

**Screening Assessment  
Petroleum Sector Stream Approach**

**Petroleum and Refinery Gases  
[Site-Restricted]**

**Chemical Abstracts Service Registry Numbers**

68307-99-3	68478-34-2
68476-26-6	68512-91-4
68476-49-3	68513-16-6
68477-69-0	68513-17-7
68477-71-4	68513-18-8
68477-72-5	68514-31-8
68477-73-6	68514-36-3
68477-75-8	68527-16-2
68477-76-9	68602-83-5
68477-77-0	68602-84-6
68477-86-1	68606-27-9
68477-87-2	68607-11-4
68477-93-0	68814-67-5
68477-97-4	68911-58-0
68478-00-2	68918-99-0
68478-01-3	68919-02-8
68478-05-7	68919-04-0
68478-25-1	68919-08-4
68478-29-5	68919-10-8
68478-32-0	68952-79-4

**Environment Canada  
Health Canada**

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## Synopsis

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

CAS RN*	Domestic Substances List (DSL) name**
68307-99-3	tail gas (petroleum), catalytic polymerized naphtha fractionation stabilizer
68476-26-6	fuel gases
68476-49-3	hydrocarbons, C <sub>2</sub> -C <sub>4</sub> , C <sub>3</sub> -rich
68477-69-0	gases (petroleum), butane splitter overhead
68477-71-4	gases (petroleum), catalytic cracked gas oil depropanizer bottom, C <sub>4</sub> -rich acid-free
68477-72-5	gases (petroleum), catalytic cracked naphtha debutanizer bottom, C <sub>3</sub> -C <sub>5</sub> -rich
68477-73-6	gases (petroleum), catalytic cracked naphtha depropanizer overhead, C <sub>3</sub> -rich acid-free
68477-75-8	gases (petroleum), catalytic cracker, C <sub>1</sub> -C <sub>5</sub> -rich
68477-76-9	gases (petroleum), catalytic polymerized naphtha stabilizer overhead, C <sub>2</sub> -C <sub>4</sub> -rich
68477-77-0	gases (petroleum), catalytic reformed naphtha stripper overhead
68477-86-1	gases (petroleum), deethanizer overhead
68477-87-2	gases (petroleum), deisobutanizer tower overhead
68477-93-0	gases (petroleum), gas concentration reabsorber distillation
68477-97-4	gases (petroleum), hydrogen-rich
68478-00-2	gases (petroleum), recycle, hydrogen-rich
68478-01-3	gases (petroleum), reformer make-up, hydrogen-rich
68478-05-7	gases (petroleum), thermal cracking distillation
68478-25-1	tail gas (petroleum), catalytic cracker refractionation absorber
68478-29-5	tail gas (petroleum), cracked distillate hydrotreater separator
68478-32-0	tail gas (petroleum), saturate gas plant mixed stream, C <sub>4</sub> -rich
68478-34-2	tail gas (petroleum), vacuum residue thermal cracker
68512-91-4	hydrocarbons, C <sub>3</sub> -C <sub>4</sub> -rich, petroleum distillates
68513-16-6	gases (petroleum), hydrocracking depropanizer off, hydrocarbon-rich
68513-17-7	gases (petroleum), light straight-run naphtha stabilizer off
68513-18-8	gases (petroleum), reformer effluent high-pressure flash drum off
68514-31-8	hydrocarbons, C <sub>1</sub> -C <sub>4</sub>
68514-36-3	hydrocarbons, C <sub>1</sub> -C <sub>4</sub> , sweetened
68527-16-2	hydrocarbons, C <sub>1</sub> -C <sub>3</sub>
68602-83-5	gases (petroleum), C <sub>1</sub> -C <sub>5</sub> , wet
68602-84-6	gases (petroleum), secondary absorber off, fluidized catalytic cracker overhead fractionater
68606-27-9	gases (petroleum), alkylation feed
68607-11-4	petroleum products, refinery gases
68814-67-5	gases (petroleum), refinery
68911-58-0	gases (petroleum), hydrotreated sour kerosine depentanizer stabilizer off
68918-99-0	gases (petroleum), crude oil fractionation off
68919-02-8	gases (petroleum), fluidized catalytic cracker fractionation off
68919-04-0	gases (petroleum), heavy distillate hydrotreater desulfurization stripper off
68919-08-4	gases (petroleum), preflash tower off, crude distillation
68919-10-8	gases (petroleum), straight-run stabilizer off
68952-79-4	tail gas (petroleum), catalytic hydrodesulfurized naphtha separator

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\*\* Revisions have been proposed to DSL names of some of the site-restricted petroleum and refinery gases. See Appendix 6 for a table of the DSL substance names used in the draft screening assessment and the revised names used in the current assessment.

These substances were identified as high priorities for action during the categorization of the Domestic Substances List, as they were determined to present greatest potential or intermediate potential for exposure of individuals in Canada and were considered to present a high hazard to human health. Although they met the categorization criteria for persistence in the environment, they did not meet the ecological categorization criteria for bioaccumulation or inherent toxicity to non-human organisms. These substances were included in the Petroleum Sector Stream Approach 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., refining, upgrading or natural gas processing facilities), are a category of saturated and unsaturated light hydrocarbons. The compositions of petroleum and refinery gases vary depending on the source of the crude oil, bitumen, or natural gas as well as the process operating conditions and processing units used. As such, petroleum and refinery gases are considered to be of Unknown or Variable composition, Complex reaction products or Biological materials (UVCBs). In order to predict 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 substance.

Site-restricted petroleum and refinery gases can serve as fuels, as intermediates for further separation of components, or as feedstocks for chemical transformation processes within a facility.

The petroleum and refinery gases considered in this screening assessment have been identified as site-restricted (i.e., they are a subset of petroleum and refinery gases that are not expected to be transported off the petroleum facility sites). According to information reported under section 71 of the *Canadian Environmental Protection Act, 1999* (CEPA 1999), and other sources of information, these 40 site-restricted petroleum and refinery gases are consumed on site or are blended into substances leaving the site under different CAS RNs. However, it has been recognized that 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. Dispersion modelling results show that unintentional releases of these site-restricted petroleum and refinery gases contribute to ambient background levels of 1,3-butadiene in the vicinity of petroleum facilities.

Based on the current available information, none of these CAS RNs contain components that meet the bioaccumulation criteria as defined in the *Persistence and Bioaccumulation Regulations*. However, many of the components of site-restricted petroleum and refinery gases persist in the atmosphere and meet the persistence criteria in the *Regulations*.

A number of regulatory and non-regulatory measures are already in place in Canada, which limit releases of site-restricted petroleum substances, including provincial/territorial operating permit requirements, and best practices and guidelines put in place by the petroleum industry at refinery, upgrader and natural gas processing facilities. Based on results of dispersion modelling, concentrations of components of

petroleum and refinery gases in air surrounding petroleum facilities are not expected to be at levels that could result in harm to the environment.

Based on the information available, it is concluded that the 40 site-restricted petroleum and refinery gases included in this screening assessment do not meet the criteria under paragraphs 64(a) and (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.

One component of petroleum and refinery gases, ethene, is being assessed in a separate assessment and its potential to cause harm is not considered in this assessment. This will allow consideration of ethene releases from industrial operations generally, rather than attempting to link its release to the specific substances that are the subject of the current assessment.

Site-restricted petroleum and refinery gases were identified as a high priority for action as they were considered to present high hazard to human health. A critical effect for categorization of human health for petroleum and refinery gases was carcinogenicity, as another jurisdiction (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, increasing the incidence of tumours at all inhalation concentrations tested. 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.

1,3-Butadiene was selected as a high hazard component to characterize potential exposure to the general population as it is considered, based on available information, to be present in these petroleum and refinery gases. While limited, 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. Furthermore, margins between high end estimates of exposure to 1,3-butadiene and estimates of cancer potency are considered potentially inadequate to address uncertainties related to health effects and exposure.

Based on the information available, it is concluded that the 40 site-restricted petroleum and refinery gases meet the criteria in 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 40 site-restricted petroleum and refinery gases listed under CAS RNs 68307-99-3, 68476-26-6, 68476-49-3, 68477-69-0, 68477-71-4, 68477-72-5, 68477-73-6, 68477-75-8, 68477-76-9, 68477-77-0, 68477-86-1, 68477-87-2, 68477-93-0, 68477-97-4, 68478-00-2, 68478-01-3, 68478-05-7, 68478-25-1, 68478-29-5, 68478-32-0, 68478-34-2, 68512-91-4, 68513-16-6, 68513-17-7, 68513-18-8, 68514-31-8, 68514-36-3, 68527-16-2, 68602-83-5, 68602-84-6, 68606-27-9,

68607-11-4, 68814-67-5, 68911-58-0, 68918-99-0, 68919-02-8, 68919-04-0, 68919-08-4, 68919-10-8 and 68952-79-4 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 presented an 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 (CMP) 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 as 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.<sup>1</sup>

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<sup>1</sup> 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 (CMP) is not relevant to, nor does it preclude, an assessment against the hazard criteria specified in the Controlled Products Regulations, which is part of the regulatory framework for the Workplace Hazardous Materials Information System (WHMIS) 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.

## Grouping of Petroleum Substances

The high-priority petroleum substances fall into nine groups of substances based on similarities in production, toxicity and physicochemical properties (Appendix 1). In order to conduct the screening assessment, each high-priority petroleum substance was placed into one of five categories (“streams”), depending on its production and uses 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<sup>2</sup>;

Stream 2: industry-restricted substances, which are substances that may leave a petroleum-sector facility and may be transported to other industrial facilities (for example, for use as a feedstock, fuel or blending component), but that 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 resulted in the determination that approximately 70 high-priority petroleum substances are site-restricted under Stream 1. Site-restricted substances are a subset of substances that are not expected to be transported off refinery, upgrader or natural gas processing facility sites as described above. These occur within four groupings: heavy fuel oils, gas oils, petroleum and refinery gases, and low-boiling-point naphthas.

These site-restricted substances were identified as having GPE or IPE during the categorization exercise based on their production volumes reported in the Domestic Substances List (DSL). Although they were considered persistent in the environment, they did not meet the ecological categorization criteria for bioaccumulation or inherent toxicity to non-human organisms. These substances were included in the Petroleum Sector Stream Approach because they are related to the petroleum sector and are all complex combinations of petroleum hydrocarbons. 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 are consumed on-site or are blended into substances leaving the site under different Chemical Abstracts Service Registry Numbers (CAS RNs), which will also be addressed under the CMP.

This final screening assessment addresses 40 site-restricted petroleum and refinery gases captured under CAS RNs 68307-99-3, 68476-26-6, 68476-49-3, 68477-69-0, 68477-71-4, 68477-72-5, 68477-73-6, 68477-75-8, 68477-76-9, 68477-77-0, 68477-86-1, 68477-87-2, 68477-93-0, 68477-97-4, 68478-00-2, 68478-01-3, 68478-05-7, 68478-25-1, 68478-29-5, 68478-32-0, 68478-34-2, 68512-91-4, 68513-16-6, 68513-17-7, 68513-18-8, 68514-31-8, 68514-36-3, 68527-16-2, 68602-83-5, 68602-84-6, 68606-27-9, 68607-11-4, 68814-67-5, 68911-58-0, 68918-99-0, 68919-02-8, 68919-04-0, 68919-08-4, 68919-10-8 and 68952-79-4. The remaining high-priority petroleum and refinery gases (under six

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<sup>2</sup> 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. In these cases, facilities are petroleum refineries, upgraders, or natural gas processing facilities.

different CAS RNs) are being assessed separately, as they belong to Streams 2 or 4 (as described above).

Included in this final screening assessment is the consideration of information on chemical properties, hazards, uses and exposure, 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, stakeholder research reports and from recent literature searches, up to December 2009 for the environmental fate and effects sections, up to September 2011 for the exposure sections and up to December 2011 for the health effects section. Key studies were critically evaluated; modelling results were used to reach conclusions.

