

Literature Review on Biomethane Impurities

July 2021

# Project number: RP3.2-09 Biomethane Impurities

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# Abbreviations

Abbreviation	Definition	
AEMO	Australian Energy Market Operator	
AGA	American Gas Association	
АРВ	Acid Producing Bacteria	
AS	Australian Standard	
BDL	Below Detection Limits	
BTEX	Benzene, Toluene, Ethylbenzene, Xylene	
BTU	British Thermal Unit	
CCST	California Council on Science and Technology	
CEC	Californian Energy Commission	
CEN	European Committee for Standardization	
CFU	Colony Forming Unit	
CPUC	Californian Public Utilities Commission	
EPCRC	Energy Pipelines Cooperative Research Centre	
EU	European Union	
FFCRC	Future Fuels Cooperative Research Centre	
GTI	Gas Technology Institute	
HHV	Higher Heating Value	
IOB	Iron Oxidising Bacteria	
LAL	Lower Action Limit	
LEL	Lower Explosive Limit	
MAOP	Maximum Allowable Operating Pressure	
MIC	Microbially Induced Corrosion	
MSW	Municipal Solid Waste	
MW	Molecular Weight	
РСВ	Polychlorinated Biphenyls	
qPCR	Quantitative Polymerase Chain Reaction	
PRCI	Pipeline Research Council International	
PSA	Pressure Swing Adsorption	
SRB	Sulphate Reducing Bacteria	
SVOC	Semi-volatile Organic Compound	
VOC	Volatile Organic Compound	
VSA	Vacuum Swing Adsorption	
WI	Wobbe Index	
WWTP	Wastewater Treatment Plant	

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Project Leader and Team	Sandra Kentish, Colin Scholes, Amanda Ellis, Erwin Macario, Holger Maier, Sam Culley.
Industry Proponent and Advisor Team	Siew Shan Foo, Shreyas Rajpurkar, Huw Evans, Joshua Moran, James McHugh, Xiaoda Xu, Justin Brown.
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# Table of Contents

Pro	oject Information	4
I	mportant Disclaimer	5
	Acknowledgement	5
F	Project Information	5
Su	mmary of Report	8
	Analysis of Biomethane quality parameters and contaminants for grid njection	8
S	Summary of Regulatory Approaches for Blomethane Injection	8
1	Next Steps and Further Studies	10
1.	Introduction	11
2.	Literature Review Overview	12
L	Literature Review Method	
3.	Biogas Feedstocks	14
4.	Upgrading Methods	18
5.	Trace Contaminants of Concern	23
I	dentification Methodology	23
r	Nonitoring Parameter Identification Studies	24
S	State of Literature Understanding	33
	Standard Monitoring Parameters	
	Non-Standard Monitoring Parameters	40
	Hydrogen	41
	Siloxanes	
	Ammonia	
	Halocarbons	
	Volatile and Semi-Volatile Organic Compounds Heavy Metals	
	Total Bacteria	
	Unregulated Monitoring Parameters and Contaminants	
6.	Regulatory Review	62
C	Global Overview	62
	Sampling Requirements	67
	Promotional Biomethane Regulations	73

7.	Conclusions	. 75
	Biogas feedstocks and upgrading methods	. 75
	Analysis of Biomethane quality parameters and contaminants for grid injection	75
	Summary of Regulatory Approaches for Blomethane Injection	. 77
8.	Next Steps and Future Work	. 79
9.	References	80
Aŗ	opendix A: VOC Database	. 83
Ap	opendix B: Biomethane Quality Specifications – EU Countries	. 86
Aŗ	opendix C: Biomethane Quality Specifications – Non-EU Countries	. 91

# **Summary of Report**

This report is a literature review for the Future Fuels Cooperative Research Centre Project RP3.2-09 (Biomethane Impurities) which aims to establish regulatory quality requirements for biomethane injection into Australian gas networks. A clear collection of biomethane quality standards will provide pipeline operators, end-users and biomethane project developers with a clear understanding of quality obligations, alongside operational and cost responsibilities. The overall project purpose is to improve industry confidence in biomethane injection, leading to increased market participation.

The technical and economic feasibility of biomethane injection into natural gas networks is evident from its widespread implementation across the world, particularly in European jurisdictions. This review utilises the wide existing body of work, including existing regulatory requirements, in combination with published academic literature, to perform the two tasks:

- Assessment of quality considerations needed to safely implement biomethane injection into the Australian gas grid.
- Determination of high-priority experimental studies to facilitate the implementation of proposed quality considerations.

The above tasks were conducted via a review of commercially utilised biomethane feedstocks and upgrading processes, followed by quantitative and holistic analysis of parameters and contaminants of concern for biomethane injection. This was performed in combination with a review of all regulatory biomethane quality requirements for all countries with > 5 operating biomethane upgrading facilities, leading to an analysis of 17 different countries / jurisdictions. This resulted in a comprehensive list of biomethane parameters to be used as inputs for future Australian biomethane quality regulations.

# ANALYSIS OF BIOMETHANE QUALITY PARAMETERS AND CONTAMINANTS FOR GRID INJECTION

To support the task of determining appropriate biomethane quality regulations, identified parameters were divided into two classifications; those that already possessed existing limit values in AS 4564 (e.g., Wobbe Index, oxygen content) and those that did not (e.g., ammonia, siloxanes). The existing AS 4564 quality requirements were assessed for their suitability for biomethane injection, with a view to determine the feasibility of relaxing existing quality requirements to promote biomethane production. Examination of AS 4564 found three potential avenues for improving the viability of biomethane production, via the relaxation of the minimum and maximum Wobbe Index and oxygen / total inerts concentrations, respectively. These initiatives are based on similar efforts found in other biomethane producing jurisdictions examined, which could be emulated for Australian biomethane production.

The second class of parameters were assessed to provide Australian decision makers with information to determine the appropriate limit values for biomethane quality for Australian pipelines. To assist with this process, the literature was reviewed for quantitative concentration values in biogas / biomethane, along with existing regulatory information as summarised in **Table 1**. This information was combined with analysis of the integrity and health-based detrimental effects associated with each parameter, and the effectiveness of biomethane upgrading methods in removing said parameter, to inform Australian decision makers.

## SUMMARY OF REGULATORY APPROACHES FOR BIOMETHANE INJECTION

The review of the various regulatory approaches for managing biomethane injection quality while promoting industry growth revealed several ideas that could be implemented in the management of Australian biomethane injection. One of the common approaches relies on feedstock-based testing requirements, due to the intrinsic relationship between certain feedstocks and the presence of adverse contaminants. The relationship between feedstocks and contaminants, alongside proposed testing schemes, are covered in detail within this report.

Other regulatory schemes that aim to promote the distribution of biomethane come in the form of allowances for pipeline blending for non-compliant biomethane. This was found in several jurisdictions, an example of which is a Swiss scheme that allows non-compliant injection on the basis that the resulting mixed gas is compliant at the first exit point of a consumer. Another detailed gas blending scheme incorporated into existing regulations is one

conducted by the Californian Council on Science and Technology, which states that pipeline blending must be evaluated on a case-by-case basis. This was also found to be the approach of German legislature, which also allowed pipeline blending subject to conditions of the local gas network.

Parameters / Contaminants	Biogas Range	Biomethane Range	Regulatory Coverage <sup>1</sup>	Limit Value Range <sup>2</sup>
Hydrogen	BDL <sup>3</sup>	BDL – 0.9 mol. %	9/13	0.1 – 5.0 mol %
Siloxanes	BDL – 14.4 mgSi/m <sup>3</sup> (8000 mg/m <sup>3</sup> ) <sup>4</sup>	BDL – 0.4 mgSi/m <sup>3</sup>	9/13	0.01 – 10 mg Si/m <sup>3</sup>
Ammonia	0.2 – 63 mg/m <sup>3</sup>	0.15 – 0.25 mg/m <sup>3</sup>	8/13	3 – 20 mg/m <sup>3</sup>
Halocarbons	BDL – 735 mgCl/m <sup>3</sup>	BDL	7/13	1 – 10 mg (Cl/F)/m <sup>3</sup>
Semi-Volatile and Volatile Organic Compounds (SVOCs and VOCs)	10 – 700 mg/m <sup>3</sup>	<1 – 100 mg/m <sup>3</sup>	3/13	< 100 mg/m <sup>3</sup> Xylene (UK) < 904 mg/m <sup>3</sup> Toluene (California, USA) < 3.7 ppm General VOC contents (Quebec, Canada)
Heavy Metals	<b>Mercury:</b> BDL – 0.02 μg/m <sup>3</sup> <b>Arsenic:</b> BDL - 8.5 μg/m <sup>3</sup>	Mercury: BDL – 0.05 μg/m <sup>3</sup> Arsenic: BDL – 0.32 μg/m <sup>3</sup>	2/13	< 1 µg/m <sup>3</sup> Mercury limit recommendation in AS 4564 is sufficient. 19 – 30 µg/m <sup>3</sup> Arsenic 30 – 60 µg/m <sup>3</sup> Copper 600 µg/m <sup>3</sup> Antimony (California, USA) 75 µg/m <sup>3</sup> Lead (California, USA)
Bacteria⁵	<b>APB<sup>6</sup>:</b> 1.23 x 10 <sup>3</sup> – 6.03 x 10 <sup>4</sup> <b>IOB<sup>5</sup>:</b> 1.02 x 10 <sup>3</sup> – 5.09 x 10 <sup>3</sup> <b>SRB<sup>5</sup>:</b> 1.1 x 10 <sup>2</sup>	<b>APB:</b> $9.69 \times 10^{1} - 2.02 \times 10^{5}$ <b>IOB:</b> $6.9 \times 10^{2} - 7.67 \times 10^{4}$ <b>SRB:</b> $1.65 \times 10^{2} - 2.52 \times 10^{4}$	1/13	4 x 10 <sup>4</sup> CFU/scf (qPCR per APB, SRB, IOB group) and commercially free of bacteria of >0.2 microns (California, USA)

#### Table 1 Biomethane Parameters / Contaminants without AS 4564 Limits

<sup>&</sup>lt;sup>1</sup> Number of jurisdictions with gas quality regulations for each parameter / contaminant. Only 13 out of 18 jurisdictions were found to have unique biomethane quality regulations.

<sup>&</sup>lt;sup>2</sup> Range of maximum contaminant limits found via the regulatory review.

<sup>&</sup>lt;sup>3</sup> BDL = Below Detection Limits.

<sup>&</sup>lt;sup>4</sup> Total siloxane concentrations of up to 8,000 mg/m<sup>3</sup> have been reported for raw landfill gas.

<sup>&</sup>lt;sup>5</sup> Concentrations presented in Colony Forming Units (CFU)/100 scf.

<sup>&</sup>lt;sup>6</sup> APB, IOB, SRB = Acid Producing Bacteria, Iron Oxidising Bacteria, Sulphate Reducing Bacteria.

Parameters / Contaminants	Biogas Range		Regulatory Coverage <sup>1</sup>	Limit Value Range <sup>2</sup>
Pesticides	Note 1	Note 1	0/13	N/A
Pharmaceuticals	Note 1	Note 1	0/13	N/A
Phosphine	Note 2	Note 2	0/13	N/A

#### Notes:

- 1. All reports of pesticide and pharmaceutical detection were either at concentrations BDL or orders of magnitude lower than recommended exposure limit concentrations.
- 2. No quantitative information could be found for phosphine contents in biogas / biomethane.

### **NEXT STEPS AND FURTHER STUDIES**

Several studies were identified to accelerate the adoption of Australian biomethane standards. The following promising studies were identified for deliberation by the RP3.2-09 project team for the next RP3.2-09 project milestone (Industry Workshop Event):

- Assessment of minimum allowable Wobbe Index specifications for biomethane injection in Australian networks.
- Assessing the work conducted in other jurisdictions for increasing allowable oxygen content and its applicability for Australian Assets (e.g., increase from 0.2 – 1.0 mol %)<sup>7</sup>.
- Detailed assessment of the effects of relaxing the AS 4564 7 mol % total inert gas limits for Australian end-users.
- Analysis of the effects of terpene odorant masking for Australian odorant compositions and concentrations.
- Assessment of the effects of propane blending on hydrocarbon dew point for likely biomethane product compositions.
- Determination of appropriate limit values for siloxane content for end-users<sup>7</sup>.

<sup>&</sup>lt;sup>7</sup> Oxygen and siloxane limit value quantification based on *end-user requirements* are the subject of an existing FFCRC project proposal.

# 1. Introduction

The use of biomethane as a renewable alternative to natural gas has been gathering momentum within the context of the Australian natural gas landscape. Biomethane, also known as renewable natural gas (RNG), is methane obtained from upgrading biogas produced via anaerobic digestion of organic feedstocks such as agricultural waste and the organic fraction of landfill waste. It is produced by "upgrading" biogas through the removal of typical biogas components such as inert gases (CO<sub>2</sub>, N<sub>2</sub>) and detrimental contaminants (H<sub>2</sub>S etc.)

The use of biomethane as a natural gas replacement is highly promising primarily since effectively no changes are required for equipment already designed to use natural gas. Through the decarbonisation of the existing natural gas grid, Australia's long-term energy security is increased. This is due to the added layer of resilience to energy supplies compared to an approach limited to electricity derived from renewable resources.

This literature review is the first report of the Future Fuels Cooperative Research Centre project RP3.2-09 (Biomethane Impurities). The aim of the project is to establish consensus on proposed regulatory requirements for biomethane injection into Australian gas networks, and by doing so improve the industry participation for biomethane production. A clear collection of gas quality and interconnection standards are critical to provide assurances to pipeline operators, their customers and biomethane project developers of gas quality requirements and operational and cost responsibilities. Standards that align with best practices, are consistent, clearly justified, and understandable can provide confidence to all relevant parties to increase industry participation.

To facilitate the widespread production of biomethane in Australia, significant work is required to ensure the suitability of biomethane with existing gas infrastructure. This includes, but is not limited to the following:

- Quantification of limit values for biomethane contaminants not present in conventional natural gas.
- Identification of existing quality requirements (e.g. AS 4564) supressing biomethane production and alternative legislative approaches.
- Consideration of new pipeline management and operational practices that promote biomethane production.

This literature review attempts to answer the above questions in the context of the significant existing body of work in numerous jurisdictions with functioning biomethane injection schemes. The aim of the review is to distil the various sources and provide useful information for Australian industry participants and regulators for the eventual regulation of biomethane injection.

With the aim of increasing biomethane market penetration, the stance taken by the review on the implementation of Australian biomethane standards is similar to that adopted by the Standards Australia ME-093 Hydrogen Technologies committee for the implementation of Australian hydrogen standards. To facilitate rapid uptake of the biomethane production technology, the implementation of already existing and well-known standards have been judged to be the best path forward. This ensures that synergistic effects between countries can be realised and that commercial solutions such as packaged biomethane treatment systems that are suitable for European markets can be utilised in Australia with little changes. Therefore, an important aspect of the review is the need to uncover the details to be considered should Australia implement existing biomethane quality standards.

# 2. Literature Review Overview

## LITERATURE REVIEW METHOD

The literature review is structured as follows:

- Overview of biomethane feedstocks: An overview of the main categories of biological feedstocks used to produce biomethane.
- Overview of biogas upgrading processes: An overview of the main technologies to process biogas produced via anaerobic digestion into biomethane, focusing on trace contaminants.
- Analysis of biomethane monitoring parameters: Analysis of all potential monitoring parameters guided by previous biomethane quality studies, within the context of the existing Australian / global regulatory limits and scientific understanding of current monitoring parameter limit values.
- Review of global biomethane specifications: A comprehensive review of global legislation and industry guidelines for biomethane production and injection into gas networks, practical sampling requirements, rates of monitoring, and other legislation designed to boost biomethane market penetration.

The literature review undertook a global approach, with a weighted focus on countries with established biomethane industries and pipeline injection history. The review of biomethane legislation and peak body documentation was limited to countries with sufficient biomethane production capacity (defined as having >5 upgrading plants), per the most recently available information. These countries are summarised in **Table 2**.

#### Exclusions

This literature review does not cover the following topics:

- **Biomethane produced by thermal gasification:** Thermal gasification was not considered due to the lack of many successfully developed plants and being characterised as a "relatively niche" industry by the International Energy Agency [1].
- Regulation regarding biomethane production incentives (biomethane certificates / mandated renewable energy targets etc.): The regulatory review was strictly limited to biomethane quality guidelines to assess considerations for the technological requirements for biomethane injection.
- Economic analysis of biogas / biomethane production and purification methods: The economic considerations for biomethane production in an Australian context are already considered in the FFCRC projects RP1.10-07, RP1.2-03 and RP1.2-04.

Country	Number of Upgrading Plants [2, 3]	Most Recent Data (Year) [2, 3]	Percentage of Upgrading Facilities Injecting into the Gas Grid [3, 4]			
EU Member	EU Members					
Germany	232	2019	> 90			
France	131	2020	> 90			
United Kingdom	80	2018	> 90			
Sweden	70	2018	< 25			
Netherlands	53	2020	> 90			
Denmark	46	2019	> 90			
Switzerland	38	2019	> 90			
Italy	18	2020	0			
Finland	17	2019	58			
Norway	16	2020	50			
Austria	15	2020	100			
Non-EU Co	untries					
U.S.A.	77	2018	-			
China	73	2017	-			
South Korea	10	2017	-			
Canada	9	2018	-			
Japan	6	2014	-			
Brazil	5	2017	-			

## Table 2 Summary of Countries with >5 Biomethane Upgrading Plants

# 3. Biogas Feedstocks

All types of biomass that contain carbohydrates, proteins, fats, cellulose and hemicelluloses as main components are suitable substrates for producing biogas. Due to the variety of available feedstocks, the resulting biogas composition, methane yield and contaminant concentrations are highly dependent on the feedstock type. The main feedstock groups and their production pathway towards biomethane injection is shown in **Figure 1**. A breakdown of the biogas production associated with individual feedstock types, categorized by country of production, is provided in **Figure 2**. This can be compared with the feedstock distribution for biomethane production in Europe as of 2020, as shown in **Figure 3**. It can be observed that feedstock distribution is similar for both biogas and biomethane production in Europe, indicating the ubiquity and indiscriminatory nature of the suitability of biogas purification for individual feedstock types.

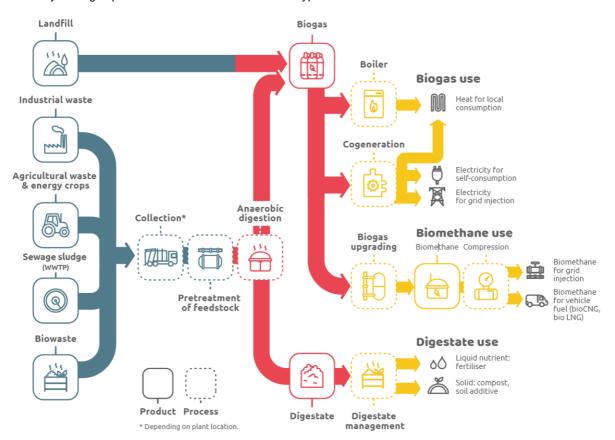
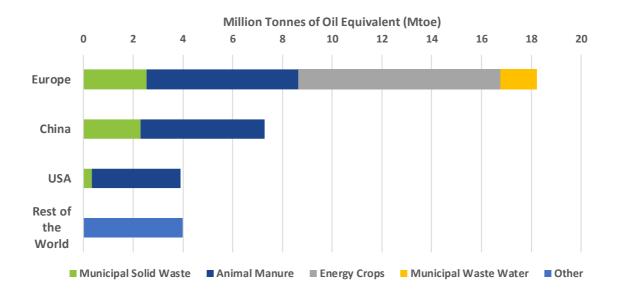
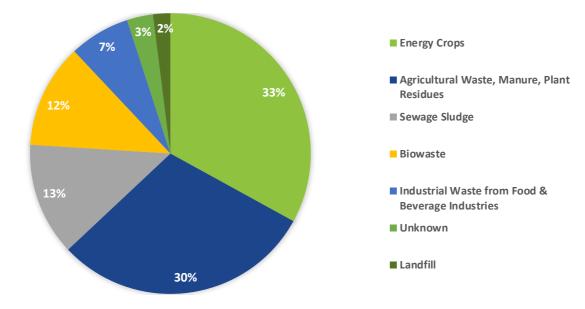


Figure 1 Biogas Value Chain, Biogas Opportunities for Australia Report [5].





### Figure 2 Biogas Production by Region and Feedstock Type (2018) [6]

## Figure 3 Biomethane Production by Feedstock Type in Europe (2020) [2]

Brief descriptions of the commercially utilised feedstock groups shown in **Figure 1** are provided in **Table 3**. The variations in biogas derived from the main feedstock types can be observed in **Table 4**. Other feedstocks, such as aquatic biomass, have not been considered within this report due to their lack of commercial applications [7].

Feedstock	Feedstock Types	Description
Group		
Landfill	Municipal Solid Waste Landfills (MSWL), Industrial Waste Landfills (IWL)	The majority of landfill-based biogas production occurs in MSWLs, with 74 % of MSWLs in the USA from 2011 – 2017 containing landfill gas collection and control systems, compared to less than 1 % of IWLs [8]. MSWLs are predominantly composed of household and council wastes that include biodegradable, recyclable and a wide range of non-degradable materials including paint, appliances, and old
		furniture. IWLs contain smaller proportions of organic waste, with a 15 %
		organic fraction of total reported waste in Australian IWLs from 2010 - 2011 [9]. This, in combination with the common presence of hazardous materials in IWLs leads to IWL based biogas production being relatively rare [10]. Many countries also have implemented legislation to reduce the use of IWLs due to the presence of impurities and heavy metals [11]
Industrial Waste	Food Industry Waste, Pulp and Paper Waste, Industrial	Industrial wastes vary widely depending on the industry. Food industry wastes are derived from hotels, restaurants,
	Wastewater	canteens, kitchen wastes and fruit and vegetable wastes from wholesale distributors.
		Waste feedstocks range from pulp and paper waste to wastewater from textile production [11].
Agricultural Waste & Energy Crops <sup>8</sup>	Animal Manure and Slurries, Crop Waste, Energy Crops,	Agricultural waste, animal manure and energy crops are the most widely utilised feedstocks for biogas production, comprising 70 % of global biogas production in 2018 [6].
	Agricultural By- products	The use of energy crops for biogas production has been predominantly localised to European countries, particularly in Germany and Austria [12]. However, support for purpose grown energy crops has been reducing in recent years due to concerns about their long-term sustainability [1].
Sludge generated from the treatment		Sewage sludge is composed of semi-solid organic matter generated from the treatment of wastewater in municipal wastewater treatment plants [13].
Biowaste	Organic Municipal Solid Waste (OMSW),	Biowaste is the organic waste from households, communities or small-scale commercial and industrial activities [5]. It is sometimes used as a co-substrate with animal manure to increase methane yield due to the rich organic nutritional value [11].

