions of temperature, relative humidity,
404 atmospheric pressure and wind velocity and direction. Meteorological conditions can
405 affect both dispersion of emitted pollutants in the atmosphere (Gallego et al., 2008) and
406 uptake rate values to calculate environmental concentrations (Strandberg et al., 2005;
407 2006). No correlations were found between temperature, relative humidity, atmospheric
408 pressure and wind velocity and 1,3-butadiene outdoor concentrations, either at El
409 Morellor in the city of Barcelona, for both active and passive samplers. On the other
410 hand, a relevant correlation was observed between active sampling and NE to SE winds
411 coming from the petrochemical sector, as already identified by other authors (Chen et
412 al., 2015). Figure 5 shows that the episodic 1,3-butadiene high concentration period
413 coincides with a large percentage of winds (between 25 and 35%) coming from the
414 petrochemical sector. The highest 1,3-butadiene concentrations during the sampling
415 period was observed on 26 June 2017, coinciding with a decrease in the percentage of
416 wind coming from the petrochemical area. However, 1,3-butadiene emissions must have
417 been so remarkably high that even though the winds also came from other sectors, these
418 ambient air concentrations were the greatest in the whole monitoring term. A second
419 period of NE to SE winds occurred during the last 4 sampling days. Nevertheless, 1,3-
420 butadiene concentrations were low, in the range of 0.04-0.4 µg m^{-3}, indicating that the

concentrations observed during the first sampling period were due to diffuse intermittent emissions rather than to the normal operation of the 1,3-butadiene plant.

4. Conclusions

The performance of two sampling methodologies, i.e. active multi-sorbent bed tubes and Radiello® passive tubes, for 1,3-butadiene analysis was evaluated. Very similar results were obtained: low detection limits, wide linearity ranges, and good precision and desorption efficiencies. The presence of 1,3-butadiene in freshly clean and refrigerator-stored tubes was non-existent or very low for both tube types. Additionally, breakthrough values for multi-sorbent bed tubes were found to meet US EPA performance criteria. Multi-sorbent bed and Radiello® tubes also exhibit similar 1,3-butadiene average concentrations in baseline periods, with Radiello® values being slightly higher. However, the use of multi-sorbent bed tubes would be advisable for significant 1,3-butadiene episodes because Radiello® tubes do not seem to yield accurate concentration results in these cases. This aspect is especially relevant when applying 325A/B methodologies of the US EPA and Regulations Respecting Reduction in the Release of Volatile Organic Compounds (Petroleum Sector)of the Government of Canada. Nonetheless, as not all worldwide petrochemical facilities would have episodic releases of 1,3-butadiene like those observed in the Tarragona region, the repetition of the same experiment near other petrochemical locations would be useful in the future.

Acknowledgements

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References

445 Arayasiri, M., Mahidol, C., Navasumrit, P., Autrup, H., Ruchirawat, M., 2010.
446 Biomonitoring of benzene and 1,3-butadiene exposure and early biological effects in
447 traffic policemen. Sci. Total Environ. 408, 48755-4862.
448 Aurell, J., Gullett, B.K., Tabor, D., Yonker, N., 2017. Emissions from prescribed
449 burning of timber slash piles in Oregon. Atmos. Environ. 150, 395-406.
450 Axelsson, G., Barregard, L., Holmberg, E., Sallsten, G., 2010. Cancer incidence in a
451 petrochemical industry area in Sweden. Sci. Total Environ. 408, 4482-4487.
452 Bari, M.A., Kindzierski, W.B., 2017. Concentrations, sources and human health risk of
453 inhalation exposure to air toxics in Edmonton, Canada. Chemosphere 173, 160-171.
454 Barro, T., Regueiro, J., Llompart, M.,Garcia-Jares, C., 2009. Analysis of industrial
455 contaminants in indoor air: Part 1. Volatile organic compounds, carbonyl compounds,
456 polycyclic aromatic hydrocarbons and polychlorinated biphenyls. J. Chromatogr. A
457 1216, 540-566.
458 Chen M.-H., Yuan, C.-S., Wang, L.-C., 2015. A feasible approach to quantify fugitive
459 VOCs from petrochemical processes by integrating open-path transform infrared
460 spectrometry measurements and industrial source complex (ISC) dispersion model.
461 Aerosol Air Qual. Res. 15, 1110-1117.
462 Curren K.C., Dann T.F., Wang, D.K., 2006. Ambient air 1,3-butadiene concentrations
463 in Canada (1995-2003): seasonal, day of week variations, trends, and source influences.
464 Atmos. Environ. 40, 170-181.
465 Czader, B.H., Rappenglück, B., 2015. Modeling of 1,3-butadiene in urban and industrial
466 areas. Atmos. Environ. 102, 30-42.
467 de Blas, M., Navazo, M., Alonso, L., Durana, N., Gómez, M.C., Iza, J., 2012.
468 Simultaneous indoor and outdoor on-line hourly monitoring of atmospheric volatile

