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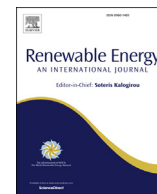
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Biogas composition from agricultural sources and organic fraction of municipal solid waste

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ABSTRACT

This paper presents an overview of biogas compositions originating from agriculture and the organic fraction of municipal solid waste. An intensive data compilation was performed from literature, plant data from an EU project (Waste2Watts) and from sampling campaigns at 5 different anaerobic digesters in Switzerland. Besides reporting the major components of biogas i.e. methane and carbon dioxide, the concentration of minor components such as nitrogen and oxygen, as well as trace amounts of sulfur compounds (H₂S, mercaptans, sulfides, etc.), silicon compounds (siloxanes, silanes), ammonia, halogenated compounds, and other volatile organic compounds (VOCs) are reported. These trace compounds can present a significant challenge to the energetic use of biogas, specifically in the use of novel, high-efficient processes such as high temperature fuel cells or catalytic fuel upgrading units. H₂S and other sulfur compounds are the major concern, as they are abundantly found in agriculture biogas; unlike silicon compounds, which are generally exist in low or undetectable levels.

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1. Introduction

The use of biogas in fuel cells presents a promising way to valorize biomass resources, especially at small scales (1–150 kW) where fuel cells hold a distinct efficiency advantage over electricity conversion via internal combustion engines. At these scales, high-temperature fuel cells (MCFCs and SOFCs) are already commercially available to be operated with natural gas (e.g., the 20 kW_e PowerPlus from Sunfire [1] or the 1.5 kW_e BlueGen from Solid-Power [2]). One of the key technical differences between natural gas and biogas for their use in fuel cells is the different chemical composition of biogas, both in bulk compounds and in trace compounds.

The first industrial size biogas-fed fuel cell system in Europe was started in 2017 in the framework of the DEMOSOFC project [3]. Two SOFC modules, for a total power of 100 kW, were installed in the SMAT Collegno wastewater treatment plant, in the Turin premises. The system has now reached more than 14'000 h of operation and

has demonstrated the advantages of biogas and fuel cells in terms of high electrical efficiency (>50%) and zero emissions to the atmosphere [4,5]. The plant concept includes a biogas cleaning system based on adsorption on activated carbons for the removal of H₂S and siloxanes (main contaminants detected in the sewage biogas locally produced from the wastewater treatment plant).

The major components of biogas are methane and carbon dioxide, where the methane fraction represents the useful energy resource. In addition to these, biogas can contain minor amounts (0–10%v levels) of nitrogen and oxygen, as well as trace amounts (ppb_v–ppm_v levels) of sulfur compounds (H₂S, mercaptans, sulfides, etc.), silicon compounds (siloxanes, silanes), ammonia, halogenated compounds, and other volatile organic compounds (VOCs). Additionally, biogas is much wetter than natural gas, generally being saturated with moisture at the temperature of the anaerobic digester (35–40 °C for mesophilic digesters, >50 °C for thermophilic digesters) or at the temperature of the downstream processes (e.g., a gas transfer line exposed to the ambient air after the digester).

The trace compounds existing in biogas can present a significant challenge to its energetic use. In particular, sulfur compounds in concentrations of a few ppm_v (or even ppb_v) can significantly

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Abbreviations

| | |
|-----------|---|
| b.d. | below detection limit |
| DMS | dimethylsulfide |
| FID | flame ionization detector |
| GC | gas chromatograph |
| ICE | internal combustion engine |
| LOD | limit of detection |
| LQ | liquid quench sampling system |
| MCFC | molten carbonate fuel cell |
| MS | mass spectrometry |
| NG | natural gas |
| n.m. | not measured |
| OFMSW | Organic Fraction of Municipal Solid Waste |
| ppmv/ppbv | parts per million/billion on a volume basis |
| SCD | sulfur chemiluminescence detector |
| SOFC | solid oxide fuel cell |
| VOC | volatile organic carbon |
| WWTP | wastewater treatment plant |

degrade any catalytic process which uses biogas. This includes novel, high-efficiency processes such as SOFCs or catalytic fuel upgrading units. The degree to which fuel cells are affected by these various compound classes was recently reviewed by Lanzini et al. [6]. According to this article, the most critical elements to be removed from biogas are sulfur compounds and siloxanes. The threshold tolerance limit of H_2S that high temperature fuel cells can withstand is 0.5 ppmv. Organic sulfur compounds decompose to H_2S at elevated temperatures (above 700 °C), therefore the same threshold tolerance can be considered for these compounds. Complete removal of siloxanes is needed as they block active pores and reduce the performance. There is no need to remove nitrogen, oxygen, VOCs and ammonia from biogas for direct use in fuel cells. Nitrogen acts as a dilutant and at small concentration levels does not affect the performance of fuel cells systems. Oxygen is a fuel reformer and as its concentration is often very low, its impact is negligible. Ammonia decomposes to H_2 at high temperatures, which then acts as a fuel for SOFCs.

