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Original
Trace contaminants in biogas: Biomass sources, variability and implications for technology applications / Pera, Lucia; Gandiglio, Marta; Marocco, Paolo; Pumiglia, Davide; Santarelli, Massimo. - In: JOURNAL OF ENVIRONMENTAL CHEMICAL ENGINEERING. - ISSN 2213-3437. - 12:6(2024). [10.1016/j.jece.2024.114478]

Publisher:
Elsevier

Published
DOI:10.1016/j.jece.2024.114478

Journal of Environmental Chemical Engineering 12 (2024) 114478

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Trace contaminants in biogas: Biomass sources, variability and implications for technology applications

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ARTICLE INFO

Keywords:
Biogas
Biogas composition
Trace contaminants
Solid oxide fuel cells
Biomethane

ABSTRACT

Biogas represents a renewable and controllable energy source. Although predominantly composed of methane and carbon dioxide, it also contains various trace contaminants that can be detrimental to the technologies used for its conversion.

The aim of this work is to comprehensively explore trace contaminants in biogas. The assessment employs a two-level approach: an extensive literature review on biogas trace contaminants, complemented with on-site analyses from real-scale biogas plants to enhance and validate the literature findings. The biogas contaminants – sulphur compounds, siloxanes, halocarbons and aromatic compounds – are quantified and categorised into four distinct groups: landfill gas, agricultural gas, gas derived from the organic fraction of municipal solid waste (OFMSW), and gas from wastewater (WWTP). This study also provides contaminant effects and required thresholds for different biogas conversion technologies, including internal combustion engines, upgrading to biomethane, and innovative solid oxide fuel cells (SOFCs).

The two-level analysis reveals significant variability in contaminant levels across different biogas sources, with H_2S being the most prevalent contaminant, averaging between 181 (WWTP) and 901 ppm (landfill gas). Other sulphur compounds show the highest average concentration in biogas from OFMSW (98 ppm), followed by agricultural and landfill gases. Siloxanes are typically more abundant in biogas from WWTP (2.55 ppm), while landfill gas exhibits the highest average concentrations of halocarbons and aromatic compounds (6 ppm and 109 ppm, respectively). Moreover, this study highlights the need for in-depth measurements of contaminants for highly sensitive technologies, such as SOFCs, to properly design tailored contaminant removal solutions.

1. Introduction

The aim of the European Union (EU), according to the European Green Deal [1] and the Paris Agreement [2], is to transition to a climate-neutral society by 2050, limiting global warming to no more than 2°C above pre-industrial levels. These initiatives involve the integration of policies and actions across key sectors, including energy, industry, mobility and agriculture, in an attempt to promote a more circular economy while reducing greenhouse gas emissions. Consequently, it has become necessary to accelerate the deployment of clean energy technologies and move away from fossil fuels in order to limit the rise in the global temperature [3].

In this framework, the adoption of biogas can help guarantee a renewable and controllable energy production. Biogas can in fact be obtained from a variety of biomass sources, including agricultural waste, manure, municipal solid waste, and wastewater sludge. Moreover, its use not only mitigates the dependence on fossil fuels but also contributes to waste management [4], thereby aligning with circular economy principles. Biogas can be employed for electricity production in internal combustion engines, micro-turbines or innovative fuel cell systems. These solutions typically enables heat recovery, and thus work as cogeneration units. In addition, biogas can be upgraded to biomethane (by removing carbon dioxide and other impurities) and then introduced into the natural gas grid [5]. Alternatively, biomethane can be liquified and employed in the transport sector. The ambition of the REPowerEU Plan [6] is to boost the sustainable production of biomethane in Europe to 35 bcm by 2030 through specific measures and incentives.

Novel end-use technologies for biogas exploitation have recently appeared on the market; fuel cell devices in particular are gaining

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https://doi.org/10.1016/j.jece.2024.114478
Received 29 April 2024; Received in revised form 23 August 2024; Accepted 15 October 2024

Acronyms

AGRO	Agricultural gas.
bcm	Billion cubic metres.
BTEX	Benzene, toluene, ethylbenzene, xylene.
CHP	Combined heat and power.
CFC	Chlorofluorocarbons.
ICE	Internal combustion engine.
LFG	Landfill gas.
LOD	Limit of detection.
OFMSW	Organic fraction municipal solid waste.
ppb	Parts per billion.
ppm	Parts per million.
SOFC	Solid oxide fuel cell.
VOC	Volatile organic compounds.
WWTP	Wastewater treatment plant.

momentum for the production of electricity in stationary applications [7]. There is a wide range of typologies of fuel cell systems, mainly depending on the electrolyte material. While some solutions are already available on the market, others are still at the research stage. Among these, increasing interest has been shown in the high-temperature solid oxide fuel cell (SOFC) technology, mainly related to the improvements that have been made in the charge transport across components and component interfaces, which have led to enhanced electrical efficiency [8]. One example of their potential use is that of fuel cell-based combined heat and power (CHP) systems for residential buildings, which have already been studied in the literature [9] but also in real demonstration projects [10,11]. Moreover, SOFCs allow high-grade heat to be recovered [12] and the operation to be reversed from fuel cell mode to electrolysis mode [13]. Fuel flexibility is another relevant advantage [14], since SOFCs can easily be fed with various fuels, including hydrogen, but also natural gas, syngas and biogas. The first industrial-sized biogas-fed SOFC plant in Europe was introduced during the DEMOSOFC project, which had the aim of demonstrating the feasibility of an SOFC coupled with a wastewater treatment plant [15]. Langnickel et al. [16] analysed the performance of the biogas-fed SOFC modules involved in DEMOSOFC and found consistently high values for the electrical (50–55 %) and total (80–90 %) efficiencies. Moreover, the integration of SOFCs in existing biogas plants has been analysed and compared with traditional cogeneration systems (internal combustion engines) to understand the technical and economic benefits of the fuel cell-based solution, even when combined in hybrid layouts with micro-turbines, adsorption process (tri-generation) or locally available solar plants [17,18].

However, low-carbon fuels of biological origin contain species that can damage the end-use technologies, by acting as contaminants. These molecules (e.g., sulphur compounds) can cause degradation and corrosion phenomena and a consequent decrease in the performance of the system [19], thus necessitating a careful monitoring. The literature on this topic has concentrated on two main aspects: the necessity of precisely detecting trace contaminants and the typology and amount of contaminants across various biomass sources. Lecharlier et al. [20] conducted a review, in the former category, of all the existing techniques used to sample and evaluate the concentrations of trace contaminants in biogas, landfill gas and biomethane. The challenges linked to the sampling procedures used to detect trace contaminants were also examined in the study by Arrhenius et al. [21]. Other literature works have focused on the analysis of the typical trace contaminant levels in biogas from different sources and have also proposed removal system layouts. Papadias et al. [22] conducted a review on the biogas impurities encountered in stationary fuel cell applications, explored their effect on the performances of fuel cells, and recommended maximum allowable concentrations for some of them. Their study reported the presence of trace contaminants in landfill gas and anaerobic digestion gas and proposed an impurity removal system based on high-temperature desulphurisation. Lanzini et al. [23] conducted a comprehensive examination of the composition of biogas, analysing the typologies and quantities of contaminants present in both landfill gas and anaerobic digestion gas. They focused on various purification techniques aimed at mitigating the presence of harmful contaminants, thereby enhancing the overall quality and usability of biogas resources. Calbry-Muzyka et al. [24] also conducted an overview of the composition of biogas originating from agriculture and the organic fraction of municipal solid waste, gathering data from both literature sources and sampling campaigns. Some studies have investigated contaminant removal and upgrading technologies for specific case studies, albeit with limited information on the actual levels of the biogas trace compounds [25,26].

1.1. Aim and novelty of the work

Despite the growing research on biogas, existing literature falls short in covering a wide array of biomass sources and associated contaminant types. Most studies refer generally to anaerobic digestion gas without differentiating between the different biomass sources, or they focus narrowly on specific biogas plants. This gap in literature underscores the need for a more comprehensive analysis that encompasses a broader spectrum of biomass sources and related biogas contaminants.