469 organic compounds in an urban building.The role of inside and outside sources. Sci.
470 Total Environ. 426**,** 327-335.
471 Delgado-Saborit, J.M., Aquilina, N.J., Meddings, Cl., Baker, S., Harrison, R.M.,
472 2011.Relationship of personal exposure to volatile organic compounds to home, work
473 and fixed site outdoor concentrations. Sci. Total Environ. 409, 478-488.
474 Dettmer, K., Engewald, W., 2003. Ambient air analysis of volatile organic compounds
475 using adsorptive enrichment.Chromatographia 57, S-339-S-347.
476 Dhaini, H.R., Salamech, T., Waked, A., Sauvage, S., Borbon, A., Formenti, P., Doussin,
477 J.-F., Locogne, N., Afif, C., 2017. Quantitative cancer risk assessment and local
478 mortality burden for ambient air pollution in an eastern Mediterranean City. Environ.
479 Sci. Pollut. Res. 24, 14151-14162.
480 Eisele, A.P., Mukerjee, S., Smith, L.A., Thoma, E.D., Whitaker, D.A., Oliver, K.D.,
481 Wu, T., Colon, M., Alston, L., Cousett, T.A., Miller, M.C., Smith, D.M., Stallings, C.,
482 2016. Volatile organic compounds at two oil and natural gas production well pads in
483 Colorado and Texas using passive samplers. J. Air Waste Assoc. 66, 412-419.
484 European Communities, 2002. 1,3-Butadiene. Summary risk assessment report.
485 European Commission, Joint Research Centre, Institute for Health and Consumer
486 Protection. European Chemicals Bureau. Ispra, Italy, pp. 24.
487 Fondazione Salvatore Maugeri-IRCCS, 2009. Adsorbing cartridge for 1,3-butadiene and
488 isoprene thermally desorbed (Cat. No. RAD141). Technical sheet no. 141-02-2009.
489 Gallego, E., Soriano, C., Roca, F.X., Perales, J.F., Alarcón, M., Guardino, X.,
490 2008.Identification of the origin of odour episodes through social participation,
491 chemical control and numerical modelling. Atmos. Environ. 42, 8150-5160.

492 Gallego, E., Roca, F.J., Perales, J.F., Guardino, X., 2009a. Use of sorbents in air quality
493 control systems. In Willis TP, editor. Sorbents: Properties, Materials and Applications.
494 New York: Nova Science Publishers, pp. 71-108.
495 Gallego, E., Roca, F.J., Perales, J.F., Guardino, X., 2009b. Simultaneous evaluation of
496 odor episodes and air quality. Methodology to identify air pollutants and their origin
497 combining chemical analysis (TD-GC/MS) social participation, and mathematical
498 simulations techniques. In: Romano GC and Conti AG, editors. Air Quality in the XXI
499 Century, New York: Nova Science Publishers, pp. 139-209.
500 Gallego, E., Roca, F.J., Perales, J.F., Guardino, X., 2010. Comparative study of the
501 adsorption performance of a multi-sorbent bed (Carbotrap, Carbopack X, Carboxen
502 569) and a Tenax TA adsorbent tube for the analysis of volatile organic compounds
503 (VOCs). Talanta 81, 916-924.
504 Gallego, E., Roca, F.J., Perales, J.F., Guardino, X., 2011. Comparative study of the
505 adsorption performance of an active multi-sorbent bed tube (Carbotrap, Carbopack X,
506 Carboxen 569) and a Radiello® diffusive sampler for the analysis of VOCs.Talanta 85,
507 662-672.
508 Gallego, E., Roca, F.J., Perales, J.F., Sánchez, G., Esplugas, P., 2012. Characterization
509 and determination of the odorous charge in the indoor air of a waste treatment facility
510 through the evaluation of volatile organic compounds (VOCs) using TD-GC/MS.
511 WasteManage. 32, 2469-81.
512 Gallego, E., Roca, F.J., Perales, J.F., Guardino, X., Gadea, E., Garrote, P., 2016. Impact
513 of formaldehyde and VOCs from waste treatment plants upon the ambient air nearby an
514 urban area (Spain).Sci. Total Environ. 568, 369-380.
515 Gallego, E., Roca, F.J., Perales, J.F., Gadea, E., 2018. Outdoor air 1,3-butadiene
516 monitoring near a petrochemical industry (Tarragona region) and in several Catalan

517 urban areas using active multi-sorbent bed tubes and analysis through TD-GC/MS. Sci.
518 Total Environ. 618, 1440-1448.
519 Gallego, E., Perales, J.F., Roca, F.J., Guardino, X., Gadea, E., 2017. Volatile methyl
520 siloxanes (VMS) concentrations in outdoor air of several Catalan urban areas.Atmos.
521 Environ. 155, 108-118.
522 Government of Canada, 2017.Regulations Respecting Reduction in the Release of
523 Volatile Organic Compounds (Petroleum Sector).http://www.gazette.gc.ca/rp-
524 pr/p1/2017/2017-05-27/html/reg2-eng.html (last accessed 8th February 2018).
525 Grant, R.L., Leopold, V., McCant, D., Honeycutt, M., 2007. Spatial and temporal trend
526 evaluation of ambient concentrations of 1,3-butadiene and chloroprene in Texas. Chem-
527 Biol. Interact. 166, 44-51.
528 Huy, L.N., Lee, S.C., Zhang, Z., 2018. Human cancer risk estimation for 1,3-butadiene:
529 An assessment of personal exposure and different microenvironments. Sci. Total
530 Environ. 616-617, 1599-1611.
531 IARC, 2012. 1,3-Butadiene, IARC Monographs 100F, 309-338.
532 Kim, Y.M., Harrad, S., Harrison, R.M., 1999. An improved method for the
533 determination of 1,3-butadiene in nonoccupational environments. Environ. Sci.
534 Technol. 33, 4342-4345.
535 Kramp, F., Paulson, S.E., 2000. The gas phase reaction of ozone with 1,3-butadiene:
536 formation yields of some toxic products. Atmos. Environ. 34, 35-43.
537 Liang, X., Chen, X., Zhang, J., Shi, T., Sun, X., Fan, L., Wang, L., Ye, D., 2017.
538 Reactivity-based industrial volatile organic compounds emission inventory and its
539 implications for ozone control strategies in China. Atmos. Environ. 162, 115-126.
540 Martin, N.A., Duckworth, P., Henderson, M.H., Swann, N.R.W., Granshaw, S.T.,
541 Lipscombe, R.P., Goody, B.A., 2005. Measurements of environmental 1,3-butadiene