The degree to which trace compounds exist in the biogas depends on a variety of factors, an overview of which are given in Fig. 1 using the example of biogas produced from manure. In this example, the biomass origins can vary, even when specifying that the primary component is manure: the manure can originate from different livestock raised under different conditions, it may be

differently available depending on the season (i.e., whether the livestock are kept in stalls or not). Then, co-substrates may also be added, which could come from different origins depending on what is available. The digester conditions (operating temperature, digester type, retention time) will also have an effect. Additionally, in-digester desulfurization methods (by micro-aeration or addition of iron compounds) can be used to reduce H_2S levels in the biogas.

The goal of this article is to present an overview of biogas compositions that can be expected from biogas originating from agriculture and organic fraction of municipal solid waste. To the best of our knowledge, this is the first scientific publication of collected data specifically on the trace compounds from these biogas sources. There is only scarce information available on the concentration of mercaptans, organic sulfur compounds and terpenes in particular. These contaminants are often found in low concentrations and do not need to be removed for traditional biogas engine applications (because of the higher tolerance limits) but are essential to be known for fuel cell applications, which have a much lower tolerance limit and where gas cleaning units must be designed taking into account all possible detrimental contaminants. Data collection is done by drawing upon available reports in the scientific and technical literature, site data from the EU project Waste2Watts [8], and sampling campaigns undertaken at three biogas production sites in Switzerland as part of a national project. The EU project Waste2Watts aims at designing innovative and low-cost cleaning solutions for fuel cells running on biogas, and a database on biogas composition is indeed fundamental in order to develop flexible gas cleaning solutions.

2. Methodology

The methodology for this article can be divided into two approaches: data collection and sampling campaigns. Data for landfill gas trace compounds has previously been compiled into a publicly available database from several plants by Papadakis and Ahmed at Argonne National Lab in 2012 [9,10]. Therefore, the exercise was not repeated here for landfill gas, and the data from Papadakis and Ahmed was used directly. Although wastewater biogas is not a focus for this project, compiled information also exists for these gases from Papadakis and Ahmed. However, there is currently a lack of summarized data available for biogas composition from agricultural and waste digestion. The lack of information especially affects non- H_2S contaminants, which are usually found in very low concentrations and are negligible – in terms of contamination – for traditional biogas engines. On the contrary, these contaminants could be, even at ppbv level, detrimental for a fuel cell system.

The data compilation focused on plants processing agricultural

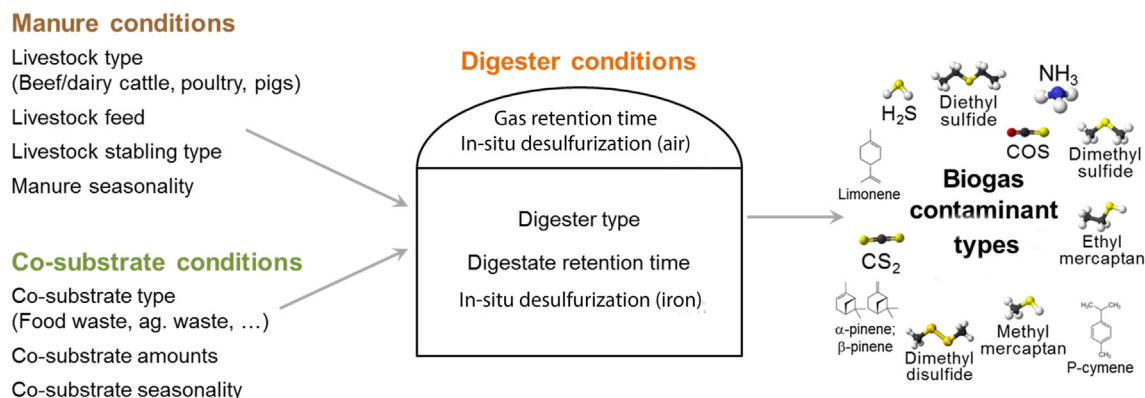


Fig. 1. Example of the variety of factors which affect trace biogas compositions, using manure biogas as the case study (Courtesy of [7]).

and food/municipal/industrial waste. This data was collected into a database inspired by the landfill gas database of Papadakis and Ahmed [9,10]. The literature and plant reports surveyed are summarized in Table 1, and overall represent data from more than 25 plants, to which data from sampling campaigns at 5 different anaerobic digesters in Switzerland are added. The complete survey including the bulk composition, sulfur, organosilicons, oxygenates, paraffin, aromatic and cyclic compounds can be found in an Excel database included as Supplementary Information.

The sampling campaigns were conducted at several Swiss biogas production plants processing manure with various amounts of co-substrates. In these sampling campaigns, bulk gas composition and trace contaminants were measured. The bulk compounds CH₄, CO₂, O₂, and N₂ in the biogas were measured offline by GC-TCD from samples of biogas collected in gas cylinders. The biogas was dried by passing through a cold solvent system, and was then compressed to 7 bar into sample gas cylinders. In order to avoid contamination from ambient air, the cylinders were filled with argon prior to sampling, and during the sampling campaign were purged twice with biogas before taking the biogas sample on the third filling process.

