Evaluation and Identification of Constituents Found in Common Carrier Pipeline Natural Gas, Biogas and Upgraded Biomethane in California

REPORT TO THE

California Air Resources Board Transportation and Toxics Division

Project # 13-418

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CleanWorld, Kiefer Landfill, New Hope Dairy, VanWarmerdam Dairy.

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LIST OF ACRONYMS

AB – assembly bill
APB – acid producing bacteria
ARB – Air Resources Board
BLAST – Basic Logical Assignment Search Tool
CEC – California Energy Commission
CNG – compressed natural gas
CPUC – California Public Utilities Commission
CSTR – continuous stirred tank reactor
DNA - deoxyribonucleic acid
FPD - flame photometric detector
GC – gas chromatography
GTI – Gas Technology Institute
H/C – hydrogen to carbon ratio
ICPMS – inductively coupled plasma mass spectrometry
IOB – iron oxidizing bacteria
LC – liquid chromatography
LOD – limit of detection
LOQ – limit of quantification
MPN – most probable number
MS – mass spectrometry
NM- no measurement
NQ – Not Quantifiable
OEHHA – office of environmental health hazard assessment
PAC – project advisory committee
PAH – polycyclic aromatic hydrocarbon
PBS – phosphate buffered saline
PCB – polychlorinated biphenyl
PCR – polymerase chain reaction
POTWS – point of treatment water systems
ppbv – parts per billion by volume
qPCR - quantitative polymerase chain reaction
qTOF - quadrupole time-of-flight
READ - Renewable Energy Anaerobic Digester
RNG – renewable natural gas
SATS - South Area Transfer Station
SRB – sulfate reducing bacteria
SVOC – semi-volatile organic compound
TCD – thermal conductivity detector
TG – thioglycolate
TSB - tryptic soy broth
VOC – volatile organic compound

ABSTRACT

Biogas is a source of renewable energy with great potential in California. Upgraded biogas (=biomethane) can potentially be used in all applications where natural gas is currently used. Many approaches can be employed to produce biogas, leading to a final fuel with a range of possible chemical compositions. Some scenarios envision that biomethane may be distributed across California through existing pipelines used for natural gas. Care must be taken to ensure that the components contained in biomethane will not cause corrosion or other damage to these pipelines. Increased use of biomethane will lead to increased population exposure to the raw gas and/or the combustion products. Biogas and biomethane must therefore be thoroughly characterized to consider the health implications of the non-methane components.

In the current study, a comprehensive set of measurements was conducted for ten different biogas / biomethane sample streams (each consisting of three different individual samples) and three different compressed natural gas streams (each consistent of a single sample). Biogas / biomethane sample streams were derived from five different production sources: two food waste digesters, two dairy farms, and one landfill. The two food waste digesters had similar designs but used different feedstocks resulting in different biogas composition. The two farms used different digester designs with one site using technology typical in California and the other site using technology typical in Europe. The landfill had two different gas streams representing the interior core of the landfill and the perimeter of the landfill. The compressed natural gas samples were obtained from three different commercial CNG refueling stations in Los Angeles.

Major components analysis showed that biogas samples contained 35% to 70.5% methane, 16 to 28% CO_2 and lesser amounts of nitrogen and oxygen. Upgraded biomethane had methane content between ~90% to ~93% which compared favorably with the ~91.5% methane content of CNG obtained from vehicle fueling stations in Los Angeles, although the residual would typically be of different compositon. Commercial CNG contained an additional ~5.5% ethane, which yielded higher energy content than biomethane, which contained primarily carbon dioxide, nitrogen and oxygen as major residual components. A small amount of air may have been entrained into the biomethane during the upgrading process, which would not be present in commercial upgrading operations.

Analysis for trace components yielded a number of relevant implications for the expanded adoption of biogas / biomethane as an energy source in California. Biogas produced from the anaerobic digestion of dairy farm waste streams had low ammonia concentrations suggesting that biogas production could have the added benefit of reducing future ammonia emissions from agriculture. The covered lagoon design for dairy digesters commonly used in California is susceptible to contamination by runoff from adjacent fields which can introduce unwanted agricultural chemicals into the biogas production stream. Future designs should incorporate features to prevent this runoff contamination. Plastics introduced into biogas production facilities contribute to halocarbon concentrations in the resulting gas. Plastics should be diverted from the biogas production feedstock as much as possible to mitigate this outcome. The alkane signature in biomethane was distinct from the alkane signature in CNG. This alkane “fingerprint” can be used to identify the biomethane content of blended fuels. Semi-volatile metals, pesticides, and PCBs were generally not detected in biogas / biomethane for the sources considered in the current study.

Bacteria were less commonly detected in California biogas than in previous measurements made using biogas outside of California. When bacteria were detected in California biogas, the concentrations were generally comparable to previous measurements. Acid forming bacteria and iron oxidizing bacteria were detected in raw biogas from agricultural digesters but not in most upgraded biomethane samples.

The results of the current study have comprehensively characterized the composition of biogas and biomethane produced by a range of possible sources in California. The composition of biogas and biomethane from additional sources (including POTWS, additional landfills, and anaerobic digesters using different types of feedstock) should be measured to fully understand the remaining possible biogas production issues specific to California.

EXECUTIVE SUMMARY

Background: Renewable energy sources are essential in California for reaching state goals for reducing greenhouse gas emissions. Biogas is a source of renewable energy with great potential in California. Biogas is produced by converting organic waste materials into a gaseous mixture of carbon dioxide and methane. Biogas can be used directly to produce electricity or it can be cleaned and upgraded to biomethane by removing carbon dioxide and other impurities so that it can potentially be used in all applications that currently use natural gas.

Despite the great potential for biogas in California, a major increase in the use of any fuel in the state must consider air quality implications and unintended outcomes for public health and infrastructure (refining facilities, pipelines, etc). The first step in this process is the thorough characterization of biogas and upgraded biomethane produced by a variety of feedstocks and anaerobic digester approaches.

Methods: A comprehensive set of measurements was conducted for ten different biogas / biomethane sample streams (each consisting of three different individual samples collected on different days) and three different compressed natural gas streams (each consistent of a single sample). Biogas / biomethane sample streams were derived from five different production sources: two food waste digesters, two dairy farms, and one landfill. The two food waste digesters had similar designs but used different feedstocks resulting in different biogas composition. The two farms used different digester designs with one site using technology typical in California and the other site using technology typical in Europe. The landfill had two different gas streams representing the interior core of the landfill and the perimeter of the landfill. The compressed natural gas samples were obtained from three different commercial CNG refueling stations in Los Angeles.

Results: Measurements are reported for approximately 350 analytes spanning 11 major compound classes. At the bulk level, the methane content of raw biogas ranged from 35% to 70.5%, the CO_2 content ranged from 16 to 28% CO_2 and the nitrogen content ranged from 7% to 38%, and the oxygen content ranged from 3% to 11%. Nitrogen and oxygen were present in the biogas either due to air injection for sulfur control or due to air entrainment at landfills. Upgraded biomethane had methane content between ~90% to ~93% which compared favorably with the ~91.5% methane content of CNG obtained from vehicle fueling stations in Los Angeles, although the residual would typically be of different composition. Commercial CNG contained an additional ~5.5% ethane which yielded higher energy content than biomethane, which contained primarily carbon dioxide, nitrogen and oxygen as major residual components. A small amount of air may have been entrained into the biomethane during the upgrading process which would not be present in commercial upgrading operations. Upgraded biomethane from all sources was successfully used as a vehicle fuel during testing supported under a separate project (CEC Project PIER#13-001).

Analysis for trace components yielded a number of relevant results for air quality in California. Biogas produced from the anaerobic digestion of dairy farm waste streams had low ammonia concentrations suggesting that biogas production could have the added benefit of reducing future ammonia emissions from agriculture. The covered lagoon design for dairy digesters commonly used in California is susceptible to contamination by runoff from adjacent fields which can

introduce unwanted agriculture chemicals into the biogas production stream. Future designs should incorporate features to prevent this runoff contamination. Plastics introduced into biogas production facilities contribute to halocarbon concentrations in the resulting gas. Plastics should be diverted from the biogas production feedstock as much as possible to mitigate this outcome. The alkane signature in biomethane was distinct from the alkane signature in CNG. This alkane "fingerprint" can be used to identify the biomethane content of blended fuels. Semi-volatile metals, pesticides, and PCBs were generally not present above detection limits in biogas / biomethane for the sources considered in the current study.

Heterotrophic and spore-forming bacteria were less commonly detected in California biogas than in previous measurements made using biogas outside of California. When bacteria were detected in California biogas, the concentrations were generally comparable to previous measurements. Acid forming bacteria and iron oxidizing bacteria were detected in raw biogas from agricultural digesters but not in most upgraded biomethane samples.

Conclusions: The composition of biogas and upgraded biomethane produced in California depends on the feedstock and the design of the anaerobic digester. The upgrading process itself can also influence the trace composition of the gas by introducing alkanes. The tests conducted to date suggest several mitigation strategies and/or best practices for management of feedstock, design of digesters, and strategies for upgrading biogas to biomethane in California.

Future Work: The composition of biogas and biomethane should be measured from California sources that have not yet been characterized including POTWS, additional landfills, and anaerobic digesters using different types of feedstock. These additional measurements will identify any remaining issues specific to biogas adoption in California.

1 INTRODUCTION

1.1 Motivation

Renewable resources are essential for reducing greenhouse gas emissions and reaching state energy goals. Bioenergy is renewable energy produced from organic waste materials such as organic urban waste, agriculture and food processing wastes, waste from sewage treatment facilities, landfills and other organic waste sources such as forest and other wood waste. Biogas is a source of renewable energy and is produced by converting organic waste materials into a gaseous mixture of carbon dioxide and methane. Biogas can be used directly to produce electricity or can be cleaned and upgraded to biomethane by removing carbon dioxide and other impurities. If biogas is upgraded to meet natural gas tariff standards or other tariffs specifically crafted for biomethane, it can be injected into the common carrier natural gas pipeline and become a replacement for fossil sources of natural gas in homes and factories. Because of this, the development of renewable natural gases (i.e. biomethane) is a high priority for the California Air Resources Board (ARB), the California Energy Commission (CEC) and other State agencies.

California is taking several actions to support the development of bioenergy from organic waste materials. The 2011 Bioenergy Action Plan prepared by the Bioenergy Interagency Working Group and the more recent 2012 update acknowledges that organic waste materials are a sustainable and dependable resource that not only can help California achieve the State's renewable energy goals but waste reduction, and climate change goals as well. However, aggressive actions must be taken to increase its use. To support bioenergy development and the use of renewable energy, the CEC funds natural gas research based on the California Public Utilities Commission (CPUC) approved annual research plan. The Natural Gas Research, Development and Demonstration Program Proposed Program Plan and Funding Request for Fiscal Year 2013-14 follows the State's "loading order." Increased use of renewable energy options is second on the loading order list. Thus the FY 13/14 budget identifies Pipeline Safety and Renewable Energy research that address the barriers to increased market penetration of renewable energy as high priority areas for natural gas research.

The California State legislature has also taken action to further advance the use of bioenergy in California by enacting legislation to promote the use of biomethane in the common carrier natural gas pipeline. Assembly Bill (AB) 1900, authored by Assemblyman Mike Gatto and chaptered into law on September 27, 2012 (Chapter 602, Statutes of 2012), requires the CPUC to develop standards for constituents in biogas to protect human health and pipeline integrity and safety, identify impediments that limit procurement of biomethane in California, and adopt policies and programs that promote the in-state production and distribution of biomethane. To support CPUC's standards development efforts, Office of Environmental Health Hazard Assessment (OEHHA) and ARB were tasked with the evaluation and identification of the health based constituents of concern in biogas and biomethane in support of developing pipeline quality renewable natural gas standards and production in California. ARB and OEHHA staff worked together to fulfill the AB1900 requirements and develop recommendations to inform the CPUC rulemaking process. The evaluation and identification of the constituents of concern in biogas, detailed in the May 15, 2013 report to the CPUC, relied on existing data and focused on the larger sources of biogas – landfills,

dairies, and sewage treatment plants (POTWs). The sites and sources evaluated were located all over the United States and were not specific to California. In future updates and as additional data becomes available, ARB and OEHHA staff will address other sources of biogas (i.e., food waste, food waste co-generation, crop residuals, energy crops, and/or woody biomass).

This report focuses on adding to the limited existing data on the constituents (both major and trace compounds) found in natural gas, biogas and biomethane from California sites or sources and on evaluating other likely sources of renewable natural gas such as the anaerobic digestion of food waste. This data will be useful to further evaluate constituents in biogas/biomethane that may pose health risks and provide critical technical support for the periodic updates mandated by AB1900.

1.2 Research Objectives

The primary objective of this project is to further understand the composition of biogas and biomethane in California and to compare the composition of biomethane to the composition of natural gas.

1.3 Project Tasks

The project was organized around the following major tasks:

Task 1a: Establish Project Advisory Group (PAC or Advisory Group).
The purpose of this task was to establish, facilitate and conduct Advisory Group meetings and work with the group to identify candidate facilities that were currently or nearly ready to produce biomethane/biogas in California. The final selection of gas streams was based on the recommendations of the Advisory group. All candidate facilities and gas streams that were selected for inclusion in the project were approved by ARB and CEC to ensure that the selections met the project goals. The final membership of the Advisory Group is listed in the Table below:

Table 1-1: List of Advisory Group Members and Affiliation

	Name	Affiliation	Contact Information
1	Valentino Tiangco	SMUD	Valentino.Tiangco@smud.org
2	Josh Rapport	CleanWorld	josh.rapport@cleanworld.com
3	Greg Kester	CASA	gkester@casaweb.org
4	Johannes Escudero	RNG Coalition	johannes@rngcoalition.com
5	Ken Kloc	OEHHA	Kenneth.Kloc@oehha.ca.gov
6	Frank Mitloehner	UC Davis	fmmitloehner@ucdavis.edu
7	John Shears	CEERT	shears@ceert.org
8	Brian Helmowski	CalRecycle	Brian.Helmowski@CalRecycle.ca.gov
9	May Lew	SoCalGas	MLew@semprautilities.com

Task 1b: Coordinate with Producers

The contractor, based on recommendations of the Advisory Group and approval of the selected sources by ARB/CEC, contacted and coordinated with the following producers to obtain permission to sample and evaluate gas streams.

Table 1-2: List of Producers Participating in Project

	Name	Contact Information
1	CleanWorld	Josh Rapport (josh.rapport@cleanworld.com)
2	Kiefer Landfill	Tim Israel (israelt@saccounty.net)
3	New Hope Dairy	Ross Buckenham (rbuckenham@calbioenergy.com)
4	VanWarmerdam Dairy	Daryl Maas (daryl@maasenergy.com)

Task 1c. Obtain Gas Samples

The original contract specified nine gas streams for sampling. The contractor sampled 10 gas streams in preparation for analytical testing using approved methods. Samples were obtained from natural gas, biogas and upgraded biomethane.

Upgraded biomethane was produced using a dual-stage membrane separation unit provided by Helee. The membranes were made from polyimide (Air Liquide). Input biogas was compressed to ~10 bar to force CO_2 and other contaminants such as O_2, H_2O, and H_2S across the membrane during the separation process. The membrane could not separate N_2 from methane, making it impossible to highly purify gas streams with significant air entrainment. Liquid and gaseous water was removed prior to the membrane using a refrigeration dryer for bulk water removal and a solid desiccant dryer for trace water removal. The upgrading unit had a maximum feed biogas capacity of 150 Nm^3/h (2500 slpm) and a maximum biomethane production capacity of ~50 Nm^3/h with methane content as high as 97%. As operated in the current study, the Helee unit processed approximately 50 Nm^3/h of feed biogas producing approximately 25 Nm^3/h of product biomethane. Typical power consumption was 16.8kW for a specific energy consumption of 0.336 kW/ (m^3/h raw gas). Figure 1-1 below shows the Helee upgrading unit.

Figure 1-1: Helee upgrading unit on transportable trailer installed at UC Davis READ biogas facility.

Table 1-3: List of Gas Samples Obtained for the Project. Planned values in the original proposal are listed first followed by actual values in parenthesis ( ). Original proposal specified 9 samples for characterization while actual project delivered 10 samples.

