

1 **Development of a method for determination of VOCs**
2 **(including methylsiloxanes) in biogas by TD-GC/MS analysis**
3 **using Supel™ Inert Film bags and multi-sorbent bed tubes**

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16
17 **Abstract**

18 An analytical method based on TD-GC/MS was developed and validated for the
19 determination of volatile organic compounds (VOCs), including linear and cyclic
20 volatile methylsiloxanes (VMSs), in biogas. Biogas was first sampled in Supel™ Inert
21 Film bags and subsequently dynamically sampled onto multi-sorbent bed tubes
22 (Carbotrap, Carboxen X and Carboxen 569) using portable pump equipment. Two
23 sample volumes, 100 and 250 ml, were evaluated. Desorption efficiency values for both
24 volumes are in the range of 99-100% for almost all studied compounds while

25 breakthrough values (%VOC on sample tube back section) are below 1% for most
26 evaluated VOCs. However, acetaldehyde, carbon disulphide, ethanol and 1,3-butadiene
27 have breakthrough values higher than 5%. Method detection limits (MDL) were in the
28 range of 0.01-0.8 ng per sample. The most abundant VOCs in biogas were terpenes with
29 concentrations between 500-700 mg m⁻³. Other important families were ketones,
30 aromatic hydrocarbons and alkanes, with concentrations in the range of 36-46 mg m⁻³,
31 20-35 mg m⁻³ and 14-16 mg m⁻³, respectively. VMSs presented average concentrations
32 of 4.9±0.4 mg m⁻³. Additionally, the SupelTM Inert Film bags were evaluated for
33 stability for 4 days at room temperature. Although several VOC families'
34 concentrations in the bag increased or decreased significantly (*t*-test; *p* ≤ 0.01, *n* = 5)
35 two days after collection, recoveries were around 70-130% for most studied VOCs. The
36 results shown demonstrate that the presented methodology is reliable and satisfactory
37 for the evaluation of VOCs in biogas and presents an alternative to the currently
38 existing biogas analytical techniques.

39

40 **Keywords:** volatile organic compounds, volatile methylsiloxanes, biogas, TD-GC/MS,
41 waste treatment

42

43 **1. Introduction**

44 Biogas, generated by anaerobic degradation of organic matter in a digestion process and
45 with levels of methane around 55-65%, can be used for producing electric energy
46 through a combustion process [1]. Anaerobic digestion is a very cost-effective treatment
47 for organic matter [2]. Additionally, the energy obtained is considered a renewable
48 energy, with its generation becoming increasingly popular [3]. Apart from methane and
49 carbon dioxide, the main components of biogas (up to 99% [3-5]), volatile organic

50 compounds (VOCs), including volatile methylsiloxanes (VMSs), can cause serious
51 corrosion-related problems in gas combustion engines [1,6-8] and affect energy
52 production efficiency [5]. VMSs, found in many domestic products, are released into
53 the gas phase by biogasification [9]. Due to the closed design of the digester, the
54 compounds emitted are found in biogas [10]. When biogas is combusted, the resulting
55 compounds are oxidized and converted into microcrystalline silicon dioxide, with
56 properties similar to those of glass [5,6,11]. This is why the determination and control
57 of these trace compounds in biogas by a reliable analytical technique is key to
58 determining whether the concentrations found exceed the critical limits established by
59 the engine manufacturer [12]. When these limits are surpassed, the possibility of gas
60 pre-treatment VOCs elimination should be considered [13], e.g. adsorption on activated
61 carbon or silica gel, refrigeration or cryogenic condensation of biogas, liquid absorption
62 in solvents, etc. [1,6,8].

63 The complexity of biogas in terms of VOCs composition (polar to non-polar
64 compounds and very volatile to semi-volatile compounds), concentration (several orders
65 of magnitude differences among analytes), volatility, and instability of several
66 compounds such as D3 and trimethylsilanol [7,14], calls for versatile sampling and an
67 analytical methodology for VOCs assessment [7,15,16]. Gas collecting bags, sorbent-
68 based, canister-based, impingers and solid-phase adsorption sampling methods have
69 been used for the collection of VOCs, including VMSs, in biogas [4-8,12,15-18]. VMSs
70 have been commonly sampled by solvent capture through impingers [1,16]. Recently,
71 reproducibility and recovery by sampling in solid adsorption media and using impingers
72 have been successfully compared [4,19]. The simplicity, short sampling time, high
73 sampling versatility, high concentration power, easy portability, low cost and easy
74 storage of sorbent tubes [12,20,21] led us to adopt a sorbent-based method for sampling

75 target compounds after the collection of biogas in gas sampling bags. Thermal
76 Desorption (TD), coupled with Gas Chromatography/Mass Spectrometry (GC/MS), was
77 the chosen instrumental technique. GC/MS methodology has been widely used in
78 biogas analysis [1,11,22], and its employment is strongly agreed on among researchers
79 [17]. It is a selective methodology which allows good chromatographic separation and
80 identification and quantification of target analytes through their characteristic mass
81 spectrum and quantification ion, respectively [21].

82 The present paper describes the development and evaluation of a TD-GC/MS method
83 for the determination of VOCs (alkanes, aromatic hydrocarbons, ketones, halocarbons,
84 aldehydes, esters, terpenes), including VMSs (trimethylsilanol (TMS), linear (L-) and
85 cyclic (C-) siloxanes), in biogas. Biogas was first sampled in SupelTM Inert Film bags
86 and then dynamically sampled onto multi-sorbent bed tubes (Carbotrap, Carbopack and
87 Carboxen 569). 100 and 250 ml sample volumes were evaluated ($n=5$ for each sampling
88 volume). It is a common practice by facility technicians to take biogas samples in bags
89 and send them to a laboratory for its analysis. The time span between the taking of the
90 sample and this analysis may be of several days. Therefore, the SupelTM Inert Film bags
91 used were studied for storage stability for 4 days at room temperature. Stability of the
92 target compounds in the bag may be affected by adsorption or absorption of the analytes
93 on the bag surface or the bag fitting and septum, reactions with other substances in the
94 sample matrix, and/or degradation due to instability of the intrinsic compounds.
95 Additionally, leaks in the bag may cause analyte loss [17,23]. The method was validated
96 with real biogas samples from a waste treatment facility.

97 Nowadays, even though several papers have been published on this topic, no
98 standardized VOCs and VMSs sampling and analytical methodologies have been
99 established for biogas matrix. The main aim of the present study was to develop a

100 simple, fast, highly versatile, with high concentration power, easy portable and low cost
101 methodology to assess VOC and VMS compounds in biogas in comparison with other
102 common techniques, for example impingers. Even though VMSs are the major
103 compounds that can cause serious drawbacks by corrosion in the traditional internal
104 combustion engines, the determination of other VOCs can also be relevant, as aromatic
105 hydrocarbons may cause corrosion and/or obstruction in the fuel cells too [7]. For other
106 applications, such as their use in vehicles, halogenated compounds concentrations have
107 also to be taken into account [22]. Additionally, molten carbonate fuel cells (MCFC)
108 have also restrictions related to hydrocarbon concentrations (C_2-C_6) in the gas [7, 24].
109 Besides, variations in VOC concentrations can indicate process changes in the biogas
110 formation [9]. Hence, their assessment would be useful to verify the correct
111 performance of the biogas production. Finally, to our knowledge, such a wide range of
112 VOCs has not been evaluated in biogas in previous studies.

113

114 **2. Materials and methods**

115 ***2.1 Chemicals and materials***

116 Standards of VOCs with a purity of no less than 98% were obtained from Aldrich
117 (Milwaukee, WI, USA), Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland).
118 Methanol and toluene for gas chromatography (SupraSolv[®]) with a purity 99.8% were
119 obtained from Merck (Darmstadt, Germany). Perkin Elmer glass tubes (Pyrex, 6 mm
120 external diameter, 90 mm long), unsilanised wool, and Carbotrap (20/40 mesh),
121 Carbopack X (40/60 mesh) and Carboxen 569 (20/45 mesh) adsorbents were purchased
122 from Supelco (Bellefonte, PA, USA).

123 ***2.2 SupelTM Inert Film bags***

124 Commercially available 1 litre SupelTM Inert Film sampling bags made from
125 polyvinylidene fluoride (PVDF) were evaluated. Supel Inert Film is a fluoropolymer
126 developed specifically for air sampling applications as an alternative to Tedlar[®] film.
127 The bags were equipped with replaceable Thermogreen[®] LB-2 septa in a screw cap
128 valve. The Thermogreen[®] polymer has the proven quality of the industries lowest bleed,
129 preventing septum contamination. The bags were obtained from Supelco (Bellefonte,
130 PA, USA).

131 ***2.3 Adsorbent tubes***

132 The multi-sorbent bed tubes were composed of Carbotrap (activated graphitized black
133 carbon, weak sorption strength, target analytes: C₅-C₁₄ (alcohols, aldehydes, ketones,
134 aromatic hydrocarbons), boiling points >75°C, 70 mg), Carbopack X (activated
135 graphitized black carbon, medium sorption strength, target analytes: C₃-C₇ (light
136 hydrocarbons, boiling points between 50-150°C), 100 mg) and Carboxen 569 (spherical
137 carbon molecular sieve, high sorption strength, target analytes: C₂-C₈ (ultra-volatile
138 hydrocarbons, boiling points between -30 and 150°C), 90 mg). They were developed in
139 an earlier study and found to be highly versatile regarding polarity and volatility of the
140 target VOCs [21]. They have been used successfully for the determination of a wide
141 range of VOC families in different applications [25-27]. Graphitized carbon blacks are
142 Class I sorbents, interacting non-specifically with all groups of adsorbates, i.e.
143 dispersion (London) forces: group A molecules (alkanes), group B molecules (aromatic
144 and chlorinated hydrocarbons), group C molecules (organo-metallic compounds) and
145 group D molecules (primary alcohols, and organic acids and bases). Carbon molecular
146 sieves are Class III sorbents, and interact specifically with adsorbates (e.g. through
147 strong dipole-dipole interactions). The characterization of sorbents and their suitability
148 for trapping pollutants is done mainly through the determination of specific retention

149 volumes (breakthrough) [20], (See section 3.2). Moisture content in biogas, up to 90%
150 [5], can complicate the collection and analysis of samples [7]; however, the sorbents are
151 highly hydrophobic and suitable for use in samplings of gases with high humidities
152 [21]. Sampling tubes were conditioned before use at 400°C, sealed with Swagelock end
153 caps fitted with PTFE ferrules and stored at 4°C for no more than 1 week before use.

154 ***2.4 Analytical instrumentation***

155 VOCs analysis was performed by TD-GC/MS using a Perkin Elmer ATD 400 (Perkin
156 Elmer, Boston, Massachusetts, USA) and a Thermo Quest Trace 2000 GC
157 (ThermoQuest, San Jose, California, USA) fitted with a Thermo Quest Trace Finnigan
158 MSD.

159 The methodology is described in the literature [21,25]. Primary thermal desorption of
160 the sampling tubes was carried out at 300°C with a helium flow rate of 50 ml min⁻¹ for
161 10 minutes. A double split was applied to the TD system (cold trap inlet and outlet splits
162 of 4 ml min⁻¹ and 7 ml min⁻¹, respectively). The cold trap (15 mg Tenax TA and 15 mg
163 Carbotrap) was maintained at -30°C. After primary desorption, the cold trap was rapidly
164 heated from -30°C to 300°C (secondary desorption) and maintained at this temperature
165 for 10 minutes. Analytes were then injected onto the capillary column (DB-624, 60 m x
166 0.25 mm x 1.4 µm) via a transfer line heated at 200°C. The column oven temperature
167 started at 40°C for 1 min, increased to 230°C at a rate of 6°C min⁻¹ and was then
168 maintained at 230°C for 5 min. Helium (99.999%) carrier gas flow in the analytical
169 column was approximately 1 ml min⁻¹ (1.4 bar).