The trace compounds H₂S and NH₃ were measured on-site using colorimetric indicators, which are commercially available from Dräger [11]. Repeat measurements were performed, at least twice per sampling point, and more often if significant variability was observed. Other trace compounds were measured offline, by first sampling the biogas using a liquid quench (LQ) sampling system, which concentrates condensable trace compounds from the biogas into a liquid solvent [12,13]. By varying the ratio of biogas flow to solvent flow ("gas/liquid ratio"), the degree to which the trace compounds are concentrated in the solvent is varied. For each sampling point, a minimum of three samples were taken and analyzed. The analysis and quantification was done using a GC-SCD

(for sulfur-containing compounds) and GC-FID (for carbon-containing compounds). Certain samples were also analyzed by GC-MS to identify unknown compounds.

2.1. Sampling campaigns

The plants visited for biogas sampling are listed in Table 2 with key descriptions of the process specifics. The choice of plants was focused on manure-based systems, with increasing amounts of co-substrates (organic waste based) going down the table. The in-digester desulfurization methods used are also listed. These vary from plant to plant, with some using addition of gas phase air, others using addition of gas phase O₂ (reducing the N₂ impurities associated with air injection), others using addition of iron compounds in solution, and in the Ag/Waste-A and Ag/Waste-B case, using a mixture of desulfurization techniques.

3. Results

3.1. Gas composition: bulk, H₂S, NH₃

Bulk gas compositions at each of the sites sampled are shown in Table 3. Methane content at these sites was between 53 and 58% by volume. Despite significant variation in manure origin and co-substrate content, there was not a large difference in methane content between these sites.

In Table 3, we see the effect of the in-situ desulfurization strategy reflected in the nitrogen and oxygen contents of the biogas. For Ag-Cow and Ag-Mix, a continuous injection of air is used for in-situ desulfurization. By contrast, the Ag/Waste-A and -B digesters use injection of pure O₂ and air simultaneously (as well as addition of FeCl₂). Pure O₂, while markedly more expensive than direct air injection, allows in-situ desulfurization without

Table 1

Overview of data collected in this document for biogas composition from agricultural and waste substrates. The complete data set can be found in the Excel database included as Supplementary Information.

| Label | Description | Source |
|---------|---|------------------------------------|
| Ag01 | Farm mesophilic biogas plant in Laukaa, Finland, processing cow manure and confectionary by-products. | Rasi et al., 2007 [14] |
| Ag02 | Mesophilic digestion plant in Germany, processing pig and cow manure, waste from sugar factory, grapes, malt grain, salad, vegetable waste | Rasi et al., 2011 [15] |
| Ag03 | Mesophilic anaerobic digestion plant in Germany, processing grass/maize | Rasi et al., 2011 [15] |
| Ag04 | Aggregate of 12 dairy manure biogas sites in the United States. | Saber & Cruz 2009 [16] |
| Ag05 | Anaerobic co-digester in the Netherlands, processing >50% manure, <50% waste from agriculture products and industry. | Internal data |
| Ag06 | Anaerobic co-digester in the Netherlands (different from Ag05), processing >50% manure, <50% waste from agriculture products and industry. | Internal data |
| Ag07 | Farm-based mesophilic anaerobic digester in Switzerland ("Ag-Cow"), 100% cattle manure, from a dairy farm. | Internal data (sampled by authors) |
| Ag08 | Farm-based mesophilic anaerobic digester in Switzerland ("Ag-Mix"). Primarily chicken and cattle manure (>80%), and some vegetable and green waste. | Internal data (sampled by authors) |
| Ag09 | Farm-based anaerobic digester in Lithuania, 90% Manure + slaughterhouse, 10% crops | Internal data |
| Waste01 | Thermophilic co-digestion plant in Finland, processing sludge from wastewater and biowaste. | Rasi et al., 2011 [15] |
| Waste02 | Mesophilic wet fermentation plant in Germany, processing 45% glycerine, ~40% fatty sludge from biodiesel production, 15% cattle manure | Salazar Gomez et al., 2016 [16] |
| Waste03 | Thermophilic dry fermentation plant in Germany, processing 87% biowaste from residential areas, 10% green/garden waste, 3% husks. | Salazar Gomez et al., 2016 [17] |
| Waste04 | Mesophilic wet fermentation plant in Germany, processing a broad variety of wastes ("the substrate composition is very broad and the percentages change continuously.") | Salazar Gomez et al., 2016 [17] |
| Waste05 | Anaerobic digestion plant in Italy, processing the organic fraction of municipal solid waste. | Internal data |
| Waste06 | Anaerobic digestion plant in Austria, processing biowaste, food waste, commercial waste and sewage sludge | Internal data |
| Waste07 | Anaerobic digestion plant in the UK, processing 100% food waste. | Internal data |
| Waste08 | Anaerobic digestion plant in the UK, processing food waste. | Internal data |
| Waste09 | Mesophilic anaerobic digester in Switzerland (industrial-scale) | Internal data (sampled by authors) |
| Waste10 | Mesophilic anaerobic digester in Switzerland (industrial-scale) | Internal data (sampled by authors) |
| Waste11 | Biogas sample taken from the combined biogas production of (1) Ag/Waste-A (Waste09); (2) Ag/Waste-B (Waste10); (3) a thermophilic batch-type anaerobic digester. | Internal data (sampled by authors) |
| Waste12 | Anaerobic digestion plant in Italy, 2015–2016 | Internal data |

