Government of Canada Gouvernement du Canada

Final Screening Assessment
Petroleum Sector Stream Approach

Petroleum and Refinery Gases
[Industry-Restricted]

Chemical Abstracts Service Registry Numbers
68131-75-9
68477-33-8
68477-85-0
68527-19-5

Environment Canada
Health Canada

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Synopsis

The Ministers of the Environment and of Health have conducted a screening assessment of the following industry-restricted petroleum and refinery gases:

CAS RN[a]	DSL[b] name
68131-75-9	Gases (petroleum), C_3–C_4
68477-33-8	Gases (petroleum), C_3–C_4, isobutane-rich
68477-85-0	Gases (petroleum), C_4-rich
68527-19-5	Hydrocarbons, C_1–C_4, debutanizer fraction[c]

[a] The Chemical Abstracts Service Registry Number (CAS RN) is the property of the American Chemical Society, and any use or redistribution, except as required in supporting regulatory requirements and/or for reports to the government when the information and the reports are required by law or administrative policy, is not permitted without the prior, written permission of the American Chemical Society.
[b] DSL, Domestic Substances List.
[c] Late information received indicated that there is no longer any evidence that CAS RN 68527-19-5 is being transported to other industrial facilities. This update therefore defines this substance as a Stream 1 (site-restricted) petroleum and refinery gas.

These substances were identified as high priorities for action during the categorization of the Domestic Substances List (DSL), as they were determined to present intermediate potential for exposure of individuals in Canada, and were considered to present a high hazard to human health. They do not meet the ecological categorization criteria for persistence, bioaccumulation potential or inherent toxicity to non-human organisms. These substances were included in the Petroleum Sector Stream Approach (PSSA) because they are related to the petroleum sector and are all complex combinations of petroleum hydrocarbons.

Petroleum and refinery gases produced from petroleum facilities (i.e., refineries, upgraders or natural gas processing facilities) are a category of saturated and unsaturated light hydrocarbons. The composition of petroleum and refinery gases varies depending on the source of the crude oil, bitumen or natural gas, as well as process operating conditions and processing units used. As such, these petroleum and refinery gases are considered to be of Unknown or Variable composition, Complex reaction products or Biological materials (UVCBs). In order to predict the overall behaviour of these complex substances for purposes of assessing the potential for ecological effects, representative structures have been selected from each chemical class in the substances.

Three petroleum and refinery gases considered in this screening assessment (CAS RNs 68131-75-9, 68477-33-8 and 68477-85-0) have been identified as industry-restricted (i.e., they are a subset of petroleum and refinery gases that may leave a petroleum sector facility and be transported to other industrial facilities). The petroleum and refinery gases can be consumed at the facility or transferred to other industrial facilities for use as feedstock or fuel or blended into substances leaving the site under different CAS RNs. Updated industry information indicated that CAS RN 68527-19-5 is not being transported to other industrial facilities. Nonetheless, this CAS RN has been included in this assessment as it was determined that this does not change the conclusions of the assessments for either site-restricted or industry-restricted petroleum and refinery gases.

According to information submitted under section 71 of the *Canadian Environmental Protection Act, 1999* (CEPA 1999) and other sources of information, these petroleum and refinery gases are transported from refineries, upgraders and natural gas processing facilities to other facilities by pipelines or in pressurized containers by train. Given the physical–chemical properties of these gases (e.g., high vapour pressures), releases of the petroleum and refinery gases into the atmosphere can occur.

Based on the available information, it is considered unlikely that these petroleum and refinery gases are causing ecological harm in Canada. One component of petroleum and refinery gases, ethene, is being addressed in a separate screening assessment and its potential to cause harm is not considered in this assessment. This will enable consideration of ethene releases from industrial operations generally, rather than attempting to link its release to the specific substances that are the subject of this assessment.

Therefore, based on the information presented in this screening assessment, it is concluded that these petroleum and refinery gases (CAS RNs 68131-75-9, 68477-33-8, 68477-85-0 and 68527-19-5) do not meet the criteria under paragraphs 64(*a*) or 64(*b*) of CEPA 1999 as they are not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity or that constitute or may constitute a danger to the environment on which life depends.

It is recognized that a small portion of the general population may be exposed to these petroleum and refinery gases in the vicinity of petroleum facilities. Exposure to the general population during handling (loading and unloading) and transportation of these industry-restricted petroleum and refinery gases is not expected given the nature of transportation systems and regulations in place to prevent or reduce any discharge during handling and transportation processes.

A critical health effect for the initial categorization of industry-restricted petroleum and refinery gas substances was carcinogenicity, based primarily on classifications by international agencies. The European Union has identified petroleum and refinery gases containing 1,3-butadiene at concentrations greater than 0.1% by weight as carcinogens. Additionally, 1,3-butadiene has been identified by Health Canada and several international regulatory agencies as a carcinogen, and was added to the List of Toxic Substances in Schedule 1 of CEPA 1999. 1,3-Butadiene was found to be a multi-site carcinogen in rodents by inhalation, increasing the incidence of tumours at all concentrations tested. 1,3-Butadiene also exhibits genotoxicity *in vitro* and *in vivo*, and a plausible mode of action for the induction of tumours involves direct interaction with genetic material.

Based on available information, 1,3-butadiene is considered to be present in the Stream 2 petroleum and refinery gases. Therefore, consistent with the approach used to assess the site-restricted (Stream 1) petroleum and refinery gases, 1,3-butadiene was selected as a high-hazard component to characterize potential exposure to the general population. It is recognized that emissions of the Stream 2 petroleum and refinery gases will contribute to a portion of the previously estimated Stream 1 releases. In that assessment it was determined that margins between the high end estimates of exposure to 1,3-butadiene, and estimates of cancer potency for inhalation exposure to 1,3-butadiene are considered potentially inadequate to address uncertainties related to the health effects and exposure databases. Margins of exposure for non-cancer endpoints are considered adequate.

Based on the contribution of these four petroleum and refinery gases to overall facility emissions, it is concluded that these substances meet the criteria under paragraph 64(*c*) of CEPA 1999 as they are entering or may enter the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health.

Based on the information available, it is concluded that the four petroleum and refinery gases listed under CAS RNs 68131-75-9, 68477-33-8, 68477-85-0 and 68527-19-5 meet one or more of the criteria set out in section 64 of CEPA 1999.

Introduction

The *Canadian Environmental Protection Act, 1999* (CEPA 1999) (Canada 1999) requires the Minister of the Environment and the Minister of Health to conduct screening assessments of substances that have met the categorization criteria set out in the Act to determine whether these substances present or may present a risk to the environment or to human health.

Based on the information obtained through the categorization process, the Ministers identified a number of substances as high priorities for action. These include substances that:

- met all of the ecological categorization criteria, including persistence (P), bioaccumulation potential (B) and inherent toxicity to aquatic organisms (iT), and were believed to be in commerce in Canada; and/or
- met the categorization criteria for greatest potential for exposure (GPE) or intermediate potential for exposure (IPE) and had been identified as posing a high hazard to human health based on classifications by other national or international agencies for carcinogenicity, genotoxicity, developmental toxicity or reproductive toxicity.

A key element of the Government of Canada's Chemicals Management Plan is the Petroleum Sector Stream Approach (PSSA), which involves the assessment of approximately 160 petroleum substances that are considered high priorities for action. These substances are primarily related to the petroleum sector and are considered to be of Unknown or Variable composition, Complex reaction products or Biological materials (UVCBs).

Screening assessments focus on information critical to determining whether a substance meets the criteria set out in section 64 of CEPA 1999. Screening assessments examine scientific information and develop conclusions by incorporating a weight-of-evidence approach and precaution.[1]

Grouping of Petroleum Substances

The high priority petroleum substances fall into nine groups of substances based on similarities in production, toxicity and physical–chemical properties (Table A1.1 in

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[1] A determination of whether one or more of the criteria of section 64 are met is based upon an assessment of potential risks to the environment and/or to human health associated with exposures in the general environment. For humans, this includes, but is not limited to, exposures from ambient and indoor air, drinking water, foodstuffs and the use of consumer products. A conclusion under CEPA 1999 on the petroleum substances in the Chemicals Management Plan is not relevant to, nor does it preclude, an assessment against the hazard criteria specified in the *Controlled Products Regulations*, which are part of the regulatory framework for the Workplace Hazardous Materials Information System for products intended for workplace use. Similarly, a conclusion based on the criteria contained in section 64 of CEPA 1999 does not preclude actions being undertaken in other sections of CEPA 1999 or other Acts.

Appendix 1). In order to conduct the screening assessments, each high priority petroleum substance was placed into one of five categories (or "streams"), depending on its production and use in Canada:

> Stream 0: substances not produced by the petroleum sector and/or not in commerce;
> Stream 1: site-restricted substances, which are substances that are not expected to be transported off refinery, upgrader or natural gas processing facility sites;[2]
> Stream 2: industry-restricted substances, which are substances that may leave a petroleum sector facility and be transported to other industrial facilities (e.g., for use as a feedstock, fuel or blending component), but do not reach the public market in the form originally acquired;
> Stream 3: substances that are primarily used by industries and consumers as fuels;
> Stream 4: substances that may be present in products available to the consumer.

An analysis of the available data determined that 16 petroleum substances are evaluated under Stream 2, as described above.[3] These occur within five of the nine substance groups: crude oils, petroleum and refinery gases, low boiling point naphthas, gas oils and heavy fuel oils.

This screening assessment addresses four petroleum and refinery gases described under Chemical Abstracts Service Registry Numbers (CAS RNs) 68131-75-9, 68477-33-8, 68477-85-0 and 68527-19-5. These substances were identified as IPE during the categorization exercise. They were not identified as high priorities for assessment of

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[2] For the purposes of the screening assessment of PSSA substances, a site is defined as the boundaries of the property where a facility is located.

[3] Based on the information collected through the "Notice with respect to certain high priority petroleum substances" (Environment Canada 2008) and the "Notice with respect to potentially industry-limited high priority petroleum substances" (Environment Canada 2009), published under section 71 of CEPA 1999, the petroleum and refinery gases listed in this screening assessment under CAS RNs 68131-75-9, 68477-33-8, 68477-85-0 and 68527-19-5 were identified as being consumed at the facility or being transferred to other industrial facilities for use as feedstock or fuel or blended into substances leaving the site under different CAS RNs.

Information received February 7, 2011 from an industrial reporter indicated an error in data previously provided in their September 2009 response to the section 71 "Notice with respect to potentially industry-limited high priority petroleum substances" (Environment Canada 2009). The data initially reported on CAS RN 68527-19-5 "Hydrocarbons, C_1–C_4, debutanizer fraction" were incorrect; as a consequence, there is no longer any evidence that CAS RN 68527-19-5 is being transported to other industrial facilities. This correction to the data reported in 2009 therefore defines this substance as a Stream 1 (site-restricted) petroleum and refinery gas.

Consequently, CAS RN 68527-19-5 has been evaluated in this assessment of industry-restricted petroleum and refinery gases using considerations consistent for site-restricted substances for the evaluation of risk both to the environment and to human health, and revisions were incorporated, where relevant, in the assessment report. Thorough evaluation of the data, considering CAS RN 68527-19-5 to be a site-restricted substance and CAS RNs 68131-75-9, 68477-33-8 and 68477-85-0 to be industry-restricted substances, revealed no impact on the conclusions under section 64 of CEPA 1999 for the petroleum and refinery gases assessed within either Stream 1 or Stream 2 of the PSSA.

ecological risk, as they were not found to contain components that met the criteria for persistence, bioaccumulation potential or inherent toxicity. According to information submitted under section 71 of CEPA 1999, voluntary industry submissions, an in-depth literature review and a search of material safety data sheets, these substances can be transported to another petroleum facility or other industry sector, but they are not sold directly to consumers. These substances were included in the PSSA because they are related to the petroleum sector and are all complex combinations of petroleum hydrocarbons.

Forty site-restricted petroleum and refinery gases were previously assessed under Stream 1, four were assessed herein under Stream 2, and two are being assessed under Stream 4 (as described above).

Included in this screening assessment is the consideration of information on chemical properties, uses, exposure and ecological and health effects, including the information submitted under section 71 of CEPA 1999. Data relevant to the screening assessment of these substances were identified in original literature, review and assessment documents and stakeholder research reports, as well as from recent literature searches, up to April 2010 for the human exposure and ecological sections of the document and up to September 2011 for the health effects section. Key studies were critically evaluated, and modelling results were used to reach conclusions.

Characterizing risk to the environment involves the consideration of data relevant to environmental behaviour, persistence, bioaccumulation and toxicity, combined with an estimation of exposure of potentially affected non-human organisms from the major sources of release to the environment. Conclusions regarding risk to the environment are based on an estimation of environmental concentrations resulting from releases and the potential for these concentrations to have a negative impact on non-human organisms. As well, other lines of evidence including fate, temporal/spatial presence in the environment and hazardous properties of the substance are taken into account. The ecological portion of the screening assessment summarizes the most pertinent data on environmental behaviour and effects and does not represent an exhaustive or critical review of all available data. Environmental models and comparisons with similar petroleum substances may have assisted in the assessment.

Evaluation of risk to human health involves consideration of data relevant to estimation of exposure (non-occupational) of the general population, as well as information on health effects (based principally on the weight-of-evidence assessments of other agencies that were used for prioritization of the substances). Decisions for risk to human health are based on the nature of the critical effect and/or margins between conservative effect levels and estimates of exposure, taking into account confidence in the completeness of the identified databases on both exposure and effects, within a screening context. The screening assessment does not represent an exhaustive or critical review of all available data. Rather, it presents a summary of the critical information upon which the conclusion is based.

This screening assessment was prepared by staff in the Existing Substances programs at Health Canada and Environment Canada and incorporates input from other programs within these departments. The human health and ecological portions of this assessment have undergone external written peer review/consultation. Comments on the technical portions relevant to human health were received from scientific experts selected and directed by Toxicology Excellence for Risk Assessment (TERA), including Dr. Michael Dourson (TERA), Dr. Stephen Embso-Mattingly (NewFields Environmental Forensics Practice, LLC), Dr. Michael Jayjock (The LifeLine Group) and Dr. Bob Benson (United States Environmental Protection Agency [U.S. EPA]). Additionally, the draft of this screening assessment was subject to a 60-day public comment period. Nonetheless, the final content and outcome of the screening assessment remain the responsibility of Health Canada and Environment Canada.

The critical information and considerations upon which the final screening assessment is based are summarized below.