542 with pumped and diffusive samplers using the sorbent Carbopack X. Atmos. Environ.
543 39, 1069-1077.
544 Mo, Z., Shao, M., Lu, S., Qu, H., Z., M., Sun, J., Gou, B., 2015.Process-specific
545 emission characteristics of volatile organic compounds (VOCs) from petrochemical
546 facilities in the Yangtze River Delta, China. Sci. Total Environ. 533, 422-431.
547 Myers, J.L., Phillips, T., Grant, R.L., 2015.Emissions and ambient air monitoring trends
548 of lower olefins across Texas from 2002 to 2012.Chem-Biol. Interact. 241, 2-9.
549 Nagpure, A.S., Gurjar, B.R., Kumar, V., Kumar, P., 2016.Estimation of exhaust and
550 non-exhaust gaseous, particulate matter and air toxics emissions from on-road vehicles
551 in Delhi. Atmos. Environ. 127, 118-124.
552 Oliver, K.D., Cousett, T.A., Whitaker, D.A., Smith, L.A., Mukerjee, S., Stallings, C.,
553 Thoma, E.D., Alston, L., Colon, M., Wu, T., Henkle, S., 2017. Sample integrity
554 evaluation and EPA method 325B interlaboratory comparison for selected volatile
555 organic compounds collected diffusively on Carbopack X sorbent tubes. Atmos.
556 Environ. 163, 99-106.
557 Özkaynak, H., Palma, T., Touma, J.S., Thurman, J., 2008.Modeling population
558 exposures to outdoor sources of hazardous air pollutants.J. Expo. Sci. Env. Epid. 18, 45-
559 58.
560 Palluau, F., Mirabel, P., Millet, M., 2007. Influence of ozone on the sampling and
561 storage of volatile organic compounds in canisters. Environ. Chem. Lett. 5, 51-55.
562 Ramos, T.D., de la Guardia M., Pastor, A., Esteve-Turrillas, F.A., 2018. Assessment of
563 air passive sampling uptakes for volatile organic compounds using VERAM devices.
564 Sci. Total Environ. 619-620, 1014-1021.
565 Ribes, A., Carrera, G., Gallego, E., Roca, X., Berenguer, M.J., Guardino, X., 2007.
566 Development and validation of a method for air-quality and nuisance odors monitoring

567 of volatile organic compounds using multi-sorbent adsorption and gas
568 chromatography/mass spectrometry thermal desorption system. J. Cromatogr. A 1140,
569 44-55.
570 Roca, F.J., Folch, J., Corruchaga, A., Cid, J., Puigjaner, L., 2003. Design and
571 development of a control system for odours and volatile organic compounds (VOC)
572 from industrial and waste treatment processes, presented at the 9th Mediterranean
573 Congress of Chemical Engineering (Barcelona, Spain).
574 Ruchirawat, M., Navasumrit, P., Settachan, D., 2010. Exposure to benzene in various
575 susceptible populations: Co-exposures to 1,3-butadiene and PAHs and implications for
576 carcinogenic risk. Chem-Biol. Interact. 184, 67-76.
577 Sakurai, K., Miyake, Y., Amagai, T., 2013. Reliable passive-sampling method for
578 determining outdoor 1,3-butadiene concentrations in air. Atmos. Environ. 80, 198-203.
579 Sapkota, A., Buckley, T.J., 2003. The mobile source effect on curbside 1,3-butadiene,
580 benzene, and particle-bound polycyclic aromatic hydrocarbons assessed at a tollbooth.
581 Air & Waste Manage. Assoc. 53, 740-748.
582 Sacco, P., 2009. Radiello diffusive sampler for monitoring 1,3-butadiene and isoprene
583 in workplace air. The Reporter 27.3, 11-12.
584 Simpson, I.J., Marrero, J.E., Batterman, S., Meinardi, S., Barletta, B., Blake, D.R.,
585 2013.Air quality in the industrial heartland of Alberta, Canada and potential impacts on
586 human health. Atmos. Environ. 81, 702-709.
587 Strandberg, B., Sunesson, A.-L., Olsson, K., Levin, J.-O., Ljungqvist, G., Sundgren, M.,
588 Sällsten, G., Barregard, L., 2005. Evaluation of two types of diffusive samplers and
589 adsorbents for measuring 1,3-butadiene and benzene in air. Atmos. Environ. 39, 4101-
590 4110.

Strandberg, B., Sunesson, A.-L., Sundgren, M., Levin, J.-O., Sällsten, G., Barregard, L., 2006. Field evaluation of two diffusive samplers and two adsorbent media to determine 1,3-butadiene and benzene levels in air. Atmos. Environ. 40, 7686-7695.

Strandberg, B., Bergemalm-Rynell, K., Sallsten, G., 2014. Evaluation of three types of passive samplers for measuring 1,3-butadiene and benzene at workplaces. Environ. Sci. Processes Impacts 16, 1008-1014.

U.S. EPA, 1999.Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Method TO-17, Center for Environmental Research Information, Office of Research and Development.