Table 2

Description of the origin biogas samples taken during the sampling campaigns.

| Label | Description | In-digester desulfurization |
|------------|---|--|
| Ag-Cow | Anaerobic digester processing dairy cow manure only, with no co-substrates. | Air addition (micro-aeration) |
| Ag-Mix | Anaerobic digester processing primarily chicken and cattle manure, and some vegetable and green waste. | Air addition (micro-aeration) |
| Ag/Waste-A | Mesophilic anaerobic digester processing a mixture of pig and cow manure (~40%) as well as waste from the food, dairy and beverage industry. | Air addition, O ₂ addition, and addition of Fe(II) solution |
| Ag/Waste-B | Mesophilic anaerobic digester processing the same feedstock as Ag/Waste-A (two parallel digesters). | Air addition, O ₂ addition, and addition of Fe(II) solution |
| Waste-Mix | Biogas sample taken from the combined biogas production of (1) Ag/Waste-A; (2) Ag/Waste-B; (3) a thermophilic batch-type anaerobic digester processing municipal green waste, horse/chicken/cow manure, garden waste, food waste, and industrial by-products. | Iron hydroxide addition in the thermophilic digester. |

Table 3Composition of bulk gases, H₂S, and NH₃ at the biogas sites surveyed. “b.d.” = below detection limit; “n.m.” = not measured.

| | CH ₄ (v%) | CO ₂ (v%) | N ₂ (v%) | O ₂ (v%) | H ₂ S (ppm _v) | NH ₃ (ppm _v) |
|-------------------|----------------------|----------------------|---------------------|---------------------|--------------------------------------|-------------------------------------|
| Ag-Cow | 54.9 | 39.0 | 5.0 | 0.9 | 400–1000 | 30–53 |
| Ag-Mix | 53.0 | 43.3 | 3.2 | 0.4 | 4–10 | b.d. (<0.25) |
| Ag/Waste-A | 57.7 | 40.8 | 1.2 | 0.3 | 18 | 70 |
| Ag/Waste-B | 56.9 | 41.3 | 1.3 | 0.5 | 2 | 70 |
| Waste-Mix | 57.2 | 42.3 | n.m. | 0.2 | 60 | n.m. |

increasing the N₂ content in the biogas. When upgrading of biogas to biomethane is the end goal, N₂ content must be kept low to meet natural gas pipeline specifications, and this is often a reason for using pure O₂ rather than air. The N₂ content in the biogas in Ag/Waste-A and -B is correspondingly lower than at the other sites, and the O₂:N₂ ratio is also higher.

Across all sites, the H₂S content varied from 2 ppm_v to 1000 ppm_v. Even at a single site, large variations could be observed. At the Ag-Cow site, six H₂S measurements were taken over the course of one sampling day, and results varied between 400 and 1000 ppm_v. The two wet digesters processing ~40% manure also had different measured H₂S contents (18 ppm_v and 2 ppm_v), despite processing the same feedstock under the same conditions, possibly indicative of different biology in-digester. Finally, although all sites used some form of in-situ desulfurization technique, the resulting H₂S content was still very variable. These results should not be used to compare H₂S results directly in order to make conclusions about the effectiveness of different desulfurization techniques on H₂S reduction; the other system variables are far too different. A systematic lab-based study would have to be done with the same feedstock in similar digesters with different desulfurization techniques to isolate these effects; this is beyond the scope of this paper. Nevertheless, it is important to report the variability in H₂S content that can exist site-to-site and even within a single day at a single site, in order to inform the operators of downstream biogas conversion systems (engines, fuel cells, methanation reactors, or otherwise) that this variability is to be expected in real systems even when in-digester desulfurization is used.

3.2. Trace compound measurements

A set of 21 sulfur compounds which could be expected in biogas were selected to calibrate the GC-SCD results and thus quantify the concentration of the compounds in the gases sampled. A set of 4 carbon-containing compounds (alpha-pinene, para-cymene, limonene, and siloxane D5) were also selected for quantification by GC-

FID. Although terpenes are not expected to harm high temperature fuel cells, they can affect the gas cleaning steps through competitive adsorption or pore blockage [7]. Siloxanes are harmful to fuel cells even at a level of 70 ppb_v [18] but are usually not expected in strictly manure-derived biogas. From the data collection performed, and discussing with biogas cleaning companies, it has been pointed out that siloxanes can be found in large agro-biogas sites, even from manure only. In particular, if stables cleaning is performed with a high level of standard detergents, which are then partially mixed with manure, it could be that siloxanes are then found in the biogas in low levels (as detected in the plant Ag09). Siloxanes are indeed linked, as demonstrated in sewage biogas applications, with the use of detergents and shampoos.