The objective of the present work is to address this gap by providing a detailed mapping of the various species – present in biogas from different sources – that can harm end-use technologies, making it crucial to understand biogas composition. Impurities (i.e., sulphur compounds, siloxanes, halocarbons and aromatic compounds) are quantified and categorised based on the source, including landfill, agriculture, organic fraction of municipal solid waste and wastewater sludge. The primary outcomes include the levels of the contaminants found in biogas, presented as minimum-maximum intervals and average values. Moreover, this study introduces a novel dataset of trace contaminant levels derived from the monitoring of real-scale biogas plants. This additional analysis not only enhances the understanding of contaminants distribution but also strengthens the validity and applicability of the findings. The study also discusses the impact of biogas impurities on various technologies, along with their tolerance levels. Specifically, three main pathways for biogas utilisation are identified: direct use in internal combustion engines, supply to high-temperature fuel cells (SOFCs) and upgrading to produce biomethane for grid injection. These pathways lead to different outcomes – with the first two primarily generating electricity (and heat) and the latter producing a purified fuel – but are explored in this study as they represent the main technological applications for biogas plants [18]. A conceptual layout of the research study is illustrated in Fig. 1.

To sum up, this review provides a detailed literature analysis of biogas contaminants, complemented by a macro-composition analysis available in the Supplementary Material, and reinforced by a novel dataset from real-scale biogas plants. It also presents an overview of the impact of these contaminants on key end-use technologies and the required tolerance levels. The ultimate goal of this comprehensive assessment is to help determine the suitability of biogas for different applications and to guide the modelling and design of appropriate cleaning, upgrading and utilisation technologies.

The paper is structured as follows: an extensive literature review of the main biogas contaminants is presented in Sections 2 and 3: data concerning impurity concentrations are collected and categorised according to the biogas source. Section 4 aims at investigating additional data from real-scale biogas plants, while maintaining the same classification based on biogas origin. Section 5 is devoted to an exploration of the limits of contaminants, focusing on solid oxide fuel cells, internal combustion engines and upgrading to biomethane. Finally, conclusions are drawn in Section 6.

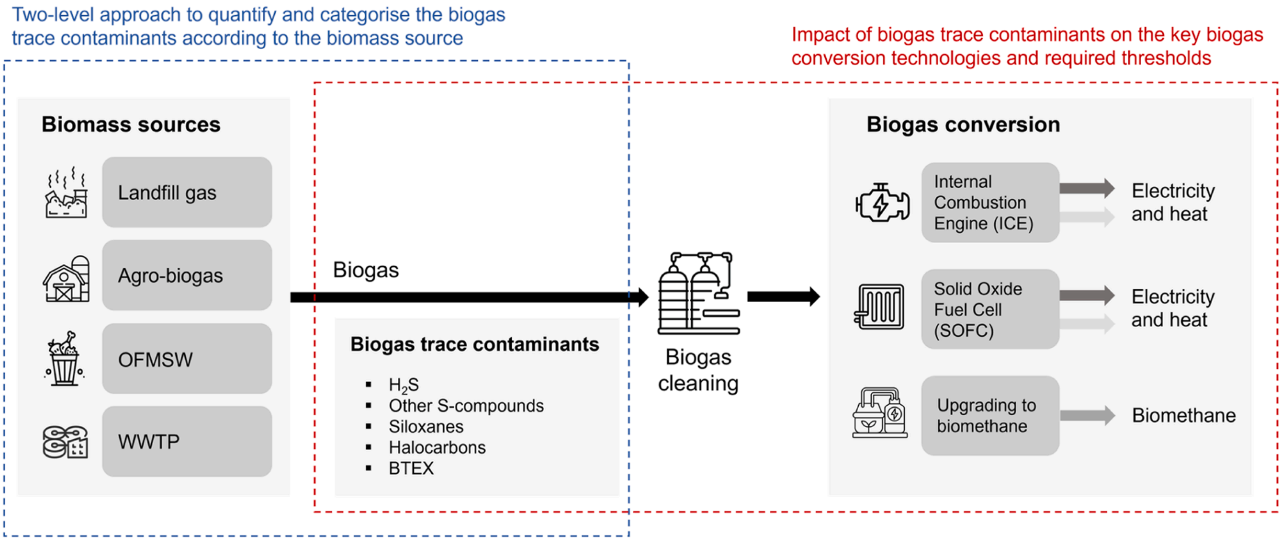

Fig. 1. Conceptual layout of the research study.

2. Biogas composition: trace contaminant analysis

This section delves into the fundamental components that constitute biogas and offers a general foundation to help understand its composition. After this first exploration, the focus is shifted to an examination of the primary contaminants that are usually detected in biogas.

Biogas is a renewable energy source that is mainly composed of a mixture of methane (CH_4) and carbon dioxide (CO_2), where the fraction of CH_4 represents the energy source. It usually contains 45–75 % per volume of CH_4 and 25–55 % per volume of CO_2 [27]. An upgrading process can be applied to remove CO_2 and impurities from biogas in order to obtain biomethane with a higher concentration of CH_4 (typically higher than 95 %vol.) [28]. Apart from the two main components (CH_4 and CO_2), biogas also contains smaller amounts of nitrogen and oxygen, which are in the 0–10 % per volume range. In addition, trace amounts of substances such as sulphur compounds, silicon compounds, ammonia, halogenated compounds and other volatile organic compounds (VOCs) are usually detected. Although the amounts of trace components are typically limited to ppb_v or ppm_v, they can have environmental and/or human health impacts and degrade any catalytic process that uses biogas [29]. The type and the concentration of biogas contaminants depend on several factors, as Calbry-Muzyka et al. [24] explained when they considered manure biogas as a reference. Indeed, in the case of manure, the conditions can differ on the basis of the livestock type (i.e., beef, dairy cattle, poultry, pigs), livestock feed, livestock stabling type and manure seasonality. In addition, the type, amounts and seasonality of co-substrates fed into the digester can also influence biogas composition. The digester type and operating conditions, such as temperature, gas and digestate retention times, and in-situ desulphurisation processes, further impact contaminant levels. Moreover, the variability of trace impurities becomes even greater when considering different biogas sources.

Fig. 2 provides a general scheme of the impurities found in biogas. Regardless of the source, the main contaminants found in biogas can be categorised into four different groups:

- Sulphur compounds, including both hydrogen sulphide (H_2S) and other sulphur-based compounds
- Siloxanes
- Halocarbons
- Benzene, Toluene, Ethylbenzene, Xylene (referred to as BTEX).

The following sub-Sections (2.1 to 2.4) offer an overview of the primary contaminants that have been found in raw biogas. An extensive investigation has been carried out, whereby data and information were collected from several literature sources. The considered sources encompass landfill gas (LFG), agricultural gas derived from livestock and green waste (AGRO), gas generated from the organic fraction of

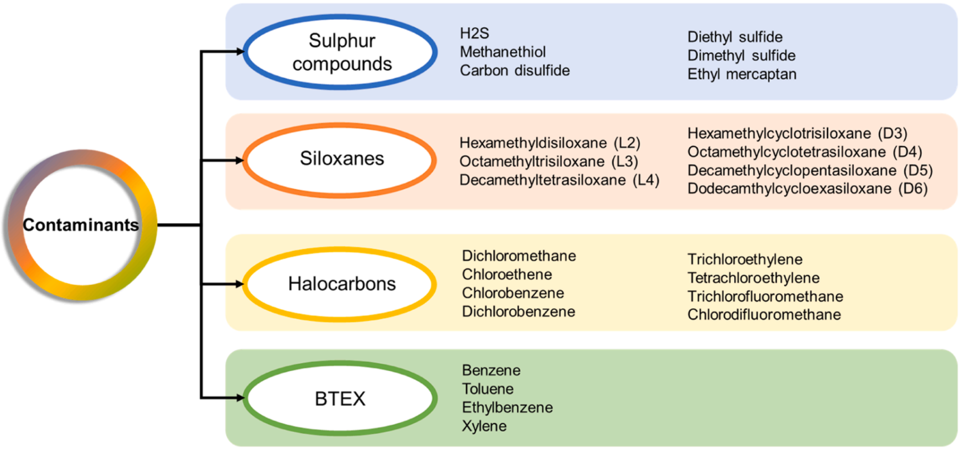

Fig. 2. The main contaminants in biogas.

municipal solid wastes (OFMSW) and gas originating from industrial wastewater (WWTP). A graph has been produced for each typology of contaminant, where the difference in concentration of each biogas source can be appreciated. In addition, since some species have a wide variation from one source of biogas to another, a zoom into each range has been made to better identify the minimum, maximum and average values. Tables containing all the literature data for the various biogas sources are available in Supplementary Material. The technical issues induced by the contaminants are discussed, along with the challenges encountered in various end-uses. Concerning the “Impact on technologies” sub-sections, this study specifically examines internal combustion engines and solid oxide fuel cells. Since there are numerous technologies for biogas upgrading to biomethane, this would require a separate ad-hoc study, which has already been addressed in [30,31]. All the values shown in this work are expressed as parts per million on a volume basis (ppm_v): for the sake of simplicity, the subscript is not specified, and the numbers are referred to as ppm.

