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

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Abstract

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

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

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

1. Introduction

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

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

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

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

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

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

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

2. Materials and methods

2.1 Chemicals and materials

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

2.2 SupelTM Inert Film bags

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

2.3 Adsorbent tubes

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

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

2.4 Analytical instrumentation

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

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

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

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

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

2.5 Sampling

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

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

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

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

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

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

2.6 Quality assurance

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

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

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

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

2.7 Data treatment

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

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

3. Results and discussion

3.1 Method performance evaluation

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

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

3.2 Breakthrough evaluation

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

3.3 Tube desorption evaluation

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

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

3.4 VOCs and VMSs concentrations in biogas

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

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

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

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

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

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

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

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

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

3.5 SupelTM Inert Film bags stability during storage

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

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

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

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

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

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

3.6 VOCs and VMSs concentrations in helium blank samples

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

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

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

4. Conclusions

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

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

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References

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

- [12] A. Narros, M.E. Del Peso, G. Mele, M. Vinot, E. Fernández, M.E. Rodríguez, presented at the Twelfth International Waste Management and Landfill Symposium, Cagliari, Sardinia, Italy, 2009.
- [13] EPRI (Electric Power Research Institute), Assessment of fuel gas cleanup systems for waste gas fuelled power generation, Palo Alto, CA, 2006, 1012763.