# Table 3 Summary of Commercially Utilised Biomethane Feedstocks

<sup>&</sup>lt;sup>8</sup> Crops grown solely for energy production.

	11	1	A surface literate l	0	Discussion
Monitoring Parameter	Units	Landfill	Agricultural Waste	Sewage Sludge	Biowaste
Energy Content (HHV)	MJ/m <sup>3</sup>	7.8 – 24.0	20.5 – 24.1	20.5 – 24.2	20.5 – 24.2
Temperature	°C	10 – 30	40 - 60	30 – 40	N.D.
Methane	mol %	20 – 70	30 – 75	55 – 77	50 - 60
Carbon Dioxide	mol %	15 – 60	15 – 50	19 – 45	34 – 38
Hydrogen Sulphide	ppm	0 – 20,000	10 – 15,800	1 – 8,000	70 – 650
Total Sulphur	mg/m³	0 – 200	N.D.	N.D.	N.D.
Nitrogen	mol %	0 – 50	0 – 5	< 8.1	0 – 5
Oxygen	mol %	0 – 10	0 – 1	0 – 2.1	0 – 1
Hydrogen	mol %	0 – 5	0	0	-
Ammonia	-	0 – 1 mol %	0 – 150 ppm	0 – 7 ppm	-
Carbon Monoxide	mol %	0 – 3	N.D.	0 – 0.01	N.D.
Non-methane Hydrocarbons	mol %	0.01 – 0.25	N.D.	N.D.	N.D.
Aromatics	mg/m³	30 – 1,900	N.D.	N.D.	0 – 200
Halogenated Compounds	mg/m³	0.3 – 2,900	0 – 0.01	0 – 2	100 – 800
Total Chlorine	mg/m³	0 – 800	0 – 100	N.D.	N.D.
Total Fluorine	mg/m³	0 - 800	0 – 100	N.D.	N.D.
Siloxanes	mg/m³	0 – 50	0 – 0.2	0 – 400	N.D.
Moisture	mol %	1 – 10	N.D.	N.D.	5 – 6
Methyl Mercaptan	ppm	0 – 3.91	N.D.	N.D.	N.D.
Dichlorobenzene	ppm	0 – 5.48	N.D.	N.D.	N.D.
Ethylbenzene	ppm	0.576 – 40.2	< 0.34	< 1	N.D.
Vinyl Chloride	ppm	0.006 - 15.6	N.D.	N.D.	N.D.
Copper	µg/m³	< 30	< 20	< 30	N.D.
Methacrolein	ppm	< 0.11	N.D.	< 0.0001	N.D.
Alkyl Thiols	ppm	6.1 – 6.8	< 7.3	1.04 – 1.15	N.D.
Toluene	mg/m³	1.7 – 340	0.2 - 0.7	2.8 – 117	N.D.

## Table 4 Composition of Biomass-Derived Gas from Various Sources [14]

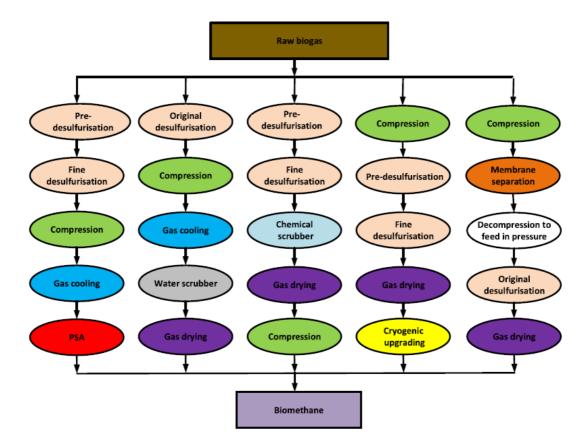
**Note:** N.D. = Not Determined or not found. Listed where contaminant is expected to be present, but concentration data was not found in the literature.

# 4. Upgrading Methods

An understanding of biogas upgrading and cleaning methods, alongside their relative strengths and weaknesses regarding contaminant removal, is necessary for understanding the existing limit values for biomethane contaminants. This section of the report provides context for understanding the capabilities of existing biogas upgrading and cleaning technologies for the specific contaminant species that will be discussed later within the review.

The upgrading methods discussed in this segment are those that are considered soon-to-be or already commercially available. A distinction also needs to be made between biogas "upgrading" and "cleaning". Upgrading is the task of primarily improving the methane composition of the biogas feed [15]. This is performed by removing the bulk of the CO<sub>2</sub> present in biogas to improve the calorific content. Depending on the upgrading method, several other contaminants can also be removed during this upgrading process [16].

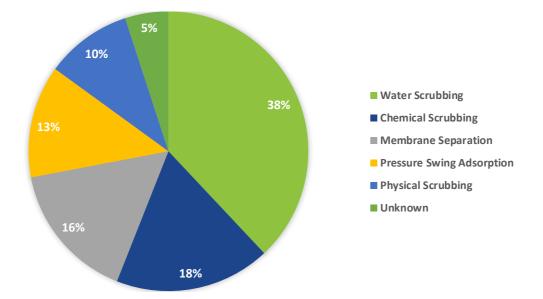
"Cleaning" can occur independently of any upgrading processes e.g., utilising landfill derived biogas for on-site power generation. This process is typically not sensitive to the large CO<sub>2</sub> composition of landfill biogas, and instead employs processes to remove corrosive compounds that could be detrimental to gas combustion engines [17]. However, when cleaning steps are combined with upgrading, the result is pipeline quality biomethane. Sample combinations of biogas cleaning and upgrading processes can be seen in **Figure 4**Error! Reference source not found.. It is important to understand that the main upgrading processes discussed often cannot achieve biomethane quality biogas without supplemental cleaning operations. Often, they are used in conjunction with simpler processes with often singular functions e.g., desulfurization before a PSA system. These individual steps can be used to fine tune the upgrading and cleaning process towards the contaminants within the unique project feedstock.



#### Figure 4 Combinations of Biogas Cleaning and Upgrading Processes [18]

The upgrading methods considered for this review are shown in **Table 5**. This collection was generated from a review of the current literature, and a recent survey of all European biomethane production facilities in 2020 [2]. As of 2020, the distribution of biomethane plants in Europe per individual biogas upgrading methods are shown

in **Figure 5**. Due to the focus of the review on biomethane monitoring parameters and trace contaminants, the detailed mechanisms of each upgrading method are not discussed within this review. However, Andan et al [19] provides a recent comprehensive description of all upgrading methods discussed here in their review paper.



## Figure 5 Distribution of Plants per Upgrading Method (Europe 2020) [2]

The achievable biomethane concentrations for the main contaminants are dependent on the upgrading method used. The compatibilities of the main contaminants with the upgrading methods are summarised in **Table 6** and **Table 7**.

# Table 5 Commercial and Soon-to-be Commercial Biomethane Upgrading Techniques [20]

Method	Sub-type	Description	
Absorption Water Scrubbing Chemical Scrubbing Physical Scrubbing		Absorption of an impurity via contacting of the gas with a liquid phase. The absorbed impurity is retained in the liquid phase for further processing. The various absorption sub-types refer to the substances used to remove CO <sub>2</sub> from the gas phase.	
Permeation Membrane separation		Permeation utilises porous membranes to selectively filter out components of the gas. These membranes can be designed to be permeable to nitrogen, ammonia, and water but not to methane.	
Adsorption	Pressure swing adsorption	Adsorption uses a chemically treated surface to capture impurities. These impurities are originally captured at the process conditions and are released when the adsorbed material is "regenerated". Regeneration occurs via the shift of a process parameter e.g. pressure or temperature. Upon regeneration, the adsorbed impurities can be removed from the chemically treated surface which is free to be re-used to capture more impurities. This method is particularly effective for removing H <sub>2</sub> S (to below 1 ppm), water, siloxanes and ammonia [20].	
Cryogenic	Cryogenic cooling	Cryogenic cooling utilises low temperatures to cool biogas to liquefy certain components of interest. Variations in boiling point between	

Method	Sub-type	Description
		methane and the other gases allow for methane to be removed in a multistage cooling process.
		While not widely used in a commercial manner, cryogenic separation has been attracting interest for the purposes of siloxane removal due to the potential for contaminant breakthrough associated with conventional siloxane removal processes e.g. activated carbon [21].

# Table 6 Allowable Contaminant Concentrations in Raw Biogas for Various UpgradingMethods [18, 22]

Upgrading technology	H <sub>2</sub> S	voc	O2/N2/H2	
Water scrubbing	300 – 2500 ppmv [23]. Main part goes to the stripper air.	Moderate concentrations. Main part removed with the condensate and stripper air.	Go to the upgraded gas.	
Chemical scrubbing	300 ppmv [23]. Main part goes to CO <sub>2</sub> stream. Polish filter may be needed in upgraded gas.	Moderate concentrations. Main part removed with the CO <sub>2</sub> and condensate streams.	Go to the upgraded gas.	
Organic physical scrubbing	< 300 ppmv. Main part goes to the stripper air.	Moderate concentrations. Main part goes to the stripper air.	Go to the upgraded gas.	
Membrane separation	Low concentrations. Some amount goes to the product gas.	Upstream removal is required.	Go to the CO <sub>2</sub> and upgraded gas stream.	
PSA	Low concentrations	Upstream removal is required.	$O_2/N_2$ go to $CO_2$ stream, $H_2$ goes to product gas.	
Cryogenic separation	< 300 ppmv. Removed during first stage refrigeration.	Moderate to high concentrations. Removed during first stage refrigeration.	Go to the upgraded gas.	

# Table 7 Allowable Contaminant Concentrations in Raw Biogas for Various UpgradingMethods Cont. [18, 22]

Upgrading technology	NH₃	Siloxanes	Halogenated Compounds
Water scrubbing	Moderate concentrations. Main part removed with process water.	Low concentrations	-

Upgrading technology	NH₃	Siloxanes	Halogenated Compounds
Chemical scrubbing	Moderate concentrations. Main part goes to the CO <sub>2</sub> stream.	Moderate concentrations	Moderate concentrations
Organic physical scrubbing	Moderate concentrations. main part goes to the stripper air.	Moderate concentrations	Moderate concentrations
Membrane separation	Usually removed with condensate during upstream drying of raw biogas.	Moderate concentrations	-
PSA	Upstream removal is required.	Moderate concentrations	Moderate concentrations
Cryogenic separation	Moderate to high concentrations. Removed during first stage refrigeration.	Moderate concentrations	-

Analysis of the various upgrading methods must be conducted within the context of costs, technological readiness and their advantages and disadvantages relative to each other. These factors can be seen in the assessment conducted by Zheng et al., presented in **Table 8**.

## Table 8 Qualitative Comparison of Different Upgrading Techniques [24]

Upgrading technology	Advantages	Disadvantages
Chemical scrubbing	<ul> <li>Minimal CH₄ loss.</li> <li>High pressure not needed.</li> <li>No pre-treatment necessary.</li> <li>Cost effective at a low heat price.</li> </ul>	Very high heat demand. Low CO <sub>2</sub> adsorption. Requires high energy for organic regeneration. Corrosive nature especially at high temperatures. Amine degradation. Disposal of wastewater. Use of process water. No removal of trace gases.
Water scrubbing	High CO <sub>2</sub> separation efficiency. Inexpensive water regeneration. Tolerance for trace impurities in biogas. No multiple stages needed.	Clogging of packing material. Low flexibility for variations in input raw biogas. High power requirement. High investment and operation cost.

Upgrading technology	Advantages	Disadvantages
	No chemicals. Reduced corrosion.	CO <sub>2</sub> -water corrosion issues that may shorten the plant lifetime.
PSA	High gas quality.	H <sub>2</sub> S pre-treatment required.
	Dry process.	Three to four parallel streams needed.
	No chemicals used.	Unstable CH <sub>4</sub> level.
	No process water demand.	Complex process.
	Partial removal of $N_2$ and $O_2$ .	High investment cost for small units.
	No bacterial contamination of gas.	
Organic physical scrubbing	No pre-treatment necessary.	Corrosive nature of the organic mixture.
Scrubbing	High CO <sub>2</sub> solubility in organic solvent.	Disposal of wastewater.
	Tolerance to low temperature (< 20 C without any extra heat supply).	Use of process water.
Membrane separation	Simple process.	Degradation of membrane over time.
Separation	No process water demand.	Pre-treatment necessary.
	No wastewater.	High energy demand.
	Container-based transportation	High investment costs.
	Space saving.	
	Less complex units (easy maintenance).	
Cryogenic separation	Liquefied methane for easy transportation.	Extremely high energy consumption and cost.
Copulation	Recovery of $CO_2$ as a by-product for market sale.	

# 5. Trace Contaminants of Concern

## **IDENTIFICATION METHODOLOGY**

The literature was comprehensively reviewed to obtain measured trace contaminant levels for biogas and biomethane associated with the different feedstocks. Trace contaminants and monitoring parameters of concern were identified via reviewing the body of work of holistic biomethane quality assessments. Within this chapter of the review, a list of trace contaminants and monitoring parameters of concern will be generated via the collation of the results of previous biomethane quality assessments. The list of parameters is assessed based on the following:

- **Standard monitoring parameters:** Parameters that already have existing limit values in AS 4564 will be assessed to determine the suitability of the existing AS 4564 requirements for biomethane injection.
- Non-standard monitoring parameters: Parameters without existing limit values in AS 4564 will be assessed to find answers to the questions in **Table 9**.

### Table 9 Assessment Criteria for Non-Standard Monitoring Parameters

Criteria	Justification
What are the pre- and post-upgrading concentration ranges associated with this contaminant for individual feedstocks?	Provision of quantitative literature information to justify evidence-based decisions for recommended biomethane quality requirements.
What are the detrimental effects of this contaminant?	Analysis of the maximum observed contaminant concentration in biogas and biomethane, and potential effects on pipeline material integrity, health and safety and downstream users.
What are the suitable removal processes and their effectiveness?	Analysis of the effectiveness of commercial removal processes to effectively quantify the risk of biomethane possessing detrimental concentrations of trace contaminants.
What is the current state of understanding of required limit values?	Verification of the above process via comparison with existing regulatory limits (See <b>Chapter 6</b> ) for each contaminant / monitoring parameter.

Trace contaminants and monitoring parameters identified in the biomethane quality assessments were classified based on the criteria identified in **Table 10**.

#### Table 10 Screening Criteria for Trace Contaminants and Monitoring Parameters

Criteria	Description
Pipeline and Distribution Infrastructure Integrity	Contaminants identified based on the following concerns [25]: Corrosion
	<ul> <li>Clogged pipes / valves</li> <li>Odorant fade / masking</li> </ul>

Criteria	Description	
Occupational Health and Safety	Contaminants identified based on the following concerns [25]:	
	Direct toxicity from confined leak	
	<ul> <li>Indirect toxicity from combustion</li> </ul>	
	<ul> <li>Water pollution from injection into storage facilities</li> </ul>	
	Air pollution	

The methodology for identifying individual contaminants of concern varied greatly throughout all references identified during the review. While the two broad topics of pipeline integrity and health and safety were present in most sources, there were many interpretations of the exact applications of each general topic. The studies used to build the list of trace contaminants and monitoring parameters of concern are discussed here.

## MONITORING PARAMETER IDENTIFICATION STUDIES

Work conducted by the Gas Technology Institute (GTI) in America on biomethane derived from dairy waste utilised two general methods to identify trace contaminants [26]. The first method utilised existing prescribed tests for natural gas quality compiled in the American Gas Association's (AGA) Report 4A – Natural Gas Contract Measurement and Quality Clauses [26]. This document compiles and references pipeline tariffs from various natural gas transmission and distribution companies in North America, allowing an effective screening of biomethane quality against existing gas quality specifications. The AGA Report 4A gas quality specifications are shown in **Table 11**, alongside the equivalent specifications in AS 4564-2011.

AGA Report 4A - 2011			AS 4564:2020
Gas Property	Contract Limits	Typical Values	Limit
Water Content	112.0 mg/m³, Maximum	32.0 – 112.0 mg/m <sup>3</sup>	Lower of water dewpoint of 0°C at the highest MAOP in the relevant transmission system or 112.0 mg/m <sup>3</sup>
Heat Content (HHV)	36.0 – 41.7 MJ/m <sup>3</sup>	37.6 – 39.5 MJ/m <sup>3</sup>	42.3 MJ/m <sup>3</sup>
Temperature	0 – 49 °C	4 – 16 °C	-
Hydrocarbon Dew Point	-9 °C Maximum at Pipeline Pressures	-18 – -9 °C at 3792 kPag	2.0 °C at 3500 kPag
Sulfur Compounds – Hydrogen Sulfide (H₂S)	5.7 – 6.9 mg/m <sup>3</sup> , Maximum	0 – 45.8 mg/m <sup>3</sup>	5.7 mg/m <sup>3</sup>

## Table 11 Gas Quality Property Specifications in AGA Report 4A vs AS 4564:2020 [25]

AGA Report 4A - 2011			AS 4564:2020
Gas Property	Contract Limits	Typical Values	Limit
Mercaptans (RSH)	No Specification	Highly Variable, 0 – 40ppm	Where required, detectable at a level not exceeding 20 % LEL.
Total Sulfur Compounds, as sulfur	114 – 458 mg/m <sup>3</sup> , Maximum	0 – 23 mg/m <sup>3</sup>	50 mg/m <sup>3</sup>
Diluent Gases Total	4 – 5 mol %, Maximum	0.5 – 3 mol %	7.0 mol %
Oxygen (O2)	0.2 mol %, Maximum 0.001 mol %, Desirable	0 – 0.001 mol %	0.2 mol %
Helium (He)	0.2 mol %, Maximum	0 – 0.1 mol %	-
Nitrogen (N2)	3 mol %, Maximum	0 – 2 mol %	-
Carbon Dioxide (CO <sub>2</sub> )	2 – 3 mol %, Maximum	0 – 2 mol %	-
Mercury (Hg)	No Specification	0 – 8 µg/m³	1.0 μg/m <sup>3</sup>
Solid Particles	3 – 15 microns, Maximum	3 – 15 microns	"Gas shall not contain materials, dust to an extent which might cause damage to, or interference with the proper operation of pipes, meters or which might cause gas to be harmful or toxic to persons having contact with it in normal work operations or usage."

GTI also employed additional internal and external testing methods to identify contaminants not normally associated with conventional natural gas. A summary of all testing methods utilised in the study is shown in **Table 12**. A total of 40 biogas / biomethane samples from 14 dairy farms (only 2 producing biomethane) in the United States were examined to identify trace contaminants.

The final output of the GTI work on dairy waste feedstocks was a list of contaminants and parameters recommended for consideration for introducing biomethane to pipeline networks. An overall methodology was not explicitly stated by the study in how the list of all detected contaminants was narrowed down into the final list included in their final report. However, the reasoning for individual contaminants, as interpreted by the review, and important parameters identified are shown in **Table 13**.

# Table 12 Summary of Trace Contaminant Testing Methods for Dairy Waste Biogas / Biomethane Production [25]

Analysis	Method Reference	Instrument Analysis / Method
Major Components	GTI Procedure	ASTM D1945/D1946
Extended Hydrocarbons	GTI Procedure	GC/FID
Sulfur	GTI Procedure	ASTM 6228
Halocarbons	GTI Procedure	ELCD/EPA TO-14
Siloxanes	GTI Procedure	GC-AED
SVOCs/PAHs	Mod NIOSH 5515	GC/MS/ EPA Method 8270C
PCBs	Mod NIOSH 5503	GC/ECD or GC/MS/ EPA Method 680
Pesticides	Mod NIOSH 5600/5601	GC/ECD, HPLC/UV
Exploratory analyses	NA	GC/MS
Pharmaceuticals/ Animal care products	TBD	LC/MS
Mercury	ASTM D5954	AAS
Volatile Metals	EPA Method 29 modified	ICP/ EPA Method 29

# Table 13 Identified Trace Contaminants for Biomethane Injection from Dairy Waste Feedstocks [26]

Parameter / Contaminant	Identification Basis	Justification
Heavy Metals	Network Integrity and End-Use Concerns	Potential corrosion of aluminium metal and alloys in gas processing equipment.
	Health and Safety	Heavy metals (e.g., mercury) may concentrate in cryogenic liquids and other processing fluids.
		Catalyst poisoning (arsenic compounds).
		Health hazards associated with presence during odorant sniff tests and end use applications.
Hydrogen	Network Integrity and End-Use Concerns	Hydrogen stress cracking / embrittlement. Reaction with sulphur and chlorine- containing compounds, forming acids.
Ammonia / Amines	Network Integrity and End-Use Concerns	Impacts on downstream gas processing equipment and odorisation. Formation of nitrogen oxides with impact on end use operations.

