Biogas Constituents of Concern and Health Protective Levels for Biomethane:

Supplement Report to OEHHA AB 1900 Biogas Recommendations

April 2023

Prepared by:

California Air Resources Board

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1 Introduction

This report is a supplement to the Office of Environmental Health Hazard Assessment's (OEHHA) "AB 1900 Biogas Recommendations"[1] (2020 Report) on recommendations regarding health-protective levels of trace constituents found in biogas, pursuant to the requirements of Assembly Bill 1900 (AB 1900, Chapter 602, Statutes of 2012). AB 1900 requires OEHHA and the California Air Resources Board (CARB) to compile a list of constituents of concern (COCs) that could pose risks to human health and that are found in varying sources of biogas at concentrations that significantly exceed the constituents in fossil natural gas. AB 1900 further requires the California Public Utilities Commission (CPUC) to adopt, by rule or order (1) standards for biomethane[2] that specify the concentrations of COCs that are reasonably necessary to protect public health and ensure pipeline integrity and safety, and (2) requirements for monitoring, testing, reporting, and recordkeeping. The bill ensures that no entity can inject biogas in a common carrier pipeline in California without meeting these standards and requirements. This supplement updates sources of COCs in biogas; COC risk management level concentrations; requirements for test methods, reporting, and recordkeeping; and realistic exposure scenarios.

2 Summary of OEHHA Updates in the 2020 Report

OEHHA and CARB published the first report to assess COCs in biogas in 2013, "Recommendations to the California Public Utilities Commission Regarding Health Protective Standards for the Injection of Biomethane into the Common Carrier Pipeline"[3] (2013 Report). In January 2020, OEHHA published the first update to the 2013 Report. The 2020 Report updates the list of COCs by removing three constituents from the 2013 list (copper, methacrolein, and toluene) and adding two new constituents (cadmium, chromium) and four chemical groups (chlorocarbons, fluorocarbons, silicon compounds, and sulfur compounds). The removal and addition of constituents and chemical groups were based on consideration of biogas combustion products, and updates to toxicity exposure factors. The 2020 Report also revised the hazard quotients (HQ) and cancer risk for all 15 COCs.

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[1] 2020 OEHHA Report. AB 1900 Biogas Recommendations, 2020. *https://oehha.ca.gov/media/downloads/air/report-document-background/biomethane010320.pdf*

[2] "Biomethane" refers to biogas that has been purified to a standard considered safe for pipeline injection. Biomethane is also commonly referred to as renewable natural gas (or "RNG").

[3] 2013 Report. Recommendations to the California Public Utilities Commission Regarding Health Protective Standards for the Injection of Biomethane into the Common Carrier Pipeline. *https://oehha.ca.gov/media/final_ab_1900_staff_report_appendices_051513.pdf*

3 CARB Updates and Recommendations

To fulfill the requirements of AB 1900 and as a supplement to OEHHA's 2020 Report, CARB staff:

1. Updated the source categories of COCs in biogas to include both "Food/Green" (food and green waste) and "Other" (additional sources without clear categorization) (Table 1).
    a. Defined Food and Green Waste
2. Updated the COCs found in study samples for each source (Table 1).
3. Determined the risk management level concentrations for COCs using updated risk values and recent cancer and non-cancer risk management thresholds (Table 2).
4. Updated recommended methods for COC testing requirements (Table 3).
5. Updated reporting and recordkeeping requirements to clarify language to the reporting schedule.

CARB staff also considered additional realistic scenarios and future work efforts as part of this supplement report.

CARB staff recommend that the above updates be accepted by CPUC to fulfill the requirements of AB 1900.

3.1 Addition of New Source Categories

CARB staff recommends biogas testing requirements for COCs (identified in the 2020 Report) from the sources shown in Table 1.

Table 1. Proposed testing requirements by biogas source.