Source Type	Raw Gas	Treated Gas[1]	Comments
Natural Gas-From Common Carrier Pipeline	number of samples		
natural gas from California utility pipelines - Northern CA		Planned=1 (Actual=0)	Planned: Either different gas sources or at different times of the year. (Actual: Samples collected in Southern California due to logistical constraints. See next row.)
natural gas from California utility pipelines - Southern CA		Planned=0 (Actual=1)	Planned: Either different gas sources or at different times of the year. (Actual: Samples obtained from 3 different CNG refueling stations in the Los Angeles area. See Section 2.7).
Biogas/Biomethane Sources			
biogas/biomethane produced from landfills (non-hazardous) - in CA	Planned=1 (Actual=2)	Planned=1 (Actual=0)	Planned: Testing at 2 different times at one site or at two different sites. (Actual: Two different gas streams sampled 3 times each at Kiefer Landfill. Gas could not be upgraded due to air intrusion and so treated gas sample not possible as discussed with Technical Advisory Committee.)
biogas/biomethane produced from food waste	Planned=1 (Actual=1)	Planned=1 (Actual=1)	(Actual: Samples collected at CleanWorld SATS facility in Sacramento)
biogas/biomethane produced from food waste possibly with codigestion of other feedstock	Planned=1 (Actual=1)	Planned=1 (Actual=1)	(Actual: Samples collected at CleanWorld READ facility in Davis)
biogas/biomethane produced from food waste and POTWs/biosolids	Planned=1 (Actual=0)	Planned=1 (Actual=0)	(Actual: POTWs not prioritized by Technical Advisory Committee)
biogas/biomethane produced from food waste and ag waste	Planned=0 (Actual=2)	Planned=0 (Actual=1)	(Actual: Samples collected at New Hope Dairy and VanWarmerdam Dairy. Samples at VanWarmerdam could not be upgraded due to air intrusion.)
	Planned=4 (Actual=6)	Planned=5 (Actual=4)	

[1] Treated gas (i.e. biomethane) is also called renewable natural gas (RNG) or upgraded biogas

Task 1d. Gas Analysis

The contractor analyzed the composition of the gas samples using the methods described below. All results from the analysis are provided in Section 3 of this report.

Compositional Dependent and Other Physical Parameters
Compressibility factor, heating value, relative density, Wobbe number, hydrocarbon dewpoint temperature, and temperature were calculated based on the composition of the biogas following standard methods.

The compressibility factor of the total gas was calculated using the weighted average of the individual components. Compressibility factors for major components at their critical points are shown in Table 1-4 below. Raw biogas was measured to have water content of approximately 6% while cleaned biomethane was measured to have water content of approximately 0.05%. These values were used in all calculations requiring saturated vs. dry parameters. Biogas and biomethane is predominantly methane and carbon dioxide, and so it is expected that compressibility factors at critical conditions will vary between 0.276 and 0.29.

Table 1-4: Compressibility factors for individual components of biogas at critical conditions.

Component	Compressibility Factor[1]
Methane	0.29
Ethane	0.285
Carbon Dioxide	0.276
Nitrogen	0.291
Oxygen	0.29

[1] All factors from Morgan and Shapiro, "Fundamentals of Engineering Thermodynamics"

The relative density of the total gas was also calculated using the weighted average of the individual components. Densities for major components are shown in Table 1-5 below. Relative density was calculated as the density of the biogas or biomethane divided by the density of air.

Table 1-5: Density for individual components of biogas and total air at standard conditions.

Component	Density[1] ($kg\ m^{-3}$)
Methane	0.656
Ethane	1.3388
Carbon Dioxide	1.98
Nitrogen	1.251
Oxygen	1.429
Air	1.29

[1]All data obtained from online databases.

Heating values of the biogas were calculated based on the methane content using a lower heating value for methane of 910 Btu ft^{-3} and a higher heating value for methane of 1012 Btu ft^{-3}.

The dry Wobbe number was calculated as the dry gas higher heating value divided by the square root of the dry gas relative density.

Motor octane number for each gas was calculated using the formulate -406.14 +508.04*(H/C)-173.55*$(H/C)^2$+20.17*$(H/C)^3$ based on guidance provided on the ARB website (www.arb.ca.gov/regact/cng-lpg/appd.pdf). The (H/C) ratio was dominated by the methane content of the gas and was close to 4 for all gases tested, yielding relatively constant motor octane numbers.

The methane number for each gas was calculated using the formula 1.624*(motor octane number) -119.1 based on guidance provided on the ARB (www.arb.ca.gov/regact/cng-lpg/appd.pdf). This value was then checked using an online calculator (www.cumminswestport.com/fuel-quality-calculator). Both values are reported in the results section of the report.

Major Component Analysis

Major components in biogas and biomethane samples are collected and analyzed using a modified version of ASTM D1945 that has been optimized based on our sampling techniques, analytical equipment, and target compounds. Biogas or biomethane samples are collected in a Tedlar sample bag (SKC Inc.) using system pressure or a "Vac-U-Chamber" (SKC Inc.) sampling apparatus, to avoid sampling pump contamination of the sample. Tedlar bags are flushed 3 times before use and are not re-used.

Analysis is conducted using an Agilent Technologies 6850 Gas Chromatograph coupled with a Thermal Conductivity Detector (GC-TCD). A system blank is analyzed before sample analysis to ensure the cleanliness of the instrument. Each sample is connected to a 250 µl sample loop for injection with split ratio of 20:1. Peak areas are recorded, and relative concentrations are calculated (in percent) using published TCD response factors. The inlet temperature is controlled at 270 °C and the inlet pressure is maintained at 16 psi. The total He flow rate is 53.7 ml/min with a column flow rate of 2.4 ml/min and a column pressure of 16 psi. Separation is accomplished using an Agilent J&W CP-Sil 5 CB for Formaldehyde (60 m x 0.32 mm x 8.00 µm) with an injection volume of 250 µl. The following temperature program is used: hold at –20 °C for 5 minutes, ramp to 150 °C at 10 °C/min, hold at 150 °C for 2 min, ramp to 280 °C at 150 °C/min and hold for 2 min. The detector temperature is maintained at 250 °C with a reference flow of 20 ml/min and a detector make-up flow of 4.6 ml/min. A major components gas standard mixture (Air Liquide) is used to prepare the standard curve and to quantify concentrations.

Extended Hydrocarbon Analysis

Extended hydrocarbons in biogas or biomethane are collected using a 8 x 100 mm 400 mg/200 mg coconut charcoal sorbent tube (SKC, Inc.) for 60 min at a flow rate of 1 l/min. Sorbent tubes are kept sealed until just prior to sampling, and flow rate is controlled with a calibrated 1-5 l/min adjustable flow meter (Dwyer Instruments, Inc.). Negative pressure is created at the back end of the sampling apparatus using an explosion-proof Teflon diaphragm pump. At the conclusion of the 60-minute sampling time, the sorbent tube is immediately capped, labeled, and placed into a cooler. Once transported back to the lab, it is stored in a 0 °C freezer until extraction. Sorbent tubes may be held at 0 °C for up to 30 days before being extracted.

To extract the sorbent material, tubes are broken open and each section of charcoal is transferred separately to appropriately labeled glass vials. Ethyl acetate (1 ml) is added to each vial, which is then capped and sonicated for 30 minutes. Samples are filtered using a 0.45 µm Teflon syringe filter. No concentration step is used, as it is expected that volatile compounds would be lost in the process.

Analysis is performed using an Agilent 7890 gas chromatograph coupled with an Agilent 7200 quadrupole time-of-flight mass spectrometer (GC-qTOF-MS). Each sample batch is analyzed with quality control samples that include a system blank, two sample blanks (1 set of unused sorbent tube extracts), calibration standards, and the samples. The injection volume is 1.0 µl and injector temperature is 250 °C. Separation is accomplished with an Agilent J&W HP5-MS UI Column (30 m x 0.25 mm x 0.25 µm) at a He carrier gas flow rate of 0.8 ml/min. The temperature program is 35 °C for 3 min, ramp from 30 °C to 325 °C at 4 °C/min, hold at 325 °C for 3 min.

A multi-point calibration curve generated from the calibration standards is used to quantify the target compounds. Analytical standards used were Sigma 8S61394-U TPH Mix 3, Sigma 29680-10ML Cyclopentane, Sigma 66490-10ML Methylcyclopentane, Sigma 442630 Isopropylbenzene, Sigma E49401-5G 2-Ethyltoluene, Sigma 47324 1,2,4-Trimethylbenzene, Sigma 442430 1-Methylnaphthalene, Sigma 36943-250MG 1,2-Dimethylnaphthalene,

Sulfur Analysis

Depending on their volatility and concentration range, sulfur compounds are collected in two different ways. Samples for hydrogen sulfide and other volatile sulfur species (e.g., dimethyl sulfide and methyl mercaptan) analysis are collected in Tedlar bags, while the semi-volatile sulfur species (e.g., thiophenes and benzothiophenes) are collected on adsorbent cartridges.

Volatile sulfur compound analyses are conducted using a modified version of ASTM D6228, "Standard test method for determination of sulfur compounds in natural gas and gaseous fuels by gas chromatography and flame photometric detection." These biogas or biomethane samples are collected in a Tedlar sample bag (SKC Inc.) using either system pressure or a "Vac-U- Chamber" (SKC Inc.) sampling apparatus, to avoid sampling pump contamination of the sample. Tedlar bags are flushed 3 times before use, and are not re-used. Samples are analyzed within 72 hours. Semi-volatile organic sulfur compounds are collected on XAD-2 adsorbent cartridges following the same procedures described below for non-sulfur containing semi-volatile organic compounds described below.

Analysis for H_2S is performed on an Agilent Technologies 6850 gas chromatograph coupled with a flame photometric detector (GC-FPD). Samples are injected on-column in splitless mode through a heated 6-port valve outfitted with a 0.1 ml or a 1 ml sample loop. Tedlar sample bags are connected directly to the inlet port of the sample loop, and negative pressure is created at the back-end of the sample introduction system using a Teflon diaphragm pump. Each sample run includes the following quality control samples: a pure nitrogen system blank, calibration standards (obtained from Air Liquide, Inc.), and the samples. A multi-point calibration curve is generated from the calibration standard using differently-sized sample loops, ranging from 0.1 ml to 1 ml.

Peak areas are recorded and calculated concentrations are subtracted by the concentrations of carbonyl sulfide (obtained as part of the volatile organic compound analysis, see below) because hydrogen sulfide and carbonyl sulfide co-elute. The inlet temperature is maintained at 50 °C and the inlet pressure is controlled at 10.4 psi. The total He flow rate is 53.3 ml/min, while the column flow rate is 2.4 ml/min. Separation is accomplished using an Agilent J&W HP-1 column (30 m x 0.32 mm x 5.00 µm) at a column pressure of 10.4 psi. The following temperature program is used for H2S analysis: hold at 35 °C for 3 min, ramp to 260 °C at 50 °C/min, and hold at 260 °C for 4 min. The detector is maintained at a temperature of 250 °C and has a H_2 flow of 50 ml/min, an air flow of 60 ml/min, and a makeup gas (N_2) flow of 57.6 ml/min. Samples are quantified against an H_2S standard (Praxair).

Volatile sulfur species other than H_2S are analyzed using an Agilent 6890/5973N GC-MS system fitted with a Markes "Unity 2" gas sampling/thermal desorption system. Periodic multi-point calibrations are performed to confirm instrument linearity. Prior to analysis, a system blank is analyzed to evaluate the cleanliness of the system. A one-point calibration is then performed using the calibration standard mixture(s) to confirm consistency in instrument response. A sulfur-specific trap material (Markes U-T6SUL-2S) is used to collect the analytes, and the trap is maintained at 25 °C during a 2.0 min sampling time with a sample flow rate of 50 mL/min. Analytes are desorbed at 300 °C held for 3.0 min. The transfer line temperature is maintained at 140 °C. The GC is operated in constant pressure mode (32 bar) with He carrier gas. Separation is achieved using an Agilent J&W DB-VRX column (60 m x 0.25 mm x 1.40 µm). The temperature program is as follows: hold at 45 °C for 3 min, ramp from 45 °C to 190 °C at 10 °C/min, ramp from 190 °C to 250 °C at 20 °C/min, hold for 8 min. A custom gas standard mixture (Air Liquide) is used to quantify analyte concentrations.

Semi-volatile organic sulfur compounds are analyzed using GC-qTOF-MS using the same methods and instrument parameters outlined below for non-sulfur containing semi-volatile organic compounds.

Aldehyde and Ketone Analysis

Carbonyl compound concentrations in biogas and biomethane samples are determined using a modified version of EPA method TO-11, "Determination of formaldehyde in ambient air using adsorbent cartridge followed by high-performance liquid chromatography." The method has been optimized for our analytical equipment and target compounds.

Biogas or biomethane samples are drawn through a pair of 8 x 115 mm DNPH-treated silica gel sorbent tubes (SKC, Inc.) for 30 sec and 1 min, respectively, at a flow rate of 1 l/min. Sorbent tubes are not unsealed until just prior to sampling, and flow rate is controlled with a calibrated 1-5 l/min adjustable flow meter (Dwyer Instruments, Inc.). Negative pressure is created at the back end of the sampling apparatus through the use of an explosion-proof Teflon diaphragm pump. At the conclusion of the 1-min sampling time, the sorbent tube is immediately capped, labeled, and placed into a cooler. Once transported back to the lab, it is stored in a 0 °C freezer prior to extraction. Sorbent tubes may be held at 0 °C for up to 30 days before being extracted. To extract the sorbent material, tubes are broken open and each section of sorbent material is transferred to a

labeled glass vial. 1 ml acetonitrile is added to each vial, which is then capped and allowed to sit for 30 minutes. The supernatant liquid is transferred to a labeled amber glass autosampler vial.

Sample analysis is carried out on an Agilent 1200 liquid chromatograph coupled with an Agilent 6530 quadrupole time-of-flight mass spectrometer (LC-qTOF-MS). Separation is accomplished using a Restek Ultra C_{18} Column (5 µm, 250 x 4.6 mm). The injection volume is 10 µl and the LC gradient is: 40% A (deionized H_2O with 1 mM CH_3COONH_4) and 60% B (ACN/H_2O, 95/5 v/v with 1 mM CH_3COONH_4) for 7 min, followed by a linear increase to 100% B at 20 min, hold at 100% B for 0.5 min. Each sample run includes a system blank, two sample blanks (1 set of sorbent tube extracts), calibration standards, and the samples. A multi-point calibration curve generated from the calibration standards (Sigma 47285-U TO-11 Standard Mix) is used to quantify the target compounds.

Halocarbon and Volatile Organic Compound Analysis

Volatile organic compounds (VOCs) and volatile halocarbons in biogas and biomethane samples are collected and analyzed using a modified version of the US EPA method TO-15, "Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially- Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)." The method has been optimized for our sampling techniques, analytical equipment, and target compounds. These compounds are analyzed in the same run, and using the same operating parameters, as the non-H_2S volatile sulfur species described above. A custom TO-15 gas standard mixture (Air Liquide) is used to quantify these compounds.

Semi-volatile Organic Compound and Polycyclic Aromatic Hydrocarbon Analysis

Semi-volatile organic compound (SVOC) and polycyclic aromatic hydrocarbon (PAH) concentrations in biogas and biomethane samples were determined using a modified version of EPA method 8270D, "Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS)." The method was optimized for our analytical equipment and target compounds.

Biogas or biomethane samples are drawn through a 8 x 110 mm 400 mg/200 mg XAD-2 sorbent tube (SKC, Inc.) for 60 minutes at a flow rate of 1 l/min. Sorbent tubes are unsealed immediately prior to sampling, and flow rate is controlled with a calibrated 1-5 l/min adjustable flow meter (Dwyer Instruments, Inc.). Negative pressure is created at the back end of the sampling apparatus using an explosion-proof Teflon diaphragm pump. At the conclusion of the 60 min sampling period, the sorbent tube is immediately capped, labeled, and placed into a cooler. Once transported back to the lab, it is stored in a 0 °C freezer until extraction. Sorbent tubes may be held at 0 °C for up to 30 days before being extracted. Sorbent tubes are extracted by breaking open each section and separately transferring the sorbent material to labeled glass vials. Ethyl acetate in the amount of one ml is added to each vial, which is then capped and sonicated for 30 minutes. The supernatant liquid is transferred to a labeled amber glass autosampler vial.

