# Screening Assessment Petroleum Sector Stream Approach

# Heavy Fuel Oils [Stream 4]

# **Chemical Abstracts Service Registry Numbers**

64741-57-7

64741-62-4

64741-67-9

64741-81-7

64742-59-2

64742-90-1

68955-27-1

# **Environment and Climate Change Canada Health Canada**

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# **Synopsis**

The Ministers of the Environment and Climate Change and of Health have conducted a screening assessment of the following heavy fuel oils (HFOs):

CAS RN <sup>a</sup>	DSL <sup>b</sup> name
64741-57-7	Gas oils (petroleum), heavy vacuum
64741-62-4	Clarified oils (petroleum), catalytic cracked
64741-67-9	Residues (petroleum), catalytic reformer fractionators
64741-81-7	Distillates (petroleum), heavy thermal cracked
64742-59-2	Gas oils (petroleum), hydrotreated vacuum
64742-90-1	Residues (petroleum), steam-cracked
68955-27-1	Distillates (petroleum), petroleum residues vacuum

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These substances were identified as priorities for assessment as they met the categorization criteria under subsection 73(1) of the Canadian Environmental Protection Act, 1999 (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 all complex combinations of hydrocarbons.

These HFOs are considered to be of Unknown or Variable composition, Complex reaction products or Biological materials (UVCBs). HFOs are composed of aromatic, aliphatic and cycloalkane hydrocarbons, primarily in the carbon range of  $C_{20}$ – $C_{50}$ . The Stream 4 HFOs have a carbon range spanning from C<sub>10</sub>–C<sub>50</sub> and have a typical boiling point range from 160-600°C. Based on information submitted under section 71 of CEPA these substances are either consumed on-site or transported from refineries and upgraders to other industrial facilities. They are intermediate products of distillation, or residues derived from refinery distillation or cracking units, and can serve as blending stocks in final heavy fuel oil products. They have been identified for use in potash processing, and for use as viscosity adjusters in asphalt emulsion road maintenance products. Based on the results of the section 71 surveys and other sources of information, these HFOs were initially identified as ingredients in consumer products available for sale to the general population; however, further investigation showed that these products are for industrial or commercial use only in Canada.

HFOs are transported in large volumes from refinery and upgrader facilities to other industrial facilities by pipelines, ships, trains and trucks. A comparison of levels expected to cause harm to organisms with estimated exposure levels for transport operations for the years 2002 to 2012 was made. This comparison, in conjunction with the relatively low expected frequency of spills to water and soil, indicates that there is a

low risk of harm to aquatic or soil organisms associated with transport of these HFOs. An analysis of use of HFOs in potash processing and road maintenance products also found a low risk of harm to soil and/or aquatic organisms.

Considering all available lines of evidence presented in this screening assessment, there is a low risk of harm to organisms and the broader integrity of the environment from these substances. It is concluded that Stream 4 HFOs (CAS RNs 64741-57-7, 64741-62-4, 64741-67-9, 64741-81-7, 64742-59-2, 64742-90-1 and 68955-27-1) do not meet the criteria under paragraphs 64(a) or (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 effect for the initial categorization of HFO substances was carcinogenicity, based primarily on classifications by international agencies. Several skin painting studies conducted in laboratory animals resulted in the development of skin tumours following repeated dermal application of HFO substances. HFOs demonstrated genotoxicity in *in vivo* and *in vitro* assays, and exhibited reproductive and developmental effects in laboratory animals.

Exposure of the general population to Stream 4 HFOs is not expected, as consumer products containing these substances were not identified.

Based on the information presented in this screening assessment, it is concluded that Stream 4 HFOs (CAS RNs 64741-57-7, 64741-62-4, 64741-67-9, 64741-81-7, 64742-59-2, 64742-90-1 and 68955-27-1) do not meet the criteria under paragraph 64(*c*) of CEPA as they are not 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.

It is concluded that Stream 4 HFOs (CAS RNs 64741-57-7, 64741-62-4, 64741-67-9, 64741-81-7, 64742-59-2, 64742-90-1 and 68955-27-1) do not meet any of the criteria set out in section 64 of CEPA.