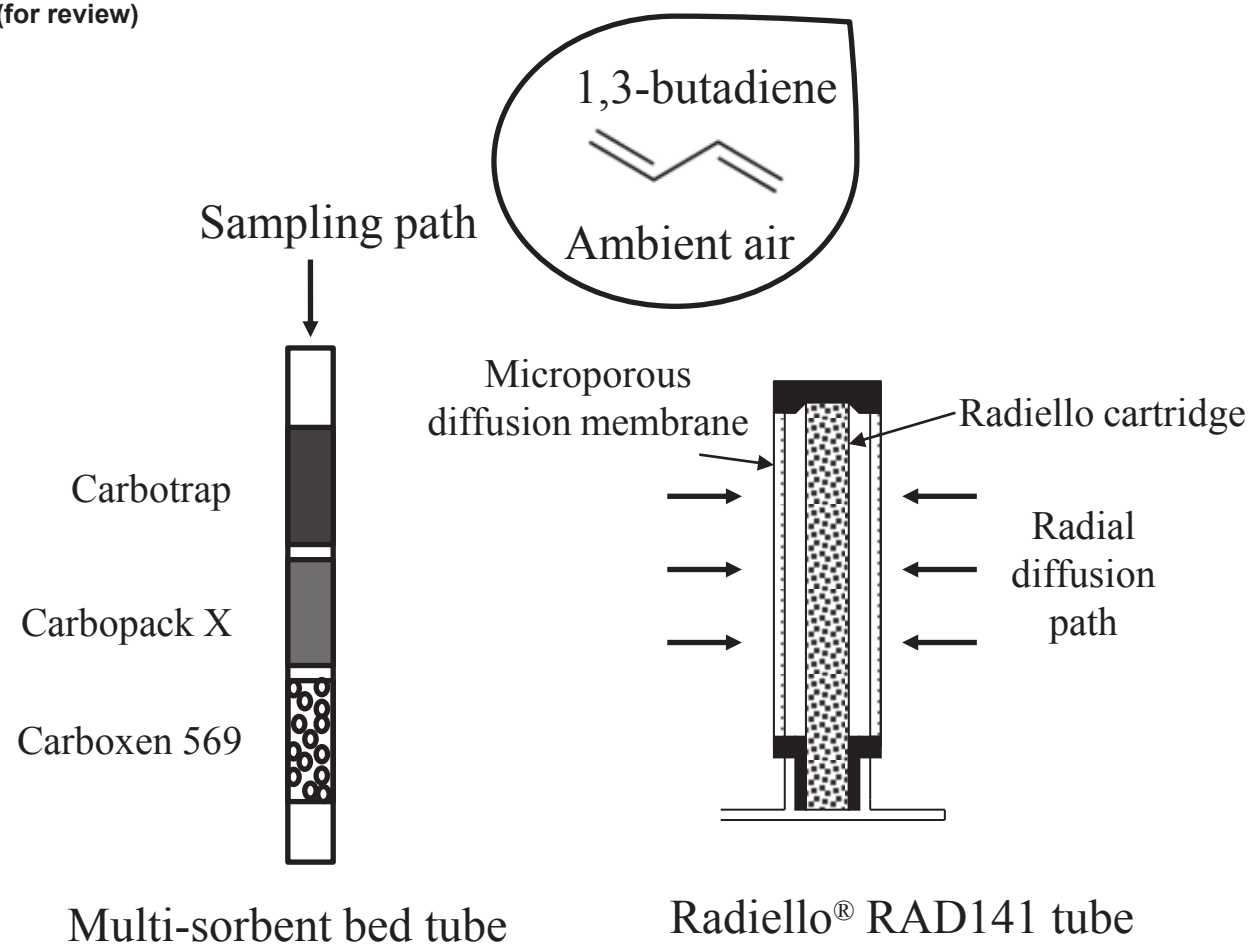
U.S. EPA, 2015a. Method 325A: Volatile Organic Compounds from Fugitive and Area Sources: Sampler Deployment and VOC Sample Collection. 40 CFR Part 63,Subpart UUU [EPA-HQ-OAR-2010-0682; FRL-9720-4], RIN 2060-AQ75, Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards. Available at: https://www.epa.gov/sites/production/files/2017-08/documents/method_325a.pdf (last accessed 8th February 2018).

U.S. EPA, 2015b. Method 325B-volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis. 40 CFR Part 63, Subpart UUU [EPAHQ-OAR-2010-0682; FRL-9720-4], RIN 2060-AQ75, Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards. Available at: https://www.epa.gov/sites/production/files/2017-08/documents/method_325b.pdf (last accessed 8th February 2018).

Vallencillos, L., Maceira, A., Marcé, R.M., Borrull, F., 2018. Evaluation of activesamplingstrategies for thedetermination of 1,3-butadiene in air. Atmos. Environ. 176, 21-29.

615 von Ehrenstein, O.S., Heck, J.E., Park, A.S., Cockburn, M., Escobedo, L., Ritz, B.,
616 2016. *In Utero* and early-life exposure to ambient air toxics and childhood brain
617 tumours: A population-based case-control study in California, USA. Environ. Health
618 Persp. 124, 1093-1099.
619 Walgraeve, C., Demeestere, K., Dewulf, J., Van Huffel K., Van Langenhove, H., 2011.
620 Diffusive sampling of 25 volatile organic compounds in indoor air: Uptake rate
621 determination and application in Flemish homes for the elderly. Atmos. Environ. 45,
622 5828-5836.
623 Zhou, J., You, Y., Bai, Z., Hu, Y., Zhang, J., Zhang, N., 2011.Health risk assessment of
624 personal inhalation exposure to volatile organic compounds in Tianjin, China. Sci.
625 Total Environ. 409, 452-459.

Graphical Abstract (for review)



Multi-sorbent bed-Radiello comparative:

-Similar analytical performances:

-low limits of detection

-low levels of blank values

-good precision and desorption efficiency

-low breakthrough for multi-sorbent bed tubes

-Radiello® samplers were not able to uptake high episodic 1,3-butadiene concentrations

Figure captions

Figure 1. Custom made multi-sorbent bed tubes (Carbotrap, Carbopack X and Carboxen 569) and Radiello® RAD141 passive samplers used in the present study.

Figure 2. Breakthrough values (%) in respect to 1,3-butadiene concentrations (µg m^{-3}) in outdoor air in El Morell, Tarragona.

Figure 3. 1,3-butadiene concentrations (µg m^{-3}) for multi-sorbent bed tubes with and without ozone scrubber in El Morell, Tarragona.