2.1. H_2S and other sulphur compounds

Among the several contaminants that can be found in biogas, sulphur compounds, including hydrogen sulphide, carbonyl sulphide, mercaptans and disulphides, are the most abundant and common to all biogas sources. The organic sulphur content ranges from ppb to a few ppm, while the bulk of sulphur species is found as H_2S at concentrations of up to several thousand parts per million.

2.1.1. Concentration

The biogas source influences the amount of H_2S [32]. Papadias *et al.* [22] stated that the highest level of sulphur was found in digester gas obtained from manure and dairy waste. Biogas from wastewater also contains H_2S, but it usually has a lower concentration. Indeed, iron salts are often used in the water treatment process to remove phosphorous, which have to satisfy limit regulations. However, these salts are also able to reduce the overall sulphur content, since Fe^{3+} oxidises sulphide chemically to elemental sulphur, reducing to Fe^{2+}, which consequently causes the formation of ferrous sulphide (FeS) [33–35]. Landfill gas (LFG) contains most of sulphur in the form of H_2S, and this reaches a high concentration when large quantities of plasterboard, wastewater sludge or flue gas desulphurisation sludge have been deposited [22].

The first analysed contaminant, i.e., hydrogen sulphide, is the most hazardous and diffused. It has emerged from several studies that this contaminant was detected in all the considered biogas sources, even though the amount changed significantly [23,36]. Fig. 3 shows the H_2S concentrations of the different sources of biogas. It is clear that there is a large variation in its content across various sources. As mentioned earlier, the largest amounts are observed in agriculture biogas, where it reaches maximum values of 6570 ppm (red bar). Landfill gas follows closely behind at 5400 ppm (green bar); however, the average value is greater than that of agricultural gas. This discrepancy can be attributed to the wide range of data collected for landfills. In fact, landfills are unstable systems, and the quality of the extracted gas depends to a great extent on its lifetime. On the other hand, in the case of agricultural gas, some papers have reported maximum values that are not so high [37,38], which has led to a reduction in the average value. Wastewater H_2S concentrations show a reduced range, which is even smaller in the case of gas originating from the organic fraction of solid waste.

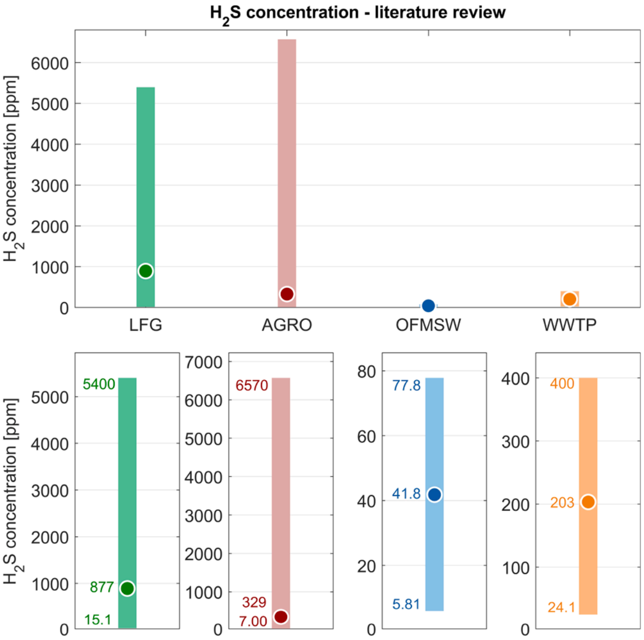

Fig. 3. Contaminant concentrations of H_2S from different sources of biogas taken from the literature review. The aim of the upper graph is to represent a comparison between the four typologies of biogas sources, while the lower graphs focus on the minimum, average and maximum values of each bar. The complete list of the data considered in the analysis can be found in the Supplementary Material section.

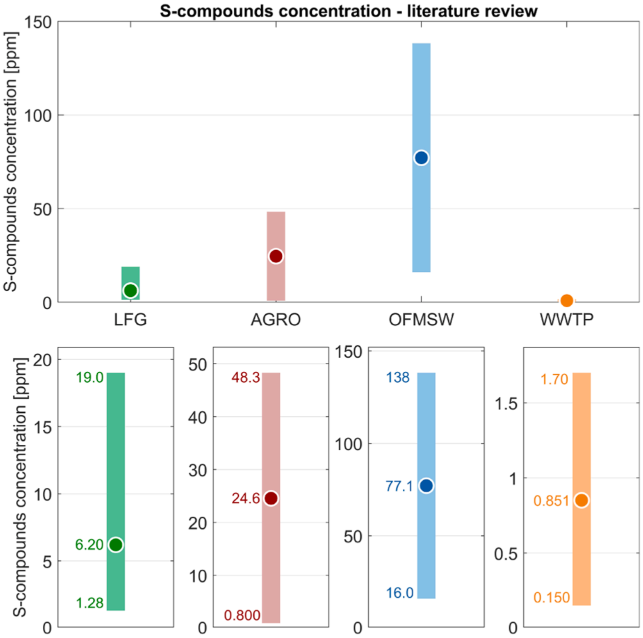

Fig. 4. Contaminants concentration of sulphur compounds (excluding H_2S) from different sources of biogas taken from the literature review. The aim of the upper graph is to represent a comparison between the four typologies of biogas sources, while the lower graphs focus on the minimum, average and maximum values of each bar. The complete list of the data considered in the analysis can be found in the Supplementary Material.

Other sulphur compounds (which are commonly referred to as S-compounds and consider all the sulphur species except H_2S) are represented using the same visual representation (Fig. 4). In this study, as also suggested in the analysis of Calbry-Muzyka et al. [36], the sulphur content does not necessarily follow the trends of H_2S. Indeed, the highest value is registered for the organic fraction of municipal solid waste (blue bar), which is the one that shows the lowest mean value of the H_2S concentration. The sulphur compound category typically encloses sulphides, mercaptans and SO_2. However, this representation does not specify the amount of each contaminant, which is discussed later on. Another toxic volatile organic sulphur compound is carbonyl sulphide (COS), which has the potential of exploding under certain mixing ratios with air. Santoni et al. [39] analysed several sorbents for the COS contaminant to understand which offered the best removal performance.

2.1.2. *Impact on technologies*

When biogas is employed in internal combustion engines (ICEs), an increased concentration of hydrogen sulphide results in oil acidification and diminishes the oil lubrification properties. Sulphur deposition occurs within the exhaust gas heat exchanger when the temperature falls below the dew point [40]. Furthermore, the presence of sulphur in the inlet gas is closely correlated with the presence of SO_x pollutants in the exhaust gases.