The results of this quantification are shown in Fig. 2. Shown on the left are the quantified carbon-containing compounds. None of the manure-based sites contained any detectable siloxanes. The only site to contain measurable siloxane D5, at a barely detectable value of 20 ppb_v, was the Waste-Mix source, which contains some industrial by-products which may be the origin of the siloxanes. Meanwhile, the amount of terpenes increased clearly with the amount of co-substrates processed. Ag-Cow, which only processes manure, had effectively no quantifiable compounds visible on GC-FID.

The 21 quantified sulfur compounds are plotted based on their chemical designation. The total sulfur is therefore separated into mercaptans (R–SH), sulfides as well as di- and tri-sulfides (R–S–R, R–S–S–R, R–S–S–S–R), thiophenes (containing a C₄H₄S ring), and sulfur heteroatoms. This category includes compounds like dimethyl sulfoxide, which contain other atoms—usually oxygen or nitrogen—beyond sulfur and a hydrocarbon base. Fuel cells are equally sensitive to sulfur atoms regardless of speciation (as noted by Madi et al. when comparing fuel cells' response to H₂S and thiophene [19]). However, classifying sulfur compounds in this way can be helpful for gas cleaning design. For example, many mercaptans are often removed well by H₂S sorbents, while volatile sulfides may not be (e.g., as observed by Ref. [20]).

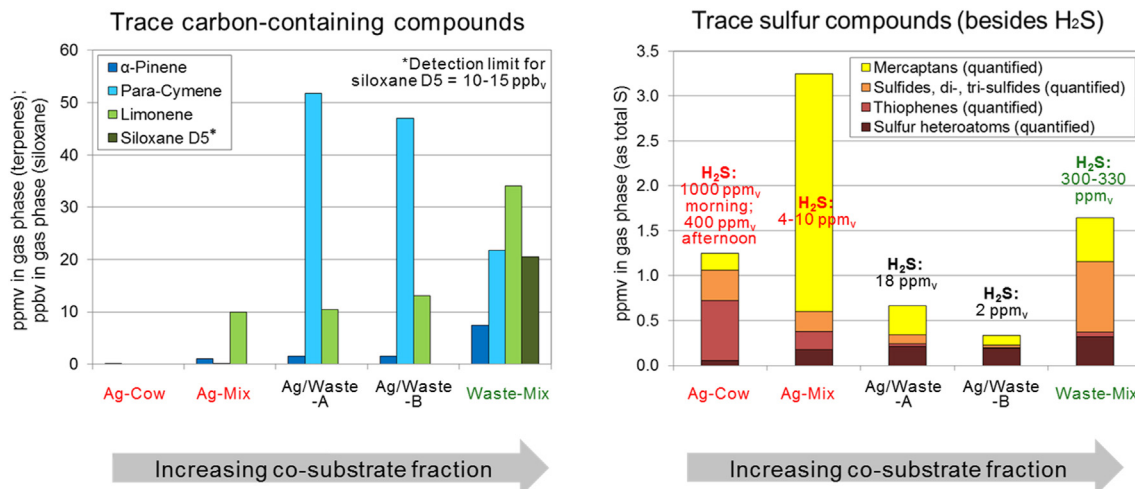


Fig. 2. Trace compounds quantified from the sampling campaigns.

From Fig. 2, it is clear that the trends in trace sulfur content do not necessarily follow the trends in H₂S content from Table 3 (which are overlaid on Fig. 2). Although the Ag-Cow site had by far the largest H₂S content, the Ag-Mix site had the largest quantifiable trace sulfur content. All sites sampled had total non-H₂S sulfur contents above the fuel cell limit of 0.5 ppm_s, except for Ag/Waste-B. Both Ag/Waste-A and Ag/Waste-B digesters had low sulfur content, both in terms of H₂S and of trace compounds. The three-fold in-digester desulfurization strategy used there may be a reason for this. However, there is a lack of knowledge regarding the effect of air/oxygen addition or iron salt addition on non-H₂S sulfur compounds, as most studies focus on the effect of these techniques on H₂S (eg. Ref. [21], for micro-aeration). One study has found that while iron chloride successfully reduces H₂S and several larger organic sulfur compounds from biogas, the volatile compound dimethyl sulfide is not affected [22].

3.3. Overview of bulk composition

The overview of the major gas compounds CH₄ and CO₂ summarized from the plants listed in Tables 1 and 2, as well as the minor compounds N₂ and O₂, is given in Table 4.

The range, median and mean values for CH₄ and CO₂ are similar for agricultural and waste biogas. However, the range is relatively broad, which means that biogas utilization techniques (fuel cells or otherwise) must account for possible significant site-to-site differences in CH₄ content—and thus in heating value. The range of expected CH₄ content in landfill gas is even wider, with older landfills producing gas with lower CH₄ fractions. In the framework of the DEMOSOFCE European project, it has been demonstrated – in a real industrial environment – that SOFC systems can work at different levels of CH₄ without any problems and guaranteeing a stable electrical efficiency level [5]. This is an advantage of fuel cell

Table 4
Summary of bulk biogas compositions.

| %v | Agricultural | | | Waste | | | Landfill | |
|-----------------|--------------|--------|------|-------|--------|------|----------|------|
| | Range | Median | Mean | Range | Median | Mean | Range | Mean |
| CH ₄ | 49–69 | 56 | 56 | 44–67 | 57 | 56 | 40–70 | 53 |
| CO ₂ | 29–44 | 39 | 40 | 30–44 | 38 | 37 | 25–40 | 35 |
| N ₂ | 0.6–13 | 3 | 3 | 0.1–6 | 1 | 1 | 0–17 | <5 |
| O ₂ | 0.2–3 | 0.6 | 0.6 | 0.1–3 | 0.4 | 0.6 | 0–3 | <1 |

systems compared to traditional biogas engines, which suffer performance drop with gases of low methane content and often require bi-fuel operation (with natural gas) in landfill gas sites.