Substance Identity

Petroleum and refinery gases are a category of petroleum light hydrocarbons produced by refineries, upgraders and natural gas processing facilities (API 2001a). The composition of petroleum and refinery gases varies depending on the source of the crude oil, bitumen or natural gas, as well as the process operating conditions and processing units involved. According to their CAS RN descriptions, these four substances are composed of a limited number of alkanes and alkenes, including C_1 (methane), C_2 (ethane, ethene), C_3 (propane, propene), C_4 (butane, isobutane, butene, butadienes) and C_5 (pentane, isopentanes).

These UVCB substances are complex combinations of hydrocarbon molecules that originate in nature or are the result of chemical reactions and processes that take place during upgrading, refining or natural gas processing. Given their complex and variable compositions, they could not practicably be formed by simply combining individual constituents.

1,3-Butadiene is a component of particular interest because of its physical–chemical properties (e.g., volatility) and toxicological properties (e.g., carcinogenicity). Although very limited data on the 1,3-butadiene content of petroleum and refinery gases are available, the American Petroleum Institute (API 2009a) reported analytical data on the 1,3-butadiene content of selected petroleum and refinery gases based on limited historical data from several US refineries from 1992 through 2002. 1,3-Butadiene was present in each of the four substances listed up to a concentration of approximately 3% by weight for CAS RN 68527-19-5, thus petroleum and refinery gases in this assessment are considered to contain 1,3-butadiene. Detection limits of the study were not reported. The compositional ranges of specific gas components may vary significantly depending on the source of crude oil, bitumen, or natural gas, operating conditions, seasonal process issues and economic cycles (API 2009a).

General descriptions of the four petroleum and refinery gases are presented in Table A2.1 (Appendix 2).

Physical and Chemical Properties

The physical–chemical properties of petroleum and refinery gases found in this assessment are listed in Table 1. Based on the available compositional information and the carbon range of petroleum and refinery gases, ten representative structures were chosen and can be found in Table A2.2 in Appendix 2. Petroleum and refinery gases are mainly composed of C_1–C_5 hydrocarbons, which consist of alkanes, isoalkanes, alkenes, cycloalkanes, cycloalkenes, dienes and cyclodienes. The proportion of each component for a substance with a particular CAS RN can be highly variable within the facility or among different facilities; this makes prediction of the physical–chemical properties of such substances inexact. Detailed physical–chemical properties of the selected representative structures are given in Table A2.2 (Appendix 2).

Table 1. General physical–chemical properties of petroleum and refinery gases (ECB 2000a,b,c,d)

Property	Range of values
Melting point (ºC)	−108.9 to −187.6
Boiling point (ºC)	−162 to 36
Vapour pressure (Pa at 25°C)	6.9×10^4 to 6×10^7
Henry's Law constant (Pa·m^3/mol)	7.5×10^3 to 1.4×10^5
Log K_{ow}	1.1 to 3.4
Log K_{oc}	1.55 to 2.9
Water solubility (mg/L at 25°C)	22 to 735

Abbreviations: K_{oc}, organic carbon–water partition coefficient; K_{ow}, octanol–water partition coefficient

CAS RNs 68131-75-9 and 68477-33-8 are mainly composed of C_3 and C_4 hydrocarbons, these being propane, propene, butane, methyl propane (isobutane), butene and butadiene. CAS RN 68477-85-0 is composed of C_1–C_5 alkanes, and 68527-19-5 is composed of C_1–C_4 alkanes (ECB 2000a,b,c,d; NCI 2006). 1,3-Butadiene has also been measured in CAS RNs 68477-85-0 and 68527-19-5 (API 2009a). Most of the components of these four petroleum and refinery gases are gaseous at environmentally relevant temperatures and are held in a liquid state under pressure. Pentane and isopentane, although liquid at environmental temperatures, are highly volatile and would evaporate readily if released. In the case of these gaseous compounds, the limitations associated with predicting the behaviour of complex mixtures based on the properties of their components in the pure form do not apply, as their boiling points will drive their behaviour in the environment. If they are released to the environment, they will quickly disperse and separate. The C_5 alkane, alkene and cyclic components that are liquids at ambient temperatures still have high vapour pressures, so that they will also evaporate readily from soil or water.

The log octanol–water partition coefficient (log K_{ow}) and log organic carbon–water partition coefficient (log K_{oc}) values are low to moderate, indicating that these four petroleum and refinery gases would not be significantly adsorbed to sediments.

Sources

The petroleum and refinery gases listed in this assessment are produced in Canadian refineries, upgraders and natural gas processing facilities. The CAS RN descriptions (NCI 2006), typical process flow diagrams (Hopkinson 2008), information submitted under section 71 of CEPA 1999 (Environment Canada 2008, 2009) and voluntary submissions of information from industry indicate that these industry-restricted petroleum and refinery gases can be intermediate streams consumed within a facility or may be transported to other industrial facilities for use as a feedstock or fuel or for blending into a substance leaving the facility under a different CAS RN.[4]

CAS RN 68131-75-9 is a general description of a gaseous combination of hydrocarbons containing predominantly C_3–C_4. It represents a substance from a gas separation unit in a refinery, upgrader or natural gas processing plant, where light hydrocarbon substances are separated into C_2 and below, C_3–C_4 and C_5 and above. API (2009a) reported a compositional range of up to approximately 0.1% by weight of 1,3-butadiene for this CAS RN.

CAS RN 68477-33-8 represents a gaseous combination of hydrocarbons (C_3–C_6), predominant with isobutane (i-C_4). It is normally a substance from an isomerization unit in a refinery or upgrader where i-C_4 is produced and will subsequently enter an alkylation unit as a feedstock. API (2009a) reported a compositional range of up to approximately 1% by weight of 1,3-butadiene for this CAS RN.

CAS RN 68477-85-0 refers to a gas stream of C_3–C_5 from a catalytic cracking process in a refinery or upgrader. The substance goes to a gas separation unit for further refining. API (2009a) reported a compositional range of up to approximately 0.5% by weight of 1,3-butadiene for this CAS RN.

CAS RN 68527-19-5 is a general description of a gaseous combination of hydrocarbons from C_1–C_4 from a distillation column in a refinery, upgrader or natural gas processing plant to remove light components (C_1–C_4). The substance often requires further recovery of individual gaseous products (e.g., fuel gas, propane, butane). API (2009a) reported a compositional range of approximately 0.1–3% by weight of 1,3-butadiene for this CAS RN.

Uses

According to information collected through the “Notice with respect to certain high priority petroleum substances” (Environment Canada 2008) and the “Notice with respect to potentially industry-limited high priority petroleum substances” (Environment Canada

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[4] Late-submitted data from industry have identified CAS RN 68527-19-5 as a site-restricted substance.

2009), published under section 71 of CEPA 1999, the petroleum and refinery gases listed in this screening assessment were identified as being consumed at the facility or transferred to other industrial facilities for use as feedstock or fuel or blended into substances leaving the site under different CAS RNs. Although these substances were identified by multiple use codes established during the development of the Domestic Substances List (DSL), it has been determined from information submitted under section 71 of CEPA 1999, voluntary industry submissions, an in-depth literature review and a search of material safety data sheets that these industry-restricted petroleum and refinery gases either do not leave the petroleum facility or are transported to other industrial facilities where they will be further refined or otherwise consumed within the facilities under the CAS RNs identified in this screening assessment.

In the rare instances when these gases leave a petroleum facility as a mixed stream, these hydrocarbon mixtures are generally sent to a fractionation plant where the gases are separated for market as individual gases (e.g., propane and butane). Alternatively, the mixed stream may be sent to a petrochemical facility where the components are separated and then used internally as petrochemical feedstocks or possibly sold as separated products (e.g., propane and butane) (ChemInfo 2009).

Releases to the Environment

Potential releases of these four petroleum and refinery gases include releases within facilities from activities associated with their processing, as well as releases related to their transportation (for CAS RNs 68131-75-9, 68477-33-8 and 68477-85-0) between industrial facilities.

Due to the complex nature of the petroleum and transportation industries, as well as the ambiguity in the literature in the use of the terminology that is critical to the understanding of the Stream 2 PSSA assessments, it is important that the definitions specific to the assessment of the industry-restricted petroleum substances are well understood. Table 2 lists the terminology specific to the present assessment.

Table 2. Definitions of terms specific to the PSSA assessments of industry-restricted petroleum substances

Terminology	Definition
Release	A generic term to define a leak, spill, vent or other release of a gaseous or liquid substance, including controlled release and unintentional release as defined below, but not including catastrophic events.
Controlled release	Any **planned** release for safety or maintenance purposes that is considered part of routine operations and occurs under controlled conditions.
Unintentional release	Any **unplanned** release of a petroleum substance. Causes can include equipment failure, poor maintenance, lack of proper operating practices, adverse weather-related events or other unforeseen factors, but can also be a routine part of normal operations. The following two categories are included under unintentional releases: (1) unintentional

Terminology	Definition
	leaks or spills that occur from processing, handling and transport of a petroleum substance; such leaks or spills can be reduced or controlled by the industry; and (2) accidental releases that may not be controllable by the industry. Only unintentional leaks or spills (category 1, defined above) are considered in the assessment of the potential of industry-restricted petroleum substances to cause ecological harm.
Fugitive release	A specific type of unintentional release. It refers to an unintentional release, which occurs under normal operating conditions, of a gaseous substance into ambient air and which may occur on a routine basis. Fugitive releases can be reduced but may not be entirely preventable due to the substance's physical–chemical properties, equipment design and operating conditions. Evaporative emission during the transportation of petroleum substances is a fugitive release and is considered in the human exposure analysis for purposes of assessing the potential of the substances to cause harm to human health.

Potential On-site Releases

Potential releases of petroleum and refinery gases from a petroleum sector facility can be characterized as either controlled or unintentional releases. Controlled releases are planned releases from pressure relief and venting valves for safety purposes or maintenance. Unintentional releases are typically characterized as spills or leaks from various equipment, valves, piping or flanges, etc. Petroleum facilities are highly regulated under various jurisdictions, and voluntary non-regulatory measures implemented by the petroleum industry are in place to manage potential releases (SENES 2009).

Controlled Releases

The petroleum and refinery gases in this screening assessment originate as overhead emissions from distillation columns in a petroleum facility. The potential locations for the controlled release of these gases include safety valves or venting systems located on the piping or the vessels (e.g., columns, reflux vessels) where these gas streams are generated.

Under typical operating conditions, controlled releases of industry-restricted petroleum and refinery gases would be captured in a closed system,[5] according to defined procedures, and directed to a flare system for combustion. However, in some instances (e.g., to relieve pressure), they may be vented directly to the atmosphere. Exposure of the general population or the environment to releases that are controlled and occur only under typical operating conditions as described above is expected to be minimal for the petroleum and refinery gases under the CAS RNs identified in this screening assessment.

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[5] For the purposes of the screening assessment of PSSA substances, a closed system is defined as a system within a facility that does not have any releases to the environment and where evaporative emissions are collected and recirculated, reused or destroyed.

Unintentional Releases

Unintentional releases (including fugitive releases and spills) occur from equipment (e.g., compressors and storage tanks), valves, pipes or flanges, pressure relief valve seals, during processing and handling of petroleum substances (e.g., loading operations), sample lines and open-ended lines (CCME 1993; CPPI 2007). Fugitive releases tend to occur more frequently when processing equipment is not properly maintained or operated and could go undetected or unfixed for periods of time ranging from days to months (CCME 1993; CAPP 2007).

Despite the fact that some measures and practices are in place to reduce the releases of petroleum substances within the facility, it has been recognized that fugitive releases of the petroleum and refinery gases into the atmosphere can occur due to the much higher volatility (lower boiling point) and higher mobility of gases compared with liquid substances (U.S. EPA 1995; CAPP 2007; CPPI 2007). Once released, gases disperse more quickly into the air with larger volumes than do liquids.

Although general population exposure is not typically expected from industry-restricted petroleum substances, the physical–chemical properties (i.e., higher volatility and vapour pressures) of the petroleum and refinery gases indicate that there is a limited potential for exposure of the general population and the environment in the vicinity of petroleum sector facility sites to the petroleum and refinery gases identified by the CAS RNs listed in this screening assessment. It is therefore considered appropriate to characterize the potential exposure of the general population from the unintentional on-site releases of petroleum and refinery gases identified by the four CAS RNs considered in this screening assessment. Detailed analysis of human exposure was conducted using gas dispersion modelling (see Potential to Cause Harm to Human Health).

Potential Releases during Transportation

In addition to the potential unintentional on-site releases, releases may also occur during the transportation of these industry-restricted petroleum and refinery gases between facilities. In general, three operating procedures are involved during the process of transportation: loading, transit and unloading. Loading and unloading of industry-restricted petroleum and refinery gases are normally conducted on industrial sites. To reduce the transported volumes and the potential for release, gases are normally transported as liquids through pressurized pipelines (Environment Canada 2009) or in pressurized containers (Noyes 1992; Kraus 1998; Miesner and Leffler 2006; Environment Canada 2009). Releases from pipeline loading and unloading processes are considered as part of operational releases by the National Energy Board (NEB 2008a,b). Pipeline loading is associated with pumping a liquid or compressing a gas stream into a pipeline system. Loading operations occur at an inlet station where storage tanks, pumps or compressors are normally located. Unloading operations occur at an outlet station where liquid streams may enter into tanks, but gas streams can enter directly into a distribution network.

Apart from the releases from loading and unloading processes, the potential releases from auxiliary pipeline components are also part of the operational releases defined by NEB (2008a,b). The auxiliary components include pump/compressor stations located along the pipelines to assist the products in moving through the pipelines and valve stations equipped along the pipelines for pipeline protection and maintenance.

No equations or data are available with respect to evaporative emission for loading into pressurized vessels. The U.S. EPA's AP 42 (U.S. EPA 2008a) states that "High-pressure storage tanks can be operated so that virtually no evaporative or working losses occur. No appropriate correlations are available to estimate vapour losses from pressure tanks." Due to the high safety and inspection standards generally applied to pressurized pipeline and container systems, regular releases from these types of pressurized systems are unlikely under normal operating conditions (European Commission 2006; U.S. EPA 2008a; OECD 2009). Therefore, only releases from pipelines are considered in this screening assessment. The potential sources of release to the environment are from unintentional leaks that occur during processing, handling and transport. These substances are gaseous at environmentally relevant temperatures, so ambient air is considered to be the primary receiving medium for all releases of industry-restricted petroleum and refinery gases.