Figure 4. Correlations between 1,3-butadiene and ozone concentrations (µg m^{-3}) during the different sampling periods.

Figure 5. 1,3-butadiene concentrations (µg m^{-3}) and NE-SE wind direction (%) during the different sampling days in El Morell, Tarragona.

Figure 1

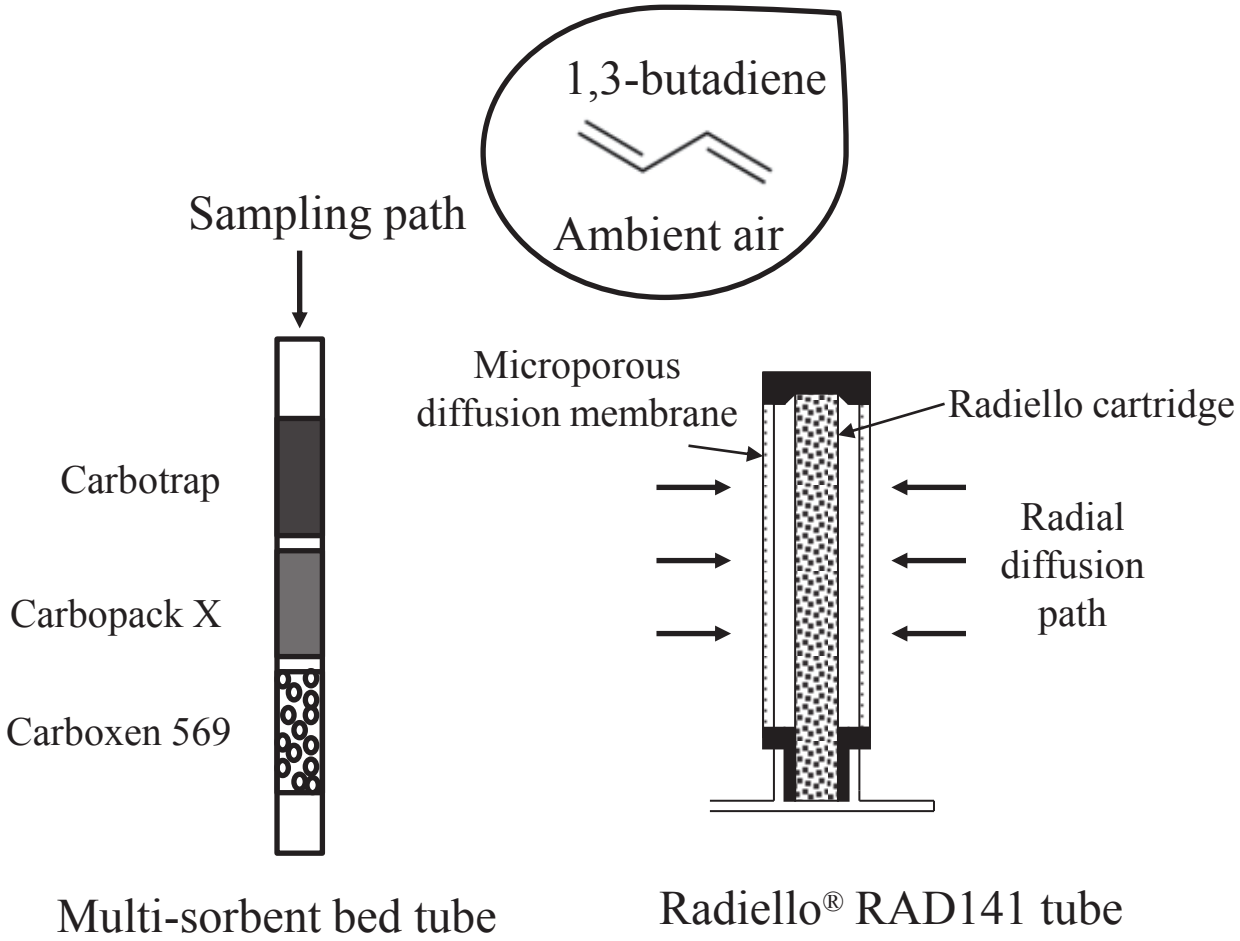

1,3-butadiene
Ambient air
Sampling path
Carbotrap
Carbopack X
Carboxen 569
Multi-sorbent bed tube
Microporous
diffusion membrane
Radiello cartridge
Radial
diffusion
path
Radiello® RAD141 tube