Although low amounts of N₂ and O₂ can come intentionally from micro-aeration to achieve in-digester desulfurization, high values of N₂ and O₂ should be treated as outliers originating from leaks or uncontrolled operation, especially in the case of anaerobic digesters.

3.4. Overview of trace sulfur compounds

The overview of sulfur compounds contained in biogas from different sources is given in Table 5. These values are given in terms of ppm_v of sulfur rather than ppm_v of individual compounds, because from the point of view of fuel cells, it is the molar concentration of sulfur which matters, as each sulfur atom has the ability to block a catalytic site.

From Table 5, it is clear that there are wide variation in the content of sulfur in biogas. The median and mean (average) values were not significantly different from source to source, although landfill gas has a slight tendency to contain more sulfur in compounds other than H₂S, relative to the other two sources. However, the main point to notice is that the sum of total non-H₂S sulfur can often be above the fuel cell limit of 0.5 ppm_s, as shown in the Fig. 2. In cases where this limit is surpassed, it will be necessary to consider a two-step desulfurization process, one focusing on H₂S removal, and another focusing on removal or transformation of all sulfur compounds which are not retained directly in the H₂S removal step.

3.5. Overview of trace silicon, halogenated, and organic compounds

The overview of trace silicon, halogenated, and organic compounds in biogas from different sources is given in Table 6. Silicon compounds are given as mg_{Si}/m³_N, because the total accumulation of Si atoms is the relevant quantity for fuel cells, as each Si has the ability to form one SiO₂. According to Madi et al. [18], at the elevated temperatures of solid oxide fuel cells, siloxanes decompose mainly to SiO₂ and this compound is responsible for the degradation in the performance of SOFCs. Volatile organic compounds (VOCs) listed here included aromatic organic compounds, cyclic organic compounds (including terpenes), higher-order alkanes, and oxygenated compounds (furans, esters, ethers, alcohols,

Table 5Summary of trace sulfur compound concentrations. Note that *thiols* and *mercaptans* refer to the same compound class (R–SH).

| ppm _v S | Agricultural | | | Waste | | | Landfill | | |
|--------------------|--------------|--------|------|--------|--------|------|----------|--------|------|
| | Range | Median | Mean | Range | Median | Mean | Range | Median | Mean |
| H ₂ S | 7–6570 | 300 | 661 | 2–3174 | 250 | 688 | 0–5143 | 115 | 437 |
| Thiols | 0.1–10 | 0.4 | 1.3 | 0–7 | 0.4 | 0.1 | 0–7.7 | 1.3 | 2.2 |
| Sulfides | 0–5.5 | 0.2 | 0.8 | 0–6 | 0.2 | 1.5 | 0.1–2.6 | 0.27 | 0.49 |
| Thiophenes | 0–0.5 | 0.1 | 0.2 | 0–0.3 | 0.0 | 0.1 | 0–3.2 | 0.0 | 0.3 |
| Others | Also present | | | | | | | | |

Table 6Summary of trace silicon, organic, and halogenated compounds. Terpenes are included as cyclic organic compounds; *alkanes* designate higher-order linear or branched alkanes; oxygenated compounds include furans, esters, ethers, alcohols, and ketones.

| | Agricultural | | | Waste | | | Landfill | | |
|--|--------------|--------|-------|--------|--------|------|----------|--------|------|
| | Range | Median | Mean | Range | Median | Mean | Range | Median | Mean |
| Siloxanes mg_{Si}/m³_N | <0.02 | <0.02 | <0.02 | 0–3.4 | 0.5 | 1.0 | 0.1–11 | 2.3 | 3.0 |
| Aromatic & cyclic mg/m³_N | 0–293 | 1.3 | 60 | 52–705 | 383 | 362 | 22–1614 | 323 | 518 |
| Alkanes mg/m³_N | 0–0.8 | 0.4 | 0.4 | 9–65 | 14 | 26 | 44–5390 | 174 | 667 |
| Oxygenates mg/m³_N | 0–49 | 40 | 30 | 0–276 | 93 | 116 | 3–157 | 66 | 67 |
| Halogens ppm_v | – | – | – | – | – | – | 1–318 | 66 | 89 |

ketones). In principle, none of these are very problematic for high-temperature fuel cells, but they can affect gas cleaning processes, such that a sorbent targeting H₂S removal (for example) may see its capacity reduced by the competitive effect of the VOCs.