In general, the petroleum industry considers three scenarios as pipeline failure (ERCB 2009):

1. Pipeline hit: typically by a vehicle, defined as striking a pipeline with or without a release of substances being transported (not considered here).
2. Pipeline leak: defined as an opening in a pipeline leading to a release of substances being transported, but not interrupting the pipeline operation.
3. Pipeline rupture: defined as an instantaneous cracking or fracturing of a pipeline leading to a relatively large release of substances being transported, and shutdown of particular pipeline segments is often required.

In pipelines regulated by the Alberta Energy Resources Conservation Board (ERCB), including those carrying crude oil, natural gas and condensates, pipeline leaks account for more than 88% of the reported failures (ERCB 2009).

As noted previously, in addition to the regulations in place to limit unintentional releases within a facility (Appendix 3), there are also various federal and provincial provisions that regulate the on-site handling of petroleum substances, including petroleum and refinery gas substances, for transportation. Such provisions cover loading and unloading and are discussed in further detail in the human health exposure assessment. Collectively, these regulations establish a set of requirements for the safe handling of petroleum substances and are intended to reduce or prevent potential releases during loading, transportation and unloading operations.

Release Estimation

According to information submitted under section 71 of CEPA 1999 (Environment Canada 2009), the industry-restricted petroleum and refinery gases (CAS RNs 68131-75-9, 68477-33-8 and 68477-85-0) are transported by pipeline or in pressurized containers by train. CAS RN 68527-19-5 is not transported in Canada and is not included in this release estimation. The total mass of these three substances transported in Canada was reported by the refining and upgrading facilities to be up to 1 million tonnes in 2006 (Environment Canada 2009).

The data sources used to estimate releases were as follows:

- Statistics Canada (2001, 2009):
  - Pipeline distances;
  - Data on "Line losses and unaccounted/adjustments."

- National Energy Board (NEB 2008a,b):
  - The numbers and volumes of liquid releases from pipelines (pipe body and non-pipe body) from 2000–2006;
  - Annual transport quantities in major pipelines (liquid and gas) from 2004–2007.

- Alberta ERCB (2009):
  - Numbers of pipeline failures (hits, leaks and ruptures) in 2005;
  - Annual numbers of releases of crude oil, natural gas and condensates in each class of release volume (smallest, secondary, large and very large) between 1995 and 2005.

The annual estimated number of releases from pipelines in Alberta was determined from historical data of the ERCB (2009). There were 311 pipeline releases of hydrocarbon liquids in 2005. The data, however, were specific to the province of Alberta. To take into account pipeline spills across Canada, the total pipeline releases in Alberta were proportionally adjusted based on each province's proportion of oil pipeline movements (Statistics Canada 2001, 2009). The release from non-pipe body is expected to be more frequent than that from pipe body. Therefore, it was assumed that 40% of spills were attributed to loading, 20% of spills to transport and 40% to unloading. The estimated annual spills of petroleum and refinery gases for loading, transport and unloading are shown in Table A4.1 (Appendix 4). These estimates are very conservative, as they were derived from all types of pipeline releases and are not specific to petroleum and refinery gases.

The estimated (upper bound) quantities released to soil and air per event for each mode of transportation (pipeline and train) are presented in Table 3. These values are used for determining the predicted environmental concentrations in the environmental exposure assessment. There are no estimated releases to air due to evaporative losses.

Table 3. Estimated (upper-bound) quantities of the three industry-restricted petroleum and refinery gases released (unintentional releases and evaporative emissions) to different media during transportation

Transportation mode	**Unintentional releases due to leaks, by medium**[a]					
	Wastewater or seawater		**Soil**		**Air**	
	(tonnes/ leak)	**(tonnes/ year)**[c]	**(tonnes/ leak)**	**(tonnes/ year)**	**(tonnes/ leak)**	**(tonnes/ year)**
Pipeline						
Loading	n.a.	n.a.	4	1018	43	10 048
Transit	n.a.	n.a.	15	1782	148	17 582
Unloading	n.a.	n.a.	4	1018	43	10 048
Ship	Not involved					
Truck	Not involved					
Train	Negligible					

[a] The generic calculation process for unintentional releases is presented in Appendix 4.

[b] Only evaporative emission under regular operating conditions is considered. Negligible evaporative emissions for pipelines or high-pressure tanks during loading, transit and unloading (U.S. EPA 2008a).

[c] Estimated releases as tonnes/year are based on estimated releases/leak × number of releases/year from Table A4.1 (Appendix 4).

The largest estimated unintentional evaporative emissions of petroleum and refinery gases to air are by pipeline transport at 148 tonnes per release event. Per event emissions for loading and unloading are estimated to be 43 tonnes each (Table 3). Unintentional losses to soil during pipeline transport were estimated to be 15 tonnes per event. An estimated maximum of 22 132 tonnes per year could be lost to soil and air during loading and unloading of pipelines, and 19 364 tonnes per year lost during pipeline transportation (Table 3). The estimated number of leak events per year is provided in Table A4.1 (Appendix 4). These data are very conservative due to the assumptions listed above and are considered as upper bounds.

Environmental Fate

Fugacity modelling has been conducted on the gases that can make up the bulk of the substances identified by these four CAS RNs. The components of these CAS RNs are gaseous at environmentally relevant temperatures; if they are released to the environment, they will volatilize and escape into ambient air.

C_1–C_5 alkanes have boiling points from −162 to 36°C. The individual components of petroleum and refinery gases are characterized by moderate water solubilities (22 to 735 mg/L), very high vapour pressures (6.9×10^4 to 6×10^7 Pa), very high Henry's Law constants (7.5×10^3 to 1.4×10^5 Pa·m^3/mol), low log K_{ow} values (1.1 to 3.4) and low to moderate log K_{oc} values (1.6 to 3.3) (Table A2.2 in Appendix 2).

If released to air, all components of petroleum and refinery gases are expected to remain in air, as they are highly volatile, with vapour pressures ranging from 6.9×10^4 to 6×10^7 Pa (Table A2.2 in Appendix 2) (EQC 2003).

If released to water, all components will largely remain in water (80 to 99%), as they have moderate solubilities (22 to 735 mg/L), with significant evaporative emissions to air likely (7 to 20%) (Table A5.1 in Appendix 5). Volatilization from water surfaces is expected to be a relatively important fate process based upon their moderate water solubilities, generally very high vapour pressures and high Henry's Law constants (7.5×10^3 to 1.4×10^5 Pa·m^3/mol). Emissions to air drop with increasing molecular size and complexity. Alkenes and dienes are less likely to evaporate from water surfaces, but will remain in the water. Petroleum and refinery gases are not expected to sorb significantly to suspended solids and sediments based upon their low to moderate estimated log K_{oc} values (Table A2.2 in Appendix 2; EQC 2003). However, there are no identified release pathways to aquatic environments, so this scenario is unlikely.

If released to soil, the alkanes and alkenes will largely volatilize, with 82 to 98% moving into the air. Dienes will have a significant component (~57%) that remains in soil, with the remainder evaporating (Table A5.1 in Appendix 5). Most components of petroleum and refinery gases are expected to have low to negligible adsorptivity to soil (i.e., expected to be highly mobile) based upon their low to moderate estimated log K_{oc} values and high vapour pressures. Volatilization from moist soil surfaces is expected to be an important fate process based upon their high to very high Henry's Law constants and vapour pressures.

Persistence and Bioaccumulation Potential

Environmental Persistence

The C_1–C_5 alkanes are relatively inert, nonpolar, hydrophobic substances that do not react with water or hydroxide ions (Lyman et al. 1990). Empirical aerobic biodegradation data (API 2001a) show that 66 to 76% biodegradation occurs over 35 days for methane and ethane in water.

As few experimental data on the degradation of other petroleum and refinery gases are available, a quantitative structure–activity relationship–based weight-of-evidence approach was also applied using the AOPWIN (2008) model (Table A5.2 in Appendix 5).

Predicted oxidation half-lives in air for petroleum and refinery gas components ranged from 0.2 to 1559 days (Table A5.2 in Appendix 5). The alkane structures in petroleum and refinery gases are slowly oxidized while the alkene and 1,3-butadiene are expected to rapidly oxidize. This is supported by calculated photodegradation values for alkanes based on equations from Atkinson (1990) that show half-life values of 3.2 to 960 days for degradation of some alkane components in contact with hydroxyl radicals in sunlight. These substances are not expected to react with other photo-oxidative species in the atmosphere, such as ozone; therefore, it is expected that reactions with hydroxyl radicals will be the most important fate process in the atmosphere for petroleum and refinery gases.

Since no empirical data were available on the degradation of petroleum and refinery gases as complex mixtures, a QSAR-based weight-of-evidence approach (Environment

Canada 2007) was applied using the BioHCWin (2008), BIOWIN 3,4,5,6 (2009), CATABOL (c2004-2008) and TOPKAT (2004) biodegradation models (Table A5.3 in Appendix 5).

Primary biodegradation (estimated with BioHCWin and BIOWIN 4) is the transformation of a parent compound to an initial metabolite. Ultimate biodegradation (estimated with BIOWIN 3, 5 and 6, CATABOL and TOPKAT) is the transformation of a parent compound to carbon dioxide and water, mineral oxides of any other elements present in the test compound and new cell material (EPI Suite 2008). BioHCWin (2008) is a biodegradation model specific to petroleum hydrocarbons. Model results are in domain for all MITI-based models (BIOWIN 5 and 6). Methane was not included as it cannot degrade.

For all of the components, both the primary and ultimate biodegradation models in BIOWIN (2009) and BioHCWin agree that these compounds would degrade quickly and would not likely be persistent (half-life < 182 days in water; Table A5.3 in Appendix 5).

Using an extrapolation ratio of 1:1:4 for a water:soil:sediment biodegradation half-life (Boethling et al. 1995), the half-life in soil for all the representative structures is also < 182 days and the half-life in sediments is < 365 days.

The atmospheric half-lives of most components of these petroleum and refinery gases are ≥ 2 days via reactions with hydroxyl radicals and are thus considered to meet the persistence criteria in air (half-life in air ≥ 2 days) as defined in the *Persistence and Bioaccumulation Regulations* of CEPA 1999 (Canada 2000a). In contrast, their half-lives in water, soil or sediments do not meet the persistence criteria for these media as defined in the *Regulations* (Canada 2000a).

Potential for Bioaccumulation

As no experimental bioaccumulation factor (BAF) or bioconcentration factor (BCF) data for petroleum and refinery gases were available, a predictive approach was applied using available BAF and BCF models. The modified Gobas BAF middle trophic level model for fish (BCFBAF 2008) predicted BAFs of 2 to 126 L/kg, indicating that none of the components of petroleum and refinery gases have the potential to bioaccumulate in fish and biomagnify in food webs (Table A5.4 in Appendix 5).

Based on the available kinetic-based modelled values, none of the components of these petroleum and refinery gases meet the bioaccumulation criterion (BAF/BCF ≥ 5000) as defined in the *Persistence and Bioaccumulation Regulations* (Canada 2000a).

Potential to Cause Ecological Harm

Ecological Effects Assessment

Aquatic Compartment

Based on the lack of a release pathway to aquatic environments, no aquatic toxicity data have been included in this assessment.

Terrestrial Compartment

There is an exposure pathway through air to terrestrial organisms. Toxicity data on small mammals were included in this assessment. Ethene was excluded from this assessment, as there is a separate assessment being prepared that discusses its toxicological significance in the environment. Environment Canada has previously assessed the ecological risks associated with the production and use of 1,3-butadiene (Canada 2000b) and found that the substance presents a low risk to terrestrial plants, soil invertebrates and wildlife. No ecotoxicological data suggesting that this conclusion should be modified have come to the attention of Environment Canada since that assessment.

Experimental data available on acute effects via inhalation in laboratory animals indicate that few of the representative structures are acutely toxic to animals (Canada 2000b; ACGIH 2001, 2005). Methane is biologically inert (Rom 1992); isobutane is toxic to rats at a concentration of 570 000 ppm (1 458 000 mg/m^3) over 15 minutes (ECB 2007); and a median lethal concentration (LC_{50}) of 620 000 mg/m^3 was noted for isobutene in rats (Shugaev 1969). Propene at 112 000 mg/m^3 over 4 hours did not produce mortality in rats (Conolly and Osimitz 1981) and at 40% (688 000 mg/m^3) produced only light anesthesia in rats (Bingham et al. 2001).

Small mammals are also not especially sensitive to these components over long periods of time. Sublethal impacts on development were not noted at relatively high concentrations for propene (17 190 mg/m^3) or 2-butene (11 460 mg/m^3) in rats exposed by inhalation during pregnancy (Waalkens-Berendsen and Arts 1992; Aveyard 1996; BASF 2002).

Ethene has previously been identified as a potentially hazardous component to terrestrial plants and is found in some of these petroleum and refinery gases. A screening assessment of ethene is ongoing, and thus it is not considered in this assessment.

Ecological Exposure Assessment

Based on the lack of an apparent pathway to aquatic environments, an aquatic exposure scenario was not developed. Due to the lack of demonstrated toxicity to small mammals via inhalation, an exposure scenario was also not developed for terrestrial animals. As ethene will be assessed separately, no exposure scenario was developed for terrestrial plants.

Characterization of Ecological Risk

The approach taken in this ecological screening assessment was to examine available scientific information and develop conclusions based on a weight-of-evidence approach as required under CEPA 1999.

The major components of petroleum and refinery gases have very low acute toxicities to small mammals (greater than 600 000 mg/m^3), such that it is highly unlikely that wild animals would be exposed to acutely toxic concentrations. There were no long-term sublethal impacts on rats exposed via inhalation to two components at 11 000 to 17 000 mg/m^3. These concentrations far exceed those that would be expected in the environment around even large spill-type releases. There was no other exposure scenario, as these substances are composed of gases, and exposure of aquatic organisms is extremely unlikely, as the substances are not transported over water.

In a scenario in which petroleum and refinery gases are released to soil via pipeline transport, these substances will not likely remain in soil, but, rather, will partition readily to air (Table A5.1 in Appendix 5). Therefore, an exposure scenario involving the release of petroleum and refinery gases to soil was not considered.

One component, ethene, is being addressed in a separate screening assessment and has not been considered here.

There was no evidence that these petroleum and refinery gases would pose a threat of harm to terrestrial organisms.

These petroleum and refinery gases are considered to contain components that meet the persistence criteria in air according to the *Persistence and Bioaccumulation Regulations* of CEPA 1999 (Canada 2000a), but none that meet the criteria for bioaccumulation.