Figure 2

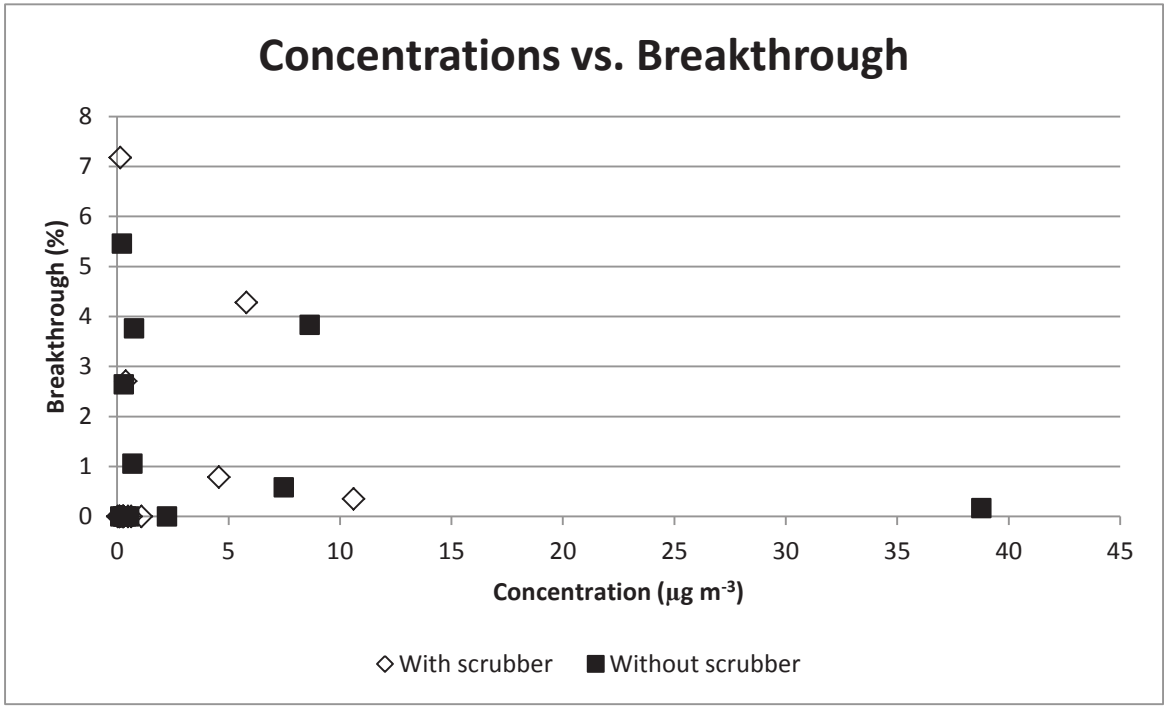

Concentrations vs. Breakthrough
Breakthrough (%)
0
1
2
3
4
5
6
7
8
0
5
10
15
20
25
30
35
40
45
Concentration (µg m-3)
With scrubber
Without scrubber

Figure 3

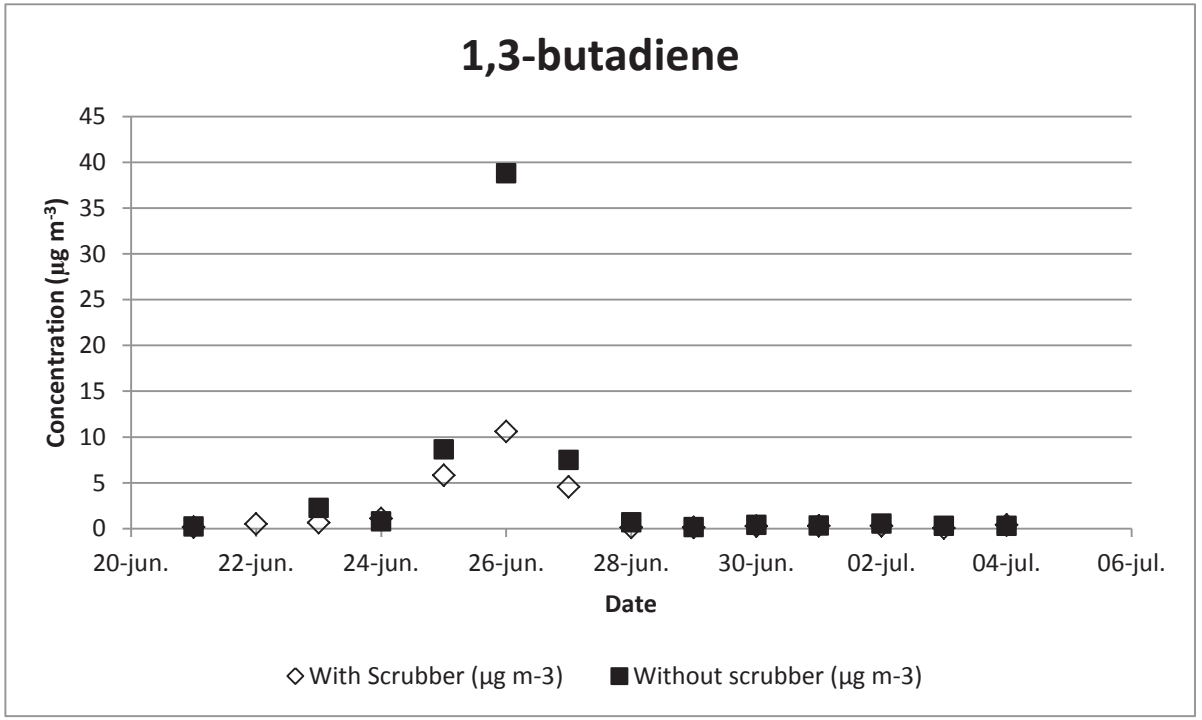
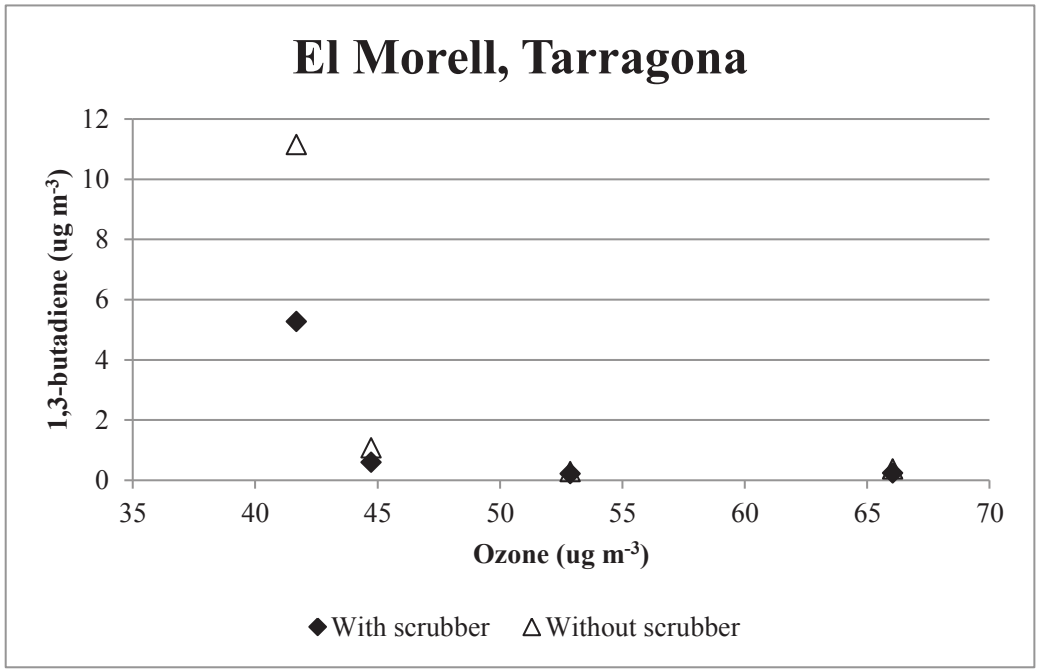