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# 1. Introduction

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

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

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

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

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

# 1.1 Grouping of Petroleum Substances

High-priority petroleum substances fall into nine groups of substances based on similarities in production, toxicity and physical-chemical properties (Table A.1 in

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<sup>&</sup>lt;sup>1</sup> A determination of whether one or more of the criteria of section 64 are met is based on 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 on the substances in the Chemicals Management Plan (CMP) Challenge is not relevant to, nor does it preclude, an assessment against the hazard criteria for WHMIS that are specified in the *Controlled Products Regulations* 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 in other sections of CEPA or other Acts.

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;<sup>2</sup> Stream 2: industry-restricted substances, which are substances that may leave a petroleum-sector facility and may be transported to other industrial facilities (for example, for use as a feedstock, fuel or blending component), but that do not reach the public market in the form originally acquired;

Stream 3: substances that are primarily used by industries and consumers as fuels; or

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 consumer products 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 (HFOs), low boiling point naphthas, natural gas condensates, solvents, petroleum and refinery gases (liquefied petroleum gases), base oils, petrolatum and waxes, and asphalt.

This screening assessment addresses seven HFO substances described under Chemical Abstracts Service Registry Numbers (CAS RNs) 64741-57-7, 64741-62-4, 64741-67-9, 64741-81-7, 64742-59-2, 64742-90-1 and 68955-27-1. These substances 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 PSSA because they are related to the petroleum sector and are all complex combinations of hydrocarbons. According to information submitted under section 71 of CEPA (Environment Canada 2008, 2009, 2011a), an in-depth literature review and a search of material safety data sheets (MSDS), these substances may be consumed on-site, blended into substances leaving the site under different CAS RNs, transported to other petroleum sector facilities for use as a feedstock, diluent or solvent, or used downstream in road maintenance products and potash processing. The information also indicated that these HFOs may be ingredients in consumer products available for sale to the general population; however, further investigation revealed these products to be of industrial or commercial use only.

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<sup>&</sup>lt;sup>2</sup> For the purposes of the screening assessment of PSSA substances, a site is defined as the boundaries of the property where a facility is located. In these cases, facilities are petroleum refineries, upgraders or natural gas processing facilities.

Included in this screening assessment is the consideration of information on chemical properties, health effects, uses and exposure, including information submitted under section 71 of CEPA. Data relevant to the screening assessment of these substances were identified in original literature, review and assessment documents, and in stakeholder research reports, submissions and correspondence, as well as from recent literature searches, up to October 2013 for the human exposure, ecological and health effects sections, and up to January 2014 for the ecological exposure section. Key studies were critically evaluated and modelling results were used to inform conclusions.

Characterization of risk to the environment involves consideration of data relevant to environmental behaviour, persistence, bioaccumulation and toxicity, combined with an estimation of exposure to potentially affected non-human organisms from the major sources of release to the environment. To predict the overall environmental behaviour and properties of complex substances such as these HFOs, representative structures were selected from each chemical class contained within these substances. Conclusions about the risk to the environment are based in part on estimation of environmental concentrations resulting from releases and the potential for these concentrations to have a negative impact on non-human organisms. As well, other lines of evidence, including fate, temporal/spatial presence in the environment and hazardous properties of the substances, are taken into account. The ecological portion of the screening assessment summarizes the most pertinent data on environmental behaviour and effects and does not represent an exhaustive or critical review of all available data. Environmental models and comparisons with similar petroleum substances were used in the assessment.

Characterization of risk to human health involves consideration of data relevant to estimation of exposure of the general population, as well as information on health effects (based principally on the weight-of-evidence assessments of other agencies that were used for prioritization of the substances). Health effects for Stream 4 HFOs were assessed using toxicological data pooled across the seven HFO CAS RNs due to insufficient data specific to each of the substances being evaluated in this assessment. Decisions for risk to human health are based on the nature of the critical effect and/or margins between conservative effect levels and estimates of exposure, taking into account confidence in the completeness of the identified databases on both exposure and effects, within a screening context. The screening assessment does not represent an exhaustive or critical review of all available data. Rather, it presents a summary of the pertinent and critical information upon which the conclusion is based.

