



Screening Assessment Petroleum Sector Stream Approach

Liquefied Petroleum Gases Stream 4 Petroleum and Refinery Gases

Chemical Abstracts Service Registry Numbers

68476-85-7

68476-86-8

**Environment and Climate Change Canada
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Synopsis

Pursuant to section 74 of the *Canadian Environmental Protection Act, 1999* (CEPA), the Ministers of the Environment and of Health have conducted a screening assessment of the following liquefied petroleum gases (LPGs):

CAS RN	Domestic Substances List name
68476-85-7	Petroleum gases, liquefied
68476-86-8	Petroleum gases, liquefied, sweetened

During the categorization exercise, LPGs under two Chemical Abstracts Service Registry Numbers (CAS RNs) 68476-85-7 and 68476-86-8 were identified as priorities for assessment, as they met the categorization criteria under subsection 73(1) of CEPA and/or were considered as a priority based on other human health concerns. These substances were included in the Petroleum Sector Stream Approach (PSSA) because they are related to the petroleum sector and are complex combinations of hydrocarbons.

LPGs are produced by petroleum facilities (i.e., refineries or natural gas processing facilities) and are a category of light, predominantly saturated, hydrocarbons (mainly C1 to C7). However, the LPGs used in consumer products are predominantly C3 and C4 hydrocarbons. LPGs from refineries may contain unsaturated hydrocarbons, such as propene and butenes. The composition of LPGs varies depending on the sources (e.g., natural gas, crude oil), as well as process operating conditions and processing units used. In order to predict overall behaviour of these complex substances for the purposes of assessing the potential for ecological effects, representative structures have been selected from each chemical class in the substances.

LPGs are used primarily as domestic and industrial fuels, as feedstocks, and as aerosol propellants in products available to consumers. It has been recognized that, given the physical-chemical properties of these substances (i.e., gases with high vapour pressures), releases of LPGs into the atmosphere can occur.

Based on the available information, exposure to LPGs by organisms is considered to be mainly through air (e.g., inhalation). Considering the low toxicities of the components of LPGs to organisms via air for non-cancer endpoints, and low predicted exposure relative to those toxicities, there is a low risk of harm to organisms and the broader integrity of the environment from LPGs. It is concluded that these two LPGs (CAS RNs 68476-85-7 and 68476-86-8) do not meet the criteria under paragraphs 64(a) and (b) of CEPA, 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.

A critical human health effect for the initial categorization of these two LPGs was carcinogenicity, as the European Union has identified petroleum and refinery gases containing 1,3-butadiene at concentrations equal to or greater than 0.1% by weight as carcinogens. 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. 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.

The general population may be exposed to LPGs through various aerosol products available in the Canadian marketplace that use LPGs as propellants. For characterization of risk of potential long-term inhalation exposure to aerosol products containing LPGs, a margin of exposure was derived based on 1,3-butadiene indoor air levels in non-smoking homes located in four Canadian cities. Compared with the cancer potency of 1,3-butadiene, the margin of exposure is considered adequate to address uncertainties related to health effects and exposure. This approach is considered conservative as multiple sources are likely to contribute to indoor air levels of 1,3-butadiene.

The general population living in the vicinity of LPG cylinder tank filling stations or LPG vehicle refuelling stations may also be exposed to LPGs. Margins of exposure were therefore derived based on potential long-term inhalation exposure to 1,3-butadiene arising from LPG releases during the fuel transfer process and are considered adequate to address uncertainties related to health effects and exposure.

A recent industry submission on testing 1,3-butadiene levels in selected gas streams at natural gas processing facilities indicates that the concentration of 1,3-butadiene was below the detection limit of 1 ppm in most of the samples tested. Based on the lines of evidence indicating a low level of 1,3-butadiene and the low hazard for other predominant gas components, the human health risks due to volatile emissions of petroleum and refinery gases including LPGs from natural gas processing facilities are considered to be low. Accordingly, emissions of LPGs from natural gas processing facilities are not identified as a source of exposure of concern.

On the basis of available information, 1,3-butadiene is considered to be present in these two LPGs when produced by petroleum refineries. These two LPGs are considered to contribute a portion of the 1,3-butadiene releases at petroleum refining facilities, as quantified in the previously published assessment on Site-Restricted Petroleum and Refinery Gases. In that assessment, it was determined that margins between high-end estimates of exposure to 1,3-butadiene and estimates of cancer potency for inhalation exposure to 1,3-butadiene were

considered potentially inadequate to address uncertainties related to health effects and exposure.

Based on the contribution of these two LPGs to overall petroleum refinery emissions, it is concluded that these two LPGs (CAS RNs 68476-85-7 and 68476-86-8) meet the criteria in paragraph 64(c) of CEPA 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 concluded that these two LPGs (CAS RNs 68476-85-7 and 68476-86-8) meet one or more of the criteria set out in section 64 of CEPA.

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1. Introduction

Pursuant to sections 68 and 74 of the *Canadian Environmental Protection Act, 1999* (CEPA) (Canada 1999), the Minister of the Environment and Climate Change and the Minister of Health conduct screening assessments of substances to determine whether these substances present or may present a risk to the environment or to human health.

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).

The high-priority petroleum substances fall into nine groups of substances based on similarities in production, toxicity and physicochemical properties (Appendix A). In order to conduct the screening assessments, 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;¹

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 determined that 67 high-priority petroleum substances may be present in products available to consumers under Stream 4, as described above. These 67 substances were further sub-grouped as follows, based on their physical and chemical properties and potential uses: aromatic extracts, gas oils, heavy fuel oils, low boiling point naphthas, natural gas condensates, solvents, petroleum and refinery gases, base oils, petrolatum and

¹ 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.

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

This screening assessment addresses two substances. These liquefied petroleum gases (LPGs) were identified as priorities for assessment, as they met the categorization criteria under section 73 of CEPA and/or were considered a priority based on human health concerns. These substances were included in the PSSA because they are related to the petroleum sector and are complex mixtures.

According to information submitted under section 71 of CEPA (Environment Canada 2009, 2012), an in-depth literature review and a search of available material safety data sheets (MSDS), these substances can be transported between industrial facilities and they are present in products available to consumers.

An analysis of exposure to LPG exhaust or combustion by-products from its use as a fuel is outside the scope of this assessment, as consideration of the contribution of fuel combustion to air pollution is assessed under different programs within the Government of Canada.

Screening assessments focus on information critical to determining whether substances within a grouping meet the criteria as set out in section 64 of CEPA, by examining scientific information to develop conclusions by incorporating a weight of evidence approach and precaution.²

This screening assessment includes consideration of information on chemical properties, environmental fate, hazards, uses and exposure, including additional information submitted by stakeholders. Relevant data were identified up to February 2014. Empirical data from key studies as well as some results from models were used to reach conclusions. When available and relevant, information presented in assessments from other jurisdictions was considered.

The screening assessment does not represent an exhaustive or critical review of all available data. Rather, it presents the most critical studies and lines of evidence pertinent to the conclusion.

² 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 is not relevant to, nor does it preclude, an assessment against the hazard criteria specified in the Controlled Products Regulations, which are part of the regulatory framework for the Workplace Hazardous Materials Information System for products intended for workplace use. Similarly, a conclusion based on the criteria contained in section 64 of CEPA does not preclude actions being undertaken under other sections of CEPA or other Acts.

This screening assessment was prepared by staff in the Existing Substances Programs at Health Canada and Environment and Climate Change 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 scientists selected by Toxicology Excellence for Risk Assessment, including Dr. Susan Griffin (U.S. Environmental Protection Agency), Dr. Calvin Willhite (Risk Sciences International & McLaughlin Centre for Population Health Risk Assessment), Dr. Donna Vorhees (Boston University School of Public Health) and Mr. Robert Lee (Neptune and Company Inc.). While external comments were taken into consideration, the final content and outcome of the screening assessment remain the responsibility of Health Canada and Environment and Climate Change Canada.

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

2. Substance Identity

LPGs are a category of petroleum light hydrocarbons produced from the extraction of natural gases or the refining of crude oils (Benz et al. 1960; Barber 2006; Thompson et al. 2011; Wiley 2007). These substances are gaseous at ambient temperature and pressure, but can be liquefied under pressurized or cooling conditions to be conveniently stored or transported (CONCAWE 1992; Thompson et al. 2011). LPGs are similar in composition to site-restricted (Stream 1) and industry-restricted (Stream 2) petroleum and refinery gases, which have been assessed by the Government of Canada (Environment Canada, Health Canada 2013, 2014a).

Below are generic CAS RN descriptions for 68476-85-7 and 68476-86-8 (NCI 2009). A general substance identity for these CAS RNs is given in Table B-1 in Appendix B. It is recognized that globally different companies may use CAS RNs according to individual preferences and internal precedent.

CAS RN 68476-85-7 is a complex combination of hydrocarbons produced by the distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C₃-C₇ and boiling in the range of approximately -40°C to 80°C.

CAS RN 68476-86-8 is a complex combination of hydrocarbons obtained by subjecting liquefied petroleum gas mix to a sweetening process to convert mercaptan or to remove acidic impurities. It consists of hydrocarbons having carbon numbers predominantly in the range of C₃ through C₇ and boiling in the range of approximately -40°C to 80°C.

Available information indicates that the hydrocarbon range and compositional proportion in the LPGs described by these two CAS RNs can vary significantly. The composition of LPGs varies depending on the types of natural gas or crude oils, process operating conditions, seasonal process issues and economic cycles; they may contain hydrocarbons from C₁ to C₈ (Barber 2006; U.S. EPA 2010). Based on limited historical sampling data (1992–2002) from several U.S. refineries primarily processing heavy sour crude oils from South America, the substances identified under CAS RNs 68476-85-7 and 68476-86-8 can contain hydrocarbons ranging from C₁ to C₈, but predominantly C₁ to C₇ (Petroleum HPV 2009a; U.S. EPA 2010).

LPGs are often simply defined as a mixture of propane and butanes. Statistics Canada (2013a,b) defines LPGs as propane, butane or a combination of the two, whereas natural gas liquids (NGLs) are a mixture of ethane, propane and butane from gas plants. The National Energy Board (NEB) defines LPGs as a term for propane and butane, whereas NGLs is a term for light hydrocarbons extracted from natural gas, including ethane, propane, butane and pentanes plus (NEB 2013). Similarly, the Canadian Association of Petroleum Producers (CAPP) defines LPG as consisting primarily of propane or butanes or a propane and butane mixture (CAPP 2013).

In addition to saturated hydrocarbon components, the LPGs from petroleum refining processes (e.g., cracking) may contain unsaturated hydrocarbons, such as propene, butenes and dienes (Benz et al. 1960; CONCAWE 1992; Thompson et al. 2011; Wiley 2007). There are limited data on the 1,3-butadiene content of the LPGs under the CAS RNs identified in this screening assessment report. One recent report by Petroleum HPV (2009a) presents a 1,3-butadiene level ranging from 0 to 0.1% w/w for CAS RNs 68476-85-7 and 68476-86-8. A search of MSDS indicates that the 1,3-butadiene level can vary from 0 to 0.3% w/w in LPGs used as a refinery feedstock (Valero 2012). 1,3-Butadiene was selected as a high hazard component in the Stream 1 and Stream 2 petroleum and refinery gases screening assessments (Environment Canada, Health Canada 2013, 2014a).

Although the substances identified under CAS RNs 68476-85-7 and 68476-86-8 can contain hydrocarbons ranging from C₁ to C₈, LPGs used in the public market with a narrow hydrocarbon range can be identified under the same CAS RNs. Available information indicates that, compared to the composition of LPGs produced at petroleum facilities, LPGs used in products available to consumers often consist of a much narrower hydrocarbon range, predominantly C₃ to C₄, i.e., propane, butanes, propene, butene, and their mixtures (Benz et al. 1960; Lewis 2007; Pohanish 2008; Petroleum HPV 2001, 2009a; Wiley 2007; Thompson et al. 2011). The presence of light hydrocarbons (< C₃) in the final products should be avoided to enhance the capability of being liquefied under moderate conditions (pressurized or refrigerated). Similarly, the amount of higher hydrocarbons (≥ C₅) should be minimized to avoid over-condensation in the gas lines or products (e.g., aerosol products). Due to such specifications, potential exposure to benzene and

hexane in the LPG end products is therefore not expected (Petroleum HPV 2001, 2009a). Trace amounts of odourants (e.g., mercaptan substances) may be added in the end-use LPG products as a safety precaution to enhance leak detection (CONCAWE 1992).

LPGs used as aerosol propellants usually consist of only propane, *n*-butane and isobutane with little or no unsaturated hydrocarbons (Barber 2006; Diversified CPC International 2012). In some MSDS, CAS RN 68476-85-7 or CAS RN 68476-86-8 is used to refer to isobutane, or a mixture of propane and isobutane, or a combination of propane, *n*-butane and isobutane (Farnam Companies 2007; Magic American Products 2008; LPS Laboratories 2008; GOJO Industries 2010; Petro-Canada Lubricants Inc. 2011).

LPGs used as home heating and cooking fuel or automotive fuel consist primarily of propane and butane (Lee et al. 2002; Gasca et al. 2004; Bozkurt et al. 2008). The mixture ratio varies among countries and/or climates. A larger quantity of propane can be added in winter (Bozkurt et al. 2008; Na and Kim 2001).

For LPGs used as a transportation fuel, propane, *n*-butane and isobutane are the major components, with the remaining minor components consisting of pentanes, alkenes, ethane and hexanes. However, their composition can vary significantly depending on their origin. Blake and Rowland (1995) compared the composition of LPGs as a vehicle fuel from Mexico City collected in February 1993 to one from Los Angeles collected in April 1995. The authors reported that the LPG vehicle fuel from Mexico City contained approximately 0.26% w/w propene, 5% w/w butenes and 0.1% w/w 1,3-butadiene. In contrast, the sample from Los Angeles showed 1.6% w/w of propene and less than 0.01% w/w of butenes and 0.01% w/w of 1,3-butadiene. Na et al. (2004) also compared LPGs used as a vehicle fuel from Korea, the United States, Egypt and Mexico. LPGs from Korea and the United States had a higher content of propane, whereas LPGs from Egypt and Mexico had a higher level of butanes. On the basis of 13 samples of LPG fuels collected from different distribution centres in Mexico City, Gamas et al. (2000) reported that C₁ to C₆ paraffins accounted for 98.9 mol% (~98.8% w/w) with the remaining as propene at 0.49 mol% (~0.41% w/w), isobutene at 0.62 mol% (~0.7% w/w) and 1,3-butadiene at 0.02 mol% (~0.02% w/w).

The information considered in this screening assessment represents the typical characteristics of LPGs. LPGs may also contain ethene. Since releases of ethene from the petroleum sector have been addressed in a separate screening assessment (Environment Canada, Health Canada 2014b), it is not further considered in this assessment.

3. Physical and Chemical Properties

The physical and chemical properties for LPGs from available literature are presented in Table 3-1. Limited information is available on the CAS RN-specific

physical and chemical properties of the LPGs. It is recognized that the physical and chemical properties vary depending on the origin of feedstock, operating or processing conditions, as well as the mix ratio of propane to butane in the final LPGs.

Table 3-1. General physical and chemical properties for LPGs

Property	Value	Reference
Molecular weight (g/mol)	42 - 58	Gamas et al. 2000, CDC 2011, Afrox 2013, HCN 2004
Melting point (°C)	-187.6 to -90.6	U.S. EPA 2010
Flash point (°C)	-74	Lewis 2007 ^a
Liquid density (kg/m ³)	~ 540 (15°C), 506 - 583(15°C)	CONCAWE 2012, Gamas et al. 2000, Afrox 2013, ECB 2000a,b
LPG vapour density (kg/m ³)	2.1 (15°C and ambient pressure)	Afrox 2013
Flammable limit, % v/v in atmosphere	Extremely flammable, 1.9 (lower), 9.5 (upper)	CDC 1978, Barber 2006, ECB 2000a,b
Boiling point (°C)	-40 to -0.5 (at ambient pressure), -42.1 to 98.5, -165 to -0.5 (at atmospheric condition) based on C ₁ to C ₄	Afrox 2013, U.S. EPA 2010, ECB 2000a,b
Vapour pressure (kPa)	500 (20°C), 60-3900 (20°C), 6 to 950 (25°C)	Afrox 2013, ECB 2000a,b, U.S. EPA 2010
Henry's Law Constant (Pa·m ³ /mol)	2.2 x 10 ⁴ to 2 x 10 ⁵	U.S. EPA 2010
Water solubility (mg/L)	3.4 to 193 (25°C), 24-61 (20 °C)	U.S. EPA 2010, ECB 2000a,b
Log K _{ow} ^a	2.36 to 4.66	U.S. EPA 2010 ^c

^a K_{ow}, octanol–water partition coefficient (dimensionless)

As shown in Table 3-1, the vapour density of LPGs is higher than that of air. This means that LPGs are heavier than air and can settle in low points and accumulate in confined spaces in the case of a leak. In addition, due to their low boiling points, once released into the atmosphere, liquid LPGs in contact with the skin can cause cold burns due to rapid evaporation (CONCAWE 1992).

LPGs are gaseous at environmentally relevant temperatures and, if released to the environment, they will quickly disperse and separate. The C₅ 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.

To predict the environmental behaviour and fate of LPGs, representative structures were chosen from each chemical class contained within the mixture (Table B-2 in Appendix B). Given that the types of petroleum hydrocarbons found in petroleum and refinery gases are similar to those found in LPGs, representative structures similar to the petroleum and refinery gases were used. Petroleum and refinery gases are mainly composed of C₁–C₆ 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 substances inexact. Detailed physical–chemical properties of the individual selected representative structures are given in Table B-2 (Appendix B).

4. Sources

The LPGs considered in this screening assessment are produced in petroleum facilities. Raw gas extracted at the wellheads of natural gas, condensate or oil wells is delivered to gas processing facilities for further purification and separation into individual products (e.g., natural gas, ethane, LPGs, condensates). According to a literature search and information submitted under section 71 of CEPA, LPGs can be produced from natural gas processing facilities as well as from various crude oil treatment processes in petroleum refineries, such as distillation, cracking or reforming. LPGs can also be generated from plants located near the main natural gas pipeline network, with any LPGs remaining in the natural gas being recovered (Purvin & Gertz 2007). Some stand-alone fractionation plants can separate raw gas streams into individual LPG products (e.g., propane/butane mixture) for commercial markets (Cheminfo 2009).

According to information submitted under section 71 of CEPA (Environment Canada 2012), in 2010, the total quantity of LPGs manufactured in Canada under CAS RNs 68476-85-7 and 68476-86-8 was between 1 and 10 million tonnes, the total imported quantity was between 10 000 and 100 000 tonnes, and the total transport and export quantities were both less than 1 million tonnes.

In addition to the information submitted under section 71 of CEPA, other production data on LPGs in Canada and worldwide were also considered. Statistics Canada (2013c) reported that the total production volume of LPGs from refineries was approximately $2.2 \times 10^6 \text{ m}^3$ (~ 1 million tonnes) in 2010. The total production of NGLs from natural gas processing facilities, including ethane, propane and butane, was approximately $2.8 \times 10^7 \text{ m}^3$ (more than 10 million tonnes) in 2010. However, these data may not be specific to the two CAS RNs identified in this screening assessment report. In the United States, each of the two CAS RNs are considered to be high production volume (HPV) chemicals, having been reported to have a total production and/or import volume of 1 billion lb (~ 0.45 million tonnes) or greater (U.S. EPA 2010). Similarly, both CAS RNs have been

identified by the Organisation for Economic Co-operation and Development (OECD) as HPV chemicals, with 1000 tonnes or more produced per year (OECD 2004). In 2009, the global production of LPGs was 244 million tonnes, with North America as the major producer (24% of total production) (Thompson et al. 2011). In North America, 60% of LPG production was from natural gas processing, with the remainder from petroleum refineries.

5. Uses

LPGs have widespread uses in industry, transportation, commerce, residences and agriculture. According to information submitted under section 71 of CEPA (Environment Canada 2012) as well as information gathered during an additional public literature search, the LPGs identified under CAS RNs 68476-85-7 and 68476-86-8 are used as a feedstock for chemical plants and petroleum refineries, domestic fuel, as well as a propellant in various types of aerosol products, including industrial blowing agents, lubricants, paints and coating products, household cleaning products, fabric treatments, automotive care products, adhesives and sealants, hair spray products, and pesticides.

One major use identified from the literature and the section 71 submission is as a chemical feedstock. For example, LPGs are used as a raw material for production of ethene, or are used to produce butane that is further blended into gasoline to increase the volatility and octane number of the fuel (CONCAWE 1992; Competition Commission 2006; Wiley 2007; Cheminfo 2009; Thompson et al. 2011). In the United States, about 35% of total LPG consumption is as a feedstock for the petrochemical industry (Wiley 2007). LPGs can also be used directly (without blending) as a high-quality fuel in industry for heating, cutting or soldering (Sullivan 1992; Thompson et al. 2011).

LPGs are used as a fuel for heating or cooking in Canada and other countries. As an end-use, LPGs are often stored in cylinders, as a convenient or mobile source for small domestic appliances, such as portable space heaters, cookers, blow lamps, camping equipment and cigarette lighters (Ames and Crowhurst 1988; Barber 2006; AFROX 2013). In Canada, LPGs are used as a fuel for barbecue tanks or for refrigerators in recreational vehicles where electricity is unavailable (Enviroharvest 2012). LPGs are also used for crop drying and powering farm equipment (Sullivan 1992; Competition Commission 2006).

LPGs are used as an alternative automotive fuel to lower vehicle exhaust emissions in some countries. In 1994, there were approximately 140 000 LPG-driven vehicles in Canada (Liu et al. 1997). More recently, LPGs have become the least competitive transportation fuel as compared to conventional fossil fuels. The number of LPG-driven fleets in Canada declined substantially, and by 2010, there were no LPG-driven passenger vehicles used in Canada (Transport Canada 2010; World LP Gas Association 2012). However, commercial taxi fleets, front-line police vehicle fleets, para-transit service fleets and mail courier company fleets in

Canada still use propane or LPGs as fuels (Propane Facts 2008; Wheels.ca 2013). Some terms, such as “autogas”, “liquefied petroleum gases”, “liquefied propane gases”, “auto propane” and “propane fuel” are sometimes used interchangeably when referring to motor fuels. The ratio of propane to butane in LPG motor fuels can vary from 20/80 up to 100% propane only (Beer et al. 2006). For example, HD5 is one special type of engine fuel, consisting predominantly of propane (> 90% v/v). LPGs are also used as a vehicle fuel by non-road vehicles (e.g., fork lift trucks) (Sullivan 1992; Competition Commission 2006).

LPGs are also found as a propellant in a variety of aerosol products available to consumers, including household cleaners, hair spray products, fabric treatment products, adhesives and paints. In addition, CAS RNs 68476-85-7 and 68476-86-8 are used as a propellant in pesticides, in therapeutic products and in the manufacturing of a coating material for food packaging in Canada. CAS RN 68476-86-8 is present as a formulant at 6 to 10% by weight in three chemical sanitizers and one insecticide in Canada (a propane-butane mix) with a 1,3-butadiene level of less than 0.1% by weight (personal communication with Health Canada’s Pest Management Regulatory Agency Feb. 2011 and Sept. 2013). In Canada, CAS RN 68476-85-7 was listed in the Therapeutic Products Directorate’s internal non-medicinal ingredients database as a non-medicinal ingredient used as a propellant in disinfectant products (for hard surface) (personal communication with Health Canada’s Therapeutic Product Directorate, May 2010). CAS RN 68476-85-7 has also been identified as a processing aid in Canada for manufacturing a coating used in food packaging, and no direct contact of residues of CAS RN 68476-85-7 with food is expected (personal communication with Health Canada’s Food Directorate, June 2013).

The composition of LPGs (even under the same CAS RN) varies depending upon the products they are used for. For example, the product used for domestic heating is primarily composed of propane (U.S. EPA 2008a), whereas high-grade or refined LPGs used for laboratory work and as an aerosol propellant contain predominantly propane and butane (Barber 2006; CONCAWE 1992; Hartop et al. 1991; U.S. EPA 2008a; Thompson et al. 2011). The CAS RNs 68476-85-7 and 68476-86-8 noted in MSDSs for aerosol consumer products often refer to propane, butanes or a combination of the two (Farnam Companies 2007; Magic American Products 2008; LPS Laboratories 2008; GOJO Industries 2010; Petro-Canada Lubricants Inc. 2011).

6. Releases to the Environment

Potential releases of LPGs include releases within facilities from activities associated with their production and processing, releases related to their transportation between industrial facilities, and release during consumer uses.

Following production at natural gas processing facilities or petroleum refineries, LPGs are liquefied under pressurized or refrigerated conditions for storage or

transportation as a final LPG product. Traditionally, large quantities of LPGs are transported under pressurized conditions by pipeline, rail, truck and ship to large-scale LPG users (e.g., industrial facilities, large commercial users) or to distribution terminals of wholesalers. From the large distribution terminals, the LPGs can be transported in pressurized road tankers to other LPG suppliers or to secondary or local distribution depots for retail sale. Small quantities of LPGs can then be delivered in specially-designed pressurized cylinders, such as barbecue tanks, to domestic end-users (Sullivan 1992; Barber 2006; Thompson et al. 2011; Wiley 2007). The potential release of LPGs can occur at any point in the LPG distribution chain, as well as from end-use products. These releases are expected to be directly to air, with any potential spills to water or soil expected to evaporate quickly if they occur. Exposure is therefore considered solely via air.

With such a high volatility, LPGs released into the environment will rapidly disperse in the atmosphere and are unlikely to cause ground or water pollution (CONCAWE 1992). The general physical and chemical properties of LPGs indicate that if released, their vapour can accumulate in low-lying areas as LPGs are heavier than air.

LPGs are not reportable under either the Canadian National Pollutant Release Inventory (NPRI 2013) or the U.S. Toxics Release Inventory (TRI 2013).

6.1. Potential On-site Releases from Production and Storage of LPGs

Petroleum facilities are highly regulated under various jurisdictions, and voluntary non-regulatory measures implemented by the petroleum industry are in place to manage potential releases (SENES 2009). Regulatory and non-regulatory tools are in place to prevent or reduce potential releases (both controlled and unintentional releases) of petroleum substances from petroleum facilities, including the LPGs identified in this screening assessment.

Despite the fact that some measures and practices are in place to reduce releases of petroleum substances within facilities, it has been recognized that fugitive releases of LPGs into the atmosphere can occur from compressor seals, processing valves, flanges etc., due to the much higher volatility (lower boiling point) and higher mobility of gases compared with liquids (U.S. EPA 1995; CAPP 2007; CPPI 2007; CCME 1993). Fugitive releases tend to occur more frequently when processing equipment is not properly maintained or operated and could go undetected or unfixed for periods ranging from days to months (CCME 1993; CAPP 2007). Once released, LPGs disperse quickly into the air.

Therefore, there is a potential for exposure of the general population and the environment in the vicinity of petroleum sector facility sites to LPGs. Detailed analysis of human exposure was conducted using a gas dispersion model (see the Potential to Cause Harm to Human Health section).

Due to their flammability and volatility, special requirements are needed for storing and handling LPGs. LPGs are usually stored under pressurized conditions (Purchon 1980; Thompson et al. 2011; Wiley 2007). The equipment for storing LPGs is fabricated according to appropriate codes with additional requirements for inspection, safety considerations and emergency guidelines. The *Liquefied Petroleum Gases Bulk Storage Regulations* made under the *Canada Transportation Act* set out standards for the placement of storage tanks and additional requirements for storage equipment, inspection, safety considerations and emergency guidelines (Canada 2013). Individual provinces can also have legislative requirements for the transport and storage of LPGs. As a result of stringent requirements for the design and operation of such pressurized storage systems, the potential for evaporative emissions of gaseous substances has been reduced (OECD 2009). The potential exposure of the general population to any release from the pressurized storage of LPGs, under normal operating conditions, is therefore considered to be minimal and is not assessed further in this report.

6.2. Potential Releases from Transportation of LPGs

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

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

No equations or data are available with respect to evaporative emissions from loading LPGs into pressurized vessels. The U.S. EPA's AP 42 (U.S. EPA 2008a) states that "High-pressure storage tanks can be operated so that virtually no evaporative or working losses occur. No appropriate correlations are available to estimate vapour losses from pressure tanks." Due to the high safety and

inspection standards generally applied to pressurized pipeline and container systems, regular releases from these types of pressurized systems are unlikely under normal operating conditions (European Commission 2006; U.S. EPA 2008a; OECD 2009). Therefore, only releases from pipelines are considered in this screening assessment. The potential sources of release to the environment are from unintentional leaks that occur during processing, handling and transport. These substances are gaseous at environmentally relevant temperatures, so ambient air is considered to be the primary receiving medium for all releases of LPGs.

Further details on potential releases of LPGs from pipelines have been addressed in a previous assessment on industry-restricted petroleum and refinery gases (Environment Canada, Health Canada 2011). Pipeline releases of industry-restricted petroleum and refinery gases were found not to be a concern for environmental exposure in that assessment. LPGs belong to the petroleum group “petroleum and refinery gases” and have similar composition and properties as those previously assessed. Due to the nature of the available information used in the assessment of industry-restricted petroleum and refinery gases (Environment Canada, Health Canada 2014a), the estimate of releases from pipelines was not restricted to the CAS RNs covered by the assessment, but instead covered all petroleum and refinery gases, including the LPGs being assessed herein. Thus, releases of LPGs from pipelines are not considered further in this assessment.

6.3. Potential Releases from Transferring of LPGs

For fuel uses, such as refuelling LPG-powered vehicles or filling a LPG barbecue tank, transferring of LPGs into a pressurized container is commonly required. Due to the high mobility and volatility of gaseous substances, there is a potential for releases of LPGs during the filling/handling process from nozzle disconnection or outage/bleeder vapour valves (to indicate whether the 80% capacity limit is reached) (Sullivan 1992; Purchon 1980).

Sullivan (1992) estimated the emissions of LPGs associated with LPG transfer operations (e.g., filling LPGs into cylinders or small storage tanks or vehicles) in several different use categories, including agricultural, commercial, engine fuel, industrial and residential, as well as from LPG distribution systems in California. The LPGs were mainly composed of propane with a small amount of butane. In this study, an average of 0.064% v/v of total LPG used was emitted into the atmosphere from transfer processes. Based on the quantity used in each use category, the emissions from engine fuel use were approximately 0.101% v/v, with emissions ranging from 0.044 to 0.057% v/v for the remaining five categories.

Similarly, Sosa et al. (2009) reported that fugitive releases of LPGs due to handling and transfer processes contributed to ambient air levels of propane and butanes. Gasca et al. (2004) examined the contribution of LPG emissions to

ambient air due to domestic combustion, fugitive emissions from cylinder distribution, and leaks from domestic appliances.

For LPG-driven vehicles, Gasca et al. (2004) and Schifter et al. (2000) examined evaporative emissions that originate from LPG fuel trapped between the vapourizer and the mixing system once the engine is stopped. The vapour consists of 43% w/w propane, 49% w/w butanes (*n*-butane and isobutane), 1% w/w pentane, and 1.5% w/w alkenes with no 1,3-butadiene identified at the detection level.

Potential long-term exposure to LPG releases from the fuel transfer process (e.g., refuelling LPG-powered vehicles or refilling LPG barbecue tanks) is considered in the Potential to Cause Harm to Human Health section.

6.4. Potential Releases from End-uses of LPGs

The widespread use of LPGs as a propellant in household products and other products available to consumers can also be a significant source of release in domestic dwellings, even though the average quantity of LPG used as a propellant is generally much smaller than that of other uses, such as heating, cooking and automotive fuels (Ames and Crowhurst 1988). Hartop et al. (1991) examined the release of LPGs (propane/butane mixture) from hair spray products containing 26% LPGs. The authors measured the peak concentration of LPGs and the 10-minute time weighted average concentration in the breathing zone of the users as well as in a bystander zone following a 10-second spray. This study is discussed further in the subsequent human exposure section, as a basis for analysis of consumer exposure to LPGs used as propellants.

7. Environmental Fate

The bulk of the substances identified as components of LPGs are gaseous at environmentally relevant temperatures and, if released to the environment, they will volatilize and escape into ambient air.

C₁–C₆ alkanes have boiling points from –162 to 69°C. The individual components of LPGs are characterized by moderate water solubilities (9.5 to 735 mg/L), very high vapour pressures (2.0×10^4 to 6×10^7 Pa), very high Henry's Law constants (7.5×10^3 to 1.8×10^5 Pa·m³/mol), low log K_{ow} values (1.1 to 3.9) and low to moderate log K_{oc} values (1.6 to 3.4) (Table B-2 in Appendix B). If released to air, all components of LPGs are expected to remain in air, as they are highly volatile.

Based on the water solubility of these components (9.5 to 735 mg/L), if a release occurs to water, these components would dissolve in water. However, volatilization from water is expected to occur quickly given their high vapour pressures and high Henry's Law constants. The majority of LPGs are composed of propane, butane and isobutane, and each of these components are highly

volatile and will volatilize quickly from water. LPGs are not expected to sorb significantly to suspended solids and sediments given their low to moderate estimated log K_{oc} values (Table B-2 in Appendix B).

If released to soil, the alkanes and alkenes are expected to volatilize. Most components of LPGs are expected to have low to negligible sorption to soil (i.e., expected to be highly mobile) given their low to moderate estimated log K_{oc} values and high vapour pressures. If released to moist soil surfaces, these components are expected to volatilize given their high to very high Henry's Law constants and vapour pressures.

8. Persistence and Bioaccumulation

8.1. Environmental Persistence

No empirical data on the persistence of LPGs were found. Because LPGs have similar components as the industry-restricted petroleum and refinery gases, assessed previously, data on the environmental persistence of industry-restricted petroleum and refinery gases were used in the determination of persistence for LPG components (Environment Canada, Health Canada 2011).

Based on Environment Canada, Health Canada (2011), the atmospheric half-lives of most components, including propane, butane and isobutane, of these LPGs are ≥ 2 days via reactions with hydroxyl. In contrast, they have relatively short half-lives in water, soil and sediments and therefore are not expected to persist in these media for long durations.

8.2. Potential for Bioaccumulation

No experimental bioaccumulation factor (BAF) or bioconcentration factor (BCF) for consumer-related LPGs or their components were found. Therefore, as LPGs consist of similar components as petroleum and refinery gases, data on the bioaccumulation potential of industry-restricted petroleum and refinery gases were used in the determination of bioaccumulation of LPG components (Environment Canada, Health Canada 2011). A predictive approach was applied using available BAF and BCF models.

Based on the available kinetic-based modelled values (Environment Canada, Health Canada 2011), the components of LPGs have very low bioaccumulation potential (BAF/BCF < 200 L/kg).

9. Potential to Cause Ecological Harm

9.1. Ecological Effects Assessment

9.1.1. Aquatic Compartment

As the components of LPGs are expected to have high to very high volatilization from water, no aquatic toxicity data have been included in this assessment.

9.1.2. Terrestrial Compartment

Terrestrial organisms may be exposed to LPGs through air. Toxicity data for rodents were available for LPGs and components of LPGs (Appendix E), and toxicity data for terrestrial organisms to 1,3-butadiene, a component of LPGs, were also available in Canada (2000).

Experimental data available on effects via inhalation in laboratory animals indicate that LPGs have very low acute, subchronic, reproductive, developmental and neurological toxicity to rodents (lowest observed adverse effect concentration (LOAEC) greater than 500 000 mg/m³; Table E-1, Appendix E). The major components of LPGs also have very low acute toxicities to rodents (LC50s greater than 100 000 mg/m³), as summarized in Appendix E. Small mammals are also not especially sensitive to these major components over longer periods of time, with reproductive and developmental LOAECs in rodents above 7000 mg/m³.

1,3-Butadiene, a minor component of LPGs, was identified as the component of LPGs having the highest toxicity. Exposure to 1,3-butadiene for 7 h caused a depletion of cellular non-protein sulfhydryl content of liver, lung or heart in mice, with a lowest-observed-effect level (LOEL) of 100 ppm (221 mg/m³) (Deutschmann and Laib 1989). In a 2-year study conducted by the U.S. National Toxicology Program (NTP1993), there was a significant increase in the incidence of ovarian atrophy in female mice exposed for up to 2 years to all concentrations tested (i.e., ≥ 6.25 ppm [≥ 13.8 mg/m³]).

1-3-Butadiene has low toxicity to plants, with low to no adverse effects reported when plants were exposed to 1,3-butadiene at 2210 mg/m³ for 7 days (Heck and Pires 1962). When exposed for 21 days, no adverse effects were observed at 22.1 mg/m³ (Heck and Pires 1962).

Due to the much greater toxicity of 1,3-butadiene to mammals compared to other components of LPGs, 1,3-butadiene is used to estimate the risk of LPGs to the environment from atmospheric exposure to LPGs. The chronic lowest observed adverse effect level (LOAEL) for rodents of 13.8 mg/m³ (13 800 μ g/m³) (NTP 1993) will be used as the chronic critical toxicity value (CTV) for the terrestrial toxicity of LPGs.

9.2. Ecological Exposure Assessment

Based on the high volatilization from aquatic environments, an aquatic exposure scenario was not developed. Two exposure scenarios for terrestrial mammals via chronic inhalation were developed: exposure due to unintentional releases from petroleum facilities and exposure near filling stations. Due to the significantly higher toxicity of 1,3-butadiene to mammals compared to other LPG components, 1,3-butadiene concentrations in the environment were estimated for exposure.

Estimated concentrations of 1,3-butadiene in air as determined in the human health section (section 10.1.1 for releases from petroleum facilities and section 10.1.3 for releases from filling stations) were used. Annual concentrations were estimated at various distances from these facilities. The highest annual concentrations estimated for any distance from the petroleum facilities and from filling stations are used here as worst-case scenarios for chronic exposure from these facilities. For releases from petroleum refining facilities, the highest annual concentration of 1,3-butadiene was $0.44 \mu\text{g}/\text{m}^3$ at 200 m (Table C-2, Appendix C). For releases from filling stations, the highest annual concentration of 1,3-butadiene was $0.86 \mu\text{g}/\text{m}^3$ at a distance of 10 m from the filling station (Table C-4, Appendix C).

9.3. Characterization of Ecological Risk

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

As these substances are composed of gases, exposure of aquatic organisms to these substances in the event that they are released to the aquatic environment is extremely unlikely due to their rapid volatilization from water.

In a scenario in which LPGs are released to soil via pipeline transport, these substances are not expected to remain in soil, but rather will partition readily to air. Therefore, an exposure scenario involving the release of LPGs to soil was not developed. Exposure to LPGs is most likely via inhalation. LPGs themselves, along with their major components, have very low acute (greater than $100\,000 \text{ mg}/\text{m}^3$) and chronic (greater than $7000 \text{ mg}/\text{m}^3$) toxicities via inhalation, such that it is highly unlikely that animals would be exposed to toxic concentrations. A minor component of LPGs, 1,3-butadiene, was identified as having much greater toxicity to organisms. However, estimated concentrations of 1,3-butadiene near petroleum facilities and filling stations are orders of magnitude below those that cause toxicity.

Therefore, based on the information presented in this screening assessment, the LPGs included in this screening assessment are unlikely to be causing ecological harm to organisms or the broader integrity of the environment. It is concluded that

these LPGs (CAS RNs 68476-85-7 and 68476-86-8) do not meet the criteria under paragraphs 64(a) or 64(b) of the *Canadian Environmental Protection Act, 1999* (CEPA) 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.

9.4. Uncertainties in Evaluation of Ecological Risk

The proportions of each component in each LPG assigned a specific CAS RN are generally not known. LPG components fall within the C₁ to C₈ range, though the majority of components are in the C₃ to C₇ range. However, the low ecological toxicity of most of these components makes this information gap relatively unimportant for the assessment of ecological risk.

There is uncertainty concerning the exposure of terrestrial organisms to LPGs. As exposure information for LPGs from petroleum facilities and filling stations was not available, effect, exposure and risk for a high-hazard component of LPGs were characterized.

10. Potential to Cause Harm to Human Health

10.1. Exposure Assessment

The general physical–chemical properties of LPGs indicate that when these substances are released, they rapidly disperse into ambient air, and the individual components of LPGs will separate and partition in accordance with their own physical–chemical properties. As such, inhalation would be the primary potential route of exposure and is therefore the focus of the exposure assessment. Dermal and oral exposures are not expected to be significant routes of exposure.

1,3-Butadiene is a high-hazard component that is found in some LPG streams. An analysis of limited samples collected from U.S. refineries from 1992 to 2002 indicated the potential presence of 1,3-butadiene at up to 0.1% by weight (w/w) for the LPGs identified under CAS RNs 68476-85-7 and 68476-86-8 (U.S. EPA 2010). Information submitted under section 71 of CEPA indicates that for the individual substances butane and isobutane, the residual level of 1,3-butadiene ranged from non-detectable to less than 1% by weight, but was typically below 0.1% by weight (Environment Canada 2007). 1,3-Butadiene is the basis for the classification of CAS RNs 68476-85-7 and 68476-86-8 as carcinogens by the European Union if the level of 1,3-butadiene is equal to or greater than 0.1% by weight (European Commission 2008a, 2009; European Union 2008).

Available information indicates that compared to LPGs consumed in industrial settings as feedstocks or industrial fuels, there is a narrower range of hydrocarbons in the LPGs used in marketplace products, especially when they

are used as aerosol propellants. (Barber 2006; CONCAWE 1992; Hartop et al. 1991; U.S. EPA 2008a; Thompson et al. 2011). As a propellant or domestic fuel (that is, for use in cooking, heating or transportation), LPGs identified under CAS RNs 68476-85-7 and 68476-86-8 are often referred to as isobutane or a combination of propane, *n*-butane and isobutane (Magic American Products 2008; LPS Laboratories 2008; GOJO Industries 2010; Farnam Companies 2007). MSDSs searches for consumer aerosol products containing LPGs gave no indication of 1,3-butadiene above 0.1%. Furthermore, according to the information submitted under section 71 of CEPA (Environment Canada 2007), 1,3-butadiene has been reported to be present in butane and isobutane as a residual at a level of non-detectable to less than 1% w/w, with a typical level below 0.1% by weight. Therefore, one approach taken in this screening assessment considered that 1,3-butadiene may be present in LPGs as a residual of up to 0.1% w/w.

The annual average concentrations of 1,3-butadiene in ambient air have been reported by various sources as less than 0.05 $\mu\text{g}/\text{m}^3$ and up 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 2000). Curren et al. (2006) reported that the average annual 1,3-butadiene concentration at urban sites in Canada between 1995 and 2003 was 0.22 $\mu\text{g}/\text{m}^3$. Additional monitoring data for 1990–2008 collected from the Clean Air Strategic Alliance data warehouse in Alberta (CASA 2008) indicate that the average annual concentrations in central Edmonton, east Edmonton and central Calgary were 0.33 $\mu\text{g}/\text{m}^3$, 0.17 $\mu\text{g}/\text{m}^3$ and 0.31 $\mu\text{g}/\text{m}^3$, respectively. As reported by the National Air Pollution Surveillance Network (NAPS 2012), the annual concentration of 1,3-butadiene in ambient air in 2009 ranged from 0.028–0.293 $\mu\text{g}/\text{m}^3$ for rural and urban areas across Canada.

Additional Canadian studies were available that measured the levels of 1,3-butadiene in both outdoor air and indoor air in Windsor, Regina, Halifax and Edmonton during the summer and winter seasons (Health Canada 2010a, 2010b, 2012 and 2013). Indoor measurements were taken in the family or living rooms of selected residential homes, and the concurrent outdoor measurements were taken in the backyards. The 45–48 non-smoking participant homes in Windsor were monitored between January 2005 and August 2006 with samples collected every 24 h for five consecutive days. Personal air samples were also taken every 24 h for five consecutive days in the 2005 study. Method detection limits (MDL) were 0.055 $\mu\text{g}/\text{m}^3$ (2005) and 0.043 $\mu\text{g}/\text{m}^3$ (2006), and 1,3-butadiene was detected in over 90% of the samples. In the Regina study, a total of 146 homes, of which 34 homes had at least one smoking participant, were monitored in both the winter and summer of 2007 with one 24-h sample and one 5-day sample collected from each household. The MDL was 0.05 $\mu\text{g}/\text{m}^3$ and the detection frequency of 1,3-butadiene was 65% and 100%, based on the season that the air samples were taken. In the Halifax study, 50 non-smoking homes were monitored in both the winter and summer of 2009 with samples collected every 24 h for seven consecutive days. The MDL was 0.022 $\mu\text{g}/\text{m}^3$ and the detection frequency was 83% and 98%, based on the season of sampling. In the Edmonton study, 50

non-smoking homes were monitored in both the winter and summer of 2010 with samples collected every 24 h for seven consecutive days. The MDL values were $0.018 \mu\text{g}/\text{m}^3$ (summer) and $0.017 \mu\text{g}/\text{m}^3$ (winter) and the sample detection frequency was above 95%.

The outdoor air measurements from the four Canadian studies showed that the levels of 1,3-butadiene for the winter monitoring periods could be up to twice as high as the summer measurements (Health Canada 2010a, 2010b, 2012, 2013). The 50th percentile concentrations of 1,3-butadiene from these studies ranged from 0.024 to $0.07 \mu\text{g}/\text{m}^3$, with 95th percentile values ranging from 0.025 to $0.385 \mu\text{g}/\text{m}^3$ (Health Canada 2010b). Such outdoor measurement values are in line with the other monitoring data across Canada (Curren et al. 2006; CASA 2007; NAPS 2012). For the assessment of risk of exposure to modelled emissions from a petroleum facility herein, an ambient background level of $0.22 \mu\text{g}/\text{m}^3$ 1,3-butadiene from Curren et al. (2006) was used as a benchmark and is consistent with the background value selected in the Stream 1 petroleum and refinery gases assessment (Environment Canada, Health Canada 2013).

The indoor air measurements from the four Canadian studies showed the 50th percentile values of 1,3-butadiene from non-smoking homes to range from 0.04 to $0.134 \mu\text{g}/\text{m}^3$ and the 95th percentile values to range from 0.16 to $0.59 \mu\text{g}/\text{m}^3$ (Health Canada 2010a, 2010b, 2012, 2013). In comparison, a much higher level of 1,3-butadiene was observed from 34 homes with at least one smoker in the Regina study, as shown by the 50th percentile values of $0.947 \mu\text{g}/\text{m}^3$ (winter) and $0.657 \mu\text{g}/\text{m}^3$ (summer), with 95th percentile values of $4.577 \mu\text{g}/\text{m}^3$ (winter) and $9.177 \mu\text{g}/\text{m}^3$ (summer) (Health Canada 2010b).

Compared to the recent studies on selected homes in Windsor, Regina, Halifax and Edmonton, other older studies that measured the indoor air level of 1,3-butadiene have shown higher MDLs and lower detection frequencies. Zhu et al. (2005) measured the 24-h indoor 1,3-butadiene levels from 75 residential houses in Ottawa, Canada, from November 2002 to March 2003. The MDL was $0.32 \mu\text{g}/\text{m}^3$ and detection frequency was 32%. The authors reported a concentration range from below the MDL up to $3.65 \mu\text{g}/\text{m}^3$, with $1.64 \mu\text{g}/\text{m}^3$ as the 90th percentile. Weisel et al. (2008) also examined the 24-h indoor air concentrations of 1,3-butadiene in 100 homes of suburban and rural areas of New Jersey, U.S., between December 2003 and April 2006, with MDLs of 0.44 to $1.1 \mu\text{g}/\text{m}^3$. Only 7 of 100 samples were tested above the MDL, with a 95th percentile of $1.3 \mu\text{g}/\text{m}^3$. The highest value was $4.4 \mu\text{g}/\text{m}^3$.

The indoor level of 1,3-butadiene in Canadian homes can be attributed to various sources, including the use of aerosol products, possible vehicle exhaust from attached garages, and cooking activities (combustion by-products) (Canada 2000). For the purpose of assessing risk from potential long-term exposure to LPGs from the use of aerosol products inside the home, the highest 50th percentile value of 1,3-butadiene for Canadian non-smoking homes was selected

from air sampling studies conducted inside homes located in four Canadian cities. This level, $0.134 \mu\text{g}/\text{m}^3$, is derived from the Regina study (Health Canada 2010b) and is considered to represent a conservative indoor air level of 1,3-butadiene to which multiple sources contribute inside the home.

As discussed in the “Releases to the Environment” section, potential sources of releases of LPGs include unintentional fugitive releases from petroleum facilities, releases during transportation of the substances, releases from transfer of LPGs into pressurized containers (e.g., refuelling LPG vehicle fuel tanks or refilling barbecue tanks), as well as releases from products containing LPGs as aerosol propellants.

10.1.1. Potential Exposure to Unintentional Releases from Petroleum Facilities

LPGs originate from petroleum refineries and natural gas processing facilities and thus upgraders are not included in this assessment. Like previously assessed Stream 1 and Stream 2 petroleum and refinery gases (Environment Canada, Health Canada 2013, 2014a), LPGs are a portion of total petroleum and refinery gases generated from petroleum facilities. LPGs may disperse into the air in the vicinity of a facility via fugitive emissions from, for example, process equipment, valves and flanges. It is recognized that releases of LPGs represent a fraction of the total fugitive releases of petroleum and refinery gases from a petroleum facility, and it is not possible to determine the proportion of total releases that are LPGs. As such, total releases of all petroleum and refinery gases containing 1,3-butadiene were characterized in the Stream 1 petroleum and refinery gases screening assessment report (Environment Canada, Health Canada 2013) and, therefore, potential exposure of the general population living in the vicinity of a petroleum refinery or natural gas processing plant to unintentional releases of LPGs (identified under the CAS RNs 68476-85-7 and 68476-86-8) has already been considered. Given the potential presence of 1,3-butadiene in these two LPGs, fugitive releases of LPGs may contribute to 1,3-butadiene concentrations in ambient air in the vicinity of petroleum facilities.

A recent report describes a mobile method (the “Aerodyne Mobile Laboratory”) that was used to detect and quantify industrial emissions, including 1,3-butadiene, from point sources (Knighton et al. 2012). However, detailed information on the estimation of total fugitive releases of 1,3-butadiene from petroleum and refinery gases at a facility in Canada was provided in the Stream 1 petroleum and refinery gases screening assessment report (Environment Canada, Health Canada 2013). SCREEN3, a tier-one air dispersion model developed by the U.S. EPA (SCREEN3 1996), was used to model the contribution of 1,3-butadiene to ambient air associated with petroleum facility fugitive releases. The results are adopted herein and are provided in Appendix C (Tables C-1 and C-2). A summary of the estimated total releases of 1,3-butadiene on which the conclusion is based is presented below.

The results of the modelled dispersion profile of 1,3-butadiene, based on distance from the release source, demonstrate that at 200 m, annual concentrations from all petroleum and refinery gases (including Stream 1 and Stream 2 petroleum and refinery gases and the LPGs in this report) contributed to ambient air by these facilities are approximately $0.44 \mu\text{g}/\text{m}^3$ on the high end (based on a ratio of 1,3-butadiene to benzene of 1:85) and approximately $0.17 \mu\text{g}/\text{m}^3$ on the low end (based on a ratio of 1,3-butadiene to benzene of 1:216). The modelled concentration decreases as the distance from the release source increases. It is estimated that for the high end ratio, the contribution of 1,3-butadiene to air associated with unintentional releases of the total petroleum and refinery gases will be equivalent to the average annual Canadian ambient urban 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 ratio, the estimated contribution of 1,3-butadiene to air from unintentional releases of petroleum and refinery gases is $0.088 \mu\text{g}/\text{m}^3$ at 500 m from the release source. Map analysis has determined that the general population may reside approximately 200 m from a potential source of release. Accordingly, releases of petroleum and refinery gases from petroleum facilities may result in long-term exposure of a limited proportion of the general population to above-background levels of 1,3-butadiene. Recent air monitoring results of sites near Canadian petroleum facilities (Simpson et al. 2013) corroborated and validated the estimated 1,3-butadiene levels obtained using SCREEN3 modelling for locations in the vicinity of a petroleum facility.

SCREEN3 is recognized as being a conservative dispersion model compared to more advanced models that require highly detailed inputs. Thus, AERSCREEN (U.S. EPA 2011a) was also used in order to conduct a sensitivity analysis. AERSCREEN is the screening model based on AERMOD (U.S. EPA 2011a). The model produces estimates of "worst-case" 1-h concentrations for a single source, without the need for hourly meteorological data, and also includes conversion factors to estimate "worst-case" 3-h, 8-h, 24-h and annual concentrations. AERSCREEN is intended to produce concentration estimates that are equal to or greater than the estimates produced by AERMOD, without a fully developed set of meteorological and terrain data (U.S. EPA 2011a). The modelling results are provided in Appendix C (Tables C-5 and C-6). 1,3-Butadiene emissions modelled with AERSCREEN at a distance of 200 m from a refinery produced estimates of $0.55 \mu\text{g}/\text{m}^3$ on the high end (based on a ratio of 1,3-butadiene to benzene of 1:85), and approximately $0.21 \mu\text{g}/\text{m}^3$ on the low end (based on a ratio of 1,3-butadiene to benzene of 1:216). AERSCREEN results suggest that the values generated by SCREEN3 are valid.

Natural gas processing facilities have different feedstocks, processing units, and operating conditions compared to petroleum refineries. A recent industry submission on testing the level of 1,3-butadiene in selected gas streams from natural gas processing facilities indicates that the concentration of 1,3-butadiene in most gas samples was below the detection limit of 1 ppm, with a single sample determined to be above the detection limit (CAPP 2014). Based on these

analytical data, in combination with the lines of evidence previously submitted by industry on the absence of 1,3-butadiene in natural gas streams, and on the removal of 1,3-butadiene from the U.S. EPA list of pollutants of concern from oil and natural gas production facilities and natural gas transmission and storage facilities, the level of 1,3-butadiene in LPGs produced by natural gas processing facilities is expected to be low. Therefore, human exposure to 1,3-butadiene due to fugitive emissions of petroleum and refinery gases, including LPGs from natural gas processing facilities, is not expected.

10.1.2. Potential Exposure to LPGs During Transportation

According to information received under section 71 of CEPA and literature review, LPGs can be transported by truck, rail, ship and pipeline (Environment Canada 2012; Thompson et al. 2011).

Pressurized or refrigerated containers are used for delivering LPGs to various users (Thompson et al. 2011; Wiley 2007). The U.S. EPA's AP 42 (U.S. EPA 2008b) states that "High-pressure storage tanks can be operated so that virtually no evaporative or working losses occur. No appropriate correlations are available to estimate vapour losses from pressure tanks." The shipment of pressurized gaseous substances generally requires stringent safety measures due to their physical-chemical properties. For example, under the *Transportation of Dangerous Goods Regulations of the Transportation of Dangerous Goods Act, 1992*, Transport Canada requires a series of standards, developed by Transport Canada, the Canadian Standards Association or the Canadian General Standards Board, for safety devices and for the design, manufacture, inspection and operation of authorized means of containment involved in the transportation of gases by rail, road and water. As well, equipment used for loading or unloading the means of containment, such as transfer hoses or loading arms, must meet design standards for appropriate pressures and temperatures (Canada 2001a). Due to the high safety and inspection standards generally applied to pressurized pipeline and container systems, regular releases from these types of pressurized systems are unlikely under normal operating conditions (European Commission 2006; U.S. EPA 2008b; OECD 2009).

There is relevant legislation in place at the federal and provincial levels for handling gaseous hydrocarbons, which is intended to reduce or prevent releases from these operations. Some of the measures outlined in these provisions apply to means of containment (i.e., transportation vessel), means of transportation (i.e., transportation vehicle) and handling equipment for transporting pressurized gases, and they indicate that each means of containment and transportation must meet specified design and safety standards. It is recognized, however, that fugitive releases of gaseous substances can occur due to their high volatility and high mobility. For example, poor maintenance of a threaded connection that may be used between a loading arm and a pressurized tank could result in fugitive

leaks. Replacing threaded connections with flange connections can help reduce such releases (Hendler et al. 2006).

Potential exposure of the general population to fugitive releases during the transportation process is considered limited and accounted for by the exposures to LPGs as detailed and assessed below.

10.1.3. Potential Exposure to LPGs from Filling Stations

As LPGs are normally stored in pressurized containers with stringent requirements for design and operation (there exist various provincial regulations), potential exposure of the general population to any fugitive emissions from such pressurized containers is not expected. However, it is recognized that a release can occur during the transfer of LPGs between containers or during a filling process, such as filling barbecue gas tank cylinders (Sullivan 1992; CONCAWE 2012). Transfer operations are typically conducted by professionals with training in the safe handling of LPGs. In addition, LPG cylinder filling stations have declined in number, generating a growing popularity of cylinder exchange services provided to customers as a convenient way to exchange an empty tank for one that was previously filled by a professional. These factors have reduced the potential for exposure of the general population to LPGs from the transfer process.

Exposure to LPGs may occur in the general population living in the vicinity of LPG cylinder tank filling stations. The filling stations can be for vehicle refuelling or for filling non-vehicle tanks, such as barbecue tanks, and are located at commercial outlets and some hardware stores. Additionally, LPG transfer may occur at centralized depots prior to delivery to the consumer market. A conservative exposure analysis was developed for considering these types of filling scenarios.

The number of LPG-powered vehicles used by the general public in Canada is unclear. Transport Canada (2010) states that as of 2010, there are no passenger vehicles running on LPG. However, commercial taxi fleets, front-line police vehicle fleets, para-transit service fleets, and a fraction of mail courier company fleets in Canada are reported to use propane or LPGs as fuel (Propane Facts 2008; Wheels.ca 2013). The terms LPG and “automotive propane” are sometimes used interchangeably in referring to alternative vehicle fuels. Other off-road vehicles, such as industrial fork-lifts and some agricultural vehicles, are also known to use LPGs (Sullivan 1992; Competition Commission 2006).

Some larger home and hardware stores provide LPG filling services. Particularly in high-demand months such as during the summer, large numbers of customers bring in empty barbecue tanks either for refilling or for direct exchange with a previously filled tank. LPG released during each cylinder tank filling process and the subsequent dispersion of this released gas in the vicinity of homes near the stores can be a potential source of long-term exposure for nearby residents.

Sullivan (1992) estimated LPG emission rates for filling of different-size stand-alone LPG storage tanks and for vehicle fuel tanks. These emissions occur at the time of nozzle disconnection and are also due to the presence of outage valves. Using factors provided by Sullivan and additional conservative assumptions regarding the number of filling events occurring at a high-throughput site, a value of 27 g per event was estimated to be a typical loss of LPGs to the atmosphere for either a single filling of a barbecue tank or a vehicle fuel tank (losses are independent of the size and purpose of the fuel tank, but dependent on the nature of the connections involved in the transfer process). Similarly, CONCAWE (2012) suggested an “inhalation transfer factor” of 0.0005 for filling a vehicle tank with 45 kg of LPGs. The emission estimate based on CONCAWE (2012) (i.e., 22.5 g/transfer) is similar to the value of 27 g/transfer calculated using parameters given by Sullivan (1992). Therefore, a total emission of 27 g of LPG per transfer event is used to characterize the risk of potential exposure in the vicinity of LPG filling stations.

The dispersion of LPGs in ambient air in the vicinity of filling stations was modelled using SCREEN3 (1996), which was developed by the U.S. EPA and which has been used in previous screening assessments (e.g., Environment Canada, Health Canada 2013). Detailed input parameters used for modelling the dispersion of LPGs for a filling scenario are listed in Table C-3. The estimated concentrations of LPGs, as well as 1,3-butadiene, contributed to ambient air are presented in Table C-4. Estimates include the maximum concentrations within 1 h and 24 h, and they account for both changing wind directions and the intermittent nature of the events. Annual estimates of 1,3-butadiene in ambient air are also determined by assuming 0.1%(w/w) of 1,3-butadiene in LPG fuels. The *Liquefied Petroleum Bulk Storage Regulations* under the *Canada Transportation Act* stipulate that the distance of LPG loading and unloading racks be not less than 200 ft (61 m) from a residence (Canada 2013). As presented in Table C-4, the annual upper-bounding estimates of 1,3-butadiene at 60 m from the LPG filling station is $0.12 \mu\text{g}/\text{m}^3$, which is below the ambient air background of $0.22 \mu\text{g}/\text{m}^3$ reported by Curren et al. (2006).

10.1.4. Potential Exposure to LPGs Used as Propellants in Aerosol Products Available to Consumers

LPGs are one of the most common aerosol propellants used in products available to consumers (Diversified CPC International 2012). In an aerosol can, LPGs are pressurized into liquid form and mixed with a liquid product. Once the pressure in the can is reduced (e.g., the nozzle is depressed and the valve opens), LPGs vapourize, forming a gas phase in the headspace of the can that exerts pressure on the liquid, effectively pushing the liquid product out of the can. As the liquid (a mixture of product and LPGs) leaves the can, the propellant rapidly expands into gas, which can further atomize the product to form a fine spray (CAPCO 2011). Accordingly, inhalation is the primary route of exposure to LPGs used as propellants.

LPGs identified under CAS RNs 68476-85-7 and 68476-86-8 are used as aerosol propellants in a variety of products across multiple brands. Based on a literature search, a summary of aerosol products containing LPGs (CAS RNs 68476-85-7 or 68476-86-8) as propellants is provided in Table 10-1, including the LPG concentration range by weight, upon which the short-term exposure analysis is based.

Table 10-1. Summary of aerosol products that use CAS RNs 68476-85-7 or 68476-86-8 as propellants^a

Type of products	Concentration of LPGs (% w/w)
Adhesive and sealants	10 – 60
Automotive care and maintenance	7 – 70
Fabric treatments	5 – 10
Fuels	40 – 55
Household cleaners (e.g., stainless steel, glass, furniture, electromechanical components)	1 – 60
Air fresheners	15 – 60
Household spot removers	5 – <100
Disinfectants (e.g., hand sanitizer, air sanitizing spray)	5 – 30
Hobbyist/art material	20 – 30
Lubricants and corrosion prevention (indoor or outdoor)	5 – 60
Paints and coatings (spray paints)	1 – 60
Hair spray	0.1 – 20
Roof coatings	10 – 30
Pesticides ^b	6 – 10

^a The information in the table is based on an MSDS search, unless specified otherwise.

^b Personal communication with Health Canada Pest Management Regulatory Agency, September 2013.

One monitoring study is available that measured indoor air levels of LPGs resulting from use of a spray product. Hartop et al. (1991) measured the concentration of LPGs in the breathing zone of an adult user and of an accompanying child (bystander) after 10 seconds of spraying with a hair spray product that contained 26% LPGs (a mixture of propane, *n*-butane and isobutane) as the propellant. The spray was conducted in a room (21 m³) without ventilation and with the door open as well as closed. The air samples were collected at heights of 1.5 m and 0.8 m from the floor and were measured by infra-red spectroscopy. The authors reported that the time-weighted average concentrations of LPGs over 10 minutes from the beginning of the spray (TWA10) were 73 ppm (~130 mg/m³ at 1.5 m from the floor) for the adult user and 80 ppm

(144 mg/m³ at 0.8 m from the floor) for the bystander. The status of the room door (open/closed) had no significant impact on the TWA10 values. As the hair spray product used in this study contained a similar level of LPGs as the products listed in Table 10-1, the measured TWA10 of 144 mg/m³ is adopted to represent an exposure that might occur for short-term use of similar products.

LPG exposures from other aerosol products were modelled with ConsExpo, version 4.1 (ConsExpo 2006). ConsExpo is a multi-tiered predictive model used to derive estimates of exposure to substances in products available to consumers via inhalation, dermal contact and oral ingestion. The IHMod version 0.198 model created by the American Industrial Hygiene Association (AIHA 2009) was also considered. Since the predictions of the LPG concentration from IHMod were similar to those from ConsExpo, only the estimates from the ConsExpo model are presented here.

As a conservative approach, a representative upper-bounding exposure scenario was selected from each use category, based on concentration, use amount or frequency. Short-term inhalation upper-bounding exposure estimates for each representative use pattern is presented in Appendix D (includes default input parameters). A summary of upper-bounding estimates for short-term inhalation exposure (i.e., amortized over 24 h) to representative aerosol products that are commonly used is presented in Table 10-2 below.

Table 10-2. Short-term inhalation exposure estimates of LPGs from the use of representative aerosol products

Products available to consumers	Max. mean concentration on day of event (mg/m ³)
Adhesive (spray)	8.46
Fabric protectors (e.g., bathroom rugs)	39.3
Household glass/stainless steel cleaners	15.5
Furniture polish and cleaners	71.6
Air fresheners	11.6
Carpet stain removers	1.64
Household specific spot removers	11
Hand sanitizers	0.034
All-purpose lubricants	19.1
Spray paints (e.g., for furniture, metal, wood, crafts and plastic items)	90.3

As shown in Table 10-2, exposure estimates vary for different products. The mean air concentrations of LPGs amortized over 24 h on the day of the event range from 0.034 mg/m³ based on an adult using a foaming hand sanitizer (containing 5% LPG propellant) to 90.3 mg/m³ based on an adult using a spray

paint (containing 60% w/w LPG propellant) in an indoor environment with good ventilation.

10.2. Health Effects Assessment

The European Commission previously classified LPGs identified by CAS RNs 68476-85-7 and 68476-86-8 as Category 1 carcinogens (“*known to be carcinogenic to humans*”) and Category 2 mutagens (“*should be regarded as if they are mutagenic to man*”) if 1,3-butadiene content is equal to or greater than 0.1% by weight (ESIS 2008; European Commission 2008a). The equivalent reclassifications of these substances by the European Commission in 2009 were Category 1A carcinogens (“*known to have carcinogenic potential for humans, classification is largely based on human evidence*”) and Category 1B mutagens (“*regarded as if they induce heritable mutations in the germ cells of humans*”) (European Commission 2008b, 2009).

Health effects information is limited for the LPGs identified under CAS RNs 68476-85-7 and 68476-86-8. A limited number of studies are available for exposure to highly refined LPG found in aerosol products containing any combination of propane, *n*-butane and isobutane. Toxicological information for other petroleum and refinery gases in the PSSA (i.e., Stream 1 and Stream 2 petroleum and refinery gases) that are similar from both a process and a physical–chemical perspective was not found. Various organizations have therefore characterized the toxicity of these substances by examining the petroleum and refinery gas component classes, including alkanes, alkenes (or olefins), alkadienes, alkynes, aromatics, mercaptans and inorganics (CONCAWE 1992; ECB 2000a,b; Petroleum HPV 2009a,b; U.S. EPA 2010). Available literature relevant to the LPGs and their individual components was therefore considered in the preparation of the screening assessment. An overview of health effects information is provided in Appendix E. Only a summary of the critical information upon which the conclusion is based is presented herein.

10.2.1. Laboratory Animal Studies (LPGs)

No studies are available to assess the acute inhalation toxicity of LPGs identified under CAS RNs 68476-85-7 and 68476-86-8. One study on a mixture of propane (17.1% v/v), *n*-butane (2.5% v/v) and isobutane (80.4% v/v) indicated an LC₅₀ of approximately 1 227 000 mg/m³ (539 600 ppm) (Aviado et al. 1977).

Acute exposure of rabbits to high levels of LPGs indicated potential toxicity. Neocortical changes and cardiac damage were reported at approximately 540 000 mg/m³ after male rabbits were continuously exposed to a mixture of ethane, propane, *n*-butane, propene and isobutane for 120 min (Komura et al. 1973). Yoshino et al. (1984) conducted histological and cytological analysis of the central nervous system of male rabbits after a 4-h exposure to a mixture of LPG (containing ≥ 95% propane) and oxygen and nitrogen. Reversible

neuropathological changes were observed at 1 260 000 mg/m³, as characterized by cytoplasmic vacuolation with reduced stainability in the V (5th) layer of the cerebral cortex, and a high-grade vacuolation of the rough endoplasmic reticulum in the peripheral region of the neurons observed at the ultrastructure level.

A no-observed-adverse-effect concentration (NOAEC) of 18 230 mg/m³ was identified for systemic effects, neurotoxicity, reproductive and developmental toxicity, following inhalation exposure of male and female rats to CAS RN 68476-85-7 for 6 h/day, 5 days/week for 13 weeks. No dose or exposure-related changes in organ weights or haematological or clinical parameters were seen (Petroleum HPV 2009b; U.S. EPA 2010). Neurotoxicity was examined, but no LPG-related effects on the functional observational battery parameters or motor activity were observed. Similarly, a NOAEC of 18 230 mg/m³ was established based on an analysis of reproductive and developmental effects. At this dose level, there was an increased incidence of abnormal sperm (4-12% of 200 sperms evaluated, with the effect occurring in 4 of 10 animals), but there was no concurrent effects on sperm count or motility. Thus, such incidences of abnormal sperm were considered to be incidental and non-treatment related (Petroleum HPV 2009b; U.S. EPA 2010).

In another study on inhalation exposure of pregnant rats to CAS RN 68476-85-7 for 6 h/day from gestation days 6 to 19 (Petroleum HPV 2009b; U.S. EPA 2010), no treatment-related effects were observed at the highest dose tested, and a NOAEC of 19 020 mg/m³ was identified.

LPGs have not demonstrated evidence of genotoxicity in an *in vivo* micronucleus assay and in an *in vitro* Ames assay. CAS RN 68476-85-7 exhibited negative results for micronuclei induction, as reported by the Petroleum HPV (2006, 2009b) and U.S. EPA (2010). There are no studies on CAS RNs 68476-85-7 and 68476-86-8 for *in vitro* genotoxicity. Only one study is available that examined the *in vitro* mutagenicity of gas mixtures of propane, isobutane and *n*-butane using the Ames assay with and without metabolic activation (Kirwin and Thomas 1980). The mixture exhibited negative mutagenicity, under both experimental conditions, after 6-h exposure to the gas mixture.

10.2.2. Human Studies (LPGs)

An epidemiology (cross-sectional) study by Sirdah et al. (2013) that characterized health effects of LPGs on workers at LPG filling and distribution stations was identified. This study included a questionnaire interview and haematological and biochemical analyses of venous blood samples. The authors reported that LPG workers were at a higher risk of health-related symptoms and clinical abnormalities, as shown by high health-related complaints and significantly increased levels of some haematological parameters (e.g., red blood cell counts, haemoglobin), as well as elevated levels of urea and creatinine (measures of kidney function) and aspartate aminotransferase (AST) and alanine

aminotransferase (ALT) (measures of liver function). The exposure metrics used in the study are not known. Confounding factors of such studies include concurrent exposures to other substances (e.g., vehicle exhaust).

Aydin and Özçakar (2003) reported a case of acute hepatitis associated with an exposure to a mixture of propane and butane during the filling of gas cylinders in an enclosed space. The symptoms resolved 10 days after cessation of exposure. Exposure time and exposure metrics were not reported in the study.

Two case studies have been reported on the use of aerosol products containing LPGs as a propellant. Weibrecht and Rhyee (2011) reported an acute pulmonary injury after a male was exposed to a spray product containing 1–10% (w/v) of LPGs for 15 minutes in an enclosed garage, with symptoms of coughing, light headedness, shortness of breath, near-syncope, chest wall tightness, vomiting, diarrhea, chills and tremor. Similarly, another case study was identified of a male repeatedly exposed to an adhesive spray containing 30–35% of butane/propane/isobutane in a poorly ventilated garage over 2 years (Pyatt et al. 1998). The authors reported effects on the liver and the central nervous system, as shown by malaise and paraesthesia in the left upper limb, and higher levels of serum alkaline phosphatase (AP) and gamma-glutamyl-transferase (γ -GT) values. All the effects and symptoms reported in these two case studies were resolved after cessation of exposure. The exposure metrics in these studies are not known and the results are confounded by likely exposure to the other substances (the actual substances that comprise the product, such as the adhesive material) present in the spray cans.

10.2.3. LPG Components

Due to limited information on the health effects of petroleum and refinery gases or LPGs, available literature relevant to the individual components present in LPGs is considered. Petroleum and refinery gases have been previously evaluated for mammalian health effects based on the assessment of individual components found in the gaseous state of these substances (API 2001a, 2009a,b; CONCAWE 2005; Petroleum HPV 2009a; U.S. EPA 2010). The results of the component evaluation facilitated the characterization of potential hazards associated with LPG mixtures. Generally, there can be multiple potentially hazardous components at various concentrations in the petroleum and refinery gases; therefore, the component that is the most highly hazardous for a particular endpoint (and present in the greatest quantity) is generally used to characterize the hazard associated with the mixture (API 2009a,b).

A brief summary of the health effects of the component classes is presented in Appendix E-2. A review of the health effects data for the predominant components of LPGs, including propane, butanes, butenes, and ethane, was undertaken as part of this screening assessment. These LPG components typically exhibit low

toxicity, having high LC₅₀ values and high NO(A)ECs and LO(A)ECs in repeated-dose studies.

For alkane components (propane, butane, isobutane), LC₅₀ values range from 570 000 to over 800 000 mg/m³ (Shugaev 1969; Clark and Tinson 1982), and *in vitro* genotoxicity assays are negative (Petroleum HPV 2009b; U.S. EPA 2010). Mixtures of butane/pentane or isobutane/isopentane have associated NOECs of 11 943 mg/m³ in subchronic exposure assays in rats (Aranyi et al. 1986). Butane and isobutane both have associated NOAECs of 21 500 mg/m³ in assays of short-term exposure and maternal/developmental toxicity, and butane exhibited a NOAEC of 21 700 mg/m³ for reproductive toxicity in SD rats (Petroleum HPV 2009b; U.S. EPA 2010). Inhalation exposure to propane has elicited some effects in animals including hematological changes in female SD rats after 2- or 4-week exposure (84 or 168 h) to 21 900 mg/m³ (Petroleum HPV 2009b). Reproductive effects in rats have been noted for propane exposure of 7180 mg/m³ (decreased live pups) and for isobutane exposures of 21 700 mg/m³ (reduced fertility index and increased post-implantation loss) (Petroleum HPV 2009b; U.S. EPA 2010). However, given that concordant effects are not seen with similar exposures to ethane, butane or other low molecular weight gases, the toxicological relevance of these effects is questionable.

Other predominant components of LPGs, such as alkenes, produce similarly negative results or unremarkable effects in toxicological assays (see Appendix E-2 for more details). Substances expected to be present only at very low levels in LPGs, such as benzene, may be associated with hazardous endpoints, but are considered not to be present at concentrations that would pose an unacceptable risk.

For the characterization of the potential risk to human health from exposure to LPGs, this screening assessment focuses on a specific component considered to conservatively represent the greatest hazard to human health. The alkadiene 1,3-butadiene was previously selected as the high-hazard component that best represents the critical health effects of petroleum and refinery gases (Environment Canada, Health Canada 2013). 1,3-Butadiene has been reported to be potentially present in LPGs (identified under CAS RNs 68476-85-7 and 68476-86-8) that are produced at petroleum refineries (U.S. EPA 2010).

1,3-Butadiene has been classified as a carcinogen by several national and international agencies. For example, the Government of Canada concluded that 1,3-butadiene met the criteria under section 64(c) of CEPA on the basis of a plausible mode of action for induction of tumours involving direct interaction with genetic material (Canada 2000). The International Agency for Research on Cancer (IARC 2008) also classified 1,3-butadiene as carcinogenic to humans (Group 1). The U.S. EPA (2002) concluded that 1,3-butadiene is carcinogenic to humans by inhalation, while the U.S. National Toxicology Program (NTP 2011a) classified 1,3-butadiene as a known human carcinogen due to sufficient evidence

of carcinogenicity in humans. For its part, the European Commission classified 1,3-butadiene as a carcinogen (Category 1A: *known to have carcinogenic potential for humans*), but also as a mutagen (Category 1B: *be regarded as if they induce heritable mutations in the germ cells of humans*) (European Commission 2008b, 2009). Based on toxicity data generated in animals, 1,3-butadiene is also in the highest (most comprehensive) category that describes the weight-of-evidence scheme in the Guidelines for Mutagenicity Risk Assessment (U.S. EPA 1986).

1,3-Butadiene was subsequently added to the List of Toxic Substances in Schedule 1 of CEPA. Appendix E-3 contains a summary of the critical health effects information on 1,3-butadiene. The critical literature for characterizing the human health effects of 1,3-butadiene as a potential high-hazard component of LPGs is presented here.

In an NTP study, the carcinogenic potential of inhaled 1,3-butadiene has been clearly demonstrated in a 2-year inhalation study in B6C3F1 mice exposed to 1,3-butadiene at concentrations of 0–625 ppm (0–1380 mg/m³) 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/m³) (NTP 1993; EURAR 2002; U.S. EPA 2002). As tumour induction was observed at all concentrations examined, it is likely that exposures lower than 6.25 ppm (13.8 mg/m³) would also cause cancer in mice (U.S. EPA 2002).

Also, mice were more sensitive to reproductive effects than rats, possibly due to production in mice of reactive 1,3-butadiene metabolites that are not formed to the same degree in rats (NTP 1993; Henderson 2001; Filser et al. 2007; Grant et al. 2010). Adverse reproductive/developmental effects are observed at lower concentrations tested in mice when compared to rats (NTP 1993). This single long-term inhalation study in rats suggests that 1,3-butadiene is also a multisite carcinogen in the rat; however, the effects were observed at air concentrations that were two to three orders of magnitude higher than in the mouse. The resistance of the rat to ovarian toxicity of 1,3-butadiene is likely due to decreased ability of the rat to produce 1,2:3,4-diepoxybutane (DEB) from 1, 3-butadiene. In a more recent study, Filser et al. (2007) were unable to detect DEB in venous blood of male Sprague-Dawley rats (detection limit 0.01 µmol/L) when they were exposed to 1200 ppm (~2650 mg/m³) for 6 h, whereas DEB was detected in B6C3F1 mice at a concentration of 3.2 µmol/L after exposure to 1280 ppm BD (~2830 mg/m³) for 6 h.

Humans are more similar to rats than mice for 1, 3-butadiene metabolism in that they do not readily produce the diepoxide metabolite (Henderson 2001). Although

there are marked differences in inter-species sensitivity to the carcinogenic properties of 1,3-butadiene that may be explained by differences in metabolism, the available data does unequivocally indicate that 1,3-butadiene is a multisite carcinogen (Owen 1981; Owen et al. 1987; Owen and Glaister 1990; U.S. EPA 2002).

Several epidemiological investigations of the carcinogenicity of 1,3-butadiene have been conducted and have served as the basis for assessment of the weight of evidence for causality of associations based on traditional criteria (Canada 2000; EURAR 2002; U.S. EPA 2002). The investigation by Delzell et al. (1995, 1996), which was a large, high quality, cohort mortality study, portrays a clear association between exposure to 1,3-butadiene in the styrene–butadiene rubber industry and leukemia in humans.

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 2000; EURAR 2002; U.S. EPA 2002).

The Government of Canada has previously developed estimates of carcinogenic potency associated with inhalation exposure to 1,3-butadiene. A tumorigenic concentration (TC_{01}) of 1.7 mg/m^3 was derived from the epidemiological investigation of Delzell et al. (1995), and the quantitative estimate of carcinogenic potency (TC_{05}) derived on the basis of data in experimental animals was 2.3 mg/m^3 for the most sensitive tumour site in mice (Canada 2000). 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 et al. 2009).

10.3. Characterization of Risk to Human Health

LPGs listed under CAS RNs 68476-85-7 and 68476-86-8 were identified as high priorities for action during categorization of the DSL because they were determined to present the greatest or intermediate potential for exposure of individuals in Canada and were considered to present a high hazard to human health. A critical effect for the initial categorization of LPGs was carcinogenicity, based primarily on classifications by international agencies. The European Union considers LPGs containing 1,3-butadiene at concentrations equal to or greater than 0.1% by weight to be carcinogens. Measured concentrations of 1,3-butadiene in the gaseous state for the two LPG substances identified in this assessment ranged from non-detectable to 0.1% by weight (U.S. EPA 2010). According to information submitted under section 71 of CEPA, the residual level of 1,3-butadiene in butane or isobutane ranges from non-detectable to less than 1% by weight and typically less than 0.1% by weight (Environment Canada 2007).

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. 1,3-Butadiene was found to be a multi-site carcinogen in rodents by inhalation, increasing the incidence of tumours at all concentrations tested. Epidemiological studies provide further evidence for an association between exposure to 1,3-butadiene in occupational environments and leukemia in humans. 1,3-Butadiene also exhibits genotoxicity *in vitro* and *in vivo*, and a plausible mode of action for induction of tumours involves direct interaction with genetic material.

Based on its carcinogenicity and presence in LPGs, 1,3-butadiene is considered to be the component representing the highest health concern for long-term inhalation exposure to LPGs. A quantitative estimate of carcinogenic potency ($TC_{05} = 2.3 \text{ mg/m}^3$) for 1,3-butadiene for the inhalation route of exposure was previously determined and represents the level that causes a 5% increase in tumours or mortality in mice (Canada 2000). The TC_{05} is used to characterize risk to the general population by deriving margins of exposure for potential long-term exposure to fugitive releases of LPGs containing 1,3-butadiene. Petroleum facilities, LPG transfer stations (where LPG tanks or LPG-powered automobiles are refuelled), and the use of aerosol products (that contain LPG as propellants) are potential sources of long-term exposure to 1,3-butadiene associated with LPG releases.

Limited studies were identified on which to base the characterization of risk for short-term inhalation exposures to LPGs. The highest inhalation NOAEC for LPGs of $19\,000 \text{ mg/m}^3$ was based on absence of maternal and developmental toxicity and is used for short-term risk characterizations through comparisons with the estimated short-term inhalation exposures (i.e., 24-h or TWA10) to LPGs from the use of aerosol products.

10.3.1. Fugitive Releases from Petroleum Facilities

LPGs identified under CAS RNs 68476-85-7 and 68476-86-8 are produced at petroleum refining and natural gas processing facilities. Fugitive releases of LPGs from petroleum refineries may contribute to the overall 1,3-butadiene concentrations in ambient air in the vicinity of the facilities. However, it is not possible to determine the proportion of such releases specifically associated with these two CAS RNs. Therefore, any risk associated with on-site fugitive releases of these two CAS RNs has been captured by the risk characterization of the total petroleum and refinery gases released at a facility in the assessment of Stream 1 petroleum and refinery gases (Environment Canada, Health Canada 2013) (summarized below).

Both air dispersion modelling and calculations based on the application of emission factors indicate that unintentional releases of petroleum and refinery gases contribute to the overall 1,3-butadiene concentration in ambient air in the

vicinity of petroleum refineries that produce or use these substances. The estimated 1,3-butadiene concentrations decline with increasing distance from these release sources. A conservative approach estimates the 1,3-butadiene concentration to be comparable to or below the Canadian urban average concentration at distances equal to or greater than 500 m from the centre of the release source. Using the estimates of carcinogenic potency previously developed by the Government of Canada (Canada 2000), together with the high and low end estimates of exposure derived from dispersion modelling of 1,3-butadiene as a high-hazard component of the petroleum and refinery gases, margins of exposure (MOEs) were derived for increasing distances from the release source (a distance of 200 m is illustrated in Table 10-3). 1,3-Butadiene to benzene ratios of 1:85 and 1:216 were used for high end and low end exposure estimates, respectively. Map analysis has determined that the general population may reside approximately 200 m from a potential source of release. Accordingly, this distance has been selected to characterize risk to the general population.

Table 10-3. MOE estimates based on air dispersion modelling of 1,3-butadiene as a high-hazard component of petroleum and refinery gases

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

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

Therefore, fugitive emissions of LPGs (CAS RNs 68476-85-7 and 68476-86-8) produced from petroleum refineries contribute to the overall site emissions of 1,3-butadiene as estimated above, accordingly contributing to the potentially inadequate margins of exposure.

Sampling results from natural gas processing facilities show that the levels of 1,3-butadiene were below the detection limit (< 1 ppm) in most gas streams, and were below 5 ppm in all samples (CAPP 2014). Given the low hazard of the other

predominant gas components, the human health risks from potential exposure to fugitive emissions of petroleum and refinery gases, including LPGs from natural gas processing facilities, are expected to be low.

10.3.2. Releases from LPG Filling Stations

The general population may be exposed to LPGs (and therefore 1,3-butadiene) in ambient air from releases that might occur during filling processes if they are living in the vicinity of such filling stations. The presence of 0.1% by weight of 1,3-butadiene in the gaseous state was assumed for each LPG release. According to the estimates in Table C-3, the annual contributions of 1,3-butadiene to ambient air associated with LPG filling events at LPG transferring stations are below the ambient background level of $0.22 \mu\text{g}/\text{m}^3$ at 200 ft (approximately 60 m) from the release source, which is a distance set out under the *Liquefied Petroleum Gases Bulk Storage Regulations* (Canada 2013). For the characterization of risk of potential long-term inhalation exposure to LPGs at a distance of 60 m from a release source, the MOE was estimated by comparing the inhalation exposure estimate for 1,3-butadiene (i.e., $0.12 \mu\text{g}/\text{m}^3$) with the TC_{05} of $2.3 \text{ mg}/\text{m}^3$, resulting in an MOE of 19 100. This MOE is considered adequate to address uncertainties in health effects and exposure.

10.3.3. Exposure to Aerosol Products Available to Consumers

The general population can be exposed to LPGs through indoor air during and after intermittent or frequent use of aerosol products containing LPGs as propellants.

For the characterization of risk of potential long-term inhalation exposure to LPGs released from the use of various aerosol products over time, the MOE was determined by comparing the highest 50th percentile of $0.134 \mu\text{g}/\text{m}^3$ for Canadian indoor air levels of 1,3-butadiene in non-smoking homes with the TC_{05} of $2.3 \text{ mg}/\text{m}^3$ ($2300 \mu\text{g}/\text{m}^3$) for 1,3-butadiene, resulting in an MOE of 17 000. This approach is considered conservative as multiple sources likely contribute to the indoor air level of 1,3-butadiene. This MOE is considered adequate to address uncertainties related to health effects and exposure.

The MOEs for short-term inhalation exposure to LPGs from different aerosol products are presented in Table 10-4. The MOEs were derived by comparing the estimated 24-h LPG concentration in indoor air from the use of each product with the highest LPG NOAEC of $19\ 000 \text{ mg}/\text{m}^3$. As shown in Table 10-4, MOE estimates range from 135 to 552 300. Given the absence of adverse effects (i.e., the MOE is based on a NOAEC) and the conservative assumptions taken within the assessment, the MOEs are considered adequate to address uncertainties related to health effects and exposure.

Table 10-4. Short-term inhalation MOEs for aerosol products containing LPGs used as propellants

Products available to consumers	Max. mean concentration on day of event (mg/m ³)	Short-term MOE
Adhesive (spray)	8.46	2200
Fabric protectors (e.g., bathroom rugs)	39.3	480
Household glass/stainless steel cleaners	15.5	1200
Furniture polish and cleaners	71.6	260
Air fresheners	11.6	1600
Carpet stain removers	1.64	11 580
Household specific spot removers	11	1700
Hand sanitizers	0.034	552 300
All-purpose lubricants	19.1	990
Spray paints (e.g., for furniture, metal, wood, crafts and plastic items)	90.3	210
Hair spray	1.5 (24-h) ^a	13 000

^a Amortized over 24-h by assuming 1.5 times/day and 10-minute per event.

10.4. Uncertainties in Evaluation of Human Health Risk

The composition of LPGs can vary depending on the source of crude oil or natural gas, operating conditions, seasonal process issues and economic cycles. Therefore, the hazard properties of LPGs may change based on the levels of component substances.

Canadian monitoring data for 1,3-butadiene in the vicinity of petroleum facilities was not identified. Therefore, general population exposures were estimated in part using computer models. There is inherent uncertainty in estimates derived with models (assumptions made in the various exposure analyses are listed in Appendix C).

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

11. Conclusion

Based on the information presented in this screening assessment, it is concluded that the LPGs listed under CAS RNs 68476-85-7 and 68476-86-8 are unlikely to be causing ecological harm to organisms or the broader integrity of the environment. Therefore, it is concluded that these two LPGs (CAS RNs 68476-85-7 and 68476-86-8) do not meet the criteria under paragraphs 64(a) and (b) of CEPA 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.

Based on the information presented in this final screening assessment, it is concluded that these two LPGs (CAS RNs 68476-85-7 and 68476-86-8) meet the criteria under paragraph 64(c) of CEPA 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 concluded that these two LPGs (CAS RNs 68476-85-7 and 68476-86-8) meet one or more of the criteria set out in section 64 of CEPA.

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Appendix A: Petroleum Substance Grouping

Table A-1. Description of the nine groups of petroleum substances

Group ^a	Description	Example
Crude oils	Complex combinations of aliphatic and aromatic hydrocarbons and small amounts of inorganic compounds, naturally occurring beneath the earth's surface or under the sea floor	Crude oil
Petroleum and refinery gases ^b	Complex combinations of light hydrocarbons, primarily from C ₁ –C ₅	Propane
Low boiling point naphthas	Complex combinations of hydrocarbons, primarily from C ₄ –C ₁₂	Gasoline
Gas oils	Complex combinations of hydrocarbons, primarily from C ₉ –C ₂₅	Diesel
Heavy fuel oils	Complex combinations of heavy hydrocarbons, primarily from C ₁₁ –C ₅₀	Fuel oil No. 6
Base oils	Complex combinations of hydrocarbons, primarily from C ₁₅ –C ₅₀	Lubricating oils
Aromatic extracts	Complex combinations of primarily aromatic hydrocarbons from C ₁₅ –C ₅₀	Feedstock for benzene production
Waxes, slack waxes and petrolatum	Complex combinations of primarily aliphatic hydrocarbons from C ₁₂ –C ₈₅	Petrolatum
Bitumen or vacuum residues	Complex combinations of heavy hydrocarbons having carbon numbers greater than C ₂₅	Asphalt

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

^b LPGs are considered to be in the petroleum and refinery gases group.

Appendix B: Physical and Chemical Data Tables for LPGs

Table B-1. Substance identity of LPGs identified in this screening assessment

CAS RN	68476-85-7	68476-86-8
DSL name	Petroleum gases, liquefied	Petroleum gases, liquefied, sweetened
Chemical group	Petroleum gases	Petroleum gases
Major components	Aliphatic hydrocarbons C ₃ – C ₄	Aliphatic hydrocarbons C ₃ –C ₄
Carbon range	C ₃ –C ₇ (NCI 2009) C ₁ –C ₈ (Petroleum HPV 2009a; U.S. EPA 2010)	C ₃ –C ₇ (NCI 2009) C ₁ –C ₈ (Petroleum HPV 2009a; U.S. EPA 2010)
1,3-Butadiene (% w/w)	0 – 0.1 (U.S. EPA 2010)	0 – 0.1 (U.S. EPA 2010)
Aromatic content (% w/w)	0 – 1 (U.S. EPA 2010)	0 – 1 (U.S. EPA 2010)

Table B-2. Physical–chemical properties of representative structures for petroleum and refinery gases^a

Substance	Melting point (°C) ^{a,b}	Boiling point (°C) ^{a,b}	Vapour pressure (Pa at 25°C) ^a	Henry's Law constant (Pa·m ³ /mol) ^a	Log K _{ow} ^a	Log K _{oc} ^a	Water solubility (mg/L at 25°C) ^a
C ₃ propane	-187.6 (exp.)	-42.1 (exp.)	9.5 × 10 ⁴ (exp.)	7 × 10 ⁴ (exp.)	2.36 (exp.)	2.05	62.4 (exp.)
C ₄ butane	-138.2 (exp.)	-0.5 (exp.)	2.4 × 10 ⁵ (exp.)	9.6 × 10 ⁴ (exp.)	2.89 (exp.)	2.5	61.2 (exp.)
C ₄ butene	-185.3 (exp.)	-6.2 (exp.)	3.0 × 10 ⁵ (exp.)	2.4 × 10 ⁴ (exp.)	2.4 (exp.)	2.08	221
C ₄ isobutane	-159.6 (exp.)	-11.7 (exp.)	3.5 × 10 ⁵ (exp.)	1.2 × 10 ⁵ (exp.)	2.8 (exp.)	1.55	49 (exp.)
C ₄ 1,3-butadiene	-108.9 (exp.)	-4.4 (exp.)	2.8 × 10 ⁵ (exp.)	7.5 × 10 ³ (exp.)	1.99 (exp.)	1.73	735
C ₅	-129.7	36	6.9 × 10 ⁴	1.3 × 10 ⁵	3.4	2.94	38 (exp.)

Substance	Melting point (°C) ^{a,b}	Boiling point (°C) ^{a,b}	Vapour pressure (Pa at 25°C) ^a	Henry's Law constant (Pa·m ³ /mol) ^a	Log K _{ow} ^a	Log K _{oc} ^a	Water solubility (mg/L at 25°C) ^a
pentane	(exp.)	(exp.)	(exp.)	(exp.)	(exp.)		
C ₅ isopentane	-159.9 (exp.)	27.8 (exp.)	9.2 × 10 ⁴ (exp.)	1.4 × 10 ⁵ (exp.)	2.7	2.4	48 (exp.)
C ₆ hexane	-95.3 (exp.)	68.7 (exp.)	2.0 × 10 ⁴ (exp.)	1.8 × 10 ⁵ (exp.)	3.90 (exp.)	3.38	9.5 (exp.)
C ₆ methyl pentane	-153.7 (exp.)	60.2 (exp.)	2.8 × 10 ⁴ (exp.)	1.7 × 10 ⁵ (exp.)	3.21	2.79	13 (exp.)

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

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

Appendix C: Air Dispersion Modelling of Potential Releases of LPGs

Table C-1. Variable inputs to SCREEN3 for modelling unintentional on-site total releases of petroleum and refinery gases^a

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

Abbreviations: DIAL, differential absorption, light detection and ranging.

^a See Environment Canada, Health Canada (2013) for detailed information on estimation of potential releases from a petroleum facility.

^b Aerial photo analysis and professional judgement.

^c Chambers et al. (2008).

^d NPRI (2000–2007) and TRI (2011).

^e Professional judgement.

^f Curry et al. (1993).

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

^h U.S. EPA (1992) and professional judgement.

ⁱ Default value in SCREEN3.

Table C-2. Modelling results of dispersion profile of 1,3-butadiene ($\mu\text{g}/\text{m}^3$) from unintentional on-site total releases of petroleum and refinery gases^a

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

^a Assumptions made in the modelling:

- (1) All unintentional releases of 1,3-butadiene from a petroleum facility are assumed to be attributed to the unintentional emission of total petroleum and refinery gases and originate from processing areas rather than bulk storage facilities.
- (2) Both LPGs identified under CAS RNs 68476-85-7 and 68476-86-8 are flagged as potentially containing 1,3-butadiene and are considered to comprise a fraction of the previously characterized Stream 1 petroleum and refinery gases.
- (3) The ratio of 1,3-butadiene to benzene (1:85 as a high end exposure range and 1:216 as a low end exposure range) in unintentional emissions is assumed to be constant over different processing units.
- (4) Unintentional emission heights of 1,3-butadiene are assumed to be 15 m and 3 m, with 80% of total emissions occurring above 15 m and 20% of emissions occurring at 3 m.
- (5) Considering the fact that the release sources are actually multiple point sources spatially distributed over the processing area, the effective processing area used for calculation of emission rate is assumed to be 80% of the total process area.
- (6) Total processing area is assumed to be 300 m × 100 m.
- (7) Adjustment factor 0.2 is used for estimation of maximum concentration over a year based on the highest 1-h concentration.

Table C-3. Variable inputs to SCREEN3 for modelling releases of LPGs from filling stations

Variables	Input variables
Source type	Area
Effective filling area ^a	5 m × 5 m
Release rate ^b	2.5×10 ⁻³ g/s·m ² (LPGs) 2.5×10 ⁻⁶ g/s·m ² (1,3-butadiene)
Number of filling events ^c	200/day
Receptor height ^d	1.74 m
Source release height ^c	1 m
Adjustment factor for wind and meteorological conditions ^e	0.4 for 24-h estimates, 0.2 for annual estimates
Urban–rural option	Urban
Meteorology ^f	1 (full meteorology)
Minimum and maximum distance to use	1–2000 m

^a Professional judgement for filling stations.

^b Estimated based on the release factor reported by Sullivan (1992).

^c Conservative professional judgement for a high-throughput BBQ cylinder tank filling station.

^d Curry et al. (1993).

^e U.S. EPA (1992) and professional judgement.

^f Default value in SCREEN3.

Table C-4. SCREEN 3 modelling results of dispersion profile of LPGs and 1,3-butadiene (µg/m³) from fugitive releases of LPGs during filling events

Distance (m)	Max. LPGs within 1-h	Max. LPGs within 24-h	Annual 1,3-butadiene ^a
1	171.8	68.72	0.034
10	4289	1715.6	0.86
20	2676	1070.4	0.54
30	1723	689.2	0.34
40	1150	460	0.23
50	805.6	322.24	0.16
60	591.3	236.52	0.12
70	451.1	180.44	0.090
80	355	142	0.071
90	286.7	114.68	0.057
100	236.4	94.56	0.047
120	169.2	67.68	0.034
160	99.49	39.796	0.020
180	80.12	32.048	0.016
200	66.07	26.428	0.013
250	44.08	17.632	0.0088
300	31.78	12.712	0.0064
350	24.18	9.672	0.0048
400	19.14	7.656	0.0038
450	15.62	6.248	0.0031

500	13.05	5.22	0.0026
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^a Assuming 0.1% by weight 1,3-butadiene in LPGs; concentration amortized based on 200 events/day for 365 days (frequency represents a high-throughput BBQ cylinder tank filling station).

Table C-5. Variable inputs to AERSCREEN for modelling unintentional on-site total releases of petroleum and refinery gases

Variables	Input variables
Source type	Area
Effective emission area ¹	300 × 100 m ²
Benzene fugitive release from process area ²	1.8 kg/h
Ratio of 1,3-butadiene to benzene ³	1:85 (upper-bounding); 1:216 (average case)
1 Receptor height ⁴	1.74 m (average adult height)
Source release height ¹	15 m (80%), 3 m (20%) ⁵
Initial vertical dimension ⁵	15 m , 3m
Population Size ⁶	100 000
Average min/max temperature (°K) ⁷	270.6 / 283.5 (Calgary)
Minimum distance to ambient air (m) ⁸	1 m
Select chemistry ⁸	No chemistry
Source elevation (m) ⁸	0
Minimum wind speed (m/s) ⁸	0.5
Anemometer height (m) ⁸	10
Adjustment factor ⁹	0.2 (average wind direction during 1 year period)
Meteorology ^{6,8}	AERMET Seasonal Tables Dominant Surface Profile /Urban / Average Moisture
Minimum and maximum distance	0–2000 m

¹ Aerial photo analysis and professional judgement.

² Chambers et al. 2008.

³ NPRI (2000–2007) and TRI (2007).

⁴ Curry et al. 1993.

⁵ 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.

⁶ Professional judgement.

⁷ Statistics Canada data <http://www.statcan.gc.ca/tables-tableaux/sum-som/l01/cst01/phys08b-eng.htm>.

⁸ Default value in AERSCREEN.

⁹ U.S. EPA (1992) and professional judgement.

Table C-6. Modelling results of AERSCREEN dispersion profile of 1,3-butadiene ($\mu\text{g}/\text{m}^3$) from unintentional on-site total releases of petroleum and refinery gases^a

Distance (m)	Concentration ($\mu\text{g}/\text{m}^3$)			
	Upper-bounding		Average case	
	Maximum 1 h	Annual	Maximum 1 h	Annual
50	3.138	0.6276	1.2349	0.2470
100	3.504	0.7008	1.3785	0.2757
200	2.7614	0.5523	1.0863	0.2173
300	1.6858	0.3372	0.6633	0.1327
400	1.1697	0.2339	0.4602	0.0920
500	0.8761	0.1752	0.3447	0.0689
600	0.6905	0.1381	0.2716	0.0543
700	0.564	0.1128	0.2219	0.0444
800	0.4727	0.0945	0.1860	0.0372
900	0.4046	0.0809	0.1592	0.0318
1000	0.3520	0.0704	0.1385	0.0277
1100	0.3104	0.0621	0.1221	0.0244
1200	0.2770	0.0554	0.1090	0.0218
1300	0.2497	0.0499	0.0982	0.0196
1400	0.2270	0.0454	0.0893	0.0179
1500	0.2080	0.0416	0.0818	0.0164
1600	0.1920	0.0384	0.0755	0.0151
1700	0.1782	0.0356	0.0701	0.0140
1800	0.1663	0.0333	0.0654	0.0131
1900	0.1560	0.0312	0.0614	0.0123
2000	0.1470	0.0294	0.0578	0.0116

^aAssumptions 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. Both LPGs identified under CAS RNs 68476-85-7 and 68476-86-8 are flagged as potentially containing 1,3-butadiene and are considered to comprise a fraction of the previously characterized Stream 1 petroleum and refinery gases.
3. The ratio of 1,3-butadiene to benzene in 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. Total processing area is assumed to be 300 m × 100 m.
6. Adjustment factor 0.2 is used for estimation of maximum concentration over a year based on the highest 1-h concentration.

Appendix D: Modelling Results for Human Exposure to LPGs from Representative Aerosol Products Available to Consumers^a

Table D-1. Estimates of potential inhalation exposure from consumer aerosol products

Product scenarios	Assumptions ^{b,c}	Estimated air concentration of LPGs ^d
Air freshener ^e	Maximum weight fraction: 0.6 Frequency: 4 events/day ^f Exposure duration: 15 min. total exposure ^f Amount of product: 10 g/event ^f Room volume: 20 m ³ Ventilation rate: 0.6 (h ⁻¹)	Mean concentration on day of exposure: 11.6 mg/m ³ Amortized mean concentration over a year: 11.6 mg/m ³
Spot remover (for chewing gum and candle wax)	Maximum weight fraction: 1.0 Frequency: 10 events/year Exposure duration: 60 min. total exposure ^g Amount of product: 7 g/event Room volume: 20 m ³ Ventilation rate: 0.6 (h ⁻¹)	Mean concentration on day of exposure: 11 mg/m ³
Furniture polish	Maximum weight fraction: 0.3 Frequency: 1 event/year Exposure duration: 240 min. Amount of product: 1.8 g/s for 0.7 min. ^h Room volume: 20 m ³ Ventilation rate: 0.6 (h ⁻¹)	Mean concentration on day of exposure: 71.6 mg/m ³
Furniture cleaner ^e	Maximum weight fraction: 0.18 Frequency: 104 events/year Exposure duration: 240 min. Amount of product: 1.8 g/s for 0.7 min. ^h Room volume: 20 m ³ Ventilation rate: 0.6 (h ⁻¹)	Mean concentration on day of exposure: 43 mg/m ³ Amortized mean

		concentration over a year: 12.2 mg/m ³
Carpet stain remover	Maximum weight fraction: 0.15 Frequency: 10 events/year Exposure duration: 60 min. ^g Amount of product: 7 g for 0.1 m ² Room volume: 20 m ³ Ventilation rate: 0.6 (h ⁻¹)	Mean concentration on day of exposure: 1.64 mg/m ³
Stainless steel/glass cleaner ^e	Maximum weight fraction: 0.3 Frequency: 365 events/year Exposure duration: 60 min. Amount of product: 0.78 g/s x 0.7 min. Room volume: 20 m ³ Ventilation rate: 0.6 (h ⁻¹)	Mean concentration on day of exposure: 15.5 mg/m ³ Amortized mean concentration over a year: 15.5 mg/m ³
Fabric protector (e.g., bathroom rug)	Maximum weight fraction: 0.1 Frequency: 1/year ^h Exposure duration: 15 min. Amount of product: 480 g ^h Room volume: 10 m ³ Ventilation rate: 2/h	Mean concentration on day of exposure: 39.3 mg/m ³
Hand sanitizer ^e	Maximum weight fraction: 0.05 Frequency: 5/day Exposure duration: 2 min. ^h Amount of product: 2g ^h Room volume: 20 m ³ Ventilation rate: 0.6 (h ⁻¹)	Mean concentration on day of exposure: 0.0344 mg/m ³ Amortized mean concentration over a year: 0.0344 mg/m ³
All-purpose lubricants (indoor) ^e	Maximum weight fraction: 0.5 Frequency: 11/year ^g Exposure duration: 50 min. ^g Amount of product: 28 g ^g Room volume: 20 m ³	Mean concentration on day of exposure: 19.1 mg/m ³

	Ventilation rate: 0.6 (h ⁻¹)	Amortized mean concentration over a year: 0.0524 mg/m ³
Automotive brake care	Maximum weight fraction: 0.7 Frequency: 2/year ⁱ Exposure duration: 30 min. ^g Amount of product: 170 g ^g Room volume: 34 m ³ (for garage) Ventilation rate: 1.5 (h ⁻¹)	Mean concentration on day of exposure: 51.3 mg/m ³
Automotive exterior coating	Maximum weight fraction: 0.4 Frequency: 1/year ^h Exposure duration: 60 min. ^g Amount of product: 310 g ^g Room volume: 34 m ³ (for garage) Ventilation rate: 1.5 (h ⁻¹)	Mean concentration on day of exposure: 78.7 mg/m ³
Spray adhesive ^e	Maximum weight fraction: 0.6 Frequency: 52/year ^j Exposure duration: 60 min. ^g Amount of product: 9 g ^j Room volume: 20 m ³ Ventilation rate: 0.6 (h ⁻¹)	Mean concentration on day of exposure: 8.46 mg/m ³ Amortized mean concentration over a year: 1.2 mg/m ³
Spray paints (e.g., for furniture, metal, wood, plastic items, can be used outdoors or indoors with good ventilation)	Maximum weight fraction: 0.6 Frequency: 2/year ^h Exposure duration: 20 min. Amount of product: 0.33g/s x 15 min. Room volume: 20 m ³ Ventilation rate: 2 (h ⁻¹)	Mean concentration on day of exposure: 90.3 mg/m ³

^a From each use category, only the products with a high concentration, a high use frequency or a high use quantity are selected for high-end exposure modelling.

^b Using "instantaneous release mode" of "exposure to vapour" in ConsExpo (RIVM 2005). All values for input parameters are from ConsExpo factsheets (RIVM 2005) unless specified.

^c Values of max. weight fraction of LPGs in products are from the maximum level reported in the MSDS for each representative consumer aerosol product.

^d Assuming a maximum level of 1,3-butadiene in LPG is 0.1% w/w, then the estimates for 1,3-butadiene air concentration from each product scenario is 0.1% x estimates for LPGs.

^e Amortized mean concentration over a year is presented for those products with a high use frequency (i.e., equal to or more than once per month).

^f ECETOC (2012).

^g U.S. EPA (2011b).

^h Professional judgement based on product information.

ⁱ Versar (1986).

^j Environment Canada, Health Canada (2010).

Appendix E: Summary of the Health Effects Information for LPGs and 1,3-Butadiene

Table E-1. Critical health effects information on LPGs identified by inhalation exposure

Toxicity type	CAS RN	Effect levels ^{a,b,c} /results
Acute toxicity	Mixture of propane (17.1% v/v), <i>n</i> -butane (2.5% v/v) and isobutane (80.4% v/v)	LC₅₀ : 539 600 ppm (1227 g/m ³) (Aviado et al. 1977).
Short-term and subchronic toxicity	Liquefied petroleum gas (assigned to CAS RN 68476-85-7 in U.S. EPA (2010))	<p>NOAEC: 18 230 mg/m³ for systemic effects (Petroleum HPV 2009b; U.S. EPA 2010)</p> <p>Sprague-Dawley (SD) rats (10/sex/dose) were exposed to 0, 1019, 5009 or 9996 ppm (0, 1860, 9140 or 18 230 mg/m³) for 6 h/day, 5 days/week for 13 weeks.</p> <p>At all dose levels, there were no dose-related changes in body weight, feed consumption.</p> <p>5009 ppm (9140 mg/m³): decreased kidney and thymus weights, but no dose-related</p> <p>Decreases in white blood cells (WBC), lymphocyte and monocyte numbers were observed in some female rats but not dose-related, and not observed in male rats.</p> <p>Significant differences in blood glucose, sodium, potassium and total protein levels were observed in some rats but not dose-related and not in both sexes.</p>
Reproductive and developmental toxicity	68476-85-7	<p>NOAEC: 9996 ppm (18 230 mg/m³) for reproductive toxicity ((Petroleum HPV 2006; 2009b).</p> <p>SD rats (10/sex/dose) were exposed to 0, 1019, 5009 or 9996 ppm (0, 1860, 9140 or 18 230 mg/m³) for 6 h/day, 5 days/week for 13 weeks.</p> <p>9996 ppm (18 230 mg/m³): increased incidence of abnormal sperm, as shown by an increased incidence of “mid-tail blob” (cytoplasmic droplet) in sperm (4-12% of the 200 sperm evaluated for each male) affected 4 out of 10 males in each group. No effects observed on sperm count and motility. Considered to be</p>

		<p>incidental and not treatment related by the author.</p> <p>No sperm count, motility and morphology examination was conducted on the other dose levels.</p>
Reproductive and developmental toxicity	Liquefied petroleum gas (assigned to CAS RN 68476-85-7 in U.S. EPA (2010))	<p>NOAEC: 10 426 ppm (19 020 mg/m³) for maternal and developmental effects (Petroleum HPV 2009b)</p> <p>Pregnant SD rats (24/dose) were exposed to 0, 1013, 5079 or 10 426 ppm (0, 1850, 9260 or 19 020 mg/m³) for 6 h/day, 7 days/week from gestation days 6 to 19.</p> <p>No test substance-related effects were observed in body weight changes, feed consumption, numbers of live and dead fetuses, number of corpora lutea, pre- and post-implantation losses, fetal body weight, and skeletal abnormalities.</p>
Genotoxicity (in vitro)	A mixture of propane, <i>n</i> -butane and isobutane at different proportions	<p>Reverse Mutations, modified Ames assay</p> <p>Negative: <i>S. typhimurium</i> (strains not identified) exposed to the test substances at various concentrations (105 to 1050 g/m³) for 6 h, with and without metabolic activation (rat liver S9) (Kirwin and Thomas 1980)</p>
Genotoxicity (in vivo)	Liquefied petroleum gas (assigned to CAS RN 68476-85-7 in U.S. EPA (2010))	<p>Micronucleus Assay:</p> <p>Negative for micronuclei induction: SD rats (5/sex/dose) were exposed to 0, 1019, 5009 or 9996 ppm (0, 1860, 9140 or 18 230 mg/m³) for 6 h/day, 5 days/week for 13 weeks. No significant differences were found for the proportion of immature cell and frequency of micronucleated immature erythrocytes (Petroleum HPV 2006, 2009b).</p>
Neurotoxicity	Liquefied petroleum gas (composed of 5.3% ethane, 49.9% propane, 11.2% <i>n</i> -butane, 27.5% propene and 4.3% isobutane)	<p>LOAEC: 540 000 mg/m³ for neocortical changes and cardiac damage (Komura et al. 1973)</p> <p>20 male 5-month rabbits were continuously exposed (whole body) to a mixture LPG and oxygen for 120 min. Electroencephalogram (EEG) and electrocardiogram (ECG) were measured at 30%, 60-70% of LPG in the gas chamber (concentration unknown, estimated to be ~540 000 mg/m³, 1 080 000 – 1 260 000 mg/m³) throughout</p>

		<p>the insufflation of LPGs.</p> <p>Licking, smacking, sniffing, jumping up occasionally and walking around were observed at the beginning of the exposure.</p> <p>For ECG: at 30% of LPG, increased pulse rate and respiratory frequency, arrhythmia with extrasystole, difficulty walking and occasional screaming; at 70% of LPG, the pulse rate and respiratory frequency decreased below the control level, appearance of temporary nystagmus, excessive salivation and weakened muscles, a depression of ST segment and an inversion of T wave.</p> <p>For EEG results, as the concentration of LPG increased, the neocortex showed a gradual change into a drowsy pattern, in contrast to hippocampus and amygdale limbic system changing into an arousal pattern.</p>
<p>Neurotoxicity</p>	<p>Mixture of oxygen, nitrogen and LPG (95+% of propane, isobutane, <i>n</i>-butane, propene and ethane)</p>	<p>LOEC: 1 260 000 mg/m³ for neuronal changes (Yoshino et al. 1984)</p> <p>21 male rabbits in a sealed chamber were exposed to the mixture at approximate levels of 720 000 mg/m³ (40%) and 1 260 000 mg/m³ (70%) for up to 4 h, with and without hypoxic conditions. Two rabbits were used as controls, but the number of tested rabbits per dose was unknown.</p> <p>1 260 000 mg/m³ (70%): Cytoplasmic vacuolation with reduced stainability were observed in the V layer of the cerebral cortex. By electron microscope, a high-grade vacuolation of the rough endoplasmic reticulum was found in the peripheral region of the neurons. Such changes were reversible, disappearing after a 24-h recovery period.</p> <p>1 260 000 mg/m³ (70%) and hypoxic conditions: shrunken neuron with hyperchromatosis of nucleus and eosinophilic cytoplasm was found in the</p>

		globus pallidus. Such changes were irreversible, but may be caused by hypoxia rather than LPG.
Neurotoxicity	Liquefied petroleum gas (assigned to CAS RN 68476-85-7 in U.S. EPA (2010))	NOAEC: 18 230 mg/m ³ for neurotoxic effects (Petroleum HPV 2009b; U.S. EPA 2010) SD rats (5/sex/dose) were exposed to 0, 1019, 5009 or 9996 ppm (0, 1860, 9140 or 18 230 mg/m ³) for 6 h/day, 5 days/week for 13 weeks. 5009 and 9996 ppm (9140 and 18 230 mg/m ³): an increase in forelimb grip strength was observed at week 13 (9140 mg/m ³) and week 4 (18 230 mg/m ³), but considered unlikely to be adverse effect by the author.
Human studies	Adhesive spray product containing 30-35% of butane/propane/isobutane, 25-35% of petroleum distillates, 10-15% of pentane and 1-5% of acetone (case study)	A male user exposed to a spray product up to 3 h/day, 2-3 times/week for 2 years in a poorly ventilated garage (Pyatt et al. 1998). The patient complained of malaise and paraesthesia in the left upper limb with abnormal liver function test results, i.e., elevated values of serum alkaline phosphatase, aspartate transaminase, alanine transaminase and gamma-glutamyl transferase. All the symptoms ceased after stopping use the product.
Human studies	Mixture of propane and butane gases (case study)	A male was chronically exposed to mixture of propane and butane gases by filling gas cylinders in an enclosed space (exposure time was not reported) (Aydin and Özçakar 2003). The patient complained of nausea, malaise and weakness of the lower limbs. Elevated levels of alanine aminotransferase and aspartate aminotransferase were observed. Recovered on day 10.
Human studies	LPG (mixture of propane and butane gases) (cross-sectional descriptive study)	Data collected from 30 male workers (34.4 ± 9.3 years old) at filling and distribution stations, including venous blood samples for haematological and biochemical analysis, and a questionnaire interview, in comparison to 30 male healthy individuals as a control group (Sirdah et al. 2013). Sample: ≥ 3 year of continuously working

		<p>at LPG stations with ≥ 6 h/day and no previous history of respiratory diseases.</p> <p>LPG workers have: significantly higher rates of health-related complaints, such as headache or fatigue at work, eye itches, redness, repeated sneezing during working hours, etc.; significantly higher values of red blood cell counts, haemoglobin, haematocrit, mean corpuscular haemoglobin concentration and platelet counts; significant lower number white blood cells; significantly higher values of serum AST and ALT and higher mean values of serum urea, creatinine and uric acid as an indication for impacts on liver and kidney function.</p>
Human studies	A canvas waterproofing spray product containing LPG (1-10% w/v), isopropanol (1-3% w/v) and ethylene glycol monobutyl ether (1-3% w/v) (case study)	A male was exposed to the product for 15-min. in an enclosed garage and developed acute pulmonary toxicity as shown by light headedness, shortness of breath, near-syncope, coughing, chest wall tightness, vomiting, diarrhea, chills and tremor. The symptoms resolved on day 4 (Weibrecht and Rhyee 2011).

^a LC₅₀, median lethal concentration; LD₅₀, median lethal dose; LOAEC, lowest-observed-adverse-effect concentration; LOAEL, lowest-observed-adverse-effect level; NOAEC, no-observed-adverse-effect concentration; NOAEL, no-observed-adverse-effect level.

^b The following formula was used for conversion of provided values into mg/m³ in air: (x ppm × MM)/24.45, assuming at 1atm and 25°C.

^c Molar mass (MM) of CAS RN 68476-85-7 reported to be 44.6 g/mol (U.S. EPA 2010).

E-2: Summary of the toxicological effects of the component classes of petroleum gases

Alkanes

As propane, *n*-butane and isobutane are the predominant components present in LPGs, key observations from toxicological studies on inhalation exposure to these components are summarized here.

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 2001a). In experimental animals, LC₅₀ values for alkanes range from 658 mg/L (658 000 mg/m³) (butane, 4-h), 570 000 ppm (isobutane, 15-min.) to greater than 800 000 ppm (1 440 000 mg/m³) (propane, 15-min.), depending on the substance, concentration and duration of acute exposure (Shugaev 1969; Clark and Tinson 1982). The European Commission has classified butane and isobutane as category 1A carcinogen (*“known to have carcinogenic potential for humans”*) and category 1B mutagen (*“known to induce heritable mutations or to be regarded as if they induce heritable mutations in the germ cells of humans”*) if each of them contains a concentration of 1,3-butadiene ≥ 0.1% by weight (European Commission 2008b, 2009).

For short-term exposure, a short-term NOAEC/LOEC of 12 168 ppm (21 900 mg/m³) was identified for propane based on decreased weight gain in male rats and increases in hemoglobin concentration, hematocrit, erythrocytes and absolute eosinophils in female SD rats after 4-week exposure at 6 h/day and 7 days/week. A NOAEC of greater than 9100 ppm (21 500 mg/m³) for butane or isobutane were reported in separate studies at 6 h/day, 7 days/week for 4 weeks (Petroleum HPV 2009b).

For reproductive toxicity, a LOAEC of 3990 ppm (7180 mg/m³) was reported based on a decrease in the number of live pups and increase in the number of stillborn pups when SD female rats were exposed to propane at 6 h/day, 7 days/week for 2 weeks prior to mating, during mating and on gestation days 0-19. Similarly, a LOAEC of 9148 ppm (21 700 mg/m³) was reported for SD female rats exposed to isobutane at 6 h/day, 7 days/week for 2 weeks prior to mating, during mating and on gestational days 0-19, as shown by a reduction in fertility index and an increase in post-implantation loss. Similar testing methodology was applied to *n*-butane in a separate study and a NOAEC of 9157 ppm (21 700 mg/m³) was reported for reproductive toxicity (Petroleum HPV 2009b; U.S. EPA 2010).

For developmental toxicity, a NOAEC/LOEC of maternal toxicity at 12 168 ppm (21 900 mg/m³) was identified for propane based on increases in hemoglobin concentration, hematocrit, erythrocytes and absolute eosinophils observed in SD female rats following exposure to propane gas at 6 h/day, 7 days/week for 2

weeks prior to mating, during mating and on gestational days 0 to 19. Following the similar testing methodology, a NOAEC of greater than 9100 ppm (21 500 mg/m³) was identified for *n*-butane and isobutane for their maternal/developmental toxicity (Petroleum HPV 2009b; U.S. EPA 2010).

For *in vitro* genotoxicity, negative results for gene mutation were exhibited in vitro Ames assay for propane and butanes. No *in vivo* genotoxicity studies are available on propane or butanes (*n*-butane and isobutane) (Petroleum HPV 2009b; U.S. EPA 2010).

A few inhalation studies are available on a mixture of C₃ to C₅. Rats were exposed to mixtures of alkanes (50% butane / 50% pentane; 50% isobutane / 50% isopentane) via inhalation for 90 days in a study designed to investigate kidney effects; a NOEC of 4489 ppm (11 943 mg/m³)^{3, 4} (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) 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).

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 (LC₅₀) are noted to range from 65 000 ppm (111 736 mg/m³)⁶ (propene; molecular weight (MW) = 42.03 g/mol) to 620 mg/L (620 000 mg/m³) (isobutene) (Shugaev 1969; Conolly and Osimitz 1981).

Short-term toxicity studies show that oral exposure to isobutene results in a 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/m³) (Fink 1968) as well as clinical and biochemical changes in rats exposed for 70 days to 100 ppm (115 mg/m³)⁶ 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 (17 190 mg/m³)⁶ for 28-day exposure to multiple concentrations of propene (MW = 42.03 g/mol) up to 17 190 mg/m³ (DuPont 2002).

³ Conversion of the provided value into mg/m³ was completed using the formula: $x \text{ ppm (MW)}/24.45$

⁴ Molecular weight of mixtures = $[0.5(58.04 \text{ g/mol}) + 0.5(72.05 \text{ g/mol})] = 65.05 \text{ g/mol}$

The lowest LOEC identified for subchronic toxicity is 500 ppm (1146 mg/m³)⁶ in a 14-week study in which male and female B6C3F1 mice and F344/N rats were exposed by inhalation to isobutene (MW = 56.10 g/mol) at concentrations up to 8000 ppm (18 336 mg/m³)⁶, 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/m³)⁶. In female rats, there was a significant increase in relative liver weights from 500 ppm (1146 mg/m³)⁶ and in absolute liver weights from 1000 ppm (2292 mg/m³)⁵. In male rats, a significant increase in relative right kidney weight was observed from 500 ppm (1146 mg/m³)⁶, with an increase in absolute right kidney weight at 4000 ppm (9168 mg/m³)⁶ (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/m³)⁶ (Krasovitskaya and Maliarova 1968).

With regard to developmental toxicity, NOEC values of 5000 ppm (5750 mg/m³) for ethene (MW = 28.02 g/mol), 10 000 ppm (17 190 mg/m³)⁶ for propene (MW = 42.03 g/mol) and 5000 ppm (11 460 mg/m³)⁶ for 2-butene (MW = 54.04 g/mol) were identified in rats exposed by inhalation (Waalkens-Berendsen and Arts 1992; Aveyard 1996). 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/m³)⁶. 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 their carcinogenicity to humans) by IARC (1994a,c). For propene, a two-year inhalation study (concentrations up to 10 000 ppm [17 190 mg/m³; MW for propene = 42.03 g/mol])⁶ 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/m³)⁶ propene 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/m³; MW of ethene = 28.02 g/mol)⁶ (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/m³; MW of isobutene = 54.04 g/mol)⁶ 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; 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 (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; Shimizu et al. 1985; Victorin and Stahlberg 1988; Wagner et al. 1992; Araki et al. 1994; NTP 1998), 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 2000; IARC 2008; U.S. EPA 2002; NTP 2011a; EURAR 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 2000). 1,3-butadiene was subsequently added to the List of Toxic Substances in Schedule 1 of CEPA. 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; Category 2: suspected human carcinogen, may cause cancer and "...reasonably anticipated to be a human carcinogen", as well as a mutagen (IRAC 1999; ESIS 2008; NTP 2011b). 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). Isoprene has also 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 (Environment Canada, Health Canada 2008).

Alkynes

Ethyne or acetylene is a simple asphyxiant (HSDB 2008); effects observed in humans after inhalation include intoxication, aggressiveness and unconsciousness at high concentrations (U.S. EPA 2008c).

Acetylene is noted to cause increased mortality in various species of experimental animals, as well as intoxication or anesthesia. Effects in the liver (LOAEC = 266.3 mg/L (266 300 mg/m³), kidneys and spleens of rats were observed following repeated exposure via inhalation. Genotoxic effects were not observed *in vitro* (U.S. EPA 2008c).

Aromatics

Benzene is noted to be a carcinogen, as classified by the Government of Canada (carcinogenic to humans; CEPA – 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 U.S. National Toxicology Program (NTP 2011c) (known human carcinogen) and the U.S. EPA (2008d) (Group A). In addition, benzene has been classified as a mutagen as Category 1B (*be regarded as if they induce heritable mutations in the germ cells of humans*) (European Commission 2008b, 2009).

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 U.S. 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 2001b).

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

Mercaptans

Two mercaptans noted to be components of petroleum and refinery gases have been evaluated or reviewed by various international or national agencies; however, for the purposes of this 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 FAO/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).

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

Endpoints	Study protocol	Effect levels ^a /results	References
Carcinogenicity	<p>B6C3F1 mice (70 of each sex per group; 90 of each sex at the highest concentration); inhalation exposure to 0, 6.25, 20, 62.5, 200 or 625 ppm (0, 13.8, 44.2, 138, 442 or 1380 mg/m³) for 6 h/day, 5 days/week, for 103 weeks. Up to 10 mice of each sex from each group were sacrificed after 9 and 15 months of exposure.</p> <p>Histopathological examination of a comprehensive range of tissues was carried out on mice in the control, on mice in the 200 and 625 ppm (442 and 1380 mg/m³) exposure groups sacrificed after 9 months, on all mice sacrificed at 15 months except females exposed to 6.25 or 20 ppm (13.8 or 44.2 mg/m³), and on all mice exposed for 2 years.</p>	<p>Lowest concentration at which tumours were observed = 6.25 ppm (13.8 mg/m³) based on a statistically significant increase in the incidence of malignant lung tumours.</p> <p>Summary of effects:</p> <p>Lymphohematopoietic system Exposure was associated with the development of malignant lymphomas (particularly lymphocytic lymphomas, which occurred as early as week 23). The incidences were significantly increased in males at 625 ppm (1380 mg/m³) ($p < 0.001$) and females at 200 and 625 ppm (442 and 1380 mg/m³) ($p < 0.001$) (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 ($p < 0.001$) and females ($p 0.002$) at 200 ppm (442 mg/m³), 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/m³) ($p 0.021$–0.051) and females at 625 ppm (1380 mg/m³) ($p 0.038$).</p> <p>Heart The incidences of cardiac hemangiosarcomas were significantly increased compared with controls in males at 62.5 ppm (138 mg/m³) and above and in females at 200 ppm (442 mg/m³) and above.</p> <p>Lungs There was evidence of increased incidences of alveolar/bronchiolar adenomas or carcinomas</p>	NTP 1993

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		<p>compared with controls in males at 62.5 ppm (138 mg/m³) and above ($p < 0.001$) and in females at all concentrations ($p < 0.001$–0.004).</p> <p>Forestomach An increased incidence of forestomach tumours (squamous cell papillomas or carcinomas) was observed in males at 200 and 625 ppm (442 and 1380 mg/m³) ($p < 0.001$) and in females at 62.5 ppm (138 mg/m³) and above ($p < 0.001$–0.044).</p> <p>Ovary Increased incidences of malignant and benign granulosa cell tumours were reported in females exposed to 62.5 ppm (138 mg/m³) and above ($p < 0.001$).</p> <p>Harderian gland The incidence of Harderian gland adenomas and carcinomas was increased in both sexes at 62.5 and 200 ppm (138 and 442 mg/m³) ($p < 0.001$–0.016).</p>	
Carcinogenicity	<p>B6C3F1 mice (50 males per group); inhalation exposure for 6 h/day, 5 days/week, at 200 ppm (442 mg/m³)^b for 40 weeks, 312 ppm (689 mg/m³)^b for 52 weeks or 625 ppm (1380 mg/m³)^b for 13 or 26 weeks.</p> <p>After exposure ceased, mice were kept in control chambers until 103 weeks and evaluated. Histopathological examination of a</p>	<p>Lowest concentration at which tumours were observed = 200 ppm (442 mg/m³) for 40 weeks based on increased incidence of cardiac hemangiosarcomas and adenomas or carcinomas in the liver.</p> <p>Summary of effects:</p> <p>Lymphohematopoietic system The incidence of malignant lymphomas (the majority of which were lymphocytic lymphomas) was markedly increased in both groups (13 and 26 weeks) exposed to 625 ppm (1380 mg/m³) ($p < 0.001$) and occurred as early as 23 weeks in the 26 weeks group.</p>	NTP 1993

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	comprehensive range of tissues was conducted on all mice.	<p>Heart The incidence of cardiac hemangiosarcomas was significantly ($p < 0.001$) increased in all groups, but particularly in mice exposed to 200 or 312 ppm (442 or 689 mg/m³).</p> <p>Lungs There was a significant ($p < 0.001$) increase in the incidence of pulmonary neoplasms (alveolar/bronchiolar adenoma or carcinoma) in all exposed groups, particularly when the figures were adjusted to account for mortality.</p> <p>Liver The incidence of adenomas or carcinomas in the liver was significantly greater in the 200 ppm (442 mg/m³) group ($p 0.004$) than in the controls and in all exposed groups when adjusted for survival ($p < 0.01-0.05$).</p> <p>Forestomach There was a significant ($p < 0.001$) increase in the incidence of squamous cell papillomas or carcinomas of the forestomach in mice exposed to 312 or 625 ppm (689 or 1380 mg/m³) (both 13 and 26 weeks).</p> <p>Harderian gland The incidence of Harderian gland adenomas or carcinomas was significantly ($p < 0.001$) increased compared with controls in all exposed groups.</p> <p>Other tumours The incidence of adenomas or carcinomas of the preputial gland was significantly ($p < 0.001-0.003$) increased in the 312 and 625 ppm (689 or 1380 mg/m³) (13 or 26 weeks) groups.</p>	

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		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 ³) for 26 weeks (1/50, 1/50, 0/50, 2/50 and 2/50).	
Carcinogenicity	SD rats (110 of each sex per group); inhalation exposure to 0, 1000 or 8000 ppm (0, 2209 or 17 669 mg/m ³) ^b for 6 h/day, 5 days/week, for 105 weeks (females) or 11 weeks (males). Ten rats of each sex from each group were sacrificed after 52 weeks of exposure.	<p>Lowest concentration at which tumours were observed = 1000 ppm (2209 mg/m³) based on increased incidence of mammary tumours.</p> <p>Summary of effects:</p> <p>Mammary gland There was a significant increase in the incidence of tumours in females in the 1000 and 8000 ppm (2209 and 17 669 mg/m³) groups (total tumour incidence: 50%, 79% and 81%; malignant tumour incidence: 18%, 15% and 26%); mammary tumours appeared earlier in treated groups compared with controls, and most of the tumours were benign.</p> <p>Thyroid gland There was a significant concentration-related positive trend in the incidence of follicular thyroid adenoma in female rats (0%, 2% and 10%).</p> <p>Testis There was a statistically significant, concentration-related increase in Leydig cell tumours in male rats (0%, 3% and 8%), but the incidence at the highest concentration is close to historical controls (0–6%).</p>	Owen 1981; Owen et al. 1987; Owen and Glaister 1990
Developmental and reproductive toxicity	Pregnant CD-1 mice; inhalation exposure to 0, 40, 200 or 1000 ppm (0, 88, 442 or 2209 mg/m ³) ^b , 6 h/day, gestation	Developmental LOAEC (mice) = 200 ppm (88 mg/m ³) based on significant reduction in body weight of male and female fetuses (15.7%). Increased skeletal variations were also	Hackett et al. 1987

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	days 6–15	observed at 200 and 1000 ppm (442 and 2209 mg/m ³).	
Developmental and reproductive toxicity	B6C3F1 mice (70 of each sex per group; 90 of each sex at the highest concentration); inhalation exposure to 0, 6.25, 20, 62.5, 200 or 625 ppm (0, 13.8, 44.2, 138, 442 or 1380 mg/m ³) for 6 h/day, 5 days/week, for 103 weeks. Up to 10 mice of each sex from each group were sacrificed after 9 and 15 months of exposure.	<p>Reproductive LOAEC (female mice) = 6.25 ppm (13.8 mg/m³) based on significantly elevated incidence of ovarian atrophy in all exposure groups compared with controls at 103 weeks. Atrophied ovaries characteristically had no evidence of oocytes, follicles or corpora lutea. At concentrations ≥ 62.5 and ≥ 200 ppm (≥ 138 and ≥ 442 mg/m³), angiectasis and germinal epithelial hyperplasia of the ovaries were reported. Uterine atrophy developed after 9 months of exposure to concentrations ≥ 200 ppm (≥ 442 mg/m³).</p> <p>Reproductive LOAEC (male mice) = 200 ppm based on testicular atrophy observed following 2 years of exposure; higher concentrations for shorter durations also induced this effect. Testes of a majority of males were atrophic at the 9- and 15-month interim evaluations and at the end of the 2-year study.</p> <p>Note: Increased mortality rates and/or tumour development also occurred at concentrations causing gonadal atrophy.</p>	NTP 1993
Human studies (carcinogenicity)	1 Canadian and 7 U.S. polymer production plants (styrene–butadiene rubber workers); cohort study using quantitative exposure estimates for 1,3-butadiene, styrene and benzene for each worker. Cohort size = 15 000 1943–1994	<p>An excess mortality for leukemia was observed in ever-hourly workers (i.e., workers who had ever been paid on an hourly basis); 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>	Delzell et al. 1995, 1996

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		The leukemia risk increased with increasing exposure level.	

^a LOAEC, lowest-observed-adverse-effect concentration.

^b Conversion of the provided value into mg/m³ was completed using the formula: x ppm (MW)/24.45.