1,3-butadiene
45
40
35
30
25
20
15
10
5
0
Concentration (µg m-3)
20-jun.
22-jun.
24-jun.
26-jun.
28-jun.
30-jun.
02-jul.
04-jul.
06-jul.
Date
With Scrubber (µg m-3)
Without scrubber (µg m-3)

Figure 4


El Morell, Tarragona
1,3-butadiene (ug m-3)
12
10
8
6
4
2
0
35
40
45
50
55
60
65
70
Ozone (ug m-3)
With scrubber
Without scrubber

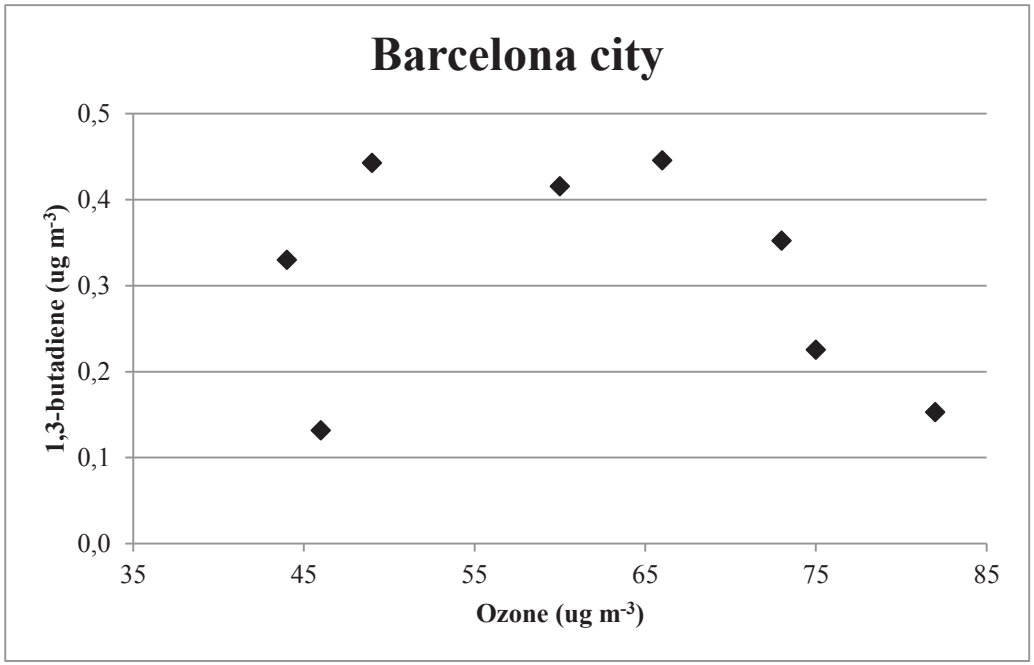

Barcelona city
1,3-butadiene (ug m-3)
0,5
0,4
0,3
0,2
0,1
0,0
35
45
55
65
75
85
Ozone (ug m-3)