Analysis is carried out on an Agilent 7890 gas chromatograph coupled with an Agilent 7200 quadrupole time-of-flight mass spectrometer (GC-qTOF-MS). Each sample run includes a system

blank, two sample blanks (1 set of sorbent tube extracts), calibration standards, and the samples. A multi-point calibration curve generated from the calibration standards (Restek 31850 8270 Megamix) is used to quantify the target compounds.

Separation is accomplished using an Agilent J&W HP5-MS UI column (30 m x 0.25 mm x 0.25 μm) with an injection volume of 1.0 μl and a flow rate of 0.8 ml/min (He). The injector temperature is 250 °C and the temperature program is: 35 °C for 3 min, ramp to 325 °C at 4°C/min, hold at 325°C for 3 minutes.

Total organic silicon, including siloxanes

Siloxanes in biogas and biomethane samples are collected and analyzed using the same approaches and parameters described above for extended hydrocarbon analysis. Briefly, samples are collected on coconut charcoal adsorbent tubes and analyzed using GC-qTOF-MS. Concentrations are quantified using the following external standards: 1,1,3,3-tetramethyldisiloxane (Sigma 235733-25G), pentamethyldisiloxane (Sigma 76840-5ML), hexamethyldisilane (Sigma 217069-5G), hexamethyldisiloxane (Sigma 205389-5ML), octamethyltrisiloxane (Sigma 235709-5ML), octamethylcyclotetrasiloxane (Sigma 43883-100MG), decamethyltetrasiloxane (Sigma 235679-25G), decamethylcyclopentasiloxane (Sigma 43217-250MG), dodecamethylpentasiloxane (Sigma 447269-10ML), and dodecamethylcyclohexasiloxane (Sigma 43216-25MG).

Pesticide and Polychlorinated Biphenyl Analysis

Pesticide and polychlorinated biphenyls (PCBs) in biogas and biomethane samples are collected and analyzed using the same procedures and instrument parameters described above for SVOCs. Pesticide concentrations are quantified using a pesticide standard mix (Sigma CRM46845 EPA 8081) and PCBs are quantified using a PCB standard mix (Supelco 47330-U PCB Congener Mix 1).

Biologicals
Biologicals were assessed via cultivation and molecular testing.

Biogas and biomethane was collected using two 47 mm in-line stainless steel filter holders (Pall Corporation, Ann Arbor, MI). Biogas flow rates ranging from 1 to 5 L min^{-1} passed through 47 mm diameter polycarbonate membrane filters (0.4-μm pore size) (VWR, Visalia, CA) placed inside stainless filter holders. Total gas collection volume ranged from 200 – 500 L per filter. Polycarbonate filters were removed from filter holders using sterile forceps and placed in a 50-ml Falcon tube containing 15 ml of sterile phosphate buffered saline (PBS, pH 7.4 ± 0.1) after sample collection. Any water that condensed in sampling lines was collected and aliquoted into two 50-ml Falcon tubes. To minimize oxygen contact for samples to be used in anaerobic bacteria cultivation, one Falcon tube was placed in a GasPak anaerobic pouch system (BD Biosciences, San Jose, CA). The other Falcon tube were kept in a clean Ziploc bag. Both Falcon tubes were immediately placed in a cooler with ice packs and transferred to a laboratory where they were stored at 4°C before analysis within 24 hrs.

The filter samples placed in 15 ml of sterile PBS were vortexed for 5 – 10 sec, hand shaken for 2 min ± 5 sec, and pooled in one tube inside a biosafety cabinet. A total of 30 ml filter suspension was divided into three parts for cultivation bacteria enumeration, spore enumeration, and quantitative polymerase chain reaction (qPCR). The MPN technique is to quantify the cultivable heterotrophic and spore-forming bacteria. MPN tests for cultivable bacteria were performed in thioglycollate medium (TG) with single dilution method that is preferred for samples with low levels of microorganisms. Samples were incubated anaerobically and aerobically at 37°C in the dark for 7 days. The number of cultivable bacteria was determined using the modified Thomas formula for a single dilution with any positive tubes (Blodgett 2010 [1]). For spore enumeration, the filter suspension was heat-treated at 80 ± 2°C in a water bath for 15 min to inactivate vegetative bacteria. The pour plate procedure modified from National Aeronautics and Space Administration (NASA) protocol for Spore Testing NHB 5340.1D [2] was applied for the first a few samples. This method was then replaced with the single dilution MPN test to increase sensitivity and accuracy. Spore-forming bacteria cultivation was performed in tryptic soy broth medium (TSB). Samples were incubated at 32°C for 3 days under aerobic and anaerobic conditions. The number of spore-forming bacteria was once again calculated modified Thomas formula (identical to procedure for cultivation bacteria enumeration). Positive wells in microplates were retrieved and used for direct PCR without DNA extraction using total bacteria assay targeting 16S rRNA of universal bacteria. The sequences were compared with publicly available BLAST database for taxonomic identification.

Filter suspension subject to qPCR analysis was centrifuged at 3500 rpm for 10 min to concentrate microorganisms. The FastDNA® SPIN KIT for Soil (MP Biomedicals, Irvine, CA) was used to extract the genomic DNA, following the manufacturer's protocol. Five real-time quantitative polymerase chain reaction (qPCR) assays were chosen from publicly available literature to analyze total bacteria and corrosion inducing bacteria including sulfate reducing bacteria (SRB), iron oxidizing bacteria (IOB) and acid producing bacteria (APB). Two separate qPCR assays were used for IOB analysis to target 16S rRNA of *Gallionella* and *Leptothrix* spp. that are widely known iron oxidizing bacteria.

Metals

Metals (including mercury) were determined via EPA Method 29 (modified) "Determination of Metals Emissions from Stationary Sources." Briefly, gas samples flowed through aqueous acid impingers followed by analysis using ICP-MS, Inductively Coupled Plasma Mass Spectrometry.

During the spring of 2016, continuing through the summer, approximately 20 samples were analyzed for mercury (Hg) by two methods: the traditional gold-coated trap method, and the metals impinger series used for all elements. Results, including detection limit performance, were comparable. Confidence in the ability to exclude incidental signal from outside the sampled gas flow was more reliable with the impinger series. For those two reasons, results from the ICP-MS method are reported.

Task 1e. Reporting

The contractor submitted quarterly progress reports and a Final Report (this document) in fulfillment of the contract deliverables.

1.4 Report Structure

This report is comprised of 4 chapters, including introduction (Chapter 1) and conclusions (Chapter 4).

Chapter 2 describes each location where biogas or upgraded biomethane was collected. The general process is described and site over-view diagrams are provided for all locations.

Chapter 3 summarizes the results of all measurements for all target analytes for biogas and upgraded biomethane. Results are provided for the mean and standard deviation of all measurements.

Chapter 4 provides preliminary conclusions about the biogas composition measurements and makes recommendations for future work.

2 SITE DESCRIPTIONS

2.1 Introduction

Biogas samples were collected at five different facilities in the current study. Two of these facilities (SATS and READ) used general food / organic waste feedstock that varied significantly over time resulting in significant process variability. Two of the facilities used dairy agricultural waste as feedstock which is relatively constant over time, but the facilities employed different sizes/forms of anaerobic digesters leading to site-to-site variations. The final facility was a landfill subdivided into the core working section of the landfill and the perimeter of the landfill producing gas streams with different methane content. All sites were reviewed and approved by the Project Advisory Committee and project managers at ARB / CEC. A more detailed description of each site is provided below.

2.2 CleanWorld South Area Transfer Station (SATS) Facility

The CleanWorld Sacramento Biodigester is located at the South Area Transfer Station (SATS) at 8550 Fruitridge Road, Sacramento CA. SATS uses a three-stage digester operating at a thermophilic temperature from 50-55ºC. It treats 25 tons day^{-1} food waste collected from restaurants and various food processors. The biogas produced from the food waste passes through an activated carbon scrubber to remove hydrogen sulfide followed by cooling to remove moisture. The cleaned gas is treated with a membrane system provided by BioCNG to separate methane from carbon dioxide. In the current project the on-site membrane system was inoperable during the time when biomethane collection occurred and so a transportable methane upgrading system constructed by Helee was used to upgrade biogas to biomethane (see Section 1.3 under Task 1c). The membranes used in the Helee system are identical to the membranes used by the on-site system, but the Helee system uses a dual-stage membrane configuration while the on-site system uses a single-stage membrane system.

The biomethane produced at SATS is used for a CNG fueling station for trucks. The tail gas from the BioCNG unit is collected and directed to an on-site flare. The site has a 190 kW engine-generator (2G-Cenergy) for electricity and heat generation but this engine is rarely used during normal operations.

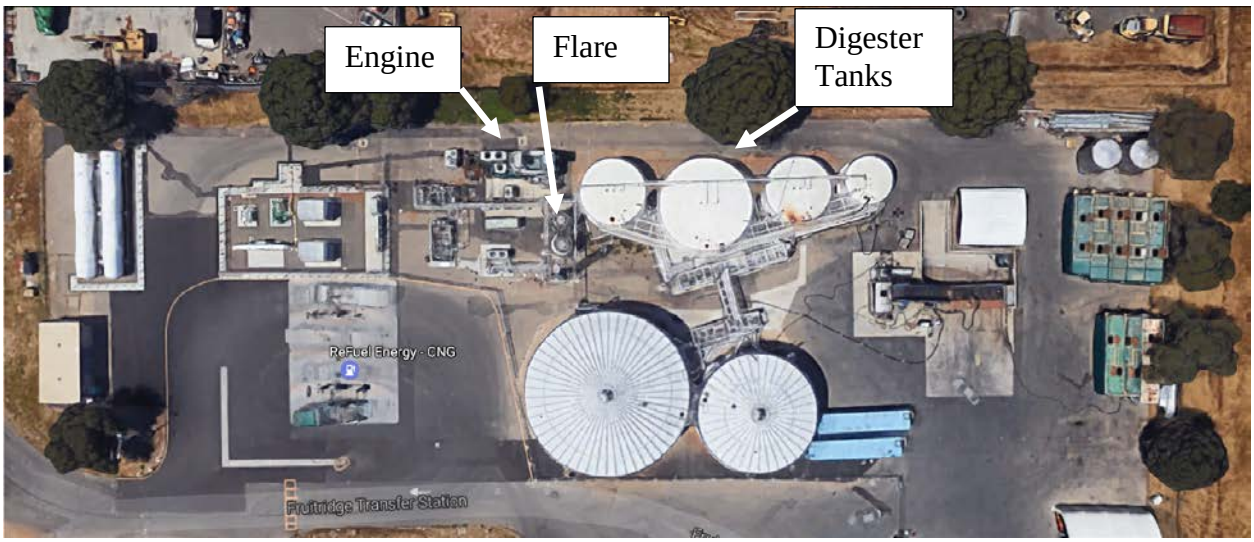

Figure 2-1: Over-view of SATS biogas production facility.

2.3 UC Davis / CleanWorld Renewable Energy Anaerobic Digester (READ) Facility

The UC Davis Renewable Energy Anaerobic Digester (READ) operated by CleanWorld is located on the campus of UC Davis. READ uses the same digester technology as the SATS facility but it operates at a larger scale. The READ facility processes 50 tons day^{-1} of mixed organic waste consisting of animal manure and bedding, food and paper waste, and other organic waste collected from the UC Davis campus and surrounding areas. The biogas produced at the READ facility is combined with gas from the UC Davis landfill to power three, 200 kW micro-turbines for electricity and heat generation. For the current project, biogas was upgraded to biomethane at the READ facility using the transportable dual-stage membrane separation unit from Helee.

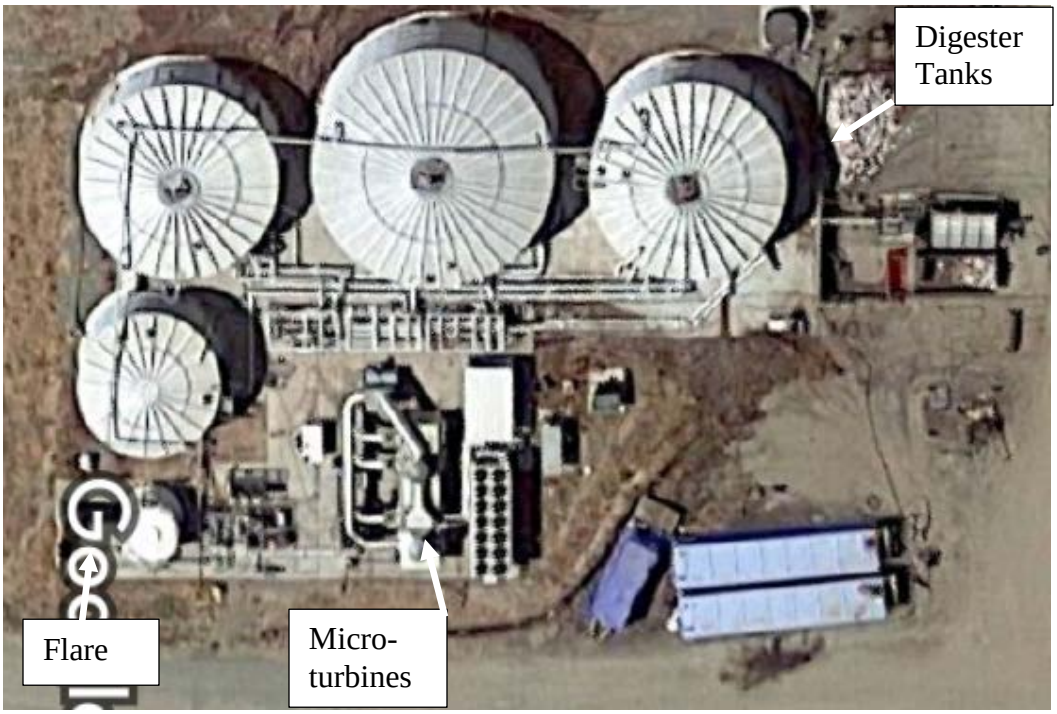

Figure 2-2: Over-view of READ biogas production facility.

2.4 Kiefer Landfill

Kiefer landfill occupies 1,084 acres near the intersection of Kiefer Boulevard and Grant Line Road to the east of Sacramento. The landfill has been accepting mixed residential and commercial waste from Sacramento and the surrounding region since 1967. Power generation from methane recovery at the landfill has been ongoing since 1999. Landfill gas at Kiefer is actively extracted by a series of blowers resulting in negative pressure at the intake which causes air intrusion through the landfill material into the system. The landfill gas stream from the core working section of the landfill has a methane content of approximately 50% and is burned in power generation turbines. The landfill gas stream from the perimeter of the landfill has a methane content of approximately 35% and is burned in a flare. Separate samples were collected from each of these gas streams in the current project. Upgraded biomethane could not be produced at Kiefer because the membrane separation unit could not remove nitrogen introduced by air intrusion.

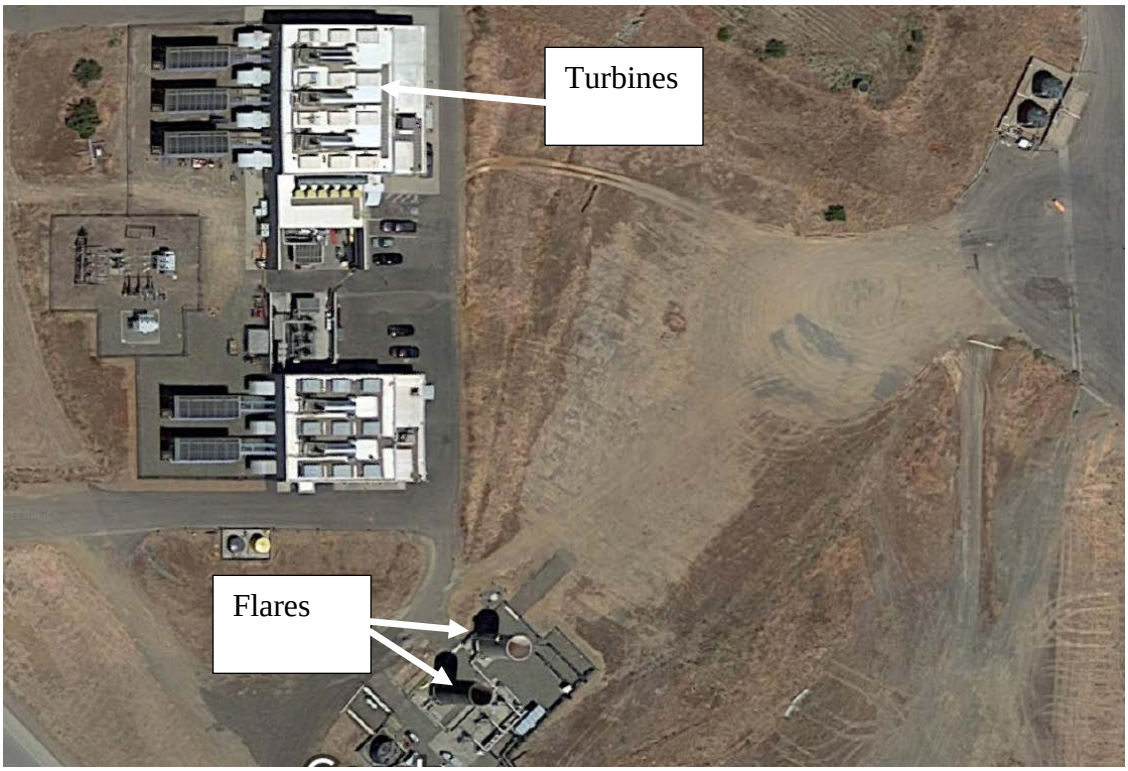

Figure 2-3: Over-view of Kiefer landfill biogas production facility.