Other sulphur compounds, such as hydrogen sulphide, carbonyl sulphide and methyl mercaptan can induce an initial drop in cell voltage in solid oxide fuel cells, typically below concentrations of 5 ppm. This is usually followed by a stable cell voltage [41]. Indeed, sulphur species deactivate the catalyst in the reformer and in the fuel cell anode by reacting with the metals to form sulphides [22]. As reported by Papurello et al. [42], hydrogen sulphide influences the performance of fuel cells, and can lead to a double degradation, which generally involves short-term and long-term effects. Among the short-term effects, the fast physisorption and chemisorption of sulphur causes the deactivation of the three-phase boundary. On the other hand, the main effect of long-term sulphur exposure is related to micro-structural changes, such as the formation of bulk nickel sulphide, Ni-particle coarsening or nickel migration. The former poisoning process leads to an initial drop in the cell voltage, while the latter causes a larger voltage drop [43,44]. Unfortunately, the harmful effects of other sulphur compounds have not been explicitly addressed in the literature.

2.2. *Siloxanes*

Siloxanes are organic, linear or cyclic silicon (Si) compounds. Organic siloxanes are semi-volatile compounds that can volatise in an anaerobic digester (where temperatures above 40°C are reached) and end up in the biogas. Cyclic siloxanes are indicated with the letter D, while linear compounds are indicated with the letter L or M [45]. The number following the letter refers to the amount of silicon in the molecules. Among the many different siloxanes in use, those most commonly found in landfill gas and biogas are L2-L5 and D3-D6. Of these, D3 is difficult to detect and quantify and, in addition, it is unstable and condenses easily. The most frequent compounds in sewage biogas are cyclic volatile polydimethylsiloxanes (D4, D5), with the D5 concentration being several times higher than D4.

2.2.1. *Concentration*

Siloxane compounds are used in many industrial processes and consumer products, such as hygiene products, cosmetics and biopharmaceuticals, adhesives and coatings, fuel additives, car waxes, detergents and defoamers. Siloxanes, because of their origin, are widespread in the sludge of wastewater treatment plants. Landfill gas contains lower amounts of these compounds. Other biogas sources show even lower amounts of siloxanes [46]. As discussed in Lanzini et al. [23], biogas from manure, pure food waste and dairy streams typically does not contain siloxanes.

These considerations were validated by referring to the data collected from literature studies, as shown in the results presented in Fig. 5. As can be noted, there are marked differences in the siloxane concentrations for different biogas sources. OFMSW biogas (blue bar) exhibits remarkably low levels (0.826 ppm as the average value), while agricultural gas registers an even lower level, which is almost negligible. On the other hand, the highest value is detected in wastewater gas (2.55 ppm), followed by landfill gas. McBean [47] provided insights into this phenomenon and explained that siloxanes have high vapour pressures and low water solubilities under the typical temperature conditions of wastewater treatment and landfill sites. Consequently, they volatise and are thus transported into the biogas stream, and this can lead to elevated concentrations in these sources.

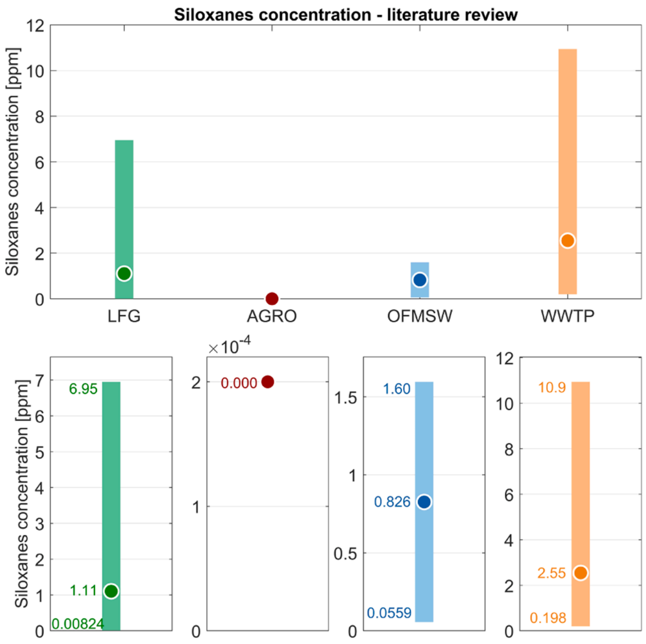

Fig. 5. Contaminant concentrations of siloxanes in different sources of biogas from the literature review. The aim of the upper graph is to represent a comparison between the four typologies of biogas sources, while the lower graphs focus on the minimum, average and maximum values of each bar. The complete list of data involved in the analysis can be found in the Supplementary Material.

2.2.2. *Impact on technologies*

Gaseous siloxanes are not reactive or corrosive as such in internal combustion engines but are transformed into hard and abrasive silica in the combustion chamber of the engine [23]. Siloxanes form a lacquer coating on any engine surface in contact with oil and can thus alter the surface finish of cylinders oil retention. As Arnold stated [40], a gaseous silica microcrystalline is formed during the combustion of siloxanes, which has similar properties to those of glass. This very hard substance causes an abrasion of the surfaces of the motor and acts as a thermal insulator on the surface. As an electrical insulator, silica compromises measurements in the combustion chamber and represses the functioning of the spark plugs. Silica, in addition to causing engine damage, covers ignition plugs, cylinders, cylinder heads, valves and emission catalysts with a white deposit, and hinders the possible catalytic treatment of exhaust gases [45].

Siloxane impurities lead to the formation of SiO_2 on the anode of the solid oxide fuel cell [48], which in turn causes a degradation of the cell voltage [23] and affects several components of the fuel cell system [22]. Siloxanes can be analysed by means of two techniques: offline analysis and online analysis. The offline analysis is based on gas-chromatography, while the online measurements only allow moderate limit of detection (LOD) values to be obtained and therefore need continuous validation through offline methods [49].

2.3. *Halocarbons*

Halocarbons refer to compounds that are emitted from anthropogenic sources, and are typically employed as solvent cleaners, refrigerants, and additives in the plastic and metal manufacturing sectors. These substances are anthropogenic in origin and contribute significantly to atmospheric pollution. Additionally, they are known to have adverse effects on the environment, including ozone depletion and greenhouse gas emissions [50]. They are mainly classified as chlorofluorocarbons (CFC), chloroalkanes, chloroaromatics, and other halocarbons [38]. The main components in the category are CFC, which are used as refrigerants, and chloroalkanes, which are commonly diffused as degreasers. Chloroalkanes include dichloromethane, trichloromethane, chloroethene, and dichloroethane [23].

2.3.1. Concentration

Li *et al.* [38] analysed different sources of biogas and found that landfill biogas has the highest total halocarbon concentration. On the other hand, dairy and food waste biogas exhibited lower halocarbon concentrations. Allen *et al.* [51] carried out a study in which they sampled landfill gases at seven sites and analysed them to identify the main potential sources of these compounds. They discovered that the majority were chlorofluoro- compounds, accounting for up to 95 % of the total chlorine measured in landfill gases. The authors also noted that the waste composition affected the variations in CFC concentrations to a great extent. CFCs are not influenced by biological decomposition processes, since they arise from the direct volatilisation of compounds contained in plastic foam, aerosol propellants and refrigerators. Some other authors have focused their attention on the removal of chlorinated compounds. For instance, Shin et al. [52] analysed purification through the use of granular activated carbon.

The data depicted in Fig. 6 are aligned with those of the existing literature. Indeed, it can be observed that the highest concentration of halocarbons is found in landfill gas (green bar, average value of 6.03 ppm). On the other hand, agricultural gas, the organic fraction of municipal solid waste and wastewater treatment plant biogas show relatively low levels of halocarbons in raw biogas. However, it should be underlined that there is limited literature available on the concentration of halocarbons in raw biogas. As a result, unambiguously understanding their quantity can be a challenging task.

2.3.2. Impact on technologies

As far as internal combustion engines are concerned, no significant information has been found in relation to the negative impact of halocarbons.

However, it has been observed that the existence of halocarbons, and in particular chlorine compounds, leads to the formation of $NiCl_2$, which results in cell degradation [25,41] in high-temperature fuel cell systems. In particular, chlorine causes an initial degradation of the cell voltage, although reversibility is possible, albeit only when the contaminant is substituted with pure gas. However, the cell suffers from a change in its anode microstructure, which is observed not only near the interface with the electrolyte, but also in the centre of the anode itself [53].

