



**Recommendations to the California Public Utilities Commission
Regarding Health Protective Standards for the
Injection of Biomethane into the Common Carrier Pipeline**

May 15, 2013

**Prepared by Staff of the
California Air Resources Board and the
Office of Health Hazard Assessment**

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EXECUTIVE SUMMARY

Biogas is created when organic waste decomposes anaerobically (without oxygen). This can occur in landfills, covered lagoons, or enclosed vessels, where access to oxygen is limited. The decomposition (or “digestion”) process involves a series of steps in which microorganisms break down the organic waste, ultimately producing primarily methane and carbon dioxide. The raw (unprocessed) mixture of methane and carbon dioxide is referred to as biogas. Biogas can be processed or upgraded to increase the percentage of methane in the gas by removing carbon dioxide and other trace components. When biogas is upgraded to pipeline quality, it is referred to as biomethane. Biomethane is interchangeable with natural gas. In addition, biomethane offers several benefits including:

- Supporting energy diversity as a renewable energy source,
- Reducing greenhouse gas emissions,
- Promoting sustainable waste management practices, and
- Creating new jobs in California.

AB 1900, authored by Assemblyman Mike Gatto and chaptered into law on September 27, 2012 (Chapter 602, Statutes of 2012), requires the California Public Utilities Commission (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, the Office of Environmental Health Hazard Assessment (OEHHA) and the Air Resources Board (ARB), in consultation with other State agencies, are to undertake certain actions.

Specifically, OEHHA is tasked with compiling a list of constituents of concern found in biogas that could pose a health risk and that are at levels that significantly exceed the concentrations of those constituents found in natural gas. OEHHA is also to determine health protective levels for these constituents. ARB is tasked with developing realistic exposure scenarios and identifying the associated health risk to utility workers and gas end users; determining the concentrations of these constituents in biogas necessary to protect public health; and identifying monitoring, testing, reporting, and recordkeeping requirements necessary to ensure that health protective standards are maintained. These tasks are to be completed on or before May 15, 2013. Per AB 1900, ARB and OEHHA are not to consider pipeline integrity and safety aspects that may be associated with the use of biogas; the CPUC will address these aspects during its rulemaking process.

ARB and OEHHA staff worked together to fulfill the AB 1900 requirements and develop recommendations to inform the CPUC rulemaking process. For the evaluation and identification of the constituents of concern in biogas, ARB and OEHHA staff focused on the larger sources of biogas – landfills, dairies, and sewage treatment plants (POTWs). For each of these three sources, data is available regarding the constituents present in the biogas. Further, these three sources have the greatest potential to economically

inject biogas into the natural gas pipeline in California. ARB and OEHHA staff will address other sources of biogas i.e., crop residuals, food waste, woody biomass, energy crops, etc., in future updates as additional data becomes available regarding constituents present in these sources of biogas. Briefly summarized below are our findings and recommendations. Additional details can be found in the chapters that follow this executive summary.

Findings and Recommendations

Based on the available data, and depending on the biogas source, there are up to 12 constituents of concern that can potentially be present in raw biogas that if not sufficiently removed during the cleaning and upgrading processes may present health concerns.¹ These constituents are listed in Table ES-1, and as shown, not all of the constituents are found in each source of biogas. All 12 constituents of concern were present in landfill biogas, 6 were present in dairy biogas and 5 in POTW biogas.

Table ES-1: Constituents of Concern in Biogas

Constituents of Concern	Biogas Source		
	Landfills	Dairies	POTWs
Antimony	✓		
Arsenic	✓		
Copper ¹	✓		
p-Dichlorobenzene	✓		✓ ²
Ethylbenzene	✓	✓	✓
Hydrogen Sulfide	✓	✓	✓
Lead	✓		
Methacrolein	✓		
n-Nitroso-di-n-propylamine	✓	✓	
Mercaptans (Alkyl Thiols)	✓	✓	✓
Toluene	✓	✓	✓
Vinyl Chloride	✓		✓

OEHHA has recommended health protective levels for these constituents of concern consistent with OEHHA health risk assessment methodologies. In our review of the available data, the majority of the constituents of concern in the biogas were either not detected or reduced to concentrations below the OEHHA recommended health

¹Copper was not detected in any of the raw biogas but was detected in some samples of landfill biomethane, raising the possibility that it was introduced in either the upgrading equipment or the sampling apparatus used for testing. As discussed in Chapter V, we recommend that the status of copper be further evaluated by ARB staff during the CPUC rulemaking process to determine whether it is appropriate to require monitoring of this compound, or if the risk management approach needs to be adjusted.

² Errata: An error in the report released on May 15, 2013 resulted in p-Dichlorobenzene being checked as a constituent of concern for dairies instead of for POTWs. This error was corrected on May 23, 2013 and is reflected in this document.

protective levels during the upgrading process to biomethane indicating that from a public health perspective, the injection of biomethane does not present additional health risk as compared to natural gas.

ARB staff has recommended a risk management strategy based on the approach outlined in ARB's Risk Management Guidelines for New and Modified Sources of Toxic Air Pollutants (ARB, 1993) wherein trigger levels and lower and upper action levels for potential cancer risk and total non-cancer hazard indexes are identified and evaluated to ensure that health protective levels are adequately maintained.

Briefly, the trigger level is set at the OEHHA health protective level for each constituent of concern and operators are required to routinely monitor (quarterly or annually) the levels of compounds above the trigger levels to verify that the total potential cancer and non-cancer risks for the constituents of concern continue to stay within the trigger level and the lower and upper action levels.³ The constituents of concern that must be measured depend on the biogas source and the frequency of monitoring is dependent on the concentration level of a constituent of concern measured during an initial pre-injection screening evaluation. A facility must be shut-off (stop injecting into the pipeline) and repaired if the lower action level is exceeded three times in a 12 month period or at any time the levels exceed the upper action level. The recommended risk management levels for the constituents of concern are presented in Table ES-2. Additional details on the recommendations are provided in Chapter V of this report.

³ Both hydrogen sulfide and mercaptans are typically addressed by natural gas tariffs. In the event there is a natural gas or other tariff for these compounds that is lower than the OEHHA health protective level (trigger) then compliance with the tariff is sufficient for demonstrating compliance with the health protective standards recommended.

Table ES-2: Recommended Risk Management Levels for Constituents of Concern

Constituent of Concern	Risk Management Levels (Health Based Standards) mg/m ³ (ppmv)		
	Trigger Level	Lower Action Level	Upper Action Level
Carcinogenic Constituents of Concern			
Arsenic	0.019 (0.006)	0.19 (0.06)	0.48 (0.15)
p-Dichlorobenzene	5.7 (0.95)	57 (9.5)	140 (24)
Ethylbenzene	26 (6.0)	260 (60)	650 (150)
n-Nitroso-di-n-propylamine	0.033 (0.006)	0.33 (0.06)	0.81 (0.15)
Vinyl Chloride	0.84 (0.33)	8.4 (3.3)	21 (8.3)
Non-carcinogenic Constituents of Concern			
Antimony	0.60 (0.12)	6.0 (1.2)	30 (6.1)
Copper	0.060 (0.02)	0.60 (0.23)	3.0 (1.2)
Hydrogen Sulfide	30 (22)	300 (216)	1,500 (1,080)
Lead	0.075 (0.009)	0.75 (0.09)	3.8 (0.44)
Methacrolein	1.1 (0.37)	11 (3.7)	53 (18)
Alkyl Thiols (Mercaptans)	N/A (12)	N/A (120)	N/A (610)
Toluene	904 (240)	9,000 (2,400)	45,000 (12,000)

ARB and OEHHA staff will continue to work with CPUC staff as they adopt standards for constituents in biomethane and address any issues pertaining to incorporating health based standards with standards to maintain pipeline integrity and safety as required by AB 1900. Staff will also work to encourage incorporation of a streamlined pathway in the regulations to allow introduction of new sources of biomethane such as crop residuals, food waste, woody biomass, etc., in the event data becomes available and it is analyzed by OEHHA and ARB staff pursuant to AB 1900. In addition, ARB and OEHHA staff will continue to evaluate available data on constituents in biogas. As required by AB 1900 we will update the list of constituents of concerns, the health protective levels, and the monitoring, testing, reporting, and recordkeeping requirements at least every five years if data warrant.

ARB staff also recommends that the CPUC consider the cost of testing for constituents of concern as they identify impediments that limit procurement of biomethane in California and adopt policies and programs that promote the in-state production and distribution of biomethane pursuant to AB 1900. During the development of the risk management strategy, concerns were raised that the cost of testing for the constituents of concern may impede the economic viability of some biomethane production facilities. In response, ARB staff developed a monitoring approach that balanced the need to demonstrate the removal efficiency of a conditioning process in the early stages of operation and to reduce testing once the functionality of a system was verified. Even so, if all the costs for testing that may be required for monitoring of the health based

standards and any additional tests required when CPUC develops requirements to maintain pipeline integrity and safety are placed on the biomethane producer, it may limit the number of biomethane production facilities that will be viable. Given the broader public benefits from the increased use of biomethane, we recommend that the CPUC explore ways to minimize the testing cost burden to the biomethane producer, while at the same time ensuring that reasonable and prudent testing is conducted to protect both public health and pipeline integrity and safety.

References

(ARB, 1993) "Risk Management Guidelines for New and Modified Sources of Toxic Air Pollutants," California Air Resources Board, July 1993.
<http://www.arb.ca.gov/diesel/documents/rmg793.pdf>

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I. INTRODUCTION

In this chapter, we provide a brief description of biogas and biomethane and Assembly Bill 1900 (AB 1900). In addition, we discuss the scope of the Air Resources Board (ARB) staff recommendations to the California Public Utilities Commission (CPUC) and provide a brief overview of the information collected by ARB and the Office of Environmental Health Hazard Assessment (OEHHA) and the process used to develop the recommendations.

A. Biogas and Biomethane

Biogas is generated from the anaerobic digestion of organic materials.⁴ This can occur in landfills, covered lagoons, or enclosed vessels, where access to oxygen is limited. The chemical composition of biogas varies and is dependent on the source material (e.g. municipal waste water, livestock manure, food wastes, or municipal solid wastes), and the environmental conditions. Raw biogas consists primarily of methane (the main component in natural gas), carbon dioxide (CO₂), and smaller amounts of nitrogen, oxygen, and hydrogen. Depending on the waste stream, several trace gases can also be produced, including hydrogen sulfide, ammonia, and various volatile organic compounds. Particulates and biological components, such as bacteria, can also be present.

Biogas can be processed or upgraded to increase the percentage of methane in the gas by removing CO₂ and other trace components. When biogas is upgraded to pipeline quality, it is referred to as biomethane. Conversion of biogas into biomethane typically requires water removal, CO₂ separation (using adsorption, absorption, membrane separation, or cryogenic distillation technology), and compression.

(DOE, 2009) During biogas upgrading, trace constituents are removed to levels comparable to or below those in traditional pipeline natural gas. (NG, 2010) This is done with the same equipment (adsorption, absorption, membrane separation, or cryogenic distillation technology) that is needed to upgrade the biogas to meet pipeline quality (tariff) specifications. (AGL, 2013) According to the Coalition for Renewable Natural Gas, if a clean-up system is removing CO₂, it is also removing trace organic and particulate compounds in the gas stream. (RNG, 2013)

Biomethane is interchangeable with natural gas, and it offers several additional benefits. It is a renewable energy source that supports energy diversity, it has the potential to reduce greenhouse gas emissions, it promotes sustainable waste management practices, and its production and use creates jobs.

There are numerous biomethane projects in the United States that inject into the natural gas pipeline. According to the American Biogas Council (ABC), there are about 60 such projects nationwide. (ABC, 2013) Specifically, the ABC reported 33 landfill projects, one

⁴ Biogas can also be generated by thermal gasification systems, where waste is exposed to very high temperatures (greater than 700° C) within a reactor vessel to produce synthesis gases (“syngas”), such as carbon monoxide, carbon dioxide, methane, and hydrogen. Thermal gasification systems are not as prevalent as anaerobic digestion processes and were not evaluated by ARB and OEHHA staff.

farm-based project, and at least 25 POTWs (sewage treatment facilities). The United States Environmental Protection Agency's (U.S. EPA) Landfill Methane Outreach Program (LMOP) maintains a data base of landfill methane projects that provides further information on the 33 projects. The LMOP database indicates that the 33 projects that upgrade landfill biogas to pipeline quality ("high BTU") biomethane are located in 13 states. (U.S. EPA, 2013) Most of these projects began operation within the last ten years, but a couple of projects (Fresh Kills, NY; Rumpke, OH) have been in operation since the 1980s.

In California, there is currently one project where biomethane is injected into the common-carrier natural gas pipeline. The project is located at the San Diego Point Loma wastewater treatment plant. The project upgrades biogas (that was previously flared) to pipeline quality gas that meets Rule 30⁵ biomethane specifications. The gas is injected into the San Diego Gas and Electric pipeline for distribution to local customers. In addition, Pacific Gas and Electric (PG&E) worked with Bioenergy Solutions in 2006-2009 to develop a biomethane injection project at Vintage Dairy, located near Fresno. PG&E received delivery of biomethane from the project from October 2008 through December 2009. However, according to PG&E, the volumes of gas being delivered were not substantial enough to sustain the project as the economy deteriorated in 2009. The project subsequently ceased operations. Regarding landfill-derived biogas in California, there are a numerous landfill gas-to-energy projects, such as those that burn landfill gas in a boiler to power a steam turbine and generate electricity. However, none of these projects currently inject biomethane into the natural gas common carrier pipeline system due to utility tariffs prohibiting this.

In California, the primary potential sources of biogas are landfills, POTWs, and dairies/animal waste operations. Of these, landfills offer the greatest potential for generation. (NREL, 2010, <http://www.nrel.gov/docs/fy10osti/48057.pdf>)

B. AB 1900

AB 1900, authored by Assemblyman Mike Gatto and chaptered into law on September 27, 2012 (Chapter 602, Statutes of 2012), establishes a process to promote and facilitate the injection and use of cleaned biogas (biomethane) in common carrier pipelines. Under AB 1900, the CPUC is tasked with multiple duties including adopting standards for constituents in biogas to protect human health and pipeline integrity and safety. In adopting these standards, the CPUC is to give due deference to recommendations from ARB and OEHHA regarding health protective concentrations and monitoring, testing, reporting, and recordkeeping requirements for constituents of concern in each source of biogas. A copy of AB 1900 is provided in Appendix A to this report.

⁵ Rule 30 created by the Southern California Gas Company (SoCalGas) is a guideline meant to demonstrate how biomethane suppliers can meet their obligation to provide merchantable gas to SoCalGas. (SoCalGas, 2013)

As noted, in support of the CPUC standards development efforts, OEHHA and ARB are to develop recommended health protective standards and identify reasonable and prudent monitoring, testing, reporting, and recordkeeping requirements for each source of biogas. More specifically, AB 1900 requires the following actions be taken and completed on or before May 15, 2013:

OEHHA Actions

- In consultation with ARB, the Department of Toxic Substances Control (DTSC), the Department of Resources Recycling and Recovery (CalRecycle), and the California Environmental Protection Agency (Cal-EPA), compile a list of constituents of concern that could pose risks to human health and that are found in biogas, as defined, at concentrations that significantly exceed the concentrations of those constituents in natural gas.
- Determine the health protective levels for the list of constituents of concern.

ARB Actions

- Identify realistic exposure scenarios and in consultation with OEHHA, identify any health risks associated with the exposure scenarios for the constituents of concern identified.
- Determine the appropriate concentrations for constituents of concern.
- Identify reasonable and prudent monitoring, testing, reporting, and recordkeeping requirements, separately for each source of biogas, that are sufficient to ensure compliance with the health protective standards.

In addition, AB 1900 requires that ARB and OEHHA update the constituents of concern and health protective levels, exposure scenarios, and the health risks associated with the exposure scenarios, at least every five years.

AB 1900 provides that actions taken pursuant to the described requirements do not constitute regulations and are exempt from the Administrative Procedure Act.

C. Development Process and Scope of Recommendations

There are many types of organic materials that can be anaerobically digested to produce biogas. For this evaluation and identification of the constituents of concern in biogas, ARB and OEHHA staff focused on the larger sources of biogas – landfills, dairies, and POTWs. These are the sources with the greatest potential to economically inject into the natural gas pipeline in California and for which data is available regarding the constituents present in the biogas. ARB and OEHHA staff will address other sources of biogas (i.e., crop residuals, food waste, woody biomass, energy crops) in future updates as additional data becomes available regarding constituents present in these sources of biogas.

Staff analyzed the constituents in both raw (untreated) biogas and upgraded biogas (or biomethane) to determine what compounds may be present, the concentration of these compounds, and the potential for control technologies to reduce or remove these

compounds. The analysis focused on potential exposure to compounds in uncombusted biogas/biomethane and not on combustion products produced when the gas is burned. This is because staff expects most of the constituents of concern to be destroyed during combustion, and there is limited information available on potential combustion products. In Table I-1 below, we provide a brief overview of the tasks undertaken to develop the recommendations to the CPUC.

Table I-1: Overview of ARB and OEHHA Tasks

Task	Actions
Identify List of Constituents and Measured Concentrations	ARB and OEHHA staff reviewed available data on the composition of natural gas and biogas/biomethane and compiled a list of constituent data (chemical name and measured concentration). For each data set, the maximum concentration measured for each constituent was identified. Data was collected for natural gas, landfill, dairy, and POTWs. Approximately 270 chemicals and chemical groups were identified in biogas.
Develop Health Values for Constituents	OEHHA staff used four main sources of toxicity data and risk values for risk evaluation: OEHHA Reference Exposure Levels (RELs) for non-carcinogens, and Cancer Slope Factors for carcinogens, U.S. EPA Reference Concentrations and Cancer Slope Factors, Agency for Toxic Substances and Disease Registry (ATSDR) Minimal Risk Levels (MRLs), and worker protection values from Occupational Safety and Health Administration (OSHA), National Institute for Occupational Safety and Health (NIOSH), or American Conference of Industrial Hygienists (ACGIH). Risk-screening values were identified for 180 constituents, defined surrogate screening values for 25 chemicals and groups.
Develop Realistic Exposure Scenarios	ARB staff developed 4 scenarios: 2 residential and 2 worker exposure scenarios. The residential scenarios consist of a household leak and the pre-ignition phase of stove use. The worker scenarios consist of a biogas worksite leak and utility worker that is exposed to an indoor leak on a service call.
Model Exposure Scenarios	ARB staff developed assumptions for each scenario to determine appropriate exposure adjustment ratios. A simple box model with a given air exchange rate was used to calculate the dilution of the gas in the household or worksite.
Conduct Health Risk Screen (HRS)	Using the model derived developed exposure adjustment factors, OEHHA staff conducted a HRS using standard calculations to find the cancer, chronic, and acute risk from each constituent.
Identify Constituents of Concern Based on HRS	Constituents were identified as a constituent of concern if, based on the HRS, it was determined that the constituent: 1) had a potential cancer risk greater than one in a million for a residential scenario or 30 in million for a worker scenario or 2) had a potential acute or chronic hazard quotient greater than 0.01 for a residential scenario and 0.3 for a worker scenario. If a constituent was observed in both natural gas and biogas and the concentration in natural gas was significantly higher than that in biogas, the constituent was removed from the list.
Determine Health Protective Levels	Health protective levels were identified by OEHHA staff for each constituent of concern and were set at the concentrations that would result in a potential cancer risk of 1 in a million for the resident or 30 in a million for the worker for the cancer risk. OEHHA staff also calculated the health protective levels for the acute and chronic constituents using 0.1 and 3.0 as limits for the hazard quotient limit for the resident and worker, respectively.
Identify Risk Management Action Concentrations for Constituents of Concern	ARB staff established recommended risk management concentrations for constituents of concern similar with the framework outlined in ARB's Risk Management Guidelines for New and Modified Sources of Toxic Air Pollutants. (ARB,1993) wherein trigger levels and lower and upper action levels for potential cancer risk and total non-cancer hazard indexes are identified and evaluated to ensure that health protective levels are adequately maintained.
Identify Monitoring, Reporting and Recordkeeping Requirements	ARB staff recommended monitoring (testing) procedures based on the risk management guidelines above. Initial pre-injection testing would need to be performed on biomethane prior to its introduction into the pipeline to demonstrate that it is pipeline quality. After injection, periodic testing would be required, with the testing frequency based on the concentrations of the constituents of concern. ARB staff also recommended recordkeeping and reporting requirements. These include reporting startup testing results for new projects, a three year records retention requirement for test data of constituents of concern, and an annual report to the CPUC on test results.

