AB 1900 Biogas Recommendations

Biogas Constituents of Concern and Health-Protective Levels for Biomethane

2020 Update

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**Biogas Constituents of Concern
and Health-Protective Levels for
Biomethane 2020 Update**

Office of Environmental Health Hazard Assessment
California Environmental Protection Agency

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Contents

1. Summary

This report updates the Office of Environmental Health Hazard Assessment's (OEHHA) 2013 analysis and recommendations regarding health-protective levels of trace constituents found in biogas, pursuant to the requirements of Assembly Bill 1900 (AB 1900, Chapter 602, Statutes of 2012). AB 1900 required OEHHA and the California Air Resources Board (CARB) to carry out a health risk evaluation of biogas constituents and provide recommendations to the California Public Utilities Commission (CPUC), defining concentration limits and monitoring requirements for constituents that could pose health hazards to exposed populations. Specifically, OEHHA was tasked with compiling the list of biogas constituents of concern and determining the health-protective levels for these constituents.

OEHHA's 2020 update incorporates new, relevant information on biogas constituents that has been identified by OEHHA since 2013. This includes additional biogas sampling data, updated toxicity and risk information, and consideration of exposure to several potentially harmful biogas combustion products. As in the 2013 biogas evaluation, OEHHA utilized risk-screening methods based on its risk assessment guidelines, which were developed as part of the Air Toxics "Hot Spots" Program (OEHHA, 2008, 2009, 2012, and 2015). In addition, OEHHA used CARB's indoor-air models from the 2013 analysis to identify constituents of concern and health-protective levels for these constituents.

The updated list of biogas constituents of concern contains 15 substances. These include six new chemicals and chemical groups that are listed mainly as a result of considering exposure to biogas combustion products. Updating other information in the assessment (e.g., toxicity and exposure factors) led to the removal of three chemicals from the original 2013 list.

OEHHA may modify the constituents of concern and health-protective levels in future updates as new information and analysis warrant.

2. Introduction

2.1 Nature and Use of Biogas and Biomethane

Biogas is generated from the anaerobic digestion of organic materials, as can occur in landfills, covered lagoons, or enclosed vessels where microbial access to oxygen is limited. The chemical composition of biogas varies and is dependent on the source material and environmental conditions. Raw biogas consists primarily of methane and carbon dioxide, along with smaller amounts of ethane, propane, nitrogen, oxygen, hydrogen, and hydrogen sulfide. A variety of trace components can also be found, including: ammonia, siloxanes, chlorofluorocarbons, organometallic compounds, and other volatile organic chemicals. Particulates and biological components, such as bacteria, may also be present.

Biogas can be processed to remove its major and minor impurities and increase its methane content. This involves the use of techniques such as compression, adsorption, absorption, membrane separation, and cryogenic distillation. When biogas is upgraded sufficiently to meet pipeline-quality standards, it is referred to as biomethane and can be used in place of, or along with, natural gas. During upgrading, the concentrations of most trace contaminants are also significantly reduced.

2.2 Required Evaluation of Biogas Chemicals Posing a Potential Health Hazard

AB 1900 requires the CPUC to develop standards for constituents in biomethane to protect human health and the integrity and safety of gas-transport pipelines. To support CPUC's

standards-development process, OEHHA and CARB were to undertake certain actions and make recommendations by May 15, 2013. AB 1900 also requires that CARB and OEHHA update their recommendations at least every five years if new information and data warrant, and that CPUC review and revise its biomethane regulations, if needed, based upon the updated recommendations.

On or before May 15, 2013, AB 1900 required OEHHA to:

- Compile a list of constituents present in biogas that could pose risks to human health and that are found at levels significantly greater than in natural gas;

- Consult with CARB, the Department of Toxic Substances Control (DTSC), CalRecycle, and CalEPA on the above task;

- Determine the health-protective levels for the identified biogas constituents.

Over the same period, CARB's responsibilities were to:

- Develop realistic exposure scenarios for biomethane end-users and biogas production workers, and identify the associated health risks for the biogas constituents identified by OEHHA;

- Consult with OEHHA on the above tasks;

- Determine the appropriate concentrations for the biogas constituents and identify reasonable and prudent monitoring, testing, reporting, and recordkeeping requirements, separately for each source of biogas, to ensure compliance with the health-protective standards. CARB was to consult with OEHHA, DTSC, CalRecycle, and CalEPA on this task.

These tasks were completed and documented in a joint CARB-OEHHA recommendations report (hereinafter referred to as "the 2013 report") submitted to CPUC (CARB-OEHHA, 2013).

2.3 OEHHA and CARB 2013 Report on Chemicals of Concern in Biogas

The 2013 report focused on biogas and biomethane from three of the larger sources in California: landfills, dairies, and wastewater treatment plants. Adequate though not extensive sample data was available for evaluating biogas from these sources,[1] and CARB staff identified biomethane deriving from such sources as having the greatest potential for injection into the natural gas pipeline. OEHHA identified several hundred trace constituents in biogas based upon the available scientific literature and other data and reports provided to CARB staff by industry stakeholders. A risk-screening process was used to define a subset of 12 constituents of concern present in biogas at levels that could present health concerns if not sufficiently removed during the upgrading process. These constituents are listed in Table 1.

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[1] The original 2013 biogas concentration database was compiled from the following sources: Gas Technology Institute (GTI) 2009 a,b,c,d; GTI, 2012; JWPCP, 2011; LACSD, 2012; PG&E, 2008, 2013; and SCAQMD, 2012. This data was from biogas collected from sites in the U.S., Canada, and California.

Table 1: Biogas Constituents of Concern Defined in the 2013 Report	
Antimony	Lead
Arsenic	Methacrolein
Copper	N-nitroso-di-n-propylamine
p-Dichlorobenzene	Mercaptans (Alkyl Thiols)
Ethylbenzene	Toluene
Hydrogen Sulfide	Vinyl Chloride

All 12 constituents of concern were found in landfill biogas, six were present in dairy biogas, and five in biogas derived from municipal wastewater. OEHHA recommended health protective levels for the constituents of concern, consistent with its health risk assessment methodology, and CARB recommended a risk management strategy based on its Risk Management Guidelines for New and Modified Sources of Toxic Air Pollutants (CARB, 1993).[2]

The 2013 report noted that other potentially large sources of biogas such as food waste, crop residuals, and woody biomass would be addressed in future updates as additional data became available. In addition, the report briefly identified several potentially harmful biogas combustion products and an exposure scenario involving combustion in a residential setting (i.e., food cooking). However, it did not evaluate the combustion scenario due to a lack of specific data on biogas combustion emissions from home appliances such as kitchen stoves.

On January 16, 2014, CPUC adopted the CARB-OEHHA recommendations as part of its standards for the injection of biomethane into the common carrier natural gas pipeline (CPUC Decision 14-01-034).

2.4 OEHHA 2020 Update Report

This report updates OEHHA's analysis of biogas constituents. OEHHA has:

- Developed and reported new information on the identity and concentration of biogas trace constituents;

- Updated the list of constituents detected in biogas, including several constituent groups that could give rise to potentially harmful substances upon combustion;

- Studied the formation of selected combustion products from biomethane, including samples containing siloxanes and halogenated volatile organic constituents;

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[2] Since biogas is known to contain hundreds of additional trace constituents, the constituents of concern can be viewed as a set of "indicator chemicals," whose concentration in biomethane indicates whether the biomethane has been adequately processed to be used safely. If concentrations of the indicator chemicals are below the health-protective levels, then it is unlikely that the biomethane would contain unhealthy levels of substances from the larger set of biogas trace constituents.

- Updated the toxicity criteria and risk calculations for the 2020 biogas constituent list;

- Updated the 2013 exposure scenarios in consultation with CARB staff;

- Revised the list of constituents of concern in biogas;

- Calculated health-protective levels for the updated constituents of concern.

A flow chart displaying these tasks, along with CARB's related update responsibilities, is presented in Figure 1. OEHHA's work on the 2020 update is discussed in the following sections.
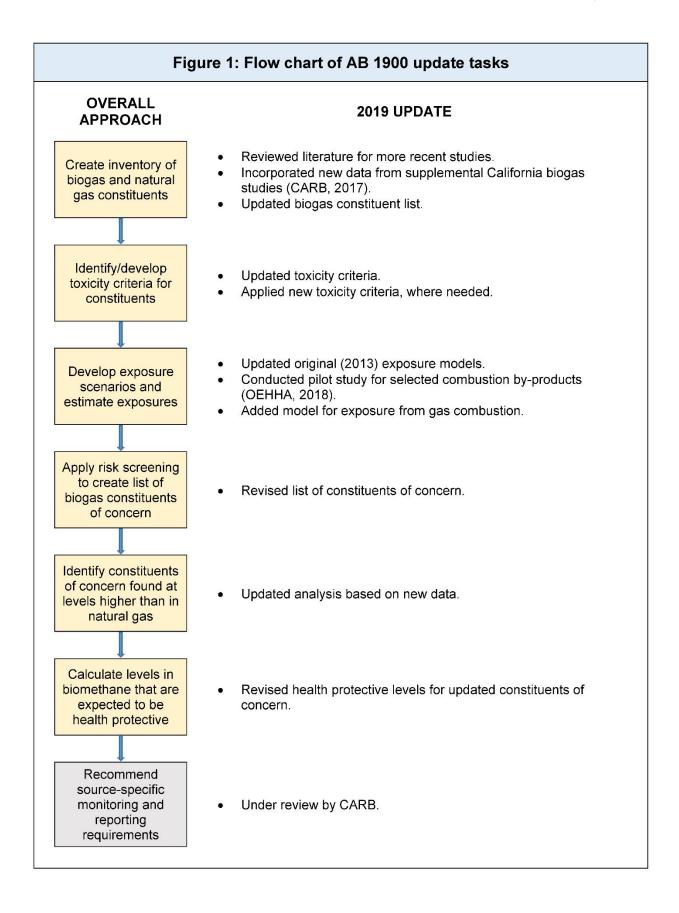
3. Biogas Constituent Update

As in the 2013 report, OEHHA used sample data from California, the US, and Canada to identify biogas constituents and to estimate exposure concentrations for the risk-screening calculations. Information from western European countries was also reviewed, but only to identify new constituents. In order to update the 2013 database, OEHHA searched the literature for studies published since 2013 that were focused on characterizing biogas trace constituents. Several reports from France, Spain, Germany, and Italy—but none from the US or Canada—were found.[3]

However, OEHHA was able to obtain recent California biogas sample data from a study commissioned by CARB and carried out by researchers at the University of California, Davis (UCD). UCD analyzed samples from two food-waste facilities, two dairy farms, and a landfill, all located in California (CARB, 2017). OEHHA identified 45 new biogas constituents based on UCD's results. These are listed in Table 2. In addition, the analytical data from the CARB-UCD study were appended to the original 2013 concentration database.

Some additional landfill gas data for hydrofluoro- and chlorofluorocarbons from a municipal landfill in Solano County was also added to the database. This data was reported in a 2016 greenhouse gas study commissioned by CARB and carried out by researchers at California Polytechnic State University, San Luis Obispo (CARB, 2016). In the study, six samples of raw biogas were taken from the landfill gas collection system, 10 meters before the landfill flare inlet. The samples were analyzed for 12 volatile fluorine-containing compounds. Three new biogas constituents measured in this study are listed in Table 2. The average total fluorine content of the biogas was 19.2 parts per million by volume (ppmv).

The updated 2020 biogas database holds concentrations for nearly 200 individual constituents. New constituents identified based upon the European studies are listed in Appendix A.

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[3] See: Cachia (2018), Paolini (2018), Hilaire (2017), Salazar Gómez (2016), Gallego (2015), and Rey (2013). The literature search was conducted in the spring of 2018.

Figure 1: Flow chart of AB 1900 update tasks

OVERALL APPROACH	2019 UPDATE
Create inventory of biogas and natural gas constituents	• Reviewed literature for more recent studies. • Incorporated new data from supplemental California biogas studies (CARB, 2017). • Updated biogas constituent list.
Identify/develop toxicity criteria for constituents	• Updated toxicity criteria. • Applied new toxicity criteria, where needed.
Develop exposure scenarios and estimate exposures	• Updated original (2013) exposure models. • Conducted pilot study for selected combustion by-products (OEHHA, 2018). • Added model for exposure from gas combustion.
Apply risk screening to create list of biogas constituents of concern	• Revised list of constituents of concern.
Identify constituents of concern found at levels higher than in natural gas	• Updated analysis based on new data.
Calculate levels in biomethane that are expected to be health protective	• Revised health protective levels for updated constituents of concern.
Recommend source-specific monitoring and reporting requirements	• Under review by CARB.