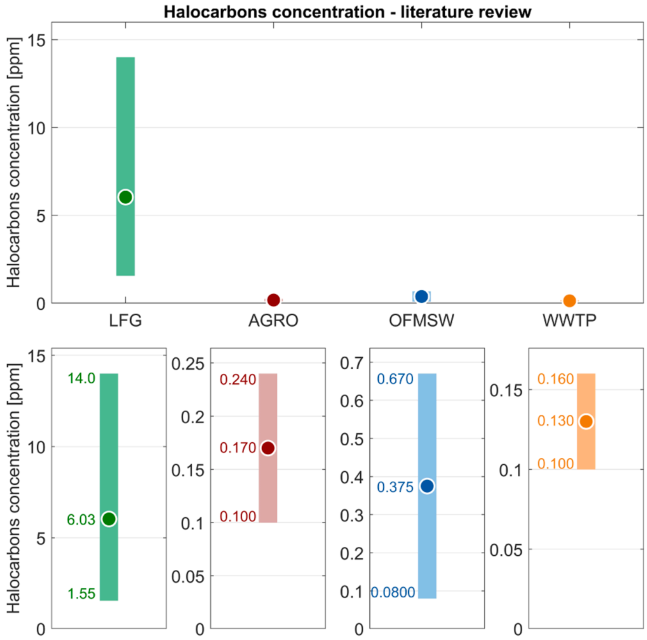

Fig. 6. Contaminant concentrations of halocarbons in different sources of biogas from the literature review. The aim of the upper graph is to represent a comparison between the four typologies of biogas sources, while the lower graphs focus on the minimum, average and maximum values of each bar. The complete list of data involved in the analysis can be found in the Supplementary Material.

2.4. Benzene, toluene, ethylbenzene, xylene (BTEX)

The aromatic compounds that occur the most in biogas are benzene, toluene, xylene and ethylbenzene, which are found at higher concentrations than other aromatic compounds. The category is called BTEX for short.

2.4.1. Concentration

The amount of the concentration of a compound depends to a great extent on the decomposition process and the source of the waste [54]. According to Salazar Gòmez et al. [55], the most significant contribution of the various aromatics is from toluene, which is a common component of landfill gas and sewage gas. In their work, they showed that the concentration of toluene in a landfill is generally higher than that of farm biogas, because it is commonly used in industry as a solvent, carrier, in rubber, printing, cosmetics, adhesives and resin. Another aromatic usually found in landfill gas is benzene, which is a natural component of crude oil, and thus is likely to be found in industry wastes [37].

Fig. 7 points out that landfill gas (green bar) has one of the highest BTEX concentrations, followed by agro-biogas (13.2 ppm as an average value), while other sources have negligible values.

2.4.2. Impact on technologies

No relevant information has been found on halocarbons in relation to the negative impact of BTEX on internal combustion engines.

This concentration is not typically hazardous for SOFC, but aromatic hydrocarbons can greatly reduce the clean-up capacity of various adsorbents used for siloxane removal [22]. No additional information is

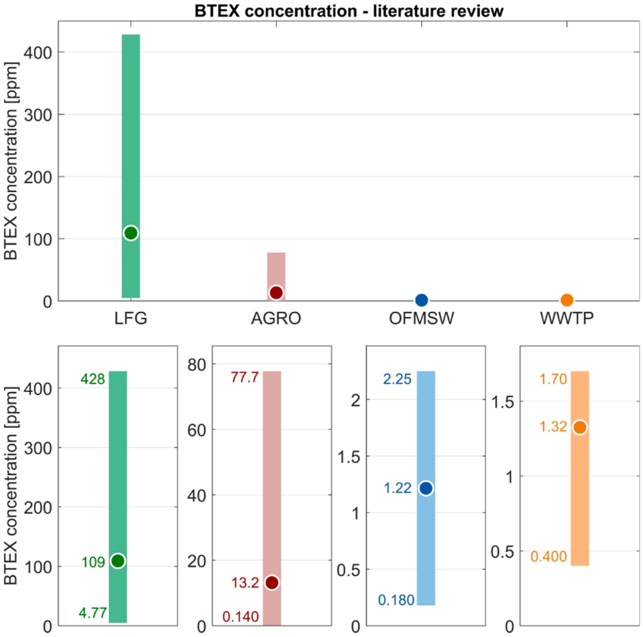

Fig. 7. Contaminant concentrations of BTEX in different sources of biogas from the literature review. The aim of the upper graph is to represent a comparison between the four typologies of biogas sources, while the lower graphs focus on the minimum, average and maximum values of each bar. The complete list of data involved in the analysis can be found in the Supplementary Material.

available about the poisoning effect of aromatic compounds in solid oxide fuel cells fed by anaerobic digestion gas. However, BTEX contaminants, especially benzene and toluene, are generally taken as representative molecules of the TARs found in syngas. In this context, although different sources of biogas considered, many studies have been conducted related to the effect of TAR contaminants from the gasification of biomasses in the SOFC field [56].

3. Biogas composition by source

After conducting an analysis on the specific categories of contaminants, a more comprehensive overview of the different sources was conducted. The aim was to give and overview on the level of contaminants for the four biogas types. Table 1 shows the ranges (minimum-maximum values) of the major contaminants discussed herein and the average values obtained from the literature review. The Supplementary Material presents additional tables listing all the data analysed, classifying the contaminants on the base of the biogas source.

A more accurate depiction of the contaminant profiles across different biogas sources was obtained by aggregating the data, and this could assist in decision-making processes regarding biogas utilisation options and contaminant mitigation strategies. In addition, the distribution of specific species within certain contaminant families was also analysed. The results (presented as average values from the literature analysis) are shown in Fig. 8.

Starting from an examination of the landfill waterfall chart (Fig. 8a), it is evident that H_2S makes the predominant contribution and accounts for approximately 90 % of the total level of contaminants (877 ppm). BTEX compounds (109 ppm) follow H_2S, while sulphur compounds, siloxanes and halocarbons contribute negligibly (< 6.2 ppm). Two pie graphs further illustrate the distribution of sulphur and BTEX within landfill gas. The majority of sulphur is attributed to the presence of methanethiol (81 %), and this is followed by dimethyl sulphide. On the other hand, the distribution of aromatic compounds is more even, with toluene and ethylbenzene each constituting around 40 % of the total BTEX, followed by xylene, while benzene accounts for a smaller portion.

H_2S is again the most abundant contaminant (329 ppm) in the case of agricultural biogas (Fig. 8b), followed by sulphur compounds, which on average account for 24.5 ppm. Almost 50 % of the sulphur, excluding H_2S, is given by sulphur dioxide, while mercaptans cover 35 %. The remaining part is instead covered by sulphides that do not include H_2S. As previously discussed, there are almost no siloxanes in agriculture biogas, small quantities of halocarbons and alkanes have been detected, and BTEX shows a level of 13.2 ppm.

It can be noted, by analysing the waterfall graph for biogas derived from the organic fraction of municipal solid waste (Fig. 8c), that H_2S contributes less to the total contaminant level than the other sources (41.8 ppm). Indeed, the predominant contaminants are sulphur compounds (77.1 ppm). Sulphur dioxide and mercaptans exhibit nearly equal proportions, each constituting about 40 % of the total, while the rest is covered by non-H_2S sulphides. This composition closely resembles that described for the agricultural source, thereby underscoring similarities in the sulphur content between these two sources. Furthermore, other contaminants are present in somewhat small amounts, which can be considered negligible (< 1.2 ppm) with respect to the total quantity of impurities.

Finally, the waterfall graph of the wastewater biogas source (Fig. 8d) shows that H_2S accounts for most of the overall contaminant level, with a mean value of 203 ppm. Conversely, sulphur compounds are limited, as are siloxanes, halocarbons and BTEX (all below 2.55 ppm). Alkanes and TVOC cover a significant percentage of the total level, that is, about 25 % and 11 %, respectively. No pie graph is provided for these sources since an insufficient amount of data was available.