ARB and OEHHA staff worked together to fulfill the AB 1900 requirements and develop recommendations to inform the CPUC rulemaking process. As noted earlier, existing sources of information were relied upon to develop the underlying technical foundation for the recommendations. To provide relevant information to interested stakeholders, a website and list serve were created. In December 2012, ARB and OEHHA staff posted an update on the website, inviting interested parties to provide comments or information that would assist with completion of the tasks under AB 1900. ARB and OEHHA staff met or consulted with several interested stakeholders including public utility representatives, representatives of the biogas industry, analytical equipment providers, Gas Technology Institute staff, U.S. EPA staff, landfill operators, biogas treatment manufacturers, and existing operators of biomethane production facilities where the biomethane is being injected into a common carrier pipeline. ARB and OEHHA staff also consulted with other State agencies including the California Energy Commission (CEC), DTSC, CalRecycle, and Cal-EPA. In addition, ARB and OEHHA staff participated in two public workshops hosted by the CPUC in support of the CPUC rulemaking activities. At each workshop, ARB and OEHHA staff provided updates on activities and presented preliminary information on the work conducted to date by ARB and OEHHA staff such as the list of constituents of concern, exposure scenarios, modeling results and monitoring, recordkeeping and reporting. One workshop was held in San Francisco on March 19, 2013 and the second was held in Sacramento on May 2, 2013. Informal discussion sessions open to all parties were held on April 10th and April 25th in Sacramento and notice of the discussion sessions were sent to the AB 1900 list serve.

References

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(U.S. EPA, 2013) "Current Landfill Methane Outreach Program (LMOP) List of Operational Projects," <http://www.epa.gov/lmop/projects-candidates/operational.html>

II. IDENTIFICATION OF BIOGAS CONSTITUENTS

Per AB 1900, OEHHA was tasked with developing a list of constituents of concern that could pose risks to human health and that are found in biogas⁶ at concentrations exceeding those found in natural gas, and to define health protective levels for these constituents. In this chapter, we summarize the primary sources of data used to identify constituents in biogas and provide the list of the constituents identified.

A. Data Sources for Constituents in Biogas

OEHHA and ARB staff compiled a list of constituents that have been identified in biogas derived mainly from landfills, dairies, and POTWs. A search was completed to identify studies published in the literature and reports from government agencies or industry groups. Staff also consulted with representatives from the Gas Technology Institute (GTI), biogas-related businesses, and California POTWs and landfills to obtain additional biogas and natural gas constituent data. Briefly summarized below are the sources of information used to identify biogas constituents:

- Five recent studies completed by GTI that identify and quantitate the constituents present in biogas derived from municipal landfills, dairies, POTWs, and natural gas in the United States and California. (GTI 2009 a, b, c, d; and GTI, 2012)⁷
- Biogas sampling data and other information for municipal landfills and POTWs in Southern California. (LACSD, 2012; SCAQMD, 2012; JWPCP, 2011)
- Reports on municipal landfill biogas constituents published by the U.S. EPA. (U. S. EPA, 2008) and the Environment Agency of the United Kingdom (UKEA, 2002)
- Emission testing results of a natural gas sample was obtained from *Air Liquide Advanced Technologies U.S. LLC*. (*Air Liquide*, 2012) A volatile fatty acid analysis of two dairy farm biomethane samples was also obtained from Pacific Gas & Electric Company. (PG&E, 2008)
- Several literature reports on specific constituents in biogases from municipal wastes and sewage sludge digestion. (Glindemann, et al. 2005; Grumping, et al. 1999; Hensel, et al. 2000; Hirner, et al. 1994; Rasi, 2009)

⁶ In this chapter we use the term biogas generally to refer to both raw biogas and upgraded biogas (i.e., biomethane).

⁷ According to GTI (GTI, 2013), Tables 23-30 were mislabeled in the GTI report titled "Pipeline Quality Biogas: Guidance Document for Dairy Waste, Wastewater Treatment Sludge and Landfill Conversion" DOT PROJECT NUMBER 250/GTI PROJECT NUMBER 20736, December 31, 2009. The units should be reported as ppb, corresponding to the data in the appendix.

Of the available data sources, the GTI reports and additional Southern California landfill and POTW data provided the most recent quantitative constituent data for landfill, dairy, POTW biogas, and natural gas, and were chosen as the primary source of constituent concentration data for the biogas evaluation. (We will refer to these studies together as the “GTI dataset.”) The GTI dataset was developed using defined and consistent analytical methodologies. The U.S. EPA and UKEA landfill gas reports and the academic papers on biogas constituents were used in a complementary way, mainly to identify additional constituents that were not analyzed or detected in the GTI dataset. The U.S. EPA and UKEA reports were particularly useful in identifying a long list of trace constituents, many of which are likely to be formed from the decomposition of biological materials present in municipal wastes. Although the number of these chemicals is large, their total content in raw landfill gas appears to be less than 0.1% (measured as non-methane organic carbon). The academic biogas studies were useful in helping to confirm the presence of volatile metallic compounds in biogas (e.g., methylated arsenic and antimony).

Although the GTI dataset was used to carry out the bulk of the risk evaluation, concentrations from the U.S. EPA landfill report (or “AP-42 update”) were used in a few instances where the primary dataset did not provide adequate coverage. In particular, we used the AP-42 update to help screen out several groups of toxicologically similar chemicals (see Section IV for details), and we used the GTI dataset together with AP-42 and *Air Liquide* data on benzene in comparing concentrations in biogas to natural gas (See Section IV).⁸

The decision to use the AP-42 concentration data in only a supplementary fashion was based upon the fact that its samples were collected mainly between 1996 and 2000. Staff judged that the AP-42 data was likely to be representative of current concentrations with regard to constituents that arise mainly from biological materials (e.g., green wastes, woody wastes, and food wastes), and would also be somewhat representative of BTEX compounds (benzene, toluene, ethylbenzene, xylene) since some Class II landfills accept petroleum-contaminated soils. However, the AP-42 data is expected to be less representative of California landfills for chemicals that have been increasingly regulated over the last two decades, for example many of the chlorinated solvents. An added reason for not using the AP-42 update as a general reference for concentration data was its variable data quality, with sample sizes ranging from 78 to 1 (landfills sampled) for any particular chemical listed.

B. Constituents in Biogas

Through this process we identified more than 300 individual constituents likely to be present in landfill, dairy, and POTW biogas, representing a broad range of chemical groups. The biogas constituents and chemical groups identified through this review process were compiled into 3 lists which are provided in Appendix B, Tables B-1

⁸ In our group risk evaluation we also used supplemental concentration data from UKEA 2002 and PG&E 2008 (See Section IV).

through B-3. Table B-1 contains constituents identified from the GTI dataset, B-2 contains a list of constituents that were found in landfill gas samples reported in the AP-42 update and the UKEA landfill report. Table B-3 contains chemicals reported in academic studies. Risk screening values were developed for as many of the chemicals on these three lists as was possible (these constituents and their screening values are listed in Chapter IV, Tables IV-1 and IV-2). In some cases, specific chemicals in the three tables of Appendix B were grouped together for the risk screening process (see Table IV-3). Further details of the risk evaluation (including the evaluation of chemical groups) are described in Section IV.

Concentrations of constituents in biogas, biomethane and natural gas from the GTI datasets are provided in Table B-4 of Appendix B. This is an Excel workbook containing individual worksheets for each set of gas data used in the health risk screening of the individual constituents. Specifically, there are 13 datasets: 3 for natural gas, 4 for landfill, 4 for POTW and 2 for dairy. Each worksheet contains data for individual constituent maximum concentrations from the specified data source and is separated by gas type (e.g. natural gas, raw dairy, clean dairy, etc.). Also included in the workbook are 3 additional worksheets summarizing the maximum concentrations for each constituent in natural gas, raw biogas, and cleaned (upgraded) biomethane.

It should be noted, that not all the constituents that have been identified in this evaluation process and listed in Appendix B could be quantitatively screened in the risk evaluation. In some cases, this was due to a lack of toxicity information (see Chapter IV Table IV-4 for a list of chemicals without criteria) and in some cases it was due to a lack of representative concentration data (in particular, this was a problem with respect to biogas combustion products, some of which we tentatively identify in Table B-3). In order to address these and other unavoidable uncertainties in our risk evaluation, we will continue to work with the CPUC in the rule-making process, and will also refine our risk analysis as more information becomes available for an update of these recommendations (which, depending upon circumstances could occur earlier than the 5-year statutory deadline for review).

Biological agents (biologicals) can also be found in both biogas and natural gas. For example, a recent report by GTI found levels of biologicals in landfill biomethane to be similar to those in natural gas. (GTI, 2012)

Based on a staff review of the available literature, there does not appear to be a significant health risk associated with biologicals in biomethane. A report prepared for the European Parliament examined the available literature and did not find any recorded examples of health problems associated with biological agents in biomethane that was injected into the natural gas pipeline. (Marcogaz, 2006) One of the studies they examined, conducted by the Swedish Institute for Veterinary Medicine (SIVM, 2005), measured biogas from four biogas plants, two sewage treatment plants and two co-digestion plants, before and after treatment. The results were compared with similar analyses of natural gas and air. The results showed very low levels of micro-organisms in biogas, similar in amount and type to natural gas. The amount of micro-organisms was found to be much lower than the levels in ambient air. Similar conclusions were

reached in a research paper that examined potential hazards in biogas. The authors concluded, based on the currently available data, that no microbial risk could be identified from the biogas injection into a gas pipeline network. (Naja et al., 2011)

In addition, the Pacific Gas and Electric Company conducted an analysis to address concerns associated with the 2008 introduction of dairy-based biomethane in the natural gas pipeline. The analysis of microbiological pathogens looked at concentrations of cells or cysts in the gas, and compared the results to minimum infectious dose levels. Based on their analysis, it was concluded that the levels found did not represent a risk of infection through exposure. (PG&E, undated)

Based on the available data, we concluded that biologicals in biomethane do not present additional health risks and did not conduct further analyses. However, we will continue to monitor for any new data and revisit biologicals in future AB 1900 updates if warranted.

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III. EXPOSURE SCENARIOS

In this chapter, we provide a description of the exposure scenarios developed and the approach used to assess the potential health risks associated with exposures to the constituents in biogas/biomethane.

A. Overview of Approach

ARB and OEHHA staff conducted a health risk assessment to assist in determining the constituents of concern present in biogas/biomethane from various sources (landfills, dairies, and POTWs). The health risk assessment consisted of two parts. First realistic exposure scenarios are defined for both residential and worker exposures. The exposure scenarios use mathematical models to estimate the concentrations of the chemical constituents to which a resident or worker could be exposed. Because the gas concentration decreases as the gas expands and is mixed with room air when it is emitted into a residence or a warehouse, these models provide exposure adjustment factors that are much less than one.

Second, established OEHHA guidelines and recommended health values are used to estimate the potential cancer risks and non-cancer health impacts (acute and chronic) for each constituent in the biogas/biomethane. The potential cancer risk is the potential for the chemical to cause cancer and is expressed as excess potential cancers in a population of one million, for a specified exposure duration (for example, 30 years for a resident and 25 years for a worker). For the chronic and acute impacts, we determined a hazard quotient (HQ), which is the ratio of the exposure concentration of the individual compound divided by its reference exposure level (REL). Only the trace components were evaluated in the assessment. The major components of the gas (methane, carbon dioxide, nitrogen, and oxygen) were not addressed and the rationale for this is discussed in Chapter IV.

In this chapter, we provide a description of the exposure scenarios and the development of exposure adjustment factors for each scenario. In Chapter IV, the exposure adjustment factors will be applied to the component concentrations and used to estimate cancer and non-cancer risks.

AB 1900 requires that we “identify realistic exposure scenarios” in evaluating the health risk. In our evaluation, we investigated four different exposure scenarios: two residential scenarios, two worker scenarios – one a biomethane production worker scenario and one utility worker scenario.⁹ A summary of the scenarios evaluated is provided in Table III-1.

⁹ On April 9, 2013 Southern California Gas Company representatives provided five additional utility worker scenarios, these scenarios are addressed qualitatively in this report.

Table III-1: Exposure Scenarios Evaluated

Scenario		Gas Streams Evaluated	Exposure Duration
Residential	Leak in home	Natural gas, 100% biogas from 3 different sources: landfill, dairy, and POTWs	24 hours a day for one year
Residential	Stovetop cooking (kitchen)		Two 2 hour cook periods per day for 30 years (24 hours per day exposure with 4 hours in kitchen and 20 hours in remainder of house)
Biomethane Production Worker	Biogas processing facility		8 hours per day, 261 days per year, working for 25 years
Utility Worker	Service call		8 hours per day, 261 days per year, working for 25 years

For all the scenarios, we modeled our approach using U.S. EPA –Indoor Air Modeling guidelines for the box model mass balance equations. (U.S. EPA, 1991) And, in each case, we applied the same models, scenarios and assumptions for evaluating each gas type, including natural gas. In our evaluation, we also relied on conservative concentration assumptions. For example, in each scenario, we assumed that there would be 100% concentration of the biogas, biomethane or natural gas in the delivery pipe and when multiple sources were included in a data set for a particular source, we used the highest measured concentrations for each compound.

B. Residential Exposure Scenarios

For residential exposures, it was assumed that an individual could potentially be exposed to biogas/biomethane indoors from an undetected leak or during cooking with a gas range.¹⁰ While there are other appliances that are typically gas fed – (i.e., furnace or hot water heater), – these appliances are typically vented to the outside air and are not expected to be a significant source of residential exposures to biogas/biomethane. The two exposure scenarios developed to represent realistic residential indoor exposures to biogas/biomethane emissions are presented below.

Residential Leak Exposure Scenario

In the residential leak scenario, the indoor exposure concentrations were modeled for residential exposure to unburned gas constituents due to a small constant gas leak. In this scenario, the indoor concentration was modeled based on a general mass balance

¹⁰ About 55% of California homes have gas stovetops. (CEC, 2005)

equation (U.S. EPA, 1991) where the steady state concentration is estimated as a function of the indoor source generation rate, the residential air exchange rate and the indoor volume. Exposure adjustment factors were estimated for a maximum 1-hour period (1 hr Max) and annual average concentrations¹¹ using the following equation:

$$C_i \left(\frac{\mu g}{m^3} \right) = C_o \left(\frac{\mu g}{m^3} \right) + \frac{S \left(\frac{\mu g}{hour} \right)}{v \left(\frac{l}{hour} \right) kV (m^3)} \quad \text{Eq. R1}$$

Where

C_i = indoor source concentration (mass/volume) for each individual constituent

C_o = outdoor source concentration (mass/volume)

v = air exchange rate (l/time)

S = indoor source generation rate (mass/time)

kV = effective indoor volume where k is a dimensionless fraction ($k=1$)

LR = gas leak rate (volume/time)

DF = modeled exposure adjustment factor (unitless)

$C_{constituent}$ = the measured concentration of the individual constituent

Only the concentration due to indoor source generation (gas stovetop or leak) was included in the model and the outside source concentration, C_o , was set to zero in this scenario. To determine the concentration of each individual constituent in the gas, the indoor source generation rate, S , is calculated as the measured concentration of the individual constituent in the gas multiplied by the gas leak rate as follows:

$$S \left(\frac{\mu g}{hour} \right) = C_{constituent} \left(\frac{\mu g}{m^3} \right) \times LR \left(\frac{m^3}{hour} \right) \quad \text{Eq. R2}$$

And the indoor concentration for each individual constituent becomes

$$C_i \left(\frac{\mu g}{m^3} \right) = C_{constituent} \left(\frac{\mu g}{m^3} \right) \times \frac{LR \left(\frac{m^3}{hour} \right)}{v \left(\frac{l}{hour} \right) kV (m^3)} \quad \text{Eq. R3}$$

Using the following formula, an exposure adjustment factor, DF was developed.

$$C_i \left(\frac{\mu g}{m^3} \right) = C_{constituent} \left(\frac{\mu g}{m^3} \right) \times DF \quad \text{Eq. R4}$$

Where the unit less exposure adjustment factor, is defined as follows:

$$DF = \frac{LR \left(\frac{m^3}{hour} \right)}{v \left(\frac{l}{hour} \right) kV (m^3)} \quad \text{Eq. R5}$$

For the residential leak exposure scenario, exposure adjustment factors for both an annual average and maximum 1-hour were calculated. In Chapter IV, the annual average exposure adjustment factor was used to calculate potential cancer and chronic

¹¹ For both the residential leak scenario and the residential stovetop scenario, the annual average exposure and calculated adjustment factor, is the same as the average 24 hour exposure since it was assumed that each day in the year had the same exposure.

non-cancer exposures and the 1-hour maximum exposure adjustment factor was used to calculate acute exposure.

The annual average was based on a 4-hour exposure to a higher concentration within the kitchen where the leak was located and a 20-hour exposure to the lower concentration within the total volume of the residence for each day.

$$DF(\text{annual average}) = \frac{4 \text{ hours} \times DF(\text{room}) + 20 \text{ hours} \times DF(\text{residence})}{24 \text{ hours}} \quad \text{Eq. R6}$$

The maximum 1-hour exposure adjustment factor was based on the highest exposure adjustment factor, calculated using the volume of the room.

For the residual leak scenario, mid-range inputs were selected for residence size, room size, and air exchange rate and are shown in Table III-2.

Table III-2: Inputs and Calculated Exposure Adjustment Factors for the Residential Leak Exposure Scenario

Input	Value	Comment
Residence Volume	396.43 m ³	1750 sq ft residence by 8 ft ceiling height
Room Volume	44.4 m ³	Room size 14 ft x 14 ft X 8 ft ceiling height or 1 room out of 9 rooms in the residence
Air Exchange Rate (ACH)	0.53 /hr	(U.S.EPA, 2002)
Leak Rate	0.003 m ³ /hr	0.75% of 122,000 ft ³ per year (0.4 m ³ /hr) consumption (1 million BTUs per year)
1-hour Maximum Exposure Adjustment Factor	1.275E-04	1-Hour maximum for acute evaluation
Annual Average Exposure Adjustment Factor	4.258E-05	Annual average for cancer and chronic evaluation

Since there was very limited data available on the possible ranges of residential leak rates, ARB staff used published values of gas losses in the natural gas delivery system to estimate leak rates. The leak rate¹² (0.003 m³/hr) was estimated based on a system wide gas loss rate of 0.75%¹³ of consumption applied to an estimated 1 million BTU per year consumption rate for a California residential consumer. While the 0.75% loss

¹² The ARB estimated leak rate of 0.003 m³/hour corresponds very well to the leak rate (0.0047 m³/hr) used in a study of allowable concentrations of renewable gas trace constituents done by IRIS Environmental for Southern California Gas Company. (IRIS, 2013)

¹³ 0.75 percent leakage rate estimate is a mid-range value between published loss rates of 0.1% (Wennberg, 2012) and 1.4% (EIA, 2012)

value also includes losses within the natural gas system prior to the consumer meter, staff felt that without more precise data, this estimate was a realistic value for a residential leak rate. Since residences can contain a large number of valves and fittings, it is possible that gas losses may be on the same magnitude as the system wide losses. A recent report on the sources of methane in the Los Angeles atmosphere provides an estimate somewhat similar to that used by ARB staff: approximately 2% loss occurring post-consumer metering (i.e. on the residential side of the gas meter) in the Los Angeles Basin. (Wennberg, 2012)

According to PG&E, the highest residential leak rate will be approximately 2.5 cubic feet per hour (0.07 m³/hr) as measured on the gas meter. (PG&E, 2013) If at this rate, the gas service worker cannot identify the leak source, then the gas service to the home must be shut off. As listed in Table III-3, a leak rate of 0.07 m³/hr would correspond to a maximum 1-hour exposure adjustment factor of 2.97E-03, about 18 times higher than the residential leak rate 1-hour maximum exposure adjustment factor presented in Table III-2.

As a further comparison to the calculated exposure adjustment factors provided in Table III-2, natural gas is federally required (CFR 192.625) to be odorized so that is detectable to a person with a normal sense of smell at a concentration of 1/5th of the lower explosive limit (LEL). For methane, the LEL is approximately 5% methane to air, by volume. Therefore, odorized methane should be detectable at concentration levels above 1%. A concentration of 1% methane to air, by volume, corresponds to a exposure adjustment factor of 0.01, which is about 60 times higher than the maximum 1-hour exposure adjustment factor provided in Table III-2. In studies done by one utility, the actual odor threshold for a resident may be as low as about 40 parts per million by volume (ppmv) (SCG, 2013). At 40 ppmv, the exposure adjustment factor would be about 4.00E-05, which is in the same range as the calculated residential exposure adjustment factor ARB staff is using.

Table III-3: Comparison of Residential Concentration Exposure Adjustment Factors to Estimated Concentrations for Gas Leak Shut Off Criteria and Odor Thresholds

Concentration or Leak Rate Assumption	Exposure Adjustment Factors
Residential leak rate scenario (leak rate at 0.003 m ³ /hr)	1.275E-04 (1-hr maximum)* 4.258E-05 (annual average)
PG&E Maximum leak rate of 0.07 m ³ /hr	2.97E-03 (1-hr maximum)* 7.73E-4 (annual average)
Odorized Concentration at 1/5 th methane lower explosive limit (CFR 192.625)	1.00E-02**
Odor threshold concentration at 40 ppmv of gas in air (0.004% gas in air). (SCG, 2013)	4.00E-05**

*We assumed that the concentration in the kitchen is higher than the concentration in the remainder of the home. Therefore, the higher 1-hour maximum adjustment factor reflects the higher exposure concentration while the resident is in the kitchen.