Figure 5

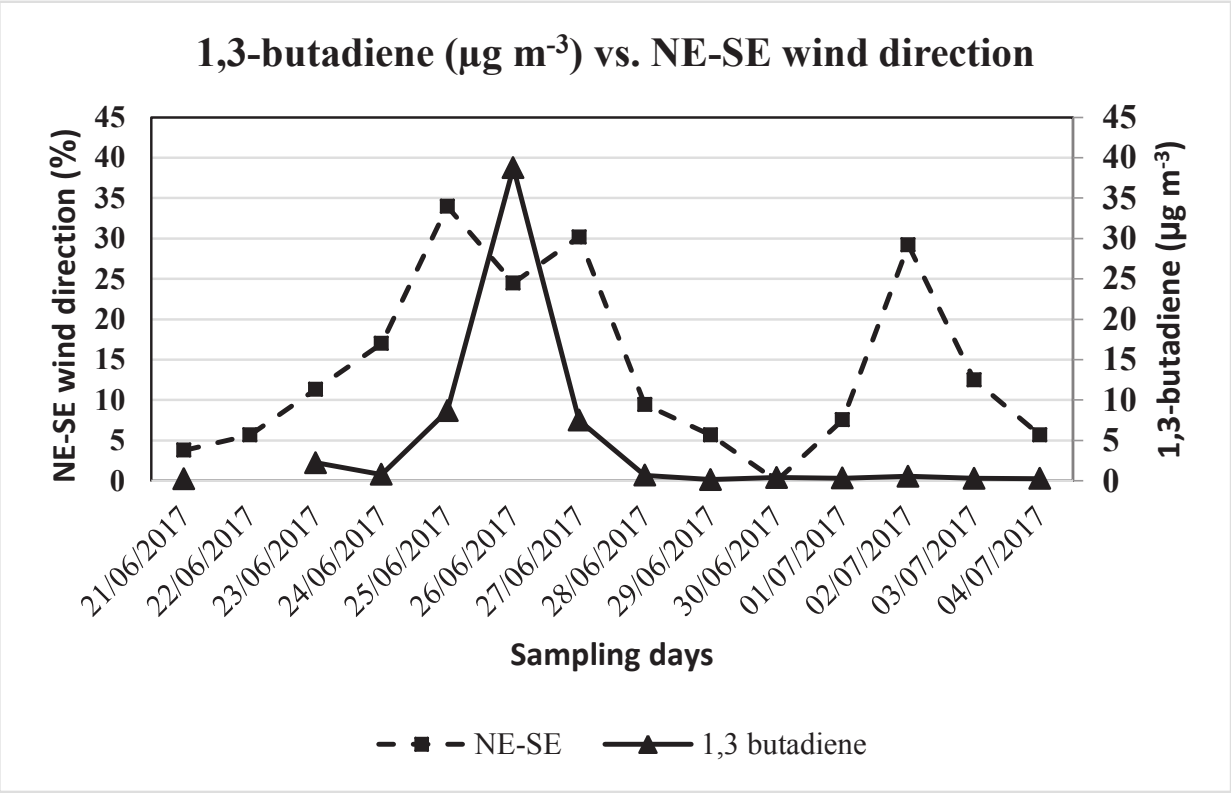

1,3-butadiene (µg m-3) vs. NE-SE wind direction
NE-SE wind direction (%)
1,3-butadiene (µg m-3)
0
5
10
15
20
25
30
35
40
45
21/06/2017
22/06/2017
23/06/2017
24/06/2017
25/06/2017
26/06/2017
27/06/2017
28/06/2017
29/06/2017
30/06/2017
01/07/2017
02/07/2017
03/07/2017
04/07/2017
Sampling days
NE-SE
1,3 butadiene

Table 1

Click here to download Table: Table 1.docx

Table 1. Quality assurance parameters for multi-sorbent bed and Radiello® tubes for 1,3-butadiene

Limit of detection (ng tube)		**Linearity range (ng)**		**Precision (RSD, %)[c]**		**MS/Rad abundance ratio[d]**	**Desorption efficiency[e] (%)**		**Blank values clean tubes[f] (ng sample)**		**Blank values 1 week refrigerator[h] (ng sample)**		**Breakthrough (%)[i]**	
MS[a]	Rad[b]	MS	Rad	MS	Rad		MS	Rad	MS	Rad	MS	Rad	MS	Rad
0.2	0.2	0.6-6500	0.6-3200	1.0	2.7	0.8 ± 0.2	98 ± 2	98 ± 4	n.d.[g]	n.d.	n.d.	1.0 ± 0.1	1.3 ± 1.9	-

[a]Multi-sorbent bed tubes

[b]Radiello® tubes

[c]Precision: Relative Standard Deviation, $n = 7$

[d]Ratio between the peak abundances in multi-sorbent bed and Radiello® tubes spiked with the same amount of standards, $n = 9$

[e]$n = 6$ for MS and Rad tubes

[f]Tubes just conditioned, $n = 2$

[g]Not detected

[h]Tubes stored 1 week in the refrigerator after conditioning, $n = 5$

[i]Samples between 81-101 l, $n = 13$

Table 2

Table 2. Outdoor air 1,3-butadiene concentrations (µg m^{-3}) for multi-sorbent bed tubes with and without ozone scrubber and ozone concentrations in El Morell, Tarragona.

	1,3-butadiene (µg m^{-3})		Ozone (µg m^{-3})
Date	**With scrubber**	**Without Scrubber**	
21-6-2017	0.1	0.2	45 ± 5
22-6-2017	0.5	-	45 ± 5
23-6-2017	0.6	2.2	45 ± 5
24-6-2017	1.1	0.8	42 ± 3
25-6-2017	5.8	8.7	42 ± 3
26-6-2017	11	39	42 ± 3
27-6-2017	4.6	7.5	42 ± 3
28-6-2017	0.1	0.7	53 ± 9
29-6-2017	0.1	0.1	53 ± 9
30-6-2017	0.3	0.4	53 ± 9
1-7-2017	0.3	0.3	66 ± 5
2-7-2017	0.3	0.5	66 ± 5
3-7-2017	0.04	0.3	66 ± 5
4-7-2017	0.4	0.3	66 ± 5

Table 3

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Table 3. Average ± standard deviation 1,3-butadiene concentrations (µg m^{-3}) for multi-sorbent bed and Radiello® tubes for each sampled period in El Morell, Tarragona.

	21-30/6/2017			1-4/7/2017		
	Average (µg m^{-3})	***n***	**Multi-sorbent/ Radiello® (%)**	**Average (µg m^{-3})**	***n***	**Multi-sorbent/ Radiello® (%)**
Multi-sorbent with scrubber	2.4 ± 3.5	10	279	0.2 ± 0.1	4	50
Multi-sorbent without scrubber	6.6 ± 12.5	10	772	0.4 ± 0.1	4	70
Radiello®	0.9 ± 0.2	4		0.5 ± 0.1	4	

Table 4. Average ± standard deviation 1,3-butadiene concentrations (µg m^{-3}) for multi-sorbent bed and Radiello® tubes in the city of Barcelona.

Barcelona city	13-21/7/2017			
	Average (µg m^{-3})	**Range (µg m^{-3})**	***n***	**Multi-sorbent/ Radiello (%)**
Multi-sorbent without scrubber	0.3 ± 0.1	0.1-0.6	16	60
Radiello®	0.5 ± 0.1	0.4-0.7	4	

Supplementary Material Figure S1

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Supplementary Material Figure S2

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Supplementary Material Figure S3

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