2.5 New Hope Dairy

New Hope Dairy Digester located near Galt CA uses scraped manure from 1200 cows as feedstock to a heated, constantly stirred tank reactor (CSTR) digester operating at mesophilic temperature (35-40 ^{o}C) with a 50 day hydraulic retention time. A small amount of air is injected into the digester to kill sulfur-producing bacteria and ferric chloride is injected into the digester to trap sulfur. The biogas produced at the site is used to power a 450 KW engine-generator (2G-Cenery) for approximately 6-8 hrs each day. The digester was designed by MT-Energie of Germany and is similar to digesters widely deployed in Europe and considered more broadly for application in California. Biogas was upgraded to biomethane at the New Hope Dairy using the transportable dual-stage membrane separation unit from Helee.

Figure 2-4: Over-view of New Hope dairy biogas production facility.

2.6 VanWarmerdam Dairy

VanWarmerdam Dairy Digester located near Galt CA consists of a covered lagoon digester operating at ambient temperature and 100 day hydraulic retention time. The digester was designed by Maas Energy and is typical of dairy digester applications in California. A small amount of air is injected into the covered lagoon to kill sulfur-producing bacteria. The biogas produced from flushed manure (1200 cows) is used to power a 600 kW engine-generator (Guascor) that operates 6-8 hrs each day. Upgraded biomethane could not be produced at VanWarmerdam because the membrane separation unit could not remove nitrogen introduced by air injection.

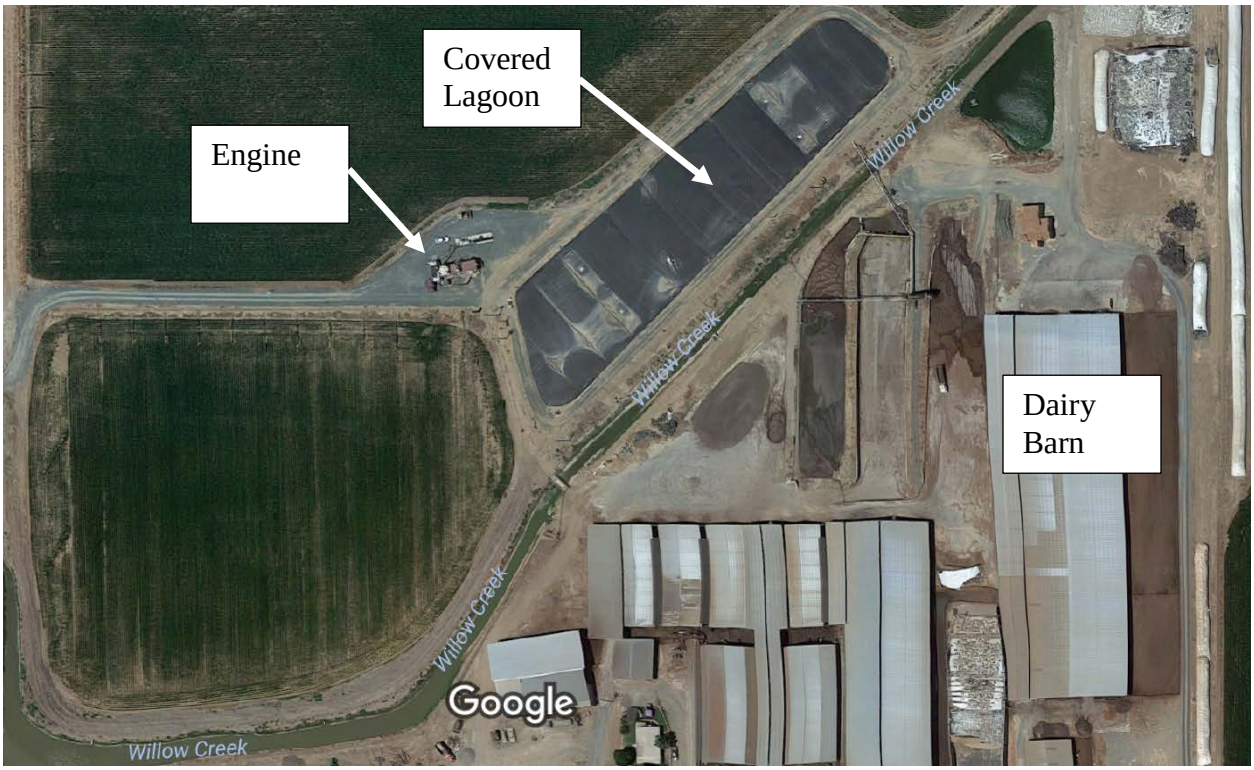

Figure 2-5: Over-view of VanWarmerdam dairy biogas production facility.

2.7 Commercial Compressed Natural Gas (CNG) Fueling Stations

Samples of Compressed Natural Gas (CNG) were obtained from the following commercial fueling stations in Los Angeles on March 23, 2017.

Station#1: Clean Energy Pasadena, 3528 Foothill Blvd., Pasadena CA 91107

Station#2: Clean Energy, 5640 Peck Rd., Arcadia CA 91006

Station#3 CNG Station, 950 N. Todd Ave., Asuza CA 91702

Approximately 200-500 psi of each gas was pumped into a transportable CNG storage tank (61 liter) using the fill nozzle at each station. Individual samples from each station were collected and analyzed separately to provide three individual samples of natural gas. All of the sample collection and analysis techniques were identical to those applied to biomethane throughout the project.

Samples of natural gas were collected in Los Angeles rather than Northern California because all of the sample collection equipment was in Los Angeles for CEC project PIER 13-001 at the time when the final report for the current project was due. CEC PIER 13-001 involved testing of emissions from vehicles powered by biomethane which employs similar analytical techniques to the testing performed for the current project. CEC PIER 13-001 was delayed by approximately 3 weeks due to a variety of unforeseen issues which disrupted the timeline of the natural gas collection for the current project. The authors believe that natural gas obtained from Los Angeles is fully representative of natural gas used in California for the purposes of the current study.

3 RESULTS

3.1 Introduction

The results shown in the following sections represent averages from multiple samples collected from the indicated source on different days to form a "sample stream". In virtually all cases three individual samples collected at different times were composited to form a "sample stream." Reported uncertainty values are one standard deviation of the individual samples.

The natural gas sample stream was constructed by collecting and analyzing CNG from three different vehicle filling stations in Los Angeles on the same day. All CNG samples were stored and handled using the same methods as the biomethane samples obtained from the biogas production sites. Compressed CNG/biomethane was stored in transportable CNG storage tanks (61 liter) with pressures ranging from 200-3600 psi. Gas passed through a two-stage brass pressure-reducing regulator prior to collection on various sampling media and subsequent analysis.

Raw biogas samples were collected directly at the production site without any intermediate steps involving compression into storage tanks or flow through a pressure-reducing regulator.

Limits of detection (LODs) for each measurement technique were defined to be the level at which a chromatographic peak could be detected but the quantification of the compound was not reliable because the signal was comparable to the baseline "noise" in the method. LODs were generally defined as 3x the baseline variability.

Limits of quantification (LOQs) for each measurement technique were defined to be the level at which quantification of the compound was possible. LOQs were generally defined as 10x the baseline variability. Measurements below their LOQ are simply reported as <LOQ in the following data tables.

All data in the report were reviewed to ensure that they met the project's quality control guidelines. If they did not, analyses were repeated (consistent with holding time limitations) or other necessary corrective actions were taken. In some cases these steps still did not produce acceptable data; in these cases the result is listed as "no measurement" (NM). Some compounds contained in biogas / biomethane samples were present at concentrations higher than the highest standard used for quantification. Samples were diluted to bring these concentrations within the range of standards where possible, but in some cases concentrations were still above the standard curve even after multiple dilutions were performed. These compounds were then quantified by extrapolating the calibration curve above the highest standard. This procedure was only used when the resulting concentrations were < 10x the highest concentration in the standard curve.

One sample of raw biogas from VanWarmerdam Dairy on 7/21/2016 was lost when the sample collection stand blew over in high winds. This caused liquid to spill from impingers and potentially compromised all sample trains. An additional sample was collected at VanWarmerdam so that the required threshold of three replicates was still achieved.

3.2 Major Component Analysis

The concentrations of major components measured in the current study are reported in Table 3-1. Methane concentrations in the raw biogas varied from 35.4% to 70.5%. The greatest variability occurred at the READ and SATS facilities due to the variable feed stock employed at these locations, but samples were only collected when biogas production was "nominal." The reported variability in methane concentrations at these sites does not fully capture the process variation over a typical year but it does represent "operating conditions."

The methane content at New Hope dairy and VanWarmerdam dairy is very different due to the different size and design of the digesters. VanWarmerdam's covered lagoon digester is considerably larger and generally more stable than the smaller CSTR digester at New Hope. As a result, methane content at New Hope had greater variability over a typical daily cycle.

The contrast in methane content produced by the core and perimeter portions of Kiefer landfill illustrate how energy from waste production at smaller landfills may be challenging. Methane content in the perimeter section of the landfill was only ~35% due to more air entrainment, while the methane content in the core section of the landfill was ~50% due to less air entrainment.

In addition to methane, the bulk of the biogas composition was made up by carbon dioxide (CO_2) with smaller amounts of nitrogen (N_2) and oxygen (O_2) (due to air intrusion) at all the biogas locations. Upgrading with the membrane separation unit effectively removed the CO_2 but did not completely remove the N_2 and O_2 in the sample stream. This prevented upgrading of biogas at Kiefer landfill and VanWarmerdam dairy. Upgrading was attempted at New Hope dairy but the resulting methane content was lower than the methane content of CNG collected in Los Angeles. Biomethane produced at READ and SATS had methane content that met or exceeded the methane content of the CNG collected in Los Angeles. Commercial CNG contained an additional ~5.5% ethane which yielded higher energy content than biomethane, which contained primarily nitrogen and oxygen as major residual components. Biomethane produced in the current study did not meet pipeline standards requiring oxygen < 0.2%, CO_2 < 3%, and total inerts <4%. It is likely that future commercial upgrading operations will be better able to achieve this standard by optimizing upgrading operations at each facility over a period of several months as opposed to several weeks available at each site in the current study. Upgraded biomethane from all sources was successfully used as a vehicle fuel during testing supported under a separate project (CEC Project PIER#13-001).

The concentrations of other potential major components listed in Table 3-1 were all below the limits of quantification.

Table 3-1: Results of Major Component Analysis (all results in %, uncertainty is 1 standard deviation)

Parameter	LOQ (%)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Nitrogen/Carbon Monoxide	0.23%	1.83± 0.65	11.2± 2.41	2.08± 0.188	6.85± 2.72	3.75± 2.04	7.9± 0.619	22.1± 24.6	4.13± 0.815	37.6± 3.32	18.1
Oxygen/Argon	0.14%	0.419± 0.303	5.97± 1.66	2.91± 0.175	6.72± 1.72	0.677± 0.307	5.81± 1.35	10.5± 8.5	2.95± 0.165	8.83± 2.12	6.62
Methane	0.76%	91.5± 0.845	56.8± 9.26	91.5± 0.576	58.8± 12.9	93.4± 2.29	70.5± 1.36	47.4± 19.6	89.5± 1.47	35.4± 7.93	49.5
Carbon Dioxide	0.72%	0.818± 0.0936	26± 9.43	3.48± 0.347	27.7± 13.6	2.13± 0.688	15.8± 3.16	20± 13.4	3.38± 1.21	18.2± 6.74	25.8
Hydrogen	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
Ethane	1.29%	5.43± 0.151	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ethene	1.08%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ethyne	1.07%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Propane	1.25%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Propene	1.07%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Propadiene	0.97%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Propyne	0.97%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
i-Butane	0.98%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
n-Butane	0.77%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
1-Butene	0.86%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
i-Butene	0.85%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
trans-2-Butene	0.72%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
cis-2-Butene	0.72%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
1,3-Butadiene	0.71%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Isoprene	0.72%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
i-Pentane	0.54%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
n-Pentane	0.54%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
neo-Pentane	0.54%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Pentenes	0.54%	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

3.3 Ammonia Analysis

The results of ammonia measurements from the 10 sample streams are summarized in Table 3-2 below. Ammonia in the direct biogas was below the LOQ (100 ppbv) in all samples except for VanWarmerdam where it was detected in a single sample. Generally speaking, better management of the waste stream on dairy farms appears to mitigate much of the ammonia emissions normally associated with these locations.

Table 3-2: Results of Ammonia Analysis (all results in ppbv, uncertainty is 1 standard deviation)

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Ammonia	100	NM	<LOQ	<LOQ	<LOQ	<LOQ	150± 300	<LOQ	<LOQ	<LOQ	<LOQ

3.4 Extended Hydrocarbon Analysis

The concentrations of extended hydrocarbons measured in the current study are reported in Table 3-3. Concentrations of straight chain alkanes with 6-12 carbons were detected in CNG samples with concentrations especially high for hexanes (6 carbons) and heptanes (7 carbons) with lower concentrations observed for higher molecular weight compounds. Straight chain alkanes were also detected in relatively high concentrations in Kiefer landfill gas with the greatest abundance observed for decane (10 carbons) and decreasing concentrations generally observed for lower and higher molecular weights than this compound. The food waste digesters and dairy digesters generally produced raw biogas with lower concentrations of straight chain alkanes. The most abundant compound from these sources was generally octane (8 carbons). Upgrading biogas to biomethane using the Helee dual-membrane unit reduced the concentration of straight chain alkanes at READ, slightly increased these concentrations at New Hope dairy and greatly increased these concentrations at SATS. The upgrading unit employs a compressor to raise the pressure of the biogas and force CO_2 across the membrane. The biogas passes through a bath of synthetic oil as part of this process. The unit was operated first at READ, second at New Hope, and third at SATS over a time period of approximately one year. This pattern approximately corresponds to the pattern of increasing alkanes in the upgraded biomethane, suggesting that the upgrading process itself may be driving the observed trends.