170 The electron impact source was obtained with an electron energy of 70 eV. Mass
171 spectral data were acquired over a mass range of 20-450 amu. Qualitative identification
172 of VOCs was based on the match of the ion ratios of the target qualifier ions using the
173 MS ChemStation Data System validated software package with the NIST05 mass

174 spectral library (NIST/EPA/NIH, Nist MS Search version 2.0 d, April 2005). VOCs
175 were verified using retention times of authentic standards of the target compounds.
176 Quantification of samples was conducted by the external standard method according to
177 [21]. Ten different levels of calibration standard solutions were prepared in methanol
178 for each evaluated compound. Stock standard solutions were prepared by adding 50-100
179 μl (via pre-weighed 100-250 μl Hamilton syringe) of each liquid neat standard or 0.05 g
180 of each solid standard into a 10 ml clean flask in methanol. This solution was further
181 diluted in methanol to obtain the different standards. 1,3-butadiene was prepared in
182 toluene. Several authors have evidenced biases between liquid and gas phase standards
183 quantifications, being these biases variable depending on the sorbents used in the
184 sampling tubes and the VOCs studied. Certain compounds or VOC families (e.g. butyl
185 acetate, isobutanol and carboxylic acids) present higher biases than others (e.g. aromatic
186 hydrocarbons, aldehydes and ketones) [28, 29]. To minimise matrix/solvent interference
187 in the chromatogram [30], 1 μl aliquots of each standard solution were spiked onto
188 clean multi-sorbent bed tubes using a conventional gas chromatograph packed column
189 injector, as recommended in U.S. EPA Compendium Method TO-17 [31]. Tubes were
190 connected to the injector through a stainless steel tube and Swagelock adapters. The
191 solvent and analytes were vaporised onto the GC injector and passed through the multi-
192 sorbent bed tube in the vapour phase, a way closely analogous to the normal air sample
193 collection process. The injector was slightly heated at 30 $^{\circ}\text{C}$ and a flow stream of 100
194 ml min^{-1} of Helium was passed through the tubes during a loading time not less than 5
195 min, a time applied allowed a good elimination of solvent [21]. Furthermore, as an
196 additional measure to reduce the matrix effect standard tubes were purged at ambient
197 temperature during 2 minutes with a Helium flow of 50 ml min^{-1} prior to their TD-
198 GC/MS analysis [30].

199 The risk of changes in instrumental sensitivity over time has been suggested by several
200 authors when samples are analyzed on different days [32]. To avoid drawbacks derived
201 from this aspect, calibration curves of all evaluated VOCs were freshly prepared, clean
202 tubes were spiked and they were injected onto the TD-GC/MS each day. Additionally,
203 the evaluation of the temporal change in sensitivity of the instrument in three days was
204 calculated. The experiment was conducted preparing each day a standard of $100 \text{ ng } \mu\text{l}^{-1}$
205 for each VOC evaluated. Their concentrations were calculated according the calibration
206 curves. The temporal change in sensitivity (%) during three days of the TD-GC/MS
207 used was found to be between 0.02-4.1%, with a 84% of the evaluated VOC presenting
208 values below 2% (Table 1). These results show that the potential changes in sensitivity
209 of the instrument during the study period are likely irrelevant [32].

210 ***2.5 Sampling***

211 Biogas samples were obtained from a mechanical-biological waste treatment (MBT)
212 plant in the metropolitan area of Barcelona during December 2013 and January 2014.
213 The plant has a processing capacity of $287,500 \text{ tons year}^{-1}$ of municipal residues:
214 selected organic fraction ($100,000 \text{ tons year}^{-1}$), waste fraction ($160,000 \text{ tons year}^{-1}$) and
215 light packaging fraction ($27,500 \text{ tons year}^{-1}$). The selected organic fraction is
216 anaerobically fermented in a methanation process to obtain biogas. The biogas used in
217 our study was collected from the main pipe just before its injection into the engines. The
218 pressure inside the pipeline was enough to fill the bags.

219 Biogas was first collected in 1 litre SupelTM Inert Film bags and then dynamically
220 sampled onto the multi-sorbent bed tubes using AirChek 2000 SKC pumps. The
221 materials used for sampling (SupelTM Inert Film bags, PTFE connectors, sampling tubes
222 (inert glass tubes for ATD 400) and unsilanized glass wool) avoided possible adsorption
223 of the target VMSs in silicon surfaces. In order to determine the appropriate sample

224 volume, 100 and 250 ml were sampled to evaluate the performance of the analytical
225 methodology in field samples. Sampling rate was set at 100 ml min^{-1} , and its value was
226 recorded both before and after the sampling. Five replicates of each sample volume
227 were taken. In order to avoid different possible adsorption patterns onto the bags inner
228 surfaces, 10 bags were sampled at the same time, being 5 bags established for 100 ml
229 sampling and another 5 bags for 250 ml sampling. The transfer of the gas to the sorbent
230 tubes was done immediately. To examine breakthrough values in the two evaluated
231 sample volumes, two tubes were connected in series with a PTFE tube for each sample,
232 with the lowest dead volume possible.

233 Additionally, the bags were evaluated for stability for a week. Four bags were filled
234 with biogas and transported to our laboratory on the same day; five 100 ml samples
235 were transferred from one of the bags to five multi-sorbent tubes one hour after
236 collection. The three remaining bags were stored in darkness at room temperature. Five
237 more samples were taken from a second bag one day after collection. Five more
238 samples were taken from a third bag two days after collection. Finally, five more
239 samples were taken from a fourth bag three days after collection. All samples were
240 taken in the same place of our laboratory and at the same time on the sampling days,
241 and were immediately injected into the TD-GC/MS system. Bags were stored at room
242 temperature to emulate the storage conditions that they are usually subjected to during
243 transport, as sometimes biogas analysis is done far away from where it has been taken,
244 and shipment can be prolonged during a couple of days. However, it will be interesting
245 to evaluate bags stability also at 4°C in future studies.

246 Stability of blank bags was evaluated throughout the process to determine the presence
247 of contamination in the bags. Four sampling bags were filled with helium and processed

248 in the same way as biogas samples, i.e. stored in darkness at room temperature and then
249 sampled immediately, 1, 2 and 3 days after helium filling.

250 **2.6 Quality assurance**

251 Extreme precautions are required to ensure reproducible quality results. Every day the
252 mass spectrometer was manually tuned at $m/z=69$, 131, 264 and 502 and air leaks ($m/z=$
253 4, 18 and 28) were controlled.

254 To avoid artifacts generation, both ATD trap and sampling tubes were properly
255 conditioned. A trap heat was done daily before analysis at 330°C for 20 min. After the
256 trap heating, analytical blank samples, i.e. two clean multi-sorbent bed tubes, were
257 analyzed before the injection of the samples and standards. As it has been said before,
258 five replicates of each sample were analyzed, and the evaluated compounds in real
259 samples generally showed repeatabilities (% relative standard deviation values, $n=5$)
260 25%, accomplishing the EPA performance criteria [31] (Table 2). Repeatabilities of
261 standards were found to be 11% (Table 1).

262 Method detection limits (MDL) were calculated through the analysis of 7 replicates of
263 the lowest concentrated standard, which presented a signal to noise factor between 2.5
264 and 10. The obtained standard deviation (SD) for the replicates concentrations was
265 multiplied for 3.14 (Student's t value at the 99% confidence interval), according to the
266 U.S. EPA (Part 136-Guidelines establishing test procedures for the analysis of
267 pollutants, Appendix B), and are presented in Table 1.

268 The linearity range of the multi-point calibration was ≥ 0.99 in for all compounds.

269 **2.7 Data treatment**

270 All experiments were conducted in five replicates. Data treatment and statistical
271 analysis were undertaken using Microsoft ExcelTM 2007 and IBM Spss Statistics
272 Version 20 (2011). Kolmogorov-Smirnov (K-S) test was used to check normal

273 distribution of the experimental data. The data sets obtained for each sampling volume
274 and each biogas and blank bags were normally distributed. *t*-test was used to evaluate
275 significant differences between obtained data.

276

277 **3. Results and discussion**

278 ***3.1 Method performance evaluation***

279 One hundred and seventeen compounds were determined qualitatively in the studied
280 biogas (alkanes (27%), aromatic hydrocarbons (15%), terpenes (14%), sulphur
281 compounds (13%), ketones (8%), siloxanes (8%), furans (3%), chlorinated compounds
282 (3%), esters (2%), aldehydes (2%) and nitrogenated compounds (2%)). In respect to
283 concentrations, aliphatic and aromatic compounds and siloxanes accounted for an
284 $88\pm 1\%$ and $0.7\pm 0.1\%$, respectively. Similar mixtures have been found in different types
285 of biogas [7,15,33], even though the specific composition of a biogas will be influenced
286 by the organic matter used and anaerobic digestion process conditions [3,5,9,11,22,33].
287 The presence of a wide range of ketones can be attributed to fermentative acidogenic
288 bacteria, which can convert sugars, amino acids and fatty acids into this type of
289 compounds [9]. In the present study, 66 compounds including a wide range of VOCs
290 families were selected as target analytes, on basis of their abundance in biogas, toxicity
291 or possibility of producing negative health effects, and odour threshold. Their
292 characteristics are presented in Table 1. Variability of VOCs and VMSs in the biogas
293 samples required working with two different concentration ranges. Hence, two
294 quantification ions were established for each studied chemical, m/z 1 (generally the
295 major characteristic ion in the spectrum) for low concentrated compounds and m/z 2
296 (minor characteristic ion) for high concentrated compounds (Table 1). Chromatographic
297 separation was good and co-eluting compounds were satisfactorily quantified using

298 characteristic ions, except *m*- and *p*-xylene, and *m*- and *p*-ethyltoluene, which were
299 quantified together because they exhibited identical mass spectra (Figure 1).

300 **3.2 Breakthrough evaluation**

301 Target compound loss during sampling due to incomplete adsorption on the sorbents is
302 an important handicap in this process [18] which can be evaluated by breakthrough
303 values. The breakthrough value for a target compound can be calculated as the
304 percentage mass of this compound found in the back tube relative to the total mass
305 found in two tubes connected in series. Typically recommended breakthrough values for
306 volatile compounds are < 5% [31]. High breakthrough values represent a transfer of
307 target compounds from the front tube to the back tube, leading to a decrease in the
308 concentrations of the sample that should be obtained and therefore underestimation of
309 results. Individual analysis of each sample showed that hardly any VOC or VMS
310 exhibited significant breakthrough for the studied sample volumes (Table 2). It can,
311 however, be observed that breakthrough values are slightly higher in 250 ml samples
312 than in 100 ml samples. Very volatile organic compounds (VVOCs) [34] such as
313 acetaldehyde, carbon disulphide, ethanol and 1,3-butadiene showed breakthrough values
314 higher than 5%, and these values were much higher in the 250 ml samples. This had
315 been reported in a previous study for low volumes (10 litres) of ambient outdoor air
316 [35]. Both 100 and 250 ml sample volumes are suitable for biogas evaluation with
317 respect to breakthrough values, except for the four above compounds.