**1-hour maximum and annual average are the same since we assumed that the exposure concentrations were the same in all parts of the home.

Stovetop Cooking Exposure Scenario

For the stovetop scenario, we developed a model to represent typical cooking on a kitchen gas stovetop. Exposures to unburned gas constituents would occur during the pre-ignition period, in this case we assumed 5 seconds after the stove is turned on and before the automatic pilot ignites the flame.¹⁴ We assumed there would be two cooking activities per day, and that a volume of gas is emitted only during the pre-ignition phase with the concentration decaying over time due to mixing with air in the kitchen and outside air exchange. The modeling approach for this scenario is similar to the methodology used by the French Agency for Health and Safety in the Environment and Workplace. (Afsset, 2008) The key model inputs are provided in Table III-4.

Table III-4: Inputs for the Residential Kitchen Scenario*

Kitchen Scenario Inputs	Values
Daily Time Spent in Kitchen	4 hours/day
Daily Time Spent in the Remainder of the House	20 hours/day
Pre-Ignition Time	5 seconds*/ignition event
Hours Between Cooking Periods	7 hours*/day
Emission Rate	0.5 m ³ /hour per burner*
Number of Burners Used	3
Air Exchange Rate (ACH)	0.54/hr
Kitchen Room Volume	44.4 m ³
Residence Volume	396.43 m ³

* (Afsset, 2008)

The following equation was used to determine the decay rate of the biogas in the kitchen and in the rest of the house. (U.S. EPA 1991)

$$C_f = C_0 + (C_i - C_0) \times e^{-v(t-t_0)}$$

Eq. S1

Where:

C_f = concentration at time t

C_0 = constant outdoor concentration. Only the concentration due to indoor source generation was included in the model and the outside source concentration, C_0 , was set to zero in this scenario

C_i = initial indoor concentration

v = air exchange rate

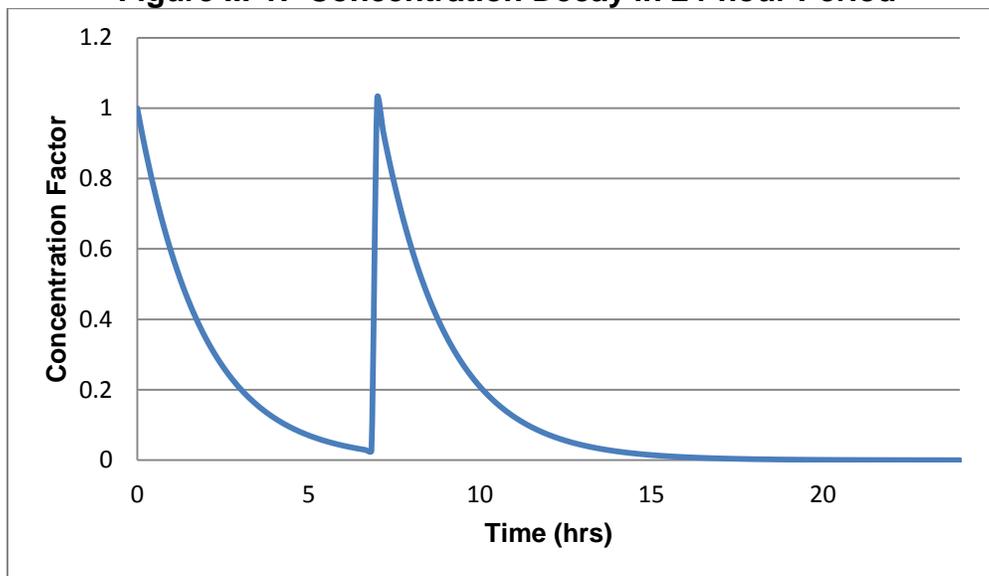
t = time (hours)

t_0 = initial time (hours)

¹⁴ In all scenarios, only the unburned gas constituents and emission rates were used. The potential combustion emission rates and combustion products were not included in the evaluation since there was limited data available on the combustion products of the trace constituents in biogas/biomethane. The major combustion components of both treated biomethane and natural gas, such as nitrogen dioxide (NO₂), carbon monoxide (CO), is likely to be similar.

In Figure III-1, we show the two concentration peaks from cooking and concentration decay after the pre-ignition phase over a 24-hour period.

Figure III-1: Concentration Decay in 24-hour Period



It was assumed that a resident would use the stovetop two times a day with 7-hours between use. The small remaining concentration from the first use is added to the second use. To determine the daily average emission factor to represent the 4 hours spent in the kitchen and 20 hours in the remainder of the house, equation S1 was integrated to find the area under the curve. The area under the curve (hours 1-2 and 7-8 spent in the kitchen) was divided by the time spent in the kitchen (4 hours) and the remaining area under the curve (hours 3-6 and 9-24 spent in the remainder of the house) was divided by the time spent in the remainder of the house (20 hours). Table III-5 below shows the average concentration factors (C/C_i) calculated for the stovetop scenario. In the potential cancer health risk evaluation in Chapter IV, we assumed that the resident would be exposed to the stovetop gas emissions for a maximum of 30 years.

Table III-5: Concentration Factors for Time Spent in the Kitchen and in the Remainder of the Residence

Exposure Location	Concentration Factor (EF)
Average Kitchen Concentration Factor (4 Hours)	$EF_k=0.629$
Average Residence Concentration Factor (20 Hours)	$EF_h=0.081$
Maximum Concentration Factor (at beginning of second cooking activity) (1 Hour)	$EF_{max}=1.02$

ARB staff used the average concentration factors to determine the final exposure adjustment factor for cancer risk and the chronic and acute hazard index. The equations for the cancer risk and chronic hazard index exposure adjustment factors are listed below in equations S2 - S4.

$$D_k = \frac{EF_k \times T_k \times ER \times T_i}{V_k} \quad \text{Eq. S2}$$

Where

D_k = exposure adjustment factor in the kitchen
 EF_k = concentration factor in the kitchen
 T_k = time spent in kitchen (hours)
 ER = emission rate of stovetop
 T_i = time of pre-ignition phase
 V_k = volume of the kitchen

$$D_h = \frac{EF_H \times T_h \times ER \times T_i}{V_h} \quad \text{Eq. S3}$$

Where

D_h = exposure adjustment factor in the residence
 EF_H = concentration factor in the residence
 T_h = time spent in remainder of house (hours)
 ER = emission rate of stovetop
 T_i = time of pre-ignition phase
 V_h = volume of the residence

$$D_T = \frac{D_k + D_h}{24 \text{ hours}} \quad \text{Eq. S4}$$

Where

D_T = annual average exposure adjustment factor

For the acute hazard index, ARB staff used the maximum 1-hour concentration factor which occurs at the start of the second use of the stovetop. The equation to find the 1-hour maximum exposure adjustment factor is listed in equation S5 as follows:

$$D_A = \frac{EF_{max} \times ER \times T_i}{V_k} \quad \text{Eq. S5}$$

Where

D_A = exposure adjustment factor in the kitchen for the 1-hour maximum acute analysis
 EF_{max} = maximum concentration factor in the kitchen

ER = emission rate of stovetop
 T_i = time of pre-ignition phase
 V_k = Volume of the kitchen

The exposure adjustment factors based on these equations are listed in Table III-6. As discussed in Chapter IV, OEHHA staff used the exposure adjustment factors and the biogas concentrations from the GTI datasets to calculate a modeled concentration factor for the stovetop scenario.

Table III-6: Exposure Adjustment Factor for the Kitchen Scenario

Kitchen Scenario Exposure Adjustment Factor	Value
1-Hour Maximum (Acute Exposure Adjustment Factor)	4.81E-05
Annual Average (Cancer and Chronic Exposure Adjustment Factors)	5.27E-06

C. Utility/Biogas Production Worker Scenarios

For workers, two scenarios were evaluated; one for a biogas production worker and one for a utility worker. These are described below. In addition, we briefly describe additional outdoor utility worker scenarios that were identified by Southern California Gas staff. While these scenarios are discussed here they were not quantitatively analyzed due to the fact that the resultant exposures would be less than the two indoor scenarios analyzed and described below.

Biomethane Production Facility Worker Leak Exposure Scenario

In the biomethane production facility worker leak scenario (biomethane worker scenario), the indoor (warehouse) exposure concentrations were determined similar to the residential leak scenario. In the biomethane worker scenario, the worker is exposed to unburned gas constituents due to a constant gas leak in the processing equipment. In this scenario, the indoor concentration was modeled based on a general mass balance, using equations R1-R5 (U.S. EPA, 1991) where the steady state concentration is estimated as a function of the indoor source generation rate (leak rate), the warehouse air exchange rate and the warehouse volume. Concentration exposure adjustment factors were calculated for a 1-hour maximum and an annual average.

In Chapter IV, the annual average exposure adjustment factor is used to calculate potential cancer risk and the chronic exposure and the 1-hour maximum exposure adjustment factor is used to calculate acute exposure. In the biomethane worker scenario, the leak concentration, the gas exposure concentration, warehouse volume and air exchange rate remain constant, therefore, the 1-hour maximum and the annual average are the same.

For the biomethane worker scenario, mid-range inputs were selected for warehouse size and air exchange rate as shown in Table III-6. Since there was no data available on the possible ranges of production facility leak rates, ARB staff estimated the leak rate as a percentage (0.1%) of a typical biogas production rate.

Table III-7: Inputs and Calculated Exposure Adjustment Factors for the Biomethane Worker Scenario

Input	Value	Comment
Warehouse volume	1417 m ³	2500 sq ft warehouse with 20 ft ceiling height
Air Exchange Rate (ACH)	1.4 /hr	(EPA, 2002)
Leak Rate	0.89 m ³ /hr	0.1% of 750000 ft ³ per day biomethane production rate (SEMPRA, 2013)
Calculated Exposure Adjustment Factors (1-hour maximum)	4.46E-04	1-hour maximum for acute evaluation
Calculated Exposure Adjustment Factors (average)	4.46E-04	Average for cancer and chronic evaluation

Utility Worker Service Call Exposure Scenario

In the utility worker service call exposure scenario (utility service worker scenario), the utility employee exposure is due to service calls to customers' residences to repair an appliance (range or stove) with a gas leak. This scenario was detailed as a realistic worker scenario in a presentation from Southern California Gas Company to ARB. (SCG, 2013) For this scenario, the worker is repeatedly exposed to unburned gas during short service calls as part of the employee's typical duties. Southern California Gas Company staff provided estimates of the number of services calls per day (3 calls per day on average) and duration of service calls (13 minutes per call) to ARB staff. In this scenario, the indoor concentration was modeled based on a general mass balance, using equations R1-R5 (U.S. EPA, 1991) where the steady state concentration is estimated as a function of the indoor source generation rate (leak rate), the residential air exchange rate and the volume of the kitchen. For consistency, ARB staff used the same leak rate (0.003 m³/hr) as was used in the residential leak rate scenario. Exposure adjustment factors were calculated for a 1-hour maximum and an annual average.

The annual average was based on 3 calls per day, each lasting 13 minutes as shown in equation U1.

$$DF (average) = \frac{13 \text{ minutes per call} \times 3 \text{ calls per day} \times DF(kitchen)}{24 \text{ hours} \times 60 \text{ minutes/hour}} \quad \boxed{\text{Eq. U1}}$$

The 1-hour maximum exposure adjustment factor was based on the highest 1-hour exposure as shown in equation U2.

$$DF (1 \text{ hour max}) = \frac{13 \text{ minutes per call} \times DF(\text{kitchen})}{60 \text{ minutes/hour}} \quad \boxed{\text{Eq. U2}}$$

For the utility service worker scenario making service call to customers' residences, the inputs were the same as the residential leak scenario and are summarized in Table III-8.

Table III-8: Inputs and Calculated Exposure Adjustment Factors for the Utility Worker Service Call Exposure Scenario

Input	Value	Comment
Room Volume (kitchen)	44.4 m ³	Room size 14 ft x 14 ft X 8 ft ceiling height or 1 room out of 9 rooms in the residence
Air Exchange Rate (ACH)	0.53 /hr	(U.S. EPA, 2002)
Leak Rate	0.003 m ³ /hr	0.75% of 122,000 ft ³ per year (0.4 m ³ /hr) consumption
Calculated Exposure Adjustment Factor (1-hour maximum)	2.76E-05	Maximum 1-hour concentration used in acute risk analysis
Calculated Exposure Adjustment Factors (average)	3.45E-06	Average concentration used in cancer and chronic risk analysis

Other Potential Utility Worker Scenarios

In a presentation to ARB and OEHHA staff, Southern California Gas staff provided five scenarios, in addition to the utility service call worker scenario modeled above. The additional scenarios included two processing/treatment operations, two transmission operations and one leak repair operation. (SCG, 2013) In all five of these scenarios, the utility worker exposure to unburned gas would occur outdoors. In outdoor exposure, the concentration of gas dilutes more rapidly, compared to an indoor exposure in a confined space. The indoor exposure scenarios developed by staff provide higher, more conservative, exposure concentrations. Therefore, the five additional outdoor exposure scenarios provided by Southern California Gas staff were not modeled in the exposure scenario evaluation.

D. Exposure Adjustment Factors

In our evaluation, we identified four realistic exposure scenarios: two residential scenarios, one biogas worker scenario and one utility worker scenario. A mass balance box model evaluation was performed for each of the scenarios to estimate the 1-hour maximum and the average exposure adjustment factor, as listed in Table III-9.

Table III-9: Calculated Exposure Adjustment Factors for the Residential and Worker Scenarios

Scenario	Annual Average Exposure Adjustment Factors	1-Hour Maximum Acute Exposure Adjustment Factors
Residential Leak Scenario	4.26E-05	1.28E-04
Residential Stovetop Scenario	5.27E-06	4.81E-05
Biomethane Production Facility Worker Leak Exposure Scenario	4.46E-04	4.46E-04
Utility Worker Service Call Exposure Scenario	3.45E-06	2.76E-05

For the two residential scenarios, the residential leak scenario has the larger factors (i.e., exposure concentrations will be higher). Therefore, in Chapter IV, the residential potential cancer and non-cancer risks are calculated using the residential leak rate scenario exposure adjustment factors. For the two worker scenario, the biomethane production facility worker scenario had the larger factors (i.e., exposure concentrations will be higher). For workers, potential cancer and non-cancer risk exposures are calculated using the biomethane production facility worker exposure adjustment factors.

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IV. CONSTITUENTS OF CONCERN AND HEALTH PROTECTIVE LEVELS

As discussed in Chapter II, we used readily available sources of information to identify more than 300 individual constituents likely to be present in biogas from landfills, dairies, and POTWs. Some of these constituents were substances of low toxicity that were judged at the outset to be of little health concern and therefore not further considered in the evaluation. One group of low-toxicity constituents was the atmospheric components: oxygen, nitrogen, hydrogen, and carbon dioxide. The second group was the low molecular weight alkanes: methane, ethane, and propane. In addition, although not considered to be low-toxicity, manganese and chromium were eliminated from further consideration since each was detected only once in all the sampling data that we reviewed. We therefore determined that these two constituents were not reliably detected in biogas.

After this initial screening process, the number of remaining biogas constituents was still quite large. However, as noted above, they are present in relatively small quantities; for instance, considered together they typically make up less than 0.1 percent of the carbon content of landfill biogas. In addition, many of the identified constituents appear to be derivatives of natural substances present in the biological materials from which the biogases originated. Examples of these types of chemicals are the groups of fatty acid esters and alkyl dienes and terpenes that have been found at trace levels in various studies (see Appendix B, Table B-2, Groups 5, 7 and 13 for specific examples of these chemicals). While toxicity information for many of these biologically-derived constituents is sparse, most of them are expected to be of relatively low concern from the perspective of health risk. In order to quantitatively evaluate as many biogas trace constituents as possible, staff carried out risk calculations for both individual chemicals where screening criteria were available, as well as for groups of chemicals likely to be toxicologically similar, and for which a suitable screening value could be developed. This process is described in more detail below.

A. Development of Health Values

OEHHA staff compiled inhalation health risk screening criteria for as many of the identified biogas, biomethane, and natural gas constituents as possible. Table IV-1 provides criteria for constituents with previously established values. Four sources of health criteria, listed in order of preference, were judged to be of sufficient quality to be included in this table and used for the biogas risk evaluation:

- OEHHA-derived toxicity criteria—e.g., Reference Exposure Levels (RELs) for non-carcinogenic toxicants and Inhalation Slope Factors (SFs) for carcinogens (including both published and proposed criteria)
- U.S. EPA toxicity criteria, which are similar to the OEHHA criteria in both form and method of derivation. U.S. EPA develops Inhalation Reference Concentrations (RfCs) for non-carcinogens and SFs for carcinogens. (In several cases, draft U.S. EPA values are used, based upon a preliminary independent

review and concurrence with the methodology upon which the criteria have been developed).

- Agency for Toxic Substances and Disease Registry (ATSDR) Acute and Chronic Minimal Risk Levels (MRLs), also similar to the OEHHA values.
- Occupational health criteria compiled by the U.S. Occupational Safety and Health Administration (OSHA) or the National Institute for Occupational Safety and Health (NIOSH). For chronic exposures, these are either OSHA Permissible Exposure Limits (PELs) for average exposures over a typical work shift, or similarly defined NIOSH Recommended Exposure Limits (RELs). Both agencies also define Short Term Exposure Limits (STELs) to protect against acute exposures. For some chemicals, NIOSH exposure limits or those recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) are more health-protective than the OSHA standards. In these cases, OEHHA used the most health-protective value available. We then applied an additional uncertainty factor (UFH) of 30 to these limits to protect sensitive members of the general population, as occupational standards are not based solely on health criteria but include cost and technical feasibility considerations. Further, they are developed for healthy working adults. An additional conversion factor was included in developing the chronic exposure criteria. This adjustment was made to account for the fact that occupational exposure guidelines are based upon an assumption of less-than-continuous workplace exposure.

Table IV-2 contains screening criteria for chemicals lacking established inhalation values, but for which surrogate values could be defined. Surrogates were based on established values for toxicologically similar chemicals, or in other cases, by route-to-route extrapolation of oral toxicity criteria for the chemicals in question. Table IV-3 contains 15 groups of chemicals whose toxicological properties are likely to be similar. Health screening criteria for total air concentrations of chemicals in these groups were defined by choosing a surrogate chemical within each group with the most restrictive individual screening value.

Table IV-4 lists chemicals and groups for which OEHHA has not identified screening criteria in the current recommendations. We propose to further evaluate these for future document updates. The development of additional toxicity information related to the biogas constituents will involve additional literature review, use of physiologically-based pharmacokinetic (PBPK) modeling, and dose-response modeling.

Conversion Calculations

The health risk criteria for inhalation exposures in Tables IV-1 are reported in units of microgram per cubic meter ($\mu\text{g}/\text{m}^3$) for non-carcinogens, and reciprocal milligrams per kilogram-day (per $\text{mg}/\text{kg}\text{-d}$) for carcinogens. For criteria derived from ATSDR MRLs (reported in units of parts-per-million) or obtained from occupational exposure limits, the published values were converted as follows.

For ATSDR MRLs:

$$\text{Risk Criterion } \left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{MRL (ppm)} \times \text{Molecular Weight } \left(\frac{\text{g}}{\text{mol}}\right) \times 1000 \left(\frac{\text{l}}{\text{m}^3}\right)}{24.45 \left(\frac{\text{l}}{\text{mol}}\right) (\text{molar volume, ideal gas at STP})^{15}}$$

To convert an OSHA PEL (or NIOSH REL or ACGIH TWA) (40-hour work week) to a biogas project screening value:

$$\text{Risk Criterion } \left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{REL } \left(\frac{\text{mg}}{\text{m}^3}\right) \times 40 \left(\frac{\text{hr}}{\text{wk}}\right) \times 1000 \left(\frac{\mu\text{g}}{\text{mg}}\right)}{168 \left(\frac{\text{hr}}{\text{wk}}\right) \times 30 (UF_H)}$$

For cases where STELs were used to develop an acute screening value, the UFH of 30 was applied without the additional adjustment for exposure duration.

Table IV-2 contains several criteria derived via route-to-route extrapolation of oral reference doses (RfDs). To obtain the inhalation values, the oral criteria were multiplied by a body weight-to-breathing rate factor of 3.5 kg/m³. The criteria presented in Table IV-3 for chemical groups are in units of parts-per-million (ppm). Estimating risk based on ppm values assumes that the toxicity of any particular member of a group is proportional to the number of molecules absorbed, as opposed to the weight absorbed. Any criteria reported in µg/m³ in the original sources were converted to ppm (see ATSDR MRL conversion above).

¹⁵ SATP = Standard Ambient Temperature and Pressure.