Characterizing risk to the environment involves consideration of data relevant to environmental behaviour, persistence, bioaccumulation and toxicity combined with an estimation of exposure to potentially affected non-human organisms from the major sources of release to the environment. Conclusions regarding risk to the environment are based in part 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 of environmental hazard 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 assist 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 substance). 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 final 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 final 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 Patricia Nance (TERA), Dr. Bob Benson (United States Environmental Protection Agency [US EPA]), Dr. Stephen Embso-Mattingly (NewFields Environmental Forensics Practice, LLC), Dr. Michael Jayjock (The Lifeline Group) and Dr. Donna Vorhees (Science Collaborative).

Additionally, the draft of this screening assessment was subject to a 60-day public comment period. While external comments were taken into consideration, 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 assessment is based are summarized below.

### Substance Identity

Petroleum and refinery gases are a category of saturated and unsaturated petroleum light hydrocarbons produced by natural gas processing, petroleum refining and upgrader facilities (API 2001a). 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 the upgrading and refining process. Given their complex and variable compositions, they could not practicably be formed by simply combining individual constituents.

Some petroleum and refinery gases may also contain inorganic components, such as hydrogen, nitrogen, hydrogen sulphide, carbon monoxide and carbon dioxide. The compositions of petroleum and refinery gases vary depending on the source of the crude oil, bitumen, or natural gas, as well as the process operating conditions and processing units involved (Speight 2007). The potential components of petroleum and refinery gases are presented in Table 1.

**Table 1. Potential components present in petroleum and refinery gases (API 2001b)**

Methane	1- <i>cis</i> -3-Pentadiene
Ethane	1- <i>trans</i> -3-Pentadiene
Propane	1,4-Pentadiene
<i>n</i> -Butane	2,3-Pentadiene
<i>n</i> -Pentane	3-Methyl-1,2-butadiene
2-Methylpropane (isobutane)	2-Methyl-1,3-butadiene (isoprene)
2-Methylbutane	Cyclopentadiene
Ethene	Ethyne
1-Propene	Benzene
1-Butene	Methanethiol
2-Butene	Ethanethiol
2-Methylpropene (isobutylene)	Hydrogen sulphide
Cyclopentane	Ammonia
Cyclopentene	Hydrogen
1,2-Propadiene	Nitrogen
1,2-Butadiene	Carbon dioxide
1,3-Butadiene	Carbon monoxide
1,2-Pentadiene	

The CAS RN descriptions are not useful in determining the exact composition of any specific petroleum and refinery gas substance, as they are written in broad, general terms with no quantitative analytical information on compositions. Because of the qualitative nature of these CAS RN descriptions, there may be significant compositional overlap between two petroleum and refinery gas substances with different CAS RNs (API 2001b).

1,3-Butadiene is a component of particular interest because of its physical-chemical properties (e.g. volatility) and toxicological properties (e.g. carcinogenicity). There are limited data on the 1,3-butadiene content of site-restricted petroleum and refinery gases. Only two recent reports were identified (API 2009a, 2009b). These reports on category analysis and hazard characterization of petroleum hydrocarbon gases and refinery gases present compositional data on the 1,3-butadiene content in selected petroleum and refinery gas substances based on limited historical data from several US refineries from 1992 through 2002. Thirty-nine of the 40 CAS RNs identified in this screening assessment were analyzed for the potential presence of 1,3-butadiene. A compositional range for 1,3-butadiene of approximately less than 0.1–4% by weight was observed in 15 of the 39 CAS RNs that were analyzed. 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. Substances containing C<sub>4</sub> through C<sub>6</sub> hydrocarbons may contain potentially carcinogenic hydrocarbon components including 1,3-butadiene and benzene at concentrations exceeding 0.1 wt% (API 2009a, 2009b). Therefore the site-restricted petroleum and refinery gases in the current assessment (which are predominately C<sub>1</sub> to C<sub>5</sub>), are considered, based on available information, to contain 1,3-butadiene.

General descriptions of the 40 site-restricted petroleum and refinery gases are presented in Table A2.1 in Appendix 2.

### **Physical and Chemical Properties**

Table 2 contains physical and chemical properties of petroleum and refinery gases that are relevant to their environmental fate. These were estimated based on modelled and experimental data available for a set of representative chemical structures. Based on the number of discrete substances and the types of petroleum hydrocarbons found in petroleum and refinery gases, the choice of representative structures was fairly straightforward. Petroleum and refinery gases are mainly composed of C<sub>1</sub>–C<sub>5</sub> hydrocarbons, which can be alkanes, isoalkanes, alkenes, cycloalkanes, cycloalkenes, dienes and cyclodienes. These components are all well-understood simple structures. The proportion of each component for a particular CAS RN can be highly variable within a facility or among different facilities; this makes prediction of the physical and chemical properties of such mixtures inexact. Information on the representative structures selected and their detailed physical and chemical properties is given in Table A2.2 in Appendix 2.

**Table 2. General physical and chemical properties of petroleum and refinery gases**

Property	Type	Value	Temperature (°C)	Reference
<b>Boiling point (°C)</b>	Experimental	-164 – 49	NA	Weast 1972
<b>Melting point (°C)</b>	Experimental	-182 – -94	NA	Weast 1972
<b>Density (kg/m<sup>3</sup>)</b>	Experimental	0.47 – 0.75	20	Weast 1972
<b>Vapour pressure (Pa)</b>	Experimental	$4 \times 10^4 - 7 \times 10^7$	25	Daubert and Danner 1994
<b>Water solubility (mg/L)</b>	Experimental	22 – 156	25	Yalkowsky and He 2003

The components of petroleum and refinery gases are gaseous at environmentally relevant temperatures. If they are released to the environment, they will quickly disperse and separate. The C<sub>5</sub> alkane, alkene and cyclic components that are liquids at ambient temperatures have high vapour pressures, so they will also evaporate quite readily from soil or water.

## Sources

Site-restricted petroleum and refinery gases are produced in Canadian refineries, upgraders and natural gas processing facilities. The CAS RN descriptions (NCI 2006), typical process flow diagrams (Hopkinson 2008), and information collected under section 71 of CEPA 1999 (Environment Canada 2008, 2009), indicate that these substances are either fuel gases consumed on-site or intermediates produced and consumed within a facility, and are not transported off-site. These site-restricted petroleum and refinery gases can be present in three types of petroleum facilities: petroleum refineries (where crude oils are converted into finished petroleum products, such as gasoline, jet fuel or base oils for lubricants); natural gas processing facilities (where crude natural gases are processed into clean natural gas and other C<sub>2</sub>–C<sub>5</sub> hydrocarbons); and upgraders (where oil sand derived bitumen is converted into synthetic crude oil for further processing at a refinery).

CAS RN 68476-26-6 represents a fractionation mixture of light gases predominantly with hydrogen and C<sub>1</sub>–C<sub>2</sub> produced from a gas separation unit in a refinery or a bitumen upgrader after acidic compounds (hydrogen sulphide, carbon dioxide) are removed. This substance is usually consumed on-site as a fuel gas.

CAS RN 68476-49-3 represents a light hydrocarbon gas mixture treated by a Merox process (i.e., sweetening process) to remove sulphide compounds in a refinery, upgrader

or natural gas processing plant. The gas mixture leaves a caustic washing and goes into an extractor to remove any mercaptan compounds.

CAS RN 68477-69-0 refers to an overhead substance stripped out of a butane splitter. It can be present in a gas separation unit of a refinery or a natural gas processing plant and may enter an alkylation unit as a feedstock.

CAS RN 68477-71-4 refers to a mixture of C<sub>3</sub>–C<sub>5</sub> from the bottom of a depropanizer distillation column treated with a catalytic cracking effluent. The gas mixture normally enters a refinery gas plant for further separation or is further processed in an isomerization unit to produce isomers for the subsequent alkylation unit.

CAS RN 68477-72-5 represents an overhead gas mixture produced from a distillation column to stabilize catalytic cracked naphtha. The gas substance can either go into a refinery gas plant for further separation or enter an isomerization unit.

CAS 68477-73-6 represents an overhead substance from a distillation column to remove C<sub>3</sub> or lighter hydrocarbons from catalytic cracked naphthas. The overhead goes into a gas separation unit for further recovery.

CAS RN 68477-75-8 refers to a mixture of light components discharged from the top of a catalytic cracking fractionation column. The mixture goes directly into a gas separation unit.

Both CAS RN 68307-99-3 and CAS RN 68477-76-9 represent a mixture of overhead light hydrocarbons discharged from a stabilization column for polymerized naphtha. CAS RN 68307-99-3 is predominantly C<sub>1</sub> to C<sub>4</sub> whereas CAS RN 68477-76-9 is predominantly C<sub>2</sub> to C<sub>3</sub>. The overhead substance normally undergoes further purification before being used as a final product (e.g., liquefied petroleum gas).

CAS RN 68477-77-0 represents an overhead light hydrocarbon from a stabilization column for reformed naphtha. The overhead goes into a gas separation unit for further recovery.

CAS RN 68477-86-1 refers to an overhead substance discharged from a deethanizer column. It usually undergoes further treatment for separating ethene and ethane.

Similar to CAS RN 68477-69-0, CAS RN 68477-87-2 refers to an overhead substance from a butane splitter in a refinery facility or a natural gas processing plant. It will enter an alkylation unit as a feedstock.

CAS RN 68477-93-0 refers to a gaseous substance discharged from the top of a stripping column. It usually returns to a gas absorber to remove any remaining acidic compounds (hydrogen sulphide and carbon dioxide) in an amine treatment process.

CAS RN 68477-97-4, CAS RN 68478-00-2 and CAS RN 68607-11-4 are generic descriptions of hydrogen-rich gaseous substances in a hydrotreating, catalytic reforming,

hydrocracking or isomerization unit. CAS RN 68477-97-4 refers to a gaseous stream flashed from a separator following the reactor and recycled to the reactor after removal of any acid compounds. CAS RN 68478-00-2 refers to a hydrogen-rich light hydrocarbon gas effluent from the reactor that contains trace acidic compounds (e.g., hydrogen sulphide and carbon dioxide). CAS RN 68607-11-4 refers to a gaseous stream similar to CAS RN 68477-97-4 in a hydrotreating, catalytic reforming, hydrocracking or isomerization unit that is normally recycled and reused in the process.

Both CAS RN 68478-01-3 and CAS RN 68513-18-8 refer to substances in a catalytic reforming process. CAS RN 68478-01-3 refers to a reactor effluent that goes into a heat exchanger to be cooled down before being flashed off in the flash tank. CAS RN 68513-18-8 represents an off-gas stream flashed from a high-pressure flash drum where light compounds are removed and will be recycled to the reactor.

CAS RN 68478-05-7 represents an overhead gas mixture produced from a fractionation column in a thermal cracking reactor (coker or visbreaker) that will go directly into a gas separation unit for further recovery.

CAS RN 68478-25-1 represents a tail gas effluent from an absorber where acid compounds are removed from the fractionation effluents in a catalytic cracking reactor. The substance is normally used as a fuel within the facility.

CAS RN 68478-29-5 represents an overhead gas discharged from a stabilization column fed with hydrotreated cracking products. The substance mainly consists of C<sub>1</sub>–C<sub>5</sub> and normally enters a gas separation unit for recovery.

CAS RN 68478-32-0 is a generic description of tail gas effluents from a distillation column to stabilize naphtha products, such as straight-run and catalytic reformed naphthas. The substance consists of C<sub>3</sub>–C<sub>6</sub> and normally enters a gas separation unit for recovery.

CAS RN 68478-34-2 represents a mixture of light overhead hydrocarbons discharged from a fractionation column in a coking or visbreaking unit. It normally goes into a gas separation unit for further treatment.

Both CAS RN 68512-91-4 and CAS RN 68918-99-0 refer to an overhead gas effluent discharged from fractionation of crude oils. The substance consists of C<sub>5</sub> and lighter hydrocarbons and will enter a gas separation unit for further treatment.

CAS RN 68513-16-6 represents an overhead gas substance leaving a fractionation column treated with a hydrocracking effluent in a refinery or an upgrader. It will normally enter a gas separation unit for further processing.

CAS RN 68513-17-7 refers to a light hydrocarbon overhead discharged from a stabilization column for straight-run naphtha prior to gasoline blending. The gaseous substance goes into a gas separation unit for further processing.

CAS RN 68514-31-8 is a generic description of a light hydrocarbon gas mixture discharged from a fractionation column in a thermal cracking process (coking or visbreaking) or from atmospheric distillation of crude oils. The gas mixture is further processed in a gas separation unit for further purification.

CAS RN 68514-36-3 is a generic description of gaseous C<sub>1</sub>–C<sub>4</sub> hydrocarbons after the removal of mercaptan or other acidic components. It will require further removal of caustic residues or gas purification.

CAS RN 68527-16-2 is a generic description of a light hydrocarbon mixture discharged from the top of a debutanizer column. It will enter a gas separation unit for further recovery.

CAS RN 68602-83-5 is a generic description of a gaseous mixture leaving atmospheric distillation of crude oils or a fractionation column in a cracking process (catalytic cracking or hydrocracking) of gas oils. It is normally discharged into a gas separation unit for further processing.

CAS RN 68602-84-6 represents an off-gas substance from a secondary absorber in a fluidized catalytic cracking unit. It will often be used as a fuel gas consumed on-site.

CAS RN 68606-27-9 refers to a hydrocarbon gas mixture discharged from a debutanizer treated with products of catalytic cracking of gas oils. The overhead substance mainly contains C<sub>3</sub>–C<sub>4</sub> and is further processed in an alkylation unit to form iso-naphtha for gasoline blending.

CAS RN 68814-67-5 is a generic description of an off-gas stream produced from various refining units, such as hydrotreating, hydrocracking, hydroreforming and cracking (catalytic and thermal). The gas mixture mainly consists of hydrogen and C<sub>1</sub>–C<sub>3</sub> and normally enters a gas separation unit for purification and recovery.

CAS RN 68911-58-0 represents an off-gas substance from a stabilization column for straight-run or cracked kerosene. It will enter a gas separation unit for recovery.

CAS RN 68919-02-8 refers to an overhead gas mixture discharged from a fractionation column in a fluidized catalytic cracking unit. It will go directly into a gas separation unit for further treatment.

CAS RN 68919-04-0 represents an off-gas mixture discharged from a distillation column following a hydrotreating process on a heavy distillate. It will normally be delivered into a gas separation unit for further processing.

CAS RN 68919-08-4 represents an off-gas mixture produced from a pre-flashed column or first distillation column of crude oils. It will go directly into a gas separation unit for further processing.

CAS RN 68919-10-8 refers to an overhead gas produced from a fractionation column following the first distillation of crude oils. It will enter a gas separation unit for further treatment.

CAS RN 68952-79-4 refers to an overhead gas substance from a stabilization column for hydrotreated naphtha. The gaseous mixture will enter a gas separation unit for further treatment.

## Uses

According to 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 substances listed in this screening assessment were identified as either being consumed at the refinery, upgrader or natural gas processing facility or blended into substances leaving the site under a different CAS RN. The site-restricted petroleum and refinery gases discussed in this screening assessment are normally consumed on-site as fuel gas or require further processing to recover each valuable component in the mixture before leaving the facility. Although these substances were identified by multiple use codes established during the development of the 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 site-restricted petroleum and refinery gases are not expected to be transported off petroleum facility sites.

## Releases to the Environment

Potential releases of petroleum and refinery gases from petroleum facilities can be characterized as either controlled or unintentional releases. Controlled releases are planned releases from pressure relief valves and venting valves, for safety purposes or maintenance, and are considered part of routine operations and occur under controlled conditions. Unintentional releases are typically characterized as unplanned releases due to spills or leaks from various equipment, valves, piping, flanges, etc., and may result from equipment failure, poor maintenance, lack of proper operating practices, adverse weather conditions or other unforeseen factors. Petroleum facilities are highly regulated and regulatory requirements established under various jurisdictions, as well as voluntary non-regulatory measures implemented by the petroleum industry, are in place to manage potential releases (SENES 2009).

### Controlled Releases

The site-restricted petroleum and refinery gas CAS RNs in this screening assessment originate as overhead emissions from distillation columns, absorbers, flash tanks and reactors in a petroleum facility. The potential locations for the controlled releases of these gases are the safety valves or venting systems located on the piping or the vessels (e.g., reflux vessels, flash tanks, reactors, towers) where the gas streams are generated.

Under typical operating conditions, controlled releases of site-restricted petroleum and refinery gases are normally collected into a closed system,<sup>3</sup> according to defined procedures, and usually go 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 only occur under typical operating conditions as described above is thus expected to be minimal for the petroleum and refinery gases under the CAS RNs identified in this screening assessment.

### **Unintentional Releases**

Unintentional releases (including fugitive releases) occur from equipment seals (e.g., compressors and storage tanks), valves, piping, flanges, etc. during processing and handling of petroleum substances and can be higher in situations of poor maintenance or operating practice. Regulatory and non-regulatory measures are in place to reduce these events at petroleum refineries and upgraders (SENES 2009). Measures have also recently been applied to natural gas processing facilities (CAPP 2007). Rather than being specific to one substance, these measures are developed in a more generic way in order to limit unintentional releases of all substances in the petroleum sector.

For the Canadian petroleum industry, requirements at the provincial/territorial level typically prevent or manage the unintentional releases of petroleum substances 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 limit unintentional releases to the environment (CanLII 2009).

Non-regulatory measures (e.g., guidelines, best practices) to reduce unintentional releases are also in place at petroleum sector facilities. Such control measures include appropriate material selection during the setup and design process, regular inspection and maintenance of storage tanks, piping 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 (SENES 2009).

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 their much higher volatility, (lower boiling point) and higher mobility as compared to liquid substances (US EPA 1995; CPPI 2005; CAPP 2007). In general, the common sources of fugitive releases from a petroleum sector facility are compressor seals, processing valves, flanges, pressure relief valve seals, storage tanks, loading operations, sample lines and open-ended lines (CCME 1993; CPPI 2005). Fugitive releases tend to occur more frequently when

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<sup>3</sup> 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 losses are collected and either recirculated, reused or destroyed.

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). Once released, gases disperse more readily into larger volumes than liquids. Although general population exposure is not typically expected from site-restricted petroleum substances, physical-chemical properties (e.g., higher volatility and vapour pressures) of the petroleum and refinery gases indicate that there is a limited potential for general population and environmental exposure in the vicinity of refinery, upgrader and/or natural gas processing facility sites. Accordingly, it is considered appropriate to quantify potential exposure to the general population from the unintentional releases of petroleum and refinery gases identified by the 40 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 section).

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

## Environmental Fate

Although these site-restricted petroleum and refinery gases are not expected to be transported from the facility, their physical-chemical properties (e.g., high volatility) dictate that any release of them within a facility may lead to their escape to the environment. Therefore, fugacity modelling was used to estimate their environmental fate.

As noted previously, the atmosphere is expected to be the primary environmental compartment into which petroleum and refinery gases are released. When released to air, all components in petroleum and refinery gases are expected to remain in air as they are highly volatile (vapour pressures are  $4 \times 10^4 - 7 \times 10^7$  Pa) (Table A2.2 in Appendix 2). Therefore, when released, petroleum and refinery gases are expected to remain in the atmosphere (EQC 2003) (Table A2.3 in Appendix 2). Releases to water and soil are not expected.

## Persistence and Bioaccumulation Potential

### Environmental Persistence

The C<sub>1</sub>-C<sub>4</sub> alkanes are relatively inert, non-polar, hydrophobic substances that do not react with water or hydroxide ions (Lyman et al. 1990). Empirical aerobic biodegradation data (API 2001a) show 66–76% biodegradation over 35 days for methane and ethane in water, but it is unlikely that these two gases would remain dissolved in water for that long under natural conditions.

As there are no experimental data on the degradation of these petroleum and refinery gases as complex mixtures, a quantitative structure-activity relationship (QSAR)-based weight-of-evidence approach (Environment Canada 2007) was applied using results from

the BIOHCWIN (2008), BIOWIN (2009) and AOPWIN (2008) models. Modelled data for primary and ultimate biodegradation obtained with BIOHCWIN (2008) and BIOWIN (2009), respectively, indicate that none of the representative structures is persistent in water or soil environments (Table A2.4 in Appendix 2). The average atmospheric half-lives for photo-oxidation of 1,3-butadiene are 0.24–10 hours, however, the half-lives of 1,3-butadiene can vary significantly, from hours up to months, under different conditions (e.g., different seasons, clear or cloudy skies) (Canada 2000a). Predicted oxidation half-lives in air for petroleum and refinery gas components were 0.08–1559 days (Table A2.5 in Appendix 2). This is supported by calculated photodegradation values for alkanes (i.e., methane) based on equations from Atkinson (1990) that suggest half-lives of 3.2–960 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.

Many petroleum and refinery gas components are predicted to have atmospheric half-lives ranging from 2.4 to 1559 days, and are considered to be persistent in air (half-life in air  $\geq 2$  days), as set out in the *Persistence and Bioaccumulation Regulations* under CEPA 1999 (Canada 2000b).

### **Potential for Bioaccumulation**

As no experimental bioaccumulation factor (BAF) or bioconcentration factor (BCF) data for petroleum and refinery gases as complex mixtures were available, a predictive approach was applied to the representative structures using available BAF and BCF models. The modified Gobas model for fish (BCFBAF 2008) predicted middle-trophic-level BAFs of 2.6–182 L/kg and BCFs of 1.7 – 55 L/kg, indicating that none of the representative structures for petroleum and refinery gases have the potential to bioaccumulate significantly in fish.

Based on the available kinetic-based modelled values, none of the components in petroleum and refinery gases meet the bioaccumulation criterion (BCF or BAF  $\geq 5000$ ) as set out in the *Persistence and Bioaccumulation Regulations* (Canada 2000b).

## **Potential to Cause Ecological Harm**

### **Ecological Effects Assessment**

#### *Aquatic Compartment*

A range of aquatic toxicity predictions for representative structures was obtained from the ECOSAR (2009) model. Predicted acute toxicity values (median lethal concentrations [LC<sub>50</sub>S]) were moderate, ranging from 10 to 167 mg/L for fish, from 11 to 164 mg/L for daphnids and from 1 to 96 mg/L for algae. Some components are not sufficiently soluble in water to reach the predicted LC<sub>50</sub> concentrations, such as the simple alkanes and

alkenes that likely make up the bulk of petroleum and refinery gases. These results indicate that, in general, these substances are not highly hazardous to aquatic organisms.

### *Terrestrial Compartment*

Experimental data available for acute effects via inhalation in laboratory animals indicate that few of the representative structures are acutely toxic to mammals (ACGIH 2001, 2005; Canada 2000a). Methane is biologically inert (Rom 1992); iso-butane is toxic to rats at a concentration of 570 000 parts per million (ppm) over 15 minutes (ESIS 2007); an LC<sub>50</sub> was noted at 620 000 mg/m<sup>3</sup> in rats for isobutylene (Shugaev 1969; BG Chemie 1991; ESIS 2000; OECD 2005); and inhalation exposure to 600 000 ppm of ethene continuously for 90 days in rats had only minor effects (Bingham et al. 2001; OECD 1998; ACGIH 2001). Propylene at 112 000 mg/m<sup>3</sup> over four hours did not produce mortality (Conolly and Osimitz 1981), and at 40% (688 000 mg/m<sup>3</sup>) produces only light anaesthesia in rats (Bingham et al. 2001).

In addition, ovarian atrophy was observed following a 2-year chronic inhalation exposure of mice to 6.25 ppm (13.8 mg/m<sup>3</sup>) of another representative structure, 1,3-butadiene, while testicular atrophy was observed following exposure to 200 ppm (442 mg/m<sup>3</sup>) (ATSDR 2009).

### **Ecological Exposure Assessment**

Although the petroleum and refinery gases in this screening assessment have been identified as site-restricted, there is limited potential for release to the ecosystem, as they are all gases that can unintentionally be released at a petroleum facility. Resulting concentrations of the components of petroleum and refinery gases in air surrounding petroleum facilities are expected to be minimal (e.g., in the low µg/m<sup>3</sup> range for 1,3-butadiene), as indicated by results of air dispersion modelling described in the exposure section of the human health portion of this assessment.

### **Characterization of Ecological Risk**

The major representative structures in petroleum and refinery gases have a very low acute and chronic toxicity to mammals (400 000 – 700 000 mg/m<sup>3</sup> and 13.8 – 442 mg/m<sup>3</sup>, respectively), such that it is highly unlikely that mammals would be exposed to concentrations causing an effect.

It is also not expected that there would be significant contamination of watercourses from gaseous fugitive release from petroleum facilities. Therefore, no exposure assessment and risk quotient estimation for aquatic organisms has been conducted.

The significance of releases of ethene to the environment will be assessed in a separate report that considers all sources of release.

None of the components in these petroleum and refinery gases meet the bioaccumulation criteria set out in the *Persistence and Bioaccumulation Regulations*, but many of their principal components meet the atmospheric persistence criteria in the *Regulations*.

Based on the available evidence, it is not expected that the fugitive emissions of these petroleum and refinery gases are causing environmental harm.

### **Uncertainties in Evaluation of Ecological Risk**

The proportions of each component in a specific petroleum and refinery gas 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 and 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 refinery, upgrader and/or natural gas processing facilities. Furthermore, when these gases are released into the air, the component chemicals 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.

Site-restricted petroleum and refinery gases 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 mixtures as a whole, it was considered appropriate to characterize the emissions of a specific component of the mixtures. 1,3-Butadiene was selected from the list of components (Table 1) 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 many of the site-restricted petroleum and refinery gases and was the basis for their classification as carcinogens by the European Union (European Commission 2004; ESIS 2008).

### ***Potential Exposure to Unintentional On-site Releases***

The annual average concentrations of 1,3-butadiene in ambient air have been reported by various sources to range from below 0.05  $\mu\text{g}/\text{m}^3$  to 0.4  $\mu\text{g}/\text{m}^3$ , depending on location. In general, automotive emissions are a major contributor to 1,3-butadiene levels in ambient air (Canada 2000a). Curren et al. (2006) reported that the average annual 1,3-butadiene concentration at urban sites in Canada over 1995–2003 was 0.22  $\mu\text{g}/\text{m}^3$ . Additional monitoring data for 1990–2007 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  $\mu\text{g}/\text{m}^3$ , 0.18  $\mu\text{g}/\text{m}^3$  and

0.32  $\mu\text{g}/\text{m}^3$ , respectively. The annual average concentration of 1,3-butadiene in ambient air ranged from below 0.05 to 0.2  $\mu\text{g}/\text{m}^3$  in 2005 based on 49 monitoring sites across Canada (NAPS 2008), from below 0.05  $\mu\text{g}/\text{m}^3$  to 0.05 - 0.1  $\mu\text{g}/\text{m}^3$  in 2006 based on 47 monitoring sites (NAPS 2008), and from 0.01 to 0.4  $\mu\text{g}/\text{m}^3$  in 2008/2009 based on 58 monitoring sites across Canada (NAPS 2010). For this assessment, 0.22  $\mu\text{g}/\text{m}^3$  was selected to represent ambient background for comparison to modelled emissions.

No measured, and limited estimated quantitative data on emissions of 1,3-butadiene from Canadian petroleum facilities were identified. Therefore, 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). Benzene emission is taken to be a measure of substance throughput in refinery facilities. To relate the substance throughput in a facility to the total 1,3-butadiene lost, it is assumed that a constant ratio holds between the total amount of 1,3-butadiene lost in the petroleum refinery gas production streams through fugitive emissions and the measured amount of benzene lost in all production streams of the facility through fugitive emissions. Thus the ratio of 1,3-butadiene to benzene in fugitive emissions was used as a scaling factor and applied to known emissions data. In general, fugitive releases of benzene in processing areas originate from processing units handling liquid substances. In comparison, fugitive releases of 1,3-butadiene in processing areas primarily originate from processing units handling gas substances. Compared with 1,3-butadiene, the amount of benzene released due to the fugitive releases in gas processing units which produce petroleum and refinery gases is considered minor. Furthermore, based on the carbon ranges reported in the CAS RN descriptions for the site-restricted petroleum and refinery gases, which are predominantly hydrocarbons ranging from  $\text{C}_1$ – $\text{C}_4$  (NCI 2006), only six of the 40 CAS RNs in this assessment may potentially contain benzene.

Data from the National Pollutant Release Inventory 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. These ratios were used to generate a range of emission rates for estimating potential 1,3-butadiene exposure concentrations. The median ratio (50th percentile of the data set) from the NPRI data (1:216) was used for estimating the low end of the emission range. However, only three to six Canadian refineries and upgraders reported fugitive emissions of 1,3-butadiene in a given year over the period 2000–2007. The median ratio from the TRI data (1:85) was used for estimating the high end of the emission range. The TRI data came from 65 US refineries and are considered representative and robust due to the reporting requirements and the large reporting base.

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; US 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 US EPA (CONCAWE 2008; US EPA 2006, 2010).

1,3-butadiene emissions were estimated based on benzene DIAL emission data (Chambers et al. 2008) and the ratios of 1,3-butadiene to benzene in the fugitive emissions of a facility (NPRI 2000-2007; TRI 2007), generating a range of emission values. The dispersion of 1,3-butadiene in air, for increasing distances from the release source, was modelled using SCREEN3 (1996) (developed by the US EPA), thereby generating a range of exposure concentrations at each distance.

SCREEN3 is a screening-level Gaussian air dispersion model based on the Industrial Source Complex (ISC) model (for assessing pollutant concentrations from various 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 (US 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 A3.1 of Appendix 3.

The modelling results from this approach are presented in Table A3.2 of Appendix 3. The results of the modelled dispersion profile of 1,3-butadiene, based on distance from the release source, demonstrate that fugitive emissions of petroleum and refinery gases from these facilities result in 1,3-butadiene concentrations in ambient air of approximately  $0.44 \mu\text{g}/\text{m}^3$  at 200 m for the high end of the emission range and approximately  $0.17 \mu\text{g}/\text{m}^3$  at 200 m for the low end of the range (Table A3.2 in Appendix 3). It is estimated that for the high end of the range ( $0.44 \mu\text{g}/\text{m}^3$ , based on an emissions ratio of 1:85), the contribution of 1,3-butadiene associated with unintentional releases of petroleum and refinery gases will be equivalent to the average annual Canadian ambient air concentration of  $0.22 \mu\text{g}/\text{m}^3$  at a distance of 500 m from the release source. For the low end of the range ( $0.17 \mu\text{g}/\text{m}^3$ , based on an emissions ratio of 1:216), the contribution of

1,3-butadiene due to the unintentional release of petroleum and refinery gases decreases to  $0.088 \mu\text{g}/\text{m}^3$  at 500 m from the release source.

Overall, the SCREEN3 air dispersion modelling suggests that the unintentional release of petroleum and refinery gases results in a contribution to ambient air concentrations of 1,3-butadiene in the vicinity of the release source. The estimated 1,3-butadiene concentrations from petroleum and refinery gases decline with increasing distance from the release source and, in conservative estimates at 500 m from the centre of the processing facility, are considered to reach values associated with the average Canadian background concentration.

A supplementary analysis of the estimated emissions data was conducted to assess the sensitivity of the exposure modelling outputs to the input parameters (as listed in Table A3.1 of Appendix 3) used in the SCREEN3 modelling. Of particular interest, an increase in the rate of release of emissions for a given site area in units of grams per second per metre squared ( $\text{g}/\text{s}\cdot\text{m}^2$ ), or release intensity, can reflect either an increase in the rate of release ( $\text{g}/\text{s}$ ) for a constant release area or release from a more localized area ( $\text{m}^2$ ), demonstrating production-volume changes that can have a significant impact on the maximum exposure estimations. Consequently, any increase in process volume at a refinery, upgrader and/or natural gas processing facility would result in increased levels, and thus exposures above the Canadian average annual ambient air concentration for greater distances from the release sources. Details of the effect of emission intensity on the estimated maximum annual exposures are shown in Figure A3.1 of Appendix 3.

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 the component 1,3-butadiene associated with the unintentional releases of petroleum and refinery gases. Accordingly, there may be limited general population exposure to petroleum and refinery gases in the vicinity of refinery, upgrader and/or 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 0.24–10 hours, the half-lives of 1,3-butadiene can vary significantly, from hours up to months, under different conditions (e.g., different seasons, clear or cloudy skies) (Canada 2000a). Therefore, as a conservative approach, losses due to photo-degradation of 1,3-butadiene are not considered in the estimation of the concentration profile of 1,3-butadiene in this screening assessment.

### **Health Effects Assessment**

Health effects information for the 40 site-restricted petroleum and refinery gas substances was not available. Toxicological information for additional petroleum and refinery gas substances in the Petroleum Sector Stream Approach that are similar from both a process and physical-chemical perspective was also not found. Therefore, in order to characterize

the toxicity of these site-restricted substances, US EPA High Production Volume Information System (HPVIS) read-across substances and petroleum and refinery gas component classes, including alkanes, alkenes, 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, as a wide range of chemical species constitute these gas substances; however, only a summary of the critical information upon which the conclusion is based is presented here.

Gases (petroleum), light steam-cracked, butadiene concentrate (CAS RN 68955-28-2), was identified as a substance similar to hydrocarbons, C<sub>3</sub>–C<sub>4</sub> rich, petroleum distillates (CAS RN 68512-91-4), a site-restricted substance, for the acute and genetic toxicity endpoints. An LC<sub>50</sub> value of  $\geq 5300 \text{ mg/m}^3$  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 CD1 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 (US EPA 2008a). CAS RN 68476-52-8, or hydrocarbons, C<sub>4</sub>, ethylene-manuf.-by-product (C<sub>4</sub> crude butadiene; 10% butadiene), was also identified through HPVIS read-across analysis as a substance similar to CAS RN 68512-91-4 for repeated-dose, 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<sup>3</sup> prior to breeding, during breeding and up to gestational day 19, for a total of approximately 36–37 days (US EPA 2008a), a no-observed-adverse-effect concentration (NOAEC) of 20 000 mg/m<sup>3</sup> was identified specifically for reproductive and developmental toxicity while a no-observed-effect concentration (NOEC) of 20 mg/L (20 000 mg/m<sup>3</sup>) was identified for repeated-dose 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 gases administered as a mixture. The petroleum and refinery gases have been previously evaluated for mammalian health hazards based on the assessment of individual components of the gas substances (API 2001b, 2009a, 2009b; 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 a petroleum and refinery gas substance (listed in Table 1); 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, 2009b). International agencies and organizations have prepared hazard profiles of the various components of the petroleum and refinery gases (API 2001a, 2001b, 2009a, 2009c; CONCAWE 2005).

A brief summary of the toxicological effects of the component classes is presented in Appendix 4; however, a critical review of all hazard data on the numerous components was not undertaken. Rather, the current screening assessment of the site-restricted petroleum and refinery gas substances focuses on a specific component considered to

conservatively represent the hazard posed by these substances as a group to human health. The alkadiene 1,3-butadiene (CAS RN 106-99-0) was selected as the high-hazard component to represent the critical health effects of the site-restricted petroleum and refinery gases, as it may be present in the 40 CAS RNs considered in this screening assessment and its critical health effects are well documented (Canada 2000a).

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 characterized the hazard data (Canada 2000a; EURAR 2002; US EPA 2002; Grant 2008; ATSDR 2009). As relevant to the current screening assessment, the critical literature for characterizing the human health effects for 1,3-butadiene as a high-hazard component for the site-restricted petroleum and refinery gases is summarized.

Appendix 5 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 Priority Substances List (PSL) 2 assessment (Canada 2000a) This substance was subsequently added to the List of Toxic Substances - Schedule 1 of CEPA 1999.

Petroleum and refinery gases have been 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). As a component of petroleum and refinery gases, 1,3-butadiene has been classified as a carcinogen by numerous national and international agencies. Under the Priority Substances Assessment Program, the Government of Canada concluded that 1,3-butadiene met the criteria under section 64c of CEPA 1999 on the basis of a plausible mode of action for induction of tumours involving direct interaction with genetic material (Canada 2000a). The International Agency for Research on Cancer (IARC 2008) has also classified 1,3-butadiene as carcinogenic to humans (Group 1); the US EPA (2002) concluded that 1,3-butadiene is carcinogenic to humans by inhalation; the US National Toxicology Program (NTP 2005) has classified 1,3-butadiene as a known human carcinogen due to sufficient evidence of carcinogenicity in humans; and the European Commission has 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 which 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 two-year inhalation study in B6C3F1 mice exposed to 1,3-butadiene at concentrations of 0 to 625 ppm (0 to 1380 mg/m<sup>3</sup>) 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<sup>3</sup>) (NTP 1993; EURAR 2002; US 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<sup>3</sup>) would also cause cancer in mice (US EPA 2002).

The single long-term inhalation study in rats suggests that 1,3-butadiene is also a multi-site 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 and Glaister 1990; Owen et al. 1987).

Although there are differences in species sensitivity to the carcinogenic properties of 1,3-butadiene, the available data provide unequivocal evidence that 1,3-butadiene is a multi-site carcinogen in rodents (US 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 2000a; EURAR 2002; US 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 international agencies have concluded that there is “sufficient evidence to consider 1,3-butadiene carcinogenic to occupationally exposed populations” (US 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 2000a; EURAR 2002; US 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  $1.7 \text{ mg/m}^3$  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  $2.3 \text{ mg/m}^3$  for the most sensitive tumour site in mice (Canada 2000a).

The US 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  $3 \times 10^{-5} (\mu\text{g/m}^3)^{-1}$  was calculated based on the Delzell et al. (1995) retrospective cohort study (US EPA 2002). More recently, an inhalation unit risk factor of  $5 \times 10^{-7} (\mu\text{g/m}^3)^{-1}$  has been calculated by the Texas Commission on Environmental Quality (TCEQ) 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 US EPA (2002) to evaluate human cancer risk.

An extensive database 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 2000a), the US EPA (2002), the European Commission (EURAR 2002) and ATSDR (2009). Consequently, this information was not included in Appendix 5.

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 2000a). Also, based on the experimental animal data, it is in the highest category described in the weight-of-evidence scheme in the Guidelines for Mutagenicity Risk Assessment (US EPA 1986).

The reproductive organs have been identified as critical targets for 1,3-butadiene-induced non-carcinogenic effects in mice and rats (Canada 2000a; EURAR 2002; US EPA 2002; Grant 2008). The most sensitive reproductive effects identified consistently across various assessments of 1,3-butadiene were observed in a two-year chronic inhalation exposure study in B6C3F1 mice; mice were exposed to concentrations of 0 to 625 ppm (0 to 1380 mg/m<sup>3</sup>). Ovarian atrophy was observed following exposure to the lowest 1,3-butadiene concentration tested, 6.25 ppm (13.8 mg/m<sup>3</sup>), while testicular atrophy was observed following exposure to 200 ppm (442 mg/m<sup>3</sup>) (NTP 1993; EURAR 2002; US 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, these effects observed in mice are considered to have a threshold and to be concentration- and duration-dependent (US 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**

A critical health effect for the initial categorization of site-restricted petroleum and refinery gas substances is 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, increasing the incidence of tumours at all concentrations tested. Epidemiological studies provide further evidence for an association between exposure to 1,3-butadiene in an occupational environment 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 indicates that unintentional releases of petroleum and refinery gases contribute to the overall 1,3-butadiene concentration in ambient air in the vicinity of refinery, upgrader and/or natural gas processing facilities. Consistent with refinery, upgrader and/or natural gas processing facilities being the primary point sources of emissions, the estimated 1,3-butadiene concentrations decline with increasing distance and are estimated to be comparable to or below Canadian average concentrations at distances of more than 500 m from the release source. Using the estimates of carcinogenic potency previously developed by the Government of Canada (Canada 2000a), together with the range of annual 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 single distance is illustrated in Table 3).

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

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

At a distance of 200 m from the release source, and using the high end of the exposure range, the margin of exposure is 5300 while at 500 m from the release source exposure approximates the Canadian average annual ambient air concentration of  $0.22 \mu\text{g}/\text{m}^3$ , with a corresponding margin of exposure of 10 500. Although the magnitude of risk would vary with the cancer potency metrics selected (e.g.,  $\text{TC}_{05}$ ; unit risks derived by US EPA and Texas Commission on Environmental Quality based on linear low-dose extrapolation models), use of a conservative cancer potency metric is considered appropriate given the uncertainties in the health effects database. The above-noted margin of exposure (5300) at 200 m from the release source for the high end of the exposure range is considered potentially inadequate to address uncertainties in the health effects and exposure databases for site-restricted petroleum and refinery gases. Uncertainties with respect to the exposure database are reflected in the model sensitivity analysis, which demonstrates that an increase in the process volume would increase the magnitude of exposure, as well as the distance from the release source before levels reached ambient levels (Figure A3.1 in Appendix 3).

With respect to non-cancer effects, reproductive toxicity was observed to be the critical endpoint. The lowest-observed-adverse-effect concentration (LOAEC) for inhalation exposure (the principal route of exposure for the general population) was 6.25 ppm ( $13.8 \text{ mg}/\text{m}^3$ ), based on ovarian atrophy characterized by the lack of oocytes, follicles and

corpora lutea in mice in a two-year chronic bioassay. Comparison of this LOAEC with the maximum annual high-end and low-end concentrations of the exposure range for 1,3-butadiene results in margins of exposure of approximately 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 exposure of the general population and the environment to site-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 refinery, upgrader, and natural gas processing facilities to concentrations in ambient air.

Uncertainties arose from utilizing NPRI and TRI data to calculate the ratio of 1,3-butadiene to benzene, and from utilizing DIAL measurements of benzene emissions at a Canadian refinery to estimate potential emissions from petroleum facilities.

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 possible 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.

It is assumed that all the estimated releases of 1,3-butadiene are attributed to the petroleum and refinery gases in this assessment.

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 which introduced uncertainty. All the assumptions made in the exposure analysis are listed in Appendix 3.

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 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 their CAS RN.

Use of a single high hazard component to characterize hazard may not reflect all hazards associated with the mixture. Uncertainties with respect to health effects include limitations of a component approach, as other hazardous components in the petroleum

and refinery gases (see Table 1) are not considered in the hazard and risk characterization.

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

## Conclusion

Based on the current available information, none of the 40 CAS RNs considered in this assessment contain components that meet the bioaccumulation criteria as defined in the *Persistence and Bioaccumulation Regulations*. Many of the components of site-restricted petroleum and refinery gases do meet the atmospheric persistence criteria defined in the *Regulations*.

Based on the information presented in this report, it is concluded that these petroleum and refinery gases do not meet the criteria under paragraphs 64(a) and (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.

On the basis of the available data, it is concluded that the site-restricted petroleum and refinery gases meet the criteria in 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 site-restricted petroleum and refinery gases (CAS RNs 68307-99-3, 68476-26-6, 68476-49-3, 68477-69-0, 68477-71-4, 68477-72-5, 68477-73-6, 68477-75-8, 68477-76-9, 68477-77-0, 68477-86-1, 68477-87-2, 68477-93-0, 68477-97-4, 68478-00-2, 68478-01-3, 68478-05-7, 68478-25-1, 68478-29-5, 68478-32-0, 68478-34-2, 68512-91-4, 68513-16-6, 68513-17-7, 68513-18-8, 68514-31-8, 68514-36-3, 68527-16-2, 68602-83-5, 68602-84-6, 68606-27-9, 68607-11-4, 68814-67-5, 68911-58-0, 68918-99-0, 68919-02-8, 68919-04-0, 68919-08-4, 68919-10-8 and 68952-79-4) meet one or more of the criteria set out in section 64 of CEPA 1999.

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**Appendix 1: Description of the nine groups of petroleum substances**

<b>Group</b>	<b>Description</b>	<b>Example</b>
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 sea floor	Crude oil
Petroleum and refinery gases	Complex combinations of light hydrocarbons primarily from C <sub>1</sub> to C <sub>5</sub>	Propane
Low boiling point naphthas	Complex combinations of hydrocarbons primarily from C <sub>4</sub> to C <sub>12</sub>	Gasoline
Gas oils	Complex combinations of hydrocarbons primarily from C <sub>9</sub> to C <sub>25</sub>	Diesel
Heavy fuel oils	Complex combinations of heavy hydrocarbons primarily from C <sub>20</sub> to C <sub>50</sub>	Fuel oil No. 6
Base oils	Complex combinations of hydrocarbons primarily from C <sub>15</sub> to C <sub>50</sub>	Lubricating oils
Aromatic extracts	Complex combinations of primarily aromatic hydrocarbons from C <sub>15</sub> to C <sub>50</sub>	Feedstock for benzene production
Waxes, slack waxes and petrolatum	Complex combinations of primarily aliphatic hydrocarbons from C <sub>12</sub> to C <sub>85</sub>	Petrolatum
Bitumen or vacuum residues	Complex combinations of heavy hydrocarbons having carbon numbers greater than C <sub>25</sub>	Asphalt

<sup>1</sup> These groups were based on classifications developed by CONCAWE and a contractor's report presented to the Canadian Petroleum Products Institute (CPPI) (Simpson 2005).

## Appendix 2: Data tables for site-restricted petroleum and refinery gases

**Table A2.1. Substance identity**

(a)

CAS RN	DSL and NCI names
68307-99-3	Tail gas (petroleum), catalytic polymerized naphtha fractionation stabilizer
68476-26-6	Fuel gases (AICS, ASIA-PAC, DSL, EINECS, TSCA)
68476-49-3	Hydrocarbons, C <sub>2</sub> -C <sub>4</sub> , C <sub>3</sub> -rich (ASIA-PAC, DSL, EINECS, TSCA)
68477-69-0	Gases (petroleum), butane splitter overhead (ASIA-PAC, DSL, ECL, EINECS, TSCA)
68477-71-4	Gases (petroleum), catalytic cracked gas oil depropanizer bottom, C <sub>4</sub> -rich acid-free (ASIA-PAC, DSL, EINECS, TSCA)
68477-72-5	Gases (petroleum), catalytic cracked naphtha debutanizer bottom, C <sub>3</sub> -C <sub>5</sub> -rich (ASIA-PAC, DSL, EINECS, TSCA)
68477-73-6	Gases (petroleum), catalytic cracked naphtha depropanizer overhead, C <sub>3</sub> -rich acid-free (ASIA-PAC, DSL, EINECS, TSCA)
68477-75-8	Gases (petroleum), catalytic cracker, C <sub>1</sub> -C <sub>5</sub> -rich (ASIA-PAC, DSL, EINECS, TSCA)
68477-76-9	Gases (petroleum), catalytic polymerized naphtha stabilizer overhead, C <sub>2</sub> -C <sub>4</sub> -rich (ASIA-PAC, DSL, EINECS, TSCA)
68477-77-0	Gases (petroleum), catalytic reformed naphtha stripper overhead (ASIA-PAC, DSL, ECL, EINECS, TSCA)
68477-86-1	Gases (petroleum), deethanizer overhead (ASIA-PAC, DSL, EINECS, TSCA)
68477-87-2	Gases (petroleum), deisobutanizer tower overhead (ASIA-PAC, DSL, EINECS, TSCA)
68477-93-0	Gases (petroleum), gas concentration reabsorber distillation (ASIA-PAC, DSL, EINECS, TSCA)
68477-97-4	Gases (petroleum), hydrogen-rich (ASIA-PAC, DSL, EINECS, TSCA)
68478-00-2	Gases (petroleum), recycle, hydrogen-rich (ASIA-PAC, DSL, EINECS, TSCA)
68478-01-3	Gases (petroleum), reformer make-up, hydrogen-rich (ASIA-PAC, DSL, EINECS, TSCA)
68478-05-7	Gases (petroleum), thermal cracking distillation (ASIA-PAC, DSL, EINECS, TSCA)
68478-25-1	Tail gas (petroleum), catalytic cracker refractionation absorber (ASIA-PAC, DSL, ECL, EINECS, TSCA)
68478-29-5	Tail gas (petroleum), cracked distillate hydrotreater separator (ASIA-PAC, DSL, ECL, EINECS, TSCA)
68478-32-0	Tail gas (petroleum), saturate gas plant mixed stream, C <sub>4</sub> -rich (ASIA-PAC, DSL, EINECS, TSCA)
68478-34-2	Tail gas (petroleum), vacuum residue thermal cracker (ASIA-PAC, DSL, ECL, EINECS, TSCA)
68512-91-4	Hydrocarbons, C <sub>3</sub> -C <sub>4</sub> -rich, petroleum distillates (ASIA-PAC, DSL, TSCA)
68513-16-6	Gases (petroleum), hydrocracking depropanizer off, hydrocarbon-rich (ASIA-PAC, DSL, EINECS, TSCA)
68513-17-7	Gases (petroleum), light straight-run naphtha stabilizer off (ASIA-PAC, DSL, EINECS, TSCA)

CAS RN	DSL and NCI names
68513-18-8	Gases (petroleum), reformer effluent high-pressure flash drum off (ASIA-PAC, DSL, EINECS, TSCA)
68514-31-8	Hydrocarbons, C <sub>1</sub> -C <sub>4</sub> (AICS, ASIA-PAC, DSL, NZIoC, TSCA)
68514-36-3	Hydrocarbons, C <sub>1</sub> -C <sub>4</sub> , sweetened (AICS, ASIA-PAC, DSL, EINECS, TSCA)
68527-16-2	Hydrocarbons, C <sub>1</sub> -C <sub>3</sub> (AICS, ASIA-PAC, DSL, EINECS, TSCA)
68602-83-5	Gases (petroleum), C <sub>1</sub> -C <sub>5</sub> , wet (ASIA-PAC, DSL, EINECS, TSCA)
68602-84-6	Gases (petroleum), secondary absorber off, fluidized catalytic cracker overhead fractionator (ASIA-PAC, DSL, TSCA)
68606-27-9	Gases (petroleum), alkylation feed (ASIA-PAC, DSL, EINECS, TSCA)
68607-11-4	Petroleum products, refinery gases (ASIA-PAC, DSL, EINECS, TSCA)
68814-67-5	Gases (petroleum), refinery (ASIA-PAC, DSL, EINECS, TSCA)
68911-58-0	Gases (petroleum), hydrotreated sour kerosine deparaffinizer stabilizer off (ASIA-PAC, DSL, EINECS, TSCA)
68918-99-0	Gases (petroleum), crude oil fractionation off (ASIA-PAC, DSL, EINECS, TSCA)
68919-02-8	Gases (petroleum), fluidized catalytic cracker fractionation off (ASIA-PAC, DSL, EINECS, TSCA)
68919-04-0	Gases (petroleum), heavy distillate hydrotreater desulfurization stripper off (ASIA-PAC, DSL, EINECS, TSCA)
68919-08-4	Gases (petroleum), preflash tower off, crude distillation (ASIA-PAC, DSL, EINECS, TSCA)
68919-10-8	Gases (petroleum), straight-run stabilizer off (ASIA-PAC, DSL, EINECS, TSCA)
68952-79-4	Tail gas (petroleum), catalytic hydrodesulfurized naphtha separator (ASIA-PAC, DSL, ECL, EINECS, TSCA)

(b)

<b>Other names</b>	Mixtures of: methane, ethane, propane, butane, isobutane, pentane, cyclopentane, 2-methylbutane, dimethylpropane, ethene, propene, butenes, pentenes, cyclopentenes, butadienes, pentadienes and cyclopentadiene
<b>Chemical group (DSL stream)</b>	Petroleum gases
<b>Major chemical class or use<sup>1</sup></b>	Mixture of light petroleum gases
<b>Major chemical subclass</b>	Variable mixtures of light hydrocarbon gases (i.e., UVCBs)

Abbreviations: AICS, Australian Inventory of Chemical Substances; ASIA-PAC, Asia-Pacific Substances Lists; CAS RN, Chemical Abstracts Service Registry Number; DSL, Domestic Substances List; ECL, Korean Existing Chemicals List; EINECS, European Inventory of Existing Commercial Chemical Substances; NCI, National Chemical Inventories; NZIoC, New Zealand Inventory of Chemicals; TSCA, *Toxic Substances Control Act* Chemical Substance Inventory; UVCB, Unknown or Variable composition, Complex reaction products or Biological materials.

<sup>1</sup> These substances are UVCBs; i.e., they are not discrete chemicals and thus may be characterized by a variety of structures.

**Table A2.2. Physical and chemical properties of representative structures for petroleum and refinery gases<sup>1</sup>**

Substance/ CAS RN	Melting point (°C)	Boiling point (°C)	Vapour pressure (Pa at 25°C)	Henry's Law constant (Pa·m <sup>3</sup> /mol)	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Water solubility (mg/L at 25°C)
Methane 74-82-8	-182.48	-164	$7 \times 10^7$	$6.7 \times 10^4$	1.1	3.34	22
Isobutane 75-28-5	-159.6	-11.7	$3.5 \times 10^5$	$1.2 \times 10^5$	2.8	1.55	49
Pentane 109-66-0	-129.7	36.1	$6.8 \times 10^4$	$1.3 \times 10^5$	3.4	1.91	38
Cyclopentane 287-92-3	-94	49	$4 \times 10^4$	$1.9 \times 10^4$	3.0	1.95	156
Ethene 74-85-1	-169.4	-102.4	$7 \times 10^6$	$2.2 \times 10^4$ (e)	1.13	0.98	131
Cyclopentene 142-29-0	-135.1	44.2	$5 \times 10^4$	$6.5 \times 10^3$ (e)	2.47	2.14	535
1,3-Butadiene 106-99-0	-108.9	-4.4	$2.8 \times 10^5$	$7.5 \times 10^3$ (e)	1.99 (e)	1.73	735
Cyclo- pentadiene 542-92-7	-97.2	41	$5.8 \times 10^4$	$8.0 \times 10^2$	2.25	1.95	1800

Abbreviations: K<sub>oc</sub>, organic carbon–water partition coefficient; K<sub>ow</sub>, octanol–water partition coefficient; (e), experimental data.

<sup>1</sup> All data on melting point, boiling point, vapour pressure and water solubility are experimentally derived, accessed from EpiSuite (2008). All other data are modelled by KOWWIN (2008), PCKOCWIN (2009) and HENRYWIN (2008).

**Table A2.3. Results of the Level III fugacity modelling for components of petroleum and refinery gases (EQC 2003)**

Release of substance to each compartment (100%)	Percentage of substance partitioning into each compartment			
	Air	Water	Soil	Sediment
<b>Methane</b>				
Air	100.0	0.0	0.0	0.0
Water	19.9	79.9	0.0	0.2
Soil	98.0	0.0	2.0	0.0
<b>Isobutane</b>				
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
<b>Pentane</b>				
Air	100.0	0.0	0.0	0.0
Water	8.6	84.4	0.0	7.0
Soil	85.9	0.0	14.1	0.0
<b>Cyclopentane</b>				
Air	100.0	0.0	0.0	0.0
Water	9.0	88.5	0.0	2.5

	<b>Soil</b>	73.1	0.2	26.7	0.0
<b>Ethene</b>					
	<b>Air</b>	100	0	0	0
	<b>Water</b>	4.26	95.6	0	0.1
	<b>Soil</b>	85.5	0.2	14.2	0
<b>Cyclopentene</b>					
	<b>Air</b>	99.9	0.02	0.03	0
	<b>Water</b>	6.7	91.6	0.0	1.7
	<b>Soil</b>	65.5	0.2	34.3	0
<b>1,3-Butadiene</b>					
	<b>Air</b>	100	0	0	0
	<b>Water</b>	0.7	99.2	0	0.1
	<b>Soil</b>	42.9	0.4	56.7	0
<b>Cyclopentadiene</b>					
	<b>Air</b>	99.9	0.05	0.04	0
	<b>Water</b>	0.3	99.5	0	0.2
	<b>Soil</b>	4.7	0.9	94.4	0

**Table A2.4. Modelled data for primary (BIOHCWIN 2008) and ultimate (BIOWIN 2009) biodegradation of representative structures for petroleum and refinery gases**

<b>Substance</b>	<b>Primary half-life (days)</b>	<b>Ultimate biodegradation result</b>	<b>Extrapolated half-life in water and soil (days)</b>
Methane	3.2	Weeks	< 182
Isobutane	3.1	Weeks	< 182
Pentane	4.0	Days-weeks	< 182
Cyclopentane	45	Weeks	< 182
Ethene	2.9	Weeks	< 182
Cyclopentene	5.5	Weeks	< 182
1,3-Butadiene	2.8	Weeks	< 182
Cyclopentadiene	3.6	Weeks	< 182

**Table A2.5. Modelled data for atmospheric degradation of petroleum and refinery gases in contact with hydroxyl radicals and ozone (AOPWIN 2008)**

<b>Substance</b>	<b>Half-life of hydroxyl oxidation reaction (days)</b>	<b>Half-life of ozone reaction (days)</b>	<b>Extrapolated half-life (days)</b>
Methane	1559	NA	≥ 2
Isobutane	4.4	NA	≥ 2
Pentane	2.6	NA	≥ 2
Cyclopentane	2.4	NA	≥ 2
Ethene	1.3	6.6	< 2
Cyclopentene	0.2	0.06	< 2
1,3-Butadiene	0.2	1.4	< 2
Cyclopentadiene	0.08	0.04	< 2

Abbreviation: NA, not applicable.

### Appendix 3: Exposure estimate modelling data and results

**Table A3.1. Variable inputs to SCREEN3 for modelling unintentional on-site releases**

Variables	Input variables
Source type	Area
Process area	300 m × 100 m <sup>1</sup>
Benzene fugitive release from processing areas (from DIAL measurements)	1.8 kg/h <sup>2</sup>
Ratio of 1,3-butadiene to benzene (for use in DIAL approach)	1:85 (high end); 1:216 (low end) <sup>3</sup>
Effective area	0.8 · (300 × 100) <sup>4</sup>
Receptor height	1.74 m <sup>5</sup>
Source release height <sup>1</sup>	15 m (80%), 3 m (20%) <sup>6</sup>
Adjustment factor for highest 1 hr to annual exposure	0.2 <sup>7</sup>
Urban/rural option	Urban
Meteorology	1 (full meteorology) <sup>8</sup>
Minimum and maximum distance to use	50–2000 m

<sup>1</sup> Aerial photo analysis and professional judgement.

<sup>2</sup> Chambers et al. 2008

<sup>3</sup> NPRI (2000–2007) and TRI (2007)

<sup>4</sup> Professional judgement

<sup>5</sup> Curry et al. 1993

<sup>6</sup> Emissions were specified at a high level (above 15 m) and a low level (3 m), in order to represent the heights of equipment involving fugitive releases of 1,3-butadiene. It is assumed that 80% of the fugitive releases occur at 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.

<sup>7</sup> US EPA (1992) and professional judgement

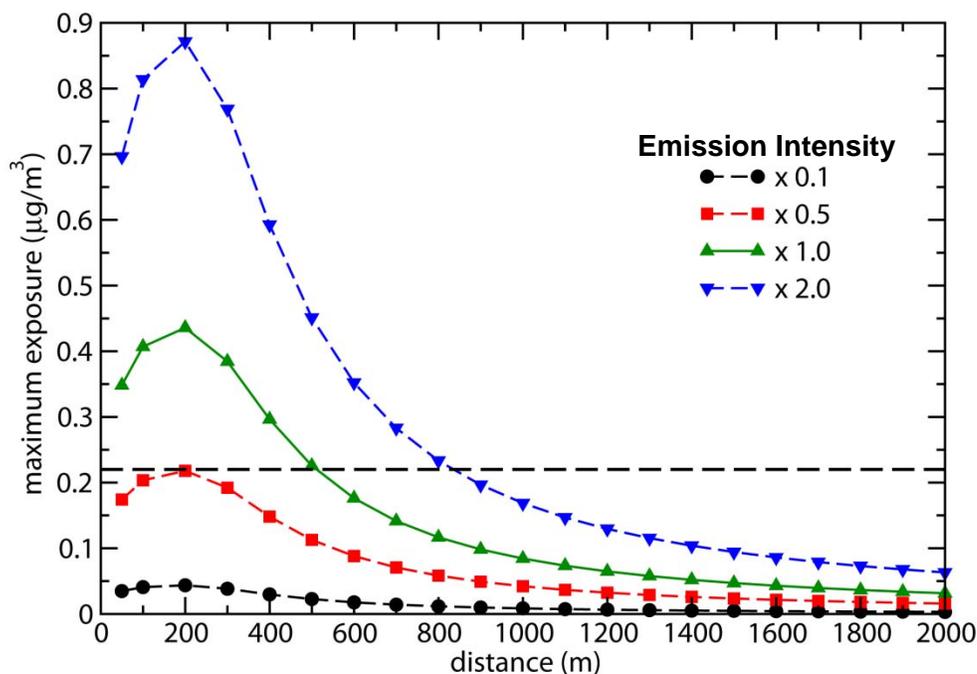
<sup>8</sup> Default value in SCREEN3

**Table A3.2. Modelling results for 1,3-butadiene dispersion profile from unintentional on-site releases of 40 petroleum and refinery gases<sup>1</sup>**

Distance (m)	Concentration ( $\mu\text{g}/\text{m}^3$ )			
	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

<sup>1</sup>Assumptions made in the modelling:

1. All releases of 1,3-butadiene from a petroleum facility are assumed to be attributed to the emissions of site-restricted petroleum and refinery gases and originate from processing areas rather than tank farms.
2. All 40 site-restricted petroleum and refinery gases are flagged as potentially containing 1,3-butadiene.
3. The ratio of 1,3-butadiene to benzene in fugitive emissions is assumed to be constant over different processing units.
4. Fugitive emission heights of 1,3-butadiene are assumed to be 15 m and 3 m, with 80% of total emissions occurring at 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  $\times$  100 m.
7. Adjustment factor 0.2 is used for estimation of maximum concentration over a year based on the highest 1-hour concentration.



**Figure A3.1.** Effect of variation of the high end 1,3-butadiene emission intensity on maximum annual exposure values for fixed facility site area of  $300 \times 100 \text{ m}^2$  and source release height of 15 m (80%) and 3 m (20%). The average background annual exposure of 1,3-butadiene ( $0.22 \text{ } \mu\text{g}/\text{m}^3$ ) is shown by the black dashed line. The maximum annual exposures for the intensity based on 1,3-butadiene emissions calculated by SCREEN3 with factors given in Table A3.1 are shown in green. The data for this curve are given in Table A3.2. This exposure is considered to arise from the “reference emission” used in the SCREEN3 calculations. To account for uncertainties in the estimated emission rate of 1,3-butadiene, maximum exposures for multiples of the reference emission are also calculated and shown with dashed lines. For example, the “ $\times 2.0$ ” values shown by the blue dashed line assume an emission intensity of 2.0 times the reference value estimated for fugitive emissions of the petroleum and refinery gases in this screening assessment. At this higher emission rate, members of the general population at distances up to 800 m would be exposed to 1,3-butadiene concentrations greater than background values. If emission rates are smaller than the reference value by a factor of 0.5 or less (black and red dashed lines), general population exposures of 1,3-butadiene from the facility will not exceed background values. In all cases, exposures of 1,3-butadiene beyond 1000 m of the facility are lower than background values.

## Appendix 4: Summary of the toxicological effects of the component classes of petroleum and refinery gases

### Alkanes

In humans, it has been observed that alkanes of low molecular weight (e.g., methane) can cause displacement of oxygen for acute exposures at high concentrations, which may lead to asphyxiation. At higher molecular weights, substances such as propane can act as mild depressants on the central nervous system (API 2001b). In experimental animals, LC<sub>50</sub> values for alkanes range from 658 mg/L (658 000 mg/m<sup>3</sup>) (butane) to greater than 800 000 ppm (1 440 000 mg/m<sup>3</sup>) (propane), depending on the substance, concentration and duration of 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 no-observed-effect level (NOEL) of 4489 ppm (11 943 mg/m<sup>3</sup>)<sup>1, 2</sup> (highest dose 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 in 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 2001a, 2001b; 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), while narcosis was noted in mice exposed to up to 70% isobutene via inhalation (Von Oettingen 1940). Acute toxicity values (LC<sub>50</sub>) are noted to range from 65 000 ppm (111 736 mg/m<sup>3</sup>)<sup>2</sup> (propene; molecular weight (MW) = 42.03 g/mol) to 620 mg/L (620 000 mg/m<sup>3</sup>) (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 (NOAEL) of 150 mg/kg body weight (kg-bw) 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<sup>3</sup>) (Fink 1968) as well as clinical and biochemical changes in rats exposed for 70 days to 100 ppm (115 mg/m<sup>3</sup>)<sup>2</sup> ethene (MW of ethene = 28.02 g/mol) (Krasovitskaya and Maliarova 1968). Exposure to propene resulted in a lowest NOEL value of 10 000 ppm

<sup>1</sup> Conversion of the provided value into mg/m<sup>3</sup> was completed using the formula:  $x \text{ ppm (MW)}/24.45$

<sup>2</sup> Molecular weight of mixtures =  $[0.5(58.04 \text{ g/mol}) + 0.5(72.05 \text{ g/mol})] = 65.05 \text{ g/mol}$

(17 190 mg/m<sup>3</sup>)<sup>2</sup> for 28-day exposure to multiple concentrations of propene (MW = 42.03 g/mol) up to 17 190 mg/m<sup>3</sup> (DuPont 2002).

The lowest lowest-observed-effect level (LOEL) identified for sub-chronic toxicity is 500 ppm (1146 mg/m<sup>3</sup>)<sup>2</sup> in a 14-week study in which male and female B6C3F1 mice and F344/N rats were exposed by inhalation to isobutene (MW = 54.04 g/mol) at concentrations up to 8000 ppm (18 336 mg/m<sup>3</sup>)<sup>2</sup> 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<sup>3</sup>)<sup>2</sup>. In female rats, there was a significant increase in relative liver weights from 500 ppm (1146 mg/m<sup>3</sup>)<sup>2</sup> and in absolute liver weights from 1000 ppm (2292 mg/m<sup>3</sup>)<sup>4</sup>. In male rats, a significant increase in relative right kidney weight was observed from 500 ppm (1146 mg/m<sup>3</sup>)<sup>2</sup> with an increase in absolute right kidney weight at 4000 ppm (9168 mg/m<sup>3</sup>)<sup>2</sup> (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<sup>3</sup>)<sup>2</sup> (Krasovitskaya and Maliarova 1968).

With regard to developmental toxicity, NOEC values of 5000 ppm (5750 mg/m<sup>3</sup>) for ethene (MW = 28.02 g/mol), 10 000 ppm (17 190 mg/m<sup>3</sup>)<sup>2</sup> for propene (MW = 42.03 g/mol) and 5000 ppm (11 460 mg/m<sup>3</sup>)<sup>2</sup> 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<sup>3</sup>)<sup>2</sup>. In addition, female rats were reported to have an increased estrus length with a related decrease in diestrus length; however, the length of the estrus 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 (1994 a, 1994c). For propene, a two-year inhalation study (concentrations up to 10 000 ppm [17 190 mg/m<sup>3</sup>; MW for propene = 42.03 g/mol])<sup>2</sup> 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<sup>3</sup>)<sup>2</sup> propylene showed no differences in tumour incidence compared with controls (Ciliberti et al. 1988). For ethene, a two-year study in rats did not result in increased tumour incidence at concentrations up to 3000 ppm (3438 mg/m<sup>3</sup>; MW of ethene = 28.02 g/mol)<sup>2</sup> (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<sup>3</sup>; MW of isobutene = 54.04 g/mol)<sup>2</sup> 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 were 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; Japan Chemical Industry Ecology-Toxicology and Information Center 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 API 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 2001b). 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 multiple national and international agencies (Canada 2000a; IARC 2008; US EPA 2002; NTP 2011a; EU RAR 2002; ESIS 2008). A thorough review of the human health effects of 1,3-butadiene was previously done under the Priority Substances List (PSL) 2 assessment (Canada 2000a). 1,3-butadiene was subsequently added to the List of Toxic Substances - 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 those 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 weight, 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,

Health 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), where effects observed in humans after inhalation include intoxication, aggressiveness and unconsciousness at high concentrations (US EPA 2008b).

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<sup>3</sup>), kidneys and spleens of rats were observed following repeated exposure via inhalation. Genotoxic effects were not observed *in vitro* (US EPA 2008b).

### *Aromatics*

Benzene is noted to be a carcinogen, as classified by the Government of Canada (carcinogenic to humans; CEPA 1999 – List of Toxic Substances) (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 US EPA (2008c) (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 sulphide 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 sulphide. The Government of Canada is currently assessing the potential impacts of hydrogen sulphide on human health from various uses and sources.

Ammonia has been evaluated by the 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 List 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 2001).

Both nitrogen and carbon dioxide have been noted to be inert pesticide ingredients by the US 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 hazard assessment, an evaluation of these component substances will not be included.

Methanethiol or methyl mercaptan has been reviewed by ATSDR (1992) and included in a review of aliphatic and aromatic sulphides 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 5: Summary of the critical health effects information on 1,3-butadiene

Endpoints	Study protocol	Effect levels <sup>1</sup> /results	References
Carcinogenicity	<p>Mice B6C3F1 (70 per sex per group; 90 per 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<sup>3</sup>) for 6 h/day, 5 days/week, for 103 weeks. Up to 10 mice of each sex from each group were killed after 9 and 15 months of exposure.</p> <p>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<sup>3</sup>) exposure groups killed after 9 months; all mice killed at 15 months except females exposed to 6.25 or 20 ppm (13.8 or 44.2 mg/m<sup>3</sup>), and all mice exposed for 2 years.</p>	<p><b>Lowest concentration</b> at which tumours were observed = 6.25 ppm (13.8 mg/m<sup>3</sup>) based on a statistically significant increase in the incidence of malignant lung tumours.</p> <p>Summary of effects:  <b>Lymphohematopoietic system</b>  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<sup>3</sup>) (p &lt; 0.001) and females at 200 and 625 ppm (442 and 1380 mg/m<sup>3</sup>) (p &lt; 0.001) (although all incidences in the females were within the range of historical control values: 8–44%).</p> <p>Histiocytic sarcomas were significantly increased in both males (p &lt; 0.001) and females (p = 0.002) at 200 ppm (442 mg/m<sup>3</sup>), 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<sup>3</sup>) (p = 0.021–0.051) and females at 625 ppm (1380 mg/m<sup>3</sup>) (p = 0.038).</p> <p><b>Heart</b>  The incidences of cardiac hemangiosarcomas were significantly increased compared with controls in males at 62.5 ppm (138 mg/m<sup>3</sup>) and above, and females at 200 ppm (442 mg/m<sup>3</sup>) and above.</p> <p><b>Lungs</b>  There was evidence of increased</p>	NTP 1993

Endpoints	Study protocol	Effect levels <sup>1</sup> /results	References
		<p>incidences of alveolar/bronchiolar adenomas or carcinomas compared with controls in males at 62.5 ppm (138 mg/m<sup>3</sup>) and above (p &lt; 0.001), and in females at all concentrations (p &lt; 0.001–0.004).</p> <p><b>Forestomach</b> 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<sup>3</sup>) (p &lt; 0.001) and females at 62.5 ppm (138 mg/m<sup>3</sup>) and above (p &lt; 0.001–0.044).</p> <p><b>Ovary</b> Increased incidences of malignant and benign granulosa cell tumours were reported in females exposed to 62.5 ppm (138 mg/m<sup>3</sup>) and above (p &lt; 0.001).</p> <p><b>Harderian gland</b> The incidence of Harderian gland adenomas and carcinomas was increased in both sexes at 62.5 and 200 ppm (138 and 442 mg/m<sup>3</sup>) (p &lt; 0.001–0.016).</p>	
	<p>Mice B6C3F1 (50 males per group); inhalation exposure for 6 h/day, 5 days/week, at 200 ppm (442 mg/m<sup>3</sup>) for 40 weeks (equivalent to a total exposure of 8000 ppm (17 669 mg/m<sup>3</sup>)<sup>2</sup> 312 ppm (689 mg/m<sup>3</sup>)<sup>2</sup> for 52 weeks (16 000 ppm [35 337 mg/m<sup>3</sup>]<sup>2</sup> or 625 ppm (1380 mg/m<sup>3</sup>) for 13 or 26 weeks (8000 and 16 000 ppm [17 669 and 35 337 mg/m<sup>3</sup>]<sup>2</sup>, respectively).</p>	<p><b>Lowest concentration</b> at which tumours were observed = 200 ppm (442 mg/m<sup>3</sup>) for 40 weeks based on increased incidence of cardiac hemangiosarcomas and adenomas or carcinomas in the liver.</p> <p>Summary of effects: <b>Lymphohematopoietic system</b> The incidence of malignant lymphomas (the majority of which were lymphocytic lymphomas) was markedly increased in both groups exposed to 625 ppm (1380 mg/m<sup>3</sup>) (p &lt; 0.001) and occurred as early as 23 weeks in the 625 ppm (1380 mg/m<sup>3</sup>) (26 weeks) group.</p> <p><b>Heart</b></p>	NTP 1993

Endpoints	Study protocol	Effect levels <sup>1</sup> /results	References
	<p>After exposure ceased, mice were kept in control chambers until 103 weeks and evaluated.</p> <p>Histopathological examination of a comprehensive range of tissues was conducted on all mice.</p>	<p>The incidence of cardiac hemangiosarcomas was significantly (<math>p &lt; 0.001</math>) increased in all groups, but particularly in mice exposed to 200 or 312 ppm (<math>442</math> or <math>689 \text{ mg/m}^3</math>)<sup>2</sup>.</p> <p><b>Lungs</b></p> <p>There was a significant (<math>p &lt; 0.001</math>) 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.</p> <p><b>Liver</b></p> <p>The incidence of adenomas or carcinomas in the liver was significantly greater in the 200 ppm (<math>442 \text{ mg/m}^3</math>) group (<math>p = 0.004</math>) than in the controls and in all exposed groups when adjusted for survival (<math>p &lt; 0.01</math>–<math>0.05</math>).</p> <p><b>Forestomach</b></p> <p>There was a significant (<math>p &lt; 0.001</math>) increase in the incidence of squamous cell papillomas or carcinomas of the forestomach in mice exposed to 312 or 625 ppm (<math>689</math> or <math>1380 \text{ mg/m}^3</math>)<sup>2</sup> (both 13 and 26 weeks).</p> <p><b>Harderian gland</b></p> <p>The incidence of Harderian gland adenomas or carcinomas was significantly (<math>p &lt; 0.001</math>) increased compared with controls in all exposed groups.</p> <p><b>Other tumours</b></p> <p>The incidence of adenomas or carcinomas of the preputial gland was significantly (<math>p &lt; 0.001</math>–<math>0.003</math>) increased in the 312 and 625 ppm (<math>689</math> or <math>1380 \text{ mg/m}^3</math>)<sup>2</sup> (13 or 26 weeks) groups.</p>	

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

Endpoints	Study protocol	Effect levels <sup>1</sup> /results	References
	<p>inhalation exposure to 0, 6.25, 20, 62.5, 200 or 625 ppm (0, 13.8, 44.2, 138, 442 or 1380 mg/m<sup>3</sup>) for 6 h/day, 5 days/week, for 103 weeks. Up to 10 mice of each sex from each group were killed after 9 and 15 months of exposure.</p>	<p>exposure groups compared with controls at 103 weeks. Atrophied ovaries characteristically had no evidence of oocytes, follicles or corpora lutea. At concentrations <math>\geq 62.5</math> and <math>\geq 200</math> ppm (<math>\geq 138</math> and <math>\geq 442</math> mg/m<sup>3</sup>), angiectasis and germinal epithelial hyperplasia of the ovaries were reported. Uterine atrophy developed after 9 months of exposure to doses <math>\geq 200</math> ppm (<math>\geq 442</math> mg/m<sup>3</sup>).</p> <p><b>Reproductive LOAEC</b> (male mice) = 200 ppm based on testicular atrophy observed following 2 years of exposure; higher doses 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.</p> <p>Note: Increased mortality rates and/or tumour development also occurred at doses causing gonadal atrophy.</p>	
Human studies (carcinogenicity)	<p>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.</p> <p>Cohort size = 15 000</p> <p>1943–1994</p>	<p>An excess mortality for leukemia was observed in ever-hourly workers; standardized mortality ratio = 143–436.</p> <p>A 4.5-fold increased leukemia risk was also noted among the highest exposure group with internal comparison.</p> <p>Excess leukemia was consistently observed across the plants that were examined.</p> <p>The leukemia risk increased with increasing exposure level.</p>	Delzell et al. 1995, 1996

<sup>1</sup> LC<sub>50</sub>, median lethal concentration; LD<sub>50</sub>, median lethal dose; LOAEC, lowest-observed-adverse-effect concentration.

<sup>2</sup> Conversion of the provided value into mg/m<sup>3</sup> was completed using the formula:  $x$  ppm (MW)/24.45.

## Appendix 6: Revisions to Domestic Substances List (DSL) names of site-restricted petroleum and refinery gases

CAS RN	DSL name used in the draft screening assessment report	Revised DSL name used in the current report
68307-99-3	tail gas (petroleum), catalytic polymerized naphtha fractionation stabilizer	no change
68476-26-6	fuel gases	no change
68476-49-3	hydrocarbons, C <sub>2</sub> -C <sub>4</sub> , C <sub>3</sub> -rich	no change
68477-69-0	gases (petroleum), butane splitter overheads	gases (petroleum), butane splitter overhead
68477-71-4	gases (petroleum), catalytic cracked gas oil depropanizer bottoms, C <sub>4</sub> -rich acid-free	gases (petroleum), catalytic cracked gas oil depropanizer bottom, C <sub>4</sub> -rich acid-free
68477-72-5	gases (petroleum), catalytic cracked naphtha debutanizer bottoms, C <sub>3</sub> -C <sub>5</sub> -rich	gases (petroleum), catalytic cracked naphtha debutanizer bottom, C <sub>3</sub> -C <sub>5</sub> -rich
68477-73-6	gases (petroleum), catalytic cracked naphtha depropanizer overhead, C <sub>3</sub> -rich acid-free	no change
68477-75-8	gases (petroleum), catalytic cracked, C <sub>1</sub> -C <sub>5</sub> -rich	gases (petroleum), catalytic cracker, C <sub>1</sub> -C <sub>5</sub> -rich
68477-76-9	gases (petroleum), catalytic polymerized naphtha stabilizer overhead, C <sub>2</sub> -C <sub>4</sub> -rich	no change
68477-77-0	gases (petroleum), catalytic reformed naphtha stripper overheads	gases (petroleum), catalytic reformed naphtha stripper overhead
68477-86-1	gases (petroleum), deethanizer overheads	gases (petroleum), deethanizer overhead
68477-87-2	gases (petroleum), deisobutanizer tower overheads	gases (petroleum), deisobutanizer tower overhead
68477-93-0	gases (petroleum), gas concentration reabsorber distillation	no change
68477-97-4	gases (petroleum), hydrogen-rich	no change
68478-00-2	gases (petroleum), recycle, hydrogen-rich	no change
68478-01-3	gases (petroleum), reformer make-up, hydrogen-rich	no change

68478-05-7	gases (petroleum), thermal cracking distn.	gases (petroleum), thermal cracking distillation
68478-25-1	tail gas (petroleum), catalytic cracker refractation absorber	no change
68478-29-5	tail gas (petroleum), cracked distillate hydrotreater separator	no change
68478-32-0	tail gas (petroleum), saturate gas plant mixed stream, C <sub>4</sub> -rich	no change
68478-34-2	tail gas (petroleum), vacuum residues thermal cracker	tail gas (petroleum), vacuum residue thermal cracker
68512-91-4	hydrocarbons, C <sub>3</sub> -C <sub>4</sub> -rich, petroleum distillates	no change
68513-16-6	gases (petroleum), hydrocracking depropanizer off, hydrocarbon-rich	no change
68513-17-7	gases (petroleum), light straight-run naphtha stabilizer off	no change
68513-18-8	gases (petroleum), reformer effluent high-pressure flash drum	gases (petroleum), reformer effluent high-pressure flash drum off
68514-31-8	hydrocarbons, C <sub>1</sub> -C <sub>4</sub>	no change
68514-36-3	hydrocarbons, C <sub>1</sub> -C <sub>4</sub> , sweetened	no change
68527-16-2	hydrocarbons, C <sub>1</sub> -C <sub>3</sub>	no change
68602-83-5	gases (petroleum), C <sub>1</sub> -C <sub>5</sub> , wet	no change
68602-84-6	gases (petroleum), secondary absorber off, fluidized catalytic cracker overheads fractionator	gases (petroleum), secondary absorber off, fluidized catalytic cracker overhead fractionater
68606-27-9	gases (petroleum), alkylation feed	no change
68607-11-4	petroleum products, refinery gases	no change
68814-67-5	gases (petroleum), refinery	no change
68911-58-0	gases (petroleum), hydrotreated sour kerosene depentanizer stabilizer off	gases (petroleum), hydrotreated sour kerosine depentanizer stabilizer off
68918-99-0	gases (petroleum), crude oil fractionation off	no change
68919-02-8	gases (petroleum), fluidized catalytic cracker fractionation off	no change
68919-04-0	gases (petroleum), heavy distillate hydrotreater desulphurization stripper off	gases (petroleum), heavy distillate hydrotreater desulfurization stripper off
68919-08-4	gases (petroleum), preflash tower	no change

	off, crude distillation	
68919-10-8	gases (petroleum), straight-run stabilizer off	no change
68952-79-4	tail gas (petroleum), catalytic hydrodesulphurized naphtha separator	tail gas (petroleum), catalytic hydrodesulfurized naphtha separator