4. Biogas composition from real-scale biogas plants

The aim of the following section has been to provide further insights into contaminant concentrations by investigating additional novel data measured in various real-scale biogas plants located throughout Northern Italy. This novel dataset has been used to supplement the existing literature findings and to provide a more comprehensive understanding of the composition of biogas. Attention was focused on several plants in the Piedmont region, and the biogas sources were distinguished and classified according to the same previously used classification, that is, landfill gas, agricultural gas, OFMSW gas and wastewater gas.

The locations of the investigated plants are reported in Fig. 9, and they are marked with different colours to better understand the source of the produced biogas. The agricultural biogas plants were selected from a database of available biogas plants in the "Consorzio Monviso Agroenergia (CMA)" [57], which includes a total of 175 plants in Piedmont. Only plants that have conducted a detailed contaminant analysis were selected for this work. The data concerning other plants for landfill, OFMSW and WWTP biogas were received directly from other companies, and historical data were averaged when available.

The analyses were typically conducted testing with regular frequency (e.g. once per year) and several datasets were thus available. The range (minimum-maximum value) and the average representative value of each contaminant were evaluated from the historical data. Data from different plants with the same biogas origin were then averaged, and the minimum and maximum levels were registered as absolute limits for that biogas category.

Biogas analyses are commonly performed in biogas plants to ensure compliance with the regulations. However, not all contaminants are routinely detected, due to the associated costs, particularly when they are not strictly necessary to satisfy the regulatory framework. Table 2 shows a summary of the contaminants obtained from the novel dataset. The term n.a. indicates contaminants that are not analysed in the plant. Additional data on the macro-composition (CH_4, CO_2, O_2, N_2, H_2, CO and NH_4) for the different biogas sources can be found in the Supplementary Material.

The detailed comparison of the four biogas sources is only presented for H_2S, because of the limited data available for other contaminant categories. The obtained results are presented in Fig. 10. The contaminant levels are highly variable over time and, as a consequence, the ranges for each source are very wide. It can be observed, by analysing

Table 1

Average values and range (min-max) of all the contaminants found in different biogas sources from the literature review. Sulphur compounds include all sulphur species except H_2S. The values are all expressed in ppm.

Literature Review								
Contaminants	**LFG**		**AGRO**		**OFMSW**		**WWTP**	
	Avg	**Range**	**Avg**	**Range**	**Avg**	**Range**	**Avg**	**Range**
H_2S	**877**	15.1–5400	**329**	7.00–6750	**41.8**	5.81–77.8	**203**	24.1–400
Sulphur compounds	**6.20**	1.28–19.0	**24.6**	0.800–48.3	**77.1**	16.0–138	**0.851**	0.150–1.70
Siloxanes	**1.11**	0.00824–6.95	**0.00**	0.00	**0.826**	0.0559–1.60	**2.55**	0.198–10.9
Halocarbons	**6.03**	1.55–14.0	**0.170**	0.100–0.240	**0.375**	0.0800–0.670	**0.130**	0.100–0.160
BTEX	**109**	4.77–428	**13.2**	0.140–77.7	**1.21**	0.180–2.25	**1.32**	0.400–1.70

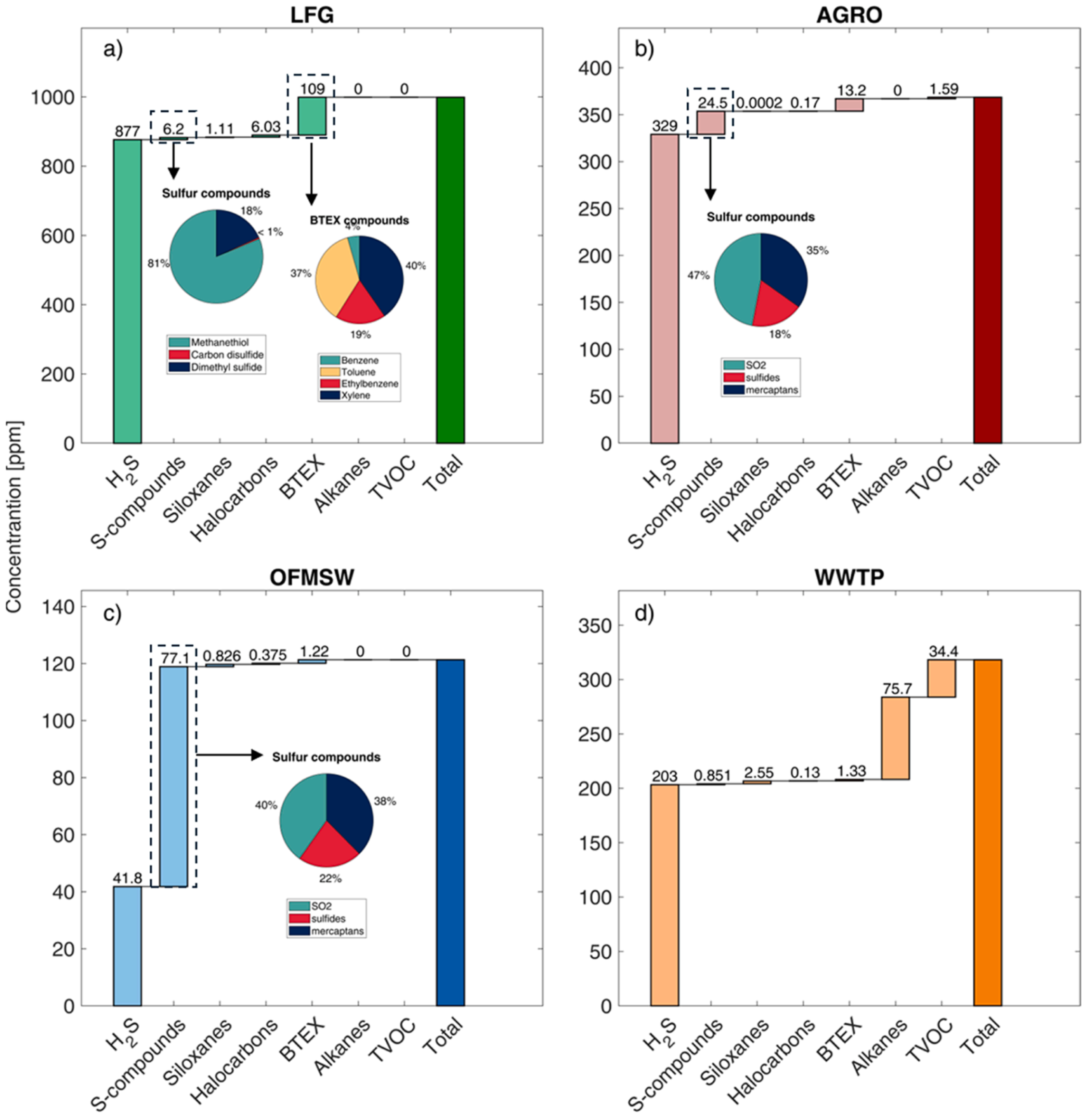

Fig. 8. Average values of the investigated trace contaminants of the different biogas sources from the literature review. (a) Landfill gas; (b) Agricultural gas; (c) OFMSW gas; (d) WWTP gas.

the average values, that the highest concentration is for landfill gas (green bar), with 975 ppm, followed by OFMSW (blue bar), agricultural biogas and, finally, by WWTP. The highest peak (maximum value) occurs for OFMSW (2144 ppm). A high variability is also present for LFG (204–1747 ppm) and AGRO (1.00–1021 ppm), while the variability is lower for WWTP. By comparing the results with the literature data shown in Fig. 3, it is possible to drawn certain considerations. First, LFG exhibits the highest values of H_2S, with an average of around 1000 ppm, and a significant variability, as pointed out in both studies. Agricultural gas shows lower values in our novel dataset, as it is likely influenced by the variability of the biomass and any pre-treatments in the digester. On the other hand, OFMSW registers higher levels of H_2S (456 ppm compared to the previous 41.8 ppm), thus suggesting a potential underestimation of this contaminant in the existing literature. WWTP remains low, at around 150–200 ppm in both cases. Finally, the variability in the novel dataset is lower than that shown in the literature: this can be expected considering the lower number of plants that were analysed.