Table IV-1: Health Risk Criteria for Biogas Constituents with Established Values^{16,17}

Constituent	CAS	Acute NC ($\mu\text{g}/\text{m}^3$)	Source Acute	Chronic NC ($\mu\text{g}/\text{m}^3$)	Source Chronic	SFi (kg-d/mg)	Source SFi
Acetaldehyde	75-07-0	4.7E+02	OEHHA REL	1.4E+02	OEHHA REL	1.0E-02	OEHHA SFi
Acetone	67-64-1	6.2E+04	ATSDR MRL	3.4E+04	ATSDR MRL		
Acetonitrile	75-05-8	3.5E+03	OSHA PEL	6.0E+01	USEPA RfC		
Acrolein	107-02-8	2.5E+00	OEHHA REL	3.5E-01	OEHHA REL		
Acrylonitrile	107-13-1	7.2E+02	OSHA PEL	5.0E+00	OEHHA REL	1.0E+00	OEHHA SFi
Allyl Chloride	107-05-1	2.0E+02	OSHA PEL	1.0E+00	USEPA RfC	2.1E-02	OEHHA SFi
Ammonia	7664-41-7	3.2E+03	OEHHA REL	2.0E+02	OEHHA REL		
Aniline	62-53-3			1.0E+00	USEPA RfC	5.7E-03	OEHHA SFi
Arsenic (inorganic and arsine)	7440-38-2	2.0E-01	OEHHA REL	1.5E-02	OEHHA REL	1.2E+01	OEHHA SFi
Benzene	71-43-2	1.3E+03	OEHHA REL	6.0E+01	OEHHA REL	1.0E-01	OEHHA SFi
Benzyl Chloride	100-44-7	2.4E+02	OEHHA REL			1.7E-01	OEHHA SFi
Bis(2-chloroethyl)ether	111-44-4					2.5E+00	OEHHA SFi
Bis(2-ethylhexyl)phthalate	117-81-7			1.0E+01	OEHHA Draft REL	8.4E-03	OEHHA SFi
Bromomethane	74-83-9	3.9E+03	OEHHA REL	5.0E+00	OEHHA REL		
Butadiene, 1,3-	106-99-0	6.6E+02	Draft OEHHA REL	7.0E+00	OEHHA Draft REL	6.0E-01	OEHHA SFi
Butane, n-	106-97-8			1.5E+04	NIOSH REL		

¹⁶ This table contains health values for constituents that were identified in the studies reviewed. Since representative biogas concentration data was not available for every table entry, risk calculations were performed on only a subset of 95 of the listed constituents. Also note that screening criteria were omitted for the following groups: Polychlorinated Dibenzodioxins/Dibenzofurans, Polychlorinated Biphenyls, and the carcinogenic Polyaromatic Hydrocarbons; these constituents were not measured above detection limits in the studies reviewed.

¹⁷ Abbreviations are defined at the end of the table.

Table IV-1: Health Risk Criteria for Biogas Constituents with Established Values^{16,17}

Constituent	CAS	Acute NC ($\mu\text{g}/\text{m}^3$)	Source Acute	Chronic NC ($\mu\text{g}/\text{m}^3$)	Source Chronic	SFi (kg-d/mg)	Source SFi
Butanol, n-	71-36-3	5.0E+03	OSHA PEL	6.0E+01	USEPA Draft RfC		
Butanone, 2-	78-93-3	1.3E+04	OEHHA REL	5.0E+03	USEPA RfC		
Butoxyethanol, 2-	111-76-2			1.9E+02	NIOSH REL		
Carbon Disulfide	75-15-0	6.2E+03	OEHHA REL	8.0E+02	OEHHA REL		
Carbon monoxide	630-08-0	2.3E+04	OEHHA REL				
Carbon Tetrachloride	56-23-5	1.9E+03	OEHHA REL	4.0E+01	OEHHA REL	1.5E-01	OEHHA SFi
Carbonyl Sulfide	463-58-1	6.5E+03	OEHHA Draft REL	2.2E+02	OEHHA Draft REL		
Chlorobenzene	108-90-7			1.0E+03	OEHHA REL		
Chloroform	67-66-3	1.5E+02	OEHHA REL	3.0E+02	OEHHA REL	1.9E-02	OEHHA SFi
Chloromethane	74-87-3	1.0E+03	ATSDR MRL	9.0E+01	USEPA RfC		
Chloroprene	126-99-8			2.0E+01	USEPA RfC	1.1E+00	USEPA IUR
Chlorotoluene, 2-	95-49-8	1.3E+04	NIOSH REL	2.0E+03	NIOSH REL		
Copper and compds.	7440-50-8	1.0E+02	OEHHA REL	2.0E-02	OEHHA Draft REL		
Cresols (methylphenol isomers)	1319-77-3			6.0E+02	OEHHA REL		
Crotonaldehyde	123-73-9			4.8E+01	OSHA PEL		
Cumene (Isopropylbenzene)	98-82-8			4.0E+02	USEPA RfC	8.4E-02	OEHHA Draft SFi
Cyclohexane	110-82-7			6.0E+03	USEPA RfC		
Cyclopentane	287-92-3			1.4E+04	NIOSH REL		
DDT, 4,4'-	50-29-3					3.4E-01	USEPA IUR
Dibromochloromethane	124-48-1					9.4E-02	OEHHA SFi
Dibromoethane, 1,2-	106-93-4	3.3E+01	NIOSH REL	8.0E-01	OEHHA REL	2.5E-01	OEHHA SFi

Table IV-1: Health Risk Criteria for Biogas Constituents with Established Values^{16,17}

Constituent	CAS	Acute NC ($\mu\text{g}/\text{m}^3$)	Source Acute	Chronic NC ($\mu\text{g}/\text{m}^3$)	Source Chronic	SFi (kg-d/mg)	Source SFi
Dichlorobenzene, 1,2-	95-50-1	1.0E+04	OSHA PEL				
Dichlorobenzene, 1,4-	106-46-7	1.2E+04	ATSDR MRL	8.0E+02	OEHHA REL	4.0E-02	OEHHA SFi
Dichlorodifluoromethane	75-71-8			1.0E+03	OEHHA Draft REL		
Dichloroethane, 1,1-	75-34-3					5.7E-03	OEHHA SFi
Dichloroethane, 1,2-	107-06-2			4.0E+02	OEHHA REL	7.2E-02	OEHHA SFi
Dichloroethene, 1,1-	75-35-4			7.0E+01	OEHHA REL		
Dichloropropane, 1,2-	78-87-5			4.0E+00	USEPA RfC	3.6E-02	OEHHA SFi
Dichloropropene, trans-1,3-	10061-02-6			2.0E+01	USEPA RfC	1.4E-02	USEPA IUR
Di-n-butyl phthalate	84-74-2			5.3E-01	OEHHA MADLi		
Dioxane, 1,4-	123-91-1	3.0E+03	OEHHA REL	3.0E+03	OEHHA REL	2.7E-02	OEHHA SFi
Endosulfan I	959-98-8			3.3E-01	CDPR RfC		
Endrin	72-20-8			7.9E-01	OSHA PEL		
Epichlorohydrin	106-89-8	1.3E+03	OEHHA REL	3.0E+00	OEHHA REL	8.0E-02	OEHHA SFi
Ethyl Chloride	75-00-3	4.0E+04	ATSDR MRL	3.0E+04	OEHHA REL		
Ethyl Mercaptan	75-08-1	4.3E+01	NIOSH REL	1.0E+01	ACGIH TLV		
Ethylbenzene	100-41-4	2.2E+04	ATSDR MRL	2.0E+03	OEHHA REL	8.7E-03	OEHHA SFi
Ethylene Oxide	75-21-8	3.0E+02	NIOSH REL	1.0E+00	OEHHA MADLi	3.1E-01	OEHHA SFi
Formaldehyde	50-00-0	5.5E+01	OEHHA REL	9.0E+00	OEHHA REL	2.1E-02	OEHHA SFi
Formic acid	64-18-6			7.1E+01	OSHA PEL		
Furanmethanol, 2-	98-00-0	2.0E+03	ACGIH STEL	3.2E+02	ACGIH TWA		

Table IV-1: Health Risk Criteria for Biogas Constituents with Established Values^{16,17}

Constituent	CAS	Acute NC ($\mu\text{g}/\text{m}^3$)	Source Acute	Chronic NC ($\mu\text{g}/\text{m}^3$)	Source Chronic	SFi (kg-d/mg)	Source SFi
Furfural	98-01-1			1.6E+02	OSHA PEL		
Heptachlor	76-44-8					4.1E+00	Cal PHG data
Heptachlor epoxide	1024-57-3					5.5E+00	Cal PHG data
Heptane, n-	8031-33-2	6.0E+04	NIOSH REL	2.8E+03	NIOSH REL		
Hexachlorobenzene	118-74-1					1.8E+00	OEHHA SFi
Hexachlorocyclopentadiene	77-47-4			2.0E-01	USEPA RfC		
Hexane, n-	110-54-3	6.0E+04	NIOSH REL	7.0E+03	OEHHA REL		
Hexanone	591-78-6			3.2E+01	NIOSH REL		
Hydrogen cyanide	74-90-8			9.0E+00	OEHHA REL		
Hydrogen Sulfide	7783-06-4	4.2E+01	OEHHA REL	1.0E+01	OEHHA REL		
Isopropanol	67-63-0	3.2E+03	OEHHA REL	2.0E+03	OEHHA Draft REL		
Lead	7439-92-1			2.5E-02	OEHHA MADLi	4.2E-02	OEHHA SFi
Mercury (alkyl compds)	593-74-8	1.3E+00	OSHA PEL	8.0E-02	OSHA PEL		
Mercury (inorganic)	7439-97-6	6.0E-01	OEHHA REL	3.0E-02	OEHHA REL		
Methacrylic Acid	79-41-4			5.6E+02	OSHA REL		
Methyl Isobutyl Ketone	108-10-1			3.0E+03	USEPA RfC		
Methyl Mercaptan	74-93-1	3.3E+01	NIOSH REL	7.9E+00	ACGIH TLV		
Methyl Methacrylate	80-62-6			1.0E+02	OEHHA Draft REL		
Methylal	109-87-5			2.5E+04	OSHA PEL		
Methylcyclohexane	108-87-2			1.3E+04	ACGIH TWA		
Methylene Chloride	75-09-2	1.4E+04	OEHHA REL	4.0E+02	OEHHA REL	3.5E-03	OEHHA SFi

Table IV-1: Health Risk Criteria for Biogas Constituents with Established Values^{16,17}

Constituent	CAS	Acute NC ($\mu\text{g}/\text{m}^3$)	Source Acute	Chronic NC ($\mu\text{g}/\text{m}^3$)	Source Chronic	SFi (kg-d/mg)	Source SFi
Methylphenol, 3-	108-39-4			6.0E+02	OEHHA REL		
Methylphenol, 4-	106-44-5			6.0E+02	OEHHA REL		
Methyl-t-butylether (MTBE)	1634-04-4			8.0E+03	OEHHA REL	1.8E-03	OEHHA SFi
Naphthalene	91-20-3			9.0E+00	OEHHA REL	1.2E-01	OEHHA SFi
Nitrobenzene	98-95-3			9.0E+00	USEPA RfC	1.4E-01	USEPA IUR
Nitrosodiethanolamine, n-	1116-54-7					2.8E+00	OEHHA SFi
Nitrosodiethylamine, n-	55-18-5					3.6E+01	OEHHA SFi
Nitrosodimethylamine, n-	62-75-9					1.6E+01	OEHHA SFi
Nitrosodi-n-butylamine, n-	924-16-3					1.1E+01	OEHHA SFi
Nitrosodi-n-propylamine, n-	621-64-7					7.0E+00	OEHHA SFi
Nitrosomorpholine, n-	59-89-2					6.7E+00	OEHHA SFi
Nitroso-n-methylethylamine, n-	10595-95-6					2.2E+01	OEHHA SFi
Nitrosornicotine, n-	16543-55-8					1.4E+00	OEHHA SFi
Nitrosopiperidine, n-	100-75-4					9.4E+00	OEHHA SFi
Nitrosopyrrolidine, n-	930-55-2					2.1E+00	OEHHA SFi
Octamethylcyclotetrasiloxane	556-67-2	4.0E+03	OEHHA REL	7.0E+02	OEHHA REL		
Pentachlorophenol	87-86-5			1.0E+02	OEHHA Draft REL	1.8E-02	OEHHA SFi
Pentane, n-	8031-35-4	6.0E+04	NIOSH REL	2.8E+03	NIOSH REL		
Perchloroethane	67-72-1			3.0E+01	USEPA RfC	3.9E-02	OEHHA SFi
Phenol	108-95-2	5.8E+03	OEHHA REL	2.0E+02	OEHHA REL		
Phosphine	7803-51-2			8.0E-01	OEHHA REL		
Polybrominated Biphenyls	13654-09-6					3.0E+01	OEHHA SFi
Propane	74-98-6			1.4E+04	OSHA PEL		
Propene	115-07-1			3.0E+03	OEHHA REL		

Table IV-1: Health Risk Criteria for Biogas Constituents with Established Values^{16,17}

Constituent	CAS	Acute NC ($\mu\text{g}/\text{m}^3$)	Source Acute	Chronic NC ($\mu\text{g}/\text{m}^3$)	Source Chronic	SFi (kg-d/mg)	Source SFi
Propionaldehyde	123-38-6			8.0E+00	USEPA RfC		
Propylene Oxide	75-56-9	3.1E+03	OEHHA REL	3.0E+01	OEHHA REL	1.3E-02	OEHHA SFi
Pyridine	110-86-1			1.2E+02	OSHA PEL		
Styrene	100-42-5	2.1E+04	OEHHA REL	9.0E+02	OEHHA REL		
Sulfur Dioxide	7446-09-5	6.6E+02	OEHHA REL	7.8E+01	Federal NAAQS		
Tetrachloroethane, 1,1,2,2-	79-34-5			5.5E+01	NIOSH REL	2.0E-01	OEHHA SFi
Tetrachloroethylene	127-18-4	2.0E+04	OEHHA REL	3.5E+01	OEHHA REL	2.1E-02	OEHHA SFi
Tetrachlorophenol, 2,3,4,6-	58-90-2			9.0E+01	OEHHA Draft REL		
Tetrahydrofuran	109-99-9			2.0E+03	USEPA RfC		
Thiophenol	108-98-5	1.7E+01	NIOSH REL				
Toluene	108-88-3	3.7E+04	OEHHA REL	3.0E+02	OEHHA REL		
Tribromomethane	75-25-2			4.0E+01	NIOSH REL		
Trichloroethane, 1,1,1-	71-55-6	6.8E+04	OEHHA REL	1.0E+03	OEHHA REL		
Trichloroethane, 1,1,2-	79-00-5					5.7E-02	OEHHA SFi
Trichloroethylene	79-01-6	3.6E+04	OSHA PEL	6.0E+02	OEHHA REL	7.0E-03	OEHHA SFi
Trichlorofluoromethane	75-69-4	1.9E+05	ACGIH STEL	2.0E+04	OEHHA Draft REL		
Trichlorophenol, 2,4,6-	88-06-2					7.0E-02	OEHHA SFi
Trimethylbenzene, 1,2,3-	95-63-6			2.0E+01	USEPA Draft RfC		
Trimethylbenzene, 1,2,4-	95-63-6			2.0E+01	USEPA Draft RfC		

Table IV-1: Health Risk Criteria for Biogas Constituents with Established Values^{16,17}

Constituent	CAS	Acute NC ($\mu\text{g}/\text{m}^3$)	Source Acute	Chronic NC ($\mu\text{g}/\text{m}^3$)	Source Chronic	SFi (kg-d/mg)	Source SFi
Trimethylbenzene, 1,3,5-	108-67-8			2.0E+01	USEPA Draft RfC		
Vinyl Acetate	108-05-4			2.0E+02	OEHHA REL		
Vinyl Chloride	75-01-4	1.8E+05	OEHHA REL	1.0E+02	USEPA RfC	2.7E-01	OEHHA SFi
Xylenes (any isomer or mixture)	1330-20-7	2.2E+04	OEHHA REL	7.0E+02	OEHHA REL		
Zinc	7440-66-6	5.0E+02	OSHA PEL (ZnO)	9.0E-01	OEHHA Draft REL		

Abbreviations:
 OEHHA REL or SFi = OEHHA Reference Exposure Level (for Acute or Chronic Non-Cancer "NC" Effects) or Inhalation Slope Factor (for carcinogens)
 USEPA RfC or IUR = USEPA Reference Concentration or Inhalation Unit Risk
 OSHA PEL or NIOSH REL = Federal OSHA Permissible Exposure Limit or NIOSH Recommended Exposure Level (adjusted for exposure duration with added UF of 30)
 ACGIH TLV = ACGIH Threshold Limit Value (adjusted for exposure duration with added UF of 30)
 OEHHA MADLi = OEHHA Maximum Allowable Dose Level (Inhalation)
 CDPR RfC = California Department of Pesticide Regulation Reference Concentration
 CalPHG = California Public Health Goal for Drinking Water

Table IV-2: Non-Cancer Health Risk Criteria for Biogas Constituents based on Route-to-Route Extrapolation or Chemical Surrogates¹

Constituent	CAS	Acute ($\mu\text{g}/\text{m}^3$)	Source Acute (Surrogate Chemical)	Chronic ($\mu\text{g}/\text{m}^3$)	Source Chronic (Surrogate Chemical)
Antimony	7440-36-0	--	--	2.0E-01	Draft OEHHA REL (SbO ₃)
Acenaphthene	83-32-9	--	--	2.1E+02	USEPA Oral RfD converted to REL
Anthracene	120-12-7	--	--	1.1E+03	USEPA Oral RfD converted to REL
Fluoranthene	206-44-0	--	--	1.4E+02	USEPA Oral RfD converted to REL
Fluorene	86-73-7	--	--	1.4E+02	USEPA Oral RfD converted to REL
Pyrene	129-00-0	--	--	1.1E+02	USEPA Oral RfD converted to REL
Methylnaphthalene, 1-	90-12-0	--	--	1.3E+01	OEHHA REL (Naphthalene)
Methylnaphthalene, 2-	91-57-6	--	--	1.3E+01	OEHHA REL (Naphthalene)
Methacrolein	78-85-3	2.5E+00	OEHHA REL (Acrolein)	3.5E-01	OEHHA REL (Acrolein)
Abbreviations: OEHHA REL = OEHHA Reference Exposure Level USEPA RfD = USEPA Oral Reference Dose					

¹ This table contains health values for constituents that were identified in the various studies reviewed. However, representative biogas concentration data was not available for every table entry such that risk calculations were performed on a subset of the listed constituents.

Table IV-3: Non-Cancer Biogas Screening Criteria for Various Chemical Groups

Group	Group Name	Description of Group Membership	Group Surrogate Chemical	Acute (ppm)	Source Acute	Chronic (ppm)	Source Chronic
1	Alkanes (6 Carbons or less) ¹	Group 1 alkanes listed in Appendix B tables	n-Pentane	20	NIOSH REL 610 ppm	0.95	NIOSH REL 120 ppm
2	Alkanes (7 Carbons or more) ¹	Group 2, Appendix B	n-Heptane	14.7	NIOSH REL 440 ppm	0.67	NIOSH REL 85 ppm
3	Cycloalkanes	Group 3, Appendix B	Cyclohexane	--	--	1.7	USEPA RfC 6 mg/m ³
4	"n-Hexane-Like" Chemicals	Group 4, Appendix B, plus n-hexane	n-Hexane	17	NIOSH REL 510 ppm	2	OEHHA REL 7 mg/m ³
5	Alkenes and Dienes	Group 5 Appendix B, plus propene	Propene	--	--	1.7	OEHHA REL 3 mg/m ³
8	Alcohols ¹	Group 8, Appendix B	n-Butanol	16.7	OSHA PEL 50 ppm	0.02	USEPA RfC (draft) 0.06 mg/m ³
9	Ethers	Group 9, Appendix B, plus tetrahydrofuran	Tetrahydrofuran	--	--	1.59	OSHA PEL 200 ppm
10	Aldehydes	Group 10, Appendix B	Propionaldehyde	--	--	0.003	USEPA RfC 0.008 mg/m ³
11	Ketones ¹	Group 11, Appendix B	Methyl Ethyl Ketone	--	--	0.34	OEHHA REL (draft) 1 mg/m ³
12	Carboxylic Acids	Group 12, Appendix B	Acetic Acid (Acute) Formic Acid (Chronic)	0.5	NIOSH REL 15 ppm	0.04	OSHA PEL 5 ppm

¹ These groups do not include chemicals that share a toxicological similarity to either n-hexane or its metabolites.