318 **3.3 Tube desorption evaluation**

319 Calibration standards and samples underwent the same procedure during analysis, then
320 the evaluation of desorption efficiency is not indispensable [36]. However, a repetition
321 of the desorption process at the same or higher temperature is usually done to check for
322 significant appearances of the target compounds in this second analysis [21,36-39]. To

323 evaluate the performance of target compound desorption of multi-sorbent tubes in real
324 biogas samples, subsequent reanalysis of already desorbed tubes was carried out at a
325 higher temperature (350°C) to remove any remaining analytes. Tube desorption values
326 of 99-100% were obtained for most target compounds for the two sample volumes
327 evaluated. Several compounds, however, exhibited lower desorption efficiency
328 percentages (e.g. benzene (90-92%), methylnaphthalenes (90-93%), phenol (90-95%)
329 and carbon disulphide (71-85%)). Similar values had already been observed for these
330 compounds in a previous study [21]. It can therefore be concluded that both 100 and
331 250 ml sample volumes are suitable for biogas evaluation with respect to desorption
332 efficiency.

333 ***3.4 VOCs and VMSs concentrations in biogas***

334 VOCs concentrations from 100 ml and 250 ml sample volumes taken on 2 December
335 2013 are presented in Table 2. 50% of the evaluated compounds showed significant
336 differences (*t*-test; $p \leq 0.01$, $n = 5$) between the concentrations from 100 ml and 250 ml
337 sample volumes, with 100 ml concentrations being higher. These results can be related
338 to the higher divisor value in the 250 ml samples, as breakthrough values were low and
339 within acceptable levels for both sample volumes. Nevertheless, the results in mg m^{-3}
340 show that differences are not so evident.

341 Terpenes, especially *p*-cymene, had the highest values (between 500-700 mg m^{-3}),
342 accounting for approximately 80% of VOC concentrations. The much higher
343 concentration of *p*-cymene compared to other terpenes has been related to the
344 conversion of limonene and other monoterpenes into *p*-cymene by rearrangement and
345 dehydrogenation by microorganisms in anaerobic conditions [10,40,41]. Ketones,
346 aromatic hydrocarbons and alkanes concentrations were in the range of 36-46 mg m^{-3} ,
347 20-35 mg m^{-3} and 14-16 mg m^{-3} , respectively. Halogenated compounds concentrations

348 were low, in the range of $200 \mu\text{g m}^{-3}$, as observed in other studies [7,33]. VOC
349 concentrations in biogas generated from anaerobic bioreactors are scarce. However, the
350 concentrations obtained in the present study are of the same order of magnitude than the
351 found in the literature, with terpenes being the highest concentrated compounds [2],
352 (Table 3). Terpenes generated from anaerobic composting processes are also very
353 similar, with *p*-cymene accounting for a 60% of all compounds of this family [10]. On
354 the other hand, VOC in landfill biogas present different concentrations, generally much
355 higher. Except for terpenes, that are one order of magnitude lower, the other VOC
356 families are from one to two orders of magnitude higher in landfill biogas than in
357 bioreactor biogas (Table 3) [42]. Waste present in landfills generally contains a wide
358 range of materials, sometimes unknown and with potentially hazardous characteristics.
359 Higher alkanes, aromatic hydrocarbons and halocarbons concentrations may be released
360 to biogas from this kind of waste buried in the landfills. On the other hand, the material
361 used to generate biogas through bioreactors is much more selected and homogeneous
362 [33,42]. Finally, VOC concentrations in biogas from aerobic composting processes are
363 much lower than the observed in anaerobic landfill and bioreactor biogas, generally one
364 order of magnitude lower.

365 1,3-butadiene values are worth noting as the concentrations obtained were very variable
366 and potentially high. 100 ml and 250 ml samples had concentrations in the range of 4-
367 136 mg m^{-3} and $1-15 \text{ mg m}^{-3}$, respectively. 1,3-butadiene is a highly reactive pollutant
368 [43] and can be quickly transformed into other types of compounds in the atmosphere
369 [44]. However, as sampling was conducted immediately after biogas capture in the
370 bags, the possibility that the results obtained were due to the reactivity of the compound
371 was ruled out. Because desorption efficiencies were around 98-99% for the two (100 ml
372 and 250 ml) sample volumes, breakthrough values are considered the main responsible

373 factor for the variability in results, as they were around $42\pm 39\%$ and $67\pm 21\%$,
374 respectively. 1,3-butadiene is classified as a human carcinogenic compound by
375 inhalation [45-47], and as said before, its presence in biogas can be relevant. Hence, its
376 concentration in biogas and fate in the combustion process should be evaluated in future
377 studies.

378 Ethanol was the only alcohol detected. Much higher levels of alcohols are found in
379 aerobic digestion than in anaerobic digestion, as reported in previous studies [2,10].
380 Alcoholic compounds tend to increase at the beginning of anaerobic digestion processes
381 [10], or when new organic material is loaded into the system, and is often related to
382 microbial processes associated with the presence of volatile fatty acids in the organic
383 matter treated [9,48]. However, their presence in landfill biogas has found to be
384 relatively low, less than 1% [48]. The concentrations of ethanol in the present case were
385 very variable, as observed in other studies [9], an aspect that was associated with the
386 anaerobic process instability. Yet, in the presented evaluation, the high breakthrough
387 values observed for this compound and the possibility of adsorption problems of this
388 type of low molecular weight alcohol in the cold trap used could also be a cause for the
389 results obtained.

390 Silicon compound concentrations were in the range of $4.9\pm 0.4 \text{ mg m}^{-3}$, below many of
391 the recommended limits set by several engine manufacturers, which are in the range of
392 $0.03\text{-}28 \text{ mg m}^{-3}$, depending on the type of engine [1,11]. The concentrations found in
393 the present study (biogas from municipal biowaste) are in the range of the observed in
394 other biogases generated both from biowaste and sewage sludge, as well as biogases
395 from landfills. On the other hand, biogas exclusively from sewage sludge present from 2
396 to 6 times higher VMSs concentrations (Table 3). Siloxanes are widely employed in
397 personal care products, such as cosmetics, and skin and hair care products, as well as in

398 household cleaning and coating agents [49-52]. They can end up in waste water
399 treatment plants, and eventually in sewage sludge [9]. Hence, the higher presence of
400 VMSs in the biogas formed from sewage sludge can be related to the use of these
401 silicon containing compounds in households and industry [22].

402 Excluding trimethylsilanol, D4 and D5 were the most abundant siloxanes, accounting
403 for 95±1% of the total, as observed in previous studies regarding biogas obtained from
404 organic matter digestion [1,9,11,17]. D3, with considerably variable concentrations, was
405 found in a previous study to be an unstable compound that can react with the gas matrix
406 and generate other compounds [53]. The proportion of studied silicon compounds is in
407 the range of that observed in Finnish biogas plants (between brackets), with values of 4-
408 11% (7-13%) TMS, 1% (1%) L2, 0.1-1% (0-6%) D3, 2% (0-1%) L3, 4-6% (22-23%)
409 D4, 1% (-) L4, 80-85 % (57-70%) D5, 0.1 % (-) L5 and 1-2% (-) D6. It has to be taken
410 into account that Finnish biogas plants digest wastewater sludge apart from municipal
411 biowaste [11].

412 **3.5 SupelTM Inert Film bags stability during storage**

413 100 ml sample volume was chosen to evaluate VOCs stability in the SupelTM Inert Film
414 bags because of its satisfactory breakthrough and desorption efficiency results.

415 VOC concentrations from the bags filled with biogas on the same day (14 January
416 2014) and sampled onto sorbent tubes on the following four days are presented in Table
417 4. Most concentrations obtained on 14 January 2014 (Table 4) are of the same order of
418 magnitude as those found on 2 December 2013 (Table 2). However, toluene and D3,
419 and ester concentrations were one order of magnitude higher and lower, respectively, on
420 14 January 2014. These differences could be attributed to changes in the operating
421 conditions of biogas production and/or in the raw materials used in the digestion process
422 [19,22].

423 Twenty-seven percent of the evaluated compounds showed significant differences (*t*-
424 test; $p \leq 0.01$, $n = 5$) in concentrations between the bag sampled on the day of collection
425 and the bags sampled on the following three days. Aggregate concentrations of alkanes,
426 siloxanes and *tert*-methyl butyl ether increased significantly (*t*-test; $p \leq 0.01$, $n = 5$) in
427 the bag the day after collection (Figure 2). These results could be related to reactions
428 inside the bags and/or septum and bag material contamination [7,23]. The bag
429 manufacturer states that the Thermogreen[®] polymer used in the septum has low bleed to
430 prevent septum contamination, and that the fluoropolymer used as bag material is
431 specifically indicated for air sampling applications as an alternative to Tedlar[®] film.
432 Additionally, a previous study observed that Supel[™] Inert film bags had a VOCs
433 background level lower than 10 ppb of the TO-15 calibration mix standard, and that the
434 recoveries of compounds decreased over time from the day of sampling [54].
435 Consequently, blank bags filled with helium were evaluated by the same procedure as
436 biogas samples to determine if the bag, the port and/or the septum materials were the
437 reason for the higher concentrations in bags sampled 2, 3 and 4 days after collection
438 (see section 3.6).

439 On the other hand, aggregated concentrations of ketones, esters and acetonitrile
440 decreased significantly (*t*-test; $p \leq 0.01$, $n = 5$) in the bag 2, 3 and 4 days after collection
441 (Table 4, Figure 2). Ketones and esters concentrations decreased to a stable value.
442 Analyte loss can result from sorption onto/into the bag material and valve ports, and/or
443 bag leaks [21,55,56]. The recoveries of these compounds (acetone, methylethylketone,
444 methylisobutylketone and ethyl acetate) after 24 and 48 hours were in the range of 89-
445 71%, that is, higher than those observed in a previous study (in the range of 66-40%)
446 [54].

447 Concentrations of several aromatic hydrocarbons, i.e. styrene, *o*-xylene, *n*-
448 propylbenzene, ethyltoluenes and trimethylbenzenes, decreased significantly (*t*-test; $p \leq$
449 0.01, $n = 5$) to a stable value on the second day after collection. Recoveries of the above
450 compounds after 24 and 48 hours were in the range of 74-51%, that is, higher than those
451 observed in a previous study (in the range of 45-19%) [54]. Benzene and toluene had
452 recoveries of around 100%, and the aggregate aromatic hydrocarbon concentrations did
453 not vary significantly over time. A previous study on Tedlar[®] bags associated the lower
454 recoveries found for the heavier molecular weight aromatics (e.g. xylenes and styrene)
455 with their potential to adsorb strongly onto the bag [56], a relationship that was not
456 found for other VOCs.

457 It is also interesting that after one hour of sampling less than 10% of the initial ethanol
458 and 1,3-butadiene concentrations were observed (Table 2, Table 4). Nonetheless, a
459 previous study using the same sampling bags showed ethanol and 1,3-butadiene
460 recoveries of 145 and 104% after 4 hours of sampling, respectively [54]. As mentioned
461 earlier, 1,3-butadiene concentrations in biogas should be assessed accurately due to its
462 toxic potential.