Constituents of Concern	Landfills	Dairies	Sewage Treatment	Food/ Green	Other
1,4-Dichlorobenzene	X	X	X	X	X
Alkyl Thiols (mercaptans)	X	X	X	X	X
Antimony	X				X
Arsenic	X				X
Cadmium[a]		X	X		X
Chlorocarbons (as Cl)[a]	X	X	X	X	X
Chromium[a, b]	X		X		X
Ethylbenzene	X	X	X	X	X
Fluorocarbons (as F)[a]	X			X	X
Hydrogen Sulfide	X	X	X	X	X
Lead	X		X		X
N-nitroso-di-n-propylamine		X			X
Silicon Compounds (as Si)[a]	X	X	X	X	X
Sulfur Compounds (as S)[a]	X	X	X	X	X
Vinyl Chloride	X	X	X	X	X

[a] COCs added in the 2020 Report

[b] Following combustion, 2% of the total measured chromium is assumed to be Cr VI (Linak et. al 1996)[4], which the OEHHA 2020 Report used to develop exposure scenarios. Given this assumption, biomethane samples only need to be evaluated for total chromium.

3.2 2020 Risk Management Levels

CARB staff recommends the risk management level concentrations for COCs identified in the 2020 Report as shown in Table 2. Except for compound classes (chlorocarbons, fluorocarbons, silicon compounds, and sulfur compounds), COC concentrations should be reported as the individual compound.

[4] Linak, WP et al. Formation and Destruction of Hexavalent Chromium in a Laboratory Swirl Flame Incinerator, Combustion Science and Technology 116 (1996) 479-498.

Table 2. Recommended risk management level concentrations (mg/m^3, except for alkyl thiols in ppmv).[a]

Constituent of Concern	Trigger Level	Cancer Risk Lower Level	Cancer Risk Upper Level	Non-Cancer Risk Lower Level	Non-Cancer Risk Upper Level
1,4-Dichlorobenzene	4.3	42	100	N/A	N/A
Alkyl Thiols (ppmv)	17	N/A	N/A	170	860
Antimony	0.062	N/A	N/A	0.62	3.1
Arsenic	0.0020[g]	0.0040	0.010	N/A	N/A
Cadmium[b]	0.0020[g]	0.0032	0.0080	N/A	N/A
Chlorocarbons (as Cl) [b,c,d]	4.9	N/A	N/A	50	250
Chromium[b]	0.0020[g]	0.0048	0.012	N/A	N/A
Ethylbenzene	20	190	490	N/A	N/A
Fluorocarbons (as F) [b,d,e]	7.4	N/A	N/A	75	370
Hydrogen Sulfide[f]	63	N/A	N/A	860	4,300
Lead	0.047	N/A	N/A	0.47	2.3
N-nitroso-di-n-propylamine	0.028[g]	0.24	0.61	N/A	N/A
Silicon Compounds (as Si) [b,c,d]	0.49	N/A	N/A	5.0	25
Sulfur Compounds (as S) [b,c,d]	13	N/A	N/A	130	640
Vinyl Chloride	0.63	6.3	15	N/A	N/A

a. mg/m^3: milligrams per cubic meter; ppmv: parts per million by volume.
b. COCs added in 2020 Report.
c. A list of compounds for these chemical classes can be found in Appendix A.
d. This group of compounds was included based on potential exposure to combustion products.
e. A list of compounds for this chemical class can be found in Section 4.4.
f. The HPL concentration for hydrogen sulfide is based on the chronic worker exposure scenario found in Table I-1 of OEHHA's 2020 Report (86.8 mg/m^3).
g. The recommended value was set to the lowest detectable concentration. This value is expected to decrease as commercial laboratories improve monitoring technologies to reach the health protective level as recommended in OEHHA's 2020 Report.

3.3 Updated Test Methods

CARB staff recommends use of the test methods listed in Table 3 to measure COCs and chemical groups identified in the 2020 Report, as part of the testing requirements.

Table 3. Recommended test methods for COCs.[a]

Constituent of Concern	Test Method[b]
Metals	-
Lead, Antimony, Arsenic, Cadmium, Chromium	EPA Method 29 (AAS/ICP/ICP-MS)
Nitroso Compounds	-
N-nitroso-di-n-propylamine	**EPA Method TO-13A (GC/MS)**, EPA Method 8270 (GC/MS), **NIOSH 5528**
Sulfur Compounds	-
Hydrogen Sulfide	ASTM D4084, D7165, D7493, ASTM D5504, D6228 (lab), **D6968**
Sulfur Compounds (as total S)	ASTM D5504, D6228 (lab), **D6968**
Alkyl Thiols	ASTM D7165, D7493, D5504, D6228, D6968
Volatile Organic Compounds (VOCs)	-
p-Dichlorobenzene, Vinyl Chloride, Ethylbenzene	EPA Method TO-15, **TO-14A** (GC/MS)
Chlorocarbons (as Cl)	EPA Method TO-15, **TO-14A (GC/MS)**
Semi-Volatile Organic Compounds (SVOCs)	-
Silicon Compounds (as total Si)	ASTM D8230-19[c]
Fluorinated Compounds	-
Fluorocarbons (as F)	EPA Method TO-15, TO-14A[d]

a. New test methods are **underlined and bold**.