Siloxanes are important to examine carefully, as even 70 ppb_v of siloxane D4 has been observed to cause degradation in fuel cells [18]. For comparison with the mg_{Si}/m³_N values given in Table 6, 70 ppb_v of siloxane D4 corresponds to 0.345 mg_{Si}/m³_N. Siloxane concentrations are generally expected to be relatively low in agricultural biogas, as indicated in this table. However, there has been at least one instance of siloxanes being measured in biogas produced from energy crops (grass silage, grass, and maize) in lab-based assays [23]. In that case, it was speculated that these siloxanes may have had their origin in the growing presence of siloxanes in the natural environment (water, etc.).

Siloxanes are present to a greater degree in biogas from waste, as the substrates become more varied. Many of the waste-based biogas contained no siloxanes, especially if originating from food wastes alone. However, of the plants in Tables 1 and 2, the waste plant with the highest siloxane content processed 87% organic fraction of municipal solid waste and 13% garden/green waste [17]. It is then unclear where the siloxanes would originate from in that case. At the levels found in some waste biogas plants, and at the levels present in most landfill gas, a solution for removal of siloxanes is therefore needed to protect the fuel cell.

Halogenated compounds are present in measurable quantities only in landfill gas, based on the plants surveyed. The range of concentration of halogenated compounds found in landfill gas may not cause a degradation of high-temperature fuel cells, as experiments with 500 ppm_v of HCl in a test gas had no detrimental effect on a fuel cell stack [24].

3.6. Discussion

Some key limitations exist when considering data of trace compounds in biogas. First, available data is often scarce and generally incomplete. Although standard compounds (CH₄, CO₂, O₂, N₂, and H₂S) are often measured online at biogas plants, trace compounds typically require a dedicated sampling and off-line measurement campaign, which can be expensive. Therefore, data is limited to point measurements, which only represent a snapshot in time.

Moreover, biogas sampling for off-line analysis can result in at least two losses of information: first, there may be losses in sampling and in sample storage, and second, it is likely that not all compounds which reach the analyzer are identified and quantified. This can be illustrated by the example of the sampling campaigns in the biogas labeled Ag-Cow and Ag-Mix in Table 2.

It is known that no single sampling technique will be enough to sample all biogas contaminants fully [25]. In particular, high boiling point compounds are often not trapped well by gas-phase sampling because they have a tendency to adsorb on the walls of the sampling vessel; meanwhile, solvent- or sorbent-based sampling methods may not trap low boiling point compounds fully. The LQ sampling system used for the field sampling campaigns in Section 2 captures a wide range of boiling points due to its trapping system at 2 bar and –20 °C. However, we do not attempt to quantify trace compounds with boiling points lower than dimethyl sulfide's (38 °C) using this system, and even dimethyl sulfide is only trapped in the solvent at 50–80% depending on the set-point of the sampling system. The sampled values therefore represent minimum values.

After the biogas has been sampled and the sample has been stored correctly, the analysis is usually focused on a certain, non-exhaustive, set of compounds. Fig. 3 shows the GC-FID and GC-SCD chromatograms used to quantify the data from the sites Ag-Cow and Ag-Mix, reported in Fig. 2. A significant effort was placed during these sampling campaigns to identify and quantify as many trace sulfur compounds as possible, as these are the primary contaminants in agricultural biogas which are relevant for fuel cells. Nevertheless, some sulfur compounds remained unidentified and therefore unquantified. The same is true of any other sampling campaign: certain compounds will be emphasized during analysis.

It is therefore important to understand, when looking at an aggregate of biogas trace compound data, that the data listed can be considered a minimum value at the time of sampling, where the concentrations can change day-to-day or even hour-to-hour, and where some losses will occur in sampling, sample storage, and analysis.

4. Conclusions

An intensive data compilation was performed from literature and plant data from the EU project Waste2Watts, representing 27