Table 3-3: Results of Extended Hydrocarbon Analysis (all results in ppbv, uncertainty is 1 standard deviation)

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Cyclopentane	1.87	740±135	30.2± 14	8.06± 2.13	<LOQ	670± 515	<LOQ	<LOQ	<LOQ	168± 238	192± 170
Methylcyclo-pentane	1.87	2150±142	126± 60.2	57.9± 22.3	53.7± 33.2	2150± 1560	12± 15.5	32.3± 60.9	4.58± 7.93	233± 329	165± 145
Cyclohexane	1.87	1720±135	490± 237	45.4± 12.5	86.2± 98.6	1880± 1330	2.54± 4.39	2± 4	4.38± 7.59	416± 589	413± 361
Methylcyclo-hexane	1.87	2940± 46.1	716± 228	50.4	3.23± 1.03	33.1	4.1± 2.13	1.77	27.9± 23.1	653± 923	535± 469
C3 Benzenes	0.0080	0.88± 0.054	15.2± 6.48	1.11	10.7± 6.43	0.235	0.295± 0.064	0.526± 0.164	0.318± 0.146	468± 313	523± 91.5
C1 Naphthalenes	0.00656	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.281± 0.192	0.184± 0.162
C2 Naphthalenes	0.0119	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Hexanes	1.87	2830± 588	140± 114	122± 79.5	144± 150	2690± 1900	40.1± 25.2	114± 212	0.869± 1.51	615± 870	238± 207
Heptanes	1.9	1040± 48.9	310± 136	72.1± 36.6	57.7± 45.3	1240± 835	7.69± 4.1	4.05± 6.28	14.3± 12.1	1100± 1550	703± 613
2,2,4-Trimethylpentane	1.87	36.2± 3.51	610± 253	1890	11.6± 13.4	263	<LOQ	<LOQ	615± 487	339± 480	326± 285
Octanes	1.87	467± 25.4	643± 215	5.34	499± 442	1420± 822	67.3± 47.3	80± 135	193± 70.7	1880± 2660	884± 766
Nonane	0.0291	145± 35.7	117± 70	3.41	124± 83.7	3.43	1.78± 0.703	3.03± 0.962	14.4± 6.38	1220± 427	1160± 361
Decane	0.00262	37.2± 5.83	82.6± 65.4	3.13	NM	1.80	0.929± 0.728	0.636± 0.308	3.19± 1.42	2880± 923	1900± 485
Undecane	0.0119	8.27± 3.18	35.9± 28.4	1.68	NM	1.56	1.05± 1.24	0.471± 0.217	2.18± 0.479	1360± 472	911± 285
Dodecane	0.00219	3.04± 1.01	4.24± 2.54	0.506	NM	0.675	0.466± 0.513	0.187± 0.054	0.971± 0.165	216± 86	162± 89.1
Tridecanes	0.00219	0.573± 0.274	0.544± 0.439	<LOQ	NM	<LOQ	0.21± 0.256	0.113± 0.0561	0.26± 0.0657	39.9± 33.4	33.6± 16.9
Tetradecane	0.0094	<LOQ	0.269± 0.197	0.0259	NM	0.0546	0.114± 0.122	0.0536± 0.0329	0.0695± 0.0178	5.49± 4.33	1.47± 1.78

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Pentadecanes	0.0094	<LOQ	<LOQ	<LOQ	NM	<LOQ	<LOQ	<LOQ	<LOQ	0.725± 0.893	<LOQ
Hexadecane	0.00165	<LOQ	<LOQ	<LOQ	NM	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptadecanes	0.00165	<LOQ	<LOQ	<LOQ	NM	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Octadecane	0.00367	<LOQ	<LOQ	<LOQ	NM	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Nonadecanes	0.00367	<LOQ	<LOQ	<LOQ	NM	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Eicosane	0.0033	<LOQ	0.0013± 0.00318	<LOQ	NM	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

3.5 Sulfur Analysis

The concentrations of sulfur species measured in the current study are reported in Table 3-4. As expected, the biogas and biomethane samples have substantially higher total concentrations of many sulfur species than the CNG, which primarily contained mercaptan and disulfide species commonly included in natural gas odorants. Upgrading removes more than 99% of the volatile sulfur species in many cases, but the relatively high starting concentrations still leave upgraded biomethane samples with total sulfur concentrations significantly higher than those in CNG. It should be noted that the large standard deviations reported in Table 3-4 (and in a number of subsequent tables) are not the result of analytical uncertainty, but instead seem to be largely driven by temperature variations. Concentrations of almost all volatile compounds (with or without sulfur) were strongly correlated with the ambient temperature at the time that sampling was conducted. That is, the variability appears to be associated with processing conditions and feedstock variation rather than with measurement uncertainty.

Table 3-4: Results of Sulfur Analysis (all results in ppbv, uncertainty is 1 standard deviation)

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Hydrogen Sulfide	298.7	<LOQ	7930± 10500	<LOQ	86800± 92200	<LOQ	<LOQ	40900± 57900	<LOQ	<LOQ	234± 203
Sulfur Dioxide	26.2	<LOQ	4030± 4610	263± 87.8	1560± 1280	<LOQ	533± 330	2660± 3100	148± 25.6	318± 394	2310± 2430
Carbonyl sulfide	15.2	<LOQ	71.4± 73.3	24.3± 5.27	362± 330	7.12± 14.2	88.8± 69.9	89.3± 115	<LOQ	76.4± 108	76.8± 71.8
Carbon disulfide	2.9	6.91± 4.6	308± 359	65.2± 5.55	3960± 2260	71.8± 51.5	25± 27.1	44.6± 89.3	9.3± 4.79	42.1± 59.5	90.6± 79.3
Methyl mercaptan	52.5	<LOQ	978± 975	258± 231	26000± 29700	15.5± 31	44± 76.2	430± 780	<LOQ	<LOQ	<LOQ
Ethyl mercaptan	7.8	172± 25.4	21.6± 43.2	42.5± 73.6	965± 1010	<LOQ	<LOQ	122± 188	<LOQ	<LOQ	<LOQ
Isopropyl mercaptan	4.9	43.7± 16.6	914± 316	205± 180	4110± 2040	136± 273	19.9± 34.4	49.4± 79.7	<LOQ	<LOQ	224± 389
n-Propyl mercaptan	4.3	12± 10.4	511± 290	63.3± 72.2	2260± 2250	27.2± 54.4	<LOQ	60.6± 88.1	<LOQ	<LOQ	<LOQ
t-Butyl mercaptan	4.4	677± 173	<LOQ	145± 194	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dimethyl sulfide	4.3	<LOQ	1630± 2780	1260± 651	4600± 3750	785± 752	20.1± 12.5	98.4± 161	119± 40.1	377± 533	826± 715
Methyl Ethyl sulfide	3.5	5.2± 0.573	74.4± 98.7	49.9± 48.2	698± 644	17.8± 12.8	5.31± 0.754	2.43± 4.85	14.6± 12.3	232± 328	385± 335
Diethyl sulfide	5.7	28.3± 0.176	<LOQ	<LOQ	13.2± 26.4	<LOQ	3.61± 6.25	3.35± 6.7	<LOQ	7.28± 10.3	4.65± 8.06
Di-tert-butyl sulfide	3.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.03± 6.06	<LOQ	<LOQ	<LOQ
Dimethyl Disulfide	0.8	<LOQ	65.6± 127	44.2± 14.6	2670± 2300	48.4± 96.8	4.82± 6.43	0.488± 0.976	88.2± 36.6	30.3± 42.8	<LOQ
Diethyl Disulfide	1.1	<LOQ	<LOQ	<LOQ	<LOQ	3.25± 2.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Thiofuran	3.0	<LOQ	<LOQ	14.4± 14	24.7± 6.12	<LOQ	9.78± 0.173	9.4± 11.6	19.9± 7.44	32.6± 46.1	56.9± 49.4

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Methyl Ethyl Disulfide	10.0	<LOQ	7.62± 8.9	31.9± 20.8	31.7± 63.4	33.7± 41.7	<LOQ	3.3± 6.6	31.9± 20	17.3± 24.5	13.2± 11.6
Methyl i-Propyl Disulfide	10.0	12.2± 21.2	3.01± 6.02	51.6± 26.1	310± 231	101± 162	<LOQ	<LOQ	70.5± 44.3	9.53± 13.5	18.7± 32.4
Methyl n-Propyl Disulfide	10.0	5.16± 8.94	16.3± 19.2	26.8± 10.1	62.2± 78.7	42.1± 40.6	<LOQ	<LOQ	61.3± 33.4	115± 163	121± 105
Methyl t-Butyl Disulfide	10.0	51.3± 11.9	<LOQ	<LOQ	<LOQ	173± 61.4	<LOQ	<LOQ	<LOQ	<LOQ	521± 453
Ethyl i-Propyl Disulfide	10.0	<LOQ	180± 102	<LOQ	522± 294	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ethyl n-Propyl Disulfide	10.0	<LOQ	<LOQ	<LOQ	<LOQ	175± 130	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ethyl t-Butyl Disulfide	10.0	4.53± 7.85	43.3± 86.6	<LOQ	18.1± 21	<LOQ	12.5± 21.7	4.23± 8.46	<LOQ	759± 1070	385± 333
Di-i-Propyl Disulfide	10.0	<LOQ	<LOQ	<LOQ	5.55± 11.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	59.3± 52.5
i-Propyl n-Propyl Disulfide	10.0	19.3± 30.1	17.9± 35.8	<LOQ	60.6± 88	13.3± 26.6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Di-n-Propyl Disulfide	10.0	3.56± 6.17	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	24.7± 34.9	<LOQ
i-Propyl t-Butyl Disulfide	10.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
n-Propyl t-Butyl Disulfide	10.0	<LOQ	<LOQ	<LOQ	7.93± 9.47	<LOQ	4.77± 8.26	<LOQ	<LOQ	<LOQ	65.9± 64.1
Di-t-Butyl Disulfide	10.0	17.1± 5.07	<LOQ	<LOQ	8.86± 17.7	37.1± 27.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dimethyl Trisulfide	0.007	<LOQ	5.17± 5.47	4.73 [a]	63.8± 111	1.68 [a]	0.137± 0.107	0.171± 0.173	0.265± 0.0802	0.778± 0.406	1.03± 0.321
Diethyl Trisulfide	0.007	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Di-t-Butyl Trisulfide	0.007	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Thiophene	10	8.65± 7.63	10.4± 13.5	8.3± 14.4	25± 12.9	<LOQ	<LOQ	4.97± 9.94	12.6± 12.2	98.2± 139	61.1± 52.9
C1-Thiophenes	10	<LOQ	109± 90.2	31.5± 16	154± 79.5	58.9 [a]	22.9± 8.77	85.5± 103	70.7± 27.3	240± 339	147± 127

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
C2-Thiophenes	0.017	<LOQ	1.55± 0.586	0.071[a]	1.87± 1.01	0.671[a]	4.24± 0.936	22.6± 10.6	0.578± 0.377	9.61± 7.11	15.9± 5.23
C3-Thiophenes	0.007	<LOQ	0.439± 0.313	0.014[a]	0.736± 0.307	0.0120[a]	0.243± 0.0552	17± 6.25	0.00652± 0.00647	2.06± 1.63	2.25± 0.37
Benzothiophene	0.007	<LOQ	0.0982± 0.0575	0.026[a]	0.0328± 0.0142	0.0182[a]	0.0399± 0.0373	0.0552± 0.0303	0.0378± 0.0094	3.37± 0.826	2.33± 0.133
C1-Benzothiophenes	0.063	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.0226± 0.0392	<LOQ	0.00303± 0.00526	2.2± 0.527	0.824± 0.171
C2-Benzothiophenes	0.006	<LOQ	0.029± 0.0159	0.018[a]	0.0332± 0.0236	0.0385[a]	0.0441± 0.0496	0.00391± 0.0044	0.0644± 0.0419	0.432± 0.336	0.0884± 0.0536
Thiophane	10	<LOQ	<LOQ	<LOQ	<LOQ	1.5± 1.29	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Thiophenol	10	<LOQ	<LOQ	<LOQ	<LOQ	1.5± 1.29	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

[a]single measurement

3.6 Halocarbon and Volatile Organic Compound Analysis

The concentrations of halocarbons and other volatile organic compounds measured in the current study are reported in Table 3-5. All halocarbon concentrations are below the LOQ for the CNG samples. Dichloropropene and associated breakdown products were detected in VanWarmerdam dairy biogas. Dichloropropene is a pesticide commonly used in agriculture and likely entered the covered lagoon at VanWarmerdam dairy through runoff from nearby fields. Notably, dichloropropene and associated breakdown products were not detected in biogas produced at New Hope dairy since the inputs to this digester are not impacted by runoff from nearby fields.

Benzene, toluene, ethylbenzene, and xylene (BTEX) compounds were present at concentrations above detection limits in all sources of biogas, biomethane, and CNG. Raw biogas likely contains BTEX compounds due to their presence in the original feedstock either through the direct incorporation of petroleum-based materials or through the use of fuels, solvents or pesticides in related processes that inadvertently become entrained into the feedstock to the digester. As discussed in section 3.4, the upgrading process directly exposed the biogas to an oil bath, which may have entrained additional BTEX compounds into the upgraded biomethane. CNG contains BTEX compounds for similar reasons.

A number of halocarbons are above LOQ in raw biogas samples from Kiefer landfill and to a lesser extent from the READ and SATS food waste digesters. These halocarbons likely originate from plastics in feedstock to these facilities. Both READ and SATS routinely accept packaged food products that have expired. An automated "depackager" shreds the containers to release the food contents, but scraps of plastic container are invariably introduced into the feedstock for these facilities. Kiefer landfill receives plastics which degrade over time and release halocarbons. It is notable that the halocarbon content of gas from the perimeter portion of the landfill is not significantly different than the halocarbon content of the gas from the core portion of the landfill.

Upgrading biogas to biomethane generally removed halocarbons from the biogas at READ and SATS.

Aromatic hydrocarbons are above LOQ for most of the samples analyzed in the present study, including CNG. Total aromatic hydrocarbon concentrations were highest in Kiefer raw biogas followed by READ raw biogas, SATS raw biogas, and then the dairy raw biogas. Aromatic hydrocarbon concentrations in the upgraded biomethane followed trends that were similar to the alkanes (discussed in Section 3.4). Initial upgrading at READ decreased aromatic hydrocarbon concentrations in the product gas by a factor of 10. Subsequent upgrading at New Hope and SATS increased aromatic hydrocarbons by a factor of ~2.75. As discussed previously, these increased concentrations may have been introduced to the gas by the upgrading process itself. Final aromatic hydrocarbon concentrations in biomethane were generally similar to those found in CNG samples (which also undergo a compression step).

Table 3-5: Results of Halocarbon and Volatile Organic Compound Analysis (all results in ppbv, uncertainty is 1 standard deviation)

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Dichlorodifluoromethane	6.0	<LOQ	87.7± 95.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	147± 166	216± 188
1,2-dichloro-1,1,2,2-tetrafluoroethane	0.9	<LOQ	9.16± 6.76	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	16.5± 17	15.1± 14.8
1,1,2-trichloro-1,2,2-trifluoroethane	2.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Trichlorofluoromethane	1.4	<LOQ	2.98± 2.7	<LOQ	0.475± 0.95	<LOQ	<LOQ	<LOQ	<LOQ	7.71± 10.9	21.6± 19.3
Methylene chloride	1.7	<LOQ	9.08± 3.05	12.7± 6.47	8.18± 9.12	<LOQ	<LOQ	<LOQ	<LOQ	54.6± 77.2	57.5± 50.6
Chloroform	2.2	<LOQ	<LOQ	<LOQ	1.15± 2.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Carbon Tetrachloride	2.3	<LOQ	10± 8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.5± 3.53	<LOQ
Chloroethane	11.7	<LOQ	25.6± 24.3	<LOQ	<LOQ	<LOQ	65.9± 114	<LOQ	<LOQ	<LOQ	20.2± 35.1
1,1-dichloroethane	2.1	<LOQ	4.69± 0.331	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	25± 35.3	18.3± 16
1,2-Dichloroethane	0.04	<LOQ	187± 126	<LOQ	24.4± 48.9	<LOQ	<LOQ	<LOQ	<LOQ	383± 542	560± 488
1,1,1-trichloroethane	2.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	6.03± 10.4
1,1,2-trichloroethane	3.7	<LOQ	4.69± 0.328	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	5.18± 7.33	4.94± 4.3
1,1,1,2-tetrachloroethane	3.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	20.2± 28.6	28.4± 24.8
1,1,2,2-tetrachloroethane	2.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.49± 2.97	1.6± 2.78	<LOQ	<LOQ
Chloroethene	2.4	<LOQ	42.7± 44.8	<LOQ	1.28± 2.55	<LOQ	2.35± 2.17	12.7± 19.6	8.01± 1.27	27± 38.2	62.8± 54.4
1,1-dichloroethene	1.5	<LOQ	2.66± 0.79	<LOQ	<LOQ	<LOQ	<LOQ	1.75± 3.5	4.91± 1.34	5.55± 7.85	3.98± 3.45
cis-1,2-Dichloroethene	2.6	<LOQ	168± 62.4	<LOQ	<LOQ	<LOQ	<LOQ	50.6± 72	<LOQ	137± 194	96.3± 86