Table IV-3: Non-Cancer Biogas Screening Criteria for Various Chemical Groups

Group	Group Name	Description of Group Membership	Group Surrogate Chemical	Acute (ppm)	Source Acute	Chronic (ppm)	Source Chronic
13	Esters	Group 13, Appendix B, plus ethyl acetate	1,3-Dimethylbutyl Acetate	--	--	0.4	NIOSH REL 50 ppm
19	Chlorofluorocarbons (CFCs)	Group 19, Appendix B	Trichlorofluoromethane (Acute) Dichlorodifluoromethane (Chronic)	33	ACGIH STEL 1000 ppm	0.24	OEHHA REL (draft) 1 mg/m ³
20	Alkyl Thiols (Mercaptans)	Group 20, Appendix B	Alkyl Thiols	0.017	NIOSH REL 0.5 ppm	0.004	ACGIH TWA 0.5 ppm
22	Siloxanes	Group 22, Appendix B	D4 Siloxane	0.3	OEHHA REL 4 mg/m ³	0.058	OEHHA REL 0.7 mg/m ³

Table IV-4: Biogas Constituents and Groups Lacking Inhalation Criteria

CAS	Constituent or Group
208-96-8	Acenaphthylene
	Alkyl sulfides (Group 21)
	Alkynes (Group 14)
	Benzenes (Alkyl; Groups 15 and 16)
	Benzenes (Chlorinated; Group 18)
	Benzenes (Styrenes; Group 17)
191-24-2	Benzo(g,h,i)perylene
95-16-9	Benzothiazole
100-51-6	Benzyl alcohol
259-79-0	Biphenylene
33617-38-8	Bis(trimethylsiloxy)benzaldehyde, 2,4-
75-27-4	Bromodichloromethane
74-96-4	Bromoethane
111-34-2	Butane, 1-(ethenyloxy)-
1615-75-4	Chloro-1-fluoroethane, 1-
95-57-8	Chlorophenol, 2-
540-54-5	Chloropropane, 1-
72-54-8	DDD, 4,4'-
5385-75-1	Dibenzo(a,e)fluoranthene
74-95-3	Dibromomethane
	Dichlorobutene
156-60-5	Dichloroethene, trans-1,2-
120-83-2	Dichlorophenol, 2,4-
27554-26-3	Diisooctylphthalate
	Dimethoxymethyl propanoate
	Dimethyl furan
1066-42-8	Dimethyldisilanol
575-43-9	Dimethylnaphthalene, 1,5-
593-80-6	Dimethyltelluride
646-06-0	Dioxolane, 1,3-
7421-93-4	Endrin aldehyde
5101-44-0	Ethynylphenol, 2-
10401-11-3	Ethynylphenol, 3-
110-00-9	Furan
72-43-5	Methoxychlor
	Methyl furan
78-94-4	Methyl vinyl ketone

Table IV-4: Biogas Constituents and Groups Lacking Inhalation Criteria

CAS	Constituent or Group
	Methyl-1,3-butadiene, 2-
625-74-1	Methyl-1-nitropropane, 2-
	Methylated Arsenic compounds
	Pentadiene, 1,3-
85-01-8	Phenanthrene
	Propanal, 3-(ethylthio)-
	Propylthiophene
1551-27-5	Propylthiophene, 2-
75-65-0	t-Butyl alcohol
	Tetrachloroethane
630-20-6	Tetrachloroethane, 1,1,1,2-
97-99-4	Tetrahydro-2-furanmethanol
110-02-1	Thiophene
95-95-4	Trichlorophenol, 2,4,5-
	Trifluorobenzene
594-10-5	Trimethylantimony
593-91-9	Trimethylbismuth
1066-40-6	Trimethylsilanol
	Trimethyltin compounds

B. Biogas Constituents of Concern

OEHHA staff completed a risk screening evaluation for individual biogas constituents having toxicity screening criteria and for the toxicity groups defined in Table IV-3. We used the exposure adjustment factors derived by ARB staff for the residential and worker scenario air models (see Chapter III section D) along with the highest measured constituent concentration values (primarily from the GTI dataset) to estimate potential health risks. High values from the GTI dataset were used for calculating potential exposure to the individual biogas constituents (See Appendix B Table B-4). For evaluating the groups, both GTI data and concentrations from the AP-42 Update, Table 2-8, were used.¹ Hazard quotients were calculated by taking the ratio of the effective exposure concentration to the appropriate non-cancer screening value for each constituent having non-cancer criteria.

Potential cancer risks were estimated for the residential and worker scenarios using OEHHA Air Toxics “Hotspots” risk assessment guidelines (OEHHA, 2012). For residential risks, the guidelines recommend age-specific values for breathing rate and time spent at home, as well as age-specific sensitivity factors. The values used for the stovetop (non-combustion) exposure scenario are provided in Table IV-5:

Table IV-5: Exposure Parameters for Cancer Risk Calculations				
Age Category (yr)	IR _i = Inhalation rate (m ³ /kg-d)	ED _i = Exposure duration (yr)	SF _i = Sensitivity factor (unitless)	FAH _i = Fraction of time at home (unitless)
3 rd Trimester	0.361	0.3	10	0.85
0 < 2	1.09	2	10	0.85
2 < 16	0.745	14	3	0.72
16 < 30	0.335	14	1	0.73

The formula to estimate the weighted-average exposure for each biogas constituent for the four age categories throughout a 30.3 year exposure period is:

$$Exposure\ Rate\ \left(\frac{mg}{kg \cdot day}\right) = C_r \times DF_r \times \left(\frac{1}{AT}\right) \sum_{i=1}^4 IR_i \times ED_i \times SF_i \times FAH_i$$

Where IR_i, ED_i, SF_i, and FAH_i are defined as above, and where:

C_r = Constituent concentration in biogas (raw and cleaned) in a residence (highest measured values, mg/m³)

¹ In two instances other data sources were used to estimate exposure concentrations, as specified in Table IV-9, below.

DF_r = Modeled long-term exposure adjustment factor for a residence (unitless)

AT = Averaging time to pro-rate less-than-lifetime exposures in cancer risk calculations (70 yr)

To calculate a “high-end” value for exposure in the 1-year residential gas-leak scenario, only the exposure parameters for the “0 < 2” year age group were used in the formula.

The equation for the worker exposure scenario is:

$$\text{Exposure Rate} \left(\frac{\text{mg}}{\text{kg} \cdot \text{day}} \right) = \frac{C_w \times DF_w \times IR_w \times EF_w \times ED_w}{AT}$$

Where:

C_w = Constituent concentration in biogas in a workplace (highest measured values, mg/m³)

DF_w = Modeled long-term exposure adjustment factor for a workplace (unitless)

IR_w = Worker 8-hour breathing rate (0.23 m³/kg-8 hr); 95th percentile for moderate exertion)

EF_w = Exposure frequency (5/7 d/d)

ED_w = Duration of employment (25 yr; 95th percentile value)

AT = Averaging time to pro-rate less-than-lifetime exposures in cancer risk calculations (70 yr)

A factor to account for the number of weeks per year worked (49/52) was not added to the exposure calculation since many production workers regularly work overtime hours (e.g., recent Department of Labor statistics indicate that the average overtime hours for production workers is approximately 4 hours per week.) The exposure rates were then multiplied by the Inhalation Slope Factors to produce estimated lifetime cancer risk estimates.

The preliminary biogas constituents of concern were then defined according to the following rationale. For chemicals with quantified risks, constituents whose risk values were greater than the following risk-thresholds were placed on the list:

- Residential Exposure Scenario: 0.01 for HQs and 1E-6 (1 chance per million) for cancer risks
- Worker Exposure Scenario: 0.3 for HQs and 3E-5 (30 chances per million) for cancer risks

The risk thresholds for the worker scenario were set at 30 times the values for the general population, which is consistent with the method used above to derive general

public health criteria from OSHA or NIOSH risk criteria (where an additional safety factor of 30 was applied to the occupational value to protect sensitive members of the general population). The potential cancer risks and the acute and chronic hazard quotients for the biogas constituents and groups are provided in Tables IV-6 through IV-9. The constituents that had cancer risks or hazard quotients greater than the screening values were placed on the list of preliminary constituents of concern. (The preliminary constituents of concern are highlighted in the tables.)

Table IV-6: Cancer Risk Estimates for Biogas/Biomethane Constituent Concentrations with the Highest Risk (top 10 risks shown; chemicals exceeding screening risks highlighted)

Raw Biogas				
Constituent	SFi ¹ (kg-d/mg)	Conc. (mg/m ³)	Risk Residential	Risk Worker
Arsenic	1.2E+01	3.39E-01	1.79E-05	1.07E-04
Benzene	1.0E-01	9.58E+00	4.21E-06	2.51E-05
Vinyl Chloride	2.7E-01	2.38E+00	2.82E-06	1.68E-05
p-Dichlorobenzene	4.0E-02	1.52E+01	2.66E-06	1.59E-05
n-Nitroso-di-n-propylamine	7.0E+00	6.23E-02	1.91E-06	1.14E-05
Ethylbenzene	8.7E-03	3.47E+01	1.33E-06	7.92E-06
Naphthalene	1.2E-01	1.14E+00	5.99E-07	3.58E-06
1,2-Dichloroethane	7.2E-02	1.82E+00	5.76E-07	3.44E-06
1,1,2-Trichloroethane	5.7E-02	2.07E+00	5.19E-07	3.10E-06
Tetrachloroethylene	2.1E-02	5.56E+00	5.13E-07	3.06E-06
Biomethane				
Constituent	SFi (kg-d/mg)	Conc. (mg/m ³)	Risk Residential	Risk Worker
Benzene	1.0E-01	3.19E+00	1.40E-06	8.37E-06
Vinyl Chloride	2.7E-01	8.44E-01	1.00E-06	5.97E-06
n-Nitroso-di-n-propylamine	7.0E+00	1.92E-02	5.89E-07	3.52E-06
Lead	4.20E-02	1.55E-01	2.86E-08	1.71E-07
Naphthalene	1.20E-01	3.67E-02	1.93E-08	1.15E-07
1,2-Dichloropropane	3.60E-02	9.10E-02	1.44E-08	8.59E-08
Acetaldehyde	1.00E-02	2.65E-01	1.16E-08	6.95E-08
Carbon Tetrachloride	1.50E-01	1.26E-02	8.33E-09	4.97E-08
Formaldehyde	2.10E-02	6.99E-02	6.45E-09	3.85E-08
Bis(2-ethylhexyl)phthalate	8.40E-03	9.74E-02	3.59E-09	2.14E-08

¹ SFi = Inhalation Slope Factor used to calculate potential cancer risk.

Table IV-7: Chronic Hazard Quotients for Biogas/Biomethane Constituent Concentrations with Highest Risk (top 10 HQs shown, chemicals exceeding screening risks highlighted)

Raw Biogas				
Constituent	Chronic Screening Value (µg/m ³)	Conc. (mg/m ³)	Residential HQ	Worker HQ
Hydrogen Sulfide	1.0E+01	9.16E+03	3.04E+01	4.08E+02
Arsenic	1.5E-02	3.39E-01	7.50E-01	1.01E+01
Antimony	2.0E-01	4.17E-01	6.92E-02	9.30E-01
Methyl Mercaptan	7.9E+00	1.20E+01	5.04E-02	6.77E-01
Methacrolein	3.5E-01	3.12E-01	2.96E-02	3.98E-01
Toluene	3.0E+02	9.80E+01	1.08E-02	1.46E-01
Sulfur Dioxide	7.8E+01	2.03E+01	8.62E-03	1.16E-01
Benzene	6.0E+01	9.58E+00	5.30E-03	7.12E-02
Tetrachloroethylene	3.5E+01	5.56E+00	5.27E-03	7.09E-02
Ammonia	2.0E+02	2.79E+01	4.63E-03	6.21E-02
Biomethane				
Constituent	Chronic Screening Value (µg/m ³)	Conc. (mg/m ³)	Residential HQ	Worker HQ
Hydrogen Sulfide	1.0E+01	2.61E+02	8.65E-01	1.16E+01
Copper and compds.	2.0E-02	2.50E-01	4.15E-01	5.58E+00
Lead	2.5E-02	1.55E-01	2.06E-01	2.77E+00
Toluene	3.00E+02	1.17E+02	1.29E-02	1.74E-01
Zinc	9.00E-01	2.53E-01	9.33E-03	1.25E-01
Methyl Mercaptan	7.94E+00	1.61E+00	6.75E-03	9.07E-02
Antimony and Compds.	2.00E-01	3.20E-02	5.31E-03	7.14E-02
Di-n-butylphthalate	5.25E-01	4.90E-02	3.10E-03	4.16E-02
Carbonyl Sulfide	2.20E+02	1.30E+01	1.96E-03	2.63E-02
Benzene	6.0E+01	3.19E+00	1.77E-03	2.37E-02

Table IV-8: Acute Hazard Quotients for Biogas/Biomethane Constituent Concentrations with Highest Risk (top 10 HQs shown, chemicals exceeding screening risks highlighted)

Raw Biogas				
Constituent	Acute Screening Value ($\mu\text{g}/\text{m}^3$)	Conc. (mg/m^3)	Residential HQ	Worker HQ
Hydrogen Sulfide	4.2E+01	9.16E+03	2.78E+01	9.73E+01
Arsenic	2.0E-01	3.39E-01	2.16E-01	7.56E-01
Methyl Mercaptan	3.3E+01	1.20E+01	4.61E-02	1.61E-01
Methacrolein	2.5E+00	3.12E-01	1.59E-02	5.57E-02
Sulfur Dioxide	6.6E+02	2.03E+01	3.91E-03	1.37E-02
Ethyl Mercaptan	4.3E+01	7.62E-01	2.24E-03	7.85E-03
Octamethylcyclotetra-siloxane	4.0E+03	6.61E+01	2.11E-03	7.37E-03
Thiophenol	1.7E+01	2.25E-01	1.69E-03	5.91E-03
Ammonia	3.2E+03	2.79E+01	1.11E-03	3.88E-03
Benzene	1.3E+03	9.58E+00	9.40E-04	3.29E-03
Biomethane				
Constituent	Acute Screening Value ($\mu\text{g}/\text{m}^3$)	Conc. (mg/m^3)	Residential HQ	Worker HQ
Hydrogen Sulfide	4.2E+01	2.61E+02	7.91E-01	2.77E+00
Methyl Mercaptan	3.3E+01	1.61E+00	6.17E-03	2.16E-02
Methacrolein	2.5E+00	1.18E-02	6.01E-04	2.10E-03
Octamethylcyclotetra-siloxane	4.00E+03	1.61E+01	5.12E-04	1.79E-03
Toluene	3.70E+04	1.17E+02	4.03E-04	1.41E-03
Copper	1.00E+02	2.50E-01	3.19E-04	1.12E-03
Benzene	1.30E+03	3.19E+00	3.13E-04	1.10E-03
Carbonyl Sulfide	6.50E+03	1.30E+01	2.54E-04	8.90E-04
Formaldehyde	5.50E+01	6.99E-02	1.62E-04	5.67E-04
Sulfur Dioxide	6.60E+02	6.55E-01	1.27E-04	4.43E-04

Table IV-9: Hazard Quotients for Chemical Groups¹

Group	Name	Screening Values (ppm)		Biogas High Conc. (ppm)	Acute HQ		Chronic HQ		Notes
		Acute	Chronic		Resident	Worker	Resident	Worker	
1	Alkanes (6 Carbons or less, minus methane, ethane, & propane)	20	0.95	124.00	0.001	0.003	0.004	0.058	GTI Data ² (Biomethane values were higher than in biogas in this instance)
2	Alkanes (7 Carbons or more)	14.7	0.67	137.00	0.001	0.004	0.007	0.091	GTI Data (Sum of Heptanes through Dodecanes)
3	Cycloalkanes	-	1.7	15.00	-	-	0.000	0.004	GTI Data ²
4	"n-Hexane-Like" Alkanes	17	2	47.00	0.000	0.001	0.001	0.010	GTI Data ²
5 & 7	Alkenes, Dienes, & Terpenes	-	1.7	149.80	-	-	0.003	0.039	USEPA 2008 (sum of alkenes) and UKEA 2002 (Table A1.7) (sum of non-aromatic Terpenes)
8	Alcohols	16.7	0.02	6.30	0.000	0.000	0.010	0.140	GTI and USEPA 2008 (sum of Ethanol, Isopropanol, and Benzyl Alcohol values)
9	Ethers	-	1.59	2.10	-	-	0.000	0.001	USEPA 2008 (sum of Tetrahydrofuran, MTBE, and 1,4-dioxane)
10	Aldehydes	-	0.003	0.60	-	-	0.007	0.089	GTI Data ² (high values were found in biomethane)

¹ The exposure adjustment factors developed in Chapter III were applied to the sum of concentrations for each group; in some cases, as noted, the highest totals were found in biomethane.

² Concentrations were based on the highest values for each detected member of in the defined group; constituents that were not detected in any sample were assumed to be absent.

Table IV-9: Hazard Quotients for Chemical Groups¹

Group	Name	Screening Values (ppm)		Biogas High Conc. (ppm)	Acute HQ		Chronic HQ		Notes
		Acute	Chronic		Resident	Worker	Resident	Worker	
11	Ketones	-	0.34	27.70	-	-	0.003	0.036	USEPA 2008 (sum of Acetone, Methyl Ethyl Ketone, and Methyl Isobutyl Ketone)
12	Carboxylic Acids	0.5	0.04	0.53	0.000	0.000	0.000	0.003	PG&E 2008; (sum of Acetic and Lactic acids; values available for biomethane only)
13	Esters	-	0.4	636.50	-	-	0.053	0.710	USEPA 2008; bounding estimate using NMOC value (as C6)
19	Chlorofluorocarbons (CFCs)	33	0.24	4.00	0.000	0.000	0.001	0.007	GTI Data ² (high values found in biomethane)
20	Alkyl Thiols (Mercaptans)	0.017	0.004	8.46	0.063	0.222	0.070	0.943	GTI Data ²
22	Siloxanes	0.3	0.058	4.22	0.002	0.006	0.002	0.032	GTI Data ²

Two of the 14 chemical groups showed screening values greater than the above stated risk thresholds: alkyl thiols and esters. Regarding the esters group, the highest HQ values were 0.05 for a resident and 0.7 for a worker. However, it was not placed on the preliminary constituents of concern list because the concentration values used in the calculation were not from analytical data for ester compounds, but were instead derived using the average Non-Methane Organic Carbon (NMOC) concentration reported in the U.S. EPA AP-42 document for municipal landfills. Using the NMOC concentration as a surrogate for the actual measurement of esters represents a highly conservative upper bound, since the NMOC value represents all carbon-containing chemicals in the biogas samples. Given that the screening HQs for esters were only above the risk cutoffs by a factor of 5 or less, and were not above 1.0, staff judged that alkyl esters normally found in biogas do not represent constituents of concern.

The alkyl thiols group values exceeded the risk thresholds and were placed on the preliminary constituents of concern list. It should be noted that methyl mercaptan and i-propyl mercaptan would have qualified to be preliminary constituents of concern based upon the individual constituent calculations. These thiols are members of the alkyl thiols group and therefore are covered by the group designation.

The final constituents of concern list was obtained from the preliminary constituents of concern list by retaining the constituents that were determined to be present in biogas at levels significantly higher than in natural gas. The limited nature of the datasets, both in sample quantity as well as coverage of the variety of biogas and natural gas streams for California, precluded a determination based on formal statistical methods. Instead, a 3-tier decision process was developed to carry out the biogas-natural gas comparison. A preliminary constituent of concern was judged to be present in levels significantly greater than in natural gas, and thus placed on the final constituent of concern list, if it met any one of the following conditions (in order):

- (i) The constituent was not found in any natural gas sample;
- (ii) Its highest measured concentration in biogas was greater than the highest concentration found in natural gas; or,
- (iii) Its average biogas value was larger than the average natural gas value.

Five of the preliminary constituents of concern were placed on the final list based upon meeting the first criterion of not being found in the natural gas samples: p-dichlorobenzene, n-nitroso-di-n-propylamine, vinyl chloride, antimony, and lead. The second criterion was met by the following constituents, which were also placed on the constituents of concern list: ethylbenzene, toluene, methacrolein, hydrogen sulfide, and copper.²⁴

Since the high concentrations of benzene and alkyl thiols in biogas were less than the respective concentrations in natural gas, the average values for these constituents were compared per the third decision criterion. Based upon this comparison, alkyl thiols were added to the list of constituents of concern since average concentrations of thiols in

²⁴ Note that in carrying out the significance comparisons, we used AP-42 Update concentrations to support and confirm the GTI dataset.

biogas were higher than in natural gas. However, based on a similar comparison, benzene did not qualify for the final list. In this case the average concentration of benzene in natural gas was more than 5 times greater than the average concentrations found in biogas. These comparisons are shown in Tables IV-10 through IV-12. The final constituents of concern list is given in Table IV-13. (Instances in which natural gas concentrations are higher than in biogas are highlighted.) Appendix C contains toxicity summaries for the final constituents of concern.