463 ***3.6 VOCs and VMSs concentrations in helium blank samples***

464 VOC concentrations from different SupelTM Inert Film bags filled with helium on the
465 same day and sampled on the following four days are presented in Table 5. 41% of the
466 studied compounds were not found in blank samples. On the other hand, VOCs detected
467 in blanks were present in low concentrations, generally below $1 \mu\text{g m}^{-3}$. *n*-hexane, *n*-
468 heptane, toluene, trimethylsilanol, carbon disulphide and tetrahydrofuran concentrations
469 in the bags increased significantly (*t*-test; $p \leq 0.01$, $n = 5$) on the three days after
470 collection. However, the concentration of VOCs was higher in biogas than in blank
471 samples, i.e. below 1% (Table 5). Nonetheless, it has to be taken into account that blank

472 values of *n*-tetradecane and D3 accounted for 2-9% and 4-6%, respectively, of the
473 concentrations in biogas.

474 The significant concentration increases observed in sampling bags for several alkanes,
475 siloxanes and *tert*-methyl butyl ether two days after collection could not be related to
476 bag film, septum and/or inlet port contamination. Hence, because biogas is composed of
477 a wide variety of VOCs which can react between themselves and thus lead to other
478 compounds [7], the type of air matrix could be the main cause of the concentration
479 increases.

480

481 **4. Conclusions**

482 A methodology for sampling and analysis of VOCs, including VMSs, in biogas using
483 TD-GC/MS was validated. Samples were initially collected in 1 litre SupelTM Inert Film
484 bags and subsequently sampled onto multi-sorbent bed tubes. Both 100 and 250 ml
485 sample volumes were found to be appropriate regarding breakthrough, desorption
486 efficiency and precision. Terpenes presented the highest values (between 500-700 mg
487 m⁻³), especially *p*-cymene (320-490 mg m⁻³), accounting for approximately 80% of
488 VOC concentrations. Ketones, aromatic hydrocarbons and alkanes concentrations were
489 in the range of 36-46 mg m⁻³ (methyl ethyl ketone 25-34 mg m⁻³), 20-35 mg m⁻³ (toluene
490 10-26 mg m⁻³) and 14-16 mg m⁻³, respectively. Twenty-seven percent of the evaluated
491 compounds showed significant differences (*t*-test; $p \leq 0.01$, $n = 5$) in concentration
492 between the bag sampled on the day of collection and the bags sampled on the
493 following three days. Global concentration values of alkanes, siloxanes and *tert*-methyl
494 butyl ether increased gradually and significantly from the second day, but this could not
495 be linked to bag film, septum and/or inlet port contamination. On the other hand, ketone
496 and ester concentrations decreased significantly to a stable value. Recoveries were

497 around 70-130% two days after collection for most studied VOCs. When the bags used
498 are not immediately sampled onto sorbent tubes, the increases or decreases in VOC
499 concentrations observed in the present study have to be taken into account.

500

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505

506 **References**

- 507 [1] E. Wheless, J. Pierce, presented at the SWANA 27 LFG conference, 2004.
- 508 [2] J. Mata-Alvarez, S. Marcé, P. Llabrés, *Bioresource Technol.* **74**, 3 (2000).
- 509 [3] L. Appels, J. Lauwers, J. Degreève, L. Helsen, B. Lievens, K. Willems, J. Van Impe,
510 R. Dewil, *Renew. Sust. Energ. Rev.* **15**, 4295 (2011).
- 511 [4] N.-J. Kim, S.-K. Chun, D.K. Cha, C. Kim, *Bull. Korean Chem. Soc.* **34**, 2353
512 (2013).
- 513 [5] G. Piechota, B. Igliski, R. Buczkowski, *Energ. Convers. Manage.* **68**, 219 (2013).
- 514 [6] L. Appels, J. Baeyens, J. Degreève, R. Dewil, *Prog. Ener. Combust.* **34**, 755 (2008).
- 515 [7] M. Arnold, T. Kajolinna, *Waste Manage.* **30**, 1011 (2010).
- 516 [8] R. Dewil, L. Appels, J. Baeyens, *Ener. Converse. Manage.* **47**, 1711 (2006).
- 517 [9] M. Kymäläinen, K. Lähde, M. Arnold, J.M. Kurola, M. Romantschuk, H. Kautola, J.
518 *Environ. Manage.* **95**, S122 (2012).
- 519 [10] E. Smet, H. Van Langenhove, I. De Bo, *Atmos. Environ.* **33**, 1295 (1999).
- 520 [11] S. Rasi, J. Lehtinen, J. Rintala, *Renew. Energ.* **35**, 2666 (2010).

- 521 [12] A. Narros, M.E. Del Peso, G. Mele, M. Vinot, E. Fernández, M.E. Rodríguez,
522 presented at the Twelfth International Waste Management and Landfill Symposium,
523 Cagliari, Sardinia, Italy, 2009.
- 524 [13] EPRI (Electric Power Research Institute), Assessment of fuel gas cleanup systems
525 for waste gas fuelled power generation, Palo Alto, CA, 2006, 1012763.
- 526 [14] R. Grümping, D. Mikolajczak, A. Hirner, Fresen. J. Anal. Chem. **361**, 133 (1998).
- 527 [15] M. Schweigkofler, R. Niessner, Environ. Sci. Technol. **33**, 3680 (1999).
- 528 [16] G. Piechota, R. Buczkowski, Intern. J. Environ. Anal. Chem. **94**, 837 (2014).
- 529 [17] M. Ajhar, B. Wens, K.H. Stollenwerk, G. Spalding, S. Yüce, T. Melin, Talanta **82**,
530 92 (2010).
- 531 [18] L. Lamaa, C. Ferronato, L. Fe, F. Jaber, J.M. Chovelon, Talanta **115**, 881 (2013)
- 532 [19] J. Raich-Montiu, C. Ribas-Font, N. de Arespachaga, E. Roig-Torres, F. Broto-
533 Puig, M. Crest, L. Bouchy, J.L. Cortina, Anal. Chim. Acta **812**, 83 (2014).
- 534 [20] E. Gallego, F.J. Roca, J.F. Perales, X. Guardino, in *Sorbents: Properties, Materials*
535 *and Applications*, edited by T.P. Willis (Nova Science Publishers, New York, 2009).
- 536 [21] A. Ribes, G. Carrera, E. Gallego, X. Roca, M.J. Berenguer, X. Guardino, J.
537 Chromatogr. A **1140**, 44 (2007).
- 538 [22] S. Rasi, J. Läntelä, J. Rintala, Energ. Convers. Manage. **52**, 3369 (2011).
- 539 [23] Y. Wang, T.S. Raihala, A.P. Jackman, R. St. John, Environ. Sci. Technol. **30**, 3115
540 (1996).
- 541 [24] C. Tomasi, M. Baratieri, B. Bosio, E. Arato, P. Baggio, J. Power Sources **157**, 765.
- 542 [25] E. Gallego, F.J. Roca, J.F. Perales, X. Guardino, in *Air Quality in the XXI Century*,
543 edited by G.C. Romano and A.G. Conti (Nova Science Publishers, New York, 2009).
- 544 [26] E. Gallego, F.J. Roca, J.F. Perales, G. Sánchez, P. Esplugas, Waste Manage **32**,
545 2469 (2012).

- 546 [27] E. Gallego, F.J. Roca, J.F. Perales, X. Guardino, *Sci Total Environ* **470-471**, 587
547 (2014).
- 548 [28] Y.-H. Kim, K.-H. Kim, *Anal. Chim. Acta* **714**, 98 (2012).
- 549 [29] Y.-H. Kim, K.-H. Kim, *Anal. Chem.* **84**, 4126 (2012).
- 550 [30] K.-H. Kim, Y.-H. Kim, R.J.C. Brown, *Anal. Bioanal. Chem.* **405**, 8397 (2013).
- 551 [31] U.S. EPA, *Compendium of Methods for the Determination of Toxic Organic*
552 *Compounds in Ambient Air, Method TO-17*, Center for Environmental Research
553 *Information, Office of Research and Development*, 1999.
- 554 [32] S.-H. Jo, K.-H. Kim, Z.-H. Shon, D. Parker, *Anal. Chim. Acta* **738**, 51 (2012).
- 555 [33] S. Rasi, A. Veokamem, J. Rintala, *Energy* **32**, 1375 (2007).
- 556 [34] WHO (World Health Organization). *Indoor air quality: organic pollutants*. Euro
557 *Reports and Studies No. 111*. Copenhagen: World Health Organisation, Regional Office
558 *for Europe*, 1989.
- 559 [35] E. Gallego, F.J. Roca, J.F. Perales, X. Guardino, *Talanta* **81**, 916 (2010).
- 560 [36] Y.-C. Chien, K.-G. Yin, *J. Environ. Monit.* **11**, 1013 (2009).
- 561 [37] P. Bruno, M. Caputi, M. Caselli, G. de Gennaro, M. de Rienzo, *Atmos. Environ.*
562 **39**, 1347 (2005).
- 563 [38] Ö.O. Kuntasal, D. Karman, D. Wang, S.G. Tuncel, G. Tuncel, *J. Chromatogr. A*,
564 **1099**, 43 (2005).
- 565 [39] C. Rodríguez-Navas, R. Forteza, V. Cerdà, *Chemosphere* **89**, 1426 (2012).
- 566 [40] S. Björkqvist, M. Fröling, H. Härelind-Ingelsten, G. Petersson, *Environ. Technol.*
567 **19**, 639 (1998).
- 568 [41] J. Harder, S. Foß, *Geomicrobiol. J.* **16**, 295 (1999).
- 569 [42] S. Rasi, PhD Thesis, University of Jyväskylä, 2009.

570 [43] I.J. Simpson, J.E. Marrero, S. Batterman, S. Meinardi, B. Barletta, D.R. Blake,
571 Atmos. Environ. **81**, 702 (2013).

572 [44] M. Doyle, K.G. Sexton, H. Jeffries, L. Jaspers, Chem-Biol. Interact. **166**, 163
573 (2007).

574 [45] IARC (International Agency for Research on Cancer), IARC Monographs on the
575 Evaluation of Carcinogenic Risks to Humans, 2013. Available from:
576 <http://monographs.iarc.fr/ENG/Classification/index.php>.

577 [46] K. Sakurai, Y. Miyske, T. Amagai, Atmos. Environ. **80**, 198 (2013).

578 [47] J.A. Swenberg, N.K. Bordeerat, G. Boysen, S. Carro, N.I. Georgieva, J.
579 Nakamura, J.M. Troutman, P.B. Upton, R.J. Albertini, P.M. Vacek, V.E. Walker, R.J.
580 Sram, M. Goggin, N. Tretyakova, Chem-Biol. Interact. **192**, 150 (2011).

581 [48] E. Davoli, M.L. Gangai, L. Morselli, D. Tonelli, Chemosphere **51**, 357 (2003).

582 [49] R.E. Dodson, M. Nishioka, L.J. Standley, L.J. Perovich, J. Green Brody, R.A.
583 Rudel, Environ. Health Persp. **120**, 935 (2012).

584 [50] A.W. Nørgaard, K.A. Jensen, C. Janfelt, F.R. Lauritsen, P.A. Clausen, P. Wolkoff,
585 Environ. Sci. Technol. **43**, 7824 (2009).

586 [51] F. Pieri, A. Katsoyiannis, T. Martellini, D. Hughes, K.C. Jones, A. Cincinelli,
587 Environ. Int. **59**, 363 (2013).

588 [52] R.A. Yucuis, C.O. Stanier, K.C. Hornbucke, Chemosphere **92**, 905 (2013).