This screening assessment was prepared by staff in the Existing Substances Programs at Health Canada and Environment and Climate Change Canada and incorporates input from other programs within these departments. The human health portions of this assessment have not undergone external written peer review/consultation due to similarity in content to previous HFO assessments. Previous Stream 1 and Stream 2 (site- and industry-restricted) HFO assessments, and the Stream 3 Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil assessments have undergone external peer review and consultation (Environment Canada, Health Canada 2011, 2013, 2014). 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

HFOs are complex combinations of hydrocarbons that are intermediate products of distillation, or residues derived from refinery distillation or cracking units, and can serve as blending stocks in final heavy fuel oil products with a typical carbon range of  $C_{20}$ – $C_{50}$  (CONCAWE 1998). The HFOs considered in this assessment are complex combinations of hydrocarbons composed of aromatic, aliphatic and cycloalkane hydrocarbons with carbon ranges spanning from  $C_{10}$ – $C_{50}$  and a boiling point range of 160– $600^{\circ}$ C (Table B.2 in Appendix B; CONCAWE 1998; API 2004). The ratio of aliphatic to aromatic hydrocarbons is important for estimating environmental behaviour and toxicity. This ratio was only found for three of the seven assessed CAS RNs. CAS RN 64741-62-4 contains approximately 58% aromatics and 42% non-aromatics, CAS RN 64741-57-7 contains approximately 60% aromatics and 40% non-aromatics, and CAS RN 64741-81-7 contains approximately 50% aromatics and 50% non-aromatics (API 2004).

CAS RNs 64741-57-7 and 68955-27-1 are complex combinations of hydrocarbons produced by the vacuum distillation of the residuum from the atmospheric distillation of crude oil. They have a typical carbon range of  $C_{20}$ – $C_{50}$  with a boiling point range of 350–600°C.

CAS RN 64741-62-4 is a complex combination of hydrocarbons produced as the residual fraction from distillation of the products from a catalytic cracking process. It has a typical carbon range of more than C<sub>20</sub> with a boiling point of more than 350°C.

CAS RN 64741-67-9 is a complex combination of hydrocarbons produced as the residual fraction from distillation of the product from a catalytic reforming process. It consists of predominantly aromatic hydrocarbons with carbon numbers ranging from  $C_{10}$ – $C_{25}$  with a boiling point range of 160–400°C.

CAS RN 64741-81-7 is a complex combination of hydrocarbons from the distillation of the products from a thermal cracking process. It consists predominantly of unsaturated hydrocarbons with carbon numbers predominantly in the range of  $C_{15}$ – $C_{36}$  with a boiling point range of 260–480°C.

CAS RN 64742-59-2 is a complex combination of hydrocarbons obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst. It consists of hydrocarbons having carbon numbers predominantly in the range of  $C_{13}$ – $C_{50}$  with a boiling point in the range of approximately 230–600°C.

CAS RN 64742-90-1 is a complex combination of hydrocarbons obtained as the residual fraction from the distillation of the products of a steam cracking process (including steam cracking to produce ethylene). It consists predominantly of unsaturated hydrocarbons having carbon numbers primarily greater than  $C_{14}$  with a boiling point range of 230–600°C.

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

To increase confidence in the available data set for these HFOs, a read-across approach to Fuel Oil No. 6 was used. Fuel Oil No. 6 (or Bunker C) is a specific type of residual fuel oil that is a complex mixture of high molecular weight components with a typical boiling point range of  $160-723^{\circ}$ C and carbon range between  $C_{20}-C_{50}$  (API 2004). Fuel Oil No. 6 includes aliphatic, aromatic and cycloalkane hydrocarbons. It also includes some asphaltenes and smaller amounts of heterocyclic components that include sulphur, nitrogen and/or oxygen (CONCAWE 1998). A comparison of available analytical data for two of the HFOs assessed and Fuel Oil No. 6 is presented in Table 2-1. Limited data were found for the other CAS RNs considered in this assessment.

Table 2-1. Available analytical data for two Stream 4 HFOs and Fuel Oil No. 6 (API 2004)

Endpoint	Vacuum distillate <sup>a</sup>	Cracked residual <sup>a</sup>	Fuel Oil No. 6 <sup>a,b,c</sup>
CAS RN	64741-57-7	64741-62-4	68553-00-4
Carbon range	$C_{20} - C_{50}$	Greater than C <sub>20</sub>	C <sub>20</sub> -C <sub>50</sub>
Specific gravity	0.93	1.07	0.98
Boiling point range (°C)	350–600	Greater than 350	160–723
Refractive index	1.515	Too dark	ND <sup>d</sup>
Non-aromatics (wt%)	40.03	41.7	55
Aromatics (wt%)	59.97	58.3	44