Table IV-10: Preliminary Constituents of Concern Detected in Biogas and Natural Gas, and Comparison of High Concentration Values (in ppmv unless otherwise noted; Natural Gas values > Biogas highlighted)

Constituent	Pipeline Quality Natural Gas	Landfills			POTWs		Dairy Farms	
		Biogas	USEPA 2008	Biomethane	Biogas	Biomethane	Biogas	Biomethane
Benzene	38.6	3.0	22	< 1	< 1	< 1	0.01	0.027
Ethylbenzene	1.0	8.0	8.8	< 1	< 1	< 1	0.34	0.003
Toluene	15.8	33	90.1	1.40	31	< 1	0.15	0.11
Methacrolein	0.001	0.11	--	0.004	< 0.0001	< 0.0001	--	--
Alkyl Thiols	9.0	6.8	6.1	< 0.05	1.04	1.15	7.3	< 0.05
Hydrogen Sulfide	0.5	152	334	0.53	300	0.16	6570	< 0.05
Copper (µg/m3)	73	< 30	--	250	< 30	< 30	< 20	< 20

Table IV-11: Benzene Average and High Values in Natural Gas and Landfill Biogas Samples (ppmv)

	Pipeline Quality Natural Gas	Landfills		
		Biogas	USEPA 2008	Biomethane
Mean ¹	13.4	1.7	2.4	< 1
Highest Site Value	38.6	3	22	< 1
Sites Sampled	8	6	41	7

Table IV-12: Alkyl Thiols Average and High Values in Natural Gas and Dairy Biogas Samples (ppmv)

	Pipeline Quality Natural Gas	Dairy	
		Biogas	Biomethane
Mean	2.1	2.7	< 0.05
Highest Site Value	9.0	7.3	< 0.05
Sites Sampled	7	12	3

Table IV-13: Final Constituents of Concern List

Alkyl Thiols (Mercaptans)
Antimony
Arsenic
Copper
p-Dichlorobenzene
Ethylbenzene
Hydrogen Sulfide
Lead
Methacrolein
n-Nitroso-di-n-Propylamine
Toluene
Vinyl Chloride

¹ Mean of site means for landfills, and mean of 8 different sources of natural gas.

C. Health Protective Levels for the Constituents of Concern

Health-protective concentrations for the constituents of concern may be defined by using the above exposure and risk formulae along with target (i.e., acceptable) risk levels. OEHHA staff based the risk levels on the values that have been typically used by the Air Pollution Control Districts for risk management under the California Air Toxics “Hotspots” program: a lifetime cancer risk of $1E-5$ (10 chances per million) for exposure to carcinogens, and a hazard index of 1.0 for non-cancer effects. Since there are several biogas constituents of concern, the potential for additive risks was taken into consideration. Thus, the target risk levels for calculating health protective levels were set at:

- An HQ of 0.1 for non-cancer risks for the general population, and of 3.0 for the unprotected worker scenario
- A lifetime additional risk of $1E-6$ (1 chance per million) for cancer risks for the general population, and $3E-5$ (30 chances per million) for the unprotected worker scenario

The resulting health-protective concentration levels for the constituents of concern are presented in Table IV-14.

Table IV-14: Health Protective Concentrations for Constituents of Concern in Biomethane²⁶

Based on Cancer Risks		
Constituent	Biomethane Concentration Level (mg/m ³)	
	Residential Leak (1E-6)	Worker Exposure Scenario (1E-5)
Arsenic ²⁷	0.019	0.032
Ethylbenzene	26	44
p-Dichlorobenzene	5.7	10
n-Nitroso-di-n-propylamine	0.033	0.055
Vinyl Chloride	0.84	1.4
Based on Chronic Non-Cancer Risks		
Constituent	Biomethane Concentration Level (mg/m ³) (in ppm for thiols group)	
	Residential Leak (HQ = 0.1)	Worker Exposure Scenario (HQ = 3.0)
Antimony	0.60	1.3
Copper	0.060	0.13
Hydrogen Sulfide	30	67
Lead	0.075	0.17
Methacrolein	1.1	2.4
Alkyl Thiols (Mercaptans) ²⁸	12 ppm	27 ppm
Toluene	904	2018

References

(OEHHA, 2012) "Air Toxics Hot Spots Program Risk Assessment Guidelines, Technical Support Document, Exposure Assessment and Stochastic Analysis, Final" August 2012.

²⁶ Assumes that the source concentrations are decreased by the exposure adjustment factors 3.3E-5 and 4.46E-4, respectively, for modeled residential leak and worker exposures.

²⁷ Residential and worker concentration limits for arsenic based on non-cancer effects would have been 0.045 and 0.10 mg/m³, respectively.

²⁸ Total of alkyl mercaptans including methyl mercaptan and i-propyl mercaptan.

V. RECOMMENDATIONS TO THE CPUC

In this chapter, we recommend health-based standards and associated monitoring, testing, reporting and recordkeeping requirements for biomethane injected into a common carrier natural gas pipeline (“pipeline”) in California.

A. Risk Management – Identification of Health-Protective Standards

As specified in AB 1900, ARB staff is to provide recommendations to the CPUC on health based standards for biomethane. The standards should identify constituents of concern found in biogas and identify concentration limits for these constituents of concern necessary to protect public health. ARB staff’s recommended health based standards rely on OEHHA’s risk analysis presented in Chapter IV and a risk management decision-making approach consistent with ARB’s Risk Management Guidelines for New and Modified Sources of Toxic Air Pollutants (Risk Management Guidelines or Guidelines). (ARB, 1993)

The Risk Management Guidelines were approved by the ARB in 1993. The approach outlined in the Guidelines continues to be used today by ARB and the local air pollution control and air quality management districts when making risk management decisions about sources of toxic air contaminants. The Guidelines identify trigger levels and lower and upper action levels for potential cancer risk and total non-cancer hazard indexes to be considered when approving a permit. The Guidelines’ risk levels reflect the uncertainty and variability in risk assessments and provide public health protection. These are summarized in Table V-1 below.

Table V-1: Risk Management Guidelines Cancer and Non-Cancer Risk Thresholds

Risk Management Levels		Potential Cancer Risk (Chances in a million)	Non-Cancer Total Hazard Index	Permitting Action
Trigger Level		1	0.2	Approve
Action Range:	Lower Level	10	1	Approve with Best Available Control Technology
	Upper Level	100	10	Deny

ARB staff is proposing a similar approach as used in the Guidelines for the biomethane health standards. Table V-2 lists the recommended risk management levels for the constituents of concern and also briefly summarizes the actions that would be taken at each risk management level. These actions are briefly described below and in more detail in Section B that follows.

Table V-2: ARB Staff Recommended Cancer and Non-Cancer Risk Management Thresholds for Biomethane Constituents of Concern

Risk Management Levels		Potential Cancer Risk (Chances in a million)	Non-Cancer Total Hazard Index	Action
Trigger Level		$\geq 1^a$	$\geq 0.1^a$	Routine Monitoring Required
Action Range:	Lower Level	$\geq 10^b$	$\geq 1^b$	After 3 exceedances in 12-month period, shut off & repair
	Upper Level	$\geq 25^c$	$\geq 5^c$	Immediate shut off and repair

- a. For any single compound
- b. Sum of all compounds exceeding the trigger level
- c. Any single compound or sum of all compounds exceeding the trigger level
- d. *The trigger level is applied to an 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.

As shown in Table V-2, ARB staff modified the non-cancer trigger level for an individual compound from 0.2 in the Guidelines to 0.1. This change was made to be consistent with OEHHA’s recommended health values. ARB staff also changed the upper level cancer action range from 100 to 25 and the upper level non-cancer action range from 10 to 5. These changes provide an additional margin of safety and are more closely aligned with local air district requirements.²⁹

Briefly, the approach used by ARB staff for risk management was to use the OEHHA health protective levels as the “trigger” for requiring routine monitoring of a constituent of concern. If an individual constituent of concern was determined to be present in the upgraded biomethane at a concentration that would result in either a potential cancer risk of ≥ 1 in a million or a hazard quotient of ≥ 0.1 , then that constituent would be subject to quarterly monitoring. Upon each quarterly monitoring event, the operator is to determine the total potential cancer risk and hazard index for the constituents of concern subject to monitoring and verify if the risk levels are below the lower action level (potential cancer risk ≥ 10 in a million or a HI of ≥ 1). If the total risk levels exceed the lower action levels 3 times in a 12-month period, the biomethane flow to the pipeline would be shut off (typically diverted to a flare) and the operator would need to determine how to bring the measured levels in the biomethane to below the lower action level. If at any time the total potential cancer risk or hazard index for the constituents of concern subject to monitoring were to exceed the upper action level (potential cancer risk ≥ 25 in a million or a HQ ≥ 5) the facility would also be subject to shut down.

²⁹ South Coast Air Quality Management District’s Rule 1402 has a maximum allowable hazard quotient of 5.

In the following sections, additional detail is provided on the monitoring, testing, reporting and recordkeeping requirements recommended by ARB staff.

B. Monitoring and Testing Requirements

ARB staff's recommended monitoring and testing requirements are based on the risk range that the constituents of concern fall under. Quarterly monitoring is recommended for any constituents of concern that exceed the trigger level identified for that compound. Operators are then required to determine the total potential cancer and non-cancer risks for all the constituents of concern that are subject to quarterly monitoring. If the combined risk exceeds the upper action level, or the lower action level three times in a 12-month period, then the flow to the pipeline must be shut off.

The constituents of concern that must be measured depend on the biogas source. In Table V-3, the constituents of concern for the three sources of biogas are noted with a checkmark, along with the trigger levels for each compound. As can be seen, landfill biomethane is to be evaluated for the presence of all 12 constituents of concern, while for POTWs there are six, and for dairies there are five.

For the AB 1900 effort, ARB staff established the recommended health based standards for individual compounds based on the potential residential exposures. This is because the residential exposures, estimated based on the health risk assessment, resulted in the highest risk values (as shown in Chapter IV, Table IV-14), and controlling emissions to protect the residential user will also protect the utility worker³⁰.

³⁰ These biomethane standards will not address worker exposure to raw biogas, which could occur at a biomethane production facility, a facility that converts raw biogas to energy on-site, a landfill gas collection system, or any facility that produces biogas. These workers would, however, be covered by OSHA standards.

Table V-3: Recommended Risk Management Levels for Constituents of Concern

Constituent of Concern	Risk Management Levels (Health Based Standards) mg/m ³ (ppmv)			Source Specific Constituents of Concern		
	Trigger Level	Lower Action Level	Upper Action Level	Land-fills	POTW	Dairy
Carcinogenic Constituents of Concern						
Arsenic	0.019 (0.006)	0.19 (0.06)	0.48 (0.15)	✓		
p-Dichlorobenzene	5.7 (0.95)	57 (9.5)	140 (24)	✓	✓	
Ethylbenzene	26 (6.0)	260 (60)	650 (150)	✓	✓	✓
n-Nitroso-di-n-propylamine	0.033 (0.006)	0.33 (0.06)	0.81 (0.15)	✓		✓
Vinyl Chloride	0.84 (0.33)	8.4 (3.3)	21 (8.3)	✓	✓	
Non-carcinogenic Constituents of Concern						
Antimony	0.60 (0.12)	6.0 (1.2)	30 (6.1)	✓		
Copper	0.060 (0.02)	0.60 (0.23)	3.0 (1.2)	✓		
Hydrogen Sulfide	30 (22)	300 (216)	1,500 (1,080)	✓	✓	✓
Lead	0.075 (0.009)	0.75 (0.09)	3.8 (0.44)	✓		
Methacrolein	1.1 (0.37)	11 (3.7)	53 (18)	✓		
Alkyl thiols (mercaptans)	N/A (12)	N/A (120)	N/A (610)	✓	✓	✓
Toluene	904 (240)	9,000 (2,400)	45,000 (12,000)	✓	✓	✓

ARB staff recommends that initial monitoring be conducted prior to the first injection of biomethane into the pipeline, and then periodic testing be performed. The frequency of the periodic testing would be dependent on whether the individual constituents are above the trigger levels, and the total potential cancer and non-cancer risks associated with all the constituents of concern above the trigger levels.

Monitoring for hydrogen sulfide and mercaptans represents a special situation because the utility companies already closely monitor these compounds. For hydrogen sulfide, this is due to health and safety concerns, and its corrosive properties in pipelines. For mercaptans, monitoring is done to ensure that proper odorant levels are maintained. Utility gas quality specifications in tariff rules (e.g., PG&E Rule 21, SoCal Gas Rule 30)

require lower levels for both of these compounds than the “trigger” levels specified above in Table V-3. For example, both PG&E and SoCal Gas tariffs prohibit hydrogen sulfide levels exceeding 4 ppm (compared to 22 ppm listed in Table V-3). Similarly, PG&E and SoCal Gas tariffs prohibit mercaptan levels (as sulfur) above 8 and 5 ppm, respectively, compared to 12 ppm in Table V-3. Furthermore, the utilities measure these compounds more frequently than the recommendations for constituents of concern discussed here. The utilities continuously measure for hydrogen sulfide from sources containing this compound, which covers most sources of pipeline gas. For mercaptans, an odorant “smell” test is performed periodically (monthly for SoCal Gas) to ensure that the gas is properly odorized. In addition, instrument-based testing is sometimes used to ensure that mercaptan levels are not too high. Given that the utility tariff levels are below the trigger levels specified above, we recommend that existing monitoring procedures used to ensure compliance with tariff requirements be used to satisfy the monitoring procedures that we are recommending, as long as the monitoring is conducted at least as frequently.

Pre-Injection Startup Testing

Prior to injecting biomethane into the pipeline, a representative sample of the biomethane should be tested for the constituents of concern specific to that biogas source (as noted in Table V-3) to determine the presence of constituents above detection levels, and where found, the associated concentrations of constituents. The recommended test methods are provided in Table V-4. ARB staff recommends that two tests be conducted over a 2-4 week period once the production facility is operational and prior to when the biomethane is first injected into the pipeline to ensure the stability and performance of the upgrading system.

The utility and the biomethane production facility should agree upon a continuous monitoring method to verify that the upgrading process is operating effectively. If a monitoring method cannot be agreed upon, then we recommend that the tariff requirements for natural gas be used as an indicator that the upgrading system is operating effectively. For biomethane injection facilities in other states, only the natural gas tariff requirements are monitored (with some exceptions for siloxanes and a few other compounds, depending on the project).

Table V-4: Recommended Test Methods for Constituents of Concern

Constituent of Concern	Test Method
Metals	
Lead, Antimony, Arsenic and Copper	EPA Method 29 (AAS and/or ICP), EPA 200.8
Nitroso Compounds	
n-Nitroso-di-n-Propylamine	EPA Method 8270 (GC/MS)
Sulfur Compounds	
Hydrogen Sulfide	ASTM D4084, D7165, D7493 (online monitoring), ASTM D5504, D6228 (lab)
Total Mercaptans	ASTM D7165, D7493 (online monitoring), ASTM D5504, D6228
SVOCs, VOCs, and Alkyl Benzenes	
p-Dichlorobenzene, Vinyl Chloride, Methacrolein, Ethylbenzene, and Toluene	TO-15 (GC/MS), TO-11A for Methacrolein (Determination of Formaldehyde Adsorbent Cartridge (HPLC))

During the pre-injection testing, if any constituent of concern in the biomethane is found to be above the lower action level, as listed in Table IV-3, then the biomethane cannot be injected into the natural gas pipeline and the operator should make modifications to the upgrading system to lower the concentrations of the constituent of concern to levels below the lower action level.

If all the constituents of concern in the biomethane are found to be below the detection level, or measured in concentrations below the lower action level in both pre-injection tests, then the biomethane may be injected into the common carrier pipeline, subject to compliance with the periodic testing requirements specified below. It is important to note, that these testing requirements do not supersede any other requirements relating to pipeline integrity, heating value, and other requirements not related to health-based standards.

Repeat of pre-injection startup testing for all the constituents of concern should be conducted with some slight modifications when:

- A change in biogas source at the facility or upgrading equipment design that the CPUC, in consultation with the ARB and OEHHA, determines will potentially increase the level of any constituent of concern over the previously measured baseline levels. Replacing a component with a functionally-equivalent component should not constitute a change in equipment design.
- Shut-off of biomethane to the pipeline due to testing that indicates a total potential cancer or non-cancer risk for the constituents of concern in biomethane

above the upper action level, or 3 exceedances of the lower action level in a 12 month period.

Under a modified startup procedure, it would not be necessary to conduct two tests over a 2-4 week period prior to reintroducing the biomethane into the pipeline. If the first test demonstrates that all the constituents are below the LAL then injection can resume and it is not necessary to retest prior to injection. However, all the constituents of concern would be reevaluated with regard to periodic testing. This would mean compounds that may have been tested biennially (because they were found to be below a trigger level twice in annual testing) or annually (because the compound is part of a group of compounds whose collective risk below the lower action level four consecutive times – see group 2 compounds below) would have to again go through the testing required to demonstrate eligibility for less frequent testing.

Periodic Testing of Constituents of Concern

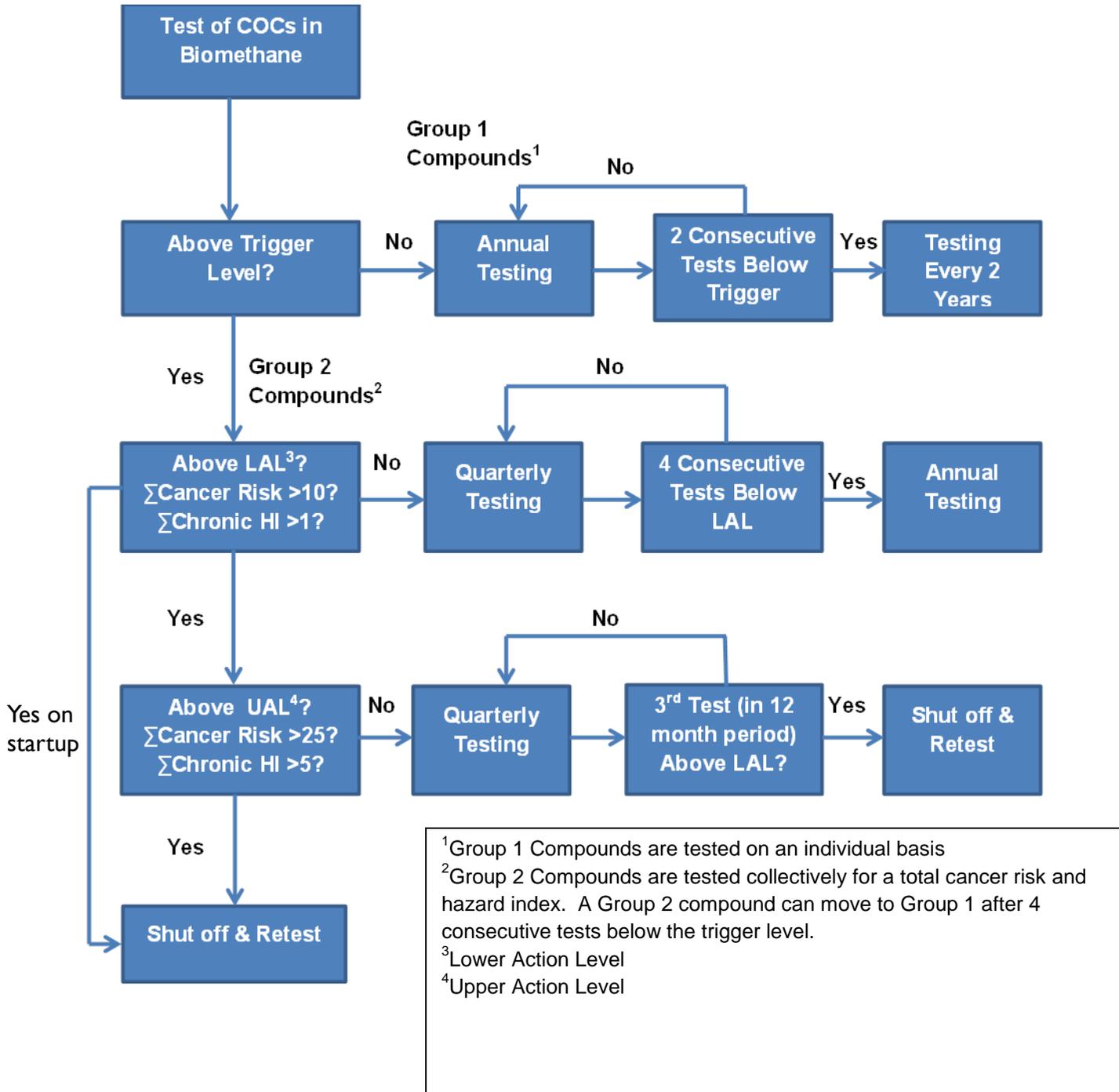
Representative samples of the biomethane being injected into a natural gas common carrier pipeline should be periodically tested for constituents of concern using the test methods specified in Table V-4 according to the frequencies specified below.