Parameter / Contaminant	Identification Basis	Justification
Siloxanes	Network Integrity and End-Use Concerns	Formation of silica (silicon dioxide) post- combustion. Silica damages internal combustion engines, turbines and air pollution control devices.
Pesticides	Network Integrity and End-Use Concerns	Risks to infrastructure and end use equipment (e.g., toxic combustion products).
Pharmaceuticals	N/A	Justification for inclusion not provided.
Higher Organics / Chlorinated Compounds (PCBs)	N/A	Justification for inclusion not provided.
Semi-Volatile and Volatile Organic Compounds (SVOCs and VOCs)	Health and Safety	Monitoring suggested to ensure no build- up to concentrations posing health or safety concerns.
Halocarbons	Network Integrity and End-Use Concerns	Gas processing problems from post- combustion formation of corrosive compounds. Production of noxious gases post- combustion.

Similar work was conducted by GTI on a guidance document for the introduction of biomethane derived from high-BTU landfills [27]. A similar list of non-standard quality parameters was created, with the parameters uniquely identified in the study shown in **Table 14**.

Table 14 Unique Trace Contaminants Identified for Biomethane Injection from Landfill
Gas [27]

Parameter / Contaminant	Identification Basis	Justification
Bacteria / Microbes	Network Integrity and End-Use Concerns	Microbial-influenced corrosion (MIC) is one of the leading causes of pipeline failure in the oil and gas industry.
		APB, IOB and SRB are considered to be the most aggressive corrosion-causing bacteria. All three species have been detected in biogas samples.
Aldehydes and Ketones	Network Integrity and End-Use Concerns	Can lead to operational problems via the degradation of odorisation quality or inducing odorant fade / masking.

Prior to the establishment of the European Committee for Standardization (CEN) Technical Committee (TC) 408 (Natural gas and biomethane for use in transport and biomethane for injection in the natural gas grid) and the creation of the current European Standards for biomethane injection quality, work was completed by the CEN/TC 234/WG 9 (Injection of non-conventional gases into the natural gas network) to standardize biogas / biomethane quality requirements [28]. Within this work, technical, gas quality and important long-term safety and integrity aspects related to the delivery of biogas injection, distribution and end use were identified. In addition to the non-standard parameters / contaminants already covered, the CEN/TC 234/WG 9 committee identified the new parameters shown in **Table 15**.

### Table 15 Unique Trace Contaminants Identified by CEN/TC 234/WG 9 [28]

Parameter / Contaminant	Identification Basis	Justification
Phosphine (PH <sub>3</sub> )	Network Integrity and End-Use Concerns	Corrosive compounds: hazard to the integrity of the gas system.
	Health and Safety	Toxic gas: health hazard.

**Note:** Polyaromatic hydrocarbons (PAHs) were also identified by CEN/TC 234/WG 9 as a biomethane contaminant of concern. However, PAHs were excluded from this study due to their formation being primarily linked with thermal gasification production methods [28].

Finally, Gas Infrastructure Europe (GIE), an association with 70 natural gas industry members across 25 European countries, created a position paper on biomethane gas quality to contribute to the discussion of quality standardisation within the EU. Within the positional paper, GIE highlighted the need to control and monitor the carbon monoxide composition of biomethane, which may significantly increase safety risks due to its toxicity [29]. However, significant carbon monoxide concentrations are associated with thermal gasification biomethane production methods [28, 30], which are outside the scope of this review. Therefore, examination of carbon monoxide was excluded from this study.

In addition to the above references, three other wholistic biomethane quality assessment studies were analysed and utilised to create **Table 16**. However, no new monitoring parameters or trace contaminants were identified within these studies.

Study Details	GTI Dairy Waste [26]	GTI Landfill Gas [27]	Interconnect Guide for Renewable Natural Gas (RNG) in New York State [31]	Evaluation and Identification of Constituents in Pipeline Natural Gas, Biogas, and Biomethane in California [17]	Canadian Gas Association Quality Guidelines (2012) [32]	Contribution to CEN/TC 408 – Requirements and Recom. For Inject. Of N.C.S Gases [28]	Perspectives for a European Standard on Biomethane (2010) [30]	GIE Position on Gas Quality Whitepaper (2011) [29]
Organisation	Gas Technology Institute	Gas Technology Institute	Northeast Gas Association	California Energy Commission	Canadian Gas Association	European Committee for Standardization (CEN) Technical Committee 234 (Gas Infrastructure) Working Group 9 (Injection of non- conventional gases into gas network)	Biogasmax	Gas Infrastructure Europe
Location	USA	USA	New York, USA	California, USA	Canada	Europe	Europe	Europe
Feedstocks	Dairy Waste	Landfill Gas	All	Wastewater Treatment, Dry Green Waste, Solid Waste, Landfills	All	All	All	All
No. of Facilities (If Sample Analysis included in Study)	14	7	N/A	7	N/A	N/A	N/A	N/A
Type of Gas	Biogas, Biomethane	Biomethane	Biomethane	Biogas, Biomethane	Biomethane	Biogas	Biomethane	Biomethane
Monitoring Parameter	1. Literature study to determine list of target	1. No identification	1. Contaminants identified via ensuring	1. No identification	1. Existing natural gas quality specifications	1. Hazard identification process	1. No identification	1. Non- comprehensive

# Table 16 Summary of Monitoring Parameters Identified in Prescriptive (Non-Legislative) Biomethane Quality Studies

Study Details	GTI Dairy Waste [26]	GTI Landfill Gas [27]	Interconnect Guide for Renewable Natural Gas (RNG) in New York State [31]	Evaluation and Identification of Constituents in Pipeline Natural Gas, Biogas, and Biomethane in California [17]	Canadian Gas Association Quality Guidelines (2012) [32]	Contribution to CEN/TC 408 – Requirements and Recom. For Inject. Of N.C.S Gases [28]	Perspectives for a European Standard on Biomethane (2010) [30]	GIE Position on Gas Quality Whitepaper (2011) [29]
Identification Methods	compounds for analytical testing. 2. Interviews and surveys of dairy farmers and biogas producers.	methodology given.	biomethane interchangeability with natural gas. 2. Trace contaminant testing requirements based on feedstock.	methodology given.	<ol> <li>Existing</li> <li>European &amp;</li> <li>American</li> <li>standards.</li> <li>3.</li> <li>Recommendations</li> <li>of the CGA</li> <li>Biomethane Task</li> <li>Force.</li> </ol>	associated with known biogas contaminants.	methodology given.	set of parameters. 2. Parameters identified based on effects on potential effects on gas infrastructure (underground storages, LNG terminals and transmission systems).
Standard Parameters								
Water Content	Х		Х		Х		Х	
Heat Content (HHV)	X	x	X	(X)	Х		X	
Wobbe Index		Х	Х	(X)	Х		Х	Х
Temperature	Х			(X)	Х			
Hydrocarbon Dew Point	Х	Х	Х		Х		Х	
Total Sulfur Compounds, as Sulfur	X	Х	X	(X)	Х		X	X
Hydrogen Sulfide (H <sub>2</sub> S)	Х	х	Х	(X)	Х		х	X
Mercaptans	Х		Х	(X)	Х		Х	
Diluent Gases Total	Х	Х	X	(X)	Х			

Study Details	GTI Dairy Waste [26]	GTI Landfill Gas [27]	Interconnect Guide for Renewable Natural Gas (RNG) in New York State [31]	Evaluation and Identification of Constituents in Pipeline Natural Gas, Biogas, and Biomethane in California [17]	Canadian Gas Association Quality Guidelines (2012) [32]	Contribution to CEN/TC 408 – Requirements and Recom. For Inject. Of N.C.S Gases [28]	Perspectives for a European Standard on Biomethane (2010) [30]	GIE Position on Gas Quality Whitepaper (2011) [29]
Oxygen (O <sub>2</sub> )	Х		Х	(X)	Х		Х	Х
Nitrogen (N <sub>2</sub> )	Х	Х	Х	(X)				
Carbon Dioxide (CO <sub>2</sub> )	Х	Х	Х	(X)	Х	Х	X	Х
Mercury (Hg)			Х	(X)			X* (LF)	
Solid Particles	Х				X		Х	Х
Non-Standard Parameters								
Heavy Metals	Х	Х	Х	(X)	Х			
Hydrogen	Х	Х	Х	(X)	Х		Х	X
Ammonia	Х	Х	Х	(X)	Х	Х	Х	Х
Siloxanes	Х	Х	Х	(X)	Х	Х	X* (LF, SS)	X
Pesticides	Х		Х	(X)				
Pharmaceuticals	Х							
Higher Organics / Chlorinated Compounds (PCBs)	х		X	(X)	Х			
Semi-Volatile and Volatile Organic Compounds (SVOCs and VOCs)		X	X	(X)	X			
Polyaromatic Hydrocarbons						X **		X **
Halocarbons	Х	X	Х	(X)	Х	Х	X* (LF, SS)	X

Study Details	GTI Dairy Waste [26]	GTI Landfill Gas [27]	Interconnect Guide for Renewable Natural Gas (RNG) in New York State [31]	Evaluation and Identification of Constituents in Pipeline Natural Gas, Biogas, and Biomethane in California [17]	Canadian Gas Association Quality Guidelines (2012) [32]	Contribution to CEN/TC 408 – Requirements and Recom. For Inject. Of N.C.S Gases [28]	Perspectives for a European Standard on Biomethane (2010) [30]	GIE Position on Gas Quality Whitepaper (2011) [29]
Total Bacteria	Х	Х	Х	(X)	Х	Х		Х
Aldehydes / Ketones		X	Х	(X)				
Phosphine						Х		
Carbon monoxide								X **

(X) Contaminant was analysed but not explicitly recommended for monitoring for injection purposes.

- \* Measurement recommended depending on specific feedstocks. LF = Landfill, SS = Sewage Sludge.
- \*\* Excluded from study scope due to primary association with thermal gasification biomethane production methods.

## STATE OF LITERATURE UNDERSTANDING

The contaminants and monitoring parameters identified in **Table 16** are a comprehensive list of contaminants that have been identified as potential trace contaminants in biomethane production. The remaining chapter will be split into the discussion of the contaminants via classification into the following topics:

- Standard monitoring parameters
- Non-standard monitoring parameters

#### Standard Monitoring Parameters

#### Australian Requirements

The implementation of standard natural gas monitoring parameters for biomethane quality is a basic requirement to ensure the continued integrity and safety of the natural gas network and end users. In Australia, the mandated natural gas quality parameters are derived from AS 4564 (Specification for General Purpose Natural Gas). Under current legislation it is assumed that all biomethane production for injection purposes must meet the AS 4564 requirements, as shown in **Table 17**. When comparing the standard gas monitoring parameters identified by the studies in **Table 16**, it can be concluded that the AS 4564 requirements encompass most standard quality parameters monitored in other jurisdictions.

The scope for discussion of the AS 4564 gas quality requirements in this review is the potential for relaxation of limit values to better accommodate biomethane injection. This has occurred in several jurisdictions for various parameters. The implementation of these limit value relaxations and their methodologies will be discussed for the individual AS 4564 gas quality characteristic and component requirements.

Characteristics and Components	Units	Limit Value
Wobbe Index <sup>9</sup>	MJ/m <sup>3</sup>	46.0 – 52.0
Higher Heating Value	MJ/m <sup>3</sup>	42.3
Oxygen	mol %	0.2
Hydrogen Sulfide (H <sub>2</sub> S)	mg/m <sup>3</sup>	5.7
Odour Intensity	-	Where required, detectable at a level not exceeding 20 % LEL
Total Sulfur	mg/m <sup>3</sup>	50
Water Content	-	Dewpoint of 0 °C at the highest MAOP in the relevant transmission system (in any case, < 112.0 mg/m <sup>3</sup> )
Hydrocarbon Dew Point	-	2 °C at 3500 kPag
Total Inert Gases	mol %	7.0
Oil	mL/TJ	20

## Table 17 AS 4564 Gas Quality Requirements

<sup>&</sup>lt;sup>9</sup> Measure of the amount of heat released by a gas burner with a constant orifice. Used to denote gas interchangeability.

#### Wobbe Index and Higher Heating Values

Due to the typically lower energy content of biomethane compared to conventional natural gas, several jurisdictions have studied the possibility of reducing minimum Wobbe Index (WI) and Higher Heating Values (HHV) to reduce the additional requirements for biomethane injection into existing networks. However, changes to these minimum parameters must be carefully examined, due to potential detrimental effects on combustion characteristics e.g., flame lifting, which can lead to carbon monoxide formation and blowout (extinguishment) [33].

A significant amount of work on this topic was conducted by the California Council on Science & Technology (CCST) on determining quality requirements for biomethane injection in Californian pipelines. In this study, both minimum Wobbe Index and HHV were independently reviewed by the CCST [33]. The study analysed the regulatory history of both parameters, alongside the literature evidence for their current limits and the cost implications of any changes to either parameter. Based on this, it concluded that minimum HHV limits could be relaxed from 990 to 970 BTU/scf (36.9 to 36.1 MJ/m<sup>3</sup>), while maintaining the existing minimum Wobbe Index requirement of 1279 BTU/scf (47.7 MJ/m<sup>3</sup>). The relaxation of the lower HHV limit enabled biomethane producers to produce a greater range of compliant biomethane compositions, while maintaining the minimum Wobbe specification still ensured safe gas interchangeability.

While no regulated minimum HHV limit exists in Australia, a similar methodology could be employed to determine the extent of allowable gas quality relaxation for biomethane injection. Reductions in the lower Wobbe Index limit would provide biomethane producers with greater flexibility for producing compliant biomethane compositions, and allow them to forgo expensive and complicated HHV upgrading methods e.g. gas blending, propane enrichment.

#### Oxygen

The maximum oxygen limit of 0.2 mol % in AS 4564 may become a significant restriction for potential biomethane producers due to the specific equipment requirements for oxygen removal (e.g., PSA, membrane upgrading). Several studies have also reported oxygen content within final biomethane products in excess of the 0.2 mol% limit, up to 2 mol % [34-36].

Two studies were found regarding the suitability of increasing the maximum oxygen limit from 0.2 to 1.0 mol % [34, 37] in natural gas networks, for the purposes of biomethane injection. Both studies concluded that concentrations up to 1 mol % oxygen were not expected to result in significant changes to the risks of using the gas, efficiency of the fuel, pollutant emissions and the operability of equipment / appliances. However, both studies reported that steel corrosion rates in the presence of water were expected to increase five-fold for the corresponding increase in oxygen concentration. The first study, conducted in 2009 in the UK, reported insignificant impacts on asset lifetimes due to the increased corrosion rate. The second, conducted in 2018 for the Irish transmission and distribution networks, reported similar results while also reinforcing the need to maintain stringent water content limits to prevent corrosion from increased oxygen concentration. Details of both studies are shown in **Table 18**.

#### Table 18 Oxygen Limit Expansion Study Details

	UK	Ireland
Study Description	A study conducted by GL Industrial Services assessing oxygen specifications for a <7 barg distribution network in Didcot, UK.	A study conducted by Penspen on the suitability of increasing oxygen concentrations up to 1 % for Irish <i>distribution</i> <i>and transmission</i> networks. Directly referenced by the Commission for Regulation of Utilities (Irish Safety Regulatory Body) in the approval of oxygen limit modifications to the Gas Networks Ireland Code of Operation [38].

	UK	Ireland
Network Materials	82 – 98 % polyethylene with "the majority of the remainder being Spun Iron and Cast Iron."	Transmission network consists of steel pipelines with maximum allowable operation pressures from 19 – 85 barg. Distribution network consists of "mostly polyethylene pipelines and steel pipelines operating at maximum allowable operating pressures of 4 barg and 7 barg respectively."
Assessment Criteria	<ul> <li>Wobbe Index</li> <li>Heating value measurement (metering)</li> <li>Combustion fundamentals (flammability, flame temperature etc.)</li> <li>Flame stability and process efficiency</li> <li>Emissions</li> <li>Utilisation equipment (appliances, gas engines, boilers etc.)</li> <li>Industrial processes (glass, fertilizer, ceramics manufacturing etc.)</li> <li>Materials of construction (pipelines, appliances and meters)</li> </ul>	Corrosion assessment Explosion assessment Change in calorific value
Notable Impacts	Possible impacts on gas engines and turbines at high pressure operations (conditions not specified). May affect performance guarantees provided by OEMs due to their basis on original gas quality information <sup>10</sup> . Potential damage to fuel cells employing internal reforming systems <sup>11</sup> . Fivefold increase in CO <sub>2</sub> corrosion rate (predominant corrosion mechanism) in iron pipelines due to increased oxygen concentration (0.2 – 1.0 mol %). Corrosion is assumed to only occur for limited periods via water ingress from upset conditions. Assuming water presence for 30 days per year, corrosion simulation software calculated an expected failure time of > 100 years. The full assumptions used are shown in <b>Table 19</b> . Increase in sulphidation of copper carcassing and coper alloy components in meters.	Threefold increase in $CO_2$ – steel corrosion rate (predominant corrosion mechanism) due to increased oxygen concentration (0.2 – 1.0 mol %). Corrosion is assumed to only occur for limited periods via water ingress from upset conditions. Assuming water presence for 4 days per year, corrosion simulation software calculated an expected failure time of > 100 years. The full assumptions used are shown in <b>Table 19</b> .

 <sup>&</sup>lt;sup>10</sup> No impacts on gas engines and turbines were predicted by the Penspen report.
 <sup>11</sup> No impacts on fuel cells were predicted by the Penspen report.

UK	Ireland
Increase of oxygen concentrations up to 1.0 mol % are expected to lead to increasing instances of appliance burners, valves / meters etc. being blocked by flaking copper sulphide. The study noted that this was not expected to be a safety hazard but could lead to increased customer inconvenience.	

## Table 19 Oxygen Limit Study Corrosion Assumptions

Parameter	Units	UK Study	Ireland Study
Pipe Material	-	Cast Iron	Steel
Diameter	mm	177.8	Not specified
Wall thickness	mm	7	10
Temperature	°C	15	15
Pressure	kPa	200	8,000
Flow velocity (liquid)	m/s	0.5	0.5
CO <sub>2</sub> Content	mol %	2.5	2.5
O <sub>2</sub> Content	mol %	0.2, 1.0	0.2, 1.0
рН	-	6.3	Not specified
Time water present	days per year	30	4

At the time of writing, the jurisdictions related to both studies above have approved the injection of biomethane of up to 1 mol % oxygen content into their natural gas networks, via the mechanisms summarised in **Table 20**. For context, the current oxygen limits for biomethane injection into natural gas networks in Europe are shown in **Table 21**. A similar undertaking may be required for the current AS 4564 oxygen limits to promote biomethane production in Australia.

#### Table 20 Gas Regulatory Oxygen Limit Increases

	UK	Ireland
Year of Approval	2013	2019
Method of Change	Exemption for biomethane injection in the Gas Safety (Management) Regulations 1996 gas quality standards [39]	Amendment to the Gas Networks Ireland Code of Operations [38]
Additional Requirements	Only applicable to biomethane entry and exit points. Biomethane must meet all other GSMR quality requirements.	Only applicable to biomethane entry and exit points.

UK	Ireland
Exemption is only for pipelines operating up to 38 bar.	

## Table 21 European Regulatory Natural Gas Oxygen Limits (2019) [40]

	FR	NL	ES	SE	DE	СН	AT	π	DK	GB	BE	CZ
Distribution (mol %)	0.01 (0.75)	0.05	1.0	1.0	3.0	0.5	0.02	0.6	0.5	1.0	1.0	0.02
Transmission (mol %)	0.01 (0.70)	0.0005 - 0.5	0.3	1.0	0.001	0.5	0.02	0.6	0.5	0.2	0.2	0.5

#### Hydrogen Sulphide

Biogas and biomethane samples contain much higher concentrations of sulphur containing compounds than natural gas, with hydrogen sulphide concentrations normally present at concentrations between 80 - 4,000 ppmv depending on feedstock [16, 17]. However an in depth study into the potential expansion of the AS 4564 hydrogen sulphide limit has not been conducted due to all biomethane upgrading technologies reporting ease of meeting the existing standards. This can be observed in quantitative data gathered by several biomethane quality studies, that show maximum observed H<sub>2</sub>S specifications from biomethane production facilities are well below the current limits in AS 4564 (**Table 22**).

## Table 22 Maximum Biomethane Hydrogen Sulphide Measured Values

Author	Landfill Maximum (mg/m³)	Dairy Maximum (mg/m³)	Wastewater (mg/m³)
California Air Resources Board, Office of Health Hazard Assessment (2013) [41]	0.765	Below Detection Limit	270*
Gas Technology Institute (2019) [36]	Below Detection Limit	Below Detection Limit	Below Detection Limit
Paolini et al. (2018) [42]	-	-	3.5 +- 1.4
California Energy Commission (2020) [17]	Below Detection Limit	-	Below Detection Limit

\* Value obtained from biogas subjected to only partial clean-up i.e., not pipeline quality biomethane.

#### Odour Intensity

Several references were found that suggest biomethane may require additional odorisation requirements in comparison to conventional natural gas, due to the possible effects of odorisation interferences from trace biomethane contaminants [43-45]. A study performed between 2016 and 2018 on odorisation interference from compounds found in Italian biomethane showed that limonene, a terpene derived from the oil of citrus fruit peels, lead to significant degradation of the odour character of natural gas odorized with THT and TBM [43]. For limonene concentrations of 173 mg/m<sup>3</sup>, 50% of rhynologists were not able to characterize samples as being odorized natural gas. This is a concern due to concentrations of terpenes in biomethane facilities being reported of up to 240 mg/m<sup>3</sup>, post upgrading and cleaning processes [46]. In a study of four different food waste facilities, the average distribution of terpenes was found to contain 91 – 94 % of D-limonene [46].