<sup>&</sup>lt;sup>a</sup> API 2004

The compositions of Fuel Oil No. 6 and the assessed HFOs are similar, thus supporting the use of a read-across approach to Fuel Oil No. 6 in the absence of further information on the composition of Stream 4 HFOs. However, Fuel Oil No. 6 contains fewer aromatics than at least CAS RNs 64741-62-4, 64741-57-7 and 64741-81-7. Fuel Oil No. 6 also likely contains a lower proportion of low boiling point components than CAS RNs 64741-67-9 and 64741-81-7. These differences may be due to differences in the crude oil from which the substances originate or the variability in the streams from which they are made (API 2011) as well as different boiling point ranges. A general hydrocarbon characterization of a Canadian Fuel Oil No. 6 sample is presented in Table 2-2.

Table 2-2. Fuel Oil No. 6 compositional data (three samples) (Fuhr 2008)

Hydrocarbon type	Range (weight %)	Average (weight %)
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<sup>&</sup>lt;sup>b</sup> Environment Canada 2010

<sup>&</sup>lt;sup>c</sup>Fuhr 2008

<sup>&</sup>lt;sup>d</sup> ND – not determined

Saturates	13–24	19.1
Alkanes	3–8	4.9
Cycloalkanes	6–9	7.4
Aromatics	35–50	43.4
Monoaromatics	4–9	5.8
Diaromatics	3–9	7.0
Three-ring aromatics	1–5	3.1
Four-ring aromatics	2–3	2.4
Five-ring aromatics	0.2–0.4	0.3
Unidentified aromatics	0.4–0.7	0.5
Aromatic sulphurs	1–2	1.3
Olefins	0-0.2	0.1
Polars	22–29	25.2
Asphaltenes	4–19	12.2
Total	100	100

As expected, aromatic hydrocarbons were predominant in the Fuel Oil No. 6 samples. The samples were also skewed toward the heavier hydrocarbons, with 64–68% of the weight having a boiling point greater than 500°C, and 2–4% of the weight with a boiling point below 200°C. These results are similar to a Fuel Oil No. 6 component analysis conducted by ATSDR (1999).

An analysis of occupational dermal exposures to various HFO substances showed the presence of different polycyclic aromatic hydrocarbon (PAH) components in two of the Stream 4 HFO substances considered in this assessment (Christopher 2011). The PAH compositions of CAS RNs 64742-90-1 and 68955-27-1 are given in Table 2-3.

Table 2-3. PAH content (mg/kg) of two Stream 4 HFO CAS RNs(Christopher 2011)

PAH compound	64742-90-1	68955-27-1
Naphthalene	5.2×10 <sup>4</sup>	less than 2
Acenaphthalene	3.3×10 <sup>3</sup>	less than 2
Acenaphthene	44	less than 2
Fluorene	4.2×10 <sup>4</sup>	less than 2
Phenanthrene	5.3×10 <sup>2</sup>	less than 2
Anthracene	9.8×10 <sup>2</sup>	less than 2
Fluoranthene	4.3×10 <sup>2</sup>	less than 2
Pyrene	$7.7 \times 10^2$	less than 2
Benz[a]anthracene	2.0×10 <sup>2</sup>	less than 2
Chrysene	2.0×10 <sup>2</sup>	less than 2
Benzo[b]fluoranthene	27	less than 2
Benzo[k]fluoranthene	less than 2	less than 2
Benzo[a]pyrene	39	less than 2

# 3. Physical and Chemical Properties

The composition and physical-chemical properties of HFOs vary depending on the sources of crude oils or bitumen and the processing steps involved, such as atmospheric distillation, cracking, vacuum distillation and reforming. A summary of experimental data on the physical-chemical properties of Stream 4 HFOs is presented in Tables 3-1 and 3-2.