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Trans-1,2-dichloroethene	1.7	<LOQ	4.83± 1.92	<LOQ	<LOQ	<LOQ	<LOQ	0.875± 1.75	<LOQ	114± 162	12.2± 10.9
Trichloroethene	4.7	<LOQ	47.3± 17.1	<LOQ	<LOQ	<LOQ	<LOQ	28.6± 44.2	<LOQ	44.5± 62.9	51.4± 46.2
Tetrachloroethene	3.8	<LOQ	25.5± 9.44	<LOQ	1± 2	<LOQ	<LOQ	10.9± 15.2	<LOQ	80.8± 114	68.7± 61.4
1,2-dichloropropane	2.8	<LOQ	<LOQ	<LOQ	3± 6	<LOQ	<LOQ	<LOQ	<LOQ	20.8± 29.4	19.4± 16.9
2,2-dichloropropane	2.3	<LOQ	0.794± 1.59	1.2± 2.08	4.73± 9.45	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	8.93± 7.79
1,2,3-trichloropropane	199.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
3-chloropropene	10.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
1,1-Dichloropropene	65.8	<LOQ	464± 821	<LOQ	2670± 3070	76± 152	26.6± 46	187± 374	<LOQ	<LOQ	327± 567
cis-1,3-dichloropropene	1.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
trans-1,3-dichloropropene	1.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
1,1,2,3,4,4-hexachloro-1,3-Butadiene	2.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Chlorobenzene	3.0	<LOQ	7.68± 1.77	<LOQ	<LOQ	<LOQ	1.33± 2.31	<LOQ	<LOQ	80.2± 113	33.3± 29.6
1,2-dichlorobenzene	3.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	34.9± 49.3	9.69± 8.87
1,3-dichlorobenzene	1.3	<LOQ	1.59± 1.85	<LOQ	2.31± 1.54	<LOQ	2.24± 1.99	1.5± 1.74	1.21± 2.1	8.58± 12.1	3.82± 3.34
1,4-Dichlorobenzene	1.5	<LOQ	18.9± 4.29	<LOQ	14.5± 1.81	<LOQ	21.9± 7.65	10.3± 7.03	4.37± 7.58	288± 408	133± 117
1,2,3-Trichlorobenzene	3.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
1,2,4-trichlorobenzene	1.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.08± 1.88	<LOQ	<LOQ	4.79± 6.78	1.28± 2.22
2-Chlorotoluene	2.7	<LOQ	3.68± 0.482	<LOQ	15.7± 18.5	6.75± 4.51	3.14± 2.76	1.45± 1.68	1.06± 1.83	115± 162	51.6± 44.9
4-Chlorotoluene	1.8	<LOQ	6.7± 2.83	<LOQ	<LOQ	<LOQ	2.18± 1.92	0.802± 1.6	0.963± 1.67	75.4± 107	26.4± 23.1
Bromomethane	4.6	<LOQ	<LOQ	<LOQ	2.4±	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	10.6± 18.3
dibromomethane	4.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Bromoform	2.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
bromochloromethane	4.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
bromodichloromethane	2.4	<LOQ	<LOQ	0.867± 1.5	<LOQ	<LOQ	<LOQ	<LOQ	2.81± 2.52	<LOQ	<LOQ
dibromochloromethane	2.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.02± 1.76	<LOQ	1.07± 1.85
1,2-dibromoethane	2.3	<LOQ	<LOQ	<LOQ	1.19± 2.38	<LOQ	<LOQ	0.958± 1.92	<LOQ	<LOQ	<LOQ
Bromochloroethane	2.3	<LOQ	2.79± 0.0972	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.34± 3.31	2.34± 2.05
1,2-dibromo-3-chloropropane	3.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
bromobenzene	2.1	<LOQ	1.46± 1.7	<LOQ	<LOQ	<LOQ	0.906± 1.57	0.658± 1.32	0.963± 1.67	8.44± 11.9	4.21± 3.67
1,3-Butadiene	1.0	<LOQ	13.6± 9.13	18± 3.82	6.26± 7.14	2.66± 5.32	<LOQ	0.43± 0.86	5.48± 1.33	45± 63.7	27± 27.7
Benzene	8.5	626± 192	84.7± 30.2	36.6± 12.3	4.88± 9.75	557± 435	11.1± 11.2	88.2± 111	7.97± 13.8	951± 1340	552± 478
Toluene	4.1	723± 91	837± 227	206± 84.2	97.3± 78.2	1080± 610	40.7± 25.1	97.5± 132	409± 176	1540± 2170	1450± 1250
Ethylbenzene	3.4	40.4± 0.774	506± 150	17± 5.28	62.4± 61.6	94.8± 20.9	23.4± 14.4	6.96± 8.04	43.2± 22.6	958± 1350	911± 786
m,p-Xylene	3.1	246± 4.75	163± 50.7	9.51± 1.66	7.12± 1.79	467± 307	16.8± 9.55	5.04± 4.2	15.7± 6.41	1030± 1450	748± 644
o-Xylene	3.0	39.1± 1.89	654± 167	26.1± 7.2	13± 5.94	93.4± 13.9	44.8± 31.4	19.5± 23	51.3± 25.9	1190± 1680	1110± 956
Styrene	2.8	<LOQ	57.8± 22.1	3.53± 0.0228	33.2± 29.2	0.922± 1.84	5.73± 1.17	4.36± 1.19	3.6± 0.148	150± 213	123± 105
Isopropylbenzene	2.8	7.54± 0.5	35.3± 10.2	4.04± 0.31	4.63± 3.87	7.65± 3.06	6.21± 2.63	1.96± 2.29	5.46± 0.832	335± 473	174± 151
4-Ethyltoluene	1.9	22.2± 0.963	36.3± 12.5	<LOQ	<LOQ	9.32± 6.52	14.1± 8.24	2.19± 4.37	<LOQ	485± 686	288± 250
n-Propylbenzene	2.5	13.2± 3.86	21.6± 6.28	3.01± 0.0725	3.98± 2.82	10.4± 4.76	7.15± 3.48	2.03± 2.42	3.33± 0.197	239± 338	129± 112
1,3,5-trimethylbenzene	2.5	10.4± 1.42	26± 8.36	4.35± 0.478	7.75± 5.12	17± 6.79	11.1± 6.25	2.94± 3.61	4.31± 0.225	332± 469	184± 160

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
tert-butylbenzene	2.6	<LOQ	3.13± 2.16	<LOQ	3.93± 3.41	<LOQ	3.74± 0.0843	1± 2	2.75± 2.44	11.1± 15.6	4.65± 4.04
1,2,4-Trimethylbenzene	6.1	<LOQ	36.7± 25.9	18.1± 0.758	20± 3.07	29.2± 4.51	26.9± 16.3	15± 10.9	17± 0.915	555± 784	17.7± 1.22
s-Butylbenzene	1.5	<LOQ	10.3± 3.44	5.51± 0.791	3.8± 4.81	1.82± 3.64	5.76± 3.02	1.11± 2.22	7.51± 1.54	96.7± 137	50± 43.4
p-Isopropyltoluene	472.8	<LOQ	845± 281	<LOQ	577± 702	124± 248	<LOQ	<LOQ	158± 274	664± 939	705± 612
n-butylbenzene	10.8	<LOQ	42.3± 73.3	<LOQ	59.8± 120	<LOQ	<LOQ	<LOQ	<LOQ	49.7± 70.2	26.1± 26.9
Naphthalene	6.1	<LOQ	18.3± 5.54	<LOQ	35.4± 40.3	45.5± 30.5	26.6± 19.6	18± 36	<LOQ	121± 171	35.2± 39
Pyridine	5.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Nitrobenzene	0.076	0.982± 0.789	0.0108± 0.0286	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

3.7 Aldehyde and Ketone Analysis

The concentrations of aldehydes and ketones measured in the current study are reported in Table 3-6. Although these compounds are frequently above quantitation limits in the raw biogas samples, and to a lesser extent in upgraded biogas samples, there is no systematic difference among concentrations in CNG and upgraded biomethane samples. The highest total aldehyde emissions were measured in READ and SATS raw biogas driven largely by acetone and butanal. These same compounds also dominated total aldehyde emissions at Kiefer landfill and both dairies, but concentrations were somewhat lower. Upgrading reduced aldehyde concentrations at READ and SATS but slightly increased these concentrations at New Hope.

Acetone was also the most prevalent aldehyde detected in CNG samples but butanal concentrations in CNG were generally not as high as butanal concentrations measured in biomethane. Compounds containing butanal can be produced as breakdown products of amino acids during the anaerobic digestion process explaining why they are more commonly detected in the biomethane.

Table 3-6: Results of Aldehyde and Ketone Analysis (all results in ppbv, uncertainty is 1 standard deviation)

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Formaldehyde	0.00621	0.844± 0.0852	0.804± 0.112	0.547	0.614± 0.235	0.712	0.864± 0.174	0.528± 0.213	0.248± 0.128	0.811± 0.381	0.407± 0.0303
Acetaldehyde	0.000847	2.23± 0.202	2.52± 1.57	1.52	1.79± 0.173	0.872	7.85± 13.1	1.66± 0.594	1.23± 0.487	3.49± 1.35	3.71± 0.789
Acetone	0.00321	44.1± 1.66	169± 146	46.2	251± 156	40	114± 84.1	37.1± 18.4	141± 168	79.2± 72.7	99.7± 25.2
Acrolein (2-propenal)	0.00333	<LOQ	0.00629± 0.00577	<LOQ	0.0104± 0.00507	0.00396	0.00741± 0.00545	0.00119± 0.00206	0.00464± 0.00173	0.00231± 0.004	0.00463± 0.000855
Propionaldehyde	0.00321	0.219± 0.0811	0.451± 0.33	0.224	0.0492± 0.0984	0.346	0.661± 1.22	0.106± 0.0985	0.327± 0.305	0.615± 0.255	0.909± 0.21
Crotonaldehyde	0.0532	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.00147± 0.00254	<LOQ
2-Butanone (MEK)	0.0259	0.0717± 0.0103	0.364± 0.274	0.358	0.147± 0.0638	0.12	0.399± 0.654	0.0954± 0.121	0.161± 0.155	1.43± 0.809	2.41± 0.517
Methacrolein (lsobutenal)	0.0532	0.0526± 0.0108	0.0397± 0.0644	0.0103	0.00209± 0.00418	0.033	0.0785± 0.0759	0.0594± 0.0535	0.0862± 0.0637	0.0818± 0.0598	0.0246± 0.00591
Butyraldehyde (Butanal)	0.00259	0.415± 0.0557	94± 89.8	15.7	71.9± 42	27.2	1.52± 2.57	0.624± 0.343	75± 81	24.3± 12.6	91.6± 25.4
Benzaldehyde	0.00176	0.0173± 0.00467	0.0227± 0.0083	0.0125	0.0171± 0.00132	0.0297	0.0147± 0.00332	0.0118± 0.00309	0.0288± 0.00386	0.028± 0.0115	0.0349± 0.00729
Valeraldehyde (Pentanal)	0.00217	<LOQ	6.51± 4.91	0.15	22.8± 11.8	4.5	0.179± 0.268	0.151± 0.0531	2.28± 2.11	2.73± 1.61	6.14± 1.67
p-Tolualdehyde	0.00155	<LOQ	<LOQ	<LOQ	<LOQ	0.00416	<LOQ	<LOQ	0.00441± 0.0035	<LOQ	<LOQ
Hexanaldehyde (Hexanal)	0.000373	0.0185± 0.00325	0.0982± 0.0829	0.0599	0.0986± 0.0222	0.0247	0.126± 0.101	0.0997± 0.0591	0.0569± 0.0114	0.109± 0.0639	0.118± 0.0173
2,5-Dimethyl-benzaldehyde *	0.00278	0.0194± 0.0247	0.0124± 0.00667	0.00184	0.00974± 0.00322	0.0172	0.00871± 0.00424	0.00403± 0.00192	0.0234± 0.0049	0.0227± 0.00987	0.0343± 0.0102
Iso-valeraldehyde*	0.000433	0.0138± 0.00293	0.0508± 0.0745	0.0542	0.0103± 0.00429	0.0179	0.137± 0.169	0.0788± 0.0547	0.0759± 0.0277	0.185± 0.149	0.124± 0.0274
m-Tolualdehyde*	0.00155	<LOQ	<LOQ	<LOQ	<LOQ	0.0075	<LOQ	<LOQ	0.0081± 0.0067	0.000901± 0.00156	0.00071± 0.00123

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
o-Tolualdehyde*	0.00155	<LOQ	<LOQ	<LOQ	<LOQ	0.00285	<LOQ	<LOQ	0.00334± 0.00181	<LOQ	<LOQ

3.8 VOC, SVOC, and PAH Component Analysis

The concentrations of additional volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs) and polycyclic aromatic hydrocarbons (PAHs) measured in the current study are reported in Table 3-7. Some of the most commonly occurring compounds in biogas and biomethane include phenol and substituted phenol compounds. Another common family of compounds apparent in the biogas and biomethane is naphthalene and substituted naphthalene compounds. Concentrations of all compounds in CNG, biogas, and biomethane are generally low.

Table 3-7: Results of Volatile Organic Compound, Semi-volatile Organic Compound, and PAH Component Analysis (all results in ppbv, uncertainty is 1 standard deviation)