b. Select test methods will need modifications to measure the corresponding COC. CARB staff will explore creating a standardized list of these test method modifications in future updates.

c. When methods are established and/or are updated so that the detection limit is below 1 mg Si/m^3, they shall supersede the current method.

d. These methods do not capture eight fluorinated compounds identified in the OEHHA 2020 Report. An extended discussion on fluorocarbon methods can be found in Section 4.4 of this report.

3.4 Updated Monitoring and Reporting Requirements for COCs

CARB staff recommends the following monitoring requirements for COCs listed in Table 4. This table supersedes Figure V-1 in the 2013 Report.[2]

Table 4. Recommended monitoring requirements for COCs.

Monitoring Result	Action
Result < Trigger Level	Annual monitoring
Result < Trigger Level for 2 consecutive years	Monitor every two (2) years
Trigger Level ≤ Result < Lower Action Level	Quarterly monitoring until Result < Trigger Level for four (4) consecutive test results, then annual monitoring
Lower Action Level ≤ Result < Upper Action Level	Quarterly monitoring
Lower Action Level ≤ Result < Upper Action Level for 3 results in 1 year (12 months)	Shut off, resolve issue and retest
Upper Action Level ≤ Result	Shut off, resolve issue and retest

CARB proposes that California's four large gas utilities present a reasonable testing plan to the CPUC for approval with their tariff applications. CARB recognizes that testing for the new COCs is important and should start promptly. Therefore, CARB recommends that newly identified COCs should begin monitoring as soon as is feasible, with a minimum of one facility monitored no later than three (3) months after the CPUC formally approves any necessary utility tariff modifications. New COC testing should be completed for all injecting facilities as soon as feasible or within 12 to 18 months of tariff approval. Gas utilities receiving biomethane from a large number of facilities may have up to 18 months to complete new COC testing to accommodate current testing schedules. CARB strongly recommends independent third-party laboratory testing of biomethane samples for COCs.

CARB further recommends that once a production facility is operational, two sets of biomethane samples should be analyzed for COCs before pipeline injection to ensure proper performance of the system in place to refine the raw biogas to pipeline injection standards. Biomethane samples should be collected over a two-to-four (2-4) week period with at least two (2) weeks between sampling events to assess COC concentration variability. Pre-injection testing would not supersede requirements relating to pipeline integrity, heating value, and other non-health-based standards.

Exemptions to the testing and monitoring requirements are not being considered for this update.

3.5 Assessment of Realistic Exposure Scenarios

AB 1900 requires CARB to identify realistic exposure scenarios and associated health risks. OEHHA considered additional constituents in the 2020 Report associated with fuel combustion, namely the four chemical groups. From OEHHA's stovetop combustion scenario, the chemical groups account for the total elemental content (e.g., silicon compounds as total Si). This CARB Supplement Report did not identify scenarios that consider exposure to the additional constituents associated with fuel combustion. However, scenarios such as exposure to biogas flaring may be included in future assessments.

4 Discussion

4.1 Determination of "Food/Green" and "Other" as Biogas Source Categories

This report adds two new source categories, which expands monitoring and reporting requirements to include biogas sources not previously considered due to a lack of information regarding COCs. Producers and utilities are required to test for COCs according to the biogas source category, as shown in Table 1.

Since the publication of the 2013 Report, CARB staff reviewed two recent studies[5, 6] to identify additional biogas sources. The studies collected untreated and treated biogas samples from the following sources:

- Dairies
- Landfills
- Wastewater treatment plants
- Food waste digesters
- Dry and wet green waste facilities
- Solid waste facilities

The studies identified three additional sources of biogas: food waste digesters, dry and wet green waste facilities, and solid waste facilities. However, instead of including three additional source categories, CARB staff recommend creating a catch-all "Other" category, as well as a "Food/Green" waste category. Adding the "Other" category enables biogas monitoring from various sources as new biomethane projects come online. This ensures maximum testing requirements for biogas whose sources vary and/or COC composition is unknown.