#### Total Sulphur

A review conducted by GL Noble Denton for the UK Health and Safety Executive in 2011 analysing hazards from the use of biomethane in gas networks concluded that total sulphur content in the final biomethane product is not expected to be more severe than the existing UK GS(M)R limits [47]. This conclusion was based on data gathered from existing clean-up technologies for both landfill and industrial / agricultural waste feedstocks. A similar conclusion was reached by the individual GTI studies for dairy waste, WWTP sludge and landfill gas feedstocks [36]. With the primary sulphur compounds in raw biogas being hydrogen sulphide [26, 47], it is likely that complying with existing AS 4564 hydrogen sulphide limits will also lead to compliant total sulphur concentrations in the biomethane product.

#### Water Content

Raw biogas is commonly saturated with water due to the moist environment in digesters[14]. Water removal for biomethane production can be performed as a separate step e.g., via glycol dehydration, or as part of the biogas upgrading process (PSA). No references were found that referred to biomethane water content being likely to exceed current tariff limits throughout the review. This is likely due to the well-established nature of glycol dehydration for conventional natural gas dehydration, alongside the supplementary water removal provided by other biogas cleaning technologies e.g. adsorption and refrigeration for removing other trace constituents [14].

#### Hydrocarbon Dew Point

No changes are expected to be required for the hydrocarbon dew point limit in AS 4564. This is due to the lack of higher hydrocarbon species in biomethane, as compared to conventional natural gas [26]. Relatively little measured information was able to be found for this parameter. However, in the GTI landfill gas dataset, all 27 biomethane samples obtained from 7 different landfill gas sites were found to possess hydrocarbon dew points all below – 73°C [48]. The only consideration for hydrocarbon dew point limits being analysed is when propane blending is required to boost calorific values of biomethane. However, no literature could be found quantifying the effects of propane blending on hydrocarbon dew point.

#### Total Inert Gases

The regulation of total inert gases (maximum limit of 7 mol % in AS 4564) is intrinsically linked to the WI and is intended to limit the levels of higher hydrocarbons in natural gas [49, 50]. The presence of high levels of non-methane hydrocarbons such as ethane or propane can lead to incorrect combustion and create soot in gas appliances [50].

The relaxation of the existing AS 4564 inert gas limits was examined in this review due to its potential to limit the feasibility of biomethane production utilising landfill gases which have been observed to produce inert concentrations of up to 10 % in the final biomethane product [36]. For context, the WI of a binary gas consisting of 93 and 7 mol % methane and nitrogen, respectively, results in the AS 4564 lower WI limit of 46.0 MJ/m<sup>3</sup>. Therefore, the relaxation of the existing AS 4564 total inert gas limits must be preceded by either lowering the AS 4564 WI limit, or the use of propane injection to ensure than biomethane mixtures with > 7 mol % total inerts meet the minimum WI requirements. The feasibility of expanding the AS 4564 inert gas limits will be examined individually under each scenario.

The literature review did not find any examples of jurisdictions that considered the raising of inert gas limits to promote a wider range of acceptable biomethane compositions. However, the feasibility of expanding the total inert gas limits has been reviewed using the guidance provided in AS 4564 and by the Australian Energy Market Operator (AEMO) [49, 50] for the purpose behind the existing 7 mol % total inert limits.

The scenario of a total inert gas limit increase following the decrease of the minimum AS 4564 WI, strictly for the purpose of biomethane injection, is not expected to defy the intention behind the existing AS 4564 total inert gas limits (See excerpts from AS 4546 and the AEMO Gas Quality Guidelines below). Under the assumption that AS 4564 WI limits have been relaxed, a corresponding increase in the total inert gas limits is not expected to lead to significant departures from the spirit of the existing AS 4564 7 mol % inert limits. For example, a decrease of the allowable minimum WI from 46.0 to 45.0 MJ/m<sup>3</sup> (AEMO gas mitigation limit)<sup>12</sup> will require a corresponding increase in allowable total inerts from 7.0 to 8.5 mol % (45.0 MJ/m<sup>3</sup> requiring a binary gas consisting of 91.5 and

<sup>&</sup>lt;sup>12</sup> Similar in scale to the lowering of Californian minimum HHV for biomethane injection from 36.9 to 36.1 MJ/m<sup>3</sup>.

8.5 mol % methane and nitrogen, respectively). A binary methane and CO<sub>2</sub> mixture with a WI of 45.0 MJ/m<sup>3</sup> would consist of 6.5 mol % CO<sub>2</sub> which is within the range of existing AS 4564 specifications. With inerts being classified as non-hazardous for the purpose of gas quality, combined with biomethane lacking higher hydrocarbons, it is expected that expanding the allowable inert gas limits in AS 4564 to correspond to a decrease in the WI will comply with the current justification for the existing AS 4564 7 mol % inert gas limits.

- Section A.3.10 AS 4564:2020: "The specification for total inert gases is intended, in conjunction with the Wobbe Index limits, to limit the levels of higher hydrocarbons. High levels of CO2 in particular could have significant implications for some gas consumers with specific needs."
- Section 5.7 AEMO Gas Quality Guidelines 2017: "Inerts in natural gas under the Gas Safety (Gas Quality) Regulations are carbon dioxide (CO<sub>2</sub>), nitrogen (N<sub>2</sub>), helium (He), argon (Ar) and oxygen (O<sub>2</sub>).
   [...] Inerts by themselves do not create a safety hazard. The specification for inerts is a method of controlling the levels of non-methane hydrocarbons such as ethane or propane. Limiting the total inerts in a gas restricts the non-methane hydrocarbons that can be present in the gas without exceeding the Wobbe Index limits. High non-methane hydrocarbon levels may cause incorrect combustion and create soot in gas appliances.

Expanding the AS 4564 total inert gas limits to facilitate the injection of biomethane containing high inerts via propane blending is also not expected to defy the intention behind the existing AS 4564 total inert gas limits. To examine this scenario, a maximum propane limit of 3 mol % was assumed for the purposes of biomethane blending. This limit was chosen by emulating the maximum propane limits found in other jurisdictions by this review (Belgium and the Czech Republic) [51]. To meet the current WI lower limit of 46.0 MJ/m<sup>3</sup>, a ternary biomethane composition maximising total inert gas requires 88.5 mol % methane, 8.5 mol % nitrogen and 3.0 mol % propane. This gas composition was compared with the test gases utilised for testing appliances under limiting conditions (e.g., testing the CO/CO<sub>2</sub> ratio for gas burners under maximum load) as described in AS/NZS 5263.0:2017 (Gas Appliances Part 0: General requirements). The range of compositions used for testing natural gas appliances are shown in **Table 23**. It can be observed that appliances are tested with natural gas compositions that contain up to 10 mol % nitrogen, and 14 mol % propane. Therefore, it is unlikely that the extension of the current AS 4564 total inert gas limits to facilitate propane blended biomethane injection will cause unacceptable sooting and combustion characteristics for gas appliances.

Test Gas Designation	Application	Composition (mol %)					Characteristics (MJ/m <sup>3</sup> )	
		Hydrogen	Methane	Propane	Nitrogen	Air	нну	WI
N	Natural Gas	-	97.5	1	1.5	-	37.8	50.0
Na	Natural Gas	-	86	14	-	-	45.7	55.0
Nb	Natural Gas	13	87	-	-	-	34.4	49.1
Nc	Natural Gas	-	90	-	10	-	34.0	44.0
S	Natural Gas	-	-	55	-	45	52.1	45.7

## Table 23 AS/NZS 5263.0:2017 Test Gas Table (Adapted)

#### Oil

The current AS 4564 limit on entrained oil is based on "good current practice" for compressor station operation and not dependent on the conveyed gas medium. No quantitative or qualitative results were found during the review of liquid contaminants being conveyed in the final biomethane product stream. It is not expected that consideration of changes to the existing entrained oil limits will be required for biomethane injection.

## Non-Standard Monitoring Parameters

The addition of non-standard monitoring parameters to facilitate biomethane production in Australia must be viewed in the context of existing global legislation. The regulatory range of limit values of each parameter of interest was obtained from the set of gas quality legislation collected by the project, along with the number of jurisdictions imposing limit values on each parameter. This is covered in further detail in **Chapter 6** of this review. The results of this analysis are provided in **Table 24**. The following can be gathered from the information:

- The addition of Australian limit values for well-regulated parameters should be given greater consideration.
- Sparsely regulated parameters should be considered during facility design and for tariff requirements primarily as a precautionary measure.

In the following section, the quantitative range of non-standard monitoring parameter concentrations within raw biogas and biomethane will be compared with existing limits in the EU standard EN 16723-1:2016, if available. This standard will be utilised as a common benchmark to assess the suitability of its adoption for Australian networks, in the context of the quantitative contaminant data within the literature. Comparison of the EU standard limit values with the concentration ranges for biogas and biomethane provide understanding of the risks of contaminant breakthrough, alongside the technical capabilities of existing upgrading methods in meeting the existing biomethane quality standards.

Parameter	No. of Appearances in Gas Quality Regulations	Regulatory Range	Comments
Hydrogen	9/13	0.1 – 5.0 mol %	High variance in limit values
Siloxanes	9/13	0.01 – 10 mg Si / m <sup>3</sup>	High variance in limit values
Ammonia	8/13	3 – 20 mg/m <sup>3</sup>	High variance in limit values
Halocarbons	7/13	1 – 10 mg Cl/F / m <sup>3</sup>	High variance in limit values
Semi-Volatile and Volatile Organic Compounds (SVOCs and VOCs)	3/13	-	Limits based on individual VOC / SVOC species.
Heavy Metals	2/13	-	Limits based on individual heavy metal species
Total Bacteria	1/13	4 x 10 <sup>4</sup> CFU/scf (qPCR per APB, SRB, IOB group) and commercially free of bacteria of >0.2 microns	-
Aldehydes / Ketones*	0/13	-	-
Pesticides	0/13	-	-
Pharmaceuticals	0/13	-	-

## Table 24 Existing Regulatory Context for Non-Standard Monitoring Parameters

Parameter	No. of Appearances in Gas Quality Regulations	Regulatory Range	Comments
Higher Organics / Chlorinated Compounds (PCBs)*	0/13	-	-
Phosphine	0/13	-	-

**Note:** Due to the lack of regulatory commentary in compounds marked with \*, their analysis will be conducted under the VOC/SVOC umbrella analysis.

## Hydrogen

What are the pre- and post-upgrading concentration ranges associated with this contaminant for individual feedstocks?

The absolute hydrogen concentration ranges for raw biogas and biomethane found during the review are shown in **Table 25**.

## Table 25 Hydrogen Concentration Range and Average Values

	Hydrogen Concentration (mg/m <sup>3</sup> )
Biogas Range	BDL
Biomethane Range	BDL – 0.9 vol. %
EN 16723-1:2016 Limit	N/A

Quantitative hydrogen concentrations found in the literature are summarised in **Table 26**. It is apparent that hydrogen content in both the biogas and biomethane product is low, with most facilities having hydrogen concentrations below detection limits. From the various feedstocks, landfill gas is reported to produce the most hydrogen content [14], as can be seen in the results of the GTI landfill gas study.

## Table 26 Quantitative Pre- and Post- Upgrading Hydrogen Concentration Data

Feedstock	Biogas concentration	Post-upgrading concentration	Treatment method	Comments	Reference
Landfill Gas	Not specified	BDL – 0.9 vol %	Not specified	Found in 21 / 27 samples obtained from 7 sites	[27]
	BDL (0.01 vol %)	Not measured	N/A	Undisclosed number of sites	[52]
Dairy Waste	BDL (0.1 vol %)	BDL (0.1 vol %)	Not specified	12 Raw samples (12 sites) 23 Biomethane samples (2 sites)	[26]
WWTP	BDL (0.1 vol %)	BDL (0.1 vol %)	Not specified	1 Site	[36]
	BDL (0.5 vol %)	BDL (0.5 vol %)	Water scrubber, dehumidifier, activated carbon, VSA	1 Site	[42]

#### What are the detrimental effects of this contaminant?

Sufficiently large hydrogen concentrations can have severe impacts on natural gas infrastructure and end-users alike. However, the relatively low concentrations associated with the quantitative data and regulatory range indicate that hydrogen content within biomethane is unlikely to cause significant issues to either the natural gas distribution network, or end users. This is supported by analysis of hydrogen mixing by the International Renewable Energy Agency (IRENA) [53], which states that hydrogen concentrations < 5 mol % are suitable for almost all applications except gas turbines, porous gas storage and other more niche applications.

#### Distribution Networks

For the hydrogen concentrations associated with biomethane production, it is possible that sufficiently high hydrogen concentrations can lead to biomethane that is unable to meet the minimum AS 4564 Wobbe Index requirements. This is based on a recent assessment of hydrogen blending into the ACT network [54]. The study analysed potential non-integrity based impacts of hydrogen blending, and found that hydrogen compositions of up to 5 mol % can cause biomethane with high inerts to fall below the minimum Wobbe Index requirement. The implications of non-negligible hydrogen concentrations for lean gas compositions are also stated in a COAG Energy Council report analysing hydrogen blending into distribution networks [55], which states noncompliance with minimum WI limits as a significant technical impact.

However, limiting the allowable inerts concentrations of biomethane to those found in currently reticulated coal seam gas will allow significantly higher hydrogen concentrations before minimum Wobbe Index requirements are not met. The assessment of hydrogen blending into the ACT network suggests limiting maximum inerts concentrations in biomethane to those found in coal seam gas will allow hydrogen concentrations of up to 30 mol % before failing to meet minimum Wobbe Index values.

Under the GPA Engineering assessment of hydrogen blending for concentrations up to 10 mol % for Australian distribution networks, no significant impacts or implications were found on gas quality, safety and risk aspects, materials, network capacity and blending.

#### What are the suitable removal processes and their effectiveness?

No facilities / references were found to have dedicated hydrogen removal stages. In combination with the "conservative" 25 mol % hydrogen limit recommended for Australian distribution networks in an EPCRC report [56], the requirement for hydrogen removal for Australian biomethane is unlikely to be required.

#### What is the current state of understanding of required limit values?

Hydrogen limit values identified during the regulatory review were mostly not associated directly with the requirements of biomethane production. Of all the hydrogen limits found, most were specified in conventional natural gas legislative documents (e.g. the Swiss hydrogen limit of 2.0 vol % is specified in SVGW G18 – Gas Quality Guideline). The only instance of hydrogen limits being included specifically with biomethane regulations is from SoCalGas Rule 30, which requires a trigger value (for increased monitoring) of 0.1 mol % for the sake of pipeline integrity. Due to the aforementioned Australian studies providing confidence of the suitability of hydrogen concentrations of up to 10 - 25 mol % for distribution network integrity, it is likely that no specific consideration is required for the appropriation of existing hydrogen limit values for Australian biomethane injection.

#### Siloxanes

Siloxanes are a family of semi-volatile man-made compounds containing oxygen-silicon (O-Si-O) bonds with methyl (CH<sub>3</sub>) groups bound to the silicon atoms. They are often used as anti-foaming agents and fire retardants in addition to being used in many consumer products such as deodorants and shampoos [57]. Due to their presence in consumer products, siloxanes are a common contaminant in biogas produced from wastewater and landfills. A summary of common biomethane siloxane contaminants is presented in **Table 27**.

## Table 27 Common Siloxane Species found in Biogas and Biomethane [21, 33]

Compound	Abbreviation	Formula	MW (g/mol)
Hexamethyldisiloxane	L2	C6H18OSi2	162

Compound	Abbreviation	Formula	MW (g/mol)
Octamethyltrisiloxane	L3	C8H24O2Si3	236
Decamethyltetrasiloxane	L4	C10H30O3Si4	310
Dodecamethylpentasiloxane	L5	C12H36O4Si5	385
Hexamethylcyclotrisiloxane	D3	C6H18O3Si3	222
Octamethylcyclotetrasiloxane	D4	C8H24O4Si4	297
Decamethylcyclopentasiloxane	D5	C10H30O5Si5	371
Dodecamethylcyclohexasiloxane	D6	C12H36O6Si6	445
Trimethylsilanol	TMS / TMSOH	C3H10OSi	90

Note: The common units for siloxane concentrations is mg Si/m<sup>3</sup> of gas.

What are the pre- and post-upgrading concentration ranges associated with this contaminant for individual feedstocks?

The absolute siloxane concentration ranges for raw biogas and biomethane found during the review are shown in **Table 28**. Quantitative siloxane concentrations from studies collected during the review are shown in **Table 29**.

A comprehensive comparison of siloxane concentrations between individual feedstocks has been conducted by Rasi et al. [58] and is presented in **Figure 6**. It can be observed that landfills and WWTPs exhibit higher ranges of siloxane values than biogas plants processing agricultural waste.

## Table 28 Siloxane Concentration Range and Average Values

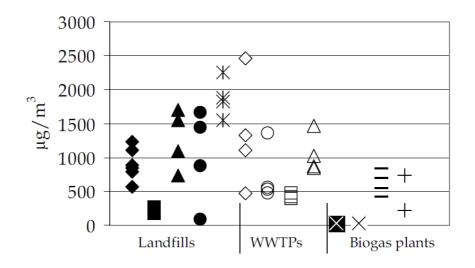
	Total Siloxane Concentration (mg Si/m <sup>3</sup> )
Biogas Range (This study)	BDL - ~14.4
Biogas Range (External Studies) <sup>13</sup>	0 – 8000 [47]
Biomethane Range (This study)	BDL - 0.4
EN 16723-1:2016 Limit (Max)	0.3 – 1.0

## Table 29 Quantitative Pre- and Post- Upgrading Siloxane Concentration Data

Feedstock	Biogas concentration	Post- upgrading concentration	Treatment method	Comments	Reference
Landfill Gas	Not specified	BDL – 0.4 mg Si/m <sup>3</sup> (D4)	Not specified	Found in 5/27 samples from 7 sites. Only siloxane detected was D4.	[27]

<sup>&</sup>lt;sup>13</sup> Total siloxane concentrations of up to 8,000 mg/m<sup>3</sup> have been reported for raw landfill gas. No qualitative information was found with siloxane concentrations near this range.

Feedstock	Biogas concentration	Post- upgrading concentration	Treatment method	Comments	Reference
	See Figure 7	Not measured	N/A	Undisclosed number of sites	[52]
Dairy Waste	BDL (0.5 ppmv Si)	BDL (0.5 ppmv Si)	Not specified	12 Raw samples (12 sites) 16 Biomethane samples (2 sites))	[26]
WWTP	Not specified	BDL (0.51 mg/m <sup>3</sup> )	Not specified	1 Site	[36]
	2.02 mg Si/m <sup>3</sup>	< 0.04 mg Si/m <sup>3</sup>	Water scrubber, dehumidifier, activated carbon, VSA	1 Site	[42]
	BDL - 22.9 ppbv (L2) 2.74 - 5.44 ppbv (L3) 4.37 - 6.52 ppbv (D4) 2.41 - 2.7 ppbv (L4) 6.64 - 11.2 ppbv (D5) 2.7 - 3.55 ppbv (L5) 6.31 - 7.74 ppbv (D6) 0.059 - 0.140 mg Si/m <sup>3</sup> (Total)	BDL (L2) BDL (L3) BDL - 0.00327 ppbv (D4) BDL - 0.0815 ppbv (L4) BDL - 0.157 (D5) BDL (L5) BDL (L5) BDL (D6) BDL - 0.0006 mg Si/m <sup>3</sup> (Total)	Site 1: Coalescing filter, PSA, activated carbon, membrane separation, activated carbon polishing, silica gel polishing. Site 2: Compression cooling, activated carbon.	6 Raw samples (2 sites) 3 Biomethane samples (1 site) 3 "Clean" gas samples (1 site) Only D5 was present in biomethane quality gas. "Clean" gas was passed through an activated carbon bed to remove siloxanes	[17]
WWTP + Bio-waste	0.15 – 5.3 mg Si/m <sup>3</sup>	N/A	Compression cooling	1 Site	[59]







## Figure 7 Siloxane Concentrations in Biogas from a Municipal Solid Waste Landfill [52]

#### What are the detrimental effects of this contaminant?

Siloxane concentrations are important due to their post-combustion impacts, via the formation of silica that can foul combustion equipment, turbines and add-on air pollution control devices [27]. The silica deposits are hard and can be abrasive to generator engine moving parts [21]. Their build-up can also foul the surfaces of heat exchangers, clog narrow tubes and collect in the oil of engines, requiring more frequent oil changes [33].

Due to the thermally insulating properties of silica, contamination can lead to the deactivation of process sensors and lead to localised overheating. Fuel cell systems can also be damaged via the clogging of catalytic fuel processing reactors and porous electrodes, resulting in performance degradation [33].

The minimum allowable limit for siloxanes may be dictated by the limits set by microturbine and gas turbine manufacturers, due to earlier experiences of turbine failure associated with biogas [58]. Engine manufacturers have specified siloxane concentration limits varying from 0.03 to 28 mg/m<sup>3</sup> [27].

#### What are the suitable removal processes and their effectiveness?

A USA nationwide survey of biogas clean-up technologies conducted by GTI provides several commercial treatment methods available for processing inlet siloxane concentrations of 100 mg/m<sup>3</sup> to concentrations ranging from <0.1 to 1.0 mg Si/m<sup>3</sup> in the biomethane product [60]. The survey results are summarised in **Table 30**.

The survey results show that most siloxane removal processes are based on adsorption processes utilising regenerative polymeric and activated carbon materials. Compliance with the existing EN 16723-1:2016 siloxane limits of between 0.3 and 1.0 mg Si/m<sup>3</sup> can also be observed, indicating the availability of suitable siloxane technologies to meet common gas quality specifications. However, the lack of available siloxane break-through detection systems indicate that siloxane associated risks are unlikely to be entirely mitigated, due to the potential for undetected breakthrough. Given the high siloxane concentrations reported for landfill gas-based feedstocks (up to 8,000 mg Si/m<sup>3</sup>), the necessity for mandated periodic siloxane testing for feedstocks associated with high siloxane contents should be considered.