589 [53] S. Saeed, S.F. Kao, G.J. Graening, presented at the AWMA Symposium on Air
590 Quality Measurement Methods and Technology, San Francisco, 2002.

591 [54] K. Schultz, J. Brown, The Reporter **30.1**, 16 (2012).

592 [55] J. Beauchamp, J. Herbig, R. Gutmann, A. Hansel, J. Breath Res. **2**, 046001 (2008).

593 [56] Y.-H. Kim, K.-H. Kim, S.-H. Jo, E.-C. Jeon, J.R. Sohn, D.B Parker, Anal. Chim.
594 Acta **712**, 162 (2012).

- 595 [57] R. Chiriac, J. De Araujos Morais, J. Carre, R. Bayard, J.M. Chovelon, R. Gourdon,
596 Waste Manage. **31**, 2294 (2011).
- 597 [58] A. Lakhout, W.N. Schirmer, T.R. Johnson, H. Cabana, A.R. Cabral, Chemosphere
598 **97**, 98 (2014).
- 599 [59] F. Tassi, G. Montegrossi, O. Vaselli, C. Liccioli, S. Moretti, B. Nisi, Sci. Tot.
600 Environ. **407**, 4513 (2009).
- 601 [60] R. Chiriac, J. Carre, Y. Perrodin, L. Fine, J.-M. Letoffe, J. Hazard. Mater. **149**, 249
602 (2007).
- 603 [61] A.I. Moreno, N. Arnáiz, R. Font, A. Carratalá, Waste Manage. **34**, 2393 (2014).
- 604 [62] A.D. Dorado, S. Husni, G. Pascual, C. Puigdemívol, D. Gabriel, Waste Manage. **34**,
605 344 (2014).
- 606 [63] E. Smet, H. Van Langenhove, I. De Bo, Atmos. Environ. **33**, 1295 (1999).
- 607 [64] K. Oshita, Y. Ishihara, M. Takaoka, N. Takeda, T. Matsumoto, S. Morisawa, A.
608 Kitayama, Water Sci. Techol. **61.8**, 2003 (2010).

Table 1. Method target VOC analytes. CAS number, molecular weight (MW, g mol⁻¹), boiling point (BP, °C, at 760 mmHg), quantification ions *m/z* 1 (low concentration range) and *m/z* 2 (high concentration range), MDL (ng in tube for *m/z* 1), Precision (*n*=7, for *m/z* 1) and Temporal Change in Sensitivity during 3 days (TCS, %). N° refers to the number assigned in the chromatogram in Figure 1.

N°	Compound	CAS	MW	BP	<i>m/z</i> 1	<i>m/z</i> 2	MDL	Precision	TCS (%)
Alkanes									
11	<i>n</i> -hexane	110-54-3	86	69	57	86	0.01	1	1.5
18	<i>n</i> -heptane	142-82-5	100	98	43	100	0.06	2	0.2
22	<i>n</i> -octane	111-65-9	114	125	43	114	0.06	2	1.9
31	<i>n</i> -nonane	111-84-2	128	150	57	128	0.05	2	0.4
42	<i>n</i> -decane	124-18-5	142	174	71	142	0.06	2	1.8
51	<i>n</i> -undecane	1120-21-4	156	195	57	156	0.06	1	0.4
55	<i>n</i> -dodecane	112-40-3	170	215	57	170	0.09	3	1.1
60	<i>n</i> -tridecane	629-50-5	184	235	57	184	0.1	3	0.7
63	<i>n</i> -tetradecane	629-59-4	198	251	57	198	0.1	7	0.7
15	<i>n</i> -cyclohexane	110-82-7	84	80	56	39	0.03	2	1.7
Aromatic hydrocarbons									
17	Benzene	71-43-2	78	80	78	51	0.05	2	1.1
21	Toluene	108-88-3	92	111	92	65	0.05	1	1.6
29	Ethylbenzene	100-41-4	106	137	106	65	0.04	2	0.1
30	<i>m+p</i> -xylene	108-38-3/106-42-3	106	139/138	106	77	0.06	2	1.1
33	Styrene	100-42-5	104	145	104	104	0.04	1	0.1
32	<i>o</i> -xylene	95-47-6	106	145	91	91	0.06	4	0.1
39	<i>n</i> -propylbenzene	103-65-1	120	159	91	120	0.05	3	0.5
40	<i>m+p</i> -ethyltoluene	620-14-4/622-96-8	120	158/162	105	120	0.05	3	0.2
44	<i>o</i> -ethyltoluene	611-14-3	120	164	105	120	0.05	3	0.2
41	1,3,5-trimethylbenzene	108-67-8	120	165	105	120	0.05	3	0.2
45	1,2,4-trimethylbenzene	95-63-6	120	168	105	120	0.05	1	0.6
56	1,2,3-trimethylbenzene	526-73-8	120	175	105	120	0.05	3	0.2
59	Naphthalene	91-20-3	128	218	128	102	0.07	2	0.5

62	2-methylnaphthalene	91-57-6	142	242	142	115	0.09	2	0.2
64	1-methylnaphthalene	90-12-0	142	245	142	115	0.07	1	0.8
52	phenol	108-95-2	94	182	94	66	0.8	2	1.6
Ketones									
4	Acetone	67-64-1	58	56	43	44	0.3	2	1.1
12	Methylethylketone	78-93-3	72	80	72	57	0.05	1	2.3
20	Methylisobutylketone	108-10-1	100	117	43	100	0.07	2	1.3
25	Ethylacetone	107-87-9	86	100	43	86	0.05	3	1.3
26	Diethylketone	96-22-0	86	102	57	86	0.05	5	1.3
34	Diisopropylketone	565-80-0	114	125	43	114	0.05	6	1.3
36	Butylmethylketone	209-731-1	100	128	43	100	0.05	2	1.3
38	Ethylisobutylketone	623-56-3	114	136	57	114	0.05	6	1.3
48	Amylmethylketone	110-43-0	114	152	43	114	0.05	10	1.3
53	Hepthylmethylketone	821-55-6	142	194	58	142	0.05	9	1.3
Halocarbons									
8	Dichloromethane	75-09-2	85	69	84	88	0.09	2	1.7
19	Trichloroethylene	79-01-6	129	87	130	134	0.05	2	3.0
24	Tetrachloroethylene	127-18-4	163	121	166	168	0.03	1	2.2
Aldehydes									
46	Benzaldehyde	100-52-7	106	178	77	106	0.08	1	0.4
1	Acetaldehyde	75-07-0	44	20	44	45	0.02	1	0.1
Esters									
7	Methyl acetate	79-20-9	74	57	74	74	0.05	9	3.4
13	Ethyl acetate	141-78-6	88	77	61	88	0.08	2	1.1
27	Butyl acetate	123-86-4	116	126	73	73	0.04	2	0.2
Terpenoids									
35	-pinene	7785-70-8	136	157	93	136	0.04	3	0.2
43	β -pinene	127-91-3	136	167	93	136	0.06	2	0.02
49	Limonene	5989-27-5	176	177	93	136	0.04	1	0.5
50	<i>p</i> -cymene	99-87-6	134	176	119	103	0.07	3	0.1

58	Camphor	76-22-2	152	204	95	96	0.05	1	2.2
Siloxanes									
9	Trimethylsilanol	1066-40-6	90	99	75	45	0.05	1	0.1
16	L2 (hexamethyldisiloxane)	107-46-0	162	100	147	73	0.09	6	2.3
28	L3 (octamethyltrisiloxane)	107-51-7	236	153	221	103	0.09	4	4.1
47	L4 (decamethyltetrasiloxane)	141-62-8	310	194	207	295	0.06	2	0.2
57	L5 (dodecamethylpentasiloxane)	141-63-9	384	230	281	249	0.08	1	2.8
23	D3 (hexamethylcyclotrisiloxane)	541-05-9	222	134	207	191	0.07	11	0.2
37	D4 (octamethylcyclotetrasiloxane)	556-67-2	296	175	281	133	0.08	1	0.5
54	D5 (decamethylcyclopentasiloxane)	541-02-6	370	210	355	339	0.09	2	0.1
61	D6 (dodecamethylcyclohexasiloxane)	540-97-6	444	245	341	207	0.07	3	1.6
Others									
5	Carbon disulphide	75-15-0	76	46	76	76	0.06	1	2.1
10	<i>tert</i> -methylbutylether	1634-04-4	88	55	73	57	0.03	2	0.4
14	Tetrahydrofuran	109-99-9	72	66	42	72	0.06	1	0.5
6	Acetonitrile	75-05-8	41	81	41	39	0.2	3	2.9
3	Ethanol	64-17-5	46	79	45	46	0.05	2	0.5
2	1,3-butadiene	106-99-0	54	-4.5	54	55	0.2	1	1.5

Table 2. VOC concentrations ($\mu\text{g m}^{-3}$), breakthrough values (%VOC found in the back tube) and precision (%RSD) from 100 ml and 250 ml samples ($n=5$).

Compound	Volume = 100 ml			Volume = 250 ml		
	Concentration	Breakthrough	Precision	Concentration	Breakthrough	Precision
CH ₄	58.1%			58.1%		
CO ₂	40.9%			40.9%		
Alkanes						
<i>n</i> -hexane*	270 ± 10	1 ± 1	2	186 ± 4	1 ± 1	2
<i>n</i> -heptane*	2380 ± 60	0.3 ± 0.3	2	1930 ± 40	0.4 ± 0.5	2
<i>n</i> -octane*	3500 ± 200	0.1 ± 0.1	5	3010 ± 80	0.1 ± 0.1	3
<i>n</i> -nonane	4200 ± 500	0.009 ± 0.004	13	4000 ± 100	0.01 ± 0.01	3
<i>n</i> -decane	2900 ± 200	0.03 ± 0.03	8	2620 ± 90	0.05 ± 0.04	4
<i>n</i> -undecane*	1700 ± 100	0	7	1390 ± 80	0.1 ± 0.1	6
<i>n</i> -dodecane*	300 ± 30	0	9	230 ± 20	0.2 ± 0.3	8
<i>n</i> -tridecane*	630 ± 40	0.8 ± 0.2	6	510 ± 30	0.31 ± 0.03	6
<i>n</i> -tetradecane*	31 ± 4	2 ± 1	14	22 ± 1	1 ± 1	6
<i>n</i> -cyclohexane*	650 ± 40	0.3 ± 0.3	7	405 ± 3	0.6 ± 0.5	1
Aromatic hydrocarbons						
Benzene*	240 ± 50	2 ± 2	19	133 ± 4	3 ± 2	3
Toluene	19,000 ± 7000	0.4 ± 0.5	37	11,000 ± 1000	2 ± 2	9
Ethylbenzene	2300 ± 300	0.01 ± 0.01	14	2170 ± 80	0.02 ± 0.03	4
<i>m+p</i> -xylene	2600 ± 400	0.05 ± 0.04	13	2400 ± 100	0.1 ± 0.1	4
Styrene	110 ± 10	0.3 ± 0.5	11	100 ± 10	2 ± 3	8
<i>o</i> -xylene	640 ± 70	0.04 ± 0.06	11	600 ± 20	0.1 ± 0.1	4
<i>n</i> -propylbenzene	230 ± 30	0.1 ± 0.1	12	240 ± 20	0.4 ± 0.4	9
<i>m+p</i> -ethyltoluene	980 ± 140	0.01 ± 0.02	14	940 ± 50	0.1 ± 0.1	5
<i>o</i> -ethyltoluene	350 ± 30	0	9	310 ± 10	0.04 ± 0.05	5
1,3,5-trimethylbenzene	570 ± 110	0.2 ± 0.3	20	460 ± 40	0.5 ± 0.5	9
1,2,4-trimethylbenzene*	970 ± 100	0.02 ± 0.02	11	720 ± 40	0.1 ± 0.1	6
1,2,3-trimethylbenzene*	640 ± 40	0	6	500 ± 40	0.03 ± 0.03	14