Therefore, based on the information presented in this screening assessment, it is concluded that these petroleum and refinery gases are unlikely to be causing ecological harm to organisms or the broader integrity of the environment. It is concluded that the petroleum and refinery gases included in this screening assessment (CAS RNs 68131-75-9, 68477-33-8, 68477-85-0 and 68527-19-5) do not meet the criteria under paragraphs 64(a) or 64(b) of the *Canadian Environmental Protection Act, 1999* (CEPA 1999) as they are not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity or that constitute or may constitute a danger to the environment on which life depends.

Uncertainties in Evaluation of Ecological Risk

The proportions of each component in each petroleum and refinery gas assigned a specific CAS RN are generally not known. However, the low ecological toxicity of most of the components makes this information gap relatively unimportant for the assessment of ecological risk.

Potential to Cause Harm to Human Health

Exposure Assessment

The general physical–chemical properties of the petroleum and refinery gases indicate that when these gaseous substances are released, they will rapidly disperse in the environment in the vicinity of refineries, upgraders and natural gas processing facilities. Furthermore, when these gases are released into the air, the individual chemicals constituting the petroleum and refinery gases will separate and partition in accordance with their own physical–chemical properties (API 2009a). As such, inhalation would be the primary potential route of exposure and is therefore the focus of the current exposure assessment.

The petroleum and refinery gases listed in this screening assessment may disperse into the air around a facility via unintentional releases from, for example, process equipment, valves and flanges. Due to limited information on emissions associated with these complex combinations of hydrocarbons as a whole, it was considered appropriate to characterize the emissions of a specific component of the substances. 1,3-Butadiene was selected from the list of components (as described in the Physical–Chemical Properties section) that confer a broad range of potential toxicities, as it is a high-hazard component representing the potential effects on human health of the petroleum and refinery gases. Furthermore, it is a component that is found in all four of these petroleum and refinery gases and was the basis for their classification as carcinogens by the European Union (European Commission 2004; ESIS 2008).

As discussed in a previous section (Releases to the Environment), potential sources of releases of these four petroleum and refinery gases are unintentional on-site releases from processing units, as well as any releases that may occur during transportation of CAS RNs 68131-75-9, 68477-33-8 and 68477-85-0 (including loading, transit and unloading).

Potential Exposure to Unintentional On-site Releases

As described in detail in the Stream 1 assessment of the site-restricted petroleum and refinery gases (Canada 2013), unintentional on-site releases can be estimated using benzene emission data and the ratio of 1,3-butadiene to benzene from refinery emissions.

The annual average concentrations of 1,3-butadiene in ambient air have been reported by various sources to range from less than 0.05 $\mu g/m^3$ to 0.4 $\mu g/m^3$, depending on location. In general, automotive emissions are a major contributor to 1,3-butadiene levels in ambient air (Canada 2000b). Curren et al. (2006) reported that the average annual 1,3-butadiene concentration at urban sites in Canada from 1995 to 2003 was 0.22 $\mu g/m^3$. Additional monitoring data for 1990 to 2007 were collected from the Clean Air Strategic

Alliance data warehouse in Alberta (CASA 2007), indicating that the average annual concentrations in central Edmonton, east Edmonton and central Calgary were 0.34 $\mu g/m^3$, 0.18 $\mu g/m^3$ and 0.32 $\mu g/m^3$, respectively. The annual average concentration of 1,3-butadiene in ambient air ranged from less than 0.05 $\mu g/m^3$ to 0.05 to 0.2 $\mu g/m^3$ in 2005 based on 49 monitoring sites across Canada (NAPS 2008), from less than 0.05 $\mu g/m^3$ to to 0.1 $\mu g/m^3$ in 2006 based on 47 monitoring sites (NAPS 2008), and from 0.01 to 0.4 $\mu g/m^3$ in 2008/2009 based on 58 monitoring sites across Canada (NAPS 2010). For this assessment, 0.22 $\mu g/m^3$ was selected to represent ambient background for comparison to modelled emissions.

Due to limited quantitative emissions data (measured or estimated) of 1,3-butadiene from petroleum facilities, potential human exposure to petroleum and refinery gases was estimated based on measured benzene emission data and the ratio of 1,3-butadiene to benzene in total refinery releases (NPRI 2000–2007; TRI 2007), as described in the Stream 1 petroleum and refinery gas assessment.

Monitoring data on benzene emissions from a Canadian refinery were reported by Chambers et al. (2008) using a differential absorption, light detection and ranging (DIAL) method. DIAL technology has been referenced as one of the best available methodologies for quantitative on-site monitoring of benzene in both refineries and storage facilities by the European Commission (EIPPCB 2003, 2006). The DIAL method has been cited as being able to provide reliable short-term emission estimates (CONCAWE 2008; U.S. EPA 2010). When short-term emission estimates are extrapolated to project annual inventory values, high estimations may occur as compared to API emission algorithms based on standardized assumptions (CONCAWE 2008). Regardless of discrepancy between DIAL and API emission estimates, DIAL measurements, based on quantitative measurements, are considered to be a reliable estimation method and have been used to assess fugitive emissions in European refineries for over 20 years, and are accepted by the U.S. EPA (CONCAWE 2008; U.S. EPA 2006, 2010).

Once the quantity of 1,3-butadiene emissions was estimated based on benzene DIAL emission data (Chambers et al. 2008), and using the ratio of 1,3-butadiene to benzene in the fugitive emissions from a facility (both average-case and upper-bounding scenarios) (NPRI 2000–2007; TRI 2007)[6], the dispersion of 1,3-butadiene in the air for increasing distances from the release source was modelled using SCREEN3 (1996), developed by the U.S. EPA.

SCREEN3 is a screening-level Gaussian air dispersion model based on the Industrial Source Complex (ISC) model (for assessing pollutant concentrations from various

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[6] Data from the National Pollutant Release Inventory (NPRI) in Canada (NPRI 2000–2007) and the US Toxics Release Inventory (TRI 2007) were used to define the ratio of 1,3-butadiene to benzene in fugitive emissions from a petroleum facility. The median ratio (50th percentile of the data set) from the NPRI (2000–2007) data (1:216) was used for average-case estimation. However, only 3–6 Canadian refineries and upgraders reported fugitive emissions of 1,3-butadiene over the period 2000 to 2007. Therefore, the median ratio from the TRI (2007) data (1:85) was used for an upper-bounding estimation, as it included data from 65 US refineries and was considered to be more representative (Canada 2012).

sources in an industry complex). The driver for air dispersion in the SCREEN3 model is wind. The maximum calculated exposure concentration is selected based on a built-in meteorological data matrix of different combinations of meteorological conditions, including wind speed, turbulence and humidity. This model directly predicts concentrations resulting from point, area and volume source releases. SCREEN3 gives the maximum concentrations of a substance at chosen receptor heights and at various distances from a release source in the direction downwind from the prevalent wind one hour after a given release event. During a 24-hour period, for point emission sources, the maximum 1-hour exposure (as assessed by the ISC Version 3) is multiplied by a factor of 0.4 to account for variable wind direction. This gives an estimate of the air concentration over a 24-hour exposure (U.S. EPA 1992). Similarly, for exposure events happening over the span of a year, it can be expected that the direction of the prevalent winds will be more variable and uncorrelated to the wind direction for a single event; thus, the maximum amortized exposure concentration for one year is determined by multiplying the maximum 1-hour exposure by a factor of 0.08. Such scaling factors are not used for non-point source emissions. However, to prevent overestimation of the exposures originating from area sources, a scaling factor of 0.2 was used to obtain the yearly amortized concentration from the value of the maximum 1-hour exposure concentration determined by SCREEN3. Detailed input parameters are listed in Table A6.1 (Appendix 6).

The modelling results from this approach are presented in Table A6.2 (Appendix 6). The SCREEN3 air dispersion modelling indicates that unintentional releases of petroleum and refinery gases contribute to the 1,3-butadiene concentration in ambient air in the vicinity of refineries, upgraders and natural gas processing facilities. The Stream 2 petroleum and refinery gases are recognized as comprising a fraction of petroleum facility releases as characterized in the Stream 1 petroleum and refinery gases assessment. The estimated total releases in the Stream 1 assessment were based on all petroleum and refinery gases at a facility. It is not possible to determine the proportion of these releases that are due to Stream 2 petroleum and refinery gases. However, at a given facility, these substances would contribute to the overall releases. The estimated overall releases are presented below.

The results of the modelled dispersion profile of 1,3-butadiene, based on distance from the release source, demonstrate that at 200 m the annual concentration of petroleum and refinery gases (for both Stream 1 and Stream 2) contributed to ambient air by these facilities is approximately 0.44 micrograms per cubic metre (μg/m^3) (high end of the range), and approximately 0.17 μg/m^3 (low end of the range) (Table A6.2 in Appendix 6). It is estimated that for the high end (1:85), the contribution of 1,3-butadiene to air associated with unintentional releases of petroleum and refinery gases will be equivalent to the average annual Canadian ambient urban air concentration of 0.22 μg/m^3 at a distance of 500 m from the release source. For the low end of the range of 0.17 μg/m^3 (1:216), the estimated contribution of 1,3-butadiene to air from unintentional release of petroleum and refinery gases is 0.088 μg/m^3 at 500 m from the release source.

An alternate approach for exposure characterization, based on application of standardized emission factors and components as described by the Canadian Chemical Producers' Association and the Canadian Petroleum Products Institute (CCPA 2008; CPPI 2007), resulted in similar outputs. Overall, available information shows that there is a contribution to ambient background levels of 1,3-butadiene associated with the unintentional releases of the industry-restricted petroleum and refinery gases. Accordingly, there may be limited general population exposure to these petroleum and refinery gases in the vicinity of refinery, upgrader and natural gas processing facilities. Atmospheric degradation of 1,3-butadiene is not considered in the exposure modelling. Although the average atmospheric half-lives for photo-oxidation of 1,3-butadiene are reported to range from approximately 14 minutes to 10 hours, the actual half-lives of 1,3-butadiene can fluctuate greatly, typically from hours to months, under different conditions (e.g., different seasons, clear or cloudy skies, etc.) (Canada 2000b). Therefore, as a conservative approach, losses due to photodegradation of 1,3-butadiene are not considered in the estimation of the concentration profile of 1,3-butadiene in this screening assessment.

Potential Exposure from Transportation

Updated information received from industry indicated that there is no evidence that CAS RN 68527-19-5 is being transported to other industrial facilities. Therefore, the transportation scenario is relevant only for CAS RNs 68131-75-9, 68477-33-8 and 68477-85-0.

Hydrocarbon gases are normally transported in pressurized systems. As a result of stringent requirements for the design and operation of pressurized systems, the potential for evaporative emissions of the gaseous substances during loading, transport and unloading processes has been significantly reduced (OECD 2009).

The shipment of pressurized petroleum gaseous substances generally requires stringent safety considerations due to their physical–chemical properties. As one example, under the *Transportation of Dangerous Goods Regulations* of the *Transportation of Dangerous Goods Act, 1992*, Transport Canada has required a series of standards, developed by the Canadian Standards Association or the Canadian General Standards Board, for design, manufacture, safety devices, inspection and operation involved in the transportation of petroleum-related gases by rail, road and water. As well, equipment for handling the substances, such as transfer hoses or loading arms, must meet design standards for appropriate pressures and temperatures (Canada 2001b).

The loading and unloading of petroleum substances are conducted in an enclosed system (European Commission 2006). However, when a threaded connection is used between a loading arm and a pressurized tank, fugitive leaks may still occur as a result of poor maintenance (Hendler et al. 2006). Such leaks are not considered to be typical releases under normal operating conditions and can be prevented (e.g., by replacing the threaded connection with a flange connection). Accordingly, releases of the gases to the environment during regular handling processes are not expected.

For the storage of liquified petroleum gases, inert gas (i.e., nitrogen) blanketing is often used around the storage tanks, as well as application of frequent leak detection programs, to prevent any flammable reaction with oxygen (Kraus 1998).

Furthermore, there is relevant legislation in place at federal and provincial levels for handling gaseous hydrocarbons, which is intended to reduce or prevent releases from these operations. Some of the measures that are outlined in these provisions apply to means of containment (i.e., transportation vessel), means of transportation (i.e., transportation vehicle) and handling equipment for transporting pressurized gases and indicate that each must meet specified design and safety standards. Such measures also include the following: a certificate and licence are normally required for handling compressed gases; regular inspection by professional personnel on pressurized vessels and pressurized piping systems is required and will be recorded; and an emergency response plan has to be developed and approved before handling or transport of the gaseous substances. In case of any foreseen or actual accidental occurrence, designated personnel have to report as soon as possible and take any reasonable measures to reduce any danger to the general population due to the releases of the substances. An inspector may inspect any matters related to the handling or transportation of these substances at any reasonable time (Alberta 2010).

Collectively, based on the preceding discussion, regular evaporative emissions from handling or during the transportation process from pressurized systems are not expected. Therefore, exposure of the general population to the regular releases of industry-restricted petroleum and refinery gases during loading, transit and unloading is not expected.

Health Effects Assessment

Health effects information for the four petroleum and refinery gases was not available. Toxicological information for additional petroleum and refinery gases in the PSSA that are similar from both a process and a physical–chemical perspective was also not found. Therefore, to characterize the toxicity of these substances, U.S. EPA High Production Volume Information System (HPVIS) read-across substances and industry-restricted petroleum and refinery gas component classes, including alkanes, alkenes (or olefins), alkadienes, alkynes, aromatics, mercaptans and inorganics, were considered. Available literature relevant to petroleum and refinery gases and their individual components was considered in the preparation of the screening assessment; however, only a summary of the critical information upon which the conclusion is based is presented in this report.

Gases (petroleum), light steam-cracked, butadiene concentrate (CAS RN 68955-28-2) was identified as a substance similar to hydrocarbons, C_3–C_4 rich, petroleum distillates (CAS RN 68512-91-4), a site-restricted petroleum and refinery gas, for the acute and genetic toxicity endpoints. An LC_{50} value of $\geq$ 5300 mg/m^3 was reported in rats for CAS RN 68955-28-2. An increased frequency of micronuclei in erythrocytes was observed in the bone marrow of male and female CD-1 mice exposed to CAS RN 68955-28-2 by inhalation for 2 days. *In vitro* genotoxicity results for CAS RN 68955-28-2 were mixed:

an increased mutation frequency was noted in mouse lymphoma cells without activation, and an increase in unscheduled deoxyribonucleic acid (DNA) synthesis was observed in mammalian cells, but negative results were reported for reverse mutation (Ames assay) and cell transformation (U.S. EPA 2008b).

CAS RN 68476-52-8, or hydrocarbons, C_4, ethylene-manuf.-by-product (C_4 crude butadiene, 10% butadiene), was also identified through HPVIS read-across analysis as a substance similar to CAS RN 68512-91-4 for repeated-exposure, reproductive and developmental toxicity endpoints. In a study in which male and female Sprague-Dawley rats were exposed by inhalation to up to 20 000 mg/m^3 before breeding, during breeding and up to gestational day 19, for a total of approximately 36–37 days (U.S. EPA 2008b), a no-observed-adverse-effect concentration of 20 000 mg/m^3 was identified specifically for reproductive and developmental toxicity, whereas a no-observed-effect concentration (NOEC) of 20 000 mg/m^3 was identified for repeated-exposure toxicity due to lack of effects observed in a variety of endpoints.

As indicated above, there were no reports in the published literature of toxicological studies on any of the petroleum and refinery gas substances. The petroleum and refinery gases have been previously evaluated for mammalian health effects based on the assessment of individual components of the gaseous substances (API 2001a, 2009a,b; CONCAWE 2005). The results of the component evaluation are useful in characterizing potential hazards associated with the mixtures. Generally, there are multiple potentially hazardous components in petroleum and refinery gases (listed under Substance Identity); therefore, the component that is the most highly hazardous for a particular endpoint is used to characterize the hazard associated with the mixture (API 2009a,b). International agencies and organizations have prepared toxicological profiles of the various components of the petroleum and refinery gases (API 2001a,b, 2009a,c; CONCAWE 2005).

A brief summary of the health effects of the component classes is presented in Appendix 7; however, a critical review of all health effects data on the numerous components was not undertaken. Rather, the current screening assessment of these petroleum and refinery gases focuses on a specific component considered to conservatively represent the greatest hazard to human health posed by these substances as a group. The alkadiene 1,3-butadiene was selected as the high-hazard component to represent the critical health effects of the petroleum and refinery gases, as it is reported to be in the four petroleum and refinery gases considered in this screening assessment, and its critical health effects are well documented (Canada 2000b).

Extensive literature is available regarding the toxicokinetics and effects of 1,3-butadiene following acute, short-term and long-term exposures, primarily via the inhalation route. Recent assessments by the Government of Canada and other organizations have thoroughly evaluated the health effects data (Canada 2000b; EURAR 2002; U.S. EPA 2002; Grant 2008; ATSDR 2009). As relevant to the current screening assessment, the critical literature for characterizing the human health effects of 1,3-butadiene as a high-hazard component of the petroleum and refinery gases is summarized.

Appendix 8 contains a summary of the critical health effects information on 1,3-butadiene. A review of the human health effects of 1,3-butadiene was previously done under the second Priority Substances List assessment (Canada 2000b). This substance was subsequently added to the List of Toxic Substances on Schedule 1 of CEPA 1999.

Petroleum and refinery gases are classified by the European Commission as a carcinogen when the concentration of 1,3-butadiene in the substance is greater than 0.1% by weight (European Commission 2004; ESIS 2008). 1,3-Butadiene has been classified as a carcinogen by several national and international agencies. Under the Priority Substances Assessment Program, the Government of Canada concluded that 1,3-butadiene met the criteria under section 64(*c*) of CEPA 1999 on the basis of a plausible mode of action for induction of tumours involving direct interaction with genetic material (Canada 2000b). The International Agency for Research on Cancer (IARC 2008) also classified 1,3-butadiene as carcinogenic to humans (Group 1); the U.S. EPA (2002) concluded that 1,3-butadiene is carcinogenic to humans by inhalation; the US National Toxicology Program (NTP 2011a) classified 1,3-butadiene as a known human carcinogen due to sufficient evidence of carcinogenicity in humans; and the European Commission classified 1,3-butadiene as a carcinogen (Category 1: may cause cancer; substances known to be carcinogenic to humans), but also as a mutagen (Category 2: may cause heritable genetic damage; substances that should be regarded as if they are mutagenic to man) (EURAR 2002; ESIS 2008).

The carcinogenic potential of inhaled 1,3-butadiene has been clearly demonstrated in a 2-year inhalation study in B6C3F1 mice exposed to 1,3-butadiene at concentrations of 0–625 ppm (0–1380 mg/m^3) in a 103-week study. 1,3-Butadiene was found to be a potent carcinogen, inducing common and rare tumours at a variety of sites in mice. In most cases, there was evidence of an exposure–response relationship in the tumour incidence and the involvement of a genotoxic mechanism. A statistically significant increase in the incidence of alveolar/bronchiolar adenocarcinomas or carcinomas in females was observed at 6.25 ppm (13.8 mg/m^3) (NTP 1993; EURAR 2002; U.S. EPA 2002). As tumour induction was observed at all concentrations examined, it is likely that exposures lower than 6.25 ppm (13.8 mg/m^3) would also cause cancer in mice (U.S. EPA 2002).

The single long-term inhalation study in rats suggests that 1,3-butadiene is also a multisite carcinogen in the rat; however, the effects were observed at air concentrations that were 2–3 orders of magnitude higher than in the mouse. In contrast to the mouse, the rat tumour profile suggests a possible non-genotoxic mechanism occurring indirectly via the endocrine system rather than directly by reactive metabolites (Owen 1981; Owen et al. 1987; Owen and Glaister 1990).

Although there are marked differences in species sensitivity to the carcinogenic properties of 1,3-butadiene, the available data provide unequivocal evidence that 1,3-utadiene is a multisite carcinogen in rodents (U.S. EPA 2002).

Several epidemiological investigations of the carcinogenicity of 1,3-butadiene have been conducted and have served as the basis for assessment of the weight of evidence for causality of associations based on traditional criteria (Canada 2000b; EURAR 2002; U.S. EPA 2002). The investigation by Delzell et al. (1995, 1996), which was a large, good quality, cohort mortality study, portrays a clear association between exposure to 1,3-butadiene in the styrene–butadiene rubber industry and leukemia in humans. On the basis of this evidence, various national and international agencies have concluded that there is "sufficient evidence to consider 1,3-butadiene carcinogenic to occupationally exposed populations" (U.S. EPA 2002) and that "butadiene should be regarded as carcinogenic in humans" (EURAR 2002).

Overall, on the basis of the available rodent and human evidence, it can be considered that 1,3-butadiene has the potential to induce tumours via a mode of action involving direct interaction with genetic material (Canada 2000b; EURAR 2002; U.S. EPA 2002).

The Government of Canada has previously developed estimates of carcinogenic potency associated with inhalation exposure to 1,3-butadiene. A tumourigenic concentration (TC_{01}) of 1.7 mg/m^3 was derived from the epidemiological investigation of Delzell et al. (1995), and the quantitative estimate of carcinogenic potency (TC_{05}) derived on the basis of data in experimental animals was 2.3 mg/m^3 for the most sensitive tumour site in mice (Canada 2000b).

The U.S. EPA (2002) derived a cancer potency from inhalation exposure using the linear relative rate model based on the same data as reported by the Government of Canada. An inhalation unit risk of 3×10^{-5} $(\mu g/m^3)^{-1}$ was calculated based on the Delzell et al. (1995) retrospective cohort study (U.S. EPA 2002). More recently, an inhalation unit risk factor of 5×10^{-7} $(\mu g/m^3)^{-1}$ was calculated by the Texas Commission on Environmental Quality based on updated human leukemia data (Grant 2008). The value derived by Grant (2008) used updated exposure estimates from the same study population that was selected as the best published exposure estimates by the U.S. EPA (2002) to evaluate human cancer risk.

An extensive database of more than 600 publications exists on the genotoxicity of 1,3-butadiene investigated in a range of *in vitro* and *in vivo* studies encompassing a variety of biological systems ranging from bacteria to humans (EURAR 2002). Detailed examinations of this database can be found in a number of recent assessments conducted by the Government of Canada (Canada 2000b), the U.S. EPA (2002), the European Commission (EURAR 2002) and ATSDR (2009). Consequently, this information is not included in Appendix 8.

To date, the studies evaluating the genotoxic potential of 1,3-butadiene in humans have produced equivocal results; however, 1,3-butadiene is clearly genotoxic in mice. The human data are too limited to allow the genotoxic potential of 1,3-butadiene in exposed humans to be dismissed (EURAR 2002; ATSDR 2009). Overall, 1,3-butadiene is considered a likely human somatic and germ cell toxicant (Canada 2000b). Also, based on the experimental animal data, 1,3-butadiene is in the highest category described in the weight-of-evidence scheme in the Guidelines for Mutagenicity Risk Assessment (U.S. EPA 1986).

The reproductive organs have been identified as critical non-carcinogenic targets for 1,3-butadiene-induced effects in mice and rats (Canada 2000b; EURAR 2002; U.S. EPA 2002; Grant 2008). The most sensitive reproductive effects identified consistently across various assessments of 1,3-butadiene were observed in B6C3F1 mice exposed to concentrations of 0–625 ppm (0–1380 mg/m^3) in a 2-year chronic inhalation study. Ovarian atrophy was observed after exposure to the lowest 1,3-butadiene concentration tested, 6.25 ppm (13.8 mg/m^3), whereas testicular atrophy was observed after exposure to 200 ppm (442 mg/m^3) (NTP 1993; EURAR 2002; U.S. EPA 2002; Grant 2008; ATSDR 2009). Based on the proposed mode of action, specifically the involvement of the diepoxide metabolite in the induction of ovarian atrophy and a decrease in serum progesterone levels, effects observed in mice are considered to have a threshold and to be concentration and duration dependent (U.S. EPA 2002; Grant 2008).

No studies were identified in the available literature regarding the effects of inhalation exposure to 1,3-butadiene on reproduction or development in humans. However, it was noted that when considering the implications of the gonadal effects observed in mice for human health, there is no indication that humans respond in a quantitatively similar manner (EURAR 2002).

Characterization of Risk to Human Health

Industry-restricted petroleum and refinery gases were identified as high priorities for action during categorization of the DSL because they were determined to present intermediate potential for exposure of individuals in Canada, and were considered to present a high hazard to human health. A critical effect for the initial categorization of industry-restricted petroleum and refinery gas substances was carcinogenicity, based primarily on classifications by international agencies. The European Union considers petroleum and refinery gases containing 1,3-butadiene at concentrations greater than 0.1% by weight as carcinogens. Measured concentrations of 1,3-butadiene in the gaseous substances considered in this assessment range from non-detectable to 3% by weight (API 2009b). Additionally, 1,3-butadiene has been identified by Health Canada and several international regulatory agencies as a carcinogen, and was added to the List of Toxic Substances in Schedule 1 of CEPA 1999. 1,3-Butadiene was found to be a multi-site carcinogen in rodents by inhalation, increasing the incidence of tumours at all concentrations tested. Epidemiological studies provide further evidence for an association between exposure to 1,3-butadiene in occupational environments and leukemia in humans. 1,3-Butadiene also exhibits genotoxicity *in vitro* and *in vivo*, and a plausible mode of action for induction of tumours involves direct interaction with genetic material.

Both air dispersion modelling and calculations based on the application of emission factors indicate that unintentional releases of petroleum and refinery gases contribute to the overall 1,3-butadiene concentration in ambient air in the vicinity of refineries, upgraders and natural gas processing facilities that produce/utilize these substances. The estimated 1,3-butadiene concentrations decline with increasing distance from these release sources. A conservative approach estimates the 1,3-butadiene concentration to be comparable to or below the Canadian urban average concentration at distances equal to or greater than 500 m from the centre of the release source. Using the estimates of carcinogenic potency previously developed by the Government of Canada (Canada 2000a), together with the high and low end estimates of exposure derived from dispersion modelling of 1,3-butadiene as a high-hazard component of the petroleum and refinery gases, margins of exposure were derived for increasing distances from the release source (a distance of 200 m is illustrated in Table 4). Map analysis has determined that the general population may reside approximately 200 m from a potential source of release. Accordingly, this distance has been selected to characterize risk to the general population.

Table 4. Margins of exposure based on air dispersion modelling of 1,3-butadiene as a high-hazard component of the petroleum and refinery gases (Stream 1 and Stream 2)

Scenario	**Distance from release source (m)**	**Annual estimate of exposure (µg/m^3)**	**Margin of exposure based on tumourigenic concentration (TC$_{05}$) of 2.3 mg/m^3 (Canada 2000a)**
Low end of exposure range	200	0.17	13 500
High end of exposure range	200	0.44	5300

For the high end of the exposure range, at a distance of 200 m from the centre of the release source, the margin of exposure is 5300. At 500 m, the margin of exposure is 10 500, which equates to an exposure concentration equal to the Canadian average annual ambient air concentration of 0.22 µg/m^3 found in urban centres. Although the magnitude of risk would vary with the cancer potency metrics selected (e.g., TC$_{05}$; unit risks derived by US EPA and Texas Commission on Environmental Quality based on linear low-dose extrapolation models etc.), use of a conservative cancer potency metric is considered appropriate given the uncertainties in the health effects database. For the high end of the exposure range, the margin of exposure at 200 m from the release source is considered potentially inadequate to address uncertainties in the health effects and exposure databases for industry-restricted petroleum and refinery gases.

The four petroleum and refinery gases in this assessment are considered to contribute to the overall site emissions estimated above, and accordingly contribute to the potentially inadequate margins of exposure.

Regarding non-cancer effects of 1,3-butadiene, reproductive toxicity was selected as the critical health effects endpoint. The lowest lowest-observed-adverse-effect concentration (LOAEC) for inhalation exposure was 6.25 ppm (13.8 mg/m^3), based on ovarian atrophy characterized by a lack of oocytes, follicles and corpora lutea in female mice in a two-year chronic bioassay. Comparison of this LOAEC with the maximum annual upper-bounding and average concentrations of 1,3-butadiene at 200 m from a release source results in margins of exposure of 31 000 and 81 000, respectively. These margins are considered adequate to address uncertainties in the non-cancer health effects and exposure databases for site-restricted petroleum and refinery gases.

Uncertainties in Evaluation of Human Health Risk

Uncertainty exists regarding the exposure of the general population and the environment to industry-restricted petroleum and refinery gases. Currently, no Canadian monitoring data are available for petroleum and refinery gases as a whole. Therefore, 1,3-butadiene was selected as a high-hazard component, and the potential unintentional releases of these gases were estimated by modelling the contribution of 1,3-butadiene emissions from refineries, upgraders and natural gas processing facilities to concentrations in ambient air.

It is assumed that all the estimated facility releases of 1,3-butadiene are attributed to the petroleum and refinery gases, and that a portion of these releases stem from the four petroleum and refinery gases in this assessment. Quantitative information for each petroleum and refinery gas CAS RN present at a given petroleum facility was not available to attribute relative contributions to emissions.

There is uncertainty regarding the potential for exposure to 1,3-butadiene from natural gas processing facilities, as exposures were modelled based on data from petroleum refineries. Uncertainty exists in the potential differences in the composition of the petroleum and refinery gases between refineries or upgraders and natural gas processing facilities arising from differences in equipment between facilities.

There is uncertainty regarding the modelling of the concentration profile of 1,3-butadiene using SCREEN3 (1996). SCREEN3 requires limited input parameters and non-site-specific meteorological data, both introducing uncertainty. Assumptions made in the exposure analysis are listed in Appendix 6.

The petroleum and refinery gases assessed may each contain multiple inorganic and organic components that contribute to the overall hazard of the category substances. The compositional ranges of specific gas components may vary significantly depending on the source of the crude oil, bitumen or natural gas, operating conditions, seasonal process issues and economic cycles. Health effects have been characterized by the health effects associated with 1,3-butadiene emitted or released to the atmosphere; however, there is uncertainty regarding the concentration of this component in each specific petroleum and refinery gas substance as identified by its CAS RN.

Use of a single high-hazard component to characterize the toxicity of petroleum and refinery gases may not reflect all health effects associated with these substance mixtures. Potential risks from exposure to other potentially hazardous components in the petroleum and refinery gases are not specifically considered in the risk characterization, but are considered to be covered by using a conservative approach and focussing on the component with the highest hazard.

Additional uncertainties relevant to the health effects evaluation of 1,3-butadiene are described in the Government of Canada Priority Substances List assessment of 1,3-butadiene (Canada 2000b).

Conclusion

Based on the information presented in this screening assessment, it is concluded that these petroleum and refinery gases are unlikely to be causing ecological harm to organisms or the broader integrity of the environment. Therefore, it is concluded that the petroleum and refinery gases included in this screening assessment (CAS RNs 68131-75-9, 68477-33-8, 68477-85-0 and 68527-19-5) do not meet the criteria under paragraphs 64(*a*) or 64(*b*) of the *Canadian Environmental Protection Act, 1999* (CEPA 1999) as they are not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity or that constitute or may constitute a danger to the environment on which life depends.

On the basis of the available data, it is concluded that these four petroleum and refinery gases meet the criteria under paragraph 64(*c*) of CEPA 1999 as they are entering or may enter the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health.

It is therefore concluded that the four petroleum and refinery gases (CAS RNs 68131-75-9, 68477-33-8, 68477-85-0 and 68527-19-5) meet one or more of the criteria set out in section 64 of CEPA 1999.

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Appendix 1. Petroleum substance grouping

Table A1.1. Description of the nine groups of petroleum substances

Group[a]	Description	Example
Crude oils	Complex combinations of aliphatic and aromatic hydrocarbons and small amounts of inorganic compounds, naturally occurring under the earth's surface or under the seafloor	Crude oil
Petroleum and refinery gases	Complex combinations of light hydrocarbons primarily from C_1–C_5	Propane
Low boiling point naphthas	Complex combinations of hydrocarbons primarily from C_4–C_{12}	Gasoline
Gas oils	Complex combinations of hydrocarbons primarily from C_9–C_{25}	Diesel
Heavy fuel oils	Complex combinations of heavy hydrocarbons primarily from C_{11}–C_{50}	Fuel Oil No. 6
Base oils	Complex combinations of hydrocarbons primarily from C_{15}–C_{50}	Lubricating oils
Aromatic extracts	Complex combinations of primarily aromatic hydrocarbons from C_{15}–C_{50}	Feedstock for benzene production
Waxes, slack waxes and petrolatum	Complex combinations of primarily aliphatic hydrocarbons from C_{12}–C_{85}	Petrolatum
Bitumen or vacuum residues	Complex combinations of heavy hydrocarbons having carbon numbers greater than C_{25}	Asphalt

[a] These groups were based on classifications developed by Conservation of Clean Air and Water in Europe (CONCAWE) and a contractor's report presented to the Canadian Petroleum Products Institute (CPPI) (Simpson 2005).

Appendix 2. Substance identity and physical and chemical properties of representative structures for the petroleum and refinery gases listed in this screening assessment

Table A2.1. Substance identity for the four petroleum and refinery gases

CAS RN	**DSL name and NCI names**[a]
68131-75-9	Gases (petroleum); C_3–C_4
68477-33-8	Gases (petroleum); C_3–C_4, isobutane-rich
68477-85-0	Gases (petroleum); C_4-rich
68527-19-5	Hydrocarbons; C_1–C_4, debutanizer fraction
Other names[b]	Mixtures of methane, ethane, propane, butane, isobutane, butylene mix, mixed (C_3–C_4) stream (petroleum), liquified petroleum gases, natural gas, butane–butylene from catalytic cracking (petroleum), C_4 fraction
Chemical group (DSL stream)	Petroleum gases
Major chemical class or use	Combinations of light petroleum gases
Major chemical subclass[c]	Complex combinations of light hydrocarbon gases (i.e., UVCBs)

Abbreviations: CAS RN, Chemical Abstracts Service Registry Number; DSL, Domestic Substances List; NCI, National Chemical Inventories; UVCBs, unknown or variable composition, complex reactions products or biological materials.

[a] NCI (2006): Asia-Pacific Substances Lists, Australian Inventory of Chemical Substances, European Inventory of Existing Commercial Chemical Substances, New Zealand Inventory of Chemicals, Toxic Substances Control Act Chemical Substance Inventory.

[b] API (2001b); NCI (2006).

[c] These substances belong to a group of UVCBs (i.e., it is not a discrete chemical and thus may be characterized by a variety of structures).

Table A2.2. Physical–chemical properties of representative structures for petroleum and refinery gases[a]

Substance	**Melting point (°C)**[a,b]	**Boiling point (°C)**[a,b]	**Vapour pressure (Pa at 25°C)**[a]	**Henry's Law constant (Pa·m^3/mol)**[a]	**Log K_{ow}**[a]	**Log K_{oc}**[a]	**Water solubility (mg/L at 25°C)**[a]
methane	−182.5	−162	6×10^7	6.7×10^4 (calc.)[c]	1.1	3.34	22
ethane	−182.8	−88.6	4.2×10^6	5.1×10^4 (calc.)	1.81	1.57	60.2
ethene	-169.0	-103.7	7.0×10^6	2.3×10^4 (calc.)	1.13	0.98	131
propane	−187.6	−42.1	9.5×10^4	7×10^4 (calc.)	2.36	2.05	62.4
butane	−138.2	−0.5	2.4×10^5	9.6×10^4	2.89	2.5	61.2

Substance	**Melting point (°C)[a,b]**	**Boiling point (°C)[a,b]**	**Vapour pressure (Pa at 25°C)[a]**	**Henry's Law constant ($Pa·m^3/mol$)[a]**	**Log K_{ow}[a]**	**Log K_{oc}[a]**	**Water solubility (mg/L at 25°C)[a]**
				(calc.)			
butene	-185.3	-6.2	3.0 × 10^5	2.4 × 10^4 (calc.)	2.4	2.08	221
isobutane	−159.6	−11.7	3.5 × 10^5	1.2 × 10^5 (calc.)	2.8	1.55	49
1,3-butadiene	−108.9	−4.4	2.8 × 10^5	7.5 × 10^3 (calc.)	1.99	1.73	735
pentane	−129.7	36	6.9 × 10^4	1.3 × 10^5	3.4	2.94	38
isopentane	−159.9	27.8	9.2 × 10^4	1.4 × 10^5	2.7	2.4	48

Abbreviations: K_{oc}, organic carbon–water partition coefficient; K_{ow}, octanol–water partition coefficient.

[a] All data on melting point, boiling point, vapour pressure, K_{ow} and water solubility are experimental. Henry's Law constants are calculated based on experimental data. K_{ow} data are from Hansch et al. (1995); melting point, boiling point and vapour pressure data are from Daubert and Danner (1994), Riddick et al. (1986), Yalkowsky and He (2003) and McAuliffe (1966).

[b] The boiling point and vapour pressure ranges for 68477-85-0 (C_1–C_5 alkanes) given in ECB (2000c) indicate that it contains only C_1–C_4 molecules, although various descriptions state that it contains pentane and isopentane.

[c] (calc.) denotes calculated data based on other experimental data. All other data are modelled by KOWWIN (2008) and KOCWIN (2009).

Appendix 3. Measures designed to prevent, reduce or manage unintentional releases

For the Canadian petroleum industry, requirements at the provincial/territorial level typically prevent or manage the unintentional releases of petroleum substances and streams within a facility through the use of operating permits (SENES 2009).

Additionally, existing occupational health and safety legislation specifies measures to reduce occupational exposures of employees, and some of these measures also serve to reduce unintentional releases (CanLII 2009).

Non-regulatory measures (e.g., guidelines, best practices) are also in place at petroleum sector facilities to reduce unintentional releases. Such control measures include appropriate material selection during the design and setup processes, regular inspection and maintenance of storage tanks, pipelines and other process equipment, the implementation of leak detection and repair or other equivalent programs, the use of floating roofs in above-ground storage tanks to reduce the internal gaseous zone and the minimal use of underground tanks, which can lead to undetected leaks or spills (SENES 2009).

For those substances containing highly volatile components (e.g., low boiling point naphthas, gasoline), a vapour recovery system is generally implemented or recommended at loading terminals of Canadian petroleum facilities (SENES 2009). Such a system is intended to reduce evaporative emissions during handling procedures.

Appendix 4. Release estimation of industry-restricted petroleum and refinery gases during transportation

Table A4.1. Estimated number of unintentional leak events per year per transport mode

Transport mode	Loading	Transport	Unloading
Train[a]	35	19	35
Pipeline[b]	235	119	235

[a] Railway occurrences for all petroleum products from TSB (2006).

[b] Historical release incident statistics for all petroleum products based on Alberta statistics from ERCB (2009) and projected to all of Canada.

Generic calculation process for release quantities (leaks only) in Table 3 in the text:

For unintentional releases due to leaks (kg/leak):

$M_G = LOSS_F \times M_T \times VPP_G$
$VPP_G = (P/P_{ATM}) / (1 + P/P_{ATM})$
$M_{SL} = M_G/NUM_S$

where:
M_G = evaporative emission quantity to air due to leaks (kg/year)
$LOSS_F$ = loss fraction, derived from historical data on reported leaks versus transport quantities from Statistics Canada and Transport Canada
M_T = transport quantities, derived from information submitted under section 71 of CEPA 1999 (Environment Canada 2009)
VPP_G = percentage partitioning into air estimated by vapour pressure only (assuming that Raoult’s Law and Dalton’s Law are valid)
P = vapour pressure of the substance at the release temperature (Pa)
P_{ATM} = ambient air pressure (Pa)
M_{SL} = evaporative emission quantity per leak event (kg/leak)
NUM_S = maximum number of leaks per year, from Table A4.1

As stated in the text, the number of pipeline leaks in Alberta was extrapolated to Canada based on a proportional analysis of the number of leaks per kilometre of Alberta pipeline and the kilometres of pipeline in each province and territory, regardless of the substance that they carried. The interprovincial pipelines were not taken into account, as they have a very different leak rate per kilometre of pipeline compared with pipelines within Alberta. The leaks considered here are leaks of all petroleum substances and are not specific to petroleum and refinery gases, as there are no data specific to petroleum and refinery gases or to other similar substances.

Appendix 5. Modelling results for environmental properties of petroleum and refinery gases

Table A5.1. Results of the Level III fugacity modelling for components of petroleum and refinery gases (EQC 2003)

Release of substance to each compartment (100%)	**% of substance partitioning into each compartment**			
methane	**Air**	**Water**	**Soil**	**Sediment**
Air	100	0	0	0
Water	19.9	79.9	0	0.2
Soil	98	0	2.0	0
ethane				
Air	100	0	0	0
Water	18.9	81.0	0	0.1
Soil	97.9	0	2.1	0
ethene				
Air	100	0	0	0
Water	4.3	95.6	0	0.1
Soil	89.9	0	10.1	0
propane				
Air	100	0	0	0
Water	12.9	87	0	0.2
Soil	96.6	0	3.4	0
butane				
Air	100	0	0	0
Water	9.3	90.4	0	0.3
Soil	93.5	0	6.5	0
butene				
Air	100	0	0	0
Water	5.8	94.0	0	0.2
Soil	89.5	0	10.4	0
isobutane				
Air	100.0	0.0	0.0	0.0
Water	11.4	87.2	0.0	1.4
Soil	95.7	0.0	4.3	0.0
1,3-butadiene				
Air	100	0	0	0
Water	0.7	99.2	0	0.1
Soil	42.9	0.4	56.7	0
pentane				
Air	100	0	0	0
Water	7.2	92.2	0	0.6
Soil	82.4	0.01	17.6	0
isopentane				
Air	100	0	0	0
Water	7.3	92.5	0	0.25
Soil	91.3	0.01	8.7	0

Table A5.2. Modelled data for atmospheric degradation of petroleum and refinery gases in contact with hydroxyl radicals (AOPWIN 2008)

Substance	Half-life of hydroxyl oxidation reaction (days)	Half-life of ozone reaction (days)	Extrapolated half-life (days)
methane	1559	n.a.	≥ 2
ethane	39.3	n.a.	≥ 2
ethene	1.3	6.5	< 2
propane	8.4	n.a.	≥ 2
butane	4	n.a.	≥ 2
butene	0.4	1.0	< 2
isobutane	4.4	n.a.	≥ 2
pentane/isopentane	2.6	n.a.	≥ 2
1,3-butadiene	0.2	1.4	≤ 2

Abbreviation: n.a., not applicable.

Table A5.3. Modelled data for primary and ultimate biodegradation of representative structures for petroleum and refinery gases.

	Primary Degradation	
	BioHCWin (2008)[a] (days)	BIOWIN 4 (BIOWIN 2009) Expert Survey[b]
Alkanes		
C_2: ethane	2.6	3.8
C_3: propane	3.0	3.8
C_4: butane	4	4.0
C_5: pentane	4.0	4.0
Isoalkanes		
C_4: methyl propane	3	3.8
C_5: isopentane	3.6	3.7
Alkenes		
C_2: ethene	2.9	3.8
C_4: butene	2.8	4.0
Dienes		
C_4: 1,3-butadiene	2.8	3.8

Table A5.3 cont. Modelled data for primary and ultimate biodegradation of representative structures for petroleum and refinery gases.

	Ultimate Degradation					
	BIOWIN 3 (BIOWIN 2009) Expert Survey[b]	BIOWIN 5 (BIOWIN 2009) MITI Linear Probability[c]	BIOWIN 6 (BIOWIN 2009) MITI Non-linear Probability[c]	CATABOL (©2004–2008) % BOD	TOPKAT (2004) Probability of Biodegradability	Extrapolated Half-life Compared with Criteria[d] (days)

	Ultimate Degradation					
	BIOWIN 3 (BIOWIN 2009) Expert Survey[b]	**BIOWIN 5 (BIOWIN 2009) MITI Linear Probability[c]**	**BIOWIN 6 (BIOWIN 2009) MITI Non-linear Probability[c]**	**CATABOL (©2004–2008) % BOD**	**TOPKAT (2004) Probability of Biodegradability**	**Extrapolated Half-life Compared with Criteria[d] (days)**
Alkanes						
C_2: ethane	3.13	0.62	0.85	98	0.009	< 182
C_3: propane	3.10	0.63	0.85	98	1	< 182
C_4: butane	3.4	0.64	0.85	98	1	< 182
C_5: pentane	3.34	0.65	0.85	98	1	< 182
Isoalkanes						
C_4: methyl propane	3.07	0.49	0.69	10.6	0.98	< 182
C_5: isopentane	3.04	0.50	0.70	6.1	1	< 182
Alkenes						
C_2: ethene	3.14	0.65	0.86	11.4	0.61	< 182
C_4: butene	3.37	0.61	0.81	0.83	1	< 182
Dienes						
C_4: 1,3-butadiene	3.1	0.6	0.76	No data	No data	< 182

Abbreviations: BOD, biochemical oxygen demand; MITI, Ministry of International Trade and Industry, Japan

[a] Half-life estimations are for non-specific media (i.e., water, soil and sediment).

[b] Output is a numerical score from 0 to 5.

[c] Output is a probability score.

[d] Based on the modelled primary and ultimate biodegradation results.

Table A5.4. Fish[a] BAF and BCF predictions for representative structures of petroleum and refinery gases using BCFBAF (2008) with metabolism

Alkanes	**Log K_{ow}**	**Metabolic rate constant[a] (k_M/day) normalized to 184 g fish at 15°C**	**BCF (L/kg ww)[b]**	**BAF (L/kg ww)[b]**
C_1: methane	1.1	3.3	2	2
C_2: Ethane	1.8	1.2	5	5
C_2: Ethene	1.1	2.5	2	2
C_3: Propane	2.4	0.9	17	17
C_4: butane	2.9 (expt)	0.6	47	47
C_4: butene	2.4	0.7	17	17
C_4: isobutane	2.8	0.7	38	38
$C_4$1,3-butadiene	2.0	1.0	7	7
C_5: pentane	3.4	0.4	126	126
C_5: isopentane	2.7	0.7	31	31

Abbreviations: BAF, bioaccumulation factor; BCF, bioconcentration factor; K_{ow}, octanol–water partition coefficient; k_M, metabolic rate constant.

[a] Metabolic rate constant normalized to middle trophic level fish in Arnot-Gobas three trophic level model (Arnot and Gobas 2004) for weight = 184 g, temperature = 15°C, lipid concentration in fish = 6.8%, based on available experimental kinetic BAF or BCF data.

[b] Arnot-Gobas BCF and BAF predictions for midde trophic level fish using three trophic level model (Arnot and Gobas 2004) using normalized rate constant and correcting for observed or estimated dietary assimilation efficiency.

Appendix 6. Modelling results for human exposure to potential releases of petroleum and refinery gases

Table A6.1. Variable inputs to SCREEN3 for modelling unintentional on-site releases

Variables	**Input variables**
Source type	Area
Process area[a]	300 m × 100 m
Benzene fugitive release from processing areas[b] (from DIAL measurements)	1.8 kg/hour
Ratio of 1,3-butadiene to benzene[c] (for use in DIAL approach)	1:85 (high end) 1:216 (low end)
Effective area[d]	0.8 · (300 × 100)
Receptor height[e]	1.74 m
Source release height[f]	15 m (80%), 3 m (20%)
Adjustment factor for highest 1 hour to annual exposure[g]	0.2
Urban–rural option	Urban
Meteorology[h]	1 (full meteorology)
Minimum and maximum distance to use	50–2000 m

Abbreviations: DIAL, differential absorption, light detection and ranging; VOC, volatile organic compound.

[a] Aerial photo analysis and professional judgement.

[b] Chambers et al. (2008).

[c] NPRI (2000–2007) and TRI (2007).

[d] Professional judgement.

[e] Curry et al. (1993).

[f] Emissions were specified at a high level (above 15 m) and a low level (3 m) to represent the heights of equipment involving unintentional releases of 1,3-butadiene. It is assumed that 80% of the unintentional releases occur above 15 m, accounting for the common discharging points, such as the top of a distillation column. The final concentration of 1,3-butadiene results from the combined high-level and low-level emissions.

[g] U.S. EPA (1992) and professional judgement.

[h] Default value in SCREEN3.

Table A6.2. Modelling results of dispersion profile of 1,3-butadiene from unintentional on-site releases of petroleum and refinery gases (site-restricted and industry restricted).[a]

Distance (m)	**Concentration (μg/m^3)**			
	High end exposure range (1:85)		**Low end exposure range (1:216)**	
	Maximum 1-hour	**Annual**	**Maximum 1-hour**	**Annual**
50	1.74	0.35	0.68	0.14
100	2.031	0.41	0.79	0.16
200	2.18	0.44	0.85	0.17
300	1.92	0.38	0.75	0.15
400	1.48	0.30	0.58	0.12
500	1.13	0.23	0.44	0.088
600	0.88	0.18	0.34	0.069
700	0.71	0.14	0.28	0.055
800	0.58	0.12	0.23	0.046
900	0.49	0.098	0.19	0.038
1000	0.42	0.084	0.16	0.033
1100	0.37	0.073	0.14	0.029
1200	0.32	0.065	0.13	0.025
1300	0.29	0.058	0.11	0.023
1400	0.26	0.052	0.10	0.020
1500	0.24	0.047	0.092	0.018
1600	0.21	0.043	0.084	0.017
1700	0.20	0.039	0.077	0.015
1800	0.18	0.036	0.071	0.014
1900	0.17	0.034	0.066	0.013
2000	0.16	0.032	0.062	0.012

[a] Assumptions made in the modelling:

1. All unintentional releases of 1,3-butadiene from a petroleum facility are assumed to be attributed to the unintentional emission of site- and industry-restricted petroleum and refinery gases and originate from processing areas rather than bulk storage facilities.
2. All four industry-restricted petroleum and refinery gases are flagged as potentially containing 1,3-butadiene and are considered to comprise a fraction of the previously characterized Stream 1 petroleum and refinery gases.

(3) The ratio of 1,3-butadiene to benzene in unintentional emissions is assumed to be constant over different processing units.
(4) Unintentional emission heights of 1,3-butadiene are assumed to be 15 m and 3 m, with 80% of total emissions occurring above 15 m and 20% of emissions occurring at 3 m.
(5) Considering the fact that the release sources are actually multiple point sources spatially distributed over the processing area, the effective processing area used for calculation of emission rate is assumed to be 80% of the total process area.
(6) Total processing area is assumed to be 300 m × 100 m.
(7) Adjustment factor 0.2 is used for estimation of maximum concentration over a year based on the highest 1-hour concentration.

Appendix 7. Summary of the toxicological effects of the component classes of petroleum and refinery gases[1]

Alkanes

In humans, it has been observed that alkanes of low molecular weight (MW) (e.g., methane) can cause displacement of oxygen for acute exposures at high concentrations, which may lead to asphyxiation. At higher MWs, substances such as propane can act as mild depressants on the central nervous system (API 2001a). In experimental animals, LC_{50} values for alkanes range from 658 mg/L (658 000 mg/m^3) (butane) to greater than 800 000 ppm (1 440 000 mg/m^3) (propane), depending on the substance, concentration and duration of the acute exposure (Shugaev 1969; Clark and Tinson 1982). Rats were exposed to mixtures of alkanes (50% butane / 50% pentane; 50% isobutane / 50% isopentane) via inhalation for 90 days in a study designed to investigate kidney effects; a NOEC of 4489 ppm (11 943 mg/m^3)[2] (highest concentration tested) was identified (Aranyi et al. 1986). Negative mutagenicity results were observed for various alkanes (propane, *n*-butane, isobutane, *n*-pentane and isopentane) that were tested via the Ames assay, although toxicity was observed with three of the gases (*n*-pentane, isopentane and isobutane) at various concentrations (Kirwin and Thomas 1980). Butane and isobutane were classified by the European Commission on the basis of carcinogenicity when they contain 1,3-butadiene (as a refinery by-product) at a concentration greater than or equal to 0.1% by weight (European Commission 2001; ESIS 2008).

Alkenes

In experimental animals exposed by inhalation, concentrations of up to 25–70% propene and 15–40% butene induced anesthesia in rats, cats and mice (Brown 1924; Riggs 1925; Virtue 1950), whereas narcosis was noted in mice exposed to up to 70% isobutene via inhalation (Von Oettingen 1940). Acute toxicity values (LC_{50}) are noted to range from greater than 65 000 ppm (111 736 mg/m^3) (propene; MW = 42.03 g/mol) to 620 mg/L (620 000 mg/m^3) (isobutene) (Shugaev 1969; Conolly and Osimitz 1981).

Short-term toxicity studies show that oral exposure to isobutene results in a no-observed-adverse-effect level of 150 mg/kg body weight per day, despite the occurrence of significant biochemical changes that fall into the historical control range (Hazleton Laboratories 1986). Short-term exposure by inhalation resulted in changes to hematology in rats exposed for a few days to 60% ethene (approximately 690 000 mg/m^3) (Fink 1968), as well as clinical and biochemical changes in rats exposed for 70 days to 100 ppm (115 mg/m^3) ethene (MW of ethene = 28.02 g/mol) (Krasovitskaia and Maliarova 1968). Exposure to propene resulted in a lowest NOEC value of 10 000 ppm (17 190

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[1] Where conversions from ppm to mg/m^3 are provided, conversion of the provided value was completed using the formula: *x* ppm (MW)/24.45.

[2] MW of mixtures = [0.5(58.04 g/mol) + 0.5(72.05 g/mol)] = 65.05 g/mol.

mg/m^3) for a 28-day exposure to multiple concentrations of propene (MW = 42.03 g/mol) up to 17 190 mg/m^3 (DuPont 2002).

The lowest lowest-observed-effect concentration identified for subchronic toxicity is 500 ppm (1146 mg/m^3) in a 14-week study in which male and female B6C3F1 mice and F344/N rats were exposed by inhalation to isobutene (MW = 56.10 g/mol) at concentrations up to 8000 ppm (18 336 mg/m^3), resulting in significant increases in absolute and relative right kidney weights in female mice. In male mice, the absolute right kidney weight was increased at 1000 and 8000 ppm (2292 and 18 336 mg/m^3). In female rats, there was a significant increase in relative liver weights from 500 ppm (1146 mg/m^3) and in absolute liver weights from 1000 ppm (2292 mg/m^3). In male rats, a significant increase in relative right kidney weight was observed from 500 ppm (1146 mg/m^3), with an increase in absolute right kidney weight at 4000 ppm (9168 mg/m^3) (NTP 1998). In addition, a 90-day continuous inhalation study conducted in newborn rats caused delays in coat appearance, tooth development and eye opening, as well as hypertension, inhibition of cholinesterase activity and behavioural changes, at an ethene (MW = 28.02 g/mol) concentration of 2.62 ppm (3 mg/m^3) (Krasovitskaia and Maliarova 1968).

With regard to developmental toxicity, NOEC values of 5000 ppm (5750 mg/m^3) for ethene (MW = 28.02 g/mol), 10 000 ppm (17 190 mg/m^3) for propene (MW = 42.03 g/mol) and 5000 ppm (11 460 mg/m^3) for 2-butene (MW = 54.04 g/mol) were identified in rats exposed by inhalation (Waalkens-Berendsen and Arts 1992; Aveyard 1996; BASF 2002). Effects on reproductive organs were observed in male rats exposed to isobutene via inhalation over 14 weeks; these include a significant increase in left epididymal weight and a decrease in epididymal sperm motility at 8000 ppm (18 336 mg/m^3). In addition, female rats were reported to have an increased estrous length with a related decrease in diestrous length; however, the length of the estrous cycle was not noted to change (NTP 1998).

Both propene and ethene have been classified as Group 3 carcinogens (not classifiable as to its carcinogenicity to humans) by IARC (1994a,b). For propene, a 2-year inhalation study (concentrations up to 10 000 ppm [17 190 mg/m^3]; MW for propene = 42.03 g/mol) showed the occurrence of hemangiosarcoma in male and female mice, as well as lung tumours (negative trend with increasing concentration) in male mice. No tumours were observed under the same protocol in rats (Quest et al. 1984; NTP 1985). A second inhalation study in mice (78 weeks) and rats (104 weeks) conducted with up to 5000 ppm (8600 mg/m^3) propylene showed no differences in tumour incidence compared with controls (Ciliberti et al. 1988). For ethene, a 2-year study in rats did not result in increased tumour incidence at concentrations up to 3000 ppm (3438 mg/m^3; MW of ethene = 28.02 g/mol) (Hamm et al. 1984). Chronic exposure of male and female F344 rats and B6C3F1 mice to isobutene at levels up to 8000 ppm (18 336 mg/m^3; MW of isobutene = 54.04 g/mol) for 104 weeks was noted to cause an increased incidence of thyroid gland follicular cell carcinoma in male rats (NTP 1998). In addition, an increased incidence of hyaline degeneration in the nose of rats and mice was reported (NTP 1998).

Ethene, propene and 1-butene were all noted to cause an increased incidence of DNA adducts *in vivo* (Segerback 1983; Tornqvist et al. 1989; Filser et al. 1992; Eide et al. 1995; Wu et al. 1995; Zhao et al. 1999; Rusyn et al. 2005; Pottenger et al. 2007), but no micronuclei were induced when rats and mice were exposed to ethene, propene or isobutene (Exxon Biomedical Sciences, Inc. 1990; Vergnes and Pritts 1994; NTP 1998; Pottenger et al. 2007). When ethene, 1-butene, 2-butene or isobutene was administered *in vitro*, negative results were obtained for mutagenicity in bacteria (Landry and Fuerst 1968; Hamm et al. 1984; Hughes et al. 1984; Staab and Sarginson 1984; Shimizu et al. 1985; Victorin and Stahlberg 1988; Thompson 1992; Wagner et al. 1992; Araki et al. 1994; NTP 1998; JETOC 2000), mouse lymphoma cells with and without activation (Staab and Sarginson 1984), micronuclei induction without activation (Jorritsma et al. 1995), chromosomal aberrations with and without activation (Riley 1996; Wright 1992) and cell transformation with and without activation (Staab and Sarginson 1984).

Other Components

The refinery gases (as part of the American Petroleum Institute grouping of petroleum gases) are noted to contain alkadienes, alkynes, aromatics, inorganics and mercaptans in addition to alkanes and alkenes, although as less abundant components in the petroleum stream (API 2001a). Many of these components are described below.

Alkadienes

As noted in the health effects section of the screening assessment, a member of the alkadienes, 1,3-butadiene, is classified as both a carcinogen and a mutagen by several national and international agencies (Canada 2000b; EURAR 2002; U.S. EPA 2002; IARC 2008; NTP 2011a). A thorough review of the human health effects of 1,3-butadiene was previously done under the second Priority Substances List (Canada 2000b). 1,3-Butadiene was subsequently added to the List of Toxic Substances on Schedule 1 of CEPA 1999. Alkadienes have been observed to have narcotic properties at high concentrations and low general toxicity (Sandmeyer 1981).

Another member of the alkadienes, 2-methyl-1,3-butadiene or isoprene, is also classified as a carcinogen (Group 2B: possibly carcinogenic to humans [IARC 1999]; Category 2: suspected human carcinogen, may cause cancer [European Commission 2004] and "reasonably anticipated to be a human carcinogen" [NTP 2011b]), as well as a mutagen (European Commission 2004; ESIS 2008). Isoprene is noted to have reproductive effects in mice (testicular atrophy, similar to that observed after 1,3-butadiene exposure), as well as developmental effects (reduced fetal body weight, increased incidence of supernumerary ribs) (Mast et al. 1989, 1990). As well, isoprene has been reported to have effects on mortality, body weight, organ weights, hematology and histopathology (stomach hyperplasia, olfactory degeneration, thymic atrophy, hepatocellular foci changes, alveolar hyperplasia, spinal cord degeneration) in mice after short- and long-term inhalation exposures (Melnick et al. 1990, 1994, 1996). On the basis of carcinogenicity, for which there may be a probability of harm at any level of exposure, the Government of Canada concluded that isoprene should be considered as a substance that may be entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health (Canada 2008).

Alkynes

Ethyne or acetylene is noted to be a simple asphyxiant (HSDB 2008); effects observed in humans after inhalation include intoxication, aggressiveness and unconsciousness at high concentrations (U.S. EPA 2008c). Acetylene is noted to cause increased mortality in various species of experimental animals, as well as intoxication or anesthesia. Effects in the liver (LOAEC = 266.3 mg/L [266 300 mg/m^3]), kidneys and spleens of rats were observed following repeated exposure via inhalation. Genotoxic effects were not observed in vitro (U.S. EPA 2008c).

Aromatics

Benzene is noted to be a carcinogen, as classified by the Government of Canada (carcinogenic to humans; List of Toxic Substances on Schedule 1 of CEPA 1999) (Canada 1993), IARC (1987) (Group 1: carcinogenic to humans), the European Commission (Category 1 carcinogen: may cause cancer) (ESIS 2008), the US National Toxicology Program (NTP 2011c) (known human carcinogen) and the U.S. EPA (2008d) (Group A). In addition, benzene has been classified as a mutagen (Category 2: may cause heritable genetic damage) (European Commission 2004; ESIS 2008).

Inorganics

Hydrogen sulfide has been evaluated by the International Programme on Chemical Safety (IPCS) in both an Environmental Health Criteria monograph (IPCS 1981) and a Concise International Chemical Assessment Document (IPCS 2003). In addition, the US Agency for Toxic Substances and Disease Registry (ATSDR 2006) has generated a toxicological profile on hydrogen sulfide. The Government of Canada is currently assessing the potential impacts of hydrogen sulfide on human health from various uses and sources.

Ammonia has been evaluated by IPCS (1986), ATSDR (2004) and the Organisation for Economic Co-operation and Development (OECD) Screening Information Dataset (SIDS) program (OECD 2007). In addition, ammonia has been evaluated by the Government of Canada under the Priority Substances Assessment Program for its presence in the aquatic environment, where “conclusions drawn on the basis of a more robust data set on environmental effects would also be protective of human health” (Canada 2001a).

Both nitrogen and carbon dioxide have been noted to be inert pesticide ingredients by the U.S. EPA (2004b). Carbon monoxide has been classified by the European Commission as a Category 1 reproductive toxin (ESIS 2008) and has also been reviewed by IPCS (1999).

Mercaptans

Two mercaptans noted to be components of petroleum and refinery gases have been evaluated or reviewed by various international or national agencies; however, for the purposes of this assessment, an evaluation of these components will not be included.

Methanethiol or methyl mercaptan has been reviewed by ATSDR (1992) and included in a review of aliphatic and aromatic sulfides and thiols by the Joint Food and Agriculture Organization of the United Nations (FAO)/World Health Organization (WHO) Expert Committee on Food Additives (JECFA) (WHO 2000). In addition, both methanethiol and ethanethiol are substances scheduled for evaluation under the OECD SIDS program, but a final review has not been made available at this time (OECD 2000).

Appendix 8. Summary of the critical health effects information for 1,3-butadiene

Table A8.1. Critical health effects information on 1,3-butadiene

Endpoints	Study protocol	Effect levels[a]/results	References
Carcinogenicity	B6C3F1 mice (70 of each sex per group; 90 of each sex at the highest concentration); inhalation exposure to 0, 6.25, 20, 62.5, 200 or 625 ppm (0, 13.8, 44.2, 138, 442 or 1380 mg/m^3) for 6 hours/day, 5 days/week, for 103 weeks. Up to 10 mice of each sex from each group were sacrificed after 9 and 15 months of exposure. Histopathological examination of a comprehensive range of tissues was carried out on mice in the control and 200 and 625 ppm (442 and 1380 mg/m^3) exposure groups sacrificed after 9 months; all mice sacrificed at 15 months except females exposed to 6.25 or 20 ppm (13.8 or 44.2 mg/m^3), and all mice exposed for 2 years.	**Lowest concentration** at which tumours were observed = 6.25 ppm (13.8 mg/m^3) based on a statistically significant increase in the incidence of malignant lung tumours. Summary of effects: **Lymphohematopoietic system** Exposure was associated with the development of malignant lymphomas (particularly lymphocytic lymphomas, which occurred as early as week 23). The incidences were significantly increased in males at 625 ppm (1380 mg/m^3) ($p < 0.001$) and females at 200 and 625 ppm (442 and 1380 mg/m^3) ($p < 0.001$) (although all incidences in the females were within the range of historical control values: 8–44%). Histiocytic sarcomas were significantly increased in both males ($p < 0.001$) and females ($p = 0.002$) at 200 ppm (442 mg/m^3), and the incidence of these tumours was marginally higher than that in controls in males at 20, 62.5 and 625 ppm (44.2, 138 and 1380 mg/m^3) ($p = 0.021$–0.051) and females at 625 ppm (1380 mg/m^3) ($p = 0.038$). **Heart** The incidences of cardiac hemangiosarcomas were significantly increased compared with controls in males at 62.5 ppm (138 mg/m^3) and above and in females at 200 ppm (442 mg/m^3) and above. **Lungs** There was evidence of increased	NTP 1993

Endpoints	Study protocol	Effect levels[a]/results	References
		incidences of alveolar/bronchiolar adenomas or carcinomas compared with controls in males at 62.5 ppm (138 mg/m^3) and above ($p < 0.001$) and in females at all concentrations ($p < 0.001–0.004$). **Forestomach** An increased incidence of forestomach tumours (squamous cell papillomas or carcinomas) was observed in males at 200 and 625 ppm (442 and 1380 mg/m^3) ($p < 0.001$) and in females at 62.5 ppm (138 mg/m^3) and above ($p < 0.001–0.044$). **Ovary** Increased incidences of malignant and benign granulosa cell tumours were reported in females exposed to 62.5 ppm (138 mg/m^3) and above ($p < 0.001$). **Harderian gland** The incidence of Harderian gland adenomas and carcinomas was increased in both sexes at 62.5 and 200 ppm (138 and 442 mg/m^3) ($p < 0.001–0.016$).	
	B6C3F1 mice (50 males per group); inhalation exposure for 6 hours/day, 5 days/week, at 200 ppm (442 mg/m^3)[b] for 40 weeks, 312 ppm (689 mg/m^3)[b,] for 52 weeks or 625 ppm (1380 mg/m^3)[b] for 13 or 26 weeks. After exposure ceased, mice were kept in control chambers until 103 weeks and evaluated. Histopathological examination of a comprehensive range	**Lowest concentration** at which tumours were observed = 200 ppm (442 mg/m^3) for 40 weeks based on increased incidence of cardiac hemangiosarcomas and adenomas or carcinomas in the liver. Summary of effects: **Lymphohematopoietic system** The incidence of malignant lymphomas (the majority of which were lymphocytic lymphomas) was markedly increased in both groups (13 and 26 weeks) exposed to 625 ppm (1380 mg/m^3) ($p < 0.001$) and occurred as early as 23 weeks in the 26 weeks group. **Heart**	NTP 1993

Endpoints	Study protocol	Effect levels[a]/results	References
	of tissues was conducted on all mice.	The incidence of cardiac hemangiosarcomas was significantly ($p < 0.001$) increased in all groups, but particularly in mice exposed to 200 or 312 ppm (442 or 689 mg/m^3). **Lungs** There was a significant ($p < 0.001$) increase in the incidence of pulmonary neoplasms (alveolar/bronchiolar adenoma or carcinoma) in all exposed groups, particularly when the figures were adjusted to account for mortality. **Liver** The incidence of adenomas or carcinomas in the liver was significantly greater in the 200 ppm (442 mg/m^3) group ($p = 0.004$) than in the controls and in all exposed groups when adjusted for survival ($p < 0.01$–0.05). **Forestomach** There was a significant ($p < 0.001$) increase in the incidence of squamous cell papillomas or carcinomas of the forestomach in mice exposed to 312 or 625 ppm (689 or 1380 mg/m^3) (both 13 and 26 weeks). **Harderian gland** The incidence of Harderian gland adenomas or carcinomas was significantly ($p < 0.001$) increased compared with controls in all exposed groups. **Other tumours** The incidence of adenomas or carcinomas of the preputial gland was significantly ($p < 0.001$–0.003) increased in the 312 and 625 ppm (689 or 1380 mg/m^3) (13 or 26 weeks) groups. The incidence of adenomas or carcinomas of the Zymbal gland was	

Endpoints	Study protocol	Effect levels[a]/results	References
		significantly ($p = 0.009$) increased in mice exposed to 625 ppm (1380 mg/m^3) for 26 weeks (1/50, 1/50, 0/50, 2/50 and 2/50).	
	Sprague-Dawley rats (110 of each sex per group); inhalation exposure to 0, 1000 or 8000 ppm (0, 2209 or 17 669 mg/m^3)[b] for 6 hours/day, 5 days/week, for 105 weeks (females) or 11 weeks (males). Ten rats of each sex from each group were sacrificed after 52 weeks of exposure.	**Lowest concentration** at which tumours were observed = 1000 ppm (2209 mg/m^3) based on increased incidence of mammary tumours. Summary of effects: **Mammary gland** There was a significant increase in the incidence of tumours in females in the 1000 and 8000 ppm (2209 and 17 669 mg/m^3) groups (total tumour incidence: 50%, 79% and 81%; malignant tumour incidence: 18%, 15% and 26%); mammary tumours appeared earlier in treated groups compared with controls, and most of the tumours were benign. **Thyroid gland** There was a significant concentration-related positive trend in the incidence of follicular thyroid adenoma in female rats (0%, 2% and 10%). **Testis** There was a statistically significant, concentration-related increase in Leydig cell tumours in male rats (0%, 3% and 8%), but the incidence at the highest concentration is close to historical controls (0–6%).	Owen 1981; Owen et al. 1987; Owen and Glaister 1990
Developmental and reproductive toxicity	Pregnant CD-1 mice; inhalation exposure to 0, 40, 200 or 1000 ppm (0, 88, 442 or 2209 mg/m^3),[b] 6 hours/day, gestation days 6–15	**Developmental LOAEC** (mice) = 200 ppm (88 mg/m^3) based on significant reduction in body weight of male and female fetuses (15.7%). Increased skeletal variations were also observed at 200 and 1000 ppm (442 and 2209 mg/m^3).	Hackett et al. 1987
	B6C3F1 mice (70 of each sex per group; 90 of each sex at the highest concentration); inhalation exposure to	**Reproductive LOAEC** (female mice) = 6.25 ppm (13.8 mg/m^3) based on significantly elevated incidence of ovarian atrophy in all exposure groups compared with	NTP 1993

Endpoints	Study protocol	Effect levels[a]/results	References
	0, 6.25, 20, 62.5, 200 or 625 ppm (0, 13.8, 44.2, 138, 442 or 1380 mg/m^3) for 6 hours/day, 5 days/week, for 103 weeks. Up to 10 mice of each sex from each group were sacrificed after 9 and 15 months of exposure.	controls at 103 weeks. Atrophied ovaries characteristically had no evidence of oocytes, follicles or corpora lutea. At concentrations ≥ 62.5 and ≥ 200 ppm (≥ 138 and ≥ 442 mg/m^3), angiectasis and germinal epithelial hyperplasia of the ovaries were reported. Uterine atrophy developed after 9 months of exposure to concentrations ≥ 200 ppm (≥ 442 mg/m^3). **Reproductive LOAEC** (male mice) = 200 ppm based on testicular atrophy observed following 2 years of exposure; higher concentrations for shorter durations also induced this effect. Testes of a majority of males were atrophic at the 9- and 15-month interim evaluations and at the end of the 2-year study. Note: Increased mortality rates and/or tumour development also occurred at concentrations causing gonadal atrophy.	
Human studies (carcinogenicity)	1 Canadian and 7 US polymer production plants (styrene–butadiene rubber workers); cohort study using quantitative exposure estimates for 1,3-butadiene, styrene and benzene for each worker. Cohort size = 15 000 1943–1994	An excess mortality for leukemia was observed in ever-hourly workers; standardized mortality ratio = 143–436. A 4.5-fold increased leukemia risk was also noted among the highest exposure group with internal comparison. Excess leukemia was consistently observed across the plants that were examined. The leukemia risk increased with increasing exposure level.	Delzell et al. 1995, 1996

[a] LOAEC, lowest-observed-adverse-effect concentration.

[b] Conversion of the provided value into mg/m^3 was completed using the formula: *x* ppm (MW)/24.45.