Table 3-1. General experimental physical-chemical properties of Stream 4 HFOs

Property	Value	Temperature (°C)	Reference
Pour point (°C)	Less than 30	-	API 2004
Boiling point (°C)	121–600	-	API 2004
Density (kg/m <sup>3</sup> )	900–1100	20	API 2004; MSDS 2007
Vapour pressure (Pa)	282.6– 3519.6	21	Rhodes and Risher 1995
Log K <sub>oc</sub> (dimensionless)	3.0–6.7	•	Rhodes and Risher 1995
Log K <sub>ow</sub> (dimensionless)	2.7–6.0	20	API 2004
Water solubility (mg/L)	Less than 100	20	API 2004

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

Table 3-2. Physical-chemical properties of five Stream 4 HFOs<sup>a</sup>

CAS RN	Boiling range (°C)	Flash point (°C)	Density at 15°C (g/cm³)	Vapour pressure (kPa)	Self-ignition temperature (°C)	Viscosity (mm²/s)
64741-57-7	350- 600 <sup>b</sup>	165– 171	0.877– 0.933	0.100	250	35 (40°C); 15–38 (50°C)
64741-62-4	more than 350⁵	-	1.092	-	-	6.8
64741-81-7	260– 480 <sub>b</sub>	64	0.868– 0.952	0.024 (120°C) 0.063 (150°C)	378	21–57 (50°C)
64742-59-2	244– 570	100– 175	0.853– 0.907	-	-	6.5–7.0 14.5 (50°C)
68955-27-1	262 (350– 600) <sup>c</sup>	150	0.981– 1.028	-	350	111 270 (40°C)

<sup>&</sup>lt;sup>a</sup> CONCAWE 2010

<sup>&</sup>lt;sup>b</sup> CONCAWE 1998

<sup>&</sup>lt;sup>c</sup>The range 350–600°C is based on its similarity to CAS RN 64741-57-7 (API 2004)

To predict the environmental behaviour and fate of complex petroleum substances such as these HFOs, representative structures were selected from each chemical class contained within the substances. Forty-seven structures were selected from a database in PetroTox (2009) based on boiling point ranges for each HFO (Table B.3 in Appendix B), the number of data on each structure and the middle of the boiling point range of similar structures. As the compositions of most HFOs are not well defined and are indeed variable, representative structures could not be chosen based on their proportion in the mixture. This resulted in the selection of representative structures for alkanes, isoalkanes, mono- and di-cycloalkanes, polycycloalkanes, cycloalkane monoaromatics, cycloalkane diaromatics and one-, two-, three-, four-, five- and six-ring aromatics ranging from  $C_{10}$ – $C_{50}$  (Table B.3 in Appendix B). Physical-chemical data for each representative structure were assembled from scientific literature and from the group of environmental models included in the Estimation Programs Interface Suite (EPI Suite 2008) of the United States Environmental Protection Agency (US EPA) (Table B.3 in Appendix B).

It should be noted that the physical and chemical behaviour of the representative structures will differ if these substances are present in a mixture, such as the HFOs. The vapour pressures of components of a mixture will be lower than their individual vapour pressures due to Raoult's Law (the total vapour pressure of an ideal mixture is proportional to the sum of the vapour pressures of the mole fractions of each individual component). Similar to Raoult's Law, the water solubilities of components in a mixture are lower than when they are present individually (Banerjee 1984). Concurrently, however, when part of a mixture, components that are normally solid under environmental conditions may have lower melting points (and therefore be in a liquid state) as well as increased vapour pressure and water solubility (Banerjee 1984).

The theoretical vapour pressures of individual components comprising HFOs are low to moderate due to their high molecular weights. However, the actual vapour pressures will be influenced by the composition of the HFO mixture in which they occur. Water solubilities of all HFOs are low, and octanol—water partition coefficient estimations vary considerably.

# 4. Sources

These HFOs are produced in refineries and upgraders in Canada, in addition to being imported into Canada (Tables 4-1 and 4-2). Information collected through the *Notice with respect to certain high priority petroleum substances* (Environment Canada 2008), the *Notice with respect to potentially industry-limited high priority petroleum substances* (Environment Canada 2009), and the *Notice with respect to certain high priority petroleum substances on the* Domestic Substances List (Environment Canada 2011a), published under section 71 of CEPA, indicated that these substances are intermediate streams consumed within a facility or are either transported off-site by truck, pipeline, ship and rail car for use as a feedstock in other industrial facilities, or for disposal.