Naphthalene*	14 ± 1	4 ± 1	8	8 ± 1	3 ± 1	16
2-methylnaphthalene*	1.5 ± 0.2	0	14	1.0 ± 0.1	0	13
1-methylnaphthalene	1.3 ± 0.4	0	29	1.0 ± 0.3	0	31
Phenol	120 ± 10	0	7	110 ± 10	0	8
Ketones						
Acetone*	7300 ± 200	0.05 ± 0.03	3	5300 ± 800	0.06 ± 0.04	15
Methylethylketone*	33,100 ± 800	0	2	26,000 ± 900	0.02 ± 0.02	3
Methylisobutylketone*	400 ± 20	0	5	340 ± 10	0	4
Ethylacetone*	2020 ± 70	0	3	1720 ± 60	0.03 ± 0.03	4
Diethylketone*	1900 ± 100	0	6	1590 ± 70	1 ± 1	5
Diisopropylketone*	240 ± 20	0	7	190 ± 10	0	6
Butylmethylketone	116 ± 3	0	2	120 ± 10	1 ± 1	7
Ethylisobutylketone	370 ± 30	0	7	330 ± 20	1 ± 1	6
Amylmethylketone	680 ± 80	0	12	680 ± 70	0.03 ± 0.04	10
Hepthylmethylketone*	39 ± 4	0	9	30 ± 3	0	9
Halocarbons						
Dichloromethane	50 ± 3	2 ± 1	7	44 ± 3	2 ± 2	8
Trichloroethylene	62 ± 2	0	4	59 ± 2	0	3
Tetrachloroethylene	46 ± 3	0	6	41 ± 1	0.3 ± 0.4	2
Aldehydes						
Benzaldehyde*	5000 ± 300	0.01 ± 0.02	6	3990 ± 80	0.05 ± 0.04	2
Acetaldehyde	3200 ± 1000	23 ± 18	32	2700 ± 500	26 ± 17	17
Esters						
Methyl acetate	50 ± 10	4 ± 2	15	38 ± 4	0	10
Ethyl acetate*	290 ± 30	1 ± 1	10	190 ± 10	1 ± 1	4
Butyl acetate*	40 ± 3	0	8	23 ± 1	0	4
Terpenes						
-pinene*	65,000 ± 5000	0	8	44,000 ± 1000	0.001 ± 0.002	2
β-pinene*	53,000 ± 4000	0	8	40,000 ± 2000	0	5
Limonene*	84,000 ± 7000	0.005 ± 0.004	8	53,000 ± 1000	0.01 ± 0.01	2

<i>p</i> -cymene*	458,000 ± 25,000	0.01 ± 0.01	5	340,000 ± 16,000	0.005 ± 0.002	5
Camphor	180 ± 20	0	9	150 ± 10	0.04 ± 0.09	8
Siloxanes						
Trimethylsilanol*	470 ± 30	1 ± 1	7	230 ± 40	1 ± 1	17
L2	50 ± 10	0	17	35 ± 3	0	8
L3	80 ± 10	0	11	76 ± 3	0	4
L4	30 ± 5	0	16	30 ± 10	0	24
L5	4.5 ± 0.3	0	7	4.6 ± 0.5	0	11
D3	20 ± 10	0	64	30 ± 10	1 ± 2	20
D4	230 ± 30	0.1 ± 0.1	12	230 ± 10	0.02 ± 0.01	6
D5	4100 ± 400	0.0004 ± 0.0006	10	4000 ± 300	0.0004 ± 0.0007	6
D6*	60 ± 10	0.3 ± 0.4	11	80 ± 10	0.01 ± 0.01	8
Others						
Carbon disulphide	2200 ± 1400	7 ± 4	60	2700 ± 1100	16 ± 10	41
<i>tert</i> -methylbutylether*	2.3 ± 0.3	0	15	1.2 ± 0.1	0	6
Tetrahydrofuran*	190 ± 10	0.5 ± 0.3	3	143 ± 4	1 ± 1	3
Acetonitrile	190 ± 40	4 ± 2	19	150 ± 10	4 ± 3	5
Ethanol*	2000 ± 1600	20 ± 30	81	310 ± 260	40 ± 30	82
1,3-butadiene*	64,000 ± 65,000	40 ± 40	102	7000 ± 6600	70 ± 20	95

*Significant differences observed between the concentrations obtained from 100 ml and 250 ml samples (*t*-test, *p* ≤ 0.01).

Table 3. VOC concentrations (mg m⁻³) in biogas from different sources.

Concentrations (mg m ⁻³)	Alkanes	Aromatic hydrocarbons	Ketones	Esters	Aldehydes	Halocarbons	Terpenes	Siloxanes	Citation
BIOGAS SOURCE									
Landfills									
Old landfill cell (40 years old)	416	340	-	-	-	-	62	-	[57]
Closed landfill (6 years)	-	-	-	-	-	n.d.	-	1.6	[7]
Recently closed landfill cell	112	298	273	-	-	-	348	-	[57]
Landfill cell	4.9	9.2	7.7	-	-	-	8.7	-	[57]
Active landfill (23 years old)	-	-	-	-	-	1-7	-	6.7-9.8	[7]
Active landfill (5 years old)	-	29-65	-	-	-	-	-	-	[58]
Active landfill	-	2.3-7.4	-	-	-	0.3-1.3	-	0.7-4.0	[33]
Active landfill	-	291	219	171	3.3	225	-	-	[42]
Active landfill	302-503	94-330	-	<0.1	-	327-739	74-152	-	[42]
Active landfill	1730-1780	8577-9430	12-211	86-282	14-25	173-357	43-44	-	[59]
Landfill open cell*	2.2-2.4	5.3-6.7	-	-	-	2.3-5.8	1.7-2.6	-	[60]
Landfill biogas leaks	-	3.7	-	-	-	-	24.1	-	[61]
Composting facilities									
Composting process*	-	0.5	-	-	-	-	38	-	[61]
Composting process*	-	0.3	2.5	0.05	0.1	-	11	-	[62]
Composting process*	-	-	-	99	181	-	72	-	[63]
Composting process	-	-	-	3.1	20	-	1812	-	[63]
Bioreactors									
Sewage sludge	-	-	-	-	-	n.d.	-	30	[7]
Sewage sludge	-	-	-	-	-	-	-	32.2	[64]
Sewage sludge	-	2.9-12	-	-	-	<0.1	-	1.5-11	[33]
Sewage sludge + Biowaste	<10	<26	-	-	-	-	1178	2.9-10	[9]
Sewage sludge + Biowaste	-	-	-	-	-	-	-	2.4-5.5	[42]
Sewage sludge + Municipal and Industrial biowaste	-	-	-	-	-	n.d.	-	2.5	[7]
Sewage and industrial sludge + Kitchen waste	-	-	-	-	-	<0.1	-	5.5	[7]
Cow manure	-	0.9-2.0	-	-	-	-	-	<0.4	[33]
Municipal biowaste	10-16	13-35	36 -53	0.3-5	6.7-8.3	0.1-0.3	477-659	4.4-4.7	This study

*Aerobic processes

Table 4. VOC concentrations ($\mu\text{g m}^{-3}$) from the different bags sampled ($n=5$).

Compound	Bag 1	Bag 2	Bag 3	Bag 4
Bag filling day	14-1-2014	14-1-2014	14-1-2014	14-1-2014
Bag sampling day [†]	14-1-2014	15-1-2014	16-1-2014	17-1-2014
CH ₄	56.9%	-	-	-
CO ₂	42.1%	-	-	-
Alkanes				
<i>n</i> -hexane	310 ± 30	320 ± 20	360 ± 30	390 ± 20*
<i>n</i> -heptane	1200 ± 200	1400 ± 100	1500 ± 100	1590 ± 90*
<i>n</i> -octane	1500 ± 200	1600 ± 200	1800 ± 200	1900 ± 100
<i>n</i> -nonane	1300 ± 200	1400 ± 200	1600 ± 200	1700 ± 100
<i>n</i> -decane	4200 ± 400	4100 ± 400	4700 ± 300	5100 ± 300
<i>n</i> -undecane	330 ± 60	390 ± 20	500 ± 20*	550 ± 20*
<i>n</i> -dodecane	80 ± 20	80 ± 10	100 ± 10	100 ± 10
<i>n</i> -tridecane	290 ± 60	190 ± 20	210 ± 20	230 ± 30
<i>n</i> -tetradecane	12 ± 2	8.3 ± 0.3	8.1 ± 0.4*	8 ± 1*
<i>n</i> -cyclohexane	440 ± 70	640 ± 50*	690 ± 50*	790 ± 50*
Aromatic hydrocarbons				
Benzene	220 ± 60	210 ± 40	230 ± 40	240 ± 40
Toluene	3500 ± 600	3200 ± 300	3300 ± 200	3400 ± 200
Ethylbenzene	2000 ± 400	1600 ± 200	1600 ± 200	1600 ± 200
<i>m</i> - <i>p</i> -xylene	2000 ± 300	1400 ± 200	1400 ± 200	1400 ± 100
Styrene	130 ± 20	60 ± 10*	60 ± 10*	60 ± 10*
<i>o</i> -xylene	670 ± 100	430 ± 60*	410 ± 50*	410 ± 40*
<i>n</i> -propylbenzene	240 ± 30	170 ± 20*	170 ± 20*	170 ± 20*
<i>m</i> - <i>p</i> -ethyltoluene	920 ± 80	560 ± 60*	550 ± 60*	560 ± 60*
<i>o</i> -ethyltoluene	330 ± 20	240 ± 20*	250 ± 20*	250 ± 30*
1,3,5-trimethylbenzene	650 ± 70	460 ± 70*	490 ± 60	510 ± 70
1,2,4-trimethylbenzene	640 ± 30	390 ± 50*	420 ± 30*	420 ± 40*
1,2,3-trimethylbenzene	600 ± 40	270 ± 20*	300 ± 20*	310 ± 40*
Naphthalene	5 ± 1	4 ± 1	4 ± 1	5 ± 1
2-methylnaphthalene	0.9 ± 0.3	0.7 ± 0.1	1.0 ± 0.2	1.5 ± 0.1
1-methylnaphthalene	0.4 ± 0.2	0.4 ± 0.1	0.35 ± 0.03	0.38 ± 0.04
Phenol	620 ± 30	610 ± 20	630 ± 30	640 ± 20
Ketones				
Acetone	7400 ± 700	6100 ± 500	6500 ± 500	6500 ± 300
Methylethylketone	38,000 ± 1000	22,000 ± 2000	21,000 ± 2000	21,000 ± 2000
Methylisobutylketone	340 ± 70	270 ± 30	250 ± 20*	260 ± 20*
Ethylacetone	2900 ± 500	2000 ± 100	1900 ± 100*	1800 ± 100*
Diethylketone	2100 ± 300	1300 ± 100*	1200 ± 100*	1200 ± 100*
Diisopropylketone	450 ± 80	370 ± 40	370 ± 40	370 ± 30
Butylmethylketone	160 ± 20	67 ± 4*	62 ± 3*	62 ± 5*
Ethylisobutylketone	320 ± 60	230 ± 20	213 ± 5*	240 ± 20
Amylmethylketone	680 ± 100	300 ± 30*	290 ± 30*	310 ± 40*
Hepthylmethylketone	17 ± 4	12 ± 1	12 ± 1	14 ± 2
Halocarbons				
Dichloromethane	140 ± 30	180 ± 10	200 ± 10*	210 ± 10*
Trichloroethylene	70 ± 10	70 ± 10	80 ± 10	84 ± 4
Tetrachloroethylene	100 ± 10	100 ± 10	110 ± 10	120 ± 10
Aldehydes				
Benzaldehyde	5400 ± 200	5100 ± 500	5700 ± 500	6100 ± 400
Acetaldehyde	1700 ± 300	1300 ± 200	1600 ± 400	1700 ± 200
Esters				
Methyl acetate	350 ± 90	330 ± 20	360 ± 20	350 ± 20
Ethyl acetate	4200 ± 400	3000 ± 100*	3000 ± 200*	2900 ± 100*
Butyl acetate	490 ± 60	310 ± 40*	310 ± 20*	310 ± 40*
Terpenes				
-pinene	65,000 ± 7000	65,000 ± 6000	71,000 ± 6000	78,000 ± 4000
β-pinene	56,000 ± 7000	53,000 ± 4000	60,000 ± 4000	64,000 ± 4000