Company	Product Type	No. of Installations	Siloxane Removal Efficiency, Outlet Siloxane Content <sup>14</sup>	Siloxane Break- through Detection
Willexa Energy	Regenerative polymeric and carbon polishing media	> 80	2 stage system with 90-95 % efficiency per stage 0.25 – 1.0 mg/m <sup>3</sup>	FTIR real time monitoring.
DCL America	Regenerative polymer media	2	> 99 % < 1 mg/m <sup>3</sup>	Method regulated in service agreement.
Parker NLI	Regenerative	~43	Not given <0.10 mg/m <sup>3</sup>	No breakthrough detection.
Venture Engineering	Regenerative polymeric resin, mole sieve, activated alumina and activated carbon polishing bed	5	Not given 0.58 mg/m <sup>3</sup>	Currently testing siloxane analysers.
Quadrogen Power Systems, Inc	Proprietary C3P technology (condensing, conversion, capture, polish)	3	Not given <0.10 mg/m <sup>3</sup>	No breakthrough detection.
Environmental Systems & Composites, Inc.	Regenerative activated carbon	3	> 95 % Not given	No breakthrough detection, method is currently being researched.
Unison Solutions Inc.	Activated carbon	70	Not given	No breakthrough detection

## Table 30 Summary of GTI Survey Siloxane Removal Technologies

<sup>&</sup>lt;sup>14</sup> Based on 100 mg/m<sup>3</sup> inlet.

Company	Product Type	No. of Installations	Siloxane Removal Efficiency, Outlet Siloxane Content <sup>14</sup>	Siloxane Break- through Detection
			<100 ppbv total siloxane species	
Pioneer Air Systems	Chill gas to (-23 to 2 °C) and carbon adsorption	25	> 99 % < 1 ppm	No breakthrough detection
Acrion Technologies	Absorption with liquid CO <sub>2</sub> generated from the biogas	2	> 99.9% < 0.1 ppm	No breakthrough detection

Arnold et al. have reported siloxane breakthrough associated with activated carbon removal methods [21]. In one application at a landfill gas-based facility, parallel activated carbon filters were installed to protect a microturbine from silica deposition. The newly installed filters were able to remove virtually all trace compounds in the gas. However, after 17 weeks of operation, the average D3, D4 and TMS removal efficiencies were reduced to an average of 10 %. The concentrations of L2-L4 species were reported to be higher in the purified gas compared to the filter inlet. The study postulated that the early breakthrough of siloxanes was likely due to the preferential adsorption of other trace contaminants, including VOCs / sulphur / moisture, that displace siloxane from the activated carbon adsorption sites.

In the same study, Arnold et al. suggests that cryogenic siloxane removal has been gaining industry interest due to the drawbacks of siloxane breakthrough experienced by activated carbon [21]. Therefore, cryogenic methods for the specific purpose of siloxane removal were analysed with the results shown below:

- Siloxane removal efficiencies vs cooling temperature as indicated in Figure 8.
- Economic feasibility of cryogenic cooling temperature vs biogas siloxane concentration per Table 31.

The results in **Table 31** indicate the substantial siloxane concentrations required in the biogas feed stream to economically utilise cryogenic cooling to temperatures of < - 30 °C. A recent 2020 survey of biomethane upgrading plants in Europe indicated a best-case scenario of 5 % market share of cryogenic cooling (5% of upgrading plant types were presented as "unknown"). Thus, it is likely that the use of cryogenic cooling to maintain biomethane siloxane levels is not commonly practiced.

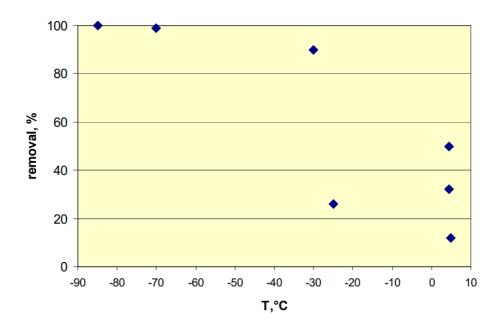


Figure 8 Siloxane Removal Efficiency vs Cooling Temperature [61]

Table 31 Siloxane Removal via Cooling and Activated Carbon Economic Applicability	
[61]	

Stage 1		Stage 2		Application Range	
Cooling and Reheating <sup>15</sup>	Siloxane Separation Efficiency (%)	Adsorption	Remaining Siloxane Concentration (mg/m <sup>3</sup> )	Biogas Siloxane Concentration (mg Siloxane/m <sup>3</sup> )	Biogas Flow Rate (m³/hr)
Heating to 35 -40 °C	0	Activated Carbon	< 1	< 10	< 150
Cooling to 2°C and heating to 10°C	< 25	Activated Carbon	< 1	< 30	> 150
Cooling < – 30°C and heating 10 °C	< 90 %	Activated Carbon	< 1	< 200 – 1,000	Unlimited

#### What is the current state of understanding of required limit values?

Biomethane siloxane concentrations, while well-regulated with 9/13 jurisdictions having limits in place, are the subject of wide debate. Regulatory limits mostly range between 0.3 - 1.0 mg Si/m<sup>3</sup>, as proposed by the EN 16723-1 standard. However, a few jurisdictions, namely California (USA), Germany and Austria, have adopted siloxane limits on the outer extremes of the regulatory range. The specification utilised by SoCalGas, one of the major Californian utility companies, is a trigger and lower action limit (LAL) at the siloxane contents of 0.01 and

<sup>&</sup>lt;sup>15</sup> Biogas is typically heated to 10 °C for activated carbon filtration.

0.1 mg Si/m<sup>3</sup> [62]. The German and Austrian specifications lie on the other end of the spectrum, having limits of 5 and 10 mg Si/m<sup>3</sup> respectively.

The SoCalGas trigger level initiates increasing siloxane testing for biomethane facilities found in breach of the specifications. The absolute values of the SoCalGas trigger and lower action limits were mandated by the Californian Public Utilities Commission (CPUC) based on a report conducted by the California Council on Science and Technology (CCST) assessing maximum allowable siloxane specifications. Within the CCST study, it was concluded that the 0.1 mg Si/m<sup>3</sup> LAL did not particularly have robust scientific evidence to support the limit, nor to support its relaxation. The LAL was characterised as an order of magnitude estimate, based on a sparse number of studies analysing existing combustion applications and reported engine specifications by manufacturers.

The higher German and Austrian siloxane limits have been specified using a similar basis but arriving at different conclusions. The recommended 5 mg Si/m<sup>3</sup> German limit in its technical standard documents DVGW G260 / G262 indicate that the limit is based on the limit "for engines", including the caveat that gas turbines "can be more sensitive" [63]. The project was unable to access the Austrian technical standard documents OVGW G31 and G B220 and could not obtain the basis for the relatively high siloxane limit specification.

## Ammonia

Ammonia is a toxic gas which can induce risk during the event of a leak. It can also induce corrosion in gas networks and increases NOx emissions when burned. It is created in the presence of organic nitrogen compounds in waste and can possibly carry over from gas treatment or via breakthrough from raw biogas [64].

What are the pre- and post-upgrading concentration ranges associated with this contaminant for individual feedstocks?

The absolute ammonia concentration ranges for raw biogas and biomethane found during the review are shown in **Table 32**.

	Ammonia Concentration (mg/m <sup>3</sup> )
Biogas Range	0.2 – 63
Biomethane Range	0.15 – 0.25
EN 16723-1:2016 Limit (Max)	10

## **Table 32 Ammonia Concentration Range and Average Values**

Ammonia was measured from 14 sample streams across 7 Californian biogas / biomethane production facilities [17]. Ammonia concentrations were below 100 ppbv for 11 out of 14 sample streams, with three facilities showing average ammonia concentrations in raw biogas per **Table 33**. Analysis of the biomethane product from those three facilities showed effective ammonia removal, with removal efficiencies of > 80% post-purification.

## Table 33 Ammonia Concentrations in Californian (USA) Biogas and Biomethane

Facility	Feedstock	Biogas (ppmv)	Biomethane (ppmv)
East Bay Municipal Utility District <sup>16</sup>	Wastewater	13.7	2.45

<sup>&</sup>lt;sup>16</sup> East Bay Municipal Utility District and the Zero Waste Energy Development "biomethane" were produced from biogas cleaning sufficient for on-site consumption and were not processed to pipeline quality biomethane specifications.

Zero Waste Energy Development	Solid Waste and Green Waste	90.2	3.39
CR&R Incorporated	Solid Waste and Green Waste	28.2	0.214

Ammonia concentration ranges compiled from the remaining studies found are summarised in Table 34.

## Table 34 Ammonia Concentrations – Various Studies

Feedstock	Biogas Concentration	Biomethane Concentration	Treatment Method	Comments	Reference
Landfill Gas	Not specified	BDL	Not specified	27 Samples from 7 sites	[27]
	0.022 – 0.055 mol %	Not specified	Not specified	Undisclosed number of sites	[52]
	BDL (1 ppm)	Not specified	Not specified	1 Site	[58]
Dairy Waste	BDL (0.001 mol %) – 0.004 mol %	BDL (0.001 mol %)	Not specified	12 Raw samples (12 sites) 16 Biomethane samples (2 sites)	[26]
Agricultural Waste	0.5 – 2.0 ppm	Not specified	Not specified	1 Site	[58]
WWTP	Not specified	BDL (10 ppmv)	Not specified	1 Site	[36]
	0.25 mg/m3	0.25 mg/m3	Water scrubber, dehumidifier, activated carbon, VSA	1 Site	[42]
	BDL (1 ppm)	Not specified	Not specified	1 Site	[58]
WWTP + Biowaste	BDL (0.2 mg/m <sup>3</sup> ) – 1.5 mg/m <sup>3</sup>	N/A	Compression cooling	1 Site	[59]

#### What are the detrimental effects of this contaminant?

Anhydrous ammonia has been known to lead to stress corrosion cracking in carbon steel [47]. However, the low concentrations of ammonia in biomethane are unlikely to lead to this issue. In the presence of oxygen, ammonia also leads to corrosion of ferrous materials (carbon steel) and non-ferrous materials (brass) alike [28]. In the presence of water, ammonia can also lead to pitting in copper-based alloys [47].

The possibility of ammonia degrading odorization quality and inducing odour fade / masking was suggested by the GTI landfill study [27]. However, no references could be found to support this concern.

The maximum observed ammonia concentration in this literature review was 63 mg/m<sup>3</sup>. This value is similar to the value obtained by a UK study for non-conventional gases, which analysed biomethane literature to produce an ammonia concentration range of 0.6 - 50 mg/m<sup>3</sup> in raw biogas.

#### What are the suitable removal processes and their effectiveness?

The removal of ammonia from biogas is reported to be highly effective, as shown by its concentration range in biomethane found via this study of  $0.15 - 0.25 \text{ mg/m}^3$ . This is supported by a Swedish study of four biomethane facilities using unique feedstocks to produce biogas with concentrations between 10 - 100 ppm ammonia. In all of the clean biomethane samples obtained from the four facilities, all ammonia concentrations were reported to be below detection limits of 1 ppmv [35]. The effectiveness of ammonia removal during the biomethane upgrading process can also be seen in the data from the Californian CR&R facility in **Table 33** which shows an effective ammonia removal rate of > 99% following a water scrubbing and VPSA system.

#### What is the current state of understanding of required limit values?

The regulatory review revealed ammonia concentrations to be well regulated, with eight out of twelve gas quality guidelines including ammonia specifications. The range of ammonia limit values is between "technically free" and 20 mg/m<sup>3</sup>.

Biomethane quality guidelines in California, USA currently contain a provision to limit ammonia concentrations to below 0.001 vol % (7 mg/m<sup>3</sup>). This was suggested by the four major utility providers during the deliberation process for Californian biomethane regulations, due to concerns about pipeline integrity. While no basis was provided for the absolute value of 7 mg/m<sup>3</sup>, it can be seen that the proposed limit is within the regulatory range implemented in various jurisdictions studied in this review. Therefore, it is likely that the basis for existing ammonia concentration limits in biomethane regulation is due to concerns for pipeline integrity.

This important factor should be considered during any attempts to implement ammonia limit values for biomethane injection into Australian gas networks. In particular, pipeline fittings and materials should be analysed for ammonia contents of up to 10 mg/m<sup>3</sup>.

Recent work conducted by the PRCI has revealed a lack of knowledge of interplay between the contaminants associated with biomethane production, including ammonia [45]. The analysis of ammonia's effects on pipeline materials must be conducted in combination with the presence of other biomethane specific contaminants, e.g. terpenes, CO etc.

### Halocarbons

Halocarbon compounds are compounds containing halogen atoms e.g., F, Cl. Their presence in biomethane originates from their use in various applications such as air conditioning systems, aerosols and firefighting agents [27]. If not directly found in the feedstock, their presence in the raw biogas is due to the degradation of the initial waste stream into volatile halocarbons. However, some species such as chlorofluorocompounds are present directly from the volatilization of compounds in plastic foam etc., and their presence is a direct function of the biogas feedstock composition [65]. The main issues from the presence of halocarbons in biomethane are their detrimental effects on gas processing, including noxious and corrosive post-combustion products.

What are the pre- and post-upgrading concentration ranges associated with this contaminant for individual feedstocks? The absolute ranges for halocarbon concentrations found during this study are shown in **Table 35**.

#### **Table 35 Halocarbon Concentration Range and Average Values**

	Halocarbon Concentration
Biogas Range	BDL – 735 mg Cl/m <sup>3</sup>
Biomethane Range	BDL
EN 16723-1:2016 Limit (Max)	Based on health assessment criteria derived by CEN/TR 17238:2018 (Proposed limit values for contaminants in biomethane based on health assessment criteria)

The University of California study on biogas and biomethane production facilities in California recorded significant halocarbon quantities in Californian landfill gas (LFG), compared to biomethane produced from non-landfill counterparts [17]. The compounds that were present at relatively high concentrations are summarised in **Table** 

**36**. It also noted that halocarbon levels were not significantly reduced by the cleaning processes used at the two landfill biogas facilities examined. The non-landfill-based facilities produced halocarbon contamination at generally lower levels, as shown in **Table 36**, and were reported to be less subject to widespread halocarbon contamination from multiple halocarbon species. The three biomethane production facilities included in the study (Point Loma Biofuels, WWTP/ CR&R, Organic Waste / Blue Line Energy, Organic Waste) were recorded with halocarbon concentrations below detection limits for all species tested in both raw biogas and biomethane streams.

	Landf	ill Gas	Non-Landfill Gas		
	Raw Biogas Facility 1, Facility 2 (ppmv)	Clean Biogas Facility 1, Facility 2 (ppmv)	Raw Biogas Range (ppmv)	Biomethane Range (ppmv)	
1,2-dichloroethane	0.718, 1.330	0.713, 1.480	BDL – 0.535	BDL	
Dichlorodifluoromethane	0.157, 0.117	0.152, 0.102	BDL - 0.008	BDL	
1,1-dichloroethene	0.036, 0.259	0.035, 0.304	BDL – 0.094	BDL	

## Table 36 Subset of Halocarbon Concentrations in Two Californian Landfills

The detection of ppmv range halocarbons is also noted in the GTI landfill gas dataset [27]. However, their results showed that not all landfill gas sites contain detectable levels of halocarbons in their cleaned biogas. Out of 27 samples, only two halocarbon species were detected (freon-12, chloroethane). Only 6 samples were found to contain Freon-12, the commonly banned refrigerant, at maximum concentrations of 2.3 ppmv. Chloroethane was found in only 3 of 27 samples, with a maximum concentration of 0.31 ppmv.

Significant halogen containing compounds were detected at a landfill site in Istanbul, Turkey, resulting in total halogenated compound concentrations of up to 67.3 mg/m<sup>3</sup> in biogas subjected to activated carbon cleaning [66]. This total concentration was composed of a variety of halocarbon products including hydrochlorofluorocarbons, volatile halogenated hydrocarbons, chlorine, and other fluorinated compounds. Notably, the chlorine concentration was found to be 22.8 mg/m<sup>3</sup> which is substantially higher than the regulatory range of halocarbon concentrations found via this review.

Rey et. al also studied the prominence of halocarbon contamination from an undisclosed number of MSW Spanish landfills [52]. Their results showed halogen contents of up to 22 mg Cl/Nm<sup>3</sup> for all samples, also exceeding the existing regulatory range of 1 - 10 mg Cl/m<sup>3</sup> limit. A study across seven landfill sites in the UK also reported substantially higher halocarbon concentrations, with landfill biogas chlorine contents of up to 735 mg/m<sup>3</sup> [65]. This shows that halocarbon concentrations have the potential to breach the safe regulatory limits, particularly for landfill gas-based feedstocks.

The relatively lower quantity of halocarbons in non-landfill gas based biomethane is shown in the remaining GTI datasets for dairy waste and wastewater treatment plants [26, 31]. All sampling, ranging from the raw biogas to the final biomethane product, produced halocarbon concentrations below detection limits of 0.1 ppmv. However, the study of biomethane from wastewater sludge by Paolini et al. shows that non-landfill gas feedstocks can also possess significant halocarbon contamination, with reported chlorine and fluorine concentrations of 26.8 and 0.17 mg/m<sup>3</sup> in wastewater sludge biogas, respectively [42]. Despite this, measurement of the quality of the resulting biomethane showed chlorine and fluorine concentrations below detection limits, showing both the effectiveness and necessity of effective halocarbon cleaning methods.

#### What are the detrimental effects of this contaminant?

The presence of halocarbons in biomethane can lead to detrimental effects for gas processing. Halocarbons in landfill gas at concentrations of approximately 600 mg/m<sup>3</sup> led to serious corrosion of gas fuelled engines in

Germany after 900 – 1000 engine hours [67]. Halocarbon combustion can also lead to noxious gases such as dioxins and furans [28].

One study reported maximum recommended chlorine concentrations for gas fuelled engines of 250 mg/m<sup>3</sup> which is well above the identified regulatory halocarbon range [67].

Quantification of halocarbon health risks have been attempted utilising existing permissible occupational exposure levels in one study [68]. Utilising the permissible exposure levels set by Californian OSHA and OEHHA bodies, total halocarbon levels in landfill biogas were found to be significantly below the permissible levels for most species studied, as shown in **Table 37**. Chloroethene, tetrachloroethene and dichlorobenzene were the only species found to be above the recommended OSHA / OEHHA limits.

# Table 37 Concentration range of selected halocarbons (mg/m<sup>3</sup>) at different landfill sites vs permissible occupational exposure levels [68]

	Biogas Concentrations			Exposure Levels	
	Landfill biogas [68]	Eklund et al. (1998) [69]	Allen et al. (1997) [67]	Cal/OSAH PEL	OEHHA
Total Halocarbons	9.90-15.65	-	246-1239	-	-
Dichlorodifluromethane	BDL-1.68	6.28	<0.5-231	-	-
Trichlorofluromethane	BDL -0.21	-	<0.5-74	4950	-
Chloroethene	BDL -0.24	-	<0.1-87	5600	0.84
1,2-Dichloroethene	BDL -1.99	-	1-182	-	-
Trichloroethene	BDL -0.48	-	<0.1-152	790	-
Tetrachloroethene	BDL -1.10	-	<0.1-255	135	-
Chlorobenzene	BDL -0.74	5.29	-	170	-
Dichlorobenzene	ND-3.99	24.35	-	46	5.7

#### What are the suitable removal processes and their effectiveness?

A comprehensive review of state-of-the-art physical, chemical and biological technologies for biogas upgrading conducted in 2015 listed regenerative activated carbon filtration as the only suitable technique for halocarbon removal [23]. However, other studies have reported individual instances of halocarbon removal via alternative techniques, including a report of halocarbon and other trace contaminant removal via cryogenic upgrading [70]. Some review studies have also documented compatibility of halocarbon removal with chemical / physical absorption and PSA [14, 22], however no specific instances of application of the technology were referenced. Therefore, it is reasonable to conclude that the most likely commercially available process for targeted halocarbon removal is via regenerative activated carbon adsorption.

#### What is the current state of understanding of required limit values?

The literature information found indicated that current halocarbon limits are configured according to health protective standards. No regulatory references were found that classified existing halocarbon limits to be dictated by pipeline integrity requirements.

The European standard EN 16723-1 explicitly recommends halocarbon limit values set by health protective standards via the process described in EN 17238. The same methodology is applied in the decision-making process for Californian biomethane regulations, with the inclusion of halocarbon limits to pipeline tariffs being

driven by the health protective concerns in a report created by the California Air Resources Board (CARB) and the Office of Health Hazard Assessment (OHHA).

## Volatile and Semi-Volatile Organic Compounds

Volatile and semi-volatile organic compounds (VOC/SVOC) are formed as intermediary products in the degradation of organic matter during anaerobic digestion [26]. Many of these compounds are potentially harmful to humans or the environment [35]. For this part of the review, VOCs and SVOCs have been defined as VOC/SVOC compounds that have not been studied on their own i.e. siloxanes / halocarbons are technically VOCs, however have been analysed individually due to their importance as a biomethane contaminant.

For this study, a list of VOC compound types of interest was compiled from compounds previously identified during this review (e.g. aldehydes / ketones) and other VOCs highlighted in the literature. The compound types are described below. VOC vs feedstock data is presented in **Appendix A**.

- Terpenes: Can lead to gas odorant masking and degradation of rubber materials [46].
- Aldehydes: Can cause operational problems for gas processing and end use applications by degrading odorisation quality or inducing odorant fade or masking [48].
- **Ketones:** Can cause operational problems for gas processing and end use applications by degrading odorisation quality or inducing odorant fade or masking [48].
- **BTEX:** Benzene, toluene, ethylbenzene and xylene (BTEX) compounds that are used in some farming operations and have toxic properties [26]
- Polychlorinated Biphenyls (PCBs): A group of 209 synthetic chlorinated compounds that have bioaccumulative and toxic properties [26].

It is important to understand that the VOC/SVOCs detailed in this study are those that have been commonly identified as compounds of interest in typical biomethane feedstocks. However, VOC/SVOCs that should be considered for individual projects / jurisdictions should be compiled from analysis of local biogas and biogas feedstocks, due to the dependence of VOC/SVOC composition on jurisdictional waste disposal rules [35].