The "Food/Green" waste category captures food waste and green waste, as well as the combination of both food and green wastes as a single source. Presently, there are multiple facilities processing combined food and green waste, with some already

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[5] Evaluation and Identification of Constituents Found in Common Carrier Pipeline Natural Gas, Biogas and Upgraded Biomethane in California. 2017. *https://ww2.arb.ca.gov/sites/default/files/2020-11/AB1900PhaseIReport.pdf*

[6] Evaluation and Identification of Constituents in Pipeline Natural Gas, Biogas, and Biomethane in California: Wastewater Treatment, Green Waste, and Landfills. 2020. *https://www.energy.ca.gov/sites/default/files/2021-05/CEC-500-2020-031.pdf*

injecting biomethane into the common carrier pipeline system and others contemplating doing so in the future. Food waste and green waste are defined as follows:

- Food waste: waste derived from plants, animals, or micro-organisms with the explicit intent of being consumed as food for humans or animals. This includes any biodegradable organic material that is typically mixed in with food waste, including but not limited to food-soiled paper or cardboard, food wrappers, egg cartons, and the like.

- Green waste: any biodegradable organic material resulting from yard, landscaping, forestry or agricultural activities, including but not limited to leaves, grass, shrubs, plants, branches, stumps and the like.

Table 1 lists COCs identified in biogas from the 2020 Report and each associated potential source. The biogas facility will be responsible for determining the source category based on the majority of their feedstock. The biogas facility will also be responsible for informing the utility operating the pipeline of this source category when negotiating the Standard Renewable Gas Interconnection Agreement. Testing and monitoring are required for individual COCs by source category.

For facilities utilizing co-digestion, where smaller amounts of different biogas source types are utilized to increase methane production from the majority source type, the source category used for monitoring would be determined by the majority biogas source type received. Should the feedstock mixture be evenly distributed between multiple categories, the facility will be required to test for all of the COCs selected for said categories. CARB staff will revisit these testing requirements as new information becomes available.

4.2 Updated COCs for each Biogas Source

Two previous research studies[4,5] identified several COCs present at very low concentrations in partially upgraded biogas or biomethane samples. However, CARB staff are not recommending that these trace COCs be included in testing requirements due to commercial lab detection limits (DLs). Research labs can achieve DLs much lower than commercial labs, a practical limitation when assigning COCs to categories and assigning testing requirements.

CARB staff added the testing requirement for a given COC based on two criteria: 1) COC presence in partially upgraded biogas or biomethane samples, and 2) COC concentrations found in published studies at levels commercial labs are capable of detecting. Based on these criteria, CARB staff made the following changes to previous monitoring requirements. The "Other" category must monitor for all 15 COCs.

- Landfills:
  - Added: chromium and 4 chemical classes (chlorocarbons, fluorocarbons, silicon compounds, sulfur compounds)
  - Removed: n-nitroso-di-n-propylamine
- Dairies:
  - Added: 1,4-dichlorobenzene, cadmium, vinyl chloride and 3 chemical classes (chlorocarbons, silicon compounds, sulfur compounds)
- Sewage Treatment:
  - Added: chromium, lead and 3 chemical classes (chlorocarbons, silicon compounds, sulfur compounds)
- Food/Green:
  - 1,4-dichlorobenzene, alkyl thiols, ethylbenzene, hydrogen sulfide, vinyl chloride and 4 chemical classes (chlorocarbons, fluorocarbons, silicon compounds, sulfur compounds)
- Other:
  - All 15 constituents

4.3 Determination of Risk Management Threshold Concentrations

4.3.1 Health Protective Level (HPL) Calculations

CARB staff determined the risk management threshold concentrations by utilizing the health protective level (HPL) concentration OEHHA calculated for each COC:

$$HPL = \frac{C_{source} \times Target\ Hazard\ Quotient\ or\ Cancer\ Risk}{Scenario\ Hazard\ Quotient\ or\ Cancer\ Risk}$$

HPL is calculated in mg/m^3 (or ppmv for alkyl thiols). C_{source} (mg/m^3 or ppmv for alkyl thiols) is the COC concentration in the biogas. The target hazard quotients, or target cancer risks, are the acceptable risk levels based on OEHHA's 2020 Report recommended risk management thresholds and are found in Table 5 of this document. The scenario hazard quotient (HQ) or scenario cancer risk is the modeled estimate concentration to which a resident or worker may be exposed to (Appendix I of the 2020 Report).

4.3.2 Risk Management Levels

CARB staff updated recommended risk management threshold concentrations for the 15 constituents/chemical groups in Table 1. Risk management threshold concentrations are the COC concentrations at or above which a biomethane production facility is required to take action. To determine the risk management level concentrations, CARB staff used the calculations described in 4.3.1 and commercially attainable DLs. Commercially attainable DLs determine the feasibility of detecting COCs at the determined risk management levels. Additional information regarding DLs is found in Section 4.3.3.

Risk management levels consist of the trigger level, lower action level, and upper action level for both cancer and non-cancer effects. The trigger level is the concentration at which an individual constituent results in a potential cancer risk of ≥1 in a million or a hazard index of ≥0.1. According to current requirements, if the COC concentration in the biogas exceeds the corresponding trigger level, then the operator is subject to quarterly monitoring for that COC. During each quarterly monitoring event, the operator determines the total potential cancer risk and hazard index for the COCs subject to monitoring and verifies if the risk levels are below the lower action level (cancer risk ≥10 in a million or a hazard index of ≥1). Table 5 summarizes recommended risk management levels for the COCs and actions if risk management levels are met or exceeded. More information on risk management levels is found in the 2013 Report.

Based on OEHHA's updated HPLs and the risk management thresholds defined in Table 5, CARB staff calculated updated trigger, lower action, and upper action levels. Table 6 lists the COCs and the trigger, lower action, and upper action level concentrations for the individual COCs. Note that OEHHA updated acute and chronic HQs in addition to cancer risk values in their 2020 Report. The risk value resulting in the most health protective risk management levels were used to update the trigger, lower action, and upper action levels in this report. In the case of sulfur compounds and alkyl thiols, risk management levels were calculated from acute HQs.

As mentioned in the 2013 report, the gas utilities monitor for sulfur compounds and alkyl thiols more frequently than is currently recommended. The gas utilities also require lower concentrations of these compounds than the proposed trigger levels. Therefore, it is unlikely these levels will be reached, let alone exceeded, due to the gas utilities' current standards and monitoring practices. If the utilities make any changes to allowable concentrations or monitoring frequency, we will reevaluate the monitoring and reporting schedule for sulfur compounds and alkyl thiols.

Table 5. Cancer and non-cancer risk management thresholds for biogas COCs

Risk Management Levels	Potential Cancer Risk (Chance in a million)	Non-Cancer Total Hazard Quotient	Action
Trigger Level [a]	≥ 1[b]	≥ 0.1[b]	Routine Monitoring Required
Action Range-Lower Level	≥ 10[c]	≥ 1[c]	After 3 exceedances in 12-month period, shut off & repair
Action Range-Upper Level	≥ 25[d]	≥ 5[d]	Immediate shut off and repair

a. The trigger level is applied to individual constituent of concern whereas the lower and upper levels are based on the sum of the potential cancer risk or hazard quotient for all the constituents of concern present at levels above the trigger level.
b. For any single compound
c. Sum of all compounds exceeding the trigger level
d. Sum of compounds exceeding the trigger level

4.3.3 Adjustments to Risk Management Level Concentrations

As previously noted, DLs in research studies are usually lower than the DLs of commercial labs. Upon reviewing commercial lab minimum DLs, CARB staff determined that they were not low enough to meet all 2020 trigger level concentrations in Table 6. This was the case for four compounds: arsenic, cadmium, chromium, and n-nitroso-di-n-propylamine. For the three metals (arsenic, cadmium, and chromium), commercial lab DLs were an order of magnitude higher than the proposed trigger level.

CARB staff adjusted the trigger levels for these four compounds to match the commercially attainable DL as the recommended (adjusted) risk management level concentrations (Table 2). CARB staff recommend adjusting risk management levels with the expectation that commercial laboratories will improve monitoring technologies and methodologies over time to improve DLs. Changes in adjusted risk management levels will be reevaluated in future updates.

Table 6. Calculated risk management level concentrations (mg/m^3, alkyl thiols in ppmv)

Constituent of Concern	Trigger Level	Cancer Risk Lower Level	Cancer Risk Upper Level	Non-Cancer Risk Lower Level	Non-Cancer Risk Upper Level
1,4-Dichlorobenzene	4.3	42	100	N/A	N/A
Alkyl Thiols (ppmv)	17	N/A	N/A	170	860
Antimony	0.062	N/A	N/A	0.62	3.1
Arsenic	0.00040[f]	0.0040	0.010	N/A	N/A
Cadmium[b]	0.00030[f]	0.0032	0.0080	N/A	N/A
Chlorocarbons (as Cl) [a,b,c]	4.9	N/A	N/A	50	250
Chromium[b]	0.00048[f]	0.0048	0.012	N/A	N/A
Ethylbenzene	20	190	490	N/A	N/A
Fluorocarbons (as F) [b,c,d]	7.4	N/A	N/A	75	370
Hydrogen Sulfide[e]	63	N/A	N/A	860	4,300
Lead	0.047	N/A	N/A	0.47	2.3
N-nitroso-di-n-propylamine	0.024[f]	0.24	0.61	N/A	N/A
Silicon Compounds (as Si) [a,b,c]	0.49	N/A	N/A	5.0	25
Sulfur Compounds (as S) [a,b,c]	13	N/A	N/A	130	640
Vinyl Chloride	0.63	6.3	15	N/A	N/A

a. A list of compounds for these chemical classes can be found in Appendix A.
b. COCs added in 2020 Report.
c. This group of compounds was included based on potential exposure to combustion products.
d. A list of compounds for this chemical class can be found in Section 4.4.
e. The HPL concentration for hydrogen sulfide is based on the chronic worker exposure scenario found in Table I-1 of the OEHHA's 2020 Report (86.8 mg/m^3).
f. These values are below current detection limits.

4.4 Recommended Test Methods

CARB staff recommends updating the test methods list from Table 3 to include newly added COCs from the 2020 Report and the corresponding recommended test method. In many cases, the recommended test method is unchanged from the 2013 Report. Certain test methods may require modifications to capture the indicated COC (e.g., NIOSH 5528 for n-nitroso-di-n-propylamine). CARB staff will explore creating a standardized list of these test method modifications in future updates.

In the case of fluorinated compounds (fluorocarbons (as F)), test methods are not readily available for many individual compounds. Several fluorinated compounds are detected by EPA Method TO-15 & TO-14A, but these methods do not capture all fluorinated compounds identified in the 2020 Report (Table 2, 2020 Report). For these and other fluorinated compounds, the most comprehensive test method found in the literature was utilized in the study "Emissions of Potential Greenhouse Gases from Appliance and Building Waste in Landfills"[7] (CARB 2016 Study), that utilized a University of California research laboratory for analysis of gas samples. The fluorinated compounds detected in the CARB 2016 Study are listed in Table 7.

A survey of available EPA methods indicates that only four methods would detect a small selection of the fluorinated compounds. EPA Methods TO-15, TO-14A, modified 8260B, and 8021B all detect the same fluorinated compounds. CARB staff recommends EPA Methods TO-15 & TO-14A given the following:

1) Compared to 8260B and 8021B, TO-15 & TO-14A would not require modifications by the laboratory, and
2) TO-15 is currently in use per 2013 Report monitoring recommendations

Staff evaluated additional test methods referenced in the CARB 2016 Study, but these methods are not standardized for commercial lab use. The first method[8] used water samples analyzed via gas chromatography and atomic adsorption resulting in the detection of two additional fluorinated compounds. The second[9] used adsorbent tubes for sample collection followed by combustion of the sample media via an oxyhydrogen torch; any acids produced are trapped in a scrubber containing water and the aqueous sample was exposed to an ion-selective electrode for analysis. These methods provide an

[7] CARB, 2016. Emissions of Potential Greenhouse Gases from Appliance and Building Waste in Landfills. *https://ww3.arb.ca.gov/research/apr/past/11-308.pdf*

[8] Haase, K. et al. Measurements of HFC-134a and HCFC-22 in groundwater and unsaturated-zone air: Implications for HFCs and HCFCs as dating tracers, Chemical Geology 385 (2014) 117–128

[9] Kissa, E. Determination of Organofluorine in Air, Environmental Science and Technology 20 (1986) 1254-1257

accurate representation of COC formation via combustion but are not a feasible option for commercial laboratories.

Table 7. Fluorinated Compounds Detected by UC (CARB 2016)

Compound	Test Method
trichlorofluoromethane	EPA Methods TO-15 & TO-14A
dichlorodifluoromethane	EPA Methods TO-15 & TO-14A
1,1,2-trichlorotrifluoroethane	EPA Methods TO-15 & TO-14A
1,2-dichlorotetrafluoroethane	EPA Methods TO-15 & TO-14A
dichlorofluoromethane	UC Research Lab
chlorodifluoromethane	UC Research Lab
1,1-dichloro-1-fluoroethane	UC Research Lab
1-chloro-1,1-difluoroethane	UC Research Lab
1-chloro-1-fluoroethane	UC Research Lab
1,1,1,2-tetrafluoroethane	UC Research Lab
1,1-difluoroethane	UC Research Lab
1,1,1,3,3-pentafluoropropane	UC Research Lab

4.5 In-State Production

CARB staff recognize that the costs of testing and monitoring requirements for AB 1900 may limit procurement of biomethane in California, such that future policies and programs to promote in-state production may be warranted. During the risk management strategy development, concerns were raised that the cost of COC testing may impede the economic viability of some biomethane production facilities. The costs of these recommended testing and monitoring requirements, along with any additional CPUC-mandated testing requirements to maintain pipeline integrity, could be placed solely on the biomethane producer and limit the number of viable production facilities.

CARB's proposed monitoring approach balances the costs for testing that may be required for COC monitoring with the need to demonstrate a process's removal efficiency in the early stages of operation. Given the potential for broad public benefits from increased use of biomethane, CARB encourages future conversations explore ways to minimize the testing cost burden on the biomethane producer, while ensuring that reasonable and prudent testing is conducted to protect both public health and pipeline integrity and safety.

5 Future Work

To better understand possible exposure scenarios, CARB may evaluate the following topics for further research:

1) Evaluation and characterization of total VOC emissions from facilities that produce biogas and/or biomethane.
    a. Monitoring VOC emissions from facilities that are converting from regular operations to biomethane production to understand possible changes in emissions.
    b. Characterize emissions from flares on-site of biogas facilities, specifically for VOCs and toxic chemicals. This would include both emergency flares and waste gas flares.
2) A follow up research study to the 2020 Report, "Chemical Toxicological Properties of Emissions from a Light-Duty Compressed Natural Gas Vehicle Fuel with Renewable Natural Gas,"[10] indicated the potential for toxicity and mutagenicity from combusted biomethane particulate matter. Mutagenic compounds can cause genetic mutations, potentially leading to heritable genetic diseases. While the previous study investigated mutagenicity of combusted biomethane from vehicle exhaust, future studies could investigate mutagenicity of combusted biomethane in other realistic exposure scenarios (e.g., stovetop cooking).
3) Further evaluate potential COCs of biogas and biomethane from non-anaerobic sources including post-combustion byproducts from other renewable gases (e.g., hydrogen, synthetic natural gas), and their sources (e.g., biomass).

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[10] Li, Y. et al. Chemical Toxicological Properties of Emissions from a Light-Duty Compressed Natural Gas Vehicle Fuel with Renewable Natural Gas. Environmental Science and Technology, 55 (2021) 2820-2830

6 References

1) 2020 OEHHA Report. AB 1900 Biogas Recommendations, 2020. *https://oehha.ca.gov/media/downloads/air/report-document-background/biomethane010320.pdf*

2) 2013 Report. Recommendations to the California Public Utilities Commission Regarding Health Protective Standards for the Injection of Biomethane into the Common Carrier Pipeline. *https://oehha.ca.gov/media/final_ab_1900_staff_report_appendices_051513.pdf*

3) Linak, WP et al. Formation and Destruction of Hexavalent Chromium in a Laboratory Swirl Flame Incinerator, Combustion Science and Technology 116 (1996) 479-498

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5) Evaluation and Identification of Constituents in Pipeline Natural Gas, Biogas, and Biomethane in California: Wastewater Treatment, Green Waste, and Landfills. 2020. *https://www.energy.ca.gov/sites/default/files/2021-05/CEC-500-2020-031.pdf*

6) CARB, 2016. Emissions of Potential Greenhouse Gases from Appliance and Building Waste in Landfills. *https://ww3.arb.ca.gov/research/apr/past/11-308.pdf*

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Appendix A: List of COCs to be Monitored for by Chemical Class

Chlorocarbons

The following chlorocarbons were monitored for in “Evaluation and Identification of Constituents Found in Common Carrier Pipeline Natural Gas, Biogas and Upgraded Biomethane in California” (2017), and “Evaluation and Identification of Constituents in Pipeline Natural Gas, Biogas, and Biomethane in California: Wastewater Treatment, Green Waste, and Landfills” (2020), using method EPA TO-15.

Dichlorodifluoromethane	2,2-dichloropropane
1,2-dichloro-1,1,2,2-tetrafluoroethane	1,2,3-trichloropropane
1,1,2-trichloro-1,2,2-trifluoroethane	3-chloropropene
Trichlorofluoromethane	1,1-Dichloropropene
Methylene chloride	cis-1,3-dichloropropene
Chloroform	trans-1,3-dichloropropene
Carbon Tetrachloride	1,1,2,3,4,4-hexachloro-1,3-Butadiene
Chloroethane	Chlorobenzene
1,1-dichloroethane	1,2-dichlorobenzene
1,2-Dichloroethane	1,3-dichlorobenzene
1,1,1-trichloroethane	1,4-Dichlorobenzene
1,1,2-trichloroethane	1,2,3-Trichlorobenzene
1,1,1,2-tetrachloroethane	1,2,4-trichlorobenzene
1,1,2,2-tetrachloroethane	2-Chlorotoluene
Chloroethene	4-Chlorotoluene
1,1-dichloroethene	Bromochloromethane
cis-1,2-Dichloroethene	Bromodichloromethane
Trans-1,2-dichloroethene	Dibromochloromethane
Trichloroethene	Bromochloroethane
Tetrachloroethene	1,2-dibromo-3-chloropropane
1,2-dichloropropane	

Silicon Compounds

ASTM D8230 currently monitors for:

Trimethylsilanol	Decamethyltetrasiloxane (L4)
Hexamethyldisiloxane (L2)	Decamethylcyclopentasiloxane (D5)
Hexamethylcyclotrisiloxane (D3)	Dodecamethylpenta-siloxane (L5)
Octamethyltrisiloxane (L3)	Dodecamethylcyclohexasiloxane (D6)
Octamethylcyclotetrasiloxane (D4)	

Sulfur Compounds

The following sulfur compounds were monitored for in "Evaluation and Identification of Constituents Found in Common Carrier Pipeline Natural Gas, Biogas and Upgraded Biomethane in California" (2017) and "Evaluation and Identification of Constituents in Pipeline Natural Gas, Biogas, and Biomethane in California: Wastewater Treatment, Green Waste, and Landfills" (2020), using method ASTM D6628.

Hydrogen Sulfide	Ethyl i-Propyl Disulfide
Sulfur Dioxide	Ethyl n-Propyl Disulfide
Carbonyl sulfide	Ethyl t-Butyl Disulfide
Carbon disulfide	Di-i-Propyl Disulfide
Carbon disulfide	i-Propyl n-Propyl Disulfide
Ethyl mercaptan	Di-n-Propyl Disulfide
Isopropyl mercaptan	i-Propyl t-Butyl Disulfide
Methyl mercaptan	n-Propyl t-Butyl Disulfide
n-Propyl mercaptan	Di-t-Butyl Disulfide
t-Butyl mercaptan	Dimethyl Trisulfide
Dimethyl sulfide	Diethyl Trisulfide
Methyl Ethyl sulfide	Di-t-Butyl Trisulfide
Diethyl sulfide	Thiophene
Di-tert-butyl sulfide	C1-Thiophenes
Dimethyl Disulfide	C2-Thiophenes
Diethyl Disulfide	C3-Thiophenes
Thiofuran	Benzothiophene
Methyl Ethyl Disulfide	C1-Benzothiophenes
Methyl i-Propyl Disulfide	C2-Benzothiophenes
Methyl n-Propyl Disulfide	Thiophane
Methyl t-Butyl Disulfide	Thiophenol