- [14] R. Grümping, D. Mikolajczak, A. Hirner, Fresen. J. Anal. Chem. **361**, 133 (1998).
- [15] M. Schweigkofler, R. Niessner, Environ. Sci. Technol. **33**, 3680 (1999).
- [16] G. Piechota, R. Buczkowski, Intern. J. Environ. Anal. Chem. **94**, 837 (2014).
- [17] M. Ajhar, B. Wens, K.H. Stollenwerk, G. Spalding, S. Yüce, T. Melin, Talanta **82**, 92 (2010).
- [18] L. Lamaa, C. Ferronato, L. Fe, F. Jaber, J.M. Chovelon, Talanta **115**, 881 (2013)
- [19] J. Raich-Montiu, C. Ribas-Font, N. de Arespachaga, E. Roig-Torres, F. Broto-Puig, M. Crest, L. Bouchy, J.L. Cortina, Anal. Chim. Acta **812**, 83 (2014).
- [20] E. Gallego, F.J. Roca, J.F. Perales, X. Guardino, in *Sorbents: Properties, Materials and Applications*, edited by T.P. Willis (Nova Science Publishers, New York, 2009).
- [21] A. Ribes, G. Carrera, E. Gallego, X. Roca, M.J. Berenguer, X. Guardino, J. Chromatogr. A **1140**, 44 (2007).
- [22] S. Rasi, J. Lantela, J. Rintala, Energ. Convers. Manage. **52**, 3369 (2011).
- [23] Y. Wang, T.S. Raihala, A.P. Jackman, R. St. John, Environ. Sci. Technol. **30**, 3115 (1996).
- [24] C. Tomasi, M. Baratieri, B. Bosio, E. Arato, P. Baggio, J. Power Sources **157**, 765.
- [25] E. Gallego, F.J. Roca, J.F. Perales, X. Guardino, in *Air Quality in the XXI Century*, edited by G.C. Romano and A.G. Conti (Nova Science Publishers, New York, 2009).
- [26] E. Gallego, F.J. Roca, J.F. Perales, G. Sánchez, P. Esplugas, Waste Manage **32**, 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. Technol. **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 $\pm$ 10	1 $\pm$ 1	2	186 $\pm$ 4	1 $\pm$ 1	2
<i>n</i> -heptane*	2380 $\pm$ 60	0.3 $\pm$ 0.3	2	1930 $\pm$ 40	0.4 $\pm$ 0.5	2
<i>n</i> -octane*	3500 $\pm$ 200	0.1 $\pm$ 0.1	5	3010 $\pm$ 80	0.1 $\pm$ 0.1	3
<i>n</i> -nonane	4200 $\pm$ 500	0.009 $\pm$ 0.004	13	4000 $\pm$ 100	0.01 $\pm$ 0.01	3
<i>n</i> -decane	2900 $\pm$ 200	0.03 $\pm$ 0.03	8	2620 $\pm$ 90	0.05 $\pm$ 0.04	4
<i>n</i> -undecane*	1700 $\pm$ 100	0	7	1390 $\pm$ 80	0.1 $\pm$ 0.1	6
<i>n</i> -dodecane*	300 $\pm$ 30	0	9	230 $\pm$ 20	0.2 $\pm$ 0.3	8
<i>n</i> -tridecane*	630 $\pm$ 40	0.8 $\pm$ 0.2	6	510 $\pm$ 30	0.31 $\pm$ 0.03	6
<i>n</i> -tetradecane*	31 $\pm$ 4	2 $\pm$ 1	14	22 $\pm$ 1	1 $\pm$ 1	6
<i>n</i> -cyclohexane*	650 $\pm$ 40	0.3 $\pm$ 0.3	7	405 $\pm$ 3	0.6 $\pm$ 0.5	1
Aromatic hydrocarbons						
Benzene*	240 $\pm$ 50	2 $\pm$ 2	19	133 $\pm$ 4	3 $\pm$ 2	3
Toluene	19,000 $\pm$ 7000	0.4 $\pm$ 0.5	37	11,000 $\pm$ 1000	2 $\pm$ 2	9
Ethylbenzene	2300 $\pm$ 300	0.01 $\pm$ 0.01	14	2170 $\pm$ 80	0.02 $\pm$ 0.03	4
<i>m+p</i> -xylene	2600 $\pm$ 400	0.05 $\pm$ 0.04	13	2400 $\pm$ 100	0.1 $\pm$ 0.1	4
Styrene	110 $\pm$ 10	0.3 $\pm$ 0.5	11	100 $\pm$ 10	2 $\pm$ 3	8
<i>o</i> -xylene	640 $\pm$ 70	0.04 $\pm$ 0.06	11	600 $\pm$ 20	0.1 $\pm$ 0.1	4
<i>n</i> -propylbenzene	230 $\pm$ 30	0.1 $\pm$ 0.1	12	240 $\pm$ 20	0.4 $\pm$ 0.4	9
<i>m+p</i> -ethyltoluene	980 $\pm$ 140	0.01 $\pm$ 0.02	14	940 $\pm$ 50	0.1 $\pm$ 0.1	5
<i>o</i> -ethyltoluene	350 $\pm$ 30	0	9	310 $\pm$ 10	0.04 $\pm$ 0.05	5
1,3,5-trimethylbenzene	570 $\pm$ 110	0.2 $\pm$ 0.3	20	460 $\pm$ 40	0.5 $\pm$ 0.5	9
1,2,4-trimethylbenzene*	970 $\pm$ 100	0.02 $\pm$ 0.02	11	720 $\pm$ 40	0.1 $\pm$ 0.1	6
1,2,3-trimethylbenzene*	640 $\pm$ 40	0	6	500 $\pm$ 40	0.03 $\pm$ 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* ≤ 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</i> + <i>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</i> + <i>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)	$0.7 \pm 0.2^*$ (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)	$0.6 \pm 0.1^*$ (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)	$1.1 \pm 0.1^*$ (<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)	$0.8 \pm 0.1^*$ (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)	$1.4 \pm 0.2^*$ (0.1 ± 0.1)	$2 \pm 1^*$ (0.2 ± 0.2)
<i>tert</i> -methylbutylether	n.d.	n.d.	n.d.	n.d.
Tetrahydrofuran	n.d.	$1.0 \pm 0.3^*$ (0.4 ± 0.1)	$1.9 \pm 0.1^*$ (0.67 ± 0.04)	$1.3 \pm 0.2^*$ (0.4 ± 0.1)
Acetonitrile	n.d.	n.d.	n.d.	n.d.
Ethanol	6 ± 3 (3 ± 2)	5 ± 4 (4 ± 3)	$14 \pm 5^*$ (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/C_0)