By joining the novel dataset with the literature review data, it is possible to derive an updated comprehensive overview of the contaminant levels. Table 3 presents the average values of the H_2S and other sulphur compounds from the two-level approach employed in this research study.

5. Technology tolerance levels

This section investigates the tolerance levels of contaminants for the various biogas conversion technologies. In order to provide a comprehensive overview of biogas impurities, it is essential to understand the tolerance limits of the technologies used in different applications to appropriately size the intermediate cleaning and purification stages [58]. Biogas is applied in several fields: it can be burnt directly in gas boilers to produce thermal power, used in engines, turbines or fuel cells to produce electricity (and heat, if cogeneration is performed), upgraded to biomethane for use as transportation fuel or injected into the natural gas grid [59]. This study has focused on the prevalent uses of biogas, such as internal combustion engines and biomethane upgrading (the currently more diffused conversion technologies for biogas [60]), while also exploring innovative solid oxide fuel cells.

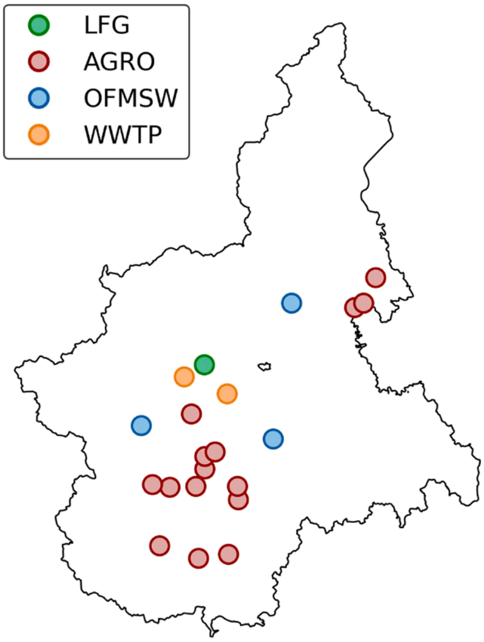

Fig. 9. Location of the biogas plants considered in the biogas contaminant analysis. The map refers to the Piedmont region, in the North-West of Italy.

5.1. *Internal combustion engines*

Table 4 shows the maximum allowed contaminant levels for biogas use in internal combustion engine (ICE). The allowed amounts of H_2S and sulphur compounds are higher than the amounts allowed in SOFCs (see Section 5.3) and for upgrading (see Section 5.2). However, when biogas is combusted, H_2S can lead to corrosion of engines and metal pipes, resulting in SO_2 emissions. Furthermore, the oxidation of trace siloxanes forms SiO_2 crystals, which can cause engine abrasion or create deposits that obstruct essential heat transfer [19]. In addition, to safeguard internal combustion engines (ICEs), the siloxane levels in the biogas should be maintained between 5 and 30 mg/m^3.

5.2. *Upgrading to biomethane*

The second end-use considered herein is the production of biomethane. The injection of biomethane into the gas grid is regulated by the gas network operator, who provides specifications regarding the quantities of contaminants in the gas. In the case of Italy, the regulatory framework is governed by ARERA, with reference to the SNAM Grid Code Biomethane ARERA Deliberation 22/11/2022 document [64]. (Table 5)

5.3. *Solid oxide fuel cells*

Unlike combustion in engines, the electrochemical conversion of biogas in SOFCs requires extremely low contaminant levels [60,64,65]. The majority of chemical species can be detrimental and cause irreversible damage to the cell materials. Lanzini et al. [23] reviewed the influence of contaminants on the SOFC stack, with the objective of defining threshold limits for high-temperature fuel cell systems. Their work focused especially on the poisoning of Ni-anodes by sulphur, chlorine and siloxanes. These impurities can poison the catalytic and electro-catalytic surfaces, leading to reduced reaction rates, increased polarization resistance, and, ultimately, a decrease in overall cell efficiency. Sulphur compounds, in particular, strongly adsorb on the anode surface, blocking active sites and hindering the electrochemical reactions essential for power generation. Additionally, siloxanes can form solid deposits, further obstructing the active areas and causing mechanical and thermal stress on the cell components. Other authors have also investigated the effects of trace contaminants on SOFCs. Papurello et al. [65] studied the behaviour of SOFC when fed with hydrogen sulphide, hydrogen chloride and D4. H_2S was found to be one of the most harmful contaminants for SOFCs. Even at low concentrations (below 1 ppm), H_2S causes rapid poisoning of the anode, significantly reducing its electrocatalytic activity. This results in an increase in polarization resistance and a decrease in the cell's power output. The damage caused by H_2S is partially reversible if the exposure is brief and promptly removed, but prolonged exposure can lead to irreversible degradation. Then, it was observed that hydrogen chloride (HCl) causes significant corrosion of the cell materials, particularly the anode and electrolyte interface. The presence of chlorine leads to the formation of corrosive products that can degrade the active material and compromise the structural integrity of the cell. Lastly, the siloxane D4 poses a threat to SOFCs due to its decomposition at high temperatures, which results in the formation of solid silica (SiO_2) deposits on the anode. These deposits can block the pores of the anode, reducing fuel access to the catalytic sites and increasing gas flow resistance, with a consequent drop in cell performance. Wasajja et al. [25] investigated the impacts of siloxanes and H_2S on SOFCs. They stated that there is no confirmed impurity concentration limit for safe SOFC operation, hence they recommended that fuel impurities should be removed as much as possible.

Table 6 shows the key limit values and references found in the literature for biogas use in SOFCs. It is widely acknowledged that it is necessary to minimise the H_2S levels, due to their potential detrimental effect on fuel cells. Concentrations below 4 ppm seem to be acceptable, while some authors have been slightly more conservative, fixing the limit at 1–2 ppm. However, these values refer to reversible degradation, as the value of voltage decreases and can subsequently be recovered after stopping the sulphur supply [23]. Additionally, the works on siloxanes have emphasised the importance of maintaining extremely low values, that is, of tolerating only some parts per billion (ppb), since even minute concentrations can damage a cell. Some additional limit values are reported for chlorine compounds and halogens.

Thus, maintaining high fuel quality through effective gas purification methods is crucial to ensure the long-term stability and performance of SOFC systems. The biogas cleaning process involves a range of technologies, often used in combination, to meet the stringent limits discussed above. Adsorption techniques using activated carbons [33] or waste-based sorbents [66] can effectively remove sulphur compounds to very low levels, while refrigeration and compression methods are

Table 2
Average and range values of the contaminants (ppm) found in different biogas sources from the novel dataset of real-scale biogas plants. Sulphur compounds include all sulphur species except H_2S. The term "n.a." indicates contaminants that are not analysed in the plant.

Novel dataset								
Contaminants	**LFG**		**AGRO**		**OFMSW**		**WWTP**	
	Avg	**Range**	**Avg**	**Range**	**Avg**	**Range**	**Avg**	**Range**
H_2S	**975**	203.7–1747	**177**	1.00–1021	**456**	0.0423–2145	**138**	16.1–260
Sulphur compounds	**0.0361**	0.0254–0.0468	**n.a.**	n.a.	**140**	8.79–270	**n.a.**	n.a.
Siloxanes	**n.a.**	n.a.	**n.a.**	n.a.	**0.486**	0.001–2.37	**1.84**	0.0676–361
Halocarbons	**n.a.**	n.a.	**n.a.**	n.a.	**n.a.**	n.a.	**n.a.**	n.a.