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
N-nitroso-dimethylamine	1.260	<LOQ	<LOQ	<LOQ	0.165± 0.331	<LOQ	0.152± 0.0741	<LOQ	<LOQ	<LOQ	<LOQ
Phenol	5.0	<LOQ	7.33± 3.69	3.07± 0.741	9.38± 13.2	3.69± 1.9	0.616± 0.871	1.09± 1.85	6.68± 2.88	30.5± 43.1	12.2± 10.6
Aniline	0.40	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Bis(2-Chloroethyl) ether	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
2-Chlorophenol	0.007	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Benzyl Alcohol	5.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
2-methylphenol	0.017	<LOQ	<LOQ	0.15	<LOQ	<LOQ	0.00718± 0.0144	<LOQ	<LOQ	<LOQ	<LOQ
bis(2-chloro-isopropyl)ether	0.055	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
N-Nitroso-di-n-propylamine	0.029	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.00495± 0.00857	<LOQ	<LOQ	<LOQ
3-methylphenol	0.017	<LOQ	16± 17.3	0.01	24.9± 13.7	<LOQ	3.38± 4.51	0.437± 0.387	<LOQ	<LOQ	<LOQ
4-methylphenol	0.003	0.57± 0.134	0.00334± 0.00819	0.06	<LOQ	<LOQ	0.00916± 0.0108	0.165± 0.1	0.111± 0.0327	<LOQ	0.0166± 0.0288
lsophorone	0.027	0.0287± 0.0254	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
2-nitrophenoI	0.013	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
2,4-dimethyl-phenol	0.031	<LOQ	<LOQ	<LOQ	<LOQ	0.05	<LOQ	<LOQ	0.113± 0.0548	<LOQ	<LOQ
Bis(2-chloro-ethoxy)methane	0.011	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
2,4-dichlorophenol	0.057	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.36± 0.452	3.04± 0.543
4-Chloroaniline	0.029	<LOQ	0.0153± 0.021	<LOQ	0.0411± 0.0282	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
4-chloro-3-methylphenol	0.003	1.36± 0.65	0.464± 0.316	0.28	0.232± 0.102	0.31	0.378± 0.504	0.0776± 0.0938	0.504± 0.0622	16.2± 3.13	8.82± 2.25
2-methyl-naphthalene	0.013	1.26± 0.599	0.458± 0.312	0.27	0.245± 0.118	0.30	0.372± 0.481	0.0763± 0.0936	0.485± 0.0632	16.2± 3.18	8.64± 2.22
1-methyl-naphthalene	0.003	0.621± 0.272	0.31± 0.206	0.15	0.148± 0.0634	0.20	0.223± 0.28	0.0446± 0.056	0.273± 0.038	10.4± 2.18	4.88± 1.31
Hexachloro-cyclopentadiene	0.014	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
2,4,6-trichloro-phenol	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
2,4,5-trichloro-phenol	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
2-chloro-naphthalene	0.006	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
2-Nitroaniline	0.068	0.14± 0.0102	0.0103± 0.0251	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.00487± 0.00844	<LOQ
1,4-dinitro-benzene	0.222	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dimethyl phthalate	0.048	<LOQ	0.0148± 0.023	<LOQ	0.0545± 0.0218	<LOQ	0.0171± 0.012	0.0248± 0.0046	<LOQ	<LOQ	<LOQ
1,3-dinitro-benzene	0.222	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
2,6-dinitro-toluene	0.102	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Acenaphthylene	0.002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.00577± 0.00562	<LOQ	<LOQ	<LOQ
1,2-dinitro-benzene	0.555	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
3-Nitroaniline	0.068	<LOQ	0.19± 0.11	<LOQ	0.317± 0.105	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Acenaphthene	0.006	0.0162± 0.00649	0.071± 0.0465	0.03	0.0676± 0.0305	0.06	0.118± 0.135	0.0243± 0.042	0.0748± 0.0123	1.37± 0.628	0.182± 0.128
2,4-dinitro-phenol	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
4-nitrophenoI	0.671	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Dibenzofuran	0.011	<LOQ	0.0356± 0.0393	0.01	0.0314± 0.0144	0.02	0.0739± 0.0812	0.015± 0.0244	0.0269± 0.0062	0.32± 0.194	0.0287± 0.0263
2,4-dinitro-toluene	0.102	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
2,3,4,6-Tetrachloro-phenol	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
2,3,5,6-Tetrachloro-phenol	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
Diethyl Phthalate	0.084	0.0554± 0.0418	0.318± 0.0324	0.20	0.205± 0.0535	0.17	0.23± 0.013	0.165± 0.028	0.123± 0.0138	0.117± 0.0283	0.138± 0.0393
Fluorene	0.022	<LOQ	0.0219± 0.0249	<LOQ	0.017± 0.00799	0.01	0.0417± 0.0464	0.00734± 0.0127	0.0146± 0.00363	0.122± 0.0795	0.00733± 0.00715
4-chlorophenyl phenyl ether	0.009	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
4-Nitroaniline	0.135	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
4,6-dinitro-2-methylphenol	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
Diphenylamine	0.011	0.0331± 0.0122	<LOQ	<LOQ	0.0142± 0.0284	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.0178± 0.0308
n-Nitroso-diphenylamine	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Azobenzene	0.021	<LOQ	0.0172± 0.00947	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
4-Bromophenyl phenyl ether	0.007	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Hexachloro-benzene	0.007	0.00364± 0.00631	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Pentachloro-phenol	1.400	<LOQ	0.487± 0.0000624	<LOQ	0.487± 0.000073 9	0.49	0.487± 0.0000209	0.487± 0.0000202	0.487± 0.0000347	0.379± 0.0937	0.487± 0.0000128
Phenanthrene	0.021	<LOQ	0.00244± 0.00419	<LOQ	0.00338 ± 0.00676	<LOQ	0.00336± 0.00398	0.00294± 0.0051	<LOQ	0.00625± 0.00552	<LOQ
Anthracene	0.052	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Carbazole	0.056	<LOQ	0.0565± 0.0214	<LOQ	0.0517± 0.0257	<LOQ	0.0171± 0.0202	0.0329± 0.00753	<LOQ	0.0383± 0.0146	0.0176± 0.0152
Di-n-butyl phthalate	0.013	<LOQ	0.0073± 0.00399	<LOQ	0.00388 ± 0.00481	<LOQ	0.00605± 0.000827	0.00612± 0.00179	<LOQ	0.00341± 0.00335	0.00227± 0.00196
Fluoranthene	0.005	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Pyrene	0.002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Benzyl butyl phthalate	0.060	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.155± 0.268
Bis(2-ethyl-hexyl)adipate	0.025	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Benzo(a) anthracene	0.008	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Chrysene	0.008	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Bis(2-ethyl-hexyl)phthalate	0.048	<LOQ	0.0323± 0.00203	0.07	0.0394± 0.0168	0.09	0.0156± 0.018	0.0103± 0.0178	0.0395± 0.00677	0.0133± 0.0115	0.0207± 0.018
Di-n-octyl phthalate	0.048	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.0249± 0.0431
Benzo(b) fluoranthene	0.037	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Benzo(k) fluoranthene	0.037	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Benzo(a)pyrene	0.037	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
lndeno(1,2,3-cd)pyrene	0.135	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dibenzo(a,h) anthracene	0.134	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Benzo[g,h,i) perylene	0.068	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

3.9 Organic Silicon Analysis

The concentrations of organic silicon compounds measured in the current study are reported in Table 3-8. These compounds mainly originate from consumer products such as shampoo. Siloxanes are not present in CNG, and siloxane concentrations from dairies were minimal. Siloxanes were detected in raw biogas samples from food waste digesters (READ and SATS). Upgrading to biomethane at these sites removed larger siloxanes but did not completely eliminate concentrations of siloxanes with fewer than 8 carbons. The READ samples had the highest measured concentrations of several siloxanes, especially hexamethyldisiloxane (L2, MM). Samples from Kiefer (perimeter or core) also had relatively high concentrations possibly due to the disposal of containers for consumer products with residual amounts of siloxanes in them.

Table 3-8: Results of Organic Silicon Analysis (all results in ppbv, uncertainty is 1 standard deviation)

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
1,1,3,3-Tetramethyldisiloxane	5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Pentamethyldisiloxane	5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Hexamethyldisilane	5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Hexamethyldisiloxane (L2,MM)	5	<LOQ	1510± 340	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	430± 609	339± 298
Octamethyltrisiloxane (L3, MOM)	0.04	<LOQ	2.79± 3.03	0.24	0.12± 0.0821	0.10	<LOQ	<LOQ	1.21± 1.08	0.296± 0.442	0.132± 0.0605
Octamethylcyclo-tetrasiloxane (04)	0.03	<LOQ	1.65± 2.63	0.33	0.952± 1.59	1.20	0.185± 0.0573	0.15± 0.0353	9.09± 6.92	7.86± 5.61	7.1± 1.49
Decamethyltetrasiloxane (L4,MD2M)	0.03	<LOQ	0.333± 0.349	0.39	0.39± 0.106	<LOQ	<LOQ	<LOQ	0.00733± 0.00635	0.00973± 0.00237	0.0298± 0.0102
Decamethylcyclo-pentasiloxane (OS)	0.03	<LOQ	49.4± 42.2	<LOQ	52.9± 34.3	<LOQ	<LOQ	<LOQ	0.28± 0.484	1.01± 0.418	3.27± 1.45
Dodecamethylpenta-siloxane (LS,MD3M)	0.02	<LOQ	0.0657± 0.0445	<LOQ	0.116± 0.0373	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.0115± 0.0023
Dodecamethylcyclo-hexasiloxane (06)	0.04	<LOQ	1.17± 0.61	0.18	1.44± 0.516	<LOQ	0.0305± 0.0424	0.0156± 0.0221	0.0672± 0.106	<LOQ	0.0379± 0.0656

3.10 Mercury Analysis

Mercury results are included in the next section.

3.11 Metals Analysis

The concentrations of metals measured in the current study are reported in Table 3-9. Few metals were detectable at statistically significant levels above zero. Notably, two elements known to produce volatile forms under reducing conditions (such as those found in our sources), arsenic and antimony produced some detections above zero at Kiefer landfill. (In the Table, '0', or 0±0, denotes <LOD for those samples. QualDet denotes qualitatively detected; NQ denotes not quantifiable.)

Table 3-9: Results of Metals Analysis (all results in µg m^{-3}, uncertainty is 1 standard deviation)

Parameter	LOD (µg m^{-3})	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Be	0.005	0± 0	0± 0	0.017	0.009± 0.009	0	0± 0	0.086± 0.097	0± 0	0± 0	0.013± 0.004
Cr	0.005	0± 0	0.34± 0.76	0	0.21± 0.24	0	0.926± 1.31	0.26± 0.37	0.061± 0.028	0.19± 0.14	0± 0
Mn	0.005	0± 0	0..48± 0.95	0	0.005± 0.008	0	0± 0	0± 0	0.067± 0.047	0.24± 0.26	0± 0
Co	0.005	0± 0	0.062± 0.14	0	0.018± 0.013	0	0.00617± 0.00873	0± 0	0.006± 0.008	0.003± 0.005	0± 0
Ni	0.02	0± 0	0± 0	0	0.074± 0.13	0	0.272± 0.384	0± 0	0.12± 0.15	0± 0	0± 0
Zn	0.2	0± 0	0.14± 0.3	0	0.56± 0.96	0	0± 0	1.5± 2.1	7.8± 8.7	0.56± 0.96	0± 0
Se	0.2	0± 0	0.45± 0.65	0	0.14± 0.24	0	0.648± 0.458	0± 0	0.21± 0.30	0.20± 0.35	0.15± 0.15
Sr	0.01	0± 0	0± 0	0	0± 0	0	0± 0	0.012± 0.017	0.005± 0.008	0.009± 0.016	0.1± 0.1
Mo	0.005	0± 0	0± 0	0	0.009± 0.009	0	0.0988± 0.114	0.21± 0.30	14.1± 20.4	0± 0	0± 0
Cd	0.005	0± 0	0.003± 0.007	0	0.005± 0.008	0	0.204± 0.249	1.0± 1.5	0± 0	0± 0	0± 0
Ba	0.02	0± 0	1.6± 2.2	0	0± 0	0	0.0247± 0.0349	0.025± 0.035	0± 0	0± 0	1.5± 1.5
Hg	0.005	0± 0	0.006± 0.014	0	0± 0	0	0± 0	0.006± 0.009	0± 0	0± 0	0.008± 0.008
Tl	0.005	0± 0	0± 0	0.017	0.014± 0.015	0	0.00617± 0.00873	0± 0	0.011± 0.016	0.003± 0.005	0± 0
Cu	0.005	0± 0	0± 0	0	0.005± 0.008	0	0± 0	0± 0	0.006± 0.008	0.20± 0.34	0± 0
As	0.005	0± 0	1.6± 1.4	0	0.23± 0.38	0	0.315± 0.432	0.012± 0.018	0.022± 0.021	4.2± 2.3	8.5± 3.4
Sb	0.005	0± 0	1.6± 1.8	0	0.31± 0.17	0	0.259± 0.184	0.006± 0.009	0.028± 0.028	1.3± 2.0	12.5± 12.5

Parameter	LOD (µg m^{-3})	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Pb	0.1	0± 0	0.14± 0.31	0	0± 0	0	1.73± 2.44	7.4± 10.5	0± 0	0.65± 1.1	0.8± 0.8
Na	2	0± 0	0± 0	0	0± 0	0	0± 0	0± 0	0± 0	0± 0	0± 0
Mg	0.2	0± 0	0± 0	0	3.0± 4.9	0	0± 0	0± 0	0.56± 0.79	0± 0	6.2± 6.2
Al	0.2	0± 0	2.2± 5.	0	0± 0	0	0± 0	0± 0	0± 0	5.6± 9.6	0± 0
K	1	0± 0	0± 0	0	1.02± 1.76	0	0± 0	3.9± 5.6	0.67± 0.94	0± 0	0± 0
Ca	1	0± 0	1.2± 2.6	0	8.3± 14.4	0	0± 0	10.5± 7.5	92.6± 89.7	14.5± 23.7	54± 52
Fe	1	0± 0	9.6± 21	0	4.4± 7.6	0	1.91± 2.71	0± 0	0± 0	0± 0	0± 0
Sn	0.02		0.05± 0.11	0	0.88± 0.19	0	0± 0	0.056± 0.079	0.011± 0.016	0.40± 0.56	0.55± 0.05
C	NQ	QualDet	0± 0	QualDet	0± 0	QualDet	QualDet	0± 0	QualDet	QualDet	QualDet
S	NQ	QualDet	0± 0	QualDet	0± 0	QualDet	QualDet	QualDet	0± 0	QualDet	QualDet
Cl	NQ	0± 0	0± 0	0	0± 0	0	QualDet	0± 0	0± 0	0± 0	0± 0

3.12 Biologicals Analysis

A total of 32 individual samples were analyzed for biological targets during the current study. In the 11 biogas samples collected from the two anaerobic digesters (READ and SATS), cultivable bacteria including heterotrophic and spore-forming bacteria were detected 5 times, ranging from 4.6 to 10 MPN per sample (Table 3-10). Cultivation positive samples were further analyzed using DNA sequencing to determine the taxonomic identification. Basic Logical Assignment Search Tool (BLAST) database comparison results indicated that cultivation positive samples found in the biogas were closely related to *Bacillus* sp. with 99% identity. Cultivable bacteria and spore-forming bacteria were below detection limits in the upgraded biomethane samples. In biogas and condensate water samples collected at the two anaerobic digesters, total bacteria concentrations as assessed by qPCR were below sample limits of detection, approximately 1400 gene copies per sample. Iron Oxidizing Bacteria (IOB) and acid producing bacteria (APB) were found once or twice in each digester, respectively, with the average means ranging from 27 to 270 gene copies per sample. DNA sequencing of qPCR amplicons revealed that IOB and APB detected by qPCR were closely related to *Leptothrix* sp. and *Clostridium* sp. that are considered as corrosion causing bacteria. Concentrations of total bacteria as well as the three corrosion causing bacteria were below sample limits of detection in upgraded biomethane samples.

Seven raw biogas and three upgraded biomethane samples were collected at the two dairy farms (New Hope and Warmerdam). Cultivable aerobic bacteria were detected in 2/3 of biogas samples collected at Warmerdam (14 ± 3.5 MPN per sample). Spore-forming bacteria were found in one of the biogas samples collected at New Hope. Blast database analysis illustrated that cultivation positive samples in the raw biogas collected from the two dairy farms were closest to *Paenibacillus* sp. and *Bacillus* sp. that are gram-positive, either aerobic or anaerobic, spore-forming bacteria found in a variety of environments such as soil, water, and rhizosphere. No cultivable bacteria were found in upgraded biomethane. In qPCR analysis, total bacteria were below sample limits of detection in all samples collected from the two dairy farms except for one upgraded biomethane sample with means of 1200 gene copies per sample. IOB were detected in 33% of raw biogas and upgraded biomethane samples with the mean range of 8.5 – 140 gene copies per sample. qPCR amplicons positive for each assay were sequenced and identified as *Gallionella capsiferriformans* and *Clostridium butylicum.*

Six raw biogas samples were collected at one landfill (Kiefer) subdivided into perimeter and core biogas based on the produced methane content (~35% versus ~50%). In the perimeter biogas samples with 35% methane content, one of three samples was positive in cultivable spore-forming bacteria analysis. It was closest relative to *Bacillus* sp. including *B. flexus, B. megaterium,* and *B. aryabhattai* in the BLAST database analysis. Results of qPCR analysis indicated that total bacteria and IOB were detected in 33% of both perimeter and core biogas samples with means of 1300 – 2300 gene copies per sample and 12 – 140 gene copies per sample, respectively.

Overall, cultivable bacteria and spore-forming bacteria were found in approximately 40% (10 of 24) of all biogas samples collected but not in any of the upgraded biomethane samples (0 of 5). The 10 positive samples contained cultivable (spore-forming) bacteria ranging from 5 to 43 MPN per sample. It should be noted that cultivation positive results in our study were observed only in

the aerobic incubation. An anaerobic pouch system was used during sample transport to minimize oxygen contact to samples that would be subjected to anaerobic cultivation. However, samples were inevitably briefly exposed to aerobic condition during sample collection and analytical processing in the lab prior to anaerobic incubation, which could affect the cultivability of anaerobic bacteria.

Although the cultivable anaerobic bacteria might be underestimated, the numbers of cultivable bacteria found in the current study are comparable to those from previous studies. Vinneras et al. [3] reported that the number of cultivable microorganisms in biogas were around 10 to 100 cfu (colony forming unit) per m^3. Gas technology institute (GTI) reports indicate that cultivable bacteria and spore-forming bacteria were detected in 4 – 25% of biomethane samples collected at landfills (GTI report project number 20736 [4] and 20792) [5]) and in 100% of raw biogas collected at dairy farms (GTI report project number 20614 [6]). GTI further noted that cultivable bacteria were present in 50% of biomethane samples collected at dairy farms. While cultivation positive samples were more often detected in the GTI studies, their concentrations were not greatly different from those in the present study when considering only the samples with positive results. GTI studies determined that the majority of spore-forming bacteria found in cultivation tests were *Bacillus* species and *Paenibacillus* species, which is consistent with the findings in the present study. Given the fact that *Bacillus* sp. are more resistant to environmental stresses, the low numbers of cultivable bacteria in biogas could be due to the loss of viability of non-spore bacteria during the anaerobic digestion/upgrading processes or biogas sampling/analytical procedure. Other parameters such as moisture content and oxygen inclusion at some sampling sites may also affect the viability of bacteria.

In the present study, the concentrations of 16S rRNA gene copies of total bacteria in biogas and upgraded biomethane were below detection limits in about 90% of samples tested. The results from the genetic quantification of the filter and condensate samples indicate how many bacteria, either live or dead, have been aerosolized from anaerobic digestion and remained in the raw biogas stream. Few studies are currently available for quantifying the microbial composition of biogas using molecular methods. Moletta et al. [7] found approximately 10^5 genome equivalents (GE) per m^3 (4×10^5 gene copies per m^3) in biogas, which was a similar number to that found in ambient air. Previous GTI projects (GTI project number 20614, 20736 and 20792) estimated that the abundance of total bacteria in biogas and biomethane collected from landfills and anaerobic digesters was around 10^6 per m^3, although it was unclear if the reported unit (#/gas volume) used the number (#) of gene copies or whether this value had been converted back to the original concentration before amplification. In the present study, the total bacteria concentration detected in biogas was approximately 10^4 gene copies per m^3. Given that our detection limits were as low as $2 – 5 \times 10^3$ gene copies per m^3, it is not likely that the total bacteria gene copies were not detected due to the selected qPCR assay. Therefore, we demonstrated that total bacteria gene copy numbers found in the biogas and upgraded biomethane samples in the current study had 1-2 orders of magnitude lower concentrations than the previously reported data.

The corrosion causing bacteria, SRB, IOB and APB tested in the current study are commonly detected in many environments. If these bacteria were present in biogas and upgraded biomethane it would pose a challenge to pipeline infrastructure used to transport gas. The qPCR results indicated that IOB and APB were present in a few of the gas samples analyzed in the present study,

but their concentrations were quite low. No SRB were found in any biogas or upgraded biomethane samples tested even though the qPCR sample limits of detection for SRB were as low as 10 gene copies per sample. SRB were rarely detected in raw biogas samples in the GTI reports (GTI report project number 20614), which is consistent with our findings. In the three natural gas samples tested in the current study, the concentrations of corrosion causing bacteria were all below sample limits of detection. The net results of this analysis suggest that SRB, IOB, and APB are not common in biomethane, but these bacteria are occasionally present in raw biogas and there is a small chance for them to propagate in pipelines used to transport this gas. Maintenance and inspection procedures should be established to regularly test for the presence of these bacteria in future pipeline applications for biomethane.

Table 3-10: Results of biological analysis (uncertainty is 1 standard deviation).

Parameter[a]	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Cultivation analysis (MPN/sample)[b]										
Live aerobic bacteria	<SLOD (3/3)	9.6 ± 2.5 (5/7)	<SLOD (1/1)	<SLOD (4/4)	<SLOD (1/1)	14 ± 3.5 (1/3)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)
Live anaerobic bacteria	<SLOD (3/3)	<SLOD (7/7)	<SLOD (1/1)	<SLOD (4/4)	<SLOD (1/1)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)
Live aerobic spore bacteria	<SLOD (3/3)	4.6 ± 1.0 (5/7)	<SLOD (1/1)	10 ± 3.9 (2/4)	<SLOD (1/1)	<SLOD (3/3)	7.1 ± 2.1 (2/3)	<SLOD (3/3)	17 ± 20 (2/3)	<SLOD (3/3)
Live anaerobic spore bacteria	<SLOD (3/3)	<SLOD (7/7)	<SLOD (1/1)	<SLOD (4/4)	<SLOD (1/1)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)
qPCR analysis (gene copies/sample)										
Total bacteria	<SLOD (3/3)	<SLOD (7/7)	<SLOD (1/1)	<SLOD (4/4)	<SLOD (1/1)	<SLOD (3/3)	<SLOD (3/3)	1200 ± 490 (2/3)	2300 ± 2100 (2/3)	1300 ± 830 (2/3)
Sulfate reducing bacteria (SRB)	<SLOD (3/3)	<SLOD (7/7)	<SLOD (1/1)	<SLOD (4/4)	<SLOD (1/1)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)
Iron oxidizing bacteria (IOB)	<SLOD (3/3)	43 ± 27 (5/7)	<SLOD (1/1)	86 ± 83 (3/4)	<SLOD (1/1)	150 ± 150 (2/3)	8.5 ± 5.8 (2/3)	140 ± 130 (2/3)	12 ± 12 (2/3)	160 ± 200 (2/3)
Acid producing bacteria (APB)	<SLOD (3/3)	350 ± 250 (5/7)	<SLOD (1/1)	72 ± 46 (2/4)	<SLOD (1/1)	84 ± 81 (2/3)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)	<SLOD (3/3)

[a] Results shown are means ± standard errors. Data below sample limits of detection (SLODs) were assumed to be one-half of the SLODs for the mean value calculation. The number of non-detects out of total samples tested is shown in parenthesis. Condensate water data were combined with raw biogas data if applicable.

[b] MPN, most probable number

3.13 Polychlorinated Biphenyls Analysis

The concentrations of polychlorinated biphenyls measured in the current study are reported in Table 3-11. The 209 polychlorinated biphenyl congeners (structural isomers) comprise ten distinct molecular formulas containing from one to ten chlorine atoms. In the results below, the specific congeners have been grouped into the appropriate molecular formula "bin" as follows: dichloro- (PCB 4-PCB 15), trichloro- (PCB 16-PCB 39), tetrachloro- (PCB 40-PCB 81), pentachloro- (PCB 82-PCB 127), hexachloro- (PCB 128-PCB 169), heptachloro- (PCB 170-PCB 193), and octachloro- (PCB 194-PCB 205). PCBs were only occasionally above the quantitation limit in raw biogas samples and were never above LOQ for any biomethane sample.

Table 3-11: Results of Polychlorinated Biphenyls Analysis (all results in ppbv, uncertainty is 1 standard deviation)

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Biphenyl, Dichloro	0.00167	<LOQ	0.00429± 0.00719	<LOQ	<LOQ	<LOQ	0.0107± 0.0115	<LOQ	<LOQ	0.0453± 0.0171	0.0032± 0.00554
Biphenyl, Trichloro	0.00724	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.00929± 0.00516	<LOQ
Biphenyl, Tetrachloro	0.00319	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Biphenyl, Pentachloro	0.00288	<LOQ	0.00512± 0.0125	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Biphenyl, Hexachloro	0.00103	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Biphenyl, Heptachloro	0.00236	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Biphenyl, Octachloro	0.00217	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

3.14 Pesticide Analysis

The concentrations of pesticides measured in the current study are reported in Table 3-12. The pesticides analyzed are all legacy compounds without current, approved uses in California. However, these compounds are considered bioaccumulative and persistent, and they are still detected in a wide variety of environmental samples. However, none of these compounds was above the quantitation limit in either raw or upgraded biomethane samples or in CNG.

Table 3-12: Results of Pesticide Analysis (all results in ppbv, uncertainty is 1 standard deviation)

Parameter	LOQ (ppbv)	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
a-BHC	0.006	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	0.013	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
g-BHC	0.013	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
d-BHC	0.006	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	0.005	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Aldrin	0.001	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor epoxide	0.002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
g-Chlordane	0.001	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endosulfan I	0.005	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
a-Chlordane	0.002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dieldrin	0.010	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
4,4'-DDE	0.006	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin	0.010	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endosulfan II	0.009	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
4,4'-DDD	0.006	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin aldehyde	0.025	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endosulfan sulfate	0.002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
4,4'-DDT	0.005	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin ketone	0.010	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Methoxychlor	0.011	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Toxaphene	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
Technical Chlordane	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM

3.15 Compositional Dependent and Other Physical Parameters

The values of parameters used to characterize raw and upgraded biomass samples determined in the current study are reported in Table 3-13.

Table 3-13: Parameters used to characterize raw and upgraded biogas (uncertainty is 1 standard deviation).

Parameter	CNG	READ Raw	READ Upgraded	SATS Raw	SATS Upgraded	Warmerdam Raw	New Hope Raw	New Hope Upgraded	Kiefer Raw Perimeter	Kiefer Raw Core
Compressibility Factor [z] (Dry)	0.29± 0.0000895	0.286± 0.00113	0.29± 0.0000386	0.286± 0.00166	0.29± 0.0000842	0.288± 0.000365	0.287± 0.0015	0.29± 0.000139	0.288± 0.000577	0.286± 0.0000936
Compressibility Factor [z] (Sat.)	0.29± 0.000175	0.27± 0.00107	0.289± 0.000107	0.27± 0.00156	0.29± 0.0000842	0.272± 0.000345	0.271± 0.00142	0.289± 0.000139	0.271± 0.000544	0.27± 0.0000883
Relative Density (Dry)	0.586± 0.00427	0.909± 0.0851	0.602± 0.00389	0.91± 0.122	0.581± 0.0102	0.781± 0.019	0.925± 0.0198	0.611± 0.0111	0.978± 0.0451	0.918± 0.00765
HHV (Dry) (Btu/ft3)	1020± 8.59	575± 81.2	926± 4.76	595± 113	946± 18.9	714± 11.2	480± 141	906± 12.2	356± 46.4	575± 7.9
HHV (Sat.) (Btu/ft3)*	1020± 8.29	542± 76.6	926± 4.95	561± 106	945± 18.9	673± 10.6	453± 133	906± 12.2	336± 43.8	542± 7.45
Wobbe Number (dry)	1290± 61.4	609± 110	1190± 9.97	635± 153	1240± 35.4	808± 22.2	501± 152	1160± 25.9	362± 55.6	600± 10.7
LHV (Dry) (Btu/ft3)	921± 7.75	517± 73	833± 4.28	535± 101	850± 17	642± 10.1	432± 126	815± 10.9	321± 41.7	517± 7.1
LHV (Sat.) (Btu/ft3)*	921± 7.48	488± 68.8	833± 4.45	505± 95.7	850± 17	605± 9.53	407± 119	814± 10.9	302± 39.4	488± 6.7
Real Gas Density (lbs/ft3)	0.0448± 0.000326	0.0459± 0.000297	0.0695± 0.00934	0.0444± 0.000782	0.0596± 0.00145	0.0706± 0.00151	0.0466± 0.000846	0.0747± 0.00345	0.0701± 0.000584	0.0694± 0.0065
Motor Octane Number	135± 0.0448	140±	140±	140±	140±	140±	140±	140±	140±	140±
Methane Number[1]	101± 0.0728	108±	108±	108±	108±	108±	108±	108±	108±	108±
Methane Number[2]	84.4± 0.478	121± 17.1	91.7± 0.45	120± 19.3	92.3± 2.18	102± 5.04	121± 2.25	89.9± 1.46	146± 23.4	124± 1.55

[1] Using Methane Number=1.624*(motor octane number) -119.1 (www.arb.ca.gov/regact/cng-lpg/appd.pdf).

[2] Using Methane Number from online calculator (www.cumminswestport.com/fuel-quality-calculator).

4 CONCLUSIONS

4.1 Summary of Results

A comprehensive set of measurements was conducted for 10 different biogas / biomethane sample streams (each consisting of three different individual samples) and three different compressed natural gas streams (each consistent of a single sample). Biogas / biomethane sample streams were derived from five different production sources: two food waste digesters, two dairy farms, and one landfill. The two food waste digesters had similar designs but used different feedstocks resulting in different biogas composition. The two farms used different digester designs with one site using technology typical in California and the other site using technology typical in Europe. The landfill had two different gas streams representing the core working section of the landfill and the perimeter of the landfill. The compressed natural gas samples were obtained from three different commercial CNG refueling stations in Los Angeles. Method detection limits for all measurements met or were lower than method detection limits used in previous biogas analysis reports published by the Gas Technology Institute (GTI).

The composition of raw biogas was predominantly methane and CO_2 with minor amounts of air intrusion depending on the process type. The methane content of the raw biogas ranged from 35% to 70.5%. Upgraded biomethane from the two food waste digesters had methane content above 90% which compared favorably with the ~91.5% methane content of CNG obtained from vehicle fueling stations in Los Angeles. The CNG contained ~5.5% ethane, however, while the biomethane contained a few percent each of nitrogen and oxygen, possibly due to leakage of the piping leading to the transportable upgrading unit. The methane content of the biomethane produced at one of the dairies was slightly lower than 90% due to additional air injection in the system which could not be removed during the upgrading process. Upgraded biomethane from all sources was successfully used as a vehicle fuel during testing supporting under a separate project (CEC Project PIER#13-001).

Ammonia concentrations in all biogas were below 100 ppb except for a single measurement at one of the dairy farms. This result suggests that better management of animal waste through anaerobic digestion may mitigate much of the ammonia emission currently associated with agricultural operations.

Alkanes were present in both CNG and upgraded biomethane but comparison to the raw biogas analysis suggests that these compounds were introduced during the upgrading process either through the purification or compression steps. The alkane signature in CNG was different than the alkane signature from upgraded biomethane. This “fingerprint” can help identify blended fuels and quantify the amount of biomethane present in those fuels.

Raw biogas contained a greater variety of sulfur compounds at significantly higher concentrations than those found in CNG. Upgrading to biomethane removed the majority of these sulfur compounds but the residual concentrations of sulfur compounds in biomethane were still higher than concentrations in CNG. The fate of these sulfur compounds after removal from the biomethane also requires thought. Burning the tail gas from the upgrading process releases sulfur to the atmosphere which will ultimately produce sulfate aerosol contributing to $PM_{2.5}$

concentrations. This finding suggests that upgrading facilities should incorporate additional steps to trap and remove sulfur containing compounds before burning tail gas or these upgrading facilities should not be located in regions where $PM_{2.5}$ concentrations are above the limits specified in the National Ambient Air Quality Standards (NAAQS).

Halocarbon measurements detected pesticides and pesticide breakdown products in the covered lagoon digester at one of the dairies. These halocarbons were likely introduced into the lagoon by runoff from adjacent fields. Concentrations in the resulting biogas were modest (<200ppb) but this finding suggests that better lagoon management may be warranted to prevent runoff intrusion from other sources when this design is employed for digesters in California. Halocarbons were also present in landfills and (to a lesser extent) in food waste digesters stemming largely from plastics in the feedstock. Better recycling programs and more careful attention to removal of residual plastics from feedstock may be warranted as future management strategies for biogas production.

Acetone was the most abundant aldehyde detected in both CNG and biomethane samples but biomethane had additionally high concentrations of butanal which was likely produced from the decomposition of amino acids in food products. Better management practices that avoid lengthy delays before processing pre-packaged foods through food waste digesters could possibly mitigate some of this butanal production.

VOCs commonly observed in biogas and upgraded biomethane include phenols and substituted phenols as well as naphthalene and substituted naphthalene compounds.

Siloxanes were detected in raw biogas samples from food waste digesters (READ and SATS). Upgrading to biomethane at these sites removed larger siloxanes but did not completely eliminate concentrations of siloxanes with fewer than 8 carbons. Landfill gas had the highest measured concentrations of siloxanes in the present study, possibly due to the disposal of containers for consumer products with residual amounts of siloxanes in them.

Few metals were detected in raw biogas or biomethane above the detection limits of 0.1-100 ng m^{-3}. Only arsenic and antimony were detected somewhat consistently and these elements are known to produce volatile forms under reducing conditions typically found in anaerobic digesters. Upgrading the gas to biomethane greatly reduced the concentrations of these metals. Mercury was detected in a single dairy sample and a single landfill sample but at concentrations lower than 1 ng m^{-3}.

Bacteria were less commonly detected in the measurements of California biogas in the current study than in previous measurements made using biogas outside of California. When bacteria were detected in California biogas, the concentrations were generally comparable to previous measurements. Acid forming bacteria and iron oxidizing bacteria were detected in raw biogas from agricultural digesters but not in most upgraded biomethane samples. Appropriate maintenance and inspection procedures should be implemented to mitigate the possibility of pipeline corrosion depending on the type of gas that is conveyed in future applications.

Polychlorinated biphenyls were not detected at concentrations that could be reliably quantified in any of the biogas / biomethane sample streams collected in the present study.

Pesticides were not detected at concentrations that could be reliably quantified in any of the biogas / biomethane sample streams collected in the present study.

4.2 Future research

The findings summarized above confirm that California has several unique issues related to biogas production and adoption as a new energy source due to the presence compounds in biogas / biomethane that are not present in natural gas. These compounds do not rule out the future use of biogas but they do require consideration to minimize potential negative effects. Additional research is needed to characterize the remaining sources of biogas / biomethane in California including POTWS, additional landfills, food waste & agriculture waste digesters, and other potential energy crop digesters. Consistent measurements are needed across all of these sources to fully characterize the range of potential biogas / biomethane production in California.

5 REFERENCES

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