Limonene	86,000 ± 7000	82,000 ± 2000	84,000 ± 2000	82,000 ± 6000
<i>p</i> -cymene	309,000 ± 14,000	254,000 ± 33,000	243,000 ± 19,000*	250,000 ± 25,000*
Camphor	110 ± 20	90 ± 10	80 ± 10	90 ± 10
Siloxanes				
Trimethylsilanol	470 ± 110	560 ± 30	630 ± 50	710 ± 70*
L2	40 ± 10	41 ± 2	50 ± 10	50 ± 10*
L3	80 ± 20	80 ± 10	90 ± 10	100 ± 10
L4	49 ± 5	48 ± 4	55 ± 5	62 ± 5*
L5	7 ± 2	5.7 ± 0.4	8 ± 2	10 ± 2
D3	8 ± 3	7 ± 2	9 ± 3	10 ± 4
D4	240 ± 10	220 ± 20	240 ± 20	280 ± 20*
D5	3740 ± 390	3600 ± 300	4500 ± 300	4800 ± 300*
D6	150 ± 30	160 ± 20	210 ± 20*	220 ± 20*
Others				
Carbon disulphide	490 ± 180	680 ± 330	790 ± 390	850 ± 470
<i>tert</i> -methylbutylether	2.0 ± 0.2	2.7 ± 0.1*	3.1 ± 0.2*	3.6 ± 0.2*
Tetrahydrofuran	320 ± 40	280 ± 20	290 ± 20	310 ± 20
Acetonitrile	170 ± 20	70 ± 2*	62 ± 2*	48 ± 4*
Ethanol	170 ± 20	120 ± 10*	130 ± 10*	130 ± 20*
1,3-butadiene	150 ± 20	160 ± 20	200 ± 40	230 ± 30*
Total VOC (mg m⁻³)	600 ± 30	520 ± 40	530 ± 30	550 ± 40

*Significant differences observed between the concentrations obtained from bags 2, 3 and 4 and the bag 1 (*t*-test, $p \leq 0.01$).

†Bags stored in darkness at room temperature

Table 5. VOC concentrations ($\mu\text{g m}^{-3}$) from the different blank bags sampled ($n=5$). Between parentheses: the percentage of VOC in blank samples in respect to biogas samples is shown.

Compound	Bag 1	Bag 2	Bag 3	Bag 4
Bag filling day	21-1-2014	21-1-2014	21-1-2014	21-1-2014
Bag sampling day†	21-1-2014	22-1-2014	23-1-2014	24-1-2014
Alkanes				
<i>n</i> -hexane	1 ± 1 (0.1 ± 0.1)	1 ± 1* (0.5 ± 0.2)	1.5 ± 0.4* (0.4 ± 0.1)	0.6 ± 0.2 (0.17 ± 0.04)
<i>n</i> -heptane	n.d.	1 ± 1 (0.1 ± 0.1)	1.4 ± 0.3* (0.09 ± 0.02)	1.5 ± 0.1* (0.10 ± 0.01)
<i>n</i> -octane	0.9 ± 0.4 (0.06 ± 0.02)	0.9 ± 0.2 (0.06 ± 0.02)	1.1 ± 0.1 (0.06 ± 0.01)	1.1 ± 0.1 (0.06 ± 0.01)
<i>n</i> -nonane	0.5 ± 0.2 (0.04 ± 0.02)	0.7 ± 0.2 (0.05 ± 0.01)	1.0 ± 0.1 (0.06 ± 0.01)	0.7 ± 0.1 (0.04 ± 0.01)
<i>n</i> -decane	2 ± 1 (0.04 ± 0.01)	1.0 ± 0.3 (0.02 ± 0.01)	2.7 ± 0.3 (0.06 ± 0.01)	1.4 ± 0.3 (0.03 ± 0.01)
<i>n</i> -undecane	1.3 ± 0.2 (0.4 ± 0.1)	0.9 ± 0.2 (0.23 ± 0.04)	1.2 ± 0.2 (0.25 ± 0.04)	1.0 ± 0.2 (0.19 ± 0.04)
<i>n</i> -dodecane	0.3 ± 0.1 (0.3 ± 0.1)	0.2 ± 0.1 (0.2 ± 0.2)	0.8 ± 0.2* (0.8 ± 0.2)	0.6 ± 0.3 (0.6 ± 0.3)
<i>n</i> -tridecane	1.2 ± 0.4 (0.4 ± 0.1)	0.6 ± 0.3 (0.3 ± 0.2)	1.1 ± 0.5 (0.5 ± 0.3)	1.5 ± 0.5 (0.7 ± 0.2)
<i>n</i> -tetradecane	0.3 ± 0.2 (2 ± 1)	0.4 ± 0.2 (4 ± 2)	0.7 ± 0.3 (9 ± 4)	0.3 ± 0.1 (4 ± 1)
<i>n</i> -cyclohexane	0.4 (0.01)	0.4 ± 0.2 (0.06 ± 0.03)	0.7 ± 0.3* (0.1 ± 0.1)	n.d.
Aromatic hydrocarbons				
Benzene	0.2 (0.1)	1 ± 1 (0.4 ± 0.3)	0.3 ± 0.3 (0.1 ± 0.1)	0.4 ± 0.3 (0.1 ± 0.1)
Toluene	1 ± 1 (0.04 ± 0.02)	2.98 ± 0.02* (0.10 ± 0.01)	9.0 ± 0.5* (0.27 ± 0.03)	3.2 ± 0.4* (0.10 ± 0.02)
Ethylbenzene	1 ± 1 (0.04 ± 0.03)	1 ± 1 (0.1 ± 0.1)	4 ± 5 (0.3 ± 0.3)	1.9 ± 0.1 (0.12 ± 0.02)
<i>m+p</i> -xylene	2 ± 2 (0.1 ± 0.1)	4 ± 2 (0.3 ± 0.1)	6 ± 1 (0.4 ± 0.2)	1 ± 1 (0.1 ± 0.1)
Styrene	1 ± 1 (1 ± 1)	0.6 ± 0.1 (0.9 ± 0.4)	1.1 ± 0.1 (2 ± 1)	0.9 ± 0.1 (1.5 ± 0.2)
<i>o</i> -xylene	2 ± 1 (0.2 ± 0.1)	2 ± 1 (0.4 ± 0.3)	2.8 ± 0.5 (0.7 ± 0.2)	0.9 ± 0.2 (0.2 ± 0.1)
<i>n</i> -propylbenzene	0.4 ± 0.3 (0.2 ± 0.1)	0.3 ± 0.1 (0.2 ± 0.1)	0.36 ± 0.02 (0.22 ± 0.03)	0.3 ± 0.1 (0.2 ± 0.1)
<i>m+p</i> -ethyltoluene	1.8 ± 0.4 (0.2 ± 0.1)	1.4 ± 0.4 (0.25 ± 0.04)	1.8 ± 0.2 (0.3 ± 0.1)	1.6 ± 0.1 (0.29 ± 0.04)
<i>o</i> -ethyltoluene	0.4 ± 0.2 (0.11 ± 0.04)	0.3 ± 0.1 (0.10 ± 0.04)	0.47 ± 0.04 (0.19 ± 0.03)	0.4 ± 0.1 (0.15 ± 0.03)
1,3,5-trimethylbenzene	0.8 ± 0.2 (0.11 ± 0.04)	0.4 ± 0.2 (0.09 ± 0.03)	0.8 ± 0.1 (0.16 ± 0.01)	0.7 ± 0.1 (0.14 ± 0.02)
1,2,4-trimethylbenzene	1.4 ± 0.4 (0.2 ± 0.1)	0.8 ± 0.3 (0.2 ± 0.1)	1.9 ± 0.2 (0.4 ± 0.1)	1.7 ± 0.1 (0.4 ± 0.1)
1,2,3-trimethylbenzene	0.6 ± 0.1 (0.10 ± 0.02)	0.5 ± 0.1 (0.2 ± 0.1)	0.65 ± 0.04 (0.22 ± 0.02)	0.5 ± 0.1 (0.15 ± 0.04)
Naphthalene	n.d.	n.d.	n.d.	n.d.
2-methylnaphthalene	n.d.	n.d.	n.d.	n.d.
1-methylnaphthalene	n.d.	n.d.	n.d.	n.d.
Phenol	n.d.	n.d.	n.d.	n.d.
Ketones				
Acetone	1 ± 1 (0.02 ± 0.01)	2.2 ± 0.3 (0.04 ± 0.01)	3.6 ± 0.5* (0.06 ± 0.01)	2.1 ± 0.2 (0.032 ± 0.002)
Methylethylketone	n.d.	n.d.	n.d.	n.d.
Methylisobutylketone	n.d.	n.d.	n.d.	n.d.
Ethylacetone	n.d.	n.d.	n.d.	n.d.
Diethylketone	n.d.	n.d.	n.d.	n.d.
Diisopropylketone	n.d.	n.d.	n.d.	n.d.
Butylmethylketone	n.d.	n.d.	n.d.	n.d.
Ethylisobutylketone	0.4 ± 0.2 (0.11 ± 0.04)	0.4 ± 0.1 (0.2 ± 0.1)	0.5 ± 0.1 (0.21 ± 0.02)	0.4 ± 0.1 (0.17 ± 0.04)
Amylmethylketone	n.d.	n.d.	n.d.	n.d.
Hepthylmethylketone	n.d.	n.d.	n.d.	n.d.
Halocarbons				
Dichloromethane	2 ± 2 (2 ± 1)	1 ± 1 (1 ± 1)	3 ± 2 (2 ± 1)	1 ± 1 (0.6 ± 0.3)
Trichloroethylene	n.d.	n.d.	n.d.	n.d.
Tetrachloroethylene	0.8 ± 0.4 (0.8 ± 0.3)	0.8 ± 0.5 (1 ± 1)	0.7 ± 0.2 (0.7 ± 0.2)	0.6 ± 0.1 (0.5 ± 0.1)
Aldehydes				
Benzaldehyde	n.d.	n.d.	n.d.	n.d.
Acetaldehyde	n.d.	n.d.	n.d.	n.d.
Esters				
Methyl acetate	0.3 (0.1)	0.6 ± 0.3* (0.2 ± 0.1)	0.2 ± 0.1 (0.06 ± 0.02)	0.1 (0.03)
Ethyl acetate	n.d.	n.d.	n.d.	n.d.
Butyl acetate	n.d.	n.d.	n.d.	n.d.
Terpenes				
-pinene	n.d.	n.d.	n.d.	n.d.
β-pinene	n.d.	n.d.	n.d.	n.d.
Limonene	9 ± 1 (<0.01)	5 ± 1* (<0.01)	9.9 ± 0.4 (<0.01)	4.8 ± 0.5* (<0.01)
<i>p</i> -cymene	8.2 ± 0.3 (<0.01)	5.2 ± 0.3* (<0.01)	6.9 ± 0.3* (<0.01)	2.8 ± 0.3* (<0.01)
Camphor	n.d.	n.d.	n.d.	n.d.
Siloxanes				
Trimethylsilanol	0.7 ± 0.4 (0.1 ± 0.1)	2.4 ± 0.5* (0.4 ± 0.1)	5 ± 1* (0.7 ± 0.2)	3.2 ± 0.5* (0.5 ± 0.1)
L2	n.d.	n.d.	n.d.	n.d.
L3	n.d.	n.d.	n.d.	n.d.