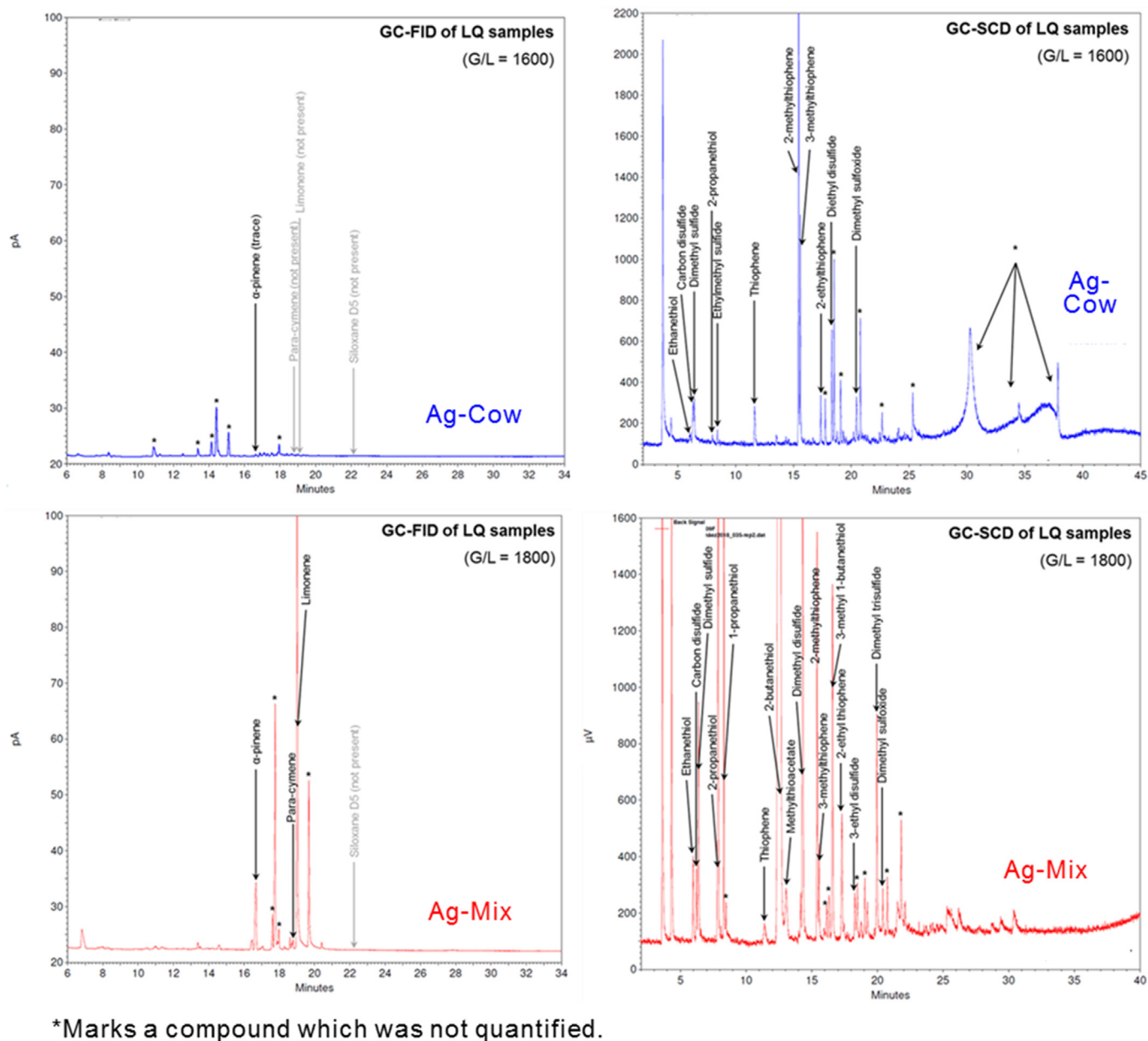


Fig. 3. GC-FID (carbon-containing compounds) and GC-SCD (sulfur-containing compounds) chromatograms of the biogas sampled at Ag-Cow and Ag-Mix.

plants either reported individually or grouped, to which data from sampling campaigns at 5 different anaerobic digesters in Switzerland were added.

Bulk analysis of the biogases shows that the range, median and mean values for CH_4 and CO_2 are similar for agricultural and waste biogas. However, the range is broad at ~45–70% CH_4 , which means that biogas utilization techniques (fuel cells or otherwise) must account for possible significant site-to-site differences in CH_4 content. Landfill gas CH_4 content can be even lower. Low amounts of N_2 and O_2 can come intentionally from micro-aeration to achieve in-digester desulfurization, but high values of N_2 and O_2 should be treated as outliers originating from leaks or uncontrolled operation, especially in the case of anaerobic digesters. Increasing the amount of food/green waste co-substrates in anaerobic digestion of manure results in an increased content of VOCs in the biogas, of which a significant fraction is present as mono-terpenes.

Trends in trace sulfur content do not necessarily follow the

trends in H_2S content – biogas with the highest H_2S content may not contain the highest trace sulfur, and vice versa. Even when in-digester desulfurization is used, the total sulfur content is still too high for fuel cells. In many cases, the sum of all trace non- H_2S sulfur content is also too high for a fuel cell, under the assumption that 0.5 ppm_v total sulfur is the maximum allowable limit. In those cases, this means that sulfur removal techniques must focus not only on H_2S but also on removing trace organic sulfur.

Silicon compounds generally exist in low or undetectable levels in agricultural biogas. They do exist above 70 ppb_v of siloxane D4, which has been shown to degrade fuel cell output [18], in some waste biogas. Most landfill gas contains siloxanes significantly above this value. This means that siloxane cleaning can generally be avoided when using agricultural gas, and in some waste biogas uses, but must be used in other waste biogas cases and for landfill gas.

When looking at data for trace biogas compounds, it is

important to remember that the data represents a minimum value at the time of sampling, where the concentrations can change day-to-day or even hour-to-hour, and where some losses will occur in sampling, sample storage, and analysis.

CRediT authorship contribution statement

Adelaide Calbry-Muzyka: Conceptualization, Methodology, Investigation, Writing – original draft. **Hossein Madi:** Writing – review & editing. **Florian Rüsche-Pfund:** Methodology, Conceptualization, Validation. **Marta Gandiglio:** Validation, Resources. **Serge Biollaz:** Conceptualization, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.renene.2021.09.100>.

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