Table 4-1. Manufactured quantities of HFOs in Canada in 2006 (Environment Canada 2009)

CAS RN	Manufacture quantity
64741-57-7	Over 10 000 000 kg
64741-62-4	Over 10 000 000 kg
64741-67-9	10 000 to 1 000 000 kg
64741-81-7	Over 10 000 000 kg
64742-59-2	Over 10 000 000 kg
64742-90-1	1 000 000 to 10 000 000 kg
68955-27-1	Over 10 000 000 kg

Table 4-2. Manufacturing, use and transportation quantities of HFOs reported in Canada in 2010 (Environment Canada 2011a)

CAS RN	Manufacture, use and transportation quantities			
64741-57-7	Over 10 000 000 kg			
64741-62-4	Over 10 000 000 kg			
64741-67-9	1000 to 10 000 kg			
64741-81-7	1 000 000 to 10 000 000 kg			
64742-59-2	Over 10 000 000 kg			
64742-90-1	No data reported			
68955-27-1	Over 10 000 000 kg			

Outside of Canada, all of these HFOs have been identified by the Organisation for Economic Co-operation and Development (OECD) as high production volume (HPV) chemicals, with 1000 tonnes or more produced per year (OECD 2004). In addition, the US EPA has also identified these HFO components as HPV chemicals (API 2004,

2011). HPV chemicals in the US are produced or imported in quantities of 1 million pounds or more per year (API 2004).

In the European Union (EU), five of these HFOs have been identified as HPV chemicals (substances produced or imported in volumes of more than 1000 tonnes per year) (ECHA 2013). However, CAS 64741-67-9 (Residues (petroleum), catalytic reformer fractionator) has been identified as a low production volume (LPV) chemical (produced or imported in volumes of 10–1000 tonnes per year) (ECHA 2013). CAS 64742-59-2 (Gas oils (petroleum), hydro treated vacuum) was not reported as a HPV or LPV chemical in the EU.

## 5. Uses

According to information collected through the *Notice with respect to certain high priority* petroleum substances (Environment Canada 2008) and the *Notice with respect to* potentially industry-limited high priority petroleum substances (Environment Canada 2009), these HFOs were initially identified as ingredients in consumer products intended for use by the general population. However, updated information collected through the *Notice with respect to certain high priority petroleum substances on the* Domestic Substances List (Environment Canada 2011a) showed these products to be for industrial or commercial use only. Industrial/commercial uses include their use as floatation oil in potash production, as a viscosity adjustor (i.e., diluents and solvents) in various applications, and as a component in road maintenance products. Other industrial uses were identified as being confidential business information.

A Health Canada contract report, which involved conducting a search of consumer product MSDS for these HFOs, also indicated that these substances were present in consumer products (Cheminfo 2011). HFOs were identified to be present in three product types: paints and coatings, sealants and adhesives, and printer ink. However, updated information from industry showed these products were discontinued, reformulated, not available in Canada and/or limited to commercial or industrial use. Accordingly, these HFO substances are not expected to contribute to releases to environmental media and exposure to the general population.

The information on the seven CAS RNs submitted under the *Notice with respect to certain high priority petroleum substances on the* Domestic Substances List (Environment Canada 2011a) reveals use patterns consistent with previous HFO assessments, including their use in industrial fuels. Additional uses identified include a solids separation agent in muriate of potash production and in road maintenance products. Site-restricted and industry-restricted uses, scenarios and potentials for exposure have been considered in the Stream 1 and Stream 2 HFO assessments (Environment Canada, Health Canada 2011, 2013) and are applicable to the substances under consideration in this assessment. In addition, exposure scenarios were developed for commercial applications of potash and road maintenance products which contain Stream 4 HFOs.

There are no registered uses of these heavy fuel oil components in pesticides in Canada (PMRA 2010, personal communication).

HFOs have been identified as being used in hydraulic fracturing fluids. CAS RN 64741-67-9 has been reported to be used as a component in hydraulic fracturing fluids used in Canada (FracFocus 2013) and in the United States (US House of Representatives 2011) for developing and unlocking natural gas supplies in shale and other unconventional oil and gas formations.

# 6. Releases to the Environment

These HFOs may be released to the environment from activities associated with production, transportation and storage, as well as from commercial or industrial use.

Fugitive releases of these HFOs were assumed to follow the same pattern as found for industry-restricted HFOs (Environment Canada, Health Canada 2013). Details on potential releases of HFOs within facilities from activities associated with processing these substances can be found in the previous assessment. There is the potential for release of HFOs to the environment through the application of potash to land or the use of road maintenance products containing HFOs. HFOs may be used in the production of potash through use as floatation oil, and trace amounts may remain in potash prior to application on agricultural soils as a commercial fertilizer. HFOs are also used to adjust the viscosity of the asphalt binