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Composition and Toxicity of Biogas Produced from Different Feedstocks in California

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Abstract

Biogas is a renewable energy source composed of methane, carbon dioxide, and other trace compounds produced from anaerobic digestion of organic matter. A variety of feedstocks can be combined with different digestion techniques that each yields biogas with different trace compositions. California is expanding biogas production systems to help meet greenhouse gas reduction goals. Here, we report the composition of six California biogas streams from three different feedstocks (dairy manure, food waste, and municipal solid waste). The chemical and biological composition of raw biogas is reported, and the toxicity of combusted biogas is tested under fresh and photochemically aged conditions. Results show that municipal waste biogas contained elevated levels of chemicals associated with volatile chemical products such as aromatic hydrocarbons, siloxanes, and certain halogenated hydrocarbons. Food waste biogas contained elevated levels of sulfur-containing compounds including hydrogen sulfide, mercaptans, and sulfur dioxide. Biogas produced from dairy manure generally had lower concentrations of trace chemicals, but the combustion products had slightly higher toxicity response compared to the other feedstocks. Atmospheric aging performed in a photochemical smog chamber did not strongly change the toxicity (oxidative capacity or mutagenicity) of biogas combustion exhaust.

Graphical Abstract

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Supporting Information

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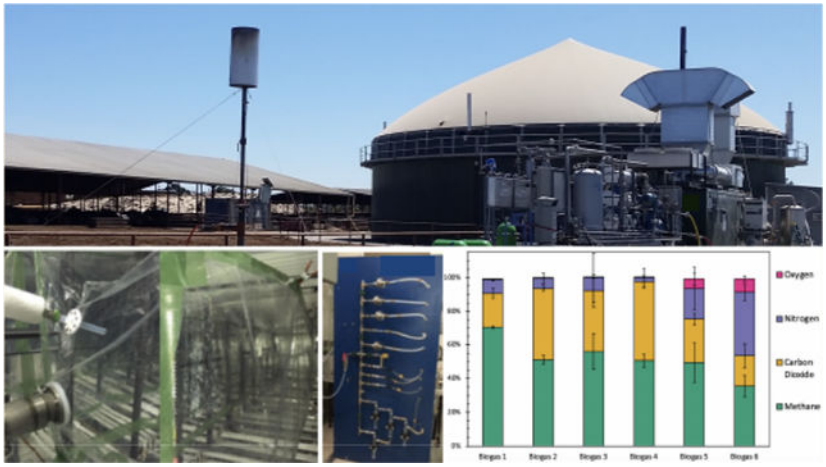

1. INTRODUCTION

Biogas is a renewable fuel produced from the anaerobic digestion of organic feedstocks including municipal waste, farm waste, food waste, and energy crops. Raw biogas typically consists of methane (50–75%), carbon dioxide (25–50%), and smaller amounts of nitrogen (2–8%). Trace levels of hydrogen sulfide, ammonia, hydrogen, and various volatile organic compounds are also present in biogas depending on the feedstock.[1] Life cycle assessment studies have shown that deploying biogas technologies can effectively reduce greenhouse gas (GHG) emissions and, therefore, reduce the climate impact of energy consumption.[2–4] Biogas production and utilization practices also help diversify energy systems while simultaneously promoting sustainable waste management practices.[1,5] California is promoting biogas utilization by mandating the low carbon fuels, offering grants to develop biogas production facilities, and providing assistance in accessing pipeline infrastructure.[6–8]

There are many environmental factors to consider when developing biogas energy sources including the potential for air quality impacts. California is home to 7 of the 10 most polluted cities in the United States[9] and so the widespread utilization of any new fuel must be carefully analyzed for effects on the air quality and human health. The concentrations of minor chemical and biological components in biogas differ from those found in other fuels. Some of these components have the potential to be toxic to human health and the environment, to form toxic substances during the combustion process, or to form toxic substances after photochemical aging in the atmosphere.

The California Air Resources Board (CARB) and the Office of Environmental Health Hazzard Assessment (OEHHA) compiled a list of 12 trace components potentially present in biogas at levels significantly above traditional fossil natural gas including carcinogens (arsenic, *p*-dichlorobenzene, ethylbenzene, *n*-nitroso-di-*n*-propylamine, vinyl chloride) and noncarcinogens (antimony, copper, hydrogen sulfide, lead, methacrolein, mercaptans, toluene). A limited dataset of measurements is available to characterize levels of these biogas components in California. Measurements of landfill biogas composition have been made over many decades around the world to identify sources of odor, to reduce ground level volatile organic compound (VOC) contamination, and to optimally recover biogas as an

energy source.[10] Trace components identified in the landfill biogas include halocarbons, aromatic hydrocarbons, and siloxanes.[11–16] Animal waste has significant biogas potential in California but often contains sulfur compounds that must be removed prior to use.[17,18] Food waste is a relatively new feedstock that has only been analyzed for biogas plant performance.[19,20] Previous studies have tested biogas or simulated biogas burning in engines or turbines, focusing on engine/turbine performance, NOx and small hydrocarbon emissions, [21–26] but these studies did not examine trace chemical compounds in the engine combustion exhaust that could pose environmental and human health concerns.

Here, we report the composition and toxicity of biogas produced and directly used for electricity production at five different facilities in California. Samples at each site were collected over 3 separate days spanning a range of environmental conditions. Comprehensive measurements were performed for 273 different features including major biogas chemical components, a variety of different organic and inorganic trace components, trace elements, and microorganisms. Concentrations were compared to previously reported measurements and to the regulatory limits specified by OEHHA and the California Division of Occupational Safety and Health (Cal/OSHA). A standard biomarker assay was used to evaluate the oxidative capacity of biogas combustion exhaust and the associated short-term inflammatory response. A carcinogen screening mutagenicity bioassay was used to evaluate the probability that biogas combustion exhaust will damage DNA, leading to increased cancer risk over longer time periods. These comprehensive measurements help to understand the potential air quality impacts of widespread biogas production and combustion for electricity generation across California.

2. MATERIALS AND METHODS

2.1. Biogas Sources.

A total of 18 sets of samples were collected from five biogas facilities: (1) dairy waste biogas produced by a flushed manure collection and covered lagoon system, (2) dairy waste biogas produced by a scraped manure collection and digester system, (3) food waste biogas, (4) food waste biogas mixed with nearby landfill gas, (5) biogas produced by the core portion of a regional landfill, and (6) biogas produced from the perimeter of the same regional landfill. The biogas production and utilization technologies used at each site are summarized in Table 1. A map showing the locations of all biogas facilities studied is present in Figure S1. All of the facilities generate electricity on-site using engines or turbines tuned to operate on biogas.

2.2. Chemical Analysis.

Biogas is a complex matrix containing hundreds of trace chemical compounds that cover a broad range of functional groups with different volatilities. Multiple sampling and analysis techniques are employed to measure the full range of compound classes. Common sampling methods include collecting high volatility compounds in Tedlar (poly(vinyl fluoride)) bags or in metal canisters, enriching lower volatility compounds onto solid sorbent tubes, and stripping polar compounds using liquid sorbents in glass impingers. The widely used analysis procedures include compound separation using gas or liquid chromatography

optionally coupled with a desorption unit followed by detectors that may be compound-specific or general mass spectrometers. Detection limits are typically tens to hundreds of parts per billion by volume for different compounds.[10,11,13–15,27–29]

The current study employed sampling and analysis techniques following the practices summarized above as published by the EPA (TO-15,[29] 8081b,[30] 8270d,[31] 8082a,[32] 29[33]) and ASTM (D1945,[34] D6228[35]) standard laboratory methods. Tedlar sample bags were collected under the positive system pressure or using a "Vac-U-Chamber" (SKC-West, Inc.) vacuum sampling apparatus if the biogas pressure was negative. Each Tedlar bag sample analysis included a pure nitrogen system blank and calibration standards. Tedlar sample bags were directly connected to the instruments summarized in Table S1 and analyzed for the 119 compounds listed in Table S2. Semivolatile and/or reactive chemical compounds were collected on three different types of sorbent tubes: XAD-2 sorbent tubes, coconut charcoal sorbent tubes, and DNPH- treated silica gel tubes. Flow through each sorbent tube was controlled at 1.0 $L \cdot min^{-1}$ using a calibrated variable area flow meter with a built-in stainless steel valve followed by a downstream Teflon diaphragm pump (R202-FP-RA1, Air Dimensions Inc.). All sorbent tubes were sealed until just prior to sampling and immediately capped at the conclusion of sampling. Each sample analysis run included a system blank, two sample blanks, and calibration standards. A multipoint calibration curve generated from the calibration standard was used to quantify the target compounds. Table S3 lists collection times, extraction methods, and analysis methods for each sorbent tube. A comprehensive list of target chemical compounds in each sampling/analysis pathway is presented in Tables S4–S6 (102 + 33 + 13 = 148 compounds total). Biogas samples for metals analysis were collected using three serial glass impingers that each contained 20 mL of 5% nitric acid and 10% hydrogen peroxide in double deionized (18.2 MΩ·cm) water. Liquid solutions from each of the impingers were transferred into separate capped vials and then analyzed with inductively coupled plasma mass spectrometry (Agilent 7500i ICP-MS, operated with a Glass Expansion AR50 MicroMist nebulizer).

2.3. Biological Analysis.

Samples for biological analysis were collected on two 47 mm polycarbonate filters (0.4 μm pore size) to support analysis for cultivable microorganisms and corrosion-inducing bacteria DNA. Sample flow rates ranged from 1 to 5 $L \cdot min^{-1}$ over times ranging from 2 to 4 h. Condensate transported along with biogas was also collected. Individual filters were placed in 50 mL Falcon tubes containing 15 mL of phosphate-buffered saline (PBS). Filters were eluted in PBS by vortexing the Falcon tube for 5 s followed by manual shaking for 2 min in a biosafety cabinet. Cultivable aerobic and anaerobic bacteria in eluates and condensates were enumerated by propagation in different growth media using the most probable number (MPN) tests.[36,37] Positive samples in the MPN tests were further characterized using DNA sequencing by conducting polymerase chain reaction (PCR) targeting 16S rRNA.[38] This allowed simultaneous identification of different bacteria species in each sample. Nucleic acids in eluates and condensates were extracted using the FastDNA SPIN Kit for Soil (MP Biomedicals, Irvine, CA) following the manufacturer's protocol. Five qPCR assays targeting total bacteria and corrosion-inducing bacteria including sulfate reducing bacteria (SRB), iron

oxidizing bacteria (IOB), and acid producing bacteria (APB) were selected from the literature.[39–43]

2.4. Toxicity Analysis.

Samples of biogas combustion exhaust were collected from five different electricity generators summarized in Table 1 after dilution with the precleaned background air. A 5.5 m^3 Teflon photochemical reaction chamber (0.051 mm NORTON FEP fluoropolymer film) installed in a 24 ft mobile trailer was used to simulate atmospheric aging of diluted exhaust under both light (daytime UV = 50 W m^{-2}) and dark (nighttime) conditions at each test facility. The reaction chamber was flushed 3 times before each test with the air that was precleaned using granulated activated carbon to remove background gases followed by a high efficiency particulate arrestance (HEPA) filter to remove background particles. Dark aging tests started by filling the reaction chamber to 50% capacity with the clean air, followed by injecting combustion exhaust through a 1/2 in. diameter insulated stainless steel transfer line at a flow rate of 26 L· min^{-1} (50–55 °C) for 255 s. The reaction chamber was then filled to 100% capacity with the clean air within 90 s, yielding a well-mixed system at a dilution ratio of approximately 50:1. The diluted exhaust was aged in the chamber for 3 h before collection onto 47 mm Teflon filters (Zefluor, 2 μm pore size) at 20 L·min^{-1} for 3.5 h. Light aging tests followed the same experimental protocol with the exception that 100 L of VOC surrogate gas (1.125 ± 0.022 ppm_v *m*-xylene and 3.29 ± 0.07 ppm_v *n*-hexane in the air, Scott Marrin, Inc.) was injected into the chamber immediately after the combustion exhaust, creating a final VOC concentration of 90 ppbv. Hydroxyl radical concentrations during the light aging tests were calculated to be (5–6) × 10^6 molecules cm^{-3} based on the decay rate of the *m*-xylene, and final ozone concentrations at the end of the 3 h experiment were measured to be 110–125 ppb.

The expression of in vitro pro-inflammatory markers was measured in human U937 macrophage cells (American Tissue Culture Collection, Manassas, VA). Macrophages are the first line of defense in human lungs, and substances in engine exhaust sample may interact with the macrophage cells though the Toll-Like Receptors (TLR), Aryl hydrocarbon Receptor (AhR), and the NF-κB protein complex to induce inflammatory responses. Biomarkers checked in this study include Cytochrome P450 monooxygenase (CYP1A1: marker for polycyclic aromatic hydrocarbons), interleukin 8 (IL-8: marker for inflammation), and cyclooxygenase (COX-2: a key enzyme for the production of prostaglandins mediating pain and inflammation). After a 6 h treatment of the exhaust filter extract, mRNA was isolated from U937 macrophage cells and reverse-transcribed into cDNA for quantitative expression analysis using qPCR. Results were normalized to housekeeping gene β-actin expression and expressed as fold increase of mRNA in treated cells relative to untreated cells.[44] The mutagenicity bioassay was carried out via a microsuspension modification of the *Salmonella*/microsome Ames assay[45,46] that is 10 times more sensitive than the standard plate incorporation test. Frame-shift mutations of *Salmonella* typhimurium tester strain TA98 were observed. TA98 requires exogenous histidine (His^-) for growth; however, substances in exhaust samples could cause deletion or addition of nucleotides in the DNA sequence of TA98 histidinegene (frame-shift), resulting in TA98's ability to manufacture histidine (His^+). The resultant colonies are referred to as

"Revertants", as the DNA sequence is changed back to its original correct form. Liver homogenate (S9) from male Aroclor-induced Sprague Dawley rats (Mol Tox, Boone, NC) was added to the assay to provide metabolic activation of the sample.

3. RESULTS AND DISCUSSION

3.1. Biogas Composition.

Concentrations of major biogas components (methane, carbon dioxide, nitrogen, and oxygen) are shown in Figure 1. Methane (CH_4) content of the different biogas streams varied from 49.5 to 70.5% with the exception of perimeter landfill biogas (biogas 6), which contained only35.4% methane due to high levels of air intrusion into the gas extraction system. Biogas produced from flushed dairy waste using a covered lagoon (biogas 1) had the highest measured methane concentration. In contrast, biogas produced from scraped dairy waste in an anaerobic digester (biogas 2) had a much lower methane concentration of 51.3%. Similar trends were reported by Saber et al., who measured the average methane concentration in a covered lagoon dairy biogas facility in the western US to be 67.6%, while the methane concentration in a complete mixed dairy biogas digester in the western US was only 60.5%.[47] In addition, the biogas 2 facility adds iron chloride to digester slurry. Iron chloride is known to inhibit anaerobic digestion processes, resulting in lower biogas methane content.[48] Core landfill biogas had an average methane concentration of 49.5%, which fell into the range reported by previous studies conducted in US and Europe.[11,12,14] The carbon dioxide content in the biogas ranged from 20.2% in lagoon dairy biogas (biogas 1) to 46.9% in food waste/landfill biogas (biogas 4). Concentrations of CH_4 and CO_2 observed in this study fall in the range commonly reported for biogas. Another important GHG formed during the life cycle of organic waste management is nitrous oxide (N_2O). N_2O is known to account for more than 20% of the total global warming potential (100 year scale) associated with GHGs emissions from organic waste storage practices,[49,50] but N_2O is unlikely to form in the anaerobic digestion process that produces biogas.[51]

Small amounts of nitrogen (N_2, <8%) and oxygen (O_2, <0.5%) were measured in biogas streams one through four. The air is commonly injected into the anaerobic digestion process at a rate of 2–6% to inhibit the formation of hydrogen sulfide.[52] The rate of anaerobic methane production does not decrease and may even increase when a small amount of oxygen is introduced, while the rate of hydrogen sulfide production is strongly reduced.[53] Higher concentrations of the air are entrained into the landfill biogas by blowers that create a negative pressure in porous collection pipes leading to air intrusion through the soil into the biogas stream. Air intrusion rates were higher at the perimeter of the landfill because less biogas was produced in this region, requiring more air intrusion to supply the extracted gas volume.

3.1.1. Sulfur-Containing Compounds.—Figure 2 shows the concentration of sulfur-containing compounds and their speciation. The amount of total sulfur-containing compounds varied significantly between different biogas facilities, reflecting the impact of both feedstock composition and primary sulfur control methods. The dairy biogas facility with covered lagoon (biogas 1) had the lowest total sulfur concentration composed mostly of

sulfur dioxide with very little hydrogen sulfide. In contrast, the dairy biogas facility with the digester (biogas 2) had the second highest total sulfur, nearly half of which (by volume) was hydrogen sulfide. Both of these dairy facilities used simple air injection to reduce H_2S production, and the digester dairy facility also added iron chloride to the digester to further control H_2S. This suggests that the covered lagoon dairy achieved optimum operating conditions for anaerobic digestion and biological desulfurization, with an effective combination of hydraulic retention time, lagoon temperature, pH, and air injection rates. Different feedstocks at the two dairy facilities may also contribute to different biogas sulfur contents. A dairy biogas study in the eastern US found that differences in water sulfur concentration explained differences in the biogas sulfur concentration from some facilities.[18] In the current study, biogas facility 1 used lagoon water to flush the dairy stalls with periodic dilution using surface water sources. Biogas facility 2 did not have access to surface water sources and so used ground water exclusively. Landfills with active blower systems inevitably have air intrusion in the biogas, which helps reduce the sulfur content. The fraction of sulfur dioxide in the perimeter landfill biogas stream is higher than that in the core landfill biogas stream, indicating a more oxidized environment in the perimeter part compared to the core. Biogas 4 included contributions from a nearby landfill, which produced a sulfur profile similar to that of the core landfill. Biogas 3 had the highest concentration of total sulfur-containing compounds. Levels of H_2S (77.7 ppm) and mercaptans (42.8 ppm) in biogas 3 both exceeded OEHHA risk management trigger levels (22 ppm for H_2S and 12 ppm for mercaptans) but were still well below the lower action level (216 ppm for H_2S and 120 ppm for mercaptans).[5] This suggests that no health risk concerns have been identified, but routine monitoring of biogas sulfur content is advisable. Overall, the total sulfur concentrations measured in the current study fell into the lower end of the range reported in previous studies.[18,47]

3.1.2. Halocarbons.—Figure 3 shows that the two landfill biogas streams (5 and 6) had the highest total halocarbon concentrations, while the dairy waste and food waste biogas facilities (1–3) produced biogas with lower total halocarbon concentrations. Biogas 4 had intermediate halocarbon concentrations because it was a mixture of food waste biogas and landfill gas. These trends reflect the halocarbon content of different feedstocks. Dairy biogas produced from the digester (biogas 2) had more chlorinated compounds than biogas produced from the covered lagoon (biogas 1) possibly due to the addition of iron chloride to the slurry, providing an additional source of chlorine. Chlorofluorocarbons (CFCs) commonly used in the past as refrigerants were present in landfill biogas. Larger chloroalkenes (trichloroethene and tetrachloroethene) commonly used as degreasers were also detected in landfill biogas, along with smaller chloroalkenes that are likely breakdown products of the anaerobic digestion process.[54] Biogas 2 (dairy digester) unexpectedly contained chloroethene, suggesting that there were some cleaning processes involved in the operation of this digester. Table S7 compares selected halocarbon species with available data from previous studies on landfill biogas, together with the Cal/OSHA permissible exposure levels (PELs) and OEHHA risk management trigger levels (if available). Levels of halocarbons fall in the wide concentration range reported by previous landfill studies and are well below the PELs, indicating negligible occupational health concern. Studies have shown that halocarbons form corrosive products during combustion in engines, resulting in earlier

failure of engine parts. However, total halocarbon concentrations found in biogas from all different streams in this study are safely below the level that might cause early engine part corrosion.[11]

3.1.3. Benzene, Toluene, Ethylbenzene, and Xylene (BTEX).—Benzene, toluene, ethylbenzene, and xylene (BTEX) compounds are regulated as "hazardous air pollutants" by the US EPA. Benzene is a known human carcinogen, while toluene, ethylbenzene, and xylenes are harmful to the human nervous system and can cause eye and throat irritation during high-level exposure. Consumer products such as paints, rubber, adhesives, cosmetics, and pharmaceuticals are major sources of BTEX.[55] Figure 4 shows that landfill biogas had much higher BTEX than food waste and dairy waste biogas because municipal solid waste contains many consumer products. Biogas 4 had intermediate BETX concentrations because it is a mixture of food waste and landfill biogas. Table S8 lists average concentrations of BTEX in each biogas stream, together with the PELs given by Cal/OSHA and risk management trigger levels by OEHHA. All of the biogas-averaged BTEX compound concentrations were below the 8 h averaged PEL. Concentrations of benzene in landfill biogas were just below the PEL, indicating that routine monitoring of BTEX concentrations is advisable at landfills.

3.1.4. Siloxanes.—Figure 5 presents siloxane concentrations from different biogas streams. Biogas 4–6 had high total siloxanes because of the many siloxane-containing compounds in the landfill feedstock including personal care products, fabric softeners, and surface treatment formulas. Notably, although biogas 4 was a mixture of food waste biogas and landfill biogas, it contained even more siloxanes than the pure landfill biogas streams (5 and 6). This indicated that the landfill site, which contributed to biogas 4, had received more siloxane-containing products compared to the landfill site producing biogas 5 and 6. Biogas 1–3 had low siloxane concentrations made up mostly by D4 (decamethyltetrasiloxane) and D5 (dodecamethylpentasiloxane) species. Table S9 lists the concentration of each siloxane species in the top three high-siloxane biogas streams (biogas 4–6), together with measured values from previous landfill studies. Siloxane concentrations in landfill gas are variable but L2 (hexamethyldisilocane), D4, and D5 are consistently found to be the most abundant species. Although siloxanes are not considered to be directly toxic to the environment or human health, siloxane combustion forms silica (SiO_2) nanoparticles (Dp < 100 nm). Silica nanoparticles can degrade engine performance and increase CO emission by abrading engine parts, depressing spark plug functionality, and deactivating emission control systems.[14,15,56] Engine manufacturers typically set siloxanes concentration limits ranging from 10 to 28 $mg \cdot m^{-3}$.[57] All of the biogas streams measured in the current study met this requirement.[57] Nanoparticles are also known to be toxic due to their large surface-to-volume ratio and ability to translocate in the human body, but the exact short- and long-term effects of Si-based nanoparticles are not yet completely understood.[58]

3.1.5. Metals.—A total of 24 different elements were analyzed in the biogas streams with all measured values reported in Table S5. Concentrations of arsenic (As), antimony (Sb), lead (Pb), copper (Cu), and aluminum (Al) are summarized in Table 2. Concentrations of antimony, lead, copper, and aluminum in biogas fall well below the Cal/OSHA PELs and

OEHHA risk management trigger levels. Arsenic concentrations in some landfill biogas samples slightly exceeded the Cal/OSHA 8-h PEL, but the average concentrations were below the PELs as well as the risk management trigger level, indicating negligible potential health risks. Possible sources of arsenic in biogas include groundwater, semiconductor electronic devices deposited into landfills or pesticides/herbicides that make it into the organic waste stream.

3.1.6. Bacteria.—Table 3 summarizes the biological entities measured in the biogas samples. Cultivable (spore-forming) bacteria were detected 2 times in 3 samples (biogas 1, dairy), 1 time in 3 samples (biogas 2, dairy), and 6 times in 11 samples (biogas 3, food waste). Cultivable biologicals were less commonly found in landfill biogas streams (2 out of 7 samples for biogas 4 and 1 out of 6 samples for biogas 5 and 6). Basic Logical Assignment Search Tool (BLAST) database analysis determined that cultivable biologicals were closely related to Bacillus spp. or *Paenibacillus* spp., which are Gram-positive, spore-forming bacteria found in a variety of environments including soil, water, and rhizosphere. Approximately, 10 to 100 MPN per m^3 were measured in the current study, which is comparable to results from previous studies reporting cultivable bacteria concentrations in biogas.[59,60]

Total bacteria concentrations assessed by qPCR were below sample limits of detection (SLODs) in most biogas streams except for the landfills. Sulfate reducing bacteria (SRB) target genes were not detected in any samples, consistent with the results from previous studies on dairy and landfill biogas.[37,59] Iron oxidizing bacteria (IOB) was found only once in most biogas streams except for biogas 4 (twice in 7 samples). DNA sequencing of qPCR amplicons revealed that IOB were closely related to *Gallionella capsiferriformans and Leptothrix* spp. Acid producing bacteria (APB) target gene *(buk)* was detected in biogas 1, 3, and 4. One-way ANOVA analysis showed that the mean values of IOB and APB were not statistically different from their SLODs ($p > 0.05$). Therefore, IOB and APB will not likely reduce the service life of biogas facilities characterized in the current study.

3.2. Biogas Engine Combustion Exhaust.

Figure 6a–d shows bioassay results measured from the particulate matter collected on filters for on-site biogas engine/turbine exhaust aged under dark and light conditions. Panels a–c present levels of biomarker expression (CYP1A1, IL-8, and COX-2, respectively) in U937 human macrophages after a 6 h treatment with the biogas engine exhaust extract. Results are expressed as fold increase above blank levels. Overall, the biomarker responses from biogas electricity generators at sites 1–5 were similar under dark conditions. Photochemical aging did not appear to strongly influence these results, with the exception that biogas 2 engine exhaust induced notably greater expression of the monooxygenase enzyme CYP1A1 and pro-inflammatory signaling protein IL-8 under light conditions. These samples likely contained polycyclic aromatic hydrocarbons, which could be metabolized into carcinogens by CYP1A1 and materials that could lead to inflammatory responses when inhaled.

Figure 6d shows the result of the mutagenic bioassay (*Salmonella*/microsome Ames assay) under dark and light conditions. The number of TA98 revertants from a field blank sample

(clean air and surrogate VOC gases aged in the photochemical reaction chamber) was subtracted from the biogas test results. No activity over spontaneous background was observed for biogas 2 dark, biogas 4 light, and biogas 5 under both dark and light conditions. Exhaust from biogas 1 showed higher mutagenicity concentrations than other biogas streams. Photochemical aging did not strongly affect the mutagenicity of exhaust, suggesting that photochemical reactions will likely not change the genotoxic properties of the particulate matter exhaust from biogas engines.

Overall, engine exhaust from dairy biogas (biogas 1 and 2) showed slightly higher bioassay activity than exhaust from other biogas sources, especially after aging under simulated UV light. A previous study indicated that the particulate matter from dairy farms can induce pro-inflammatory responses with toxic and immunogenic substances such as histamine, endotoxins, different antigens, and microorganisms.[44] The observed higher activities in dairy biogas combustion exhaust may actually be driven by the dairy farm background air drawn into the engines during the combustion process, rather than the combustion products of biogas itself. Moreover, a previous study by Xue et al. showed that ultrafine particle emission from biogas-fueled engines is influenced more strongly by the engine and combustion technology than by the fuel composition.[61] The relationships between the properties of the fuel, the properties of the gas-phase combustion exhaust, the properties of the PM in the combustion exhaust, and the toxicity of the PM are not fully understood in the current study, but the current results suggest that the toxicity of the dairy biogas combustion exhaust merits further investigation.

4. IMPLICATIONS

Calculated emission factors (EFs) of SO_2 and selected organic compounds are summarized in Tables 4 and 5 to support future predictions of the aerosol formation potential of biogas burning in engines. $SO_2 EFs \left(\frac{\text{g-SO}_2 (\text{or mg-SO}_2)}{\text{m}^3 - \text{biogas}} \text{or} \frac{\text{lb-SO}_2}{10^6 \text{Btu energy}} \right)$ were estimated for each biogas stream, assuming that all of the S-containing compounds in the fuel are converted to SO_2 under stoichiometric combustion conditions. Calculations were carried out for both raw biogas and for upgraded biogas (biomethane), as summarized in Table 4. SO_2 EFs range from1.71×10^{-4} lb $MMBtu^{-1}$ to 3.5×10^{-2} lb $MMBtu^{-1}$ in raw biogas due to variability in fuel sulfur and methane content. SO_2 EFs for biomethane range from 1.06 to 4.07×10^{-4} lb $MMBtu^{-1}$ because the precleaning steps for the upgrading process remove sulfur from the fuel.[62] For reference, the SO_2 EF from natural gas-fired stationary reciprocating engines[63] is 5.88×10^{-4} lb $MMBtu^{-1}$, which is comparable to the biomethane EFs calculated in the current study.

Concentrations of different semivolatile organic compounds, PAHs, and extended hydrocarbons in the engine exhaust were measured after injection into the photochemical reaction chamber and aging under dark or light conditions. Note that concentrations were diluted by a factor of ~50 to represent true atmospheric conditions, which resulted in low measured values close to method detection limits. Concentrations vary from site to site due to this issue and so median results across all locations are shown rather than results for individual locations. Table 5 summarizes concentrations of various organic compounds in

exhaust as well as the calculated EFs. Median values are reported along with minimum and maximum values in the parentheses. EFs for 4-stroke lean-burn natural gas-fired reciprocating engines[63] are listed in the last column of Table 5 as a reference point. EFs of various organic compounds from biogas-fired engines are generally comparable or lower than EFs from natural gas-fired engines.

The current study characterizes the range of trace composition profiles for California biogas produced from different feedstocks. These trace component characteristics play a central role in determining what upgrading steps are required to enable biogas energy recovery[62] and what routine monitoring protocols are needed to protect pipeline infrastructure and public health. Quantifying the broad array of trace contaminants in biogas is challenging for two reasons. First, the composition of biogas varies with feedstock, weather condition, digester operating parameters, etc. Second, different laboratories employ different sampling and analysis techniques that can lead to different detection limits. Characterizing the distribution of concentrations for each contaminant requires repeated measurements across multiple seasons using identical methods followed by statistical analysis. The biogas industry should agree on a set of sampling and analysis protocols to facilitate the intercomparison of results from different laboratories.

No strong evidence of potential occupational health risk was detected at any of the five California biogas sites. This study also found no obvious differences between the toxicity of different biogas combustion exhaust streams after atmospheric dilution and aging. Future studies should continue to characterize the variability of the trace chemical composition of biogas combustion exhaust to enable a more detailed statistical analysis of potential public health impacts of large biogas energy recovery facilities.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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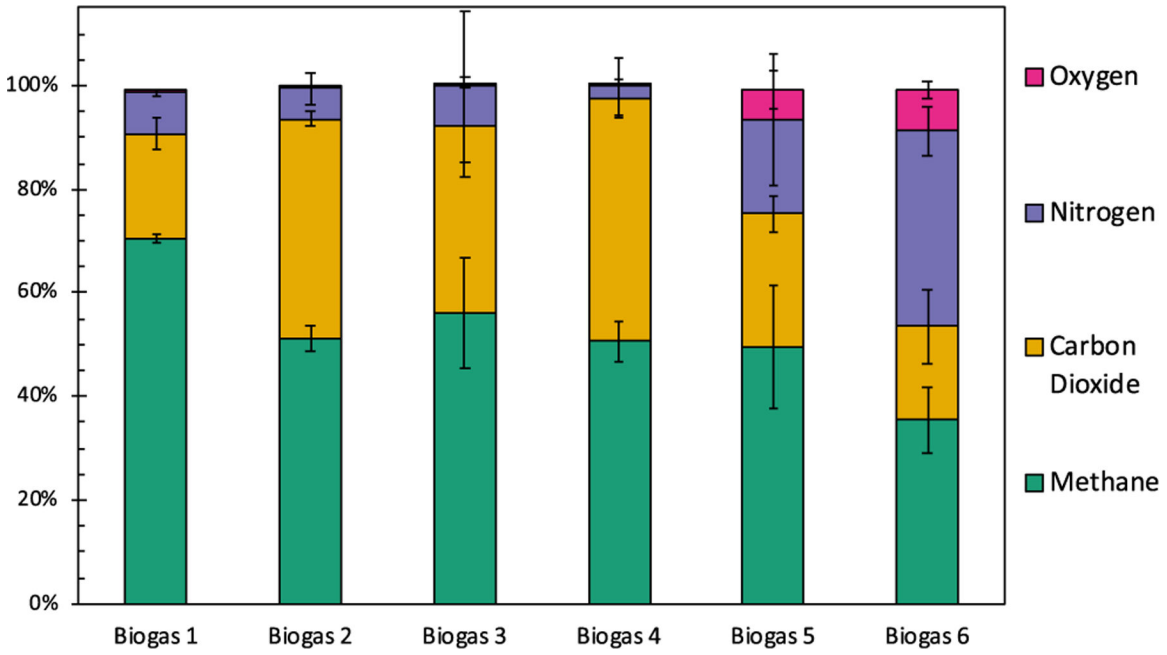

Figure 1.
Major component concentrations by volume in dry biogas streams.

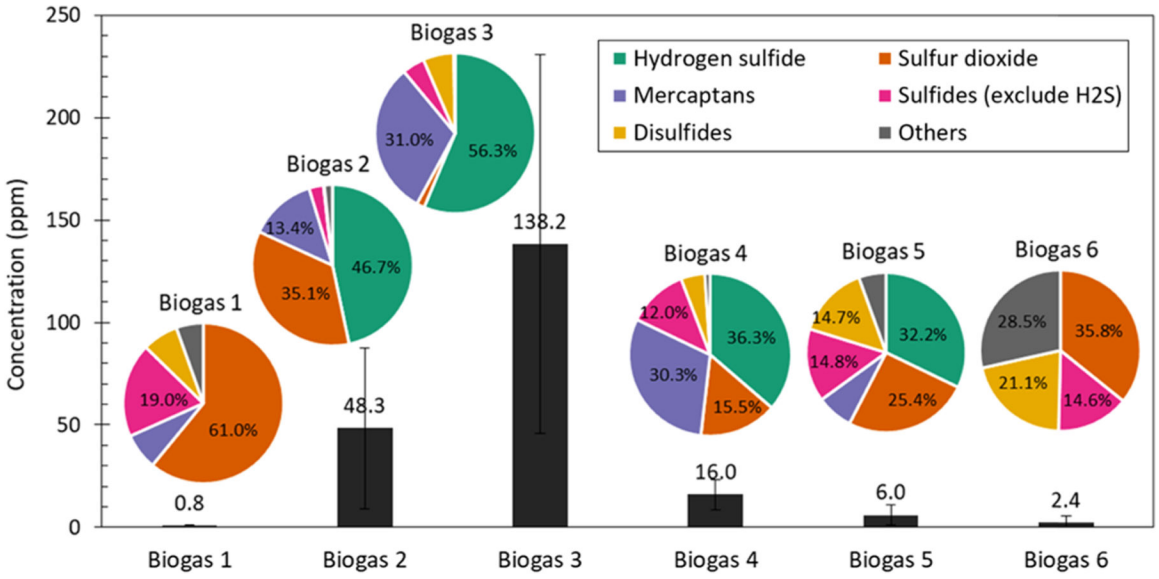

Figure 2.

Total sulfur-containing compound concentration (ppm_v) and speciation in different biogas streams.

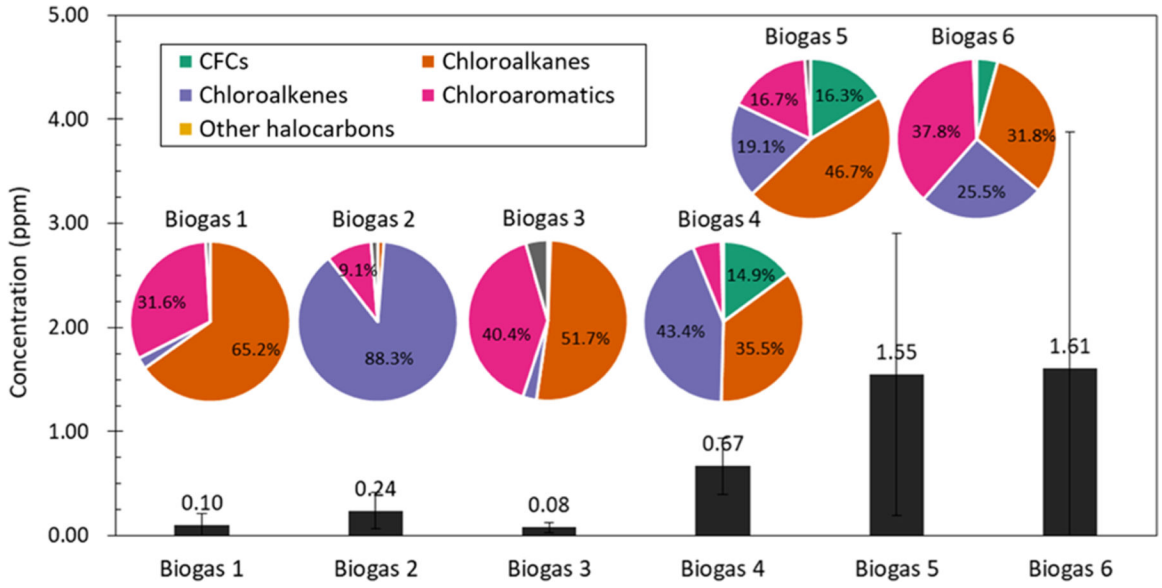

Figure 3.
Total halocarbon concentration (ppm_v) and speciation in different biogas streams.

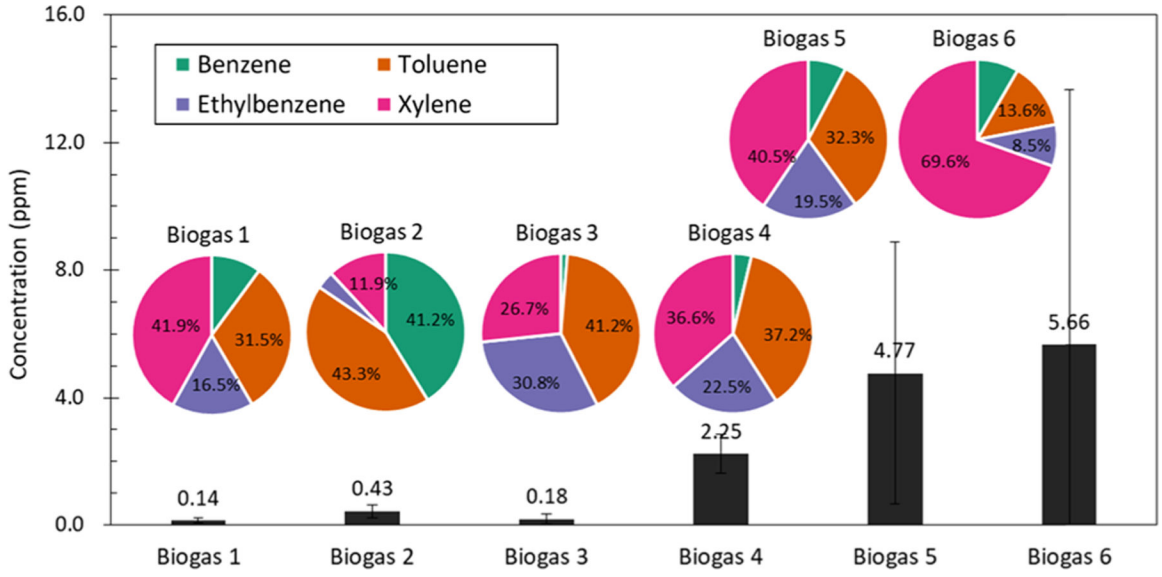

Figure 4.

Total BTEX concentration (ppm_v) and speciation in different biogas streams.

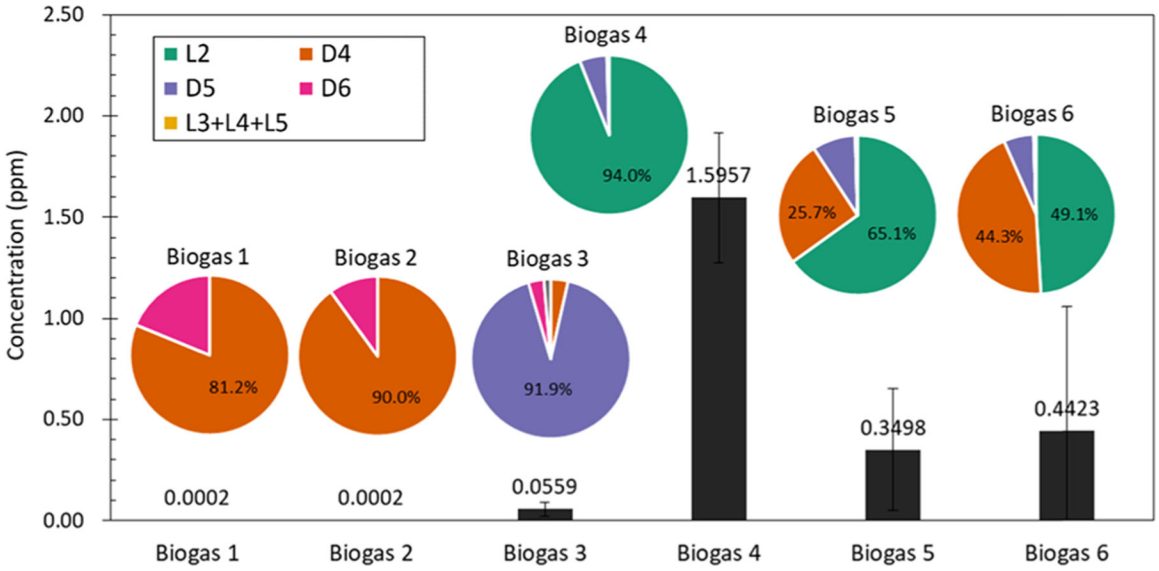

Figure 5.

Total siloxane concentration (ppm_v) and speciation in different biogas streams L2 (hexamethyldisiloxane), L3 (hexamethylcyclotrisiloxane), L4 (decamethyltetrasiloxane), L5 (dodecamethylpentasiloxane), D4 (octamethylcyclotetrasiloxane), D5 (decamethylcyclopentasiloxane), D6 (dodecamethylcyclohexasiloxane).

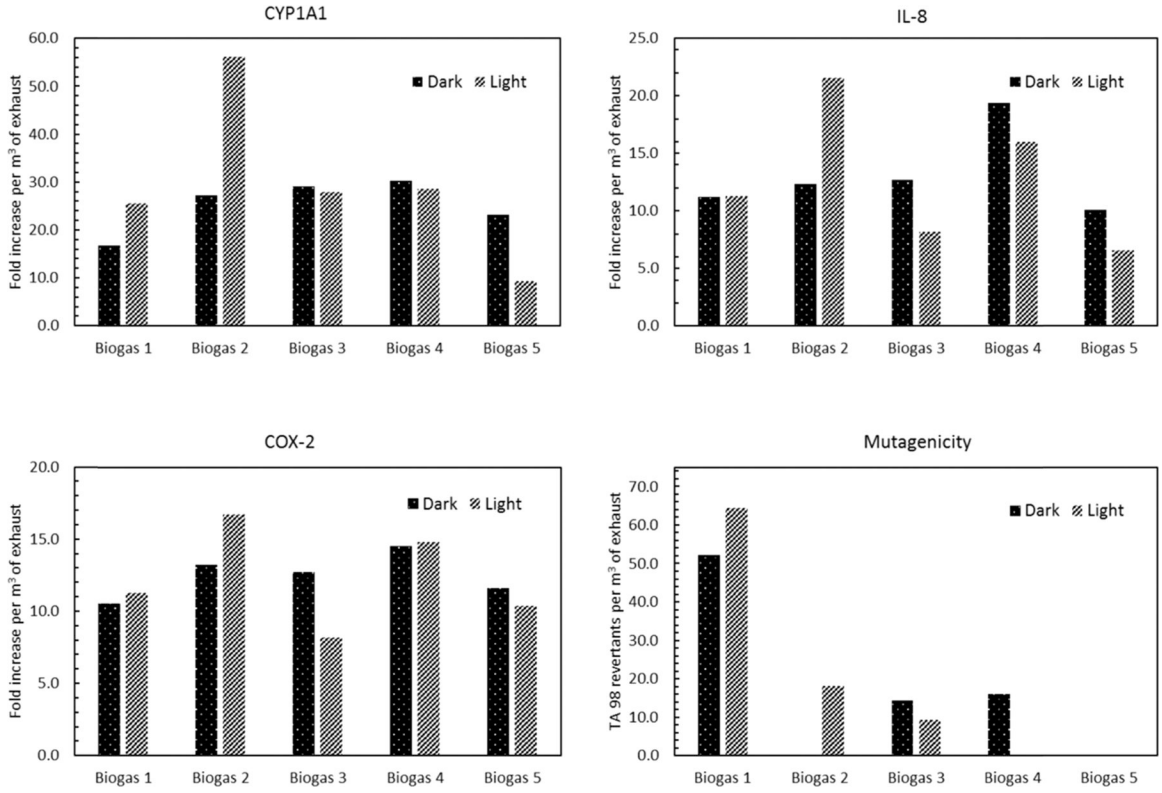

Figure 6.

Bioassay results of on-site biogas engine/turbine exhaust aged under dark and light conditions: (a) fold increase of CYP1A1 per m^3 of engine exhaust, (b) fold increase of IL-8 per m^3 of engine exhaust, (c) fold increase of COX-2 per m^3 of engine exhaust, and (d) number of TA98 net revertants per m^3 of engine exhaust.

Table 1.

Summary of Biogas Production Sites Characterized in This Study

biogas streams	type of feedstock	biogas production technology	gas end use
1	Dairy farm cow manure (flushed). 1200 cows total. Surface water.	Covered lagoon. Lower mesophilic (20–30 °C). Retention time 100 days	Fuel for internal combustion engine to generate electricity
2	Dairy farm cow manure (scraped). 1200 cows total. Ground water.	Single continuously stirred digester. Mesophilic (35–40 °C). Retention time 50 days	Fuel for internal combustion engine to generate electricity
3	Food waste 25 tons per day	Three-stage digester Thermophilic (50–55 °C). Retention time 21 days	(a) Fuel for internal combustion engine to generate electricity, (b) upgrade to biomethane using membrane system
4	Varying amount of food waste, animal bedding and waste, municipal organic waste	Three-stage digester. Thermophilic (50–55 °C). Retention time 21 days	Fuel for microgas turbines to generate electricity
	Landfill	15 acres since early 1970s	
5	Landfill (core part)	Residential and commercial waste since 1967 (1084 acres)	Fuel for gas turbines to generate electricity
6	Landfill (perimeter)	Residential and commercial waste since 1967 (1084 acres)	Flared

Table 2.

Concentration of Arsenic (As), Antimony (Sb), Lead (Pb), Copper (Cu), and Aluminum (Al) in different biogas streams ($\mu g \cdot m^{-3}$)[a,b]

element	As	Sb	Pb	Cu	Al
LOD	0.005	0.005	0.1	0.005	0.2
biogas 1	0.315 ± 0.432	0.259 ± 0.184	1.7 ± 2.4	0.000 ± 0.000	0.0 ± 0.0
biogas 2	0.012 ± 0.018	0.006 ± 0.009	7.4 ± 10.5	0.000 ± 0.000	0.0 ± 0.0
biogas 3	0.230 ± 0.380	0.310 ± 0.170	0.0 ± 0.0	0.005 ± 0.008	0.0 ± 0.0
biogas 4	1.600 ± 1.400	1.600 ± 1.800	0.1 ± 0.3	0.000 ± 0.000	2.2 ± 5.0
biogas 5	8.500 ± 3.400	12.500 ± 12.500	0.8 ± 0.8	0.000 ± 0.000	0.0 ± 0.0
biogas 6	4.200 ± 2.300	1.300 ± 2.000	0.7 ± 1.1	0.200 ± 0.340	5.6 ± 9.6
Cal/OSHA 8 h average PEL[64]	10	500	50	100	5000
OEHHA trigger level[64]	19	600	75	60	

[a] Results expressed in (average value ± 1 standard deviation).

[b] Concentrations below limit of detection (LOD) are denoted as 0 ± 0.

Table 3.

Results of Biological Analysis (Cultivation and qPCR)

parameter[a]	biogas 1	biogas 2	biogas 3	biogas 4	biogas 5	biogas 6
Cultivation Analysis (MPN m^{-3})[b]						
live aerobic bacteria	34 ± 7 (2/3)	<SLOD (0/3)	<SLOD (0/4)	87 ± 39 (2/7)	<SLOD (0/3)	<SLOD (0/3)
live anaerobic bacteria	<SLOD (0/3)	<SLOD (0/3)	<SLOD (0/4)	<SLOD (0/7)	<SLOD (0/3)	<SLOD (0/3)
live aerobic spore bacteria	<SLOD (0/3)	22 ± 10 (1/3)	32 ± 14 (2/4)	32 ± 13 (2/7)	<SLOD (0/3)	29 ± 19 (1/3)
live anaerobic spore bacteria	<SLOD (0/3)	<SLOD (0/3)	<SLOD (0/4)	<SLOD (0/7)	<SLOD (0/3)	<SLOD (0/3)
qPCR Analysis (gene copies m^{-3}) total bacteria	<SLOD (0/3)	<SLOD (0/3)	<SLOD (0/4)	<SLOD (0/7)	3600 ± 2300 (1/3)	4300 ± 4000 (1/3)
sulfate reducing bacteria (SRB)	<SLOD (0/3)	<SLOD (0/3)	<SLOD (0/4)	<SLOD (0/7)	<SLOD (0/3)	<SLOD (0/3)
iron oxidizing bacteria (IOB)	450 ± 440 (1/3)	29 ± 23 (1/3)	190 ± 190 (1/4)	170 ± 100 (2/7)	430 ± 550 (1/3)	23 ± 24 (1/3)
acid producing bacteria (APB)	180 ± 180 (1/3)	<SLOD (0/3)	160 ± 100 (2/4)	800 ± 560 (2/7)	<SLOD (0/3)	<SLOD (0/3)

[a] Results shown are means ± standard errors. Data below sample limits of detection (SLODS) were assumed to be the half of the SLODS for mean calculation. The median SLODS of cultivation tests were 23 MPN per m^3. The median SLODS of qPCR were 3200, 22, 140, 13, and 16 gene copies per m^3 for total bacteria, SRB, IOB, and APB, respectively. The number of 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.

Table 4.

Concentration of Total S-Containing Compounds in Biogas and Biomethane Streams and Emission Factors of SO_2 from Burning These Gas Streams

	biogas			biomethane		
	total S in fuel[a] (ppm)	**EF - SO_2 (g m^{-3}-biogas)**	**EF - SO_2 (lb/MMBtu)**	**total S in fuel[a] (ppm)**	**EF - SO_2 (mg m^{-3}-biomethane)**	**EF - SO_2 (lb/MMBtu)**
biogas 1	0.81 ± 0.29	0.002 ± 0.001	$(1.71 \pm 0.74) \times 10^{-4}$			
biogas 2	48.28 ± 39.33	0.117 ± 0.095	$(1.52 \pm 0.99) \times 10^{-2}$	0.648 ± 0.197	1.56 ± 0.48	$(1.06 \pm 0.32) \times 10^{-4}$
biogas 3	138.19 ± 92.51	0.334 ± 0.223	$(3.50 \pm 2.32) \times 10^{-2}$	1.706 ± 0.697	4.12 ± 1.68	$(2.71 \pm 1.12) \times 10^{-4}$
biogas 4	15.95 ± 7.50	0.039 ± 0.018	$(4.18 \pm 1.88) \times 10^{-3}$	2.583 ± 1.296	6.23 ± 3.13	$(4.07 \pm 2.08) \times 10^{-4}$
biogas 5	6.00 ± 4.96	0.014 ± 0.012	$(1.81 \pm 1.25) \times 10^{-3}$			

[a]Concentration results expressed as (average value ± 1 standard deviation).

Table 5.

Concentration of Selected Compounds in Diluted and Atmospherically Aged Engine Exhaust, Their Emission Factors from Burning in Biogas Engines, and Corresponding Emission Factors for Natural Gas Engines

compounds	concentration[a] (ppb)	EF[a] (mg m^{-3}-biogas)	EF[a] (lb $MMBtu^{-1}$)	natural gas engines[63] EF (lb $MMBtu^{-1}$)
1,3-dichlorobenzene	0.003 (0–0.014)	0.007 (0–0.034)	$0.78\ (0–3.53) \times 10^{-6}$	
1,4-dichlorobenzene	0.003 (0–0.015)	0.007 (0–0.364)	$0.07\ (0–3.78) \times 10^{-5}$	
benzyl alcohol	0.008 (0–0.053)	0.014 (0–0.095)	$1.50\ (0–9.89) \times 10^{-6}$	
m,*p*-cresol	0.011 (0–0.028)	0.020 (0–0.051)	$2.08\ (0–5.29) \times 10^{-6}$	
2,4-dichlorophenol	0.009 (0–0.015)	0.025 (0–0.040)	$2.55\ (0–4.14) \times 10^{-6}$	
naphthalene	0.035 (0–0.075)	0.075 (0–0.160)	$0.78\ (0–1.66) \times 10^{-5}$	7.44×10^{-5}
2-methylnaphthalene	0.005 (0–0.015)	0.012 (0–0.035)	$1.24\ (0–3.68) \times 10^{-6}$	3.32×10^{-5}
1-methylnaphthalene	0.010 (0–0.033)	0.024 (0–0.078)	$2.47\ (0–8.07) \times 10^{-6}$	
dimethyl phthalate	0.004 (0–0.011)	0.014 (0–0.034)	$1.44\ (0–3.58) \times 10^{-6}$	
2,4-dinitrotoluene	0.052 (0–0.139)	0.158 (0–0.423)	$1.65\ (0–4.40) \times 10^{-5}$	
diethyl phthalate	0.012 (0–0.037)	0.044 (0–0.136)	$0.46\ (0–1.42) \times 10^{-5}$	
phenanthrene	0.002 (0–0.007)	0.005 (0–0.020)	$0.55\ (0–2.05) \times 10^{-6}$	1.04×10^{-5}
di-*n*-butyl phthalate	0.002 (0–0.006)	0.007 (0–0.028)	$0.76\ (0–2.92) \times 10^{-6}$	
bis(2-ethylhexyl) phthalate	0.003 (0–0.011)	0.020 (0–0.074)	$2.04\ (0–7.66) \times 10^{-6}$	
(1-methylethyl) benzene	0.011 (0–0.090)	0.021 (0–0.181)	$0.22\ (0–1.89) \times 10^{-5}$	
1,2,4-trimethylbenzene	0.009 (0–0.064)	0.019 (0–0.128)	$0.20\ (0–1.33) \times 10^{-5}$	1.43×10^{-5}
1,3,5-trimethylbenzene	0.035 (0–0.242)	0.071 (0–0.487)	$0.74\ (0–5.06) \times 10^{-5}$	3.38×10^{-5}
decane	0.020 (0–0.346)	0.047 (0–0.822)	$0.49\ (0–8.55) \times 10^{-5}$	
tetradecane	0.013 (0–0.048)	0.044 (0–0.157)	$0.45\ (0–1.64) \times 10^{-5}$	
hexadecane	0.017 (0–0.048)	0.064 (0–0.183)	$0.67\ (0–1.91) \times 10^{-5}$	
octadecane	0.013 (0–0.021)	0.053 (0–0.091)	$5.53\ (0–9.46) \times 10^{-6}$	
eicosane	0.015 (0–0.024)	0.073 (0–0.115)	$0.76\ (0–1.20) \times 10^{-5}$	

[a]Median value across all biogas streams. Values inside parentheses are minimum and maximum.