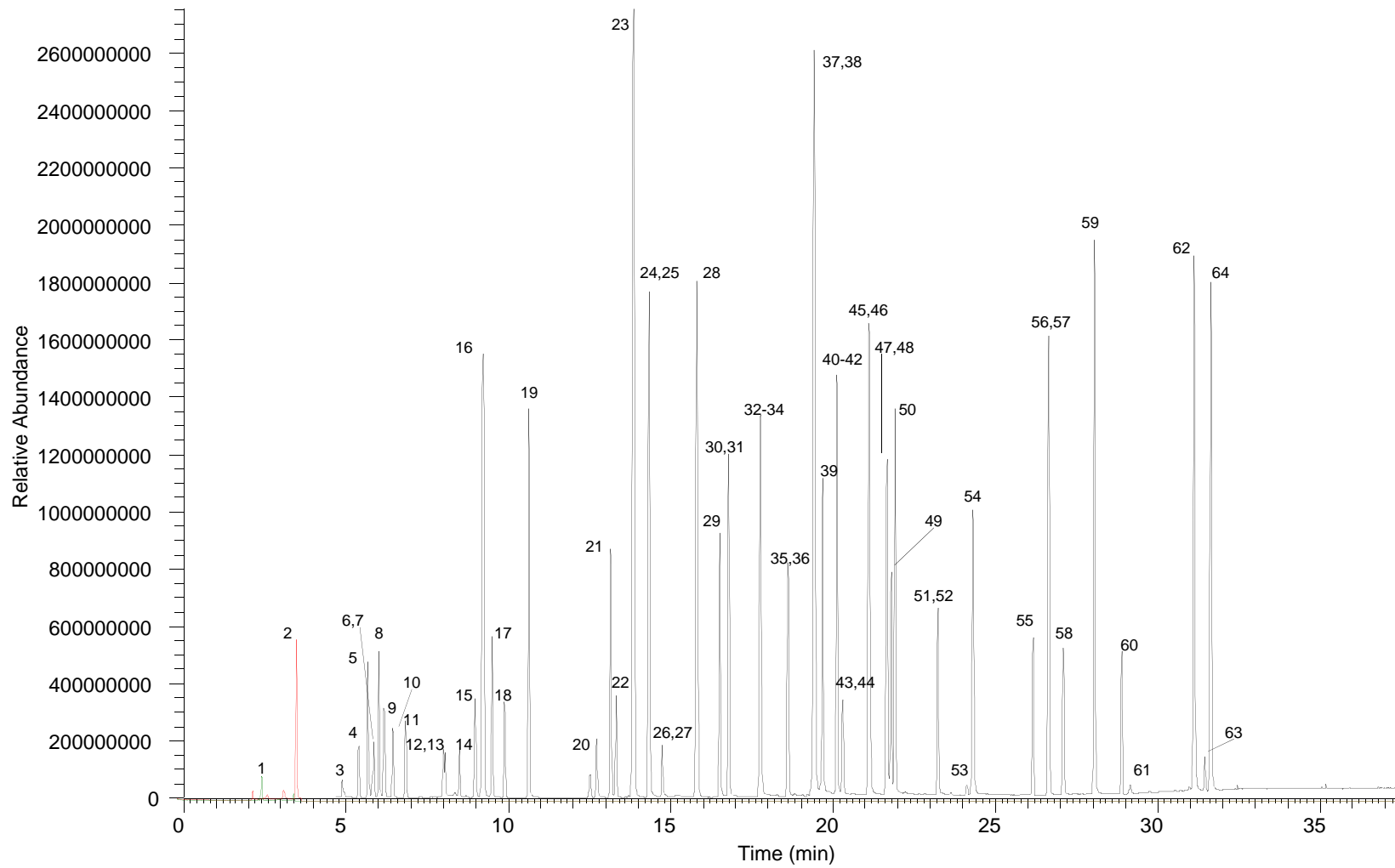
L4	n.d.	n.d.	n.d.	n.d.
L5	n.d.	n.d.	n.d.	n.d.
D3	0.4 ± 0.1 (6 ± 3)	0.3 ± 0.1 (4.2 ± 0.7)	0.7 ± 0.2* (6 ± 2)	0.5 ± 0.1 (6 ± 3)
D4	0.4 ± 0.1 (0.14 ± 0.04)	0.3 ± 0.1 (0.14 ± 0.03)	0.6 ± 0.1* (0.3 ± 0.1)	0.4 ± 0.1 (0.15 ± 0.04)
D5	0.5 ± 0.1 (<0.01)	0.5 ± 0.2 (<0.01)	1.1 ± 0.1* (<0.01)	0.7 ± 0.2 (<0.01)
D6	0.4 ± 0.1 (0.3 ± 0.1)	0.4 ± 0.2 (0.2 ± 0.1)	0.8 ± 0.1* (0.4 ± 0.1)	0.4 ± 0.3 (0.2 ± 0.1)
Others				
Carbon disulphide	0.01 (<0.01)	0.3 ± 0.2 (0.04 ± 0.04)	1.4 ± 0.2* (0.1 ± 0.1)	2 ± 1* (0.2 ± 0.2)
<i>tert</i> -methylbutylether	n.d.	n.d.	n.d.	n.d.
Tetrahydrofuran	n.d.	1.0 ± 0.3* (0.4 ± 0.1)	1.9 ± 0.1* (0.67 ± 0.04)	1.3 ± 0.2* (0.4 ± 0.1)
Acetonitrile	n.d.	n.d.	n.d.	n.d.
Ethanol	6 ± 3 (3 ± 2)	5 ± 4 (4 ± 3)	14 ± 5* (12 ± 5)	0.5 (0.5)
1,3-butadiene	n.d.	n.d.	n.d.	n.d.

*Significant differences observed between the concentrations obtained from bags 2, 3 and 4 and the bag 1 (*t*-test, $p \leq 0.01$).

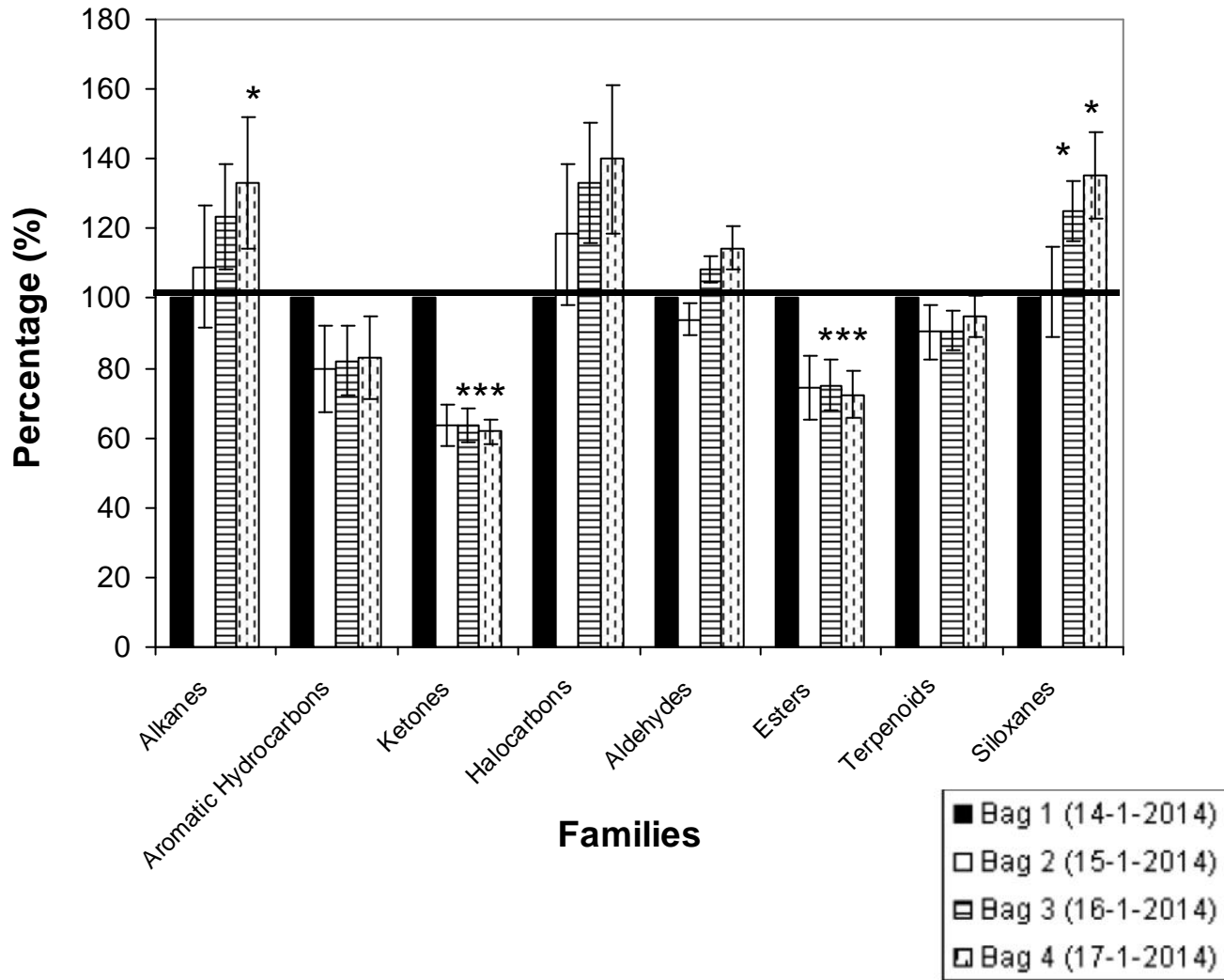
†Bags stored in darkness at room temperature

Figure 1. GC chromatogram for stock standard solution. Acetaldehyde (green) and butadiene (red) are injected separately as they elute before the solvent. Peak numbers are related to compounds listed in Table 1.

Figure 2. Percentages of VOC losses or increases for families and individual compounds in respect to the bag sampled the same day of its filling with biogas. (*) Indicates significant differences (*t*-test, $p \leq 0.01$) between the concentrations obtained from bags 2, 3 and 4 and bag 1.



Recoveries (C/C₀)



Recoveries (C/C₀)