- Constituents of concern not found above test method detection levels in biomethane or below the trigger level (i.e., group 1 compounds) should be monitored at least once for every 12 months of injection into the common carrier pipeline. Individual constituents found to be below trigger levels during two consecutive annual tests can then be tested once every two years.
- Any constituents of concern found at or above the trigger level for that constituent of concern (i.e., group 2 compounds) should be monitored quarterly (at least once every 3 months of injection into the common carrier pipeline) and the total potential cancer risk and non-cancer risk estimated.
 - ✓ The total potential cancer risk for group 2 compounds can be estimated by summing the individual potential cancer risk for each carcinogenic constituent of concern found in Table V-3. Specifically, the cancer risk can be calculated using the ratio of the concentration of the constituent in biomethane to the health protective (“trigger”) concentration value corresponding to one in a million cancer risk for that specific constituent found in Table VI-3, and then summing the risk for all the group 2 constituents. To calculate the total non-cancer chronic risk, the process is similar. The risk can be calculated using the ratio of the concentration of the constituent in biomethane to the health protective concentration value corresponding to a hazard quotient of 0.1 for that specific noncarcinogenic constituent found in Table V-3, then multiplying the ratio by 0.1, and then summing the noncancer chronic risk for all these group 2 constituents. ARB staff will develop a spreadsheet tool that biomethane producers can use to calculate the combined cancer or noncancer chronic risk.

- ✓ If the quarterly testing over a 12 month period demonstrates that an individual constituent of concern within the group 2 compounds is below the trigger level four consecutive times, then monitoring for that constituent can be reduced to once every 12 months of injection.
 - ✓ If the quarterly testing over a 12 month period demonstrates that the total potential cancer risk or non-cancer risks for the group 2 constituents being monitored is at a level below the lower action level, monitoring can be reduced to once for every 12 months of injection for all the constituents of concern.
- If, in a 12 month period, there are three exceedances of the lower action level for the constituents of concern (with the exceedances being lower than the upper action level), the operator will shut off the supply of the biomethane and determine necessary adjustments to bring the potential cancer and non-cancer risks for the constituents of concern to levels below the lower action level.
 - If any test result indicates the potential cancer or non-cancer risks for the constituents of concern is above the upper action level, the operator will shut off the supply of the biomethane to the pipeline and determine necessary adjustments/modifications to bring the potential cancer and non-cancer risk levels to below the lower action level.

A flow chart depicting the recommended monitoring plan is provided in Figure V-1. Note that the flow chart and above description is meant to provide a general structure for monitoring procedures. It does not address all potential testing scenarios. For example, a group 1 compound subject to annual or biennial testing, could subsequently revert to quarterly testing if it is monitored and found above the trigger level.

Figure V-1: Flowchart of ARB Staff Recommended Monitoring for Constituents of Concern



Based on the available data, for most biomethane projects it is unlikely that the constituents of concern will be above the trigger level. In Table V-5, we provide a comparison of the trigger level, lower action level, and the maximum concentration that was noted for each biomethane source in the data analyzed. As can be seen, for most compounds, the maximum values found are well below the trigger levels. In all cases, the maximum levels are below the lower action level which indicates that from a public health perspective, the injection of biomethane does not present additional health risk as compared to natural gas. For hydrogen sulfide, the high level noted in Table V-5 (187 ppm) is an anomaly because the raw biogas at this site was subjected to only partial clean up and was not intended to produce a pipeline quality product gas.

Based on the data in Table V-5, and the testing recommended in this document, we do not believe more frequent testing by the utilities should be necessary to demonstrate compliance with the recommended risk management strategy, except in special situations where the CPUC, in consultation with ARB and OEHHA, agree that more frequent monitoring is appropriate. We also believe that any additional utility testing should count toward the periodic testing requirements recommended here.

Table V-5: Comparison of Trigger Level, Lower Action Level and Observed Maximum Biomethane Concentrations for the Constituents of Concern

Constituent	Trigger Level OEHHA Health Protective Limit (ppm)	Risk Mgmt. Lower Action Level Standard (ppm)	Landfill Maximum (ppm)	Dairy Maximum (ppm)	POTW Maximum (ppm)
Vinyl Chloride	0.33	3.30	0.330	BDL*	BDL
Dichlorobenzenes (as p- Dichlorobenzene)	0.95	9.47	0.002	BDL	BDL
n-Nitroso-di-n- propylamine	0.006	0.06	BDL	0.004	BDL
Ethylbenzene	6	60	0.001	0.003	
Arsenic	0.006	0.06	BDL	BDL	BDL
Hydrogen Sulfide	22	216	0.530	BDL	187**
Antimony	0.12	1.2	0.006	BDL	BDL
Methacrolein	0.37	3.7	0.004	BDL	BDL
Toluene	240	2400	1.4	0.11	31**
Alkyl thiols (Mercaptans)	12	120	BDL	BDL	1.15**
Copper	0.02	0.23	0.096	BDL	BDL
Lead	0.009	0.09	0.018	BDL	BDL

*BDL= Below detection level.

** Each of these values were from biogas that was only subject to partial cleanup and not intended for pipeline injection.

We believe that copper merits some additional evaluation. Copper was not found in any of the raw biogas samples analyzed, and only in a few of the biomethane samples in a 2009 GTI report (GTI, 2009). Furthermore, it was found in one of the field blanks in a 2012 GTI report (GTI, 2012). This raises the possibility that it was introduced in either the upgrading equipment or the sampling apparatus used for testing. We intend to further investigate copper as the CPUC rulemaking progresses to determine whether it is appropriate to require monitoring of this compound, or if the risk management approach needs to be adjusted.

C. Reporting and Recordkeeping Requirements

AB 1900 directs Air Resources Board staff to provide recommendations on reporting and recordkeeping requirements. Discussed below are our general recommendations. Our expectation is that some of the details would be further developed through the CPUC regulatory process to ensure that the recordkeeping and reporting associated with ensuring public health aligns with the requirements to ensure pipeline integrity. Our recommendations are summarized below:

- Biomethane producers (“producers”) shall notify the CPUC (and the CPUC shall notify the ARB and OEHHA) within 30 days of the date when they first inject into the natural gas common carrier pipeline, the producer company name, contact person, location of facility and injection point.
- The testing entity (utility or producer) shall provide the CPUC (and the CPUC shall provide the ARB and OEHHA) with the “Startup Testing” results (concentrations of constituents of concern and associated test methods and concentrations of any additional constituents beyond those recommended in this document, if applicable) within 30 days of receiving the test data. The testing entity will also note whether monitoring and recordkeeping of hydrogen sulfide and mercaptans conducted subject to utility tariff requirements will be used to meet the monitoring and recordkeeping recommended in this document for constituents of concern.
- The testing entity (utility or producer) shall maintain records of all test results (concentrations of constituents of concern and associated test methods) for at least 3 years from the date when the tests were conducted. These records would not be required for hydrogen sulfide and mercaptans when these compounds are monitored continuously, or more frequently than recommended for constituents of concern in this document, and are subject to utility tariff monitoring and reporting requirements.
- The producers and utility shall provide an annual report to the CPUC (and the CPUC shall provide the report to ARB and OEHHA) containing the following information:
 - ✓ All test data (concentrations of constituents of concern and identification of associated test methods) received during the report period
 - ✓ Annual biomethane production rate
 - ✓ Monitoring parameters used to ensure that the upgrading system is operating effectively

- ✓ Dates of any shutoff events, the reason for the shutoff, the actions taken to resume injection into the pipeline, and the start of re-injection into the pipeline (if applicable).
- If the utility is the testing entity, the utility shall provide the following test data to the producer:
 - ✓ Test results of constituents of concern within two weeks of receiving the data
 - ✓ Test results of constituents of concern within 24 hours of receiving the data when it results in shutoff of biomethane to the pipeline.
- If the producer is the testing entity, the producer shall provide the above information to the utility.

References

(ARB, 1993) Risk Management Guidelines for New and Modified Sources of Toxic Air Pollutants, California Air Resources Board, July 1993.

<http://www.arb.ca.gov/diesel/documents/rmg793.pdf>

(GTI, 2009) "Pipeline Quality Biogas: Guidance Document for Dairy Waste, Wastewater Treatment Sludge and Landfill Conversion, Final Reports: Tasks 1, 2, 3, and 4," Gas Technology Institute, December 2009.

(GTI, 2012) "Guidance Document for the Introduction of Landfill-Derived Renewable Gas into Natural Gas Pipelines," Gas Technology Institute, 2009.

APPENDIX A

AB 1900

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Assembly Bill No. 1900

CHAPTER 602

An act to amend Section 25420 of, and to repeal and add Section 25421 of, the Health and Safety Code, to add Section 25326 to the Public Resources Code, and to add Sections 399.24 and 784 to the Public Utilities Code, relating to energy.

[Approved by Governor September 27, 2012. Filed Secretary of State September 27, 2012.]

BILL TEXT

THE PEOPLE OF THE STATE OF CALIFORNIA DO ENACT AS FOLLOWS:

SECTION 1.

Section 25420 of the Health and Safety Code is amended to read:

25420.

For purposes of this chapter, the following definitions apply:

- (a) "Biogas" means gas that is produced from the anaerobic decomposition of organic material.
- (b) "Biomethane" means biogas that meets the standards adopted pursuant to subdivisions (c) and (d) of Section 25421 for injection into a common carrier pipeline.
- (c) "Board" means the State Air Resources Board.
- (d) "CalRecycle" means the Department of Resources Recycling and Recovery.
- (e) "Commission" means the Public Utilities Commission.
- (f) "Common carrier pipeline" means a gas conveyance pipeline, located in California, that is owned or operated by a utility or gas corporation, excluding a dedicated pipeline.
- (g) "Dedicated pipeline" means a conveyance of biogas or biomethane that is not part of a common carrier pipeline system, and which conveys biogas from a biogas producer to a conditioning facility or an electrical generation facility.
- (h) "Department" means the Department of Toxic Substances Control.
- (i) "Gas corporation" has the same meaning as defined in Section 222 of the Public Utilities Code and is subject to rate regulation by the commission.

(j) "Hazardous waste landfill" means a landfill that is a hazardous waste facility, as defined in Section 25117.1.

(k) "Office" means the Office of Environmental Health Hazard Assessment.

(l) "Person" means an individual, trust, firm, joint stock company, partnership, association, business concern, limited liability company, or corporation. "Person" also includes any city, county, district, and the state or any department or agency thereof, or the federal government or any department or agency thereof to the extent permitted by law.

SEC. 2.

Section 25421 of the Health and Safety Code is repealed.

SEC. 3.

Section 25421 is added to the Health and Safety Code, to read:

25421.

(a) On or before May 15, 2013, all of the following shall be completed:

(1) The office, in consultation with the board, the department, CalRecycle, and the California Environmental Protection Agency, shall compile a list of constituents of concern that could pose risks to human health and that are found in biogas at concentrations that significantly exceed the concentrations of those constituents in natural gas. The office, in consultation with the board, the department, CalRecycle, and the California Environmental Protection Agency, shall update this list at least every five years.

(2) The office shall determine health protective levels for the list of constituents of concern identified pursuant to paragraph (1). In determining those health protective levels, the office shall consider potential health impacts and risks, including, but not limited to, health impacts and risks to utility workers and gas end users. The office shall update these levels at least every five years.

(3) The board shall identify realistic exposure scenarios and, in consultation with the office, shall identify the health risks associated with the exposure scenarios for the constituents of concern identified by the office pursuant to paragraph (1). The board shall update the exposure scenarios, and, in consultation with the office, the health risks associated with the exposure scenarios, at least every five years.

(4) Upon completion of the responsibilities required pursuant to paragraphs (1) through (3), the board, in consultation with the office, the department, CalRecycle, and the California Environmental Protection Agency shall determine the appropriate concentrations of constituents of concern. In determining those concentrations, the board shall use the health protective levels identified pursuant to paragraph (2) and the exposure scenarios identified pursuant to paragraph (3). The concentrations shall be updated at least every five years by the board in consultation with the office, the department, CalRecycle, and the California Environmental Protection Agency.

(5) The board, in consultation with the office, the department, CalRecycle, and the California Environmental Protection Agency, shall identify reasonable and prudent monitoring, testing, reporting, and recordkeeping requirements, separately for each source of biogas, that are sufficient to ensure compliance with the health protective standards adopted pursuant to subdivision (d). The board, in consultation with the office, the department, CalRecycle and the California Environmental Protection Agency shall update the monitoring, testing, reporting, and recordkeeping requirements at least every five years.

(b) Actions taken pursuant to subdivision (a) shall not constitute regulations and shall be exempt from the administrative regulations and rulemaking provisions of the Administrative Procedure Act (Chapter 3.5 (commencing with Section 11340) of Division 2 of Title 2 of the Government Code).

(c) On or before December 31, 2013, for biomethane that is to be injected into a common carrier pipeline, the commission shall, by rule or order, adopt standards that specify, for constituents that may be found in that biomethane, concentrations that are reasonably necessary to ensure both of the following:

(1) The protection of human health. In making this specification, the commission shall give due deference to the determinations of the board pursuant to paragraph (4) of subdivision (a).

(2) Pipeline and pipeline facility integrity and safety.

(d) To ensure pipeline and pipeline facility integrity and safety, on or before December 31, 2013, the commission, giving due deference to the board's determinations, shall, by rule or order, adopt the monitoring, testing, reporting, and recordkeeping requirements identified pursuant to paragraph (5) of subdivision (a).

(e) Every five years, or earlier if new information becomes available, the commission shall review and update the standards for the protection of human health and pipeline integrity and safety adopted pursuant to subdivision (c), as well as the monitoring, testing, reporting, and recordkeeping requirements adopted pursuant to subdivision (d).

(f) (1) A person shall not inject biogas into a common carrier pipeline unless the biogas satisfies both the standards set by the commission pursuant to subdivision (c), as well as the monitoring, testing, reporting, and recordkeeping requirements of subdivision (d).

(2) The commission shall require gas corporation tariffs to condition access to common carrier pipelines on the applicable customer meeting the standards and requirements adopted by the commission pursuant to subdivisions (c) and (d).

(g) (1) A person shall not knowingly sell, supply, or transport, or knowingly cause to be sold, supplied, or transported, biogas collected from a hazardous waste landfill to a gas corporation through a common carrier pipeline.

(2) A gas corporation shall not knowingly purchase gas collected from a hazardous waste landfill through a common carrier pipeline.

SEC. 4.

Section 25326 is added to the Public Resources Code, to read:

25326.

(a) The commission shall hold public hearings to identify impediments that limit procurement of biomethane in California, including, but not limited to, impediments to interconnection. The commission shall offer solutions to those impediments as part of the integrated energy policy report prepared pursuant to Section 25302.

(b) For the purposes of this section, “biomethane” means biogas that meets the standards adopted pursuant to subdivisions (c) and (d) of Section 25421 of the Health and Safety Code for injection into a common carrier pipeline.

SEC. 5.

Section 399.24 is added to the Public Utilities Code, to read:

399.24.

(a) To meet the energy and transportation needs of the state, the commission shall adopt policies and programs that promote the in-state production and distribution of biomethane. The policies and programs shall facilitate the development of a variety of sources of in-state biomethane.

(b) For the purposes of this section, “biomethane” means biogas that meets the standards adopted pursuant to subdivisions (c) and (d) of Section 25421 of the Health and Safety Code for injection into a common carrier pipeline.

SEC. 6.

Section 784 is added to the Public Utilities Code, to read:

784.

For each gas corporation, the commission shall adopt pipeline access rules that ensure that each gas corporation provides nondiscriminatory open access to its gas pipeline system to any party for the purposes of physically interconnecting with the gas pipeline system and effectuating the delivery of gas.

SEC. 7.

This act shall become operative only if this act and Assembly Bill 2196 of the 2011–12 Regular Session are both enacted and become effective on or before January 1, 2013.

SEC. 8.

No reimbursement is required by this act pursuant to Section 6 of Article XIII B of the California Constitution because the only costs that may be incurred by a local agency or school district will be incurred because this act creates a new crime or infraction, eliminates a crime or infraction, or changes the penalty for a crime or infraction, within the meaning of Section 17556 of the Government Code, or changes the definition of a crime within the meaning of Section 6 of Article XIII B of the California Constitution.

APPENDIX B

Lists of Constituents

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Appendix B

Lists of Constituents and Chemical Groups Found in Biogas and Natural Gas Sources

Appendix B provides a compilation of the list of constituents identified by ARB and OEHHA staff as present or likely to be present in biogas derived from landfills, dairies, and POTWs. The constituents are provided in four tables, B-1 through B-4, and are based upon information reported in the environmental science literature, as well as government and industry reports. Additional data for biogas from municipal landfills, wastewater treatment, and natural gas was obtained from biogas-related businesses operating in the United States.

The list of identified constituents was divided into tables based upon the sources from which the information was obtained. Table B-1 contains chemicals and chemical groups that have been identified in recent analyses of biogas samples in the United States by the Gas Technology Institute, and using additional California-specific data for landfills and POTWs. (GTI 2009 a, b, c, d; and GTI 2012, LACSD 2012; SCAQMD 2012; JWPCP 2011) As noted in Chapter II of this report, these were chosen as the primary quantitative data sources for the risk evaluation. Several of these studies also analyzed trace constituents in pipeline-quality natural gas and any unique chemicals found in the natural gas samples were included in the table. The “Table B-1” constituents were categorized into chemical groups for ease of review, as well as to assist in the risk evaluation. As is discussed in Chapter IV of this report, several of these groups are treated as sets of toxicologically similar chemicals and a single risk screening value is developed for them). The last section of Table B-1 contains a “group of groups,” (Group 27). This is a list of various chemical categories that were reported in the reference studies but which were, for the most part, not used in the risk evaluation.

Table B-2 is compiled from municipal landfill gas data reported by the U.S. EPA (U.S. EPA 2008) and from a municipal landfill study by the United Kingdom Environment Agency (UKEA) (UKEA 2002). These were used as supplementary information sources in the risk evaluation. The biogas data reviewed in the U.S. EPA report was obtained mainly during the mid-1990s and early 2000s. The UKEA concentration data was from 2001 and 2002, although its list of trace constituents was based on a wider set of data including pre-1990s information from U.K. municipal landfills. Both the U.S. EPA and UKEA reports identified many of the same chemicals that have been found at municipal landfill sites in the “Table B-1” reference studies. However, they also listed a variety of chemicals that likely derive from microbial action upon materials such as papers, wood, foods, and other biological wastes. Table B-2 only includes the additional landfill gas constituents not already listed in Table B-1. These were also organized into chemical groups.

Table B-3 includes several additional biogas constituents that have been reported in the environmental science literature (Rasi 2009; Grumping, et al. 1999; Hensel, et al. 2000; Hirner, et al. 1994; Glindemann, et al. 2005). Finally, Table B-3 lists several chemicals that are likely to be produced upon combustion of biogas and will be evaluated in future

updates to these recommendations. The information from the academic studies was used primarily in a qualitative way, for example, to identify additional constituents that were not looked for in other studies, or else to confirm the identification of chemicals reported in the primary data sources.

Concentrations of constituents in biogas, biomethane and natural gas from the GTI datasets are provided in Table B-4. This is an Excel workbook containing individual worksheets for each set of gas data used in the health risk assessment of the individual constituents. Each worksheet contains data for individual constituent maximum concentrations from the specified data source and is separated by gas type (e.g. natural gas, raw dairy, clean dairy, etc.). Also included in the workbook are three additional sheets summarizing the maximum concentrations for each constituent in natural gas, raw biogas and cleaned (upgraded) biomethane.

(References noted in Appendix B are provided in Chapter II of the report)

Table B-1

Constituents and Chemical Groups Identified in Recent Samples of Biogas from Municipal Landfills, Wastewater Treatment Plants and Dairy Farms in the U.S. and California³¹

Group	Constituent	CAS
1	Alkanes (C6 and lower)	
	Ethane	74-84-0
	i-Butane	75-28-5
	i-Pentane	78-78-4
	Methane	74-82-8
	n-Butane	106-97-8
	n-Pentane	109-66-0
	Propane	74-98-6
2	Alkanes (C7 and greater)	
	2,2,4-Trimethylpentane	540-84-1
	n-Heptane	8031-33-2
3	Alkanes (Cyclic)	
	1-Ethyl-2-methylcyclohexane	3728-54-9
	Cyclohexane	110-82-7
	Cyclopentane	287-92-3
	Methylcyclohexane	108-87-2
	Methylcyclopentane	96-37-7
4	Alkanes (Hexane-Like)	
	3-Ethylhexane	619-99-8
	n-Hexane	110-54-3
5	Alkenes and Dienes	
	1,3-Butadiene	106-99-0
	Propene	115-07-1
8	Alcohols	
	Benzyl Alcohol	100-51-6
	Butanol	71-36-3
	Ethanol	64-17-5
9	Ethers	
	Tetrahydrofuran	109-99-9
10	Aldehydes	

³¹ Data sources: GTI 2009a, b, c, and d, GTI 2012, LACSD 2012; SCAQMD 2012; JWPCP 2011.