#### What are the pre- and post-upgrading concentration ranges associated with this contaminant for individual feedstocks?

A study of VOCs and semi-VOCs in biogas produced from dairy waste showed low concentrations of VOCs and SVOCs [26]. Out of 115 target compounds, 34 compounds were found above detection limits. The highest absolute concentration for one compound was found to be 0.147 ppmv for toluene. This was compared to the OSHA recommended exposure limit of 200 ppm, suggesting that VOC/SVOCs from dairy waste feedstocks are unlikely to lead to health concerns. This trend was observed for all 34 compounds detected. All compounds with available exposure limit information were found at concentrations several of orders of magnitude below said limits in the final biomethane product.

A significant piece of work quantifying VOC concentrations pre- and post-upgrading was conducted by Arrhenius et al. [35]. The report includes analysis of VOC removal with respect to different feedstocks and upgrading processes. The results of the study are shown in **Table 38**. Unfortunately, the VOC values weren't separated into individual compounds for further analysis.

	Units	Organic Waste Plant	Waste Water Treatment Plant	Organic Waste Plant + Waste Water Treatment Plant	Energy Crop and Food Industry By- products	Manure
No. of Sites	-	2	2	3	3	1

## Table 38 Comparison of VOC Removal by Biogas Feedstock and Upgrading Method

	Units	Organic Waste Plant	Waste Water Treatment Plant	Organic Waste Plant + Waste Water Treatment Plant	Energy Crop and Food Industry By- products	Manure
Average VOCs in biogas	mg/m <sup>3</sup>	700	200	400	10-30	20
VOCs after PSA	mg/m <sup>3</sup>	5	3	-	-	-
VOCs after Water Scrubbing	mg/m <sup>3</sup>	100	-	70, <5	<1 x 3	<1
VOCs after Amine Scrubbing	mg/m <sup>3</sup>	-	10	10	-	-

The 2020 study of 7 different facilities by the Californian Energy Commission (CEC) provides insight into the presence of BTEX, aldehydes, ketones and PCBs in biogas and biomethane [17]. BTEX was found to be above detection limits for most biogas samples, however were found to be consistently below concentrations found in conventional natural gas.

Analysis of aldehydes and ketones in the 2020 CEC study provided similar profiles to conventional natural gas except for the components listed below. Facilities that did not upgrade biogas to biomethane quality indicated significantly higher concentrations of aldehydes and ketones.

- Acetone was found at 240 ppbv in wastewater biomethane, compared to BDL in conventional natural gas.
- Methylethylketone and valeraldehyde were found at levels 190 300 times higher in clean biogas vs conventional natural gas.

Analysis of PCBs in the CEC study revealed BDL concentrations for five out of the seven facilities, with the two landfill facilities being the ones producing measurable PCB concentrations. However, the clean biogas from one of the landfill facilities also produced BDL PCB concentrations, indicating the effectiveness of the cleaning process (water condensation / activated alumina / silica gel / molecular sieve / carbon polishing) in removing PCBs. PCB concentrations in the entire GTI USA dataset (containing dairy waste, WWTP and landfill feedstocks) were found to be below detection limits for all sampling studies conducted [31].

Biogas obtained from farms was found to contain lower total VOCs (5 – 8 mg/m3) compared to other feedstocks. In comparison, landfill and WWTP found TVOCs between  $46 - 173 \text{ mg/m}^3$  and  $13 - 268 \text{ mg/m}^3$  respectively [58].

#### What are the detrimental effects of this contaminant?

As previously discussed in this review, terpenes observed in biomethane have been shown to lead to significant degradation of odorisation character for natural gases odorized with TBM and THT [43]. The effects of terpenes on rubber materials have been studied by Arrhenius et al. [46]. The study compares the suitability of O-ring materials with terpenes found in biogas plants, as recommended by O-ring manufacturers. The information is shown in **Table 39**. However, the basis for material compatibility was not stated.

Material	Brand	Paracymene	Cymene or pCymene	Dipentene, limonene	Pinene	Camphene
NBR	Nitrile	Х	4	2	2	2
EPDM	EPDM	Х	4	4	4	4
CR	Neoprene	4	4	4	3	4
SBR	SBR	4	4	4	4	4
VMQ	Silicone	Х	4	4	4	Х
lir	Butyl	4	4	4	4	4
ACM	Polyacrylate	4	4	4	4	4
CSM	Hypalon	4	4	4	4	4
FKM	Viton	1	1	1	1	1
AU, EU	Polyurethane	3	4	4	3	3
FVMQ	Fluorosilicone	2	2	2	2	2
FEPM	Aflas	Х	Х	Х	Х	Х
FFKM	Kalrez	1	1	1	1	1

## Table 39 O-Ring Material Compatibility with Terpenes [46]

Note: 1 = Satisfactory, 2 = Fair, 3 = Doubtful, 4 = Unsatisfactory, X = Insufficient Data

#### What are the suitable removal processes and their effectiveness?

The work conducted by Arrhenius et al. provides significant insight into the suitability and efficiency of VOC removal from different feedstocks and upgrading methods (See **Table 38**).

The study analysed the removal effectiveness for individual VOC compounds and came to the following conclusions:

- Amine scrubbing is particularly effective for removing ketones and esters while not being particularly
  effective in removing other VOCs. The gas drying stage post-amine scrubbing was reported to have a
  removal efficiency of 95 % of the remaining VOCs.
- Water scrubbing was reported to be less effective than other upgrading methods at VOC removal. In two participating plants, clean gases upgraded with water scrubbing contained considerably more VOCs than gas upgraded in parallel utilising other upgrading techniques.
- The facilities utilising PSA upgrading were reported to have activated carbon pre-treatment for the PSA feed. The activated carbon was reported to remove most contaminants, apart from chlorinated hydrocarbons, with removal efficiencies of more than 90 %.

#### What is the current state of understanding of required limit values?

Three out of thirteen jurisdictions possessed biomethane quality limit values for VOC/SVOCs considered in this review. Two were based on BTEX components, with California, USA and the UK regulating a maximum 904 mg/m<sup>3</sup> toluene and 100 mg/m<sup>3</sup> xylene limits, respectively. Both limits have been imposed for the purposes of biomethane injection, with the Californian standard based on health protective limits based on permissible exposure concentrations [71]. The derivation process for the 100 mg/m<sup>3</sup> xylene recommendation could not be found by the review, however the limit is intrinsically linked to biomethane due to its introduction via the

Biomethane from Waste quality protocol produced by the UK Environmental Agency for biomethane injection into natural gas networks [72].

The third implementation of VOC limits are contained in the guidelines for biomethane injection in Quebec, Canada. The limit specified is a maximum total VOC content of 3.7 ppm [32]. However, the project was not able to access the necessary regulatory documents to determine the methodology behind the implemented value.

Little information could be found for the remaining VOC/SVOC families examined. Work by the PRCI has proposed the derivation of limit values for terpenes due to their disposition to heavily affect natural gas odorisation schemes [45], however much research is required before definitive limits are established.

#### Heavy Metals

Heavy metals in biomethane can be produced through the volatilization of metal via the degradation of concentrated plant materials and metal-containing products e.g., copper containing fungicides for dairy waste feedstocks [26]. They can lead to toxicological and environmental problems, alongside potential corrosion of aluminium metal and alloys used in gas network infrastructure.

#### What are the pre- and post-upgrading concentration ranges associated with this contaminant for individual feedstocks?

The GTI dairy dataset tested for arsenic, cadmium, copper, lead, molybdenum, selenium and mercury from biogas and biomethane derived from dairy waste feedstocks from 14 unique facilities in the USA [26]. The results are summarised in **Table 40**.

Gas Type	Number of Facilities Sampled	Number of Samples	Results
Raw Biogas	9	9	2 samples above DL. Copper concentration of up to 60 μg/m <sup>3</sup> Molybdenum concentration of up to 2 μg/m <sup>3</sup> Mercury concentration of up to 0.02 μg/m <sup>3</sup>
Clean Biogas	5	7	2 samples above DL. Mercury concentration of up to 0.06 μg/m <sup>3</sup>
Biomethane	2	23	All heavy metals BDL.

### **Table 40 Heavy Metal Presence in Dairy Waste Feedstocks**

The 2020 CEC review of biogas and biomethane facilities in California, USA also detected sporadic heavy metal concentrations [17]. The concentrations of a total of 17 heavy metals were analysed. The metals known to produce volatile compounds under the reducing conditions of anaerobic digesters, arsenic and antimony, produced several detections. However, it was reported that arsenic vapor was removed at efficiencies of > 90% by the clean-up processes at the sites where it was detected. Notably, the study postulates that most of the heavy metal detections for certain species (Cr, Mn, Ni and Zn) were likely associated with aerosolised particles of a mechanical origin and not from volatilization into the biogas. This was attributed to the metals being as likely to be detected in clean vs raw biogas. The maximum heavy metal concentrations detected in the study are shown in **Table 42**.

# Table 41 Maximum Average Heavy Metal Concentrations in Californian Biogas / Biomethane

Metal Species	Metal Concentration (µg/m <sup>3</sup> )	Gas Type	Feedstock
Ве	BDL	Biogas	Landfill
Cr	6	Biogas	Landfill
Mn	6	Biogas	Landfill
Со	0.322	Biogas	Landfill
Ni	60.2	Biogas	Landfill
Cu	11.9	Biomethane	WWTP
Zn	113	Biogas	Landfill
As	8.36	Biogas	Landfill
Se	0.0844	Biogas	Landfill
Sr	0.511	Biogas	Landfill
Мо	0.747	Biogas	Landfill
Cd	0.6	Biomethane	WWTP
Sb	2.02	Biogas	Landfill
Ва	7.22	Biogas	Landfill
Hg	0.00627	Biogas	WWTP
ті	0.000378	Biomethane	Organic Waste
Pb	3.9	Biogas	WWTP

The GTI landfill gas dataset displayed similar results to the CEC 2020 study [27]. Mercury content was found in 6 / 27 samples from 7 unique facilities between  $0.03 - 0.05 \ \mu g/m^3$ . No arsenic was found, and smaller concentrations of other volatile metals were found in only 3 / 27 samples.

Another study of 24 different heavy metals of Californian biogas from 6 facilities utilising 3 unique feedstocks showed that levels of antimony (Sb), lead (Pb), copper (Cu) and aluminium (Al) in biogas fell well below the Californian OSHA and OEHHA risk management trigger levels [68]. However, arsenic concentrations in some landfill gas samples were found to slightly exceed the 8-hour permissible exposure limit, but not by a significant factor (arsenic concentrations of 8.5 +- 3.4 vs PEL of 10 µg/m<sup>3</sup>).

#### What are the detrimental effects of this contaminant?

The detrimental effects of heavy metals can be characterised into health risks and risks to pipeline integrity. Analysis of the suitability of biomethane for pipeline injection into the UK gas network states that the heavy

metals of most concern are arsenic and mercury [47]. Other studies have highlighted exposure based health risks from heavy metals at concentrations found in biogas / biomethane, particularly for arsenic, antimony, copper and lead in the case of a scientific report produced for Californian legislators [41].

The consequences of mercury ingress into natural gas networks from an integrity standpoint are the formation of amalgams and consequent corrosion of aluminium alloys. However, this corrosion process requires the presence of liquid water. Mercury can also lead to liquid metal embrittlement (LME) which can lead to rapid intergranular cracking in copper alloys and intergranular cracking / pitting corrosion in aluminium alloys. According to [47], general industrial practice recommends mercury concentrations of > 10  $\mu$ g/m<sup>3</sup> to be risk assessed for potential integrity concerns. Due to the potential for low mercury concentration gases to build-up concentrated pockets of liquid mercury over time, if the mercury dew point of the gas is reached, assessments for the necessity of mercury removal equipment and potential mercury concentrating mechanisms have been recommended for facilities with mercury presence in the biogas feedstock [47].

#### What are the suitable removal processes and their effectiveness?

Generally, the low levels of volatile metals in biogas do not necessitate the use of a dedicated removal process [47]. Activated carbon, a commonly used polishing unit for various biomethane upgrading methods, has also been reported to effectively remove traces of mercury in both conventional natural gas and biomethane to concentrations of  $0.1 \ \mu g/m^3$  [30].

#### What is the current state of understanding of required limit values?

The recommended limit for mercury in natural gas in AS 4564 is 1  $\mu$ g/m<sup>3</sup>. The limit is based on the background atmospheric concentration of mercury in air of 0.02  $\mu$ g/m<sup>3</sup>, which would not be significantly impacted with the introduction of 1  $\mu$ g/m<sup>3</sup> mercury after consideration of post-combustion dilution effects. Compliance towards this standard for biomethane injection in Australia is likely to lead to sufficient health and integrity protection, while not significantly hampering the development of biomethane injection. This is due to the < 1 $\mu$ g/m<sup>3</sup> concentrations observed in both biogas and biomethane data collected by this study, alongside the detrimental effects of mercury corrosion being associated with larger concentrations of > 10 $\mu$ g/m<sup>3</sup>.

Regulatory limit values for non-mercury based heavy metals were only found in two jurisdictions (California, USA and Canada) due to health protective concerns. Both jurisdictions regulated copper and arsenic, with California also regulating lead and antimony concentrations [73]. The implementation of similar health-based limit values in Australia would need to consider the prominence of these four species, alongside other heavy metals, in promising biogas feedstocks to determine if such limits are required for the unique Australian waste compositions.

## Total Bacteria

#### What are the pre- and post-upgrading concentration ranges associated with this contaminant for individual feedstocks?

Quantitative bacterial concentrations were analysed for 7 biogas / biomethane production facilities in California via the CEC 2020 study [17]. The study showed aerobic and anaerobic spore-forming bacteria in 50 and 25 % of biogas and biomethane samples, respectively. Similar analysis conducted on conventional natural gas resulted in spore-forming bacteria below detection limits. Absolute bacterial concentrations were found to be in similar orders of magnitudes to other biogas studies, measuring between 10 - 100 colony forming units per m<sup>3</sup>.

DNA sequencing of the bacteria collected in the 2020 CEC study showed most cultivable bacteria found at relatively high concentrations were Bacillus species that were resistant to adverse conditions such as heat, cold, desiccation and radiation. Quantitative PCR analysis of the species also revealed sulphate reducing bacteria (SRB), iron oxidizing bacteria (IOB) and acid producing bacteria (APB) all below detection limits for all samples collected.

The results of the GTI study on dairy waste feedstocks report similar conclusions [26], with 25 % of total biomethane samples containing spore forming bacteria compared to a 70 % in "clean" biogas. The study also noted that the detection rate for total anaerobic bacteria (including spore and non-spore forming) increased between "clean" biogas (1/7 samples) and biomethane (10/22) samples, indicating that total anaerobic bacteria may also be growing or accumulating in biomethane clean-up unit parts. In contrast to the 2020 CEC study, the main bacterial species found in raw biogas samples were APB and IOB. The GTI study also noted slight

reductions in the total (alive or dead) number of bacteria in the final biomethane product compared to raw biogas, however this effect was not very pronounced.

Examination of bacteria in landfill gas resulted in total bacterial counts between 5.13 x 10<sup>5</sup> to 3.29 x 10<sup>8</sup> per 100 scf [27]. Out of 27 samples, all were found to contain bacteria, with some presenting higher and some lower values when compared to natural gas. Analysis of IOB, SRB and APB species also revealed similar concentrations to those found in natural gas samples.

Another study of 6 Californian facilities utilising various feedstocks also revealed statistically insignificant quantities of IOB, SRB and APB within all biogas samples collected. The study concluded that the IOB and APB concentrations were unlikely to reduce the service life of the facilities characterized in that particular study [68]

#### What are the detrimental effects of this contaminant?

The most pressing detrimental effect from bacterial presence in biomethane is the opportunity for microbial influenced corrosion (MIC) which can degrade the integrity, safety and reliability of pipeline operations and is one of the leading causes of pipeline failure in the oil and gas industry [27]. MIC is facilitated by five basic bacterial groups (APB, IOB, SRB, denitrifying bacteria (DNB) and methanogens). APB, SRB and IOB are the most concerning species in terms of corrosion.

In terms of health and safety, the inhalation of microorganisms from unprocessed biogas is considered to be much lower consequence that the inhalation of hydrogen sulphide and ammonia at biogas concentrations [25]. Inhalation of biomethane has been assumed have similar effects to inhalation of conventional natural gas, due to preliminary testing results by the Swedish University of Agricultural Sciences indicating similar microorganism densities [74]. Due to the low volumes of gas inhaled during typical exposure activities e.g. from stovetop cookers, the risk of spreading disease via biogas / biomethane was judged to be very low. However, the study did not identify individual pathogens, and others suggest that further study is required to draw specific conclusions for individual biomethane feedstocks [25].

#### What are the suitable removal processes and their effectiveness?

A small scale study of parallel filters for the removal of live bacteria was conducted by GTI for dairy waste feedstocks. The study showed effectiveness for the removal of live bacteria utilising filters sized from 0.2 to 1 micron, however more detailed results were not made available.

#### What is the current state of understanding of required limit values?

The only jurisdiction with specific bacteria limit values are those in the Californian legislature that require biological concentrations of  $< 4 \times 10^4$  / scf and commercially free of bacteria > 0.2 microns. However, this limit was contentiously debated by biomethane producers during the deliberation process of the Californian biomethane quality standards. Proponents claimed that the proposed limits were far in excess of high efficiency particulate air (HEPA) filter standards, which removes particles > 0.3 microns at 99.97% efficiency. Biomethane proponents also asserted that the biological limits were in excess of those suggested by the World Health Organization for filtration sterilization. However, the CPUC upheld the existing biological limits of  $< 4 \times 10^4$  / scf and commercially free of bacteria > 0.2 microns, on the basis of pipeline integrity protection.

Other jurisdictions with no regulatory requirements for bacterial testing have also opposed the inclusion of bacterial testing requirements in individual pipeline quality agreements. Within the UK, certain companies have reported bacterial testing to "incur large annual cost[s]", while not detecting significant bacterial content [75].

## Unregulated Monitoring Parameters and Contaminants

#### Pesticides, Pharmaceuticals

The use of pesticides and pharmaceuticals for the agriculture industry has led to concerns of these compounds being retained in agricultural waste feedstocks used for biomethane production [47]. Health related risks have been raised due to some pesticides being considered persistent and bio accumulative [17]. Pharmaceuticals and pesticides were previously included in biomethane gas tariffs for utility providers in California, USA, however have been eliminated as constituents of concern in the most recent biomethane quality legislation [73]. However, the decision behind their removal from pipeline tariffs were not able to be found by this review.

In a review of quantitative pesticide and pharmaceutical contents in biogas and biomethane, very little instances of concentrations above detection limits were observed. Analysis of the GTI dairy waste feedstock report showed maximum pesticide concentrations 4 orders of magnitude below OSHA recommended exposure limits [26]. Across 7 different Californian facilities utilising a range of biogas feedstocks, analysis of biogas and biomethane for 21 different pesticides revealed no samples above detection limits for all facilities / gases tested.

Similar reports of pharmaceuticals below detection limits were observed [26].

#### Phosphine

Little information could be found for phosphine content of biogas / biomethane. Phosphine is a colourless, flammable and toxic gas that is reported to be present in landfill and other biogas feedstocks by several sources [18, 28]. Despite this, no significant literature was found that recorded qualitative or quantitative evidence of its presence in biogas / biomethane production facilities.

# 6. Regulatory Review

# **GLOBAL OVERVIEW**

A global review of biomethane quality specifications for pipeline injection was conducted. The countries considered were countries which operated greater than five biomethane production / biogas upgrading facilities. A summary of the status of global biomethane quality specifications is shown in **Table 42**.

## Table 42 Global Biomethane Injection Quality Standards Summary

Country	Number of Upgrading Plants [2, 3]	Most Recent Data (Year) [2, 3]	Consistent National Standard for Biomethane Injection [3]
EU Countrie	S		
Germany	232	2019	Yes
France	131	2020	Yes
United Kingdom	80	2018	Yes
Sweden	70	2018	No
Netherlands	53	2020	Yes
Denmark	46	2019	Yes
Switzerland	38	2019	Yes
Italy	18	2020	Yes
Finland	17	2019	Yes
Norway	16	2020	Unknown
Austria	15	2020	Yes
Non-EU Cou	Intries	1	
U.S.A.	77	2018	No
China	73	2017	Yes
South Korea	10	2017	Yes
Canada	9	2018	No
Japan	6	2014	No
Brazil	5	2017	Yes

A qualitative assessment of the regulatory schemes for each jurisdiction is shown in **Table 43**. Another set of supra-national guidelines for biomethane quality comes in the form of the European Union standard EN 16723-1:2016 (Natural Gas and Biomethane for use in Transport and Biomethane for Injection in the Natural Gas Network – Part 1: Specifications for Biomethane for Injection in the Natural Gas Network). This standard is currently being utilised by several EU member nations and is likely to be the most promising standard to emulate for Australian biomethane injection quality.

Out of the 17 jurisdictions in **Table 42**, only 12 possessed their own unique quality standards for biomethane injection. From the review, three of the European jurisdictions appear to solely rely on the European Union standard EN 16723-1:2016 to define biomethane quality limits. Therefore, for the purposes of the regulatory analysis, the three countries were combined into one jurisdiction befalling under the EN 16723-1:2016 quality specifications.

No regulatory information could be found for Norway, South Korea or Japan.

It is important to note that many of the original regulatory documents were written in the native language of their jurisdictions. The interpretations of the regulations within this review rely on the accuracy of widely available online translation software.

To analyse the current understanding of limit values for the trace contaminants identified in earlier sections of this report, the full quality standards of the 13 jurisdictions were documented (12 unique and 1 EN Standard), and are shown in **Appendix B**. This information was used to determine the regulatory understanding for each trace contaminant, by assessing the number of times each component appears in regulations and the variance and range of its limit values.

The regulatory review also covered the following topics which will be discussed within this chapter:

- Analysis of allowable feedstocks for biomethane injection into the natural gas network (See Table Table 43).
- Analysis of contaminant sampling requirements.
- Analysis of schemes or methods that are conducive to wider implementation of biomethane production and injection.

Country	Gas Quality Legislation	Comments	Reference
Germany	DVGW 260 – Gas Quality (Conventional Gas Regulations) DVGW 262 – Usage of Gases from Renewable Sources in the Public Gas Supply (Biomethane Regulations)	Could not access DVGW 260 / 262 for detailed review. Landfill gas injection is forbidden.	[33, 76, 77]
France	AFG 562-2 - Injection of biomethane into natural gas transmission networks (Biomethane Regulations)	<ul><li>Biomethane producers must have buffer systems to manage off-spec gas.</li><li>Quality standards are based on technical specifications of the transporter.</li><li>Biomethane producers may be required to provide equipment (e.g. buffer storage) to ensure non-compliant gas does not enter the transmission network.</li><li>Sewage gas injection is forbidden.</li></ul>	[33, 78]
United Kingdom	Gas Safety (Management) Regulations 1996 (Conventional Gas Regulations) Biomethane Quality Protocol (Technical Standard) (Biomethane Regulations)	Exemption for biomethane injection in the Gas Safety (Management) Regulations 1996 gas quality standards for higher allowable oxygen limit (0.2 to 1.0 mol %).	[39, 40]
Sweden	SS-EN 16726:2015 (Conventional Gas Regulations) SS-EN 16723-1: 2016 (Biomethane Regulations)	Confirmed by the Swedish Energy Agency.	[40]

Country	Gas Quality Legislation	Comments	Reference
Netherlands	Regulation of the Minister of Economic Affairs of 11 July 2014, no. WJZ / 13196684 (Biomethane Regulations)	Confirmed by Gasunie Transport Services (Netherlands). All feedstocks (including landfill gas) are allowed for biomethane injection.	[16, 79]
Denmark	Executive Order on Gas Quality (21/03/2018) (Biomethane Regulations)	•	[80, 81]
Switzerland	Directive SVGW G18 – Gas Quality Guideline (Conventional Gas Regulations) Directive SVGW G13 – Injection of Renewable Gases (Biomethane Regulations)	<ul> <li>Could not access SVGW G13 / G18 for detailed review.</li> <li>Possible to inject non-compliant gas into network as long as it can be proved that the gas is compliant at the first exit point of a consumer.</li> <li>Inlet gas must be at least 50% combustible components.</li> <li>Landfill gas injection is forbidden.</li> </ul>	[33, 82]
Italy	Resolution January 29, 2019 27/2019/R/gas – Update of the directives for the connection of biomethane plants to natural gas networks and implementation of the provisions of the decree of 2 March 2018. (Biomethane Regulations)	Resolution 27/2019/R/gas defers to biomethane quality standards in the Italian UNI EN 16723-1 standard.	[83]
Finland	SFS-EN 16723-1:2016 (Biomethane Regulations)	Confirmed by the Finnish Safety and Chemicals Agency	
Norway	-	No relevant documents were able to be found	
Austria	Directive OVGW G31 – Natural gas in Austria (Conventional Gas Regulations) Directive OVGW G B220 – Regenerative Gases (Biomethane Regulations)	Could not access OVGW G31 / G B220 for detailed review. Confirmed by the Austrian Association for Gas and Water Specialists (OVGW). Both guidelines to be superseded by new guideline document G B210 – Gas Quality on the 1 <sup>st</sup> of June 2021.	[33, 54]

Country	Gas Quality Legislation	Comments	Reference
		Landfill and sewage gas injection is forbidden.	
U.S.A.	No legislated national biomethane quality guidelines SoCalGas Rule 30 (Biomethane Regulations)	The regulatory study was conducted on the well-developed Californian legislation for biomethane quality requirements. California was chosen due to it being the largest biomethane producing state. Hazardous waste landfill gas injection is forbidden.	[84]
China	GB 17820-2012 – Natural Gas (Conventional Gas Regulations) T/BGLM 0003.01-2018 – Quality requirements for Bio Natural Gas entering natural gas pipe networks (Biomethane Industry Guidelines) T/BGLM 0004.01-2018 – Bio Natural Gas (Biomethane Industry Guidelines)	Could not access GB 17820-2012 for review. Biomethane should be tested in early summer and early winter to assess seasonal variations.	[24]
South Korea	-	No relevant documents could be found	
Canada	No legislated national biomethane quality guidelines BNQ 3672-100 – Biomethane - Quality Specifications for Injection into Natural Gas Distribution and Transmission Systems (Biomethane Regulations)	The regulatory study was conducted on the BNQ 3672-100 specifications for the Quebec natural gas network as this was the only standard found during the review.	[85]
Japan	-	No relevant documents could be found	
Brazil	Resolution No. 8 January 30 2015 (Biomethane Regulations)	Only allows for biomethane injection from agricultural feedstocks. Biomethane producers must use 0.2 µm filtration before pipeline injection.	[86]

## Sampling Requirements

A summary of sampling requirements by jurisdiction is shown in **Table 44**. Substantial amounts of information were available for the individual sampling regimes of each jurisdiction, alongside the decision-making process behind the sampling requirements. A common trend amongst the sampling regimes was the waiving of sampling requirements for individual contaminants depending on feedstock usage. For instructive purposes, two of the publicly available detailed sampling regimes will be described here:

- SoCalGas Sampling Requirements in California, USA
- GTI Recommendations for Sampling Requirements for New York, USA

#### SoCalGas Rule 30 Sampling Requirements

A publicly available comprehensive sampling and monitoring scheme for the Californian natural gas network is available online via the SoCalGas RNG Toolkit document [62], which contains the biomethane quality specifications through SoCalGas' Rule 30. The sampling and monitoring requirements are largely driven by the recommendations established in the two scientific studies regarding health protective standards for biomethane injection, and detailed analysis of HHV and siloxane specifications [33, 41].

The major details of the sampling scheme are as follows:

- "Biomethane [...] shall be subject to periodic testing and monitoring based on the biogas source.": Health Protective Constituents identified in Californian legislation are subject to testing based on the likelihood of appearing in individual feedstocks (see Table 45).
- Health Protective Constituents deviations can cause supply shut-in based on calculated cancer and non-cancer risks: A methodology is provided to calculate potential cancer risks and hazard indexes from carcinogenic and non-carcinogenic Health Protective Constituents, respectively. Trigger, LAL and UAL are established for these metrics that can allow the grid operator to shut-in biomethane supplies from non-compliant suppliers.
- Pre-injection testing shall occur over a 2–4-week period: During pre-injection testing, both Pipeline Integrity Protective Constituents (ammonia, siloxanes etc.) and Health Protective Constituents must be below their corresponding LALs before biomethane can be accepted by the grid operator.
- Biomethane certified to originate from specific feedstocks are subjected to reduce siloxane testing: See next section (Promotional Biomethane Regulations).
- Constituents found below trigger levels during pre-injection testing (Group 1 Compounds) shall be tested once every 12-month period: If the Constituent is found below the trigger level for two consecutive annual tests after the first 12-month period, the Constituent may be tested once every 2year period.
- Constituents found above trigger levels during pre-injection testing (Group 2 Compounds) shall be tested quarterly.
- Group 1 Compounds will become a Group 2 Compound if testing indicates a concentration above the trigger level. A Group 2 Compound will become a Group 1 Compound if testing indicates concentrations below the trigger level for 4 consecutive tests.
- Testing shall be by the methods adopted in the CPUC legislation document D.14-04-034.
- Producers must supply PFDs when substantial changes are made to biogas source / upgrading and conditioning facilities.

## Table 44 Sampling Requirements in EU Countries

	DEU	FRA	SWE	NLD	CHE	ITA	AUT
Methane	Online	#N/A	Online	Onine	Online	#N/A	Online
Propane	Online	#N/A	-	#N/A	#N/A	#N/A	-
Carbon Dioxide	Online	Online	-	Online	Online	Online	-
Hydrogen Sulphide	Online	Online	-	Online	Batch	Online	Online
Oxygen	Online	Online	-	Online	Online	Online	-
Inerts	Online	#N/A	-	Online	Batch	#N/A	-
Water dew point	Online	Online	-	Online	Batch	Online	Online
Hydrocarbon dew point	Online	#N/A	-	Batch	Batch	Online <sup>17</sup>	-
Total Sulphur	Batch	Batch + Online	-	Batch	Batch	Batch	-
Mercaptans	Online	Batch	-	#N/A	Batch	Batch	-
Gross Calorific Value	Online	Online	Online	Online	Batch	Online	-
Wobbe Index	Online	Online	-	Online	Batch	Online	-
Density (rel)	Online	Online	-	#N/A	Batch	Online	-

<sup>17</sup> Only in case of injection of LPG in the biomethane

	DEU	FRA	SWE	NLD	CHE	ITA	AUT
Odorisation	Online	Online	-	Online	Batch	Batch <sup>18</sup>	-
Ammonia	Batch	-	-	-	-	Batch	-
Hydrogen	Online	-	-	-	-	Batch	-
Carbon Monoxide	Batch	-	-	-	-	Batch	-
Reference	[40]	[40]	[40]	[40]	[40]	[40]	OVGW G B 220

<sup>&</sup>lt;sup>18</sup> See prescriptions in UNI 7133 for odorisation control and for odorizability of the biomethane.

Parameter	Landfill	Agricultural and Clean Organics	WWTP
Arsenic	~	-	-
p-Dichlorobenzene	~	-	~
Ethylbenzene	~	~	~
n-Nitroso-di-n-propylamine	~	~	-
Vinyl Chloride	~	-	~
Antimony	~	-	-
Copper	~	-	-
Hydrogen Sulphide	~	~	~
Lead	~	-	-
Methacrolein	~	-	-
Alkyl thiols (mercaptans)	~	~	~
Toluene	~	~	~

## Table 45 Sampling Requirements vs Feedstocks (Californian CoCs) [73]

#### Interconnect Guide for Renewable Natural Gas (RNG) in New York State

GTI produced an industry guidance document for the introduction of RNG into the gas distribution network for New York, USA for the Northeast Gas Association [36]. The guidance document contains, amongst many other items, a comprehensive set of recommendations for sampling requirements for biomethane producers. The document relies on the comprehensive quantitative dataset collected by GTI for biomethane production, one of the largest identified during this literature review, and establishes a "good science and common sense" approach to establishing the biomethane requirements for grid injection.

The key tenets of the sampling scheme recommendations are summarised as follows:

- Testing requirements are to be aligned with expected contaminants: See Table 46. If a
  contaminant is not reasonably expected above background levels at the point of interconnect, testing
  may not be required.
- The responsibility to affirm and demonstrate contaminant levels at the point of interconnection below background levels lies with the biomethane developer / producer: Producers must demonstrate that reasonably expected contaminant concentrations in the raw gas (based on raw gas analysis / similar processing experience / prior engineering studies) will be removed and / or limited to concentrations typically found at the interconnect location.
- Producers must verify an agreed list of technical considerations: Producers must demonstrate compliance to a list of contaminant classes (e.g. ammonia, siloxanes) agreed to by the pipeline operator. Testing of the natural gas supply near the proposed interconnect point is also required as a basis for comparison.
- Reduction in testing frequencies once the upgrading process and biogas source are shown to be in control and meet design specifications: A proposed sampling schedule is shown in Table 47.

 Online monitoring parameters e.g., HHV, Wobbe Index, H<sub>2</sub>S, can be utilised as surrogate monitoring parameters for trace contaminants: Trace constituents that are shown to be within specification in parallel with major gas monitoring parameters during start-up testing can be presumed to be in control during routine "maintenance monitoring", if major parameters are also shown to be in control.

## Table 46 Sampling Requirements vs Feedstocks (GTI Interconnect Guide) [31]

Parameter	Landfill	Agricultural and Clean Organics	WWTP	Source Separated Organics and Facility Separated Organics
Water Content	~	~	~	~
Sulphur (including H <sub>2</sub> S)	~	~	~	~
Hydrogen	~	~	~	~
Carbon Dioxide	~	~	~	~
Nitrogen	~	~	~	~
Oxygen	~	~	~	~
Ammonia	~	~	~	~
Biologicals	~	~	~	~
Mercury	~	-	~	-
Volatile Metals	~	-	-	-
Siloxanes	~	-	~	~
Volatile Organic Compounds	~	-	~	-
Semi-volatile Organic compounds	✓	-	-	-
Halocarbons	~	-	~	-
Aldehydes and Ketones	~	-	-	-
Polychlorinated Biphenyls	~	-	-	-
Pesticides <sup>19</sup>	-	-	-	-

<sup>&</sup>lt;sup>19</sup> Not required unless the facility has a verified history of PCB / Pesticide contamination or use.

## Table 47 Parameter and Sample Frequency Considerations by GTI [31]

Parameter	Frequency	
Heating Value	Continuous real-time or near-real time GC monitoring and periodic field samples for independent confirmation.	
Temperature	Continuously measured on-line	
Pressure	Continuously measured on-line	
Water Content	Continuously measured on-line	
Sulphur	Continuous real-time or near-real time GC monitoring and periodic field samples for independent confirmation	
Hydrogen	Continuous real-time or near-real time monitoring and periodic field samples for independent confirmation	
Carbon dioxide	Continuous real-time or near-real time monitoring and periodic field samples for independent confirmation	
Nitrogen	Continuous real-time or near-real time monitoring and periodic field samples for independent confirmation	
Oxygen	Continuous real-time or near-real time monitoring and periodic field samples for independent confirmation	
Biologicals (If reasonably expected)	Incorporation of a 0.2-micron filter would mitigate need for testing if bacteria/spores are reasonably expected	
Mercury (if reasonably expected)	Minimum of three samples over a three-month period, with increased frequency, depending upon concentration at first sample point	
Siloxanes	Minimum of three samples over a three-month period, with increased frequency, depending upon concentration at first sample point	
Semi-volatile and Volatile Compounds (if reasonably expected)	Minimum of three samples over a three-month period, with increased frequency, depending upon concentration at first sample point	
Halocarbons (if reasonably expected, Examples are freons, chloroethane and vinyl chloride)	Minimum of three samples over a three-month period, with increased frequency, depending upon concentration at first sample point	
Aldehydes and Ketones (if reasonably expected)	Minimum of three samples over a three-month period, with increased frequency, depending upon concentration at first sample point	
PCBs/Pesticides (if reasonably expected)	Minimum of three samples over a three-month period, with increased frequency, depending upon concentration at first sample point	

### Promotional Biomethane Regulations

#### Simplified and Reduced Testing Schemes

Feedstock based testing has been regulated in California to enable biomethane producers that can certify that their biogas is only sourced from non-siloxane containing feedstocks (e.g. dairy, animal manure, forest residues) to have reduced siloxane testing requirements [87]. With the reduced testing requirements, if producers can satisfy pre-injection testing of < 0.01 mg Si/m<sup>3</sup>, then the standard periodic testing requirements are waived. A similar event occurs for pre-injection siloxane concentrations < 0.1 mg Si/m<sup>3</sup>, where quarterly siloxane testing is required for one year to ensure adherence to the 0.1 mg Si/m<sup>3</sup> Lower Action Level. Once the yearly review period is over, periodic siloxane testing can be discontinued [62]. This change was amended to the Californian legislation due to the recommendations of the CCST 2018 siloxanes and HHV study, which concluded that sources not expected to produce siloxanes should be held to a reduced and simplified verification regime [33].

#### Extension of Existing Limit Value Boundaries

Extensions of existing limit value boundaries have been described in **Chapter 5** of this report for the individual parameters. The discussion for the methodologies behind limit value increases are contained in the discussion for the individual parameters. The parameters found to have undergone expansion of existing limit values to accommodate biomethane injection are shown below:

- **Higher Heating Values:** Minimum HHV has been decreased to allow for a larger number of acceptable biomethane compositions.
- **Oxygen:** Maximum oxygen limits for pipeline injection have been increased due to the difficulty of oxygen removal for biomethane production.

#### Blending Allowances

Another significant regulatory amendment to stimulate biomethane producers is the decision made by the CPUC on allowing blending requests for biomethane producers if adequate blending can occur in the pipeline before the biomethane is delivered to customers. If blending is rejected, the Californian utilities must provide written explanation to the injector and the Californian Energy Division.

The blending allowance is managed on a case-by-case exception process, where the utility determines the feasibility of allowing a biomethane producer to inject biomethane with a lower than minimum heating value specification into the pipeline.

Within the deliberation documents for the regulatory ruling, the four major Californian utility companies (SocalGas, SDG&E, Southwest Gas and PG&E) expressed concern about the difficulty in monitoring blending, and the impacts of changes to the pipeline system, location and magnitude of customer demand [71]. During their deliberation, the CPUC deferred to the recommendations of the CCST study, which concluded that blending might be safe when the biomethane volume is small relative to local consumption, after evaluation on a case-by-case basis.

The CPUC mandated the allowance of blending, after consideration of the following factors:

- The proposed volume, timing, method and location of injection of biomethane;
- The proposed minimum heating value and Wobbe Number;
- The daily location-specific operational conditions, including but not limited to the proximity to gas customers, customer demand, historic heating value and Wobbe Number of gas received by the downstream customers, the volume and flow of other sources of natural gas in the pipeline;
- Pipeline system characteristics;
- Seasonal variations in demand that require limits on the authorization for blending in the pipeline;
- How long the authorization for blending in the pipeline is valid before it must be renewed; and
- Whether authorization for blending in the pipeline can be granted only with certain other conditions.

• Other relevant factors as decided by the utility.

A similar scheme is mandated in Switzerland, whereby non-compliant biomethane is allowed to be injected into the natural gas network. However, the injected gas must be able to mix into the available gas stream so that the gas is compliant at the first exit point of a consumer [82]. The injected gas must also consist of at least 50 % combustible components.

While the study could not access copies of the German conventional gas and biomethane quality regulatory documents (DVGW G260/262), a report by Kreeft et al. [82] states that the injection of non-compliant gases is allowed, subject to the local conditions of the gas network.

### 7. Conclusions

It is clear from both technological and commercial perspectives that biomethane injection into natural gas networks is feasible from the abundance of biomethane injection facilities operating in the over 18 different countries / jurisdictions analysed within this review. To facilitate similar success in biomethane injection into Australian gas networks, a significant amount of work is required to ensure that a consistent collection of standards can be created that balances the critical safety and operational requirements of pipeline owners / operators and downstream end-users, while also ensuring that no unnecessary barriers are created for prospective biomethane producers.

To facilitate the creation of such standards, this review has assessed the following information from the literature:

- Biogas feedstocks and commercial upgrading methods for biomethane production.
- Quantitative, holistic analysis of biogas and biomethane quality for the purpose of grid injection and the identified monitoring parameters / contaminants of concern.
- The detrimental effects caused by the inadvertent introduction of said parameters to the natural gas network.
- The effectiveness of biomethane upgrading / cleaning methods in manipulating said parameters / contaminants of concern.
- The current regulatory approach of the 17 individual jurisdictions for implementing limit values for biomethane injection.

### **BIOGAS FEEDSTOCKS AND UPGRADING METHODS**

A review of the current utilisation of biogas feedstocks in Europe for biomethane production shows that the majority (63 %) of biomethane is produced via the anaerobic digestion of energy crops and agricultural residues. This is followed by WWTP sludge and bio and municipal waste at 13 and 12 % respectively. The remaining is comprised of industrial organic waste, and landfill gas which comprises of 2 % of total European biomethane production. While energy crops aren't produced in Australia [88], it is likely that the biomethane injection industry will follow a similar trend in feedstock utilisation, with agricultural residues also making up the bulk of biogas feedstocks in other jurisdictions e.g. China and the USA.

Analysis of commercially available upgrading methods can also provide a similar projection for the Australian biomethane industry. Biogas upgrading by absorption (water, physical and chemical scrubbing) was found to have the largest market share of biomethane production in the EU, comprising of 66 % of total biomethane facilities. Membrane separation was found to be the second most common method, followed by pressure swing adsorption at 16 and 13 % of total market share respectively. The remaining 5 % of total upgrading methods comprise of less common techniques such cryogenic upgrading.

The development of the future work packages and analyses for the current FFCRC project (RP3.2-09) will consider these factors to focus efforts on areas and developments that are most likely to occur for the Australian biomethane injection industry.

# ANALYSIS OF BIOMETHANE QUALITY PARAMETERS AND CONTAMINANTS FOR GRID INJECTION

The analysis process utilised the results of 8 different biomethane quality reviews utilising a wide variety of feedstocks in different jurisdictions to create a comprehensive list of biomethane quality parameters and contaminants that have been identified as being important to monitor for grid injection. This list contained individual compounds e.g., ammonia, alongside entire compound families (siloxanes etc.) and other important monitoring parameters (HHV, Wobbe Index etc.) identified within the 8 studies.

The list formed the basis of the remainder of the literature review, with each parameter / contaminant addressed to determine properties summarised in **Table 48** and **Table 49**. The review divided the parameters / contaminants into two classes, the first being those that already possessed limit values in the existing Australian

natural gas quality standard, AS 4564. The suitability of the existing AS 4564 limit values, including the possibility of extending the current range of AS 4564 limits was assessed for this first class of parameters / contaminants, with the results shown in **Table 48**.

The second list of parameters / contaminants were those that had no existing Australian limit values. These were assessed at a greater depth, to provide Australian decision makers with the information to determine the appropriate limit values for biomethane quality for Australian pipelines. To assist with this process, the literature was reviewed for quantitative concentration values in biogas / biomethane, along with existing regulatory information as summarised in **Table 49**.

Parameter / Contaminant	Limit Value	Assessment
Wobbe Index	46.0 – 52.0 MJ/m <sup>3</sup>	Possibility of expanding lower Wobbe Index limit to increase acceptable biomethane composition ranges.
Higher Heating Value	42.3 MJ/m <sup>3</sup>	No changes to maximum heating value limit.
Oxygen	0.2 mol %	Possibility of increasing oxygen limits based on similar efforts in other jurisdictions specifically for the purpose of biomethane injection.
Hydrogen Sulphide (H <sub>2</sub> S)	5.7 mg/m <sup>3</sup>	No changes necessary.
Odour Intensity	Where required, detectable at a level not exceeding 20 % LEL	No changes to odour intensity requirements. Consideration required for management of biomethane facilities with terpene species at concentrations known to affect odorant character e.g., D-limonene.
Total Sulphur	50 mg/m <sup>3</sup>	No changes necessary.
Water Content	Dewpoint of 0 °C at the highest MAOP in the relevant transmission system (in any case, < 112.0 mg/m <sup>3</sup> )	No changes necessary.
Hydrocarbon Dew Point	2 °C at 3500 kPag	No changes necessary.
Total Inert Gases	7.0 mol %	Possibility of increasing limits to facilitate landfill gas feedstocks. The review observed an absence of similar efforts to increase limits in the other jurisdictions examined, however preliminary examination indicates that expansion of inert limits (particularly to allow the injection of off-spec high inerts biomethane via propane blending) remains within the range of gas compositions used to test existing gas appliances via AS/NZS 5263.0:2017.
Oil	20 mL/TJ	No changes necessary.

### Table 48 Biomethane Parameters / Contaminants with AS 4564 Limits

Parameters / Contaminants	Biomethane Range	Limit Value Range
Hydrogen	BDL – 0.9 mol. %	0.1 – 5.0 mol %
Siloxanes	BDL – 0.4 mgSi/m <sup>3</sup>	0.01 – 10 mg Si/m <sup>3</sup>
Ammonia	0.15 – 0.25 mg/m <sup>3</sup>	3 – 20 mg/m <sup>3</sup>
Halocarbons	BDL	1 – 10 mg Cl/F / m <sup>3</sup>
Semi-Volatile and Volatile Organic Compounds (SVOCs and VOCs)	<1 – 100 mg/m <sup>3</sup>	< 100 mg/m <sup>3</sup> Xylene (UK) < 904 mg/m <sup>3</sup> Toluene (California, USA) < 3.7 ppm General VOC contents (Quebec, Canada)
Heavy Metals	<b>Mercury:</b> BDL – 0.05 μg/m <sup>3</sup> <b>Arsenic:</b> BDL – 0.32 μg/m <sup>3</sup>	< 1 µg/m <sup>3</sup> Mercury limit recommendation in AS 4564 is sufficient. 19 – 30 µg/m <sup>3</sup> Arsenic 30 – 60 µg/m <sup>3</sup> Copper 600 µg/m <sup>3</sup> Antimony (California, USA) 75 µg/m <sup>3</sup> Lead (California, USA)
Bacteria <sup>20</sup>	<b>APB:</b> 9.69 x 10 <sup>1</sup> – 2.02 x 10 <sup>5</sup> <b>IOB:</b> 6.9 x 10 <sup>2</sup> -7.67 x 10 <sup>4</sup> <b>SRB:</b> 1.65 x 10 <sup>2</sup> – 2.52 x 10 <sup>4</sup>	4 x 10 <sup>4</sup> CFU/scf (qPCR per APB, SRB, IOB group) and commercially free of bacteria of >0.2 microns (California, USA)
Pesticides	Note 1	-
Pharmaceuticals	Note 1	-
Phosphine	Note 2	-

### Table 49 Biomethane Parameters / Contaminants without AS 4564 Limits

Notes:

- 1. All reports of pesticide and pharmaceutical detection were either at concentrations BDL or orders of magnitude lower than recommended exposure limit concentrations.
- 2. No quantitative information could be found for phosphine contents in biogas / biomethane.

### SUMMARY OF REGULATORY APPROACHES FOR BIOMETHANE INJECTION

The review of the various regulatory approaches for managing biomethane injection quality while promoting industry growth revealed several ideas that could be implemented in the management of Australian biomethane injection. One of the common approaches relied on feedstock-based testing requirements, due to the intrinsic relationship between certain feedstocks and the presence of adverse contaminants e.g. lack of siloxane testing requirements for agricultural feedstocks. This particular approach has been included in gas quality regulations in

<sup>&</sup>lt;sup>20</sup> Concentrations presented in CFU/100 scf

some jurisdictions, with Californian (USA) quality requirements completely waiving post-start up siloxane testing upon certification of the use of a limited number of specific feedstocks.

Other regulatory schemes that aim to promote the distribution of biomethane come in the form of allowances for pipeline blending for non-compliant biomethane. This was found in several jurisdictions, an example of which is a Swiss scheme that allows non-compliant injection on the basis that the resulting mixed gas is compliant at the first exit point of a consumer. Another detailed gas blending scheme incorporated into existing regulations is one conducted by the Californian Council on Science and Technology, which states that pipeline blending must be evaluated on a case-by-case basis. This was found to be the approach of German legislature, which also allowed pipeline blending subject to conditions of the local gas network.

### 8. Next Steps and Future Work

The next step of the RP3.2-09 project is to process the results of this review and collaborate with industry participants to determine the most effective mechanisms for managing biomethane quality standards within Australia. This may take form in an instructive Appendix to be included in the next revision of AS 4564 that stipulates common biomethane contaminants, akin to the instructive concentrations provided for mercury, radiation and elemental sulphur included in the existing standard. An alternative approach is to directly emulate the work conducted by the Standards Australia ME-093 Hydrogen Technologies committee in the adoption of ISO hydrogen standards for Australian utilization. This could be achieved utilising the existing European biomethane quality standard EN 16723-1:2016. The deliberation for the best effective mechanisms to facilitate biomethane quality requirements will take place during a workshop event attended by industry participants and key regulatory stakeholders.

To accomplish the adoption of biomethane standards, foundational research is required to answer the topics that are the subject of debate amongst the biomethane producing jurisdictions. The following areas of work have been identified within this review:

- Assessment of minimum allowable Wobbe Index specifications for biomethane injection in Australian networks.
- Assessing the work conducted in other jurisdictions for increasing allowable oxygen content and its applicability for Australian Assets (e.g., increase from 0.2 – 1.0 mol %)<sup>21</sup>.
- Detailed assessment of the effects of relaxing the AS 4564 7 mol % total inert gas limits for Australian end-users.
- Analysis of the effects of terpene odorant masking for Australian odorant compositions and concentrations.
- Assessment of the effects of propane blending on hydrocarbon dew point for likely biomethane product compositions.
- Determination of appropriate limit values for siloxane content for end-users<sup>21</sup>.
- Assessment of off-grid or in-pipe gas blending to meet gas quality specifications.

These studies, along with those proposed and discussed in the oncoming industry workshop event will be ranked in priority by industry participants to guide the remainder of the research work for RP 3.2-09.

<sup>&</sup>lt;sup>21</sup> Oxygen and siloxane limit value quantification based on end-user requirements are the subject of an existing FFCRC project proposal.

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## Appendix A: VOC Database

### Table 50 VOC vs Feedstock Data – Hydrocarbons [35]

	Sewage sludge	Household waste	Slaughterhouse waste	Residual products	Manure	Landfill
Terpenes	Х	Х	(X)	Х	(X)	Х
P-cymene		D		X		D
D-limonene	X	D	(X)	X	()	D
α-pinene				X	(X)	
β-pinene						
Alkanes	X	X	(X)		(X)	Х
Decane	X		(D)		(X)	Х
Undecane	D		(D)		(X)	Х
Dodecane	X		(D)		(X)	Х
Pentanes						Х
C6, C7, C8, C9						X
Alkenes			(X)			
Decene			(X)			
Undecene			(X)			
Cyclical hydrocarbons	X					Х
Cyclohexane						Х
Decahydronaphthalene	X					
Methyl decahydronaphtalene	X					
Aromatic hydrocarbons	X					Х
Toluene	D					Х
Xylenes	X					Х
Tri-, tetramethylbenzenes	Х					Х

	Sewage sludge	Household waste	Slaughterhouse waste	Residual products	Manure	Landfill
Dioxolanes	Х			Х		
Ethyl methyl dioxolane	Х					
Trimethyl dioxolane				Х		
Furans			(X)	Х		
Tetrahydrofuran			(X)			
Methylfuran			(X)	Х	(X)	
Ketones		Х		Х		
2-butanone		Х		D	(X)	
Pentanones		Х		Х		
C6-, C7-, C8-ketones				X		

### Table 51 VOC vs Feedstock Data – Oxygenated Substances [35]

### Table 52 VOC vs Feedstock Data – Other Substances [35]

	Sewage sludge	Household waste	Slaughterhouse waste	Residual products	Manure	Landfill
Nitrogen compounds				Х		
Ethyl methyl pyridine				Х		
Sulphur compounds		Х			(X)	
1-propanethiol		Х			(X)	
Methyl mercaptan				D	(X)	
Dimethyl sulphide				D	(X) (X)	
Dimethyl disulphide				Х		
Thiophenes					(X)	

Chlorinated and fluorinated	Х		Х	Х
hydrocarbons	Х		Х	Х
Di-, tri-, tetrachloroethylene				Х
Fluorodichloromethane,				
chlorofluoroethane				
Siloxanes	Х		Х	Х
D4	D		Х	Х
D5			Х	Х

D: dominant, i.e. the quantities correspond to more than 10% of the total content of contaminants measured for a specific substrate

X: present

(X) and (D): identified, but insufficient data

	Units	DEU	FRA	GBR	SWE	NLD	DNK	СНЕ	ITA	AUT
GCV	(MJ/m <sup>3</sup> , 15/15)	28.7 - 44.7	32.4 - 35.9 (L) 36.5 - 43.7 (H)	-	-	-	-	38.5 - 47.2 <sup>6</sup>	35.0 - 45.3	32.4 - 46.1 <sup>6</sup>
WI	(MJ/m <sup>3</sup> , 15/15)	37.6 - 44.4 (L) 46.4 - 53.6 (H)	42.7 - 44.6 (L) 46.6 - 53.6 (H)	49.8 - 54.18	-	41.23 - 42.13	48.2 - 55.8	47.9 – 56.5 <sup>6</sup>	47.3 - 52.3	48.6 - 55.86
Relative Density	-	0.55-0.75	0.555-0.70	-	0.555-0.7	-	0.555-0.7	0.55 – 0.70	0.555-0.7	-
Reference conditions: Combustion / Volume	-	25°C/ 0 °C, 103.25 kPa	0°C / 0°C, 103.25 kPa	15°C/ 15 °C, 103.25 kPa	15°C/ 15 °C, 103.25 kPa	25°C/ 0 °C, 103.25 kPa	25ºC/ 0 ºC, 103.25 kPa	?	15°C/ 15 °C, 103.25 kPa	?
Water dew point	(°C at 70 bara)	-	< -5 At MOP	<-10 for MOP < 7 barg < -10 at MOP	≤-8	<ul> <li>≤ -8 (High pressure L - HTL)</li> <li>≤ -8</li> <li>(Regional L - RTL)</li> <li>≤ -10 at 8 bar abs</li> <li>(Distribution L - RNB)</li> </ul>	-8	-	≤-5	<-8
Water	(mg/m³)	< 50 (MOP > 10bar) < 200 (MOP <10 bar)	-	-	-	-	-	< 60	-	-

# Appendix B: Biomethane Quality Specifications – EU Countries

	Units	DEU	FRA	GBR	SWE	NLD	DNK	СНЕ	ITA	AUT
HC Dew Point	(°C at 1- 70 bara)	< -2	< -2	<-2	<5	≤ 80 (mg/m3(n) at 3°C	-2	-	≤0	<0
Total Sulphur	mgS/m <sup>3</sup>	< 6 < 8 (after odorisation)	< 30	< 50	<pre>≤ 20 (without odorant) ≤ 30 (with odorant)</pre>	$\leq$ 5.5 ( $\leq$ 20) (High pressure L - HTL) (before odorisation) $\leq$ 5.5 ( $\leq$ 20) (Regional L - RTL) (before odorisation) $\leq$ 5.5 ( $\leq$ 20) (Distribution L - RNB) (before odorisation) $\leq$ 15.5 ( $<$ 31) (Regional L - RTL) (after odorisation) $\leq$ 15.5 ( $<$ 31) (Distribution L RNB) (after odorisation)	< 30	< 30	≤ 20 (without odorisation)	<1 20
Mercaptan Sulphur	mgS/m <sup>3</sup>	< 6	< 6	-	≤ 6 (without odorant)	≤ 6	-	-	< 6	-
Mercaptans	mgS/m <sup>3</sup>						< 6			< 16.9
H₂S + COS	mgS/m <sup>3</sup>	< 5	< 5	-	≤ 5	≤ 5	< 5	-	-	< 6.8
H <sub>2</sub> S	mgS/m <sup>3</sup>	-	-	≤ 5	-	-	-	< 5	≤ 5	-

	Units	DEU	FRA	GBR	SWE	NLD	DNK	СНЕ	ITA	AUT
CO2	mol %	< 10 L- gas* < 5 H- gas*	< 2.5 (Exemptions exist for the DSO system: up to 3,5% (H gas) / up to 11,7% (L gas))	<2.5	≤ 4	≤3 (High pressure L HTL) ≤10.3 (Regional L – RTL) ≤10.3 (Distribution L – RNB)	<2.5 transmission <3 distribution	< 4	≤ 2.5	<2
N <sub>2</sub> + CO <sub>2</sub>	mol %	-	-	-	-	-	-	-	-	-
O <sub>2</sub>	mol %	< 0.001 (MOP > 16bar) < 3 (MOP <16 bar)	0.01 (exemption: up to 0.7% in the transmission grid / up to 0,75% in the distribution grid)	< 0.2 < 1 for MOP< 38 bar	≤ 1	$\leq$ 0.0005 (High pressure L HTL) $\leq$ 0.5 (Regional L – RTL) $\leq$ 0.5 (Distribution L – RNB)	< 0.5	< 0.5	≤ 0.6	< 0.02
Hg	µg/m³	-	< 1	-	-	-	-	-	-	-
NON-AS 4564 Constituents										
CI	mg/m <sup>3</sup>	-	< 1	≤ 1.5 <sup>3</sup>	Acc. to CEN/TR (WI 00408007)	≤ 5	-	-	< 1	-
F	mg/m <sup>3</sup>	-	< 10	≤ 5 <sup>3</sup>	Acc. to CEN/TR (WI 00408007)	≤ 5	-	< 1	< 3	-

	Units	DEU	FRA	GBR	SWE	NLD	DNK	СНЕ	ITA	AUT
H2	mol %	< 2**	< 6	< 0.1	≤ 2	≤0.02 (High pressure L HTL) ≤0.02 (Regional L - RTL) ≤0.5 (Distribution L - RNB)		< 5	≤ 0.5	-
NH <sub>3</sub>	mg/m <sup>3</sup>	Technically free*	< 3	≤ 20 <sup>3</sup>	≤ 10	-	< 3	-	≤ 10	-
Amines	-	Technically free*	-	-	≤ 10 (mg/m3)	-	-	-	≤ 10	-
со	mol %		< 2	-	≤ 0.1	≤2900 mg/m3	-	-	≤ 0.1	-
Siloxanes	mg/m <sup>3</sup>	< 5*		≤ 0.5 as Si	≤ 0.3 as Si	<0.1 as Si	< 1		≤ 1	< 10
Impurities	mg/m <sup>3</sup>	Technically free	-	-	Technically free	-	-	Technically free	-	-
Dust	mg/m <sup>3</sup>	Technically free	-	-	Technically free	≤ 100 Size > 5µm	-		Technically free	-
VOCs	mg/m <sup>3</sup>	-	-	≤ 100 <sup>3</sup> (Xilene)	-	-	-	-	-	-
Standards / Reference	-	DVGW G260 *DVGW G262 ** DIN 51624	GRTgaz Prescriptions Techniques, V3, 1/02/2007 Arrêté du 28/03/1980 Arrêtés du 28/01/1981	Gas Safety (Management ) Regulation, 1996 Network Entry Agreements	EN 16726 EN 16723-1 EN 16723- 2	ISO 6326 ISO 6327 ISO 6570 ISO 6974 ISO 6976 ISO 15970 Richtignen R- 16-46, 18/08/2016	-	-	UNI TR 11537	LOOK INTO OVGW G B210 to see if there have been any updates since marcogaz

	Units	DEU	FRA	GBR	SWE	NLD	DNK	СНЕ	ITA	AUT
			GRDF, Prescriptions techniques du distributeur							
Last Update	-	March 2018	March 2018	March 2018	February 2019	March 2018	March 2018	-	March 2018	-

Country codes via ISO 3166-1 alpha-3

# Appendix C: Biomethane Quality Specifications – Non-EU Countries

	Units	California [62], USA	China [89]**, ***	Canada [90] ****	Brazil
нни	MJ/m <sup>3</sup>	36.1 – 42.8	34.0 (Type I) 31.4 (Type II)	36 - 41.34	>96.5 (mol % CH₄)
WI	MJ/m <sup>3</sup>	1279 -	39.04 – 44.84 (For Urban Use)	47.23 - 51.16	-
Relative Density	-	-	-	-	-
Reference conditions: Combustion / Volume	-	-	101.325 kPa, 20°C	-	101.325 kPa, 20 °C
Water dew point	-	< 6.67 °C for delivery pressures > 5516 kPag	5 °C lower than minimum ambient temperature	-10 °C	Dew point of – 45°C at 1 atm.
Water	(mg/m³)	< 112 for delivery pressures < 5516 kPag	-	35	-
HC Dew Point	-	< 7.22 °C at 2758 kPag for delivery pressures < 2758 kPag < -6.67 at 2758 kPag	5 °C lower than minimum ambient temperature	-	-
Total Sulphur	mgS/m³	12.6 (ppm)	20 (Type I) 100 (Type II)	115	70
Mercaptan Sulphur	mgS/m <sup>3</sup>	5 (ppm)	-	-	-
Mercaptans	mgS/m <sup>3</sup>	-	-	-	-
H₂S + COS	mgS/m <sup>3</sup>	-	-	-	-
H₂S	mg/m³	5.7	6 (Type I) 20 (Type II)	7 (Distribution) 23 (Transmission)	10

	Units	California [62], USA	China [89]**, ***	Canada [90] ****	Brazil
CO2	mol %	3	3 (Type I)	2	3
N <sub>2</sub> + CO <sub>2</sub>	mol %	-	-	-	-
O <sub>2</sub>	mol %	-	-	0.4	0.5
Hg	µg/m³	80	-	0.05	-
Total Inerts	mol %	4	-	4	3.5
NON-AS 4564 Constituents					
CI	mg/m³	-	-	10	-
F	mg/m³	-	-	1	-
Halogens	mg/m³	-	-	-	-
H <sub>2</sub>	mol %	0.1	-	0.1	-
NH <sub>3</sub>	mg/m³	7	-	3	-
Amines	-	-	-	-	-
СО	mol %	-	-	-	-
Siloxanes	mg/m³	0.01 mg Si/m <sup>3</sup>	-	1 (ppmv)	-
Biologicals	-	4 x 104 CFU/scf (qPCR per APB, SRB, IOB group) and commercially free of bacteria of >0.2 microns (California, USA)	-	-	-
Dust	mg/m³	Shall not contain dust at levels that would be injurious to Utility facilities or that would cause gas to be unmarketable.	-	-	-
Heavy Metals	µg/m³	19 (Arsenic) <sup>x</sup>	-	30 (Arsenic, Copper)	-

	Units	California [62], USA	China [89]**, ***	Canada [90] ****	Brazil
		600 <sup>×</sup> (Antimony) 60 <sup>×</sup> (Copper) 75 <sup>×</sup> (Lead)			
VOC	mg/m3	904 (Toluene)	-	3.7 (ppm)	-
Carcinogenic Substances	mg/m³	5.7 <sup>×</sup> (p-Dichlorobenzene) 26 <sup>×</sup> (Ethylbenzene) 0.033 <sup>×</sup> (n-Nitroso-di-n- propylamine) 0.84 <sup>×</sup> (Vinyl Chloride)	-	1 (Vinyl Chloride)	-
Non-Carcinogenic Health Protective Constituents	mg/m³	1.1 $^{\times}$ (Methacrolein) 12 $^{\times}$ (Alkyl thiols)	-	-	-
Standards / Reference	-	SoCalGas Rule 30	T/BGLM 0004.01-2018 T/BGLM 0003.01-2018	BNQ 3672-100	Resolution No. 8 January 30 2015 (Biomethane Regulations)
Last Update	-	2020	2019	2012	2015

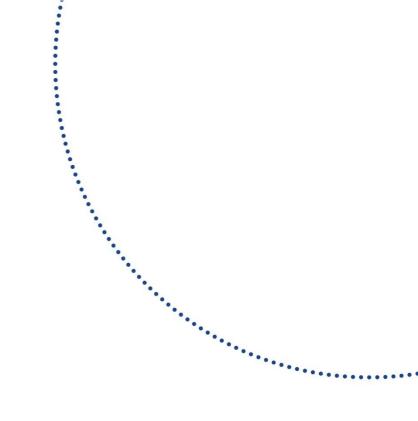
<sup>×</sup> Value is trigger level (Triggers additional periodic testing)

\*\* For Class I gas, if total sulphur or hydrogen sulphide does not meet the respective requirements, biomethane can still be accepted if total sulfur and hydrogen sulphide are continuously monitored so long as instantaneous values are not greater than 30 and 10 mg/m<sup>3</sup> respectively. Averaged 8-hour values also cannot exceed 20 and 6 mg/m<sup>3</sup> for total sulphur and hydrogen sulphide, respectively.

\*\*\* Class II gas are not allowed into long-distance transmission pipelines.

\*\*\*\* Specifications based on values presented in the public consultation version of Standard BNQ 3672-100. A copy of the finalised version could not be found by the project.





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