Table 2: Additional Biogas Constituents Identified in the CARB (2016 and 2017) Studies

1,1-Difluoroethane	Dimethylphthalate[a]
1,1,1,2-Tetrafluoroethane	Di-n-octylphthalate
1,1,1,3,3-Pentafluoropropane	Di-n-propyl disulfide
2,2-Dichloropropane	Diphenylamine[a]
2,5-Dimethylbenzaldehyde	Di-tert-butyl disulfide
2-Nitroaniline[a]	Di-tert-butyl sulfide
3-Nitroaniline	Dodecamethylpentasiloxane
4-Chloro-3-methylphenol	Ethyl-t-butyl disulfide
Aluminum[a]	Isopropyl-n-propyl disulfide
Azobenzene[a]	Iron[a]
Barium[a]	Isovaleraldehyde
Benzothiophene	Magnesium[a]
Benzylbutylphthalate[a]	Manganese[a]
Beryllium[a]	Methyl-tert-butyl disulfide
Bromobenzene[a]	Molybdenum[a]
Bromochloroethane[a]	m-Tolualdehyde
C1-Benzothiophenes	Nickel[a]
C2-Benzothiophenes	n-Propyl-tert-butyl disulfide
Cadmium[a]	o-Tolualdehyde
Calcium[a]	Pentachlorophenol[a]
Carbazole[a]	Potassium
Chromium[a]	Selenium[a]
Cobalt[a]	Strontium
Di-isopropyl disulfide	Thallium

[a] Chemical has toxicity criteria.

In the 2013 analysis, manganese (Mn) and chromium (Cr) were not evaluated since each was found only once in the Gas Technology Institute (GTI) dataset, which contained measurements on more than 50 samples of biogas and biomethane. At the time, these two metals were considered to be unreliably detected in biogas at the detection limit of the analytical method (30 ug/m^3). However, the recent CARB-UCD study, which used a more sensitive method with a detection limit of 0.005 ug/m^3, found low levels (< 1 ug/m^3) of these metals in five out of six of its biogas samples and one of three biomethane samples.[4] Therefore, the 2020 update includes an

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[4] The UCD study results were corroborated by a recent French study that also found low concentrations of metallic constituents in several landfill and green-waste biogas samples (See: Cachia, 2018).

evaluation of Mn and Cr exposure. The UCD measurements for these two metals were used in place of the higher-concentration GTI data, since the accuracy of the GTI data for these particular constituents is still in doubt. In the absence of data on chemical speciation, chromium is assumed to be present as insoluble Cr III particulate in unburned biogas. For the combustion analysis, 2% of chromium is assumed to be Cr VI, a value based on a study by Linak *et al.* (1996).

4. Combustion By-Products

The biogas constituents that could give rise to potentially harmful combustion gases are presented in Table 3, along with their likely combustion products. These were originally listed in Appendix Table B-4 of the 2013 report.

Table 3: Biogas Constituents that Could Pose a Hazard to Human Health Upon Combustion	
Biogas Constituents	*Combustion Products*
Chlorinated organics	Hydrogen chloride (HCl)
Fluorinated organics	Hydrogen fluoride (HF)
Metallic constituents	Metal oxides
Siloxanes	Silica (pyrogenic)
Sulfur-containing chemicals	Sulfur dioxide

OEHHA funded a pilot study conducted by UCD to measure selected combustion products from biomethane and natural gas samples (OEHHA, 2018). The study provided information for a residential exposure scenario involving cooking with biomethane. Fully-processed (clean) biomethane samples derived from food-waste and wastewater biogas were combusted using the stove-top burners on a typical residential kitchen stove and the exhaust was analyzed. The study also measured emissions from biomethane samples with added siloxanes and chlorinated/fluorinated volatile organic chemicals (VOCs) in order to evaluate the emission of silica particles and HCl/HF.

Combustion gases were analyzed for VOCs and semivolatile organic compounds (SVOCs), low-molecular weight aldehydes and ketones, phosgene, and chlorinated dioxins/furans. No phosgene or chlorinated dioxins/furans were found in the combustion samples. With the exception of several aldehydes and ketones, listed in Appendix B, emissions from biomethane contained similar or lower concentrations of VOCs and SVOCs, as compared to a sample of compressed natural gas. Given the limited number and type of combustion samples examined in the pilot study, it is uncertain whether there is a difference in the level of aldehydes and ketones emitted by the two combustion-exhaust streams. For the purpose of demonstration, OEHHA assumed that there is a difference, and included the Appendix B chemicals in the risk screening analysis. The screening indicated that the measured aldehydes and ketones in biomethane exhaust did not produce risk values large enough to qualify as constituents of concern.

Production of fine silica particulate has frequently been reported with respect to the use of siloxane-containing biomethane in industrial combustion equipment, and also in laboratory flame studies (See Jalali, 2013, and references cited therein). The pilot study indicated that

stove-top combustion of biomethane with siloxanes produces amorphous silica nanoparticles with a high conversion ratio (essentially 100% of siloxane impurities appear to be converted to amorphous silica).

Regarding the combustion of biomethane spiked with halogenated VOCs, it was expected that most of the halogenated impurities would be converted to their respective acid gases. This was confirmed for the two compounds used in the study: Stove-top combustion of biomethane containing added methylene chloride and/or dichlorodifluoroethane (in the range of 10 to 100 ppm) resulted in conversion efficiencies of (94 ± 9) % for HCl and (119 ± 26) % for HF.

Aside from the constituents listed in Table 3, OEHHA does not have sufficient information to determine whether raw or insufficiently processed biogas would produce higher quantities of various combustion products than natural gas.

5. Toxicity Criteria Update

For this update, OEHHA used a risk-screening methodology similar to that used in the 2013 report. This included the procedure for selecting toxicity criteria, the formulae and exposure assumptions used for the risk calculations, and the choice of acceptable-risk thresholds used to identify the constituents of concern as a subset of the list of all biogas constituents.

The toxicity-screening criteria for the biogas constituents were compiled by defining three tiers of preferred values. The first tier consisted of Criteria developed by OEHHA for assessing risks from inhalation exposures: Reference Exposure Levels (RELs) for non-cancer effects of toxicants and Inhalation Slope Factors (SFi) for cancer effects of toxicants,[5] including both published and proposed criteria, where appropriate. In addition, for several phthalate compounds, the toxicity criteria were based on Safe Harbor Levels defined under the California Proposition 65 regulations.

If toxicity values were not available from the first-tier sources, a second tier of inhalation criteria was used:

- US Environmental Protection Agency (US EPA) toxicity criteria. Values were obtained from the Integrated Risk Information System (IRIS) and Provisional Peer-Reviewed Toxicity Values (PPRTV) databases.

- Agency for Toxic Substances and Disease Registry (ATSDR) Acute and Chronic Minimal Risk Levels (MRLs).

When several values were available for a chemical in this tier, OEHHA generally chose the most health-protective value.

If toxicity values were not available from the second-tier sources, a third tier was used. This consisted of occupational health criteria compiled by the California Department of Occupational Safety and Health (CalOSHA), US Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Safety and Health (NIOSH), or the American Conference of Governmental Industrial Hygienists (ACGIH). We applied an additional uncertainty factor of 30 to these limits to protect sensitive members of the general population, since occupational standards are developed for healthy working adults, and may include cost and technical

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[5] OEHHA defines its cancer-risk criteria in two ways: as SFi's with units of reciprocal (mg/kg-day), and as Unit Risk Factors, in units of reciprocal ($\mu g/m^3$).

feasibility considerations. Additional adjustments were made to the occupational health criteria to account for the fact that these limits are based on exposure assumptions and breathing rates that differ from those used for non-occupational values.

As was done for tier two, when there were several choices of toxicity values, the most health-protective values were chosen for estimating risks.

In a few cases, criteria from other sources were chosen for the analysis when deemed appropriate. For instance, OEHHA used the National Ambient Air Quality Standards (NAAQS) to screen non-cancer risk due to lead exposure via inhalation. For some constituents lacking toxicity values, chemical surrogates with published criteria could be identified based on chemical and toxicological similarity. In some other cases, route-to-route extrapolation of oral exposure criteria was used to obtain a toxicity value for inhalation exposure.

Using the above data sources, toxicity criteria were identified for more than 140 constituents in the updated biogas concentration database. When needed, the values were adjusted as noted above and converted into consistent units of measurement (see Appendix C for additional details). A list of the toxicity criteria (and sources) used for the updated calculations is provided in Appendix D.

6. Update of Risk Calculations

As in the 2013 report, OEHHA carried out a risk evaluation of several likely exposure scenarios to identify the subset of constituents of concern from the full list of biogas trace constituents. This involved use of the 2013 indoor-air models developed by CARB staff, calculation of potential exposure concentrations, estimation of chemical intakes via inhalation, and characterization of the associated health risks.

Potential cancer and non-cancer risks were estimated using OEHHA Air Toxics "Hot Spots" risk assessment guidelines. For non-cancer toxic effects, inhalation hazard quotients were calculated for one-hour ("acute") exposures and long-term average ("chronic") exposures. A hazard quotient is the ratio of estimated exposure to an "acceptable" exposure level. Acceptable exposure is determined by the toxicity value (e.g., a reference concentration or reference dose), which is set at a level below which toxic effects are unlikely to be observed, even in sensitive members of the population. A hazard quotient of one or less indicates a level of exposure that is unlikely to produce a toxic effect in those exposed. Cancer risks are calculated using toxicity values called "cancer potency factors" or "unit risk factors" or "slope factors" that estimate an increase of lifetime cancer risk per unit of chemical intake. Appendix E provides additional details of the risk-screening methods used in the update.

In the 2013 report, CARB defined two residential exposure scenarios and two worker exposure scenarios. For residential exposures, CARB assumed that an individual could be exposed to biomethane from an undetected leak in the home, or to uncombusted gas emitted from a kitchen stove while turning on the burners.[6] The worker scenarios looked at exposures to biomethane-production and gas-utility workers from equipment leaks. Simple mass-balance models (single-zone) were developed by CARB to estimate source-gas dilution factors that were

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[6] CARB also assumed that 100 percent biomethane would be delivered to residences situated close to pipeline injection points and receiving relatively large flows of biomethane. Recent pipeline-flow modeling carried out by the California Council on Science and Technology (CCST, 2018) shows this to be a reasonable assumption.

used to calculate short- and long-term, indoor-air exposure concentrations for these scenarios. Of the four models evaluated, the residential-leak model produced the largest list of constituents of concern and the most health-protective levels for these constituents.[7]

The highest-measured constituent concentrations from the biogas database were chosen by CARB staff for exposure modeling. This was based upon several factors: (1) the biogas concentration database contained data from relatively few samples over a limited time interval, at a small number of sites, (2) a high level of variability was seen among gases from the different sources, and (3) the data for some of the detected chemicals were significantly left-censored.[8]

In the updated risk-screening calculations, OEHHA continued to use CARB's 2013 indoor air models for the biomethane-worker and the residential-exposure scenarios. The worker model and the source-gas dilution factors derived from it were used without revision. [9] On the other hand, several changes were made to the residential-exposure models based on updated information, as well as, to accommodate the combustion-emission analysis. Additional details of the residential models are discussed further below (the model equations and source-gas dilution factors are provided in Appendix F).

Elements from the 2013 residential indoor-air models that were retained are:

- The highest concentrations from the biogas database were generally used as source-gas inputs in the models since the data issues noted above were still present in the updated biogas database.[10]
- House and kitchen volumes of 396.43 m^3 and 44.4 m^3, respectively, were used for both residential scenarios.
- The long-term average, indoor-air concentrations were estimated separately for an isolated kitchen volume and the whole-house volume. Individual exposure was then calculated as a weighted average of these two concentrations, assuming that a resident would spend four hours-per-day in the kitchen (i.e., two meal activities, each lasting two hours).
- The one-hour average, indoor-air concentrations were calculated as the average, isolated kitchen concentrations during a cooking period.[11]
- The residential leak was assumed to occur in the kitchen area.
- The stove-combustion model assumed daily residential use of the stove two times a day with 7 hours between uses.

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[7] Of the two worker scenarios, the biomethane production-worker indicated higher risk levels.

[8] A "left censored" data set is one where some values are reported as less-than the detection limit of the analytical method.

[9] However, in order to correct an oversight in the 2013 analysis, an air-intake adjustment factor was used to calculate the non-cancer HQs for biomethane workers (See Appendix E for additional details).

[10] Except for Cr and Mn, as discussed earlier in the report. For these metals, the lower-concentration results from the CARB-UCD study (CARB, 2017) were used.

[11] A small modification to the averaging method was made. The one-hour average was calculated 30 minutes after the start of burner-use until 30 minutes after the end of use. This provided a slightly larger 1-hour value than averaging from the start of burner-use.

The following model elements were revised in the 2020 update:

- The median air exchange rate for the residence was revised from 0.54 to 0.43 per hour, based on information presented in a recent update of US EPA's Exposure Factors Handbook (US EPA, 2018).

- For the residential-leak model, the gas-leak rate was reduced from 0.003 m^3/hour to 0.000923 m^3/hour based upon a recent study of natural gas leaks in 75 California homes (Fischer, 2018). The concentration-decay factor for organic constituents was maintained at zero-per-hour as in the original model. This factor was revised for the metallic constituents which, with the exception of arsenic and antimony,[12] were assumed to be present as fine particles. A decay factor was 0.2 was chosen to be consistent with the stove-combustion model (see below).

- The 2013 models assumed that the kitchen area was isolated from the rest of the house for four hours each day. The updated models also assume that the kitchen space is isolated for four hours per day, but for only one of every two days. This was judged to better reflect normal cooking behavior, where kitchen doors may be opened at times to maintain a comfortable atmosphere (i.e., to reduce steam, heat, and odors) in the kitchen during cooking.

- The following revisions were specific to the stove-combustion model:[13]

  - The emission source-term was changed from three burners operating at full capacity for five seconds twice per day, to two burners operating at half-capacity for one hour, twice per day. The daily cooking times were chosen based upon a home-cooking survey carried out by Lawrence Berkeley National Laboratory (Klug, 2011) that focused primarily on California residences. Data from this study included the combined use of the stove-top and oven burners.

  - The concentration-decay factor was changed from zero-per-hour to 0.2-per-hour for the metallic constituents and silica, and to one-per-hour for the acid-gas emissions, to account for sorption, deposition, and decomposition processes. The concentration-decay factors were chosen by considering information presented in a US EPA indoor-air modeling handbook (US EPA, 1991) and the Exposure Factors Handbook (US EPA, 2018). The decay factor for acid gases was based upon studies looking at the behavior of sulfur dioxide in indoor environments.

The stove-combustion model required an estimation of biogas silicon, chlorine, fluorine, and sulfur content. These concentrations were obtained by choosing the biogas or biomethane sample having the highest total elemental content, or if multiple samples from the same site were available, an average of sample values was used. For example, the chlorine concentration was based upon the average total chlorine content of two biogas samples taken at a landfill with

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[12] Both arsenic and antimony were assumed to be present as organometallic compounds in uncombusted gas.

[13] Experimental data supporting the choice of input values for these parameters is not extensive. OEHHA judged the revised source-term values to be representative of higher-than-average exposures and to be reasonably health-protective in combination with the other factors used in the risk evaluation.

the highest values (sample numbers "LF04BG01" and "LF04BG02") reported by GTI (2009d). Appendix G provides additional information on the source concentrations for these constituents.

The biogas halogens, silicon, sulfur, and metals were assumed to be fully converted to their respective combustion products. This was judged to be a reasonably health-protective assumption based on the scientific literature dealing with landfill-gas combustion, as well as flame studies using low molecular-weight hydrocarbon fuels, such as methane. In the case of siloxanes and halogenated hydrocarbons, additional support for this assumption is provided by OEHHA's pilot study (OEHHA, 2018) discussed earlier.

As noted above, the indoor-air models provided dilution factors for converting biomethane constituent concentrations to indoor-air exposure concentrations for use in the risk calculations. (Abbreviated tables of these calculations are provided in Appendix H.) Constituents whose hazard quotients or cancer risk values were greater than the following risk thresholds were placed on a preliminary list of constituents of concern:

- Residential Exposure Scenario: 0.1 for hazard quotients and one cancer per million people exposed, for cancer risks

- Worker Exposure Scenario: 1.0 for hazard quotients and 10-per-million for cancer risks

The update uses non-cancer risk thresholds that differ from those previously employed. In the 2013 report, non-cancer hazard quotients of 0.01 (residential) and 0.3 (worker) were used for listing constituents, and 0.1 (residential) and 3.0 (worker) were used in defining the health-protective levels. For the update, OEHHA uses a single set of threshold values, 0.1 (residential) and 1.0 (worker) for listing chemicals as well as for defining their health-protective levels.

A hazard quotient of 0.1 was judged to provide adequate protection in situations where individuals are simultaneously exposed to elevated levels of multiple biogas constituents at home. Regarding the biomethane worker scenario, the 2013 risk thresholds were set at 30 times the values for the general population in order to be consistent with levels of exposure typically allowed under the state and federal occupational safety regulations, which consider the worker population to be more resilient to toxic exposures. This was also consistent with the method used by OEHHA in the 2013 biogas report to derive general public health criteria from occupational health criteria (where an additional factor of 30 was applied to the occupational value to protect sensitive members of the general population, such as infants and individuals with pre-existing health problems).

In the present analysis, OEHHA is reducing the acceptable risk thresholds for workers to 1.0 (for non-cancer hazard quotients) and 10 per million (for cancer risks) in order to provide an additional measure of protection, and in consideration of simultaneous exposure to multiple constituents of concern and the potential for additive risks.

Table 4 presents the constituents of concern and their qualifying risk values, as determined from the two residential exposure scenarios. The aggregate risk values for the residential scenarios were also calculated since an individual could be simultaneously exposed via both pathways. The risk values generated from biomethane-worker scenario were generally not high enough above the acceptable-risk thresholds to determine additional constituents of concern or to set health protective levels. Hydrogen sulfide was the exception, where the chronic hazard quotient for the worker scenario provided the lowest (i.e., most restrictive) health-protective concentration value.

The Table 4 constituents were all determined to be present in biogas at levels higher than in natural gas using the decision method described in the 2013 report and the sample data for natural gas contained in the updated biogas database. As in 2013, benzene was the only preliminary constituent of concern eliminated from the risk evaluation for this reason.

7. Health-Protective Levels for the Constituents of Concern

The health-protective levels (HPLs) for the constituents of concern are presented in Table 5. They were calculated using the aggregated risk values from the updated risk-screening analysis, according to the following formula:

$$HPL = \frac{C_{Source} \; x \; (Target \; Hazard \; Quotient \; or \; Cancer \; Risk)}{(Scenario \; Hazard \; Quotient \; or \; Cancer \; Risk)}$$

where HPL is calculated in mg/m^3 (or ppmv for alkyl thiols) and C_{source} is the biogas concentration used in the risk calculations, also in mg/m^3 (or ppmv for alkyl thiols). The most restrictive of the available values was chosen as the HPL for each constituent of concern. As such, the HPLs are mostly based upon risk values estimated in the long-term residential exposure scenarios (both chronic non-cancer and cancer risks). One exception is hydrogen sulfide, where the HPL was defined using the biomethane-worker chronic risk estimate. Two other exceptions are alkyl thiols and combusted sulfur compounds, where the risks from acute residential exposures determined the protective level. The scenario-specific values from which the final HPLs were chosen are provided in Appendix I.

Constituent or Combustion Product	Kitchen Stove-Combustion Exposure Scenario			Residential Gas Leak Exposure Scenario			Aggregated Risk Values		
	Acute HQ	Chronic HQ	Cancer Risk[a]	Acute HQ	Chronic HQ	Cancer Risk[a]	Acute HQ	Chronic HQ	Cancer Risk[a]
1,4-Dichlorobenzene						3.5			3.5
Alkyl Thiols				0.2	0.1		0.2	0.1	
Antimony		0.7						0.7	
Arsenic	6.5	7.1	823.7	0.1	0.2	23.8	6.6	7.3	847.5
Cadmium			3.0			0.1			3.1
Chlorine (organic)		0.5						0.5	
Chromium (2% Cr VI)			1.9						1.9
Ethylbenzene						1.8			1.8
Fluorine (organic)	0.2	0.2					0.2	0.2	
Hydrogen Sulfide				10.6	8.2		10.6	8.2	
Lead		0.3	1.3					0.3	1.3
N-nitroso-di-n-propylamine						2.5			2.5
Silicon (organic)		5.8						5.8	
Sulfur (compounds)	66.9						66.9		
Vinyl Chloride						3.7			3.7

Table 4: Biogas Constituents of Concern with Qualifying Risk Values
Hazard Quotients (HQs) ≥ 0.1, Cancer Risks ≥ one-per-million)

[a] Risk values are the number of additional cancers expected in a population of one-million people exposed to the constituent according to the modeled exposure scenario over a 70-year period.

| Table 5: Health-Protective Concentrations for Constituents of Concern in Biomethane ||
Biogas Constituent (or Group)	Concentration (mg/m^3) (or ppmv as indicated)
1,4-Dichlorobenzene [a]	4.3
Alkyl Thiols [a]	17 (ppmv)
Antimony [a,b]	0.062
Arsenic [a,b]	0.00040
Cadmium [b]	0.00032
Chlorocarbons (as Cl) [b,c]	4.9
Chromium [b]	0.00048
Ethylbenzene [a]	20
Fluorocarbons (as F) [b,c]	7.4
Hydrogen Sulfide [a]	63 [d]
Lead [a,b]	0.047
N-nitroso-di-n-propylamine [a]	0.024
Silicon compounds (as Si) [b,c]	0.49
Sulfur compounds (as S) [b,c]	13
Vinyl Chloride [a]	0.63

(a) The constituent was also on the 2013 list.

(b) The health-protective concentrations for these chemical groups are based upon their expected combustion products.

(c) The health-protective concentration for these groups is defined in terms of the total concentration of the element giving rise to the combustion product of concern. For example, the value 0.49 mg/m^3 for "Silicon compounds (as Si)" indicates that the health-protective level is based on the silicon content of the gas.

(d) The health protective level for hydrogen sulfide is based upon the chronic worker-exposure scenario, which in this instance, provides a more restrictive value than the 87 and 111 mg/m^3 values (acute and chronic) obtained from the residential-leak scenario.

8. Ongoing Work

Both the 2013 report and this update have identified a number of biogas constituents for which toxicity criteria are currently unavailable. These are listed in Table IV-4 of the 2013 report, with additional chemicals (based upon updated information) presented above in Table 2 and Appendix A. OEHHA will develop toxicity screening criteria for these biogas constituents as information becomes available. In addition, OEHHA will continue to consult with CARB on updates of the available biogas sample data and/or revised exposure scenarios and air-modeling results. OEHHA may modify the constituents of concern and health-protective levels in future updates as new information and analysis warrant.

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Appendix A:
Additional Biogas Constituents Identified
in Recent Western European Studies

Table A-1: Additional Biogas Constituents Identified in Recent Western European Studies				
Study	**Country**	**Biogas Sources**	**Analysis**	**Constituents Reported** [14]
Paolini (2018)	Italy	Sewage sludge	VOCs, Siloxanes	Iodomethane Trimethyl cyclohexane Methyl ethyl cyclohexane
Cachia (2018)	France	Municipal landfill, agricultural wastes	Metals	Aluminum, Barium, Cadmium, Chromium, Molybdenum, Nickel, Selenium, Silver, Vanadium
Hilaire (2017)	France	Municipal landfill, wastewater treatment, agricultural wastes	VOCs	4-Methyl-2-pentanone cis-Decalin
Salazar Gomez (2016)	Germany	Green and food wastes, cattle manure	VOCs	2-Carene 2-Ethylfuran 2-Heptanone 2-Pentylfuran 3-Pentanone Dipropyl disulphide Methyl propyl sulphide
Gallego (2015)	Spain	Municipal landfill	VOCs, Siloxanes	2-Nonanone 3-Pentanone Amylmethylketone Diisopropylketone Dodecamethylpentasiloxane (L5) Ethylisobutylketone

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[14] Constituents that were not previously listed in the 2013 report.

Table A-1: Additional Biogas Constituents Identified in Recent Western European Studies				
Study	**Country**	**Biogas Sources**	**Analysis**	**Constituents Reported [14]**
Rey (2013)	Spain	Municipal landfill	VOCs, Siloxanes	1,2,3,4,4α,5,6,8α-Octahydro-7-methyl-4-methylene-1-(1-methylethyl)-(1α,4aα,8aα)-naphthalene 1-p-Menthene 2,5-Dimethylfuran 2,6-Dimethyl-2-trans-6-octadiene 2-Ethyl-1-decanol 2-Ethyl-5-methylfuran 2-Methyl-3-ethyl-2-heptene 3,7-Dimethyl-1,6-octadiene 3-p-Menthene 3-Pentanone Borneol Butanoic acid 1-methylpropyl ester Butanoic acid 2-methyl-, ethyl ester L-Camphor Carane cis-Caryophyllene Caryophyllene α-Cubebene p-Cymenene Eucalyptol Fenchol Fenchone Hexanoic acid butyl ester Hexanoic acid ethyl ester Humulene Menthol Propene sulphide α-Terpineol Terpinolene α,α,4-Trimethylbenzenemethanol

Appendix B:
Selected Aldehydes and Ketones
in Biomethane Combustion Emissions

Table B-1 lists seven alkyl carbonyl compounds measured in the pilot combustion study (OEHHA, 2018) that appeared to be present in biomethane combustion emissions at levels above those found with natural gas. Given the limited amount of sample data collected for the study, OEHHA regards this information as uncertain. However, for the purpose of demonstration, OEHHA included the Table B-1 chemicals in its risk screening analysis. The screening indicated that the measured aldehydes and ketones in biomethane exhaust did not produce risk values large enough to qualify as constituents of concern.

Table B-1: Aldehydes and ketones found in biomethane combustion emissions at levels potentially higher than in natural gas (OEHHA 2018) (parts-per-billion by volume, ppbv)		
Constituent	*Natural Gas*	*Biomethane*
2-Butanone	0.0206	0.036
Acetaldehyde	0.126	0.352
Benzaldehyde	0.0051	0.009
Crotonaldehyde	< 0.003	0.003
Formaldehyde	0.960	1.328
Hexanal	0.0134	0.017
Propionaldehyde	0.0153	0.027

Appendix C:
Toxicity Value Conversion Calculations

For the purposes of the risk calculations, some of the toxicity values were adjusted for differences in exposure time and breathing rates, and/or converted to uniform units of measurement. For non-carcinogens, the HQ calculations are carried out in air-concentration units of microgram per cubic meter ($\mu g/m^3$). For carcinogens, risks are estimated per milligram of chemical intake, per kilogram body-weight, per day (per mg/kg-d).

For non-cancer toxicity criteria reported in units of parts-per-million, such as ATSDR Minimal Risk Levels (MRLs), the published values were converted as follows:

$$Toxicity\ Value\left(\frac{\mu g}{m^3}\right) = \frac{MRL\ (ppm)\ x\ Molecular\ Weight\left(\frac{g}{mol}\right) x\ 1000\left(\frac{l}{m^3}\right)}{24.45\left(\frac{l}{mol}\right)(molar\ volume, ideal\ gas\ at\ SATP)^{15}}$$

Occupational exposure limits: CalOSHA Permissible Exposure Levels (PELs), NIOSH Recommended Exposure Levels (RELs), and ACGIH Time Weighted Averages (TWAs) were adjusted for differences in exposure time and breathing rate,[15] and an additional uncertainty factor of 30 was applied to protect sensitive members of the general population:

$$Toxicity\ Value\left(\frac{\mu g}{m^3}\right) = \frac{Occup.Value\left(\frac{mg}{m^3}\right) x\ 10\left(\frac{m^3}{day}\right) x\ 5\left(\frac{days}{week}\right) x\ 1000\left(\frac{\mu g}{mg}\right)}{20\left(\frac{m^3}{day}\right) x\ 7\left(\frac{days}{week}\right) x\ 30}$$

For cases where occupational Short-Term Exposure Limits (STELs) or Ceiling Limits were used to develop an acute criterion, an uncertainty factor of 30 was applied together with an adjustment for exposure duration.[16] Specifically, OEHHA converted from a 15-minute STEL or Ceiling to an equivalent 1-hour exposure using the modified form of Haber's law, per our non-cancer risk assessment guidelines (OEHHA, 2008). In this case, the default Haber's law adjustment consists of multiplication by 0.25, corresponding to a Haber's law exponent of one. For alkyl thiols, OEHHA used an exponent of 2, based on Appendix G of the guidelines. This is equivalent to multiplying the STEL by one-half.

For non-cancer criteria derived by route-to-route extrapolation of oral reference doses, the values in units of mg/kg-day were multiplied by a standard adult body weight-to-breathing rate factor of 3.5 kg/m^3 and by 1000 µg/mg. This assumes equivalent absorption by ingestion or inhalation, as well as, inconsequential toxicokinetic differences between each route of intake. Cancer unit risk values in units of reciprocal µg/m^3 (e.g., US EPA IRIS values) were converted to reciprocal mg/kg-day in the same manner: multiplying by 3.5 kg/m^3 and by 1000 µg/mg.

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[15] The update uses the standard occupational breathing-rate ratio of 10 (m^3/day) per 20 (m^3/day) to adjust an occupational exposure to an equivalent general-population exposure; the 2013 analysis used an adjustment factor based on time spent at work.

[16] The 2013 analysis did not apply this additional adjustment.

Appendix D:
Biogas Constituent Toxicity Criteria

Table D-1: Acute Toxicity Criteria					
Constituent	**Source**	**Type**	**Value**	**Units**	**Adjusted Value** ($\mu g/m^3$ or ppbv as indicated)
1,1,1-trichloroethane	OEHHA	REL	6.80E+04	ug/m^3	6.80E+04
1,2,4-Trichlorobenzene	CalOSHA	Ceiling	4.00E+01	mg/m^3	3.33E+02
1,2-Dibromoethane	NIOSH	Ceiling	1.00E+00	mg/m^3	8.33E+00
1,2-Dichlorobenzene	CalOSHA	Ceiling	3.00E+02	mg/m^3	2.50E+03
1,2-Dichloroethane	CalOSHA	STEL	8.00E+00	mg/m^3	6.67E+01
1,2-Dichloropropane	ATSDR	MRL	5.00E-02	ppmv	2.31E+02
1,3-Butadiene	OEHHA	REL	6.60E+02	ug/m^3	6.60E+02
1,4-Dichlorobenzene	ATSDR	MRL	2.00E+00	ppmv	1.20E+04
1,4-Dioxane	OEHHA	REL	3.00E+03	ug/m^3	3.00E+03
2-Butanone	OEHHA	REL	1.30E+04	ug/m^3	1.30E+04
2-Chlorotoluene	NIOSH	STEL	3.75E+02	mg/m^3	3.13E+03
Acetaldehyde	OEHHA	REL	4.70E+02	ug/m^3	4.70E+02
Acetone	ATSDR	MRL	2.60E+01	ppmv	6.18E+04
Acetonitrile	CalOSHA	STEL	1.05E+02	mg/m^3	8.75E+02
Acrolein	OEHHA	REL	2.50E+00	ug/m^3	2.50E+00
Alkyl Thiols	NIOSH	Ceiling	5.00E-01	ppm	8.33E+00 (ppbv)
Ammonia	OEHHA	REL	3.20E+03	ug/m^3	3.20E+03
Arsenic	OEHHA	REL	2.00E-01	ug/m^3	2.00E-01
Beryllium	CalOSHA	STEL	2.00E-03	mg/m^3	1.67E-02
bis(2-chloroethyl)ether	CalOSHA	STEL	6.00E+01	mg/m^3	5.00E+02
Bromomethane	OEHHA	REL	3.90E+03	ug/m^3	3.90E+03
Carbon Disulfide	OEHHA	REL	6.20E+03	ug/m^3	6.20E+03
Carbon Tetrachloride	OEHHA	REL	1.90E+03	ug/m^3	1.90E+03
Carbonyl Sulfide	OEHHA	REL	6.60E+02	ug/m^3	6.60E+02
Chloroethane	ATSDR	MRL	1.50E+01	ppmv	3.96E+04
Chloroform	OEHHA	REL	1.50E+02	ug/m^3	1.50E+02
Chloromethane	ATSDR	MRL	5.00E-01	ppmv	1.03E+03

Table D-1: Acute Toxicity Criteria					
Constituent	**Source**	**Type**	**Value**	**Units**	**Adjusted Value** ($\mu g/m^3$ or ppbv as indicated)
Chromium (2% Cr VI)	CalOSHA	Ceiling for Cr (VI) adj. for 2%	1.00E-01	mg/m^3	4.17E+01
Copper	OEHHA	REL	1.00E+02	ug/m^3	1.00E+02
Crotonaldehyde	CalOSHA	Ceiling	8.60E-01	mg/m^3	7.17E+00
Dichlorodifluoromethane	CalOSHA	Ceiling	3.07E+04	mg/m^3	2.56E+05
Dichloromethane	OEHHA	REL	1.40E+04	ug/m^3	1.40E+04
Ethylbenzene	ATSDR	MRL	5.00E+00	ppmv	2.17E+04
Formaldehyde	OEHHA	REL	5.50E+01	ug/m^3	5.50E+01
Heptane	NIOSH	Ceiling	1.80E+03	mg/m^3	1.50E+04
Heptanes	ACGIH	Ceiling	2.05E+03	mg/m^3	1.71E+04
Hexanes	NIOSH	Ceiling (excl. n-hexane)	1.80E+03	mg/m^3	1.50E+04
Hydrogen Chloride	OEHHA	REL	2.10E+03	ug/m^3	2.10E+03
Hydrogen Fluoride	OEHHA	REL	2.40E+02	ug/m^3	2.40E+02
Hydrogen Sulfide	OEHHA	REL	4.20E+01	ug/m^3	4.20E+01
Manganese	NIOSH	STEL	3.00E+00	mg/m^3	2.50E+01
Mercury	OEHHA	REL	6.00E-01	ug/m^3	6.00E-01
Methylisobutyl ketone	CalOSHA	STEL	3.00E+02	mg/m^3	2.50E+03
Methyl-t-Butyl Ether	ATSDR	MRL	2.00E+00	ppmv	7.21E+03
n-butanol	CalOSHA	Ceiling	1.50E+02	mg/m^3	1.25E+03
n-Heptane	CalOSHA	STEL	2.00E+03	mg/m^3	1.67E+04
Nickel	OEHHA	REL	2.00E-01	ug/m^3	2.00E-01
Octamethylcyclotetrasiloxane	OEHHA	Draft REL	4.00E+03	ug/m^3	4.00E+03
Perchloroethylene	OEHHA	REL	2.00E+04	ug/m^3	2.00E+04
Phenol	OEHHA	REL	5.80E+03	ug/m^3	5.80E+03
Styrene	OEHHA	REL	2.10E+04	ug/m^3	2.10E+04
Sulfur Dioxide	OEHHA	REL	6.60E+02	ug/m^3	6.60E+02
Thiophenol	NIOSH	Ceiling	5.00E-01	mg/m^3	4.17E+00
Toluene	OEHHA	Draft REL	5.00E+03	ug/m^3	5.00E+03
trans-1,2-Dichloroethene	ATSDR	MRL	2.00E-01	ppmv	7.93E+02

Table D-1: Acute Toxicity Criteria					
Constituent	**Source**	**Type**	**Value**	**Units**	**Adjusted Value** ($\mu g/m^3$ or ppbv as indicated)
Trichloroethylene	CalOSHA	STEL	5.37E+02	mg/m^3	4.48E+03
Trichlorofluoromethane	OEHHA	Draft REL	1.90E+05	ug/m^3	1.90E+05
Trimethylbenzenes	OEHHA	Draft REL	4.20E+03	ug/m^3	4.20E+03
Vinyl Chloride	OEHHA	REL	1.80E+05	ug/m^3	1.80E+05
Xylenes	OEHHA	REL	2.20E+04	ug/m^3	2.20E+04
Zinc	OEHHA	Draft REL	1.70E+01	ug/m^3	1.70E+01

Table D-2: Chronic Toxicity Criteria					
Constituent	**Source**	**Type**	**Value**	**Units**	**Adjusted Value** ($\mu g/m^3$ or ppbv as indicated)
1,1,1-trichloroethane	OEHHA	REL	1.00E+03	ug/m^3	1.00E+03
1,1,2,2-Tetrachloroethane	CalOSHA	PEL	7.00E+00	mg/m^3	8.33E+01
1,1,2-Trichloroethane	CalOSHA	PEL	4.50E+01	mg/m^3	5.36E+02
1,1-Dichloroethane	CalOSHA	PEL	4.00E+02	mg/m^3	4.76E+03
1,1-Dichloroethene	OEHHA	REL	7.00E+01	ug/m^3	7.00E+01
1,2,4-Trichlorobenzene	EPA	PPRTV	2.00E-03	mg/m^3	2.00E+00
1,2-Dibromoethane	OEHHA	REL	8.00E-01	ug/m^3	8.00E-01
1,2-Dichlorobenzene	EPA	HEAST[17]	2.00E-01	mg/m^3	2.00E+02
1,2-dichloroethane	OEHHA	REL	4.00E+02	ug/m^3	4.00E+02
1,2-Dichloroethylene	CalOSHA	PEL	7.90E+02	mg/m^3	9.40E+03
1,2-Dichloropropane	EPA	IRIS	4.00E-03	mg/m^3	4.00E+00
1,2-Dichlorotetrafluoroethane	CalOSHA	PEL	7.00E+03	mg/m^3	8.33E+04
1,3-Butadiene	OEHHA	REL	2.00E+00	ug/m^3	2.00E+00
1,4-Dichlorobenzene	OEHHA	REL	8.00E+02	ug/m^3	8.00E+02
1,4-Dioxane	ATSDR	MRL	2.00E-01	ppmv	7.21E+02
2-Butanone	EPA	IRIS	5.00E+00	mg/m^3	5.00E+03
2-Chlorotoluene	CalOSHA	PEL	2.50E+02	mg/m^3	2.98E+03

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[17] US EPA Health Effects Assessment Summary Tables.

Table D-2: Chronic Toxicity Criteria					
Constituent	**Source**	**Type**	**Value**	**Units**	**Adjusted Value** (µg/m³ or ppbv as indicated)
2-Nitroaniline	EPA	PPRTV	5.00E-05	mg/m³	5.00E-02
4,4'-DDT	NIOSH	PEL	5.00E-01	mg/m³	5.95E+00
Acenaphthene	EPA	IRIS RfDo converted	6.00E-02	mg/kg-d	2.10E+02
Acetaldehyde	OEHHA	REL	1.40E+02	ug/m³	1.40E+02
Acetone	ATSDR	MRL	1.30E+01	ppmv	3.09E+04
Acetonitrile	EPA	IRIS	6.00E-02	mg/m³	6.00E+01
Acrolein	OEHHA	REL	3.50E-01	ug/m³	3.50E-01
Alkyl Thiols	NIOSH	REL	5.00E-01	ppm	6.00E+00 (ppbv)
Aluminum	EPA	PPRTV	5.00E-03	mg/m³	5.00E+00
Ammonia	OEHHA	REL	2.00E+02	ug/m³	2.00E+02
Aniline	EPA	IRIS	1.00E-03	mg/m³	1.00E+00
Antimony	EPA	IRIS (SbO_3)	2.00E-04	mg/m³	2.00E-01
Arsenic	OEHHA	REL	1.50E-02	ug/m³	1.50E-02
Barium	CalOSHA	PEL	5.00E-01	mg/m³	5.95E+00
Benzylbutylphthalate	OEHHA	MADL	1.20E+03	ug/d	7.00E+01
Beryllium	OEHHA	REL	7.00E-03	ug/m³	7.00E-03
bis(2-Chloroethyl)ether	ATSDR	MRL	2.00E-02	ppmv	1.17E+02
bis(2-Ethylhexyl)phthalate	OEHHA	MADL	4.06E+02	ug/d	2.03E+01
Bromobenzene	EPA	IRIS	6.00E-02	mg/m³	6.00E+01
Bromomethane	OEHHA	REL	5.00E+00	ug/m³	5.00E+00
Cadmium	OEHHA	REL	2.00E-02	ug/m³	2.00E-02
Calcium oxide	CalOSHA	PEL	2.00E+00	mg/m³	2.38E+01
Carbon Disulfide	OEHHA	REL	8.00E+02	ug/m³	8.00E+02
Carbon Tetrachloride	OEHHA	REL	4.00E+01	ug/m³	4.00E+01
Carbonyl Sulfide	OEHHA	REL	1.00E+01	ug/m³	1.00E+01
Chlorobenzene	OEHHA	REL	1.00E+03	ug/m³	1.00E+03
Chloroethane	OEHHA	REL	3.00E+04	ug/m³	3.00E+04
Chloroform	ATSDR	MRL	5.00E-02	ppmv	2.44E+02
Chloromethane	EPA	IRIS	9.00E-02	mg/m³	9.00E+01

Table D-2: Chronic Toxicity Criteria					
Constituent	**Source**	**Type**	**Value**	**Units**	**Adjusted Value** ($\mu g/m^3$ or ppbv as indicated)
Chromium (2% Cr VI)	ATSDR	Used MRL for insoluble Cr (III)	5.00E-03	mg/m^3	5.00E+00
Chromium (Cr III)	ATSDR	MRL for insoluble particulate	5.00E-03	mg/m^3	5.00E+00
Cobalt	EPA	PPRTV	6.00E-06	mg/m^3	6.00E-03
Copper	CalOSHA	PEL	1.00E-01	mg/m^3	1.19E+00
Cresols	OEHHA	REL	6.00E+02	ug/m^3	6.00E+02
Cyclohexane	EPA	IRIS	6.00E+00	mg/m^3	6.00E+03
Cyclopentane	CalOSHA	PEL	1.72E+03	mg/m^3	2.05E+04
Dichlorodifluoromethane	OEHHA	Draft REL	1.00E+03	ug/m^3	1.00E+03
Dichlorofluoromethane	CalOSHA	PEL	4.00E+01	mg/m^3	4.76E+02
Dichloromethane	OEHHA	REL	4.00E+02	ug/m^3	4.00E+02
Diethylphthalate	CalOSHA	PEL	5.00E+00	mg/m^3	5.95E+01
Dimethylphthalate	CalOSHA	PEL	5.00E+00	mg/m^3	5.95E+01
Di-n-butylphthalate	OEHHA	MADL	8.70E+00	ug/d	5.25E-01
Diphenylamine	CalOSHA	PEL	1.00E+01	mg/m^3	1.19E+02
Endosulfan I	CDPR[18]	RfC	3.30E-04	mg/m^3	3.30E-01
Endrin	CalOSHA	PEL	1.00E-01	mg/m^3	1.19E+00
Ethyl Acetate	EPA	PPRTV	7.00E-02	mg/m^3	7.00E+01
Ethylbenzene	OEHHA	REL	2.00E+03	ug/m^3	2.00E+03
Fluorene	EPA	IRIS RfDo converted	4.00E-02	mg/kg-d	1.40E+02
Formaldehyde	OEHHA	REL	9.00E+00	ug/m^3	9.00E+00
Heptachlor	CalOSHA	PEL	5.00E-02	mg/m^3	5.95E-01
Heptane	EPA	PPRTV	4.00E-01	mg/m^3	4.00E+02
Heptanes	ACGIH	TWA	1.64E+03	mg/m^3	1.95E+04
Hexane	OEHHA	REL	7.00E+03	ug/m^3	7.00E+03
Hexanes	NIOSH	TWA	3.50E+02	mg/m^3	4.17E+03
Hydrogen Chloride	OEHHA	REL	9.00E+00	ug/m^3	9.00E+00

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[18] California Department of Pesticide Regulation.

Table D-2: Chronic Toxicity Criteria					
Constituent	**Source**	**Type**	**Value**	**Units**	**Adjusted Value** ($\mu g/m^3$ or ppbv as indicated)
Hydrogen Fluoride	OEHHA	REL	1.40E+01	ug/m^3	1.40E+01
Hydrogen Sulfide	OEHHA	REL	1.00E+01	ug/m^3	1.00E+01
Iron	CalOSHA	PEL, Soluble salts	1.00E+00	mg/m^3	1.19E+01
Isopropylbenzene	EPA	IRIS	4.00E-01	mg/m^3	4.00E+02
Lead	EPA	NAAQS	1.50E-04	mg/m^3	1.50E-01
Magnesium oxide	ACGIH	TWA	1.00E+01	mg/m^3	1.19E+02
Manganese	OEHHA	REL	9.00E-02	ug/m^3	9.00E-02
Mercury	OEHHA	REL	3.00E-02	ug/m^3	3.00E-02
Methoxychlor	CalOSHA	PEL	1.00E+01	mg/m^3	1.19E+02
Methylcyclohexane	CalOSHA	PEL	1.60E+03	mg/m^3	1.90E+04
Methylisobutyl ketone	EPA	IRIS	3.00E+00	mg/m^3	3.00E+03
Methyl-t-Butyl Ether	ATSDR	MRL	7.00E-01	ppmv	2.52E+03
Molybdenum	ATSDR	MRL	4.00E-04	mg/m^3	4.00E-01
Naphthalene	OEHHA	REL	9.00E+00	ug/m^3	9.00E+00
n-Butane	CalOSHA	PEL	1.90E+03	mg/m^3	2.26E+04
n-butanol	CalOSHA	PEL	1.50E+02	mg/m^3	1.79E+03
Nickel	OEHHA	REL	1.40E-02	ug/m^3	1.40E-02
Nitrobenzene	EPA	IRIS	9.00E-03	mg/m^3	9.00E+00
N-nitrosodimethylamine	EPA	PPRTV	4.00E-05	mg/m^3	4.00E-02
Nonane	EPA	PPRTV	2.00E-02	mg/m^3	2.00E+01
n-Propylbenzene	EPA	PPRTV	1.00E+00	mg/m^3	1.00E+03
Octamethylcyclotetrasiloxane	OEHHA	Draft REL	7.10E+02	ug/m^3	7.10E+02
Octanes	ACGIH	TWA	1.40E+03	mg/m^3	1.67E+04
Pentachlorophenol	OEHHA	Draft REL	1.00E+02	ug/m^3	1.00E+02
Perchloroethane	EPA	RfC	3.00E-02	mg/m^3	3.00E+01
Perchloroethylene	OEHHA	REL	3.50E+01	ug/m^3	3.50E+01
Phenol	OEHHA	REL	2.00E+02	ug/m^3	2.00E+02
Propane	CalOSHA	PEL	1.80E+03	mg/m^3	2.14E+04
Propene	OEHHA	REL	3.00E+03	ug/m^3	3.00E+03

Table D-2: Chronic Toxicity Criteria					
Constituent	**Source**	**Type**	**Value**	**Units**	**Adjusted Value** (µg/m^3 or ppbv as indicated)
Propionaldehyde	EPA	IRIS	8.00E-03	mg/m^3	8.00E+00
Pyridine	CalOSHA	PEL	1.50E+01	mg/m^3	1.79E+02
Selenium	OEHHA	REL	2.00E+01	ug/m^3	2.00E+01
Silica (pyrogenic)	TCEQ[19]	OEHHA adjusted Chronic ReV	6.60E+00	ug/m^3	3.30E+00
Styrene	OEHHA	REL	9.00E+02	ug/m^3	9.00E+02
Thallium	ACGIH	TWA	2.00E-02	mg/m^3	2.38E-01
Thiophenol	CalOSHA	PEL	2.00E+00	mg/m^3	2.38E+01
Tin	CalOSHA	PEL, Oxide and soluble salts	2.00E+00	mg/m^3	2.38E+01
Toluene	OEHHA	Draft REL	4.15E+02	ug/m^3	4.15E+02
trans-1,2-Dichloroethene	ATSDR	MRL	2.00E-01	ppmv	7.93E+02
trans-1,3-Dichloropropene	EPA	RfC	2.00E-02	mg/m^3	2.00E+01
Trichloroethylene	ATSDR	MRL	4.00E-04	ppmv	2.15E+00
Trichlorofluoromethane	OEHHA	Draft REL	2.00E+04	ug/m^3	2.00E+04
Trimethylbenzenes	OEHHA	Draft REL	2.60E+01	ug/m^3	2.60E+01
Valeraldehyde	CalOSHA	PEL	1.75E+02	mg/m^3	2.08E+03
Vinyl Chloride	ATSDR	MRL	3.00E-02	ppmv	7.67E+01
Xylenes	OEHHA	REL	7.00E+02	ug/m^3	7.00E+02
Zinc	OEHHA	Draft REL	9.00E-01	ug/m^3	9.00E-01

Table D-3: Cancer Risk Criteria					
Constituent	**Source**	**Type**	**Value**	**Units**	**Adjusted Value** (per mg/kg-d)
1,1,1,2-tetrachloroethane	US EPA	URi	7.40E-06	per µg/m^3	2.59E-02
1,1,2,2-Tetrachloroethane	OEHHA	SFi	2.00E-01	per mg/kg-d	2.00E-01

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[19] Texas Commission on Environmental Quality. TCEQ publishes inhalation Reference Values (ReVs) to protect public health, some of which are based on analysis methods similar to those of OEHHA. In this case, using the same toxicity data for silica, OEHHA would derive a chronic REL similar to the TCEQ value, but with an additional applied uncertainty factor of 2.

Table D-3: Cancer Risk Criteria					
Constituent	**Source**	**Type**	**Value**	**Units**	**Adjusted Value** (per mg/kg-d)
1,1,2-Trichloroethane	OEHHA	SFi	5.70E-02	per mg/kg-d	5.70E-02
1,1-Dichloroethane	OEHHA	SFi	5.70E-03	per mg/kg-d	5.70E-03
1,2-Dibromoethane	OEHHA	URi	7.10E-05	per µg/m^3	2.50E-01
1,2-dichloroethane	OEHHA	URi	2.10E-05	per µg/m^3	7.20E-02
1,2-Dichloropropane	OEHHA	SFi	3.60E-02	per mg/kg-d	3.60E-02
1,1,1,2-tetrachloroethane	EPA	IRIS	7.40E-06	per ug/m^3	2.59E-02
1,1,2,2-Tetrachloroethane	OEHHA	SFi	2.00E-01	per mg/kg-d	2.00E-01
1,1,2-Trichloroethane	OEHHA	SFi	5.70E-02	per mg/kg-d	5.70E-02
1,1-Dichloroethane	OEHHA	SFi	5.70E-03	per mg/kg-d	5.70E-03
1,2-Dibromoethane	OEHHA	SFi	2.50E-01	per mg/kg-d	2.50E-01
1,2-dichloroethane	OEHHA	SFi	7.20E-02	per mg/kg-d	7.20E-02
1,2-Dichloropropane	OEHHA	SFi	3.60E-02	per mg/kg-d	3.60E-02
1,3-Butadiene	OEHHA	SFi	6.00E-01	per mg/kg-d	6.00E-01
1,4-Dichlorobenzene	OEHHA	SFi	4.00E-02	per mg/kg-d	4.00E-02
1,4-Dioxane	OEHHA	SFi	2.70E-02	per mg/kg-d	2.70E-02
4,4'-DDD	OEHHA	SFi	2.40E-01	per mg/kg-d	2.40E-01
4,4'-DDT	OEHHA	SFi	3.40E-01	per mg/kg-d	3.40E-01
Acetaldehyde	OEHHA	SFi	1.00E-02	per mg/kg-d	1.00E-02
Aniline	OEHHA	SFi	5.70E-03	per mg/kg-d	5.70E-03
Arsenic	OEHHA	SFi	1.20E+01	per mg/kg-d	1.20E+01
Azobenzene	OEHHA	SFi	1.10E-01	per mg/kg-d	1.10E-01
Beryllium	OEHHA	SFi	8.40E+00	per mg/kg-d	8.40E+00
bis(2-Chloroethyl)ether	OEHHA	SFi	2.50E+00	per mg/kg-d	2.50E+00
bis(2-Ethylhexyl)phthalate	OEHHA	SFi	8.40E-03	per mg/kg-d	8.40E-03
Bromochloroethane	EPA	PPRTV-X	6.00E-04	per ug/m^3	2.10E+00
Bromodichloromethane	OEHHA	SFi	1.30E-01	per mg/kg-d	1.30E-01
Cadmium	OEHHA	SFi	1.50E+01	per mg/kg-d	1.50E+01
Carbazole	OEHHA	NSRL	1.70E-01	per mg/kg-d	1.70E-01
Carbon Tetrachloride	OEHHA	SFi	1.50E-01	per mg/kg-d	1.50E-01
Chloroform	OEHHA	SFi	1.90E-02	per mg/kg-d	1.90E-02

Table D-3: Cancer Risk Criteria					
Constituent	**Source**	**Type**	**Value**	**Units**	**Adjusted Value (per mg/kg-d)**
Chromium (2% Cr VI)	OEHHA	SFi for Cr (VI) adj. for 2%	5.10E+02	per mg/kg-d	1.02E+01
Cobalt	EPA	PPRTV	9.00E-03	per ug/m^3	3.15E+01
Dibromochloromethane	OEHHA	SFi	9.40E-02	per mg/kg-d	9.40E-02
Dichloromethane	OEHHA	SFi	3.50E-03	per mg/kg-d	3.50E-03
Ethylbenzene	OEHHA	SFi	8.70E-03	per mg/kg-d	8.70E-03
Formaldehyde	OEHHA	SFi	2.10E-02	per mg/kg-d	2.10E-02
Heptachlor	EPA	IRIS	1.30E-03	per ug/m^3	4.55E+00
Heptachlor epoxide	EPA	IRIS	2.60E-03	per ug/m^3	9.10E+00
Isopropylbenzene	OEHHA	Draft SFi	8.40E-02	per mg/kg-d	8.40E-02
Lead	OEHHA	SFi	4.20E-02	per mg/kg-d	4.20E-02
Methyl-t-Butyl Ether	OEHHA	SFi	1.80E-03	per mg/kg-d	1.80E-03
Naphthalene	OEHHA	SFi	1.20E-01	per mg/kg-d	1.20E-01
Nickel	OEHHA	SFi	9.10E-01	per mg/kg-d	9.10E-01
Nitrobenzene	EPA	IRIS	4.00E-05	per ug/m^3	1.40E-01
N-nitrosodimethylamine	OEHHA	SFi	1.60E+01	per mg/kg-d	1.60E+01
N-nitroso-di-n-propylamine	OEHHA	SFi	7.00E+00	per mg/kg-d	7.00E+00
Pentachlorophenol	OEHHA	SFi	1.80E-02	per mg/kg-d	1.80E-02
Perchloroethane	OEHHA	SFi	3.90E-02	per mg/kg-d	3.90E-02
Perchloroethylene	OEHHA	SFi	2.10E-02	per mg/kg-d	2.10E-02
trans-1,3-Dichloropropene	EPA	IRIS	4.00E-06	per ug/m^3	1.40E-02
Trichloroethylene	OEHHA	SFi	7.00E-03	per mg/kg-d	7.00E-03
Vinyl Chloride	OEHHA	SFi	2.70E-01	per mg/kg-d	2.70E-01

Appendix E:
Additional Details of the Risk Screening Calculations

Potential cancer risks were estimated for the residential and worker scenarios in the same manner as in the 2013 report, using OEHHA Air Toxics "Hotspots" risk assessment guidelines (OEHHA, 2012 and 2016). The incremental life-time cancer risk is calculated as the product of the inhalation slope factor and the life-time average daily rate of chemical intake by inhalation. The formula to estimate the intake rates of biogas constituents for the residential indoor-air scenarios is:

$$Intake\ Rate\ \left(\frac{mg}{kg \cdot day}\right) = BC_r\ x\ DF_r\ x\ SAI_r$$

where:

BC_r = Constituent concentration in biomethane used in a residence (represented by the highest measured values found in biogas or biomethane, mg/m^3)

DF_r = Modeled dilution factor for estimating residential air concentrations produced by a given indoor source of trace constituents from a biomethane leak or from biomethane combustion (unitless) (See Appendix F, Table F-1)

SAI_r = Sensitivity-adjusted, average intake of residential air per body-weight per day (m^3/kg-day)

For calculating residential risks, OEHHA's guidelines recommend estimating the SAI_r factor with age-specific values for breathing rate and time spent at home. In addition, to account for the potential increased sensitivity of infants and children, the guidelines recommend modifying the intake rate with age-specific sensitivity factors. The values used for the calculation are provided below in Table E-1.

Table E-1: Air-Intake and Sensitivity 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)
3rd 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 SAI_r for the residential exposure scenarios is:

$$SAI_r\ \left(\frac{m^3}{kg \cdot day}\right) = \left(\frac{1}{AT}\right) \sum_{i=1}^{4} IR_i\ x\ ED_i\ x\ SF_i\ x\ FAH_i$$

where: IR_i, ED_i, SF_i, and FAH_i are defined as in Table E-1, and where AT is the averaging-time to pro-rate less-than-lifetime exposures in cancer risk calculations (70 yr).

Exposures from the uncombusted gas-leak and stove-combustion scenarios were assumed to occur over 30 years, which represents a value in the high end (i.e., the 90th or 95th percentile) of the range of residential tenure in a single home.[20] The SAI$_r$ value obtained for the residential scenarios is 0.649.

The long-term average intake equation for the worker exposure scenario is:

$$Intake\ Rate \left(\frac{mg}{kg \cdot day}\right) = BC_w\ x\ DF_w\ x\ AI_w = BC_w\ x\ DF_w\ x\ \left(\frac{IR_w\ x\ EF_w\ x\ ED_w}{AT}\right)$$

where:

BC$_w$ = Constituent concentration in biogas in a workplace (highest measured values, mg/m^3)

DF$_w$ = Modeled long-term exposure adjustment factor (biogas dilution factor) for a workplace (4.46 E-04) (unitless)

AI$_w$ = Long-term average, workplace air-intake factor (0.0587 m^3/kg-day)

IR$_w$ = Worker 8-hour breathing rate (0.23 m^3/kg-8 hr) x (8 hr/day); 95%ile for moderate exertion

EF$_w$ = Exposure frequency factor (5/7 day/day)

ED$_w$ = Duration of employment (25 year; 95%ile value)

AT = Averaging time to prorate less-than-lifetime exposures in cancer risk calculations (70 year)

For non-cancer risks in the residential scenario, the acute and chronic hazard quotients were calculated by taking the ratio of the estimated short- or long-term air concentrations to their respective toxicity criteria (e.g., acute or chronic RELs). For the biomethane worker scenario, the acute hazard quotients were calculated in the same way. For the chronic worker hazard quotients, the long-term average air concentration was modified by an additional intake factor to account for less-than-continuous exposure, as follows:

$$Hazard\ Quotient = BC_w\ x\ DF_w\ x\ \frac{5\ days}{7\ days}\ x\ \frac{10\ m^3/day}{20\ m^3/day}\ x\ 1000\ x\ \left(\frac{1}{REL}\right)$$

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[20] Note that the 2013 report assumed a 1-year exposure to uncombusted gas leaks. This value was revised for the 2018 update in consultation with CARB staff. Recently published information on undetected, low-level home gas leaks indicates that they are quite common (Fischer, 2018). Use of a 30-year exposure period is also consistent with OEHHA risk assessment guidelines.

Appendix F:
The CARB 2013 Indoor-Air Models and Adaptations

CARB's 2013 single-zone, indoor-air model was used to estimate the exposure concentrations of biogas constituents in the residential-leak and stove-combustion scenarios. As in the 2013 evaluation, the model was used to separately estimate indoor air concentrations for an isolated kitchen space, as well as, for a house volume (assuming an open kitchen space). The results from these two simulations were then used to estimate composite exposures to individuals using the kitchen space for four hours per day and the rest of the house for the remaining hours. The equations for estimating air concentrations in the kitchen or whole living space are described below.

For the residential-leak scenario, steady-state concentrations were calculated with the following formula:[21]

$$C_{ss} = \left(\frac{s}{\alpha V}\right) = C_s \left(\frac{LR}{\alpha V}\right) = C_s * DF$$

Where:

C_{ss}	=	steady-state concentration (mg/m^3)
s	=	indoor-source emission rate (mg/hour)
α	=	sum of the air-exchange rate (0.43), and concentration-decay rate (0.2, or zero for particulates or organic vapors, respectively) (hour $^{-1}$)
V	=	room volume (44.4 and 396.43 m^3)
C_s	=	constituent concentration in biogas (mg/m^3)
LR	=	indoor biogas leak-rate (9.23E-4 m^3/hour)
DF	=	biogas source to indoor-air dilution factor (unitless)

The leak-rate was derived from a natural gas leak study by Fischer, et al. (2018). The 95th percentile of methane leak-rates measured in 75 representative California houses (20.3 grams per day) was initially decreased by a factor of (2/3) based on a recommendation of Fischer to account for a portion of the measured leakage that does not enter into living spaces.[22] The reduced rate was converted into an equivalent volume of methane at ambient temperature (0.657 grams per liter) and then to a natural gas equivalent (0.93 liters of methane per liter of natural gas), and finally to cubic meters per hour.

Based on the above equation and input values, the DFs for the isolated kitchen space and whole house volume are, respectively, 4.84 E-5 and 5.42 E-6. A single-day, weighted average exposure, assuming a resident spends four meal-time hours in a kitchen that is also isolated from the rest of the house for the same hours is:

$$\frac{4}{24} * (4.84\ E - 5) + \frac{20}{24} * (5.42\ E - 6) = 1.26\ E - 5$$

Assuming that the kitchen is closed off during meal times from the rest of the house for only one of every two days gives the following long-term, daily average concentration:

$$\frac{1}{2} * (1.26\ E - 5) + \frac{1}{2} * (5.42\ E - 6) = 9.0\ E - 6$$

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[21] The models assume no outdoor air contribution to indoor air concentrations.

[22] From a personal communication with Marc L. Fischer, 2018.

The following equation was used for the stove-combustion scenario, where the build-up and decay of indoor concentrations over the course of a day were modeled:[23]

$$C_t = C_0 e^{-\alpha \Delta t} + \left(\frac{s}{\alpha V}\right)\left(1 - e^{-\alpha \Delta t}\right)$$

Where:

C_t	=	concentration at time (t) (mg/m³)
C_0	=	initial indoor air concentration (mg/m³)
Δt	=	difference between time (t) and initial model time (hours)
s	=	indoor-source emission rate (mg/hour)
α	=	sum of the air-exchange rate, and concentration-decay rate (hour⁻¹)
V	=	room volumes (m³)

The corresponding mass-balance equation for the model may be written as:

$$V\left(\frac{dC}{dt}\right) = s - (\alpha)(V)(C)$$

In order to facilitate calculations, this equation was translated into Berkeley Madonna code, as presented below in Figure F-1. The model input values are defined in the code.

The updated concentration-dilution factors for the two residential exposure scenarios are presented in Table F-1, along with the unmodified factors for the biomethane-worker scenario.

Table F-1: Source-to-Indoor Air Concentration-Dilution Factors (unitless)		
Exposure Scenario	Long-Term Average Concentration (for Chronic HQ & Cancer Risk)	One-Hour Average Concentration (for Acute HQ)
Residential Leak	9.00 E-06 (organics) 6.14 E-06 (metal particulates)	4.84 E-05 (organics) 3.30 E-05 (metal particulates)
Residential Stove-combustion	3.92 E-04 (organics) 3.12 E-04 (metal particulates) 1.79 E-04 (acid gases)	4.46 E-03 (organics) 3.84 E-03 (metal particulates) 2.56 E-03 (acid gases)
Biomethane Worker	4.46 E-04	4.46 E-04

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[23] This model assumes no outdoor air contribution to indoor air concentrations.

**Figure F-1: Berkeley Madonna Code
for the Stove-Combustion Indoor-Air Model**

```
{Method = RK4}
STARTTIME = 0  STOPTIME= 24
DT = 0.001

sgcon = 1                       ; source gas concentration; mg/m3
vk = 44.4                       ; volume kitchen, m3
vh = 396.43                     ; volume house, m3
brn = 2                         ; number of burners
bcap_e = 10000                  ; burner energy capacity, Btu/hr
gcf = 36621                     ; conversion factor, Btu/m3
bcap_v = bcap_e/gcf             ; burner volume capacity, m3/hr
buf = 0.5                       ; burner use factor, unitless
gfr = (brn*buf*bcap_v)          ; gas flow rate, m3/hr
src = sgcon*gfr                 ; constituent emission rate, mg/hr
nu = 0.43                       ; air exchange rate, 1/hr
lamda = 1                       ; decay rate, 1/hr, lamda = 1, 0.2,
                                ; or zero for acid gases, particles,
                                ; or organic vapors, respectively


Init m = 0 Limit m >= 0         ; mass in mg
Init cxt_a = 0 Limit cxt_a >=0  ; concentration x time, 1 hour exposure
Init cxt1 = 0  Limit cxt1 >=0   ; concentration x time, toggles between
                                ; kitchen and house
Init cxt2 = 0  Limit cxt2 >=0   ; house conc x time

src_t = If (Mod(Time,7)<=1) AND (Time<=9) THEN (src) ELSE 0

m' = src_t-((nu+lamda)*m)

ck = m/vk  ; concentration in isolated kitchen space, mg/m3
ch = m/vh  ; concentration in house assuming kitchen is open to the house,
           ; mg/m3

cxt_a'= IF (Time>=7.5 and Time<=8.5) THEN (ck) ELSE 0 ; one-hour exposure
                                            ; concentration, mg/m3

cxt1' = IF (Mod(Time,7)<=2) AND (Time<=9) THEN (ck) ELSE (ch)
cavg1 = (cxt1)/24 ; average exposure concentration for composite of isolated
                  ; kitchen (4 hours) and whole house (20 hours), mg/m3

cxt2'= ch
cavg2= (cxt2)/24  ; average exposure concentration in whole house with open
                  ; kitchen, mg/m3

clt=0.5*(cavg1+cavg2) ; long-term average exposure concentration, mg/m3

DISPLAY cxt_a, clt
```

Appendix G:
Total Elemental Concentrations Used in Stove-Combustion Scenario

(Highest Values from the 2020 Biogas Database)

Table G-1: Chlorine Content of Landfill Biogas Sample DL=0.1 ppmv, (GTI, 2009d)					
Chemical	LF4BG01TB	LF4BG02TB	Average	Cl #	Cl ppmv
Dichlorodifluoromethane	0.31	0.67	0.49	2	0.98
1,2-Dichlorotetrafluoroethane	0.05	0.52	0.29	2	0.57
Trichlorofluoromethane	0.05	0.59	0.32	3	0.96
Dichloromethane	0.05	2.08	1.07	2	2.13
Chloroethane	0.43	4.59	2.51	1	2.51
1,1-Dichloroethane	0.05	0.11	0.08	2	0.16
1,2-Dichloroethane	0.05	0.21	0.13	2	0.26
Vinyl Chloride	1.50	2.32	1.91	1	1.91
cis-1,2-Dichloroethene	2.32	1.14	1.73	2	3.46
Trichloroethene	0.23	0.62	0.43	3	1.275
Tetrachloroethene	0.39	1.15	0.77	4	3.08
Total Chlorine					17.3

Table G-2: Fluorine Content of Landfill Biogas (CARB, 2016)			
Chemical	Concentration (pptv)*	F #	F ppmv
trichlorofluoromethane	6.69E+04	1	0.067
dichlorodifluoromethane	1.21E+06	2	2.420
1,1,2-trichlorotrifluoroethane	3.15E+03	3	0.009
1,2-dichlorotetrafluoroethane	1.08E+05	4	0.432
dichlorofluoromethane	2.74E+04	1	0.027
chlorodifluoromethane	1.94E+06	2	3.880
1,1-dichloro-1-fluoroethane	8.28E+05	1	0.828
1-chloro-1,1-difluoroethane	1.23E+05	2	0.246
1-chloro-1-fluoroethane	1.34E+05	1	0.134
1,1,1,2-tetrafluoroethane	2.16E+06	4	8.640
1,1-difluoroethane	1.21E+06	2	2.420
1,1,1,3,3-pentafluoropropane	2.60E+04	5	0.130
Total Fluorine			19.2

* Average of 6 samples; pptv = parts-per-trillion by volume.

Table G-3: Sulfur Content of Dairy Farm Biogas Sample, 081227-001, DL=0.05 ppmv (GTI, 2009b)

Chemical	S ppmv
Hydrogen Sulfide	6570
Sulfur Dioxide	0.19
Carbonyl Sulfide	2.97
Carbon Disulfide	0.07
Methyl Mercaptan	2.84
Ethyl Mercaptan	0.26
i-Propyl Mercaptan	0.35
Dimethyl Sulfide	1.09
Thiophene	0.06
Total Sulfur	6580

Table G-4: Silicon Content of Wastewater Biogas Sample, WWTP2BG01TB, ppmv as Si, DL=0.5 ppmv (GTI, 2009d)

Chemical	ppmv as Si
Octamethylcyclotetrasiloxane (D4)	21.8
Decamethylcyclopentasiloxane (D5)	2.8
Total Silicon	24.6

Appendix H:
Abbreviated Risk-Screening Calculations

Table H-1: Acute Non-Cancer Hazard Quotients (Non-Combustion, Top 20)					
$$Hazard\ Quotient\ (HQ) = \frac{C_S\ (mg/m^3)\ x\ Dilution\ Factor\ (DF)\ x\ 1000}{Acute\ REL}$$					
Constituent	Source Gas Concentration (C$_s$) mg/m^3 (or ppmv as indicated)	Modeled Exposure Concentration ug/m^3 (or ppbv as indicated)		Acute REL ug/m^3 (or ppbv as indicated)	Acute HQ	
		Residential Leak	Worker Scenario		Residential Leak	Worker Scenario
Hydrogen Sulfide	9.16E+03	4.43E+02	4.08E+03	4.20E+01	1.06E+01	9.72E+01
Alkyl Thiols	3.64E+01 (ppmv)	1.76E+00 (ppbv)	1.62E+01 (ppbv)	8.33E+00 (ppbv)	2.11E-01	1.95E+00
Arsenic	3.39E-01	1.64E-02	1.51E-01	2.00E-01	8.20E-02	7.56E-01
Methacrolein	3.12E-01	1.51E-02	1.39E-01	2.50E+00	6.05E-03	5.57E-02
Thiophenol	2.25E-01	1.09E-02	1.00E-01	4.17E+00	2.62E-03	2.41E-02
1,2-Dichloroethane	2.27E+00	1.10E-01	1.01E+00	6.67E+01	1.65E-03	1.52E-02
Sulfur Dioxide	2.03E+01	9.80E-01	9.03E+00	6.60E+02	1.49E-03	1.37E-02
Toluene	1.17E+02	5.65E+00	5.21E+01	5.00E+03	1.13E-03	1.04E-02
Crotonaldehyde	1.55E-01	7.49E-03	6.90E-02	7.17E+00	1.05E-03	9.63E-03
Carbonyl Sulfide	1.30E+01	6.28E-01	5.79E+00	6.60E+02	9.51E-04	8.77E-03
Octamethylcyclotetrasiloxane	6.60E+01	3.19E+00	2.94E+01	4.00E+03	7.98E-04	7.36E-03
1,2-Dibromoethane	9.22E-02	4.46E-03	4.11E-02	8.33E+00	5.36E-04	4.93E-03
Zinc	2.53E-01	8.35E-03	1.13E-01	1.70E+01	4.91E-04	6.64E-03
Ammonia	2.79E+01	1.35E+00	1.24E+01	3.20E+03	4.21E-04	3.88E-03
Heptane	1.27E+02	6.15E+00	5.67E+01	1.67E+04	3.69E-04	3.40E-03
Xylenes	7.99E+01	3.87E+00	3.56E+01	2.20E+04	1.76E-04	1.62E-03
Beryllium	8.60E-05	2.84E-06	3.84E-05	1.67E-02	1.70E-04	2.30E-03
Carbon Disulfide	1.23E+01	5.97E-01	5.50E+00	6.20E+03	9.63E-05	8.87E-04
Mercury	1.70E-03	5.61E-05	7.58E-04	6.00E-01	9.35E-05	1.26E-03
Copper	2.50E-01	8.25E-03	1.12E-01	1.00E+02	8.25E-05	1.12E-03

Table H-2: Acute Non-Cancer Hazard Quotients (Stove Combustion, All)

$$Hazard\ Quotient\ (HQ) = \frac{C_S\ (mg/m^3)\ x\ Dilution\ Factor\ (DF)\ x\ 1000}{Acute\ REL}$$

Constituent	Source Gas Concentration (Cs) (mg/m³)	Modeled Exposure Concentration (ug/m³)	Acute REL (ug/m³)	Residential Acute HQ
Sulfur (compounds as SO₂)	1.72E+04	4.41E+04	6.60E+02	6.69E+01
Arsenic	3.39E-01	1.30E+00	2.00E-01	6.51E+00
Fluorine (organic, as HF)	1.57E+01	4.03E+01	2.40E+02	1.68E-01
Zinc	2.53E-01	9.71E-01	1.70E+01	5.71E-02
Chlorine (organic, as HCl)	2.58E+01	6.60E+01	2.10E+03	3.14E-02
Beryllium	8.60E-05	3.30E-04	1.67E-02	1.98E-02
Mercury	1.70E-03	6.53E-03	6.00E-01	1.09E-02
Copper	2.50E-01	9.60E-01	1.00E+02	9.60E-03
Nickel	2.72E-04	1.04E-03	2.00E-01	5.22E-03
Formaldehyde	1.63E-03	7.27E-03	5.50E+01	1.32E-04
Chromium (2% Cr VI)	9.26E-04	3.56E-03	4.17E+01	8.53E-05
Manganese	4.80E-04	1.84E-03	2.50E+01	7.37E-05
Acetaldehyde	6.34E-04	2.83E-03	4.70E+02	6.02E-06
Crotonaldehyde	8.60E-06	3.84E-05	7.17E+00	5.35E-06

Table H-3: Chronic Non-Cancer Hazard Quotients (Non-Combustion, Top 20)

$$Hazard\ Quotient\ (HQ) = \frac{C_S\ (mg/m^3)\ x\ Dilution\ Factor\ (DF)\ x\ Intake\ Factor\ (IF)\ x\ 1000}{Chronic\ REL}$$

Constituent	Source Gas Concentration (C$_s$) mg/m^3 (or ppmv as indicated)	Modeled Exposure Concentration ug/m^3 (or ppbv as indicated)		Chronic REL ug/m^3 (or ppbv as indicated)	Chronic HQ	
		Residential Leak	Worker Scenario		Residential Leak	Worker Scenario
Hydrogen Sulfide	9.16E+03	8.24E+01	4.08E+03	1.00E+01	8.24E+00	1.46E+02
Arsenic	3.39E-01	3.05E-03	1.51E-01	1.50E-02	2.03E-01	3.60E+00
Alkyl Thiols	3.64E+01 (ppbv)	3.28E-01 (ppbv)	1.62E+01 (ppbv)	6.00E+00 (ppbv)	5.46E-02	9.66E-01
Antimony	4.17E-01	3.75E-03	1.86E-01	2.00E-01	1.88E-02	3.32E-01
Carbonyl Sulfide	1.30E+01	1.17E-01	5.79E+00	1.00E+01	1.17E-02	2.07E-01
Methacrolein	3.12E-01	2.81E-03	1.39E-01	3.50E-01	8.03E-03	1.42E-01
Lead	1.55E-01	9.52E-04	6.91E-02	1.50E-01	6.34E-03	1.65E-01
Trichloroethylene	1.50E+00	1.35E-02	6.71E-01	2.15E+00	6.30E-03	1.12E-01
Nonane	6.40E+00	5.76E-02	2.85E+00	2.00E+01	2.88E-03	5.10E-02
Heptane	1.27E+02	1.14E+00	5.67E+01	4.00E+02	2.86E-03	5.06E-02
Toluene	1.17E+02	1.05E+00	5.21E+01	4.15E+02	2.53E-03	4.48E-02
Zinc	2.53E-01	1.55E-03	1.13E-01	9.00E-01	1.73E-03	4.48E-02
Perchloroethylene	5.56E+00	5.01E-02	2.48E+00	3.50E+01	1.43E-03	2.53E-02
Copper	2.50E-01	1.53E-03	1.12E-01	1.19E+00	1.29E-03	3.34E-02
Ammonia	2.79E+01	2.51E-01	1.24E+01	2.00E+02	1.25E-03	2.22E-02
Naphthalene	1.14E+00	1.02E-02	5.07E-01	9.00E+00	1.14E-03	2.01E-02
1,2-Dibromoethane	9.22E-02	8.30E-04	4.11E-02	8.00E-01	1.04E-03	1.84E-02
Xylenes	7.99E+01	7.19E-01	3.56E+01	7.00E+02	1.03E-03	1.82E-02
1,2,4-Trimethylbenzene	2.73E+00	2.46E-02	1.22E+00	2.60E+01	9.44E-04	1.67E-02
Aniline	9.97E-02	8.97E-04	4.45E-02	1.00E+00	8.97E-04	1.59E-02

Table H-4: Chronic Non-Cancer Hazard Quotients (Stove Combustion, Top 20)

$$Hazard\ Quotient\ (HQ) = \frac{C_S\ (mg/m^3)\ x\ Dilution\ Factor\ (DF)\ x\ 1000}{Chronic\ REL}$$

Constituent	Source Gas Concentration (Cs) (mg/m³)	Modeled Exposure Concentration (ug/m³)	Chronic REL (ug/m³)	Residential Chronic HQ
Arsenic	3.39E-01	1.06E-01	1.50E-02	7.05E+00
Silicon (organic)	6.09E+01	1.90E+01	3.30E+00	5.76E+00
Antimony	4.17E-01	1.30E-01	2.00E-01	6.51E-01
Chlorine (organic)	2.58E+01	4.62E+00	9.00E+00	5.13E-01
Lead	1.55E-01	4.84E-02	1.50E-01	3.22E-01
Fluorine (organic)	1.57E+01	2.82E+00	1.40E+01	2.01E-01
Zinc	2.53E-01	7.89E-02	9.00E-01	8.77E-02
Copper	2.50E-01	7.80E-02	1.19E+00	6.55E-02
Mercury	1.70E-03	5.30E-04	3.00E-02	1.77E-02
Cadmium	1.00E-03	3.12E-04	2.00E-02	1.56E-02
Molybdenum	1.41E-02	4.40E-03	4.00E-01	1.10E-02
Nickel	2.72E-04	8.49E-05	1.40E-02	6.06E-03
Beryllium	8.60E-05	2.68E-05	7.00E-03	3.83E-03
Cobalt	6.20E-05	1.93E-05	6.00E-03	3.22E-03
Calcium	1.30E-01	4.04E-02	2.38E+01	1.70E-03
Manganese	4.80E-04	1.50E-04	9.00E-02	1.66E-03
Aluminum	5.60E-03	1.75E-03	5.00E+00	3.49E-04
Iron	9.60E-03	3.00E-03	1.19E+01	2.52E-04
Barium	1.60E-03	4.99E-04	5.95E+00	8.39E-05
Formaldehyde	1.63E-03	6.39E-04	9.00E+00	7.10E-05

Table H-5: Cancer Risk Calculations (Non-Combustion, Top 20)

$$Cancer\ Risk = C_s\ (mg/m^3)\ x\ Dilution\ Factor\ (DF)\ x\ Intake\ Factor\ (IF)\ x\ Slope\ Factor\ (SF_i)$$

Constituent	Source Gas Concentration (C_s) (mg/m³)	Modeled Exposure Concentrations (mg/m³)		Inhalation Slope Factor (SF_i) (kg-d/mg)	Cancer Risk	
		Residential Leak	Worker Scenario		Residential Leak	Worker Scenario
Arsenic	3.39E-01	3.05E-06	1.51E-04	1.20E+01	2.38E-05	1.07E-04
Vinyl Chloride	2.38E+00	2.14E-05	1.06E-03	2.70E-01	3.75E-06	1.68E-05
1,4-Dichlorobenzene	1.52E+01	1.36E-04	6.76E-03	4.00E-02	3.54E-06	1.59E-05
N-nitroso-di-n-propylamine	6.23E-02	5.61E-07	2.78E-05	7.00E+00	2.55E-06	1.14E-05
Ethylbenzene	3.47E+01	3.13E-04	1.55E-02	8.70E-03	1.77E-06	7.91E-06
1,2-Dichloroethane	2.27E+00	2.04E-05	1.01E-03	7.20E-02	9.53E-07	4.27E-06
Isopropylbenzene	1.65E+00	1.48E-05	7.35E-04	8.40E-02	8.08E-07	3.62E-06
Naphthalene	1.14E+00	1.02E-05	5.07E-04	1.20E-01	7.97E-07	3.57E-06
1,1,2-Trichloroethane	2.07E+00	1.87E-05	9.25E-04	5.70E-02	6.90E-07	3.09E-06
Perchloroethylene	5.56E+00	5.01E-05	2.48E-03	2.10E-02	6.82E-07	3.06E-06
1,3-Butadiene	1.24E-01	1.11E-06	5.53E-05	6.00E-01	4.34E-07	1.95E-06
Bromochloroethane	1.64E-02	1.47E-07	7.30E-06	2.10E+00	2.01E-07	9.00E-07
Dichloromethane	8.61E+00	7.75E-05	3.84E-03	3.50E-03	1.76E-07	7.89E-07
2-Methylnaphthalene	1.94E-01	1.75E-06	8.66E-05	1.20E-01	1.36E-07	6.10E-07
1,2-Dibromoethane	9.22E-02	8.30E-07	4.11E-05	2.50E-01	1.35E-07	6.03E-07
Carbon Tetrachloride	1.01E-01	9.06E-07	4.49E-05	1.50E-01	8.82E-08	3.95E-07
bis(2-Chloroethyl)ether	5.77E-03	5.19E-08	2.57E-06	2.50E+00	8.42E-08	3.77E-07
1-Methylnaphthalene	9.25E-02	8.32E-07	4.12E-05	1.20E-01	6.48E-08	2.91E-07
Trichloroethylene	1.50E+00	1.35E-05	6.71E-04	7.00E-03	6.15E-08	2.76E-07
Cadmium	1.00E-03	6.14E-09	4.46E-07	1.50E+01	5.98E-08	3.93E-07

Table H-6: Cancer Risk (Stove Combustion, All)

$$Cancer\ Risk = C_s\ (mg/m^3)\ x\ Dilution\ Factor\ (DF)\ x\ Intake\ Factor\ (IF)\ x\ Slope\ Factor\ (SF_i)$$

Constituent	Source Gas Concentration (C_s) (mg/m^3)	Modeled Exposure Concentration (mg/m^3)	Inhalation Slope Factor (SF_i) (kg-d/mg)	Residential Cancer Risk
Arsenic	3.39E-01	1.06E-04	1.20E+01	8.24E-04
Cadmium	1.00E-03	3.12E-07	1.50E+01	3.04E-06
Chromium (2% Cr VI)	9.26E-04	2.89E-07	1.02E+01	1.91E-06
Lead	1.55E-01	4.84E-05	4.20E-02	1.32E-06
Cobalt	6.20E-05	1.93E-08	3.15E+01	3.95E-07
Beryllium	8.60E-05	2.68E-08	8.40E+00	1.46E-07
Nickel	2.72E-04	8.49E-08	9.10E-01	5.01E-08
Formaldehyde	1.63E-03	6.39E-07	2.10E-02	8.71E-09
Acetaldehyde	6.34E-04	2.49E-07	1.00E-02	1.61E-09

Appendix I: Scenario-Specific Health Protective Levels

Table I-1: Candidate Health Protective Levels (HPLs) mg/m³ (or ppmv where noted)									
Chemical	**Residential Exposure Scenarios (adjusted) [a]**			**Worker Exposure Scenario**			**Minimum HPL (Acute)**	**Minimum HPL (Chronic and Cancer)**	**Minimum HPL (Overall)**
	Acute	**Chronic**	**Cancer**	**Acute**	**Chronic**	**Cancer**			
1,4-Dichlorobenzene	2.5E+04	8.9E+03	4.3E+00		5.0E+03	9.5E+00	2.5E+04	4.3E+00	4.3E+00
Alkyl Thiols (ppmv)	1.7E+01	6.7E+01		1.9E+01	3.8E+01		1.7E+01	1.9E+01	1.7E+01
Antimony		6.2E-02			1.3E+00			6.2E-02	6.2E-02
Arsenic	5.1E-03	4.7E-03	4.0E-04		9.4E-02	3.2E-02	5.1E-03	4.0E-04	4.0E-04
Cadmium		6.3E-03	3.2E-04		1.3E-01	2.5E-02		3.2E-04	3.2E-04
Chlorocarbons (as Cl)	8.0E+01	4.9E+00					8.0E+01	4.9E+00	4.9E+00
Chromium	1.1E+00		4.8E-04				1.1E+00	4.8E-04	4.8E-04
Ethylbenzene	4.5E+04	2.2E+04	2.0E+01		1.3E+04	4.4E+01	4.5E+04	2.0E+01	2.0E+01
Fluorocarbons (as F)	8.9E+00	7.4E+00					8.9E+00	7.4E+00	7.4E+00
Hydrogen Sulfide	8.7E+01	1.1E+02		9.4E+01	6.3E+01		8.7E+01	6.3E+01	6.3E+01
Lead		4.7E-02	1.2E-01		9.4E-01	9.1E+00		4.7E-02	4.7E-02
N-nitroso-di-n-propylamine			2.4E-02			5.5E-02		2.4E-02	2.4E-02
Silicon compounds (as Si)		4.9E-01						4.9E-01	4.9E-01
Sulfur compounds (as S)	1.3E+01						1.3E+01		1.3E+01
Vinyl Chloride	3.7E+05	8.5E+02	6.3E-01		4.8E+02	1.4E+00	3.7E+05	6.3E-01	6.3E-01

(a) The HPLs for organic chlorine, fluorine, silicon, and sulfur compounds were converted from initial values based on their respective combustion products (hydrogen chloride, hydrogen fluoride, silicon dioxide, and sulfur dioxide) to values based on elemental content.