Table B-1 (continued)		
Group	Constituent	CAS
	Acetaldehyde	75-07-0
	Benzaldehyde	100-52-7
	Butanal	123-72-8
	Hexanaldehyde	66-25-1
	Pentanaldehyde (Valeraldehyde)	110-62-3
	Propionaldehyde	123-38-6
	p-Tolualdehyde	104-87-0
11	Ketones	
	2-Butanone	78-93-3
	Acetone	67-64-1
	Methyl Isobutyl Ketone (MIBK)	108-10-1
15	Benzenes (monoalkyl)	
	Ethylbenzene	100-41-4
	Isopropylbenzene (cumene)	98-82-8
	n-Butylbenzene	104-51-8
	n-Propylbenzene	103-65-1
	sec-Butylbenzene	135-98-8
	t-Butylbenzene	98-06-6
	Toluene	108-88-3
16	Benzenes (polyalkyl)	
	1,2,4-Trimethylbenzene	95-63-6
	1,3,5-Trimethylbenzene	108-67-8
	4-Ethyltoluene	622-96-8
	m/p-Xylenes	179601-23-1
	m-Xylene	108-38-3
	o-Xylene	95-47-6
	p-Isopropyltoluene (Cymene)	99-87-6
	p-Xylene	106-42-3
	Xylene (mixed isomers)	1330-20-7
17	Benzenes (styrenes)	
	Styrene	100-42-5
18	Benzenes (chlorinated)	
	1,2,3-Trichlorobenzene	87-61-6
	1,2,4-Trichlorobenzene	120-82-1
	1,2-Dichlorobenzene	95-50-1
	1,3-Dichlorobenzene	541-73-1
	1,4-Dichlorobenzene	106-46-7
	Chlorobenzene	108-90-7

Table B-1 (continued)		
Group	Constituent	CAS
19	Chlorofluorocarbons (CFCs)	
	1,2-Dichlorotetrafluoroethane (CFC-114)	76-14-2
	Dichlorodifluoromethane	75-71-8
	Trichlorofluoromethane (Freon 11)	75-69-4
20	Alkyl Thiols	
	Ethyl Mercaptan	75-08-1
	i-Propyl Mercaptan	75-33-2
	Methyl Mercaptan	74-93-1
	n-Propyl Mercaptan	107-03-9
	t-Butyl Mercaptan	75-66-1
21	Alkyl Sulfides	
	Carbon Disulfide	75-15-0
	Carbonyl Sulfide	463-58-1
	Diethyl Disulfide	110-81-6
	Dimethyl Disulfide	624-92-0
	Dimethyl Sulfide	75-18-3
	Dimethyl Trisulfide	3658-80-8
	Methyl Ethyl Sulfide	625-80-9
	Tetrahydrothiophene	110-01-0
22	Organosilicon Compounds	
	Decamethylcyclopentasiloxane (D5)	541-02-6
	Decamethyltetrasiloxane (L4)	141-62-8
	Hexamethylcyclotrisiloxane (D3)	541-05-9
	Hexamethyldisiloxane (L2)	107-46-0
	Octamethylcyclotetrasiloxane (D4)	556-67-2
	Octamethyltrisiloxane (L3)	107-51-7
23	Volatile Organics (VOCs)	
	1,1,1-Trichloroethane	71-55-6
	1,1,2,2-Tetrachloroethane	79-34-5
	1,1,2-Trichloroethane	79-00-5
	1,1-Dichloroethane	75-34-3
	1,1-Dichloroethene	75-35-4
	1,2-Dibromoethane	106-93-4
	1,2-Dichloroethane	107-06-2
	1,2-Dichloroethylene	540-59-0
	1,2-Dichloropropane	78-87-5
	1,4-Dioxane	123-91-1
	1-Bromo-2-methylpropane	78-77-3

Table B-1 (continued)		
Group	Constituent	CAS
	2-Chlorotoluene	95-49-8
	2-Methyl-1-nitropropane	625-74-1
	4-Chlorotoluene	106-43-4
	Acetonitrile	75-05-8
	Acrolein	107-02-8
	Acrylonitrile	107-13-1
	Allyl Chloride	107-05-1
	Benzene	71-43-2
	Benzyl Chloride	100-44-7
	bis(2-Chloroethyl)ether	111-44-4
	bis(2-Chloroisopropyl)ether	108-60-1
	Bromodichloromethane	75-27-4
	Bromomethane	74-83-9
	Carbon Tetrachloride	56-23-5
	Chloroform	67-66-3
	Chloromethane	74-87-3
	Chloroprene	126-99-8
	cis-1,2-Dichloroethylene	156-59-2
	Crotonaldehyde	123-73-9
	Dibromochloromethane	124-48-1
	Epichlorohydrin	106-89-8
	Ethyl Acetate	141-78-6
	Ethyl Chloride	75-00-3
	Ethylene Oxide	75-21-8
	Formaldehyde	50-00-0
	Methacrolein	78-85-3
	Methylene Chloride	75-09-2
	Methyl-t-Butyl Ether (MTBE)	1634-04-4
	Perchloroethane	98299-61-7
	Phosgene	75-44-5
	Propylene Oxide	75-56-9
	Tetrachloroethylene	127-18-4
	trans-1,2-Dichloroethene	156-60-5
	trans-1,3-Dichloropropene	10061-02-6
	Tribromomethane (Bromoform)	75-25-2
	Trichloroethylene	79-01-6
	Vinyl Acetate	108-05-4
	Vinyl Chloride	75-01-4

Table B-1 (continued)		
Group	Constituent	CAS
24	Semivolative Organics (SVOCs)	
	1-Methylnaphthalene	90-12-0
	2,4-Dimethylphenol	105-67-9
	2-Chlorophenol	95-57-8
	2-Methylnaphthalene	91-57-6
	4,4'-DDD	72-54-8
	4,4'-DDT	50-29-3
	4-Chloroaniline	106-47-8
	4-Nitrophenol	100-02-7
	Acenaphthene	83-32-9
	Aniline	62-53-3
	bis(2-Ethylhexyl)adipate	103-23-1
	bis(2-Ethylhexyl)phthalate	117-81-7
	Bromo-2-fluorobenzene	1072-85-1
	Cresols (mixed isomers)	1319-77-3
	Dibenzofuran	132-64-9
	Diethylphthalate	84-66-2
	Di-n-butylphthalate	84-74-2
	Endosulfan I	959-98-8
	Endosulfan II	33213-65-9
	Endosulfan sulfate	1031-07-8
	Endrin	72-20-8
	Endrin aldehyde	7421-93-4
	Fluorene	86-73-7
	Heptachlor	76-44-8
	Heptachlor epoxide	1024-57-3
	Hexachlorocyclopentadiene	77-47-4
	m/p-cresols (3,4-methylphenols)	15831-10-4
	Methoxychlor	72-43-5
	Naphthalene	91-20-3
	Nitrobenzene	98-95-3
	N-Nitroso-di-n-propylamine	621-64-7
	Phenanthrene	85-01-8
	Phenol	108-95-2
	Pyridine	110-86-1
	Thiophene	110-02-1
	Thiophenol	108-98-5

Table B-1 (continued)		
Group	Constituent	CAS
25	Metallic Compounds	
	Antimony	7440-36-0
	Arsenic	7440-38-2
	Chromium (assumed Cr III)	7440-47-3
	Copper	7440-50-8
	Lead	7439-92-1
	Manganese	7439-96-5
	Mercury	7439-97-6
	Zinc	7440-66-6
26	Inorganic Compounds	
	Ammonia	7664-41-7
	Carbon Dioxide	124-38-9
	Hydrogen	1333-74-0
	Hydrogen Sulfide	7783-06-4
	Nitrogen	7727-37-9
	Oxygen	7782-44-7
	Sulfur Dioxide	7446-09-5
27	Multi-Chemical Groupings	
	Aldehydes and Ketones	--
	Biologicals	--
	C1-Thiophenes	--
	C2-Thiophenes	--
	C3 Benzenes	--
	C5-C7 Cycloalkanes	--
	Chlorinated Phenols	--
	Decanes	--
	Dialkyl Nitrosamines	--
	Dichlorobenzenes	--
	Dodecanes	--
	Halocarbons	--
	Halogenated Compounds	--
	Heptanes	--
	Hexanes	--
	Hexanes plus	--
	Individual Unidentified Sulfur Compounds (all as monosulfides)	--
	Mercaptans	--
	Nonanes	--
	Octanes	--

Table B-1 (continued)		
Group	Constituent	CAS
	Organosilicon Compounds	--
	Oxygen/Argon	--
	Polychlorinated Biphenyls	--
	Polychlorinated Dibenzofurans	--
	Polychlorinated Dibenzo-p-Dioxins	--
	Polynuclear Aromatic Hydrocarbons (PAHs)	--
	Siloxanes	--
	SVOCs (Semivolatile Organics)	--
	Tetradecanes	--
	Total from Cyclopentane to Eicosanes +	--
	Total Sulfur (ppm)	--
	Total TO-14 Halocarbons	--
	Tridecanes	--
	Undecanes	--
	VOCs (Volatile Organics)	--
	Volatile Metals	--

Table B-2
Additional Constituents Identified in Municipal Landfill Biogas from the U.S.,
Canada, and the U.K.³²

(list includes only unique chemicals not reported in other biogas reference studies)

Group 1 Alkanes (C6 and lower)	2,2-dimethylbutane 2,2-dimethylpropane	2,3-dimethylbutane 2-methylbutane	2-methylpentane 3-methylpentane
Group 2 Alkanes (C7 and greater)	2,2,3-trimethylbutane 2,3,3-trimethylpentane 2,3,4-trimethylhexane 2,3,4-trimethylpentane 2,2,5-trimethylhexane 2,4,6-trimethylheptane 2,2-dimethylhexane 2,2-dimethylpentane 2,3-dimethylheptane 2,3-dimethylpentane 2,4-dimethylpentane 2,4-dimethylheptane 2,4-dimethylhexane 2,5-dimethylheptane 2,5-dimethylhexane 2,6-dimethylheptane 2,6-dimethyloctane 2,6-dimethylnonane	3,3-dimethylpentane 3,5-dimethyloctane 3,6-dimethyloctane 2-methyldecane 2-methylheptane 2-methylhexane 2-methylnonane 2-methyloctane 3-ethyl-4-methylheptane 3-ethylpentane 3-methyldecane 3-methylheptane 3-methylnonane 3-methyloctane 4-methyldecane 4-methylheptane 4-methylnonane 4-methyloctane	5-methyldecane eicosane heneicosane heptadecane hexadecane n-decane n-dodecane n-nonane n-octane nonadecane n-tetradecane n-tridecane n-undecane octadecane pentadecane tetradecane trimethylhexane
Group 3 Alkanes (Cyclic)	1,1,3-trimethylcyclohexane 1,2,4-trimethylcyclohexane 1,2,4-trimethylcyclopentane 1,3,5-trimethylcyclohexane 1,1-dimethylcyclopropane 1,2-dimethylcyclohexane (cis) 1,2-dimethylcyclopropane 1,3-dimethylcyclohexane (cis) 1,3-dimethylcyclohexane (trans) 1,3-dimethylcyclopentane 1,3-dimethylcyclopentane (trans) 1,4-dimethylcyclohexane (cis) 1,4-dimethylcyclohexane (trans)	(1-methylethyl)cyclohexane 1-ethyl-2-methylcyclohexane 1-ethyl-2-methylcyclopentane 1-ethyl-3-methylcyclohexane 1-ethyl-3-methylcyclopentane 1-ethyl-4-methylcyclohexane 1-methyl-2-propylcyclopentane 2-methylpropylcyclohexane butylcyclohexane cyclobutane cycloheptane decahydronaphthalene dimethylcyclohexane	dimethylcyclopentane ethylcyclohexane ethylcyclopentane ethylcyclopropane ethylmethylcyclohexane methylcycloheptane methylcyclobutane methylcyclopropane methylethylcyclohexane propylcyclohexane tetramethylcyclohexane trimethylcyclopentane

³² References: USEPA 2008, Table 2-8, UKEA 2002.

Table B-2 (continued)

Group 4 Alkanes (Hexane-Like)	3-ethylhexane 3-methylhexane		
Group 5 Alkenes and Dienes	1,10-undecadiene 1,11-dodecadiene 1,4-pentadiene 1,6-heptadiene 1,8-nonadiene 1,9-decadiene 1-butene 1-decene 1-heptene 1-hexene 1-methylcyclohexene 1-methylcyclopentene 1-nonene 1-octene 1-pentene 1-undecene 2,5-dimethylpentene 2-butene (cis) 2-butene (trans)	2-ethyl-1-butene 2-heptene (cis) 2-heptene (trans) 2-hexene (cis) 2-hexene (trans) 2-methyl-1-butene 2-methyl-1-pentene 2-methyl-1-propene 2-methyl-2-butene 2-octene (cis) 2-octene (trans) 2-pentene (cis) 2-pentene (trans) 3-heptene (cis) 3-methyl-1-butene 3-methyl-1-pentene 3-methyl-2-pentene (cis) 3-methyl-2-pentene (trans)	4-methyl-1-hexene 4-methyl-1-pentene 4-methyl-2-pentene (cis) 4-methyl-2-pentene (trans) butene cyclohexene cyclopentene dodecene ethene hexadiene methylene-cyclohexane n-decene nonene n-undecene octadiene pentene propadiene (allene) propene
Group 6 1,3-Dienes	1,3-butadiene 1,3-pentadiene	2-methyl-1,3-butadiene	
Group 7 Terpenes	3-carene 4-carene camphene carene	decahydro-4,8,8-trimethyl-9-methylene-(1 α ,3 α ,4 α ,8 α) -1,4-methanoazulene limonene phellandrene	β -pinene thujene α -pinene γ -terpinene
Group 8 Alcohols	1-propanol 2-(2-hydroxypropoxy)-1-propanol 2-butanol 2-ethyl-1-butanol 2-methyl-1-propanol	2-ethyl-1-hexanol 3-methyl-2-butanol 3-methyl-2-pentanol 3-pentanol amyl alcohol	3-methyl-1-butanol n-hexanol methanol methyl isobutyl carbinol
Group 9 Ethers	dimethyl ether dipropyl ether	methyl ethyl ether	tetrahydrofuran

Table B-2 (continued)

Group 10 Aldehydes	benzaldehyde butanal	decanal nonanal	octanal
Group 11 Ketones	1-phenyl-1-propanone 2-ethyl-cycloheptanone 2-pentanone 3-methyl-2-butanone	acetophenone cyclohexanone cyclopentanone dimethyl-3-pentanone	methyl ethyl ketone methyl isobutyl ketone methyl isopropyl ketone
Group 12 Carboxylic Acids	acetic acid benzoic acid	2,2-dimethylpropanoic acid butyric acid	propionic acid
Group 13 Esters	amyl acetate (mixed isomers) butyl acetate butyl butyrate butyl formate dimethylethyl methanoate ethyl 2-methyl butyrate ethyl butyrate ethyl caproate ethyl dimethyl propanoate ethyl isovalerate ethyl pentanoate	ethyl propionate hexyl methanoates isobutyl formate methyl 2-methylbutanoate methyl acetate methyl butyrate methyl caproate methylethyl butanoate methylethyl propanoate methyl isobutyrate	methyl isovalerate methyl pentanoate methyl propanoate methylpropyl ethanoate n-butyl propionate n-propyl acetate n-propyl butyrate pentyl methanoate propylmethyl propanoate propyl propionate
Group 14 Alkynes	acetylene butynes	propyne	
Group 16 Benzenes (Polyalkyl)	1,2,3-trimethylbenzene 1,2-diethylbenzene 1,3-diethylbenzene 1,4-diethylbenzene 1-ethyl-2,3-dimethylbenzene	1-methyl-2-propylbenzene 1-methyl-3-propylbenzene 1-methyl-4-propylbenzene 2-ethyl-1,3-dimethylbenzene 2-ethyltoluene	3-ethyltoluene isobutylbenzene β-cymene tetramethylbenzene
Group 17 Benzenes (Styrenes)	1-ethenyl-3-ethylbenzene dimethyl styrene	ethyl vinyl benzene methyl-4- isopropenylbenzene	vinyl toluene
Group 18 Benzenes (Chlorinated)	1,2,3,4-tetrachlorobenzene 1,2,3-trichlorobenzene	1,2,4-trichlorobenzene	pentachlorobenzene
Group 19 CFCs	1,1,1,2-tetrafluorochloroethane 1,1,1-trichlorotrifluoroethane 1,1,1-trifluorochloroethane 1,1,2,2-tetrafluoroethane 1,1,2-trichlorotrifluoroethane	1,1-difluoro-1-chloroethane 1,2-dichloro-1-fluoroethane 1,2-dichlorotetrafluoroethane 1-chloro-1,1-difluoroethane	chlorofluoromethane chlorotrifluoroethene chlorotrifluoromethane dichlorofluoromethane

	1,1,2-trifluoro-1,2-dichloroethane 1,1,2-trifluoro-1-chloroethane 1,1-chlorofluoroethane 1,1-dichlorotetrafluoroethane	2,2-difluoropropane bromochlorodifluoromethane bromochlorofluoromethane carbon tetrafluoride chlorodifluoromethane	dichlorodifluoromethane tetrafluoroethane trichlorofluoromethane
Group 20 Alkyl Thiols	1-butanethiol 1-pentanethiol 2-butanethiol	2-methyl-1-propanethiol 2-propene-1-thiol amyl mercaptan	heptanethiol n-hexanethiol
Group 21 Alkyl Sulfides	1-(ethylthio)butane dibutyl sulfide dibutyl trisulfide diethyl sulfide dimethyl tetrasulfide dipropyl sulfide dipropyl trisulfide ethyl butyl trisulfide ethyl isobutyl disulfide	ethyl isopropyl disulfide ethyl n-propyl disulfide ethyl propyl trisulfide methyl butyl disulfide methyl butyl trisulfide methyl ethyl disulfide methyl ethyl sulfide methyl ethyl trisulfide	methyl isopropyl sulfide methyl isopropyl disulfide methyl propyl disulfide methyl propyl trisulfide n-butyl disulfide pentyl trisulfide propyl butyl disulfide propyl butyl trisulfide
Group 22 Organosilicon Compounds	dodecamethylcyclohexasiloxane		
Table IV-1 Constituents (See Section IV of the main document; these constituents have established criteria)	2-butoxyethanol 2-furanmethanol 2-hexanone camphor carbon monoxide formic acid	furfural hexachlorobenzene hexachlorobutadiene hydrogen chloride hydrogen cyanide	methacrylic acid methylal methyl methacrylate sulphuric acid tribromomethane
Table IV-4 Constituents (See Section IV of the main document; these constituents do not have criteria and will require additional research.)	1-(ethenyloxy)-butane 1,1,1,2-tetrachloroethane 1,3-dioxolane 1,3-dichloropropene (cis) 1,4-dichlorobutane 1,6-dimethylnaphthalene 2,5-dimethylthiophene 2-ethylthiophene 2-ethynylphenol 2-propyl thiophene 3-(ethylthio)propanal 3-ethynylphenol	3-methylthiophene benzothiazole biphenylene bromodichloromethane bromoethane dibromochloromethane dibromomethane dichlorobutene di-isooctylphthalate dimethoxymethyl propanoate dimethyl furan	furan hexylbenzene indane (2,3-dihydroindene) methyl furan methyl vinyl ketone pentylbenzene propylthiophene t-butyl alcohol tetrachloroethane tetrahydro-2-furanmethanol trifluorobenzene

Table B-3
Constituents Identified in Biogas from Selected Academic Studies
and Possible Combustion Products³³

(includes unique chemicals not reported in other biogas reference studies)

Group	Constituent
Group 19: Chlorofluorocarbons (CFCs)	1-Chloro-1-fluoroethane
Group 22: Organosilicon Compounds	Trimethylsilanol Dimethyldisilanol 2,4-bis(trimethylsiloxy)benzaldehyde
Group 23: Volatile Organics (VOCs)	1-Chloropropane
Group 24: Semivolatile Organics (SVOCs)	Methylthiophenes Ethylthiophenes
Group 25: Metallic Compounds	Dimethyl Tellurium Trimethyl Bismuth Trimethyl Antimony Trimethyl Tin Compounds Arsine and Methyl Arsines
Group 26: Inorganic Compounds	Phosphine
Group 28: Possible Combustion Products	Hydrogen Bromide Hydrogen Chloride Hydrogen Fluoride Metal Oxides Phosphates/Phosphoric Acid Silica (crystalline) Sulfur Dioxide/Sulfates

³³ References: AFSSET 2008, Grumping, et al. 1999, Glindemann, et al. 2005, Hensel, et al. 2000, Hirner, et al. 1994, Rasi 2009.

Table B-4
Constituent Concentration Data for Biogas, Biomethane, and Natural Gas
from the GTI Datasets

Table B-4 provides a link to an Excel workbook containing individual worksheets for each set of gas data used in the health risk assessment of the individual constituents. The Excel file can be found at <http://www.arb.ca.gov/energy/biogas/biogas.htm>

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APPENDIX C

Toxicity Reviews for the Constituents of Concern

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Appendix C provides a link to a pdf file with toxicity summaries for the final constituents of concern. The summaries are, for the most part, excerpts of toxicology reviews that have been published by OEHHA to support the development of Reference Exposure Levels (RELs) and Cancer Slope Factors and other health risk screening values. Also included are several toxicity summaries published by the National Institute for Occupational Safety and Health (NIOSH) for cases in which a NIOSH screening value was used. The pdf file can be found at <http://www.arb.ca.gov/energy/biogas/biogas.htm>