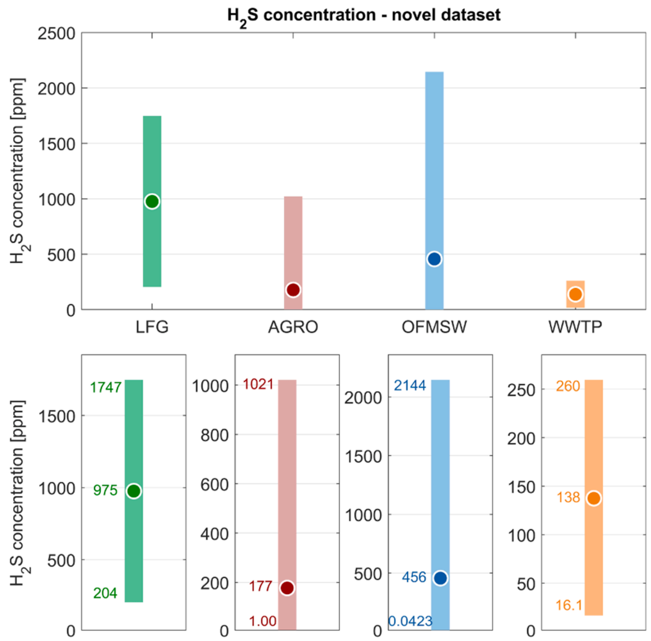

Fig. 10. Contaminant concentrations of H_2S in the different sources of biogas from the novel dataset of real-scale plants. The aim of the upper graph is to represent a comparison between the four sources, while the lower graphs focus on the minimum, average and maximum values of each bar. The complete list of data involved in the analysis can be found in the Supplementary Material.

Table 3
Mean values of H_2S and other sulphur compound contaminants in different sources of biogas. S-compounds include all sulphur species except H_2S.

Biogas	Data source	H_2S [ppm]	S-compounds [ppm]
LFG	Literature review	892	6.20
	Novel dataset	975	0.0361
	Average	**901**	**4.66**
AGRO	Literature review	329	24.6
	Novel dataset	177	n.a.
	Average	**204**	**24.6**
OFMSW	Literature review	41.8	0.851
	Novel dataset	456	140
	Average	**338**	**97.9**
WWTP	Literature review	203	0.851
	Novel dataset	138	n.a.
	Average	**181**	**0.851**

Table 4
The tolerance levels of biogas contaminants for internal combustion engines.

Contaminant	Limit	Ref.
H_2S	50–500 ppm	[61]
	200 ppm	[62]
Sulphur	70 mg/kWh*	[63]
	20 mg/kWh**	[63]
	30 mg/m^3	[45]
Siloxanes	5–30 mg/m^3	[19]
Halogens	10 mg/kWh*	[63]
	2 mg/kWh**	[63]

* Without catalyst

** With catalyst

commonly used to eliminate siloxanes. Additionally, chemical or biological scrubbers can efficiently handle bulk sulphur removal, reducing the load on downstream adsorption beds. A comprehensive assessment of the various biogas cleaning technologies and their applications can be found in [61,67,68].

Table 5
The tolerance levels of biogas contaminants for biomethane.

Contaminant	Limit	Ref.
H_2S	5 mg/Sm^3 (3.59 ppm)	[64]
COS	5 mg/Sm^3 (sulphur from H_2S+sulphur from COS, 3.59 ppm)	[64]
Mercaptans	6 mg/Sm^3 (3.05 ppm, methanethiol equivalent)	[64]

Table 6
The tolerance levels of biogas contaminants for SOFC.

Contaminant	Limit	Ref.
H_2S	2 ppm	[65]
	1–2 ppm	[23]
	2 ppm	[23]
	1 ppm	[25]
	4 ppm	[69]
	2 ppm	[70]
COS	550 ppb	[70]
CS_2	150 ppb	[70]
Mercaptans	200 ppb	[70]
Thiophenes	200 ppb	[70]
$H_2S/COS/CH_3SH$	5 ppm	[41]
Sulphur compounds	0.5 ppm	[71]
Siloxanes	70 ppb	[48]
	70 ppb	[36]
	10 ppb, 100 ppb	[25]
	Trace at ppb levels	[23]
D4	Units of ppb	[65]
D5	0.5 ppm	[23]
	1 ppm	[23]
HCl	No influence up to 40 ppm	[65]
	100 ppm	[23]
	160 ppm	[23]
	500 ppm	[23]
HCl, Cl_2, CH_3Cl	8 ppm	[23]
Halogens (F, Cl_2, CH_3Cl)	4 ppm	[69]
	5 ppm	[22]
NH_3	1 ppm	[69]

6. Conclusions

The aim of this work has been to provide a clear understanding of the issue of trace contaminants within biogas, focusing on its main end-use applications.

The analysis applied a two-level methodology, beginning with an extensive literature review on biogas trace contaminants, followed by on-site analyses at real-scale biogas plants to refine and validate the findings. In the first phase, biogas composition was examined by comparing data from the literature and classifying them according to the biogas source. The contaminants – sulphur compounds, siloxanes, halocarbons, and aromatic (BTEX) compounds – were quantified (minimum, maximum and average values) and categorized into four distinct groups: landfill gas (LFG), agricultural gas (AGRO), gas derived from the organic fraction of municipal solid waste (OFMSW), and wastewater treatment plant gas (WWTP). The second phase, which focused on contaminants detected in real-scale biogas plants (novel dataset), revealed that most of these facilities primarily monitor H_2S, as it requires constant measurement to ensure regulatory compliance. In contrast, other trace contaminants were often neglected since their monitoring is not explicitly mandated by current regulatory frameworks.

The obtained average values of H_2S from the novel dataset do not diverge significantly from the results in the literature review data collection, with the only exception being for OFMSW. The composition of biogas exhibits a significant variability, even for gases from the same source. This is mainly related to the type of waste, its seasonality and several additional factors that make the trace compound concentrations vary to a great extent. Among the various impurities, H_2S shows the most substantial variation. AGRO biogas displays H_2S concentration in the range of 1 to 6570 ppm, while the range is 15.1–5400 ppm in LFG. BTEX variation is also significant in both AGRO and landfill gas.

When considering the average values from the two-level assessment, LFG contains the largest amount of H_2S, at approximately 900 ppm, followed by OFMSW (338 ppm), AGRO (204 ppm) and WWTP (181 ppm). Other sulphur compounds show the highest average concentration in biogas from OFMSW (98 ppm), followed by agricultural (25 ppm) and landfill (4.7 ppm) gases. Biogas from WWTP, on the other side, exhibits near-zero (0.85 ppm) S-compounds.

Based on average values from the literature review, siloxanes are typically detected in biogas from WWTP (2.55 ppm), landfill (1.11 ppm) and OFMSW (0.83 ppm), but are absent in AGRO. Landfill gas also exhibits high average concentrations of halocarbons and BTEX compounds (6 ppm and 109 ppm, respectively). Aromatic compounds are found in agricultural biogas (13 ppm), whereas biogas from OFMSW and WWTP contains low content (< 1.5 ppm) of halocarbons and BTEX.

Finally, this study also addressed the tolerance limits for various biogas conversion technologies. It is found that there are no stringent specifications for internal combustion engines (ICEs), except for H_2S. However, the ongoing transition in power generation, from ICEs to SOFCs, necessitates a deep understanding of trace contaminants as these systems are highly sensitive and require an effective cleaning solution. Lastly, biogas can be alternatively upgraded to biomethane and injected into the natural gas grid. This application show contaminant thresholds comparable with those of SOFCs, which must be met by a properly designed upgrading solution.

CRediT authorship contribution statement

Massimo Santarelli: Writing – review & editing, Supervision, Project administration, Funding acquisition. **Paolo Marocco:** Writing – review & editing, Supervision, Methodology, Investigation, Conceptualization. **Davide Pumiglia:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Lucia Pera:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marta Gandiglio:** Writing – review & editing, Visualization, Supervision, Methodology, Investigation, Conceptualization.

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

Acknowledgements

This research was funded by the European Union - NextGenerationEU from the Italian Ministry of Environment and Energy Security, POR H2 AdP MEES/ENEA with the involvement of the CNR and RSE, PNRR - Mission 2, Component 2, Investment 3.5 "Ricerca e sviluppo sull'idrogeno", CUP: I83C22001170006.

The authors would like to thank all the companies that provided data on biogas contaminants for the analysis and took part in valuable discussions to elucidate the detected trends. Special thanks are due to: Consorzio Monviso Energia (Dr. Andrea Chiabrando), ACEA Pinerolese (Dr. Denis Bona), GAIA SpA (Dr. Andrea Artusio), SMAT SpA, and all the other companies that have not been explicitly mentioned.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2024.114478.

Data availability

The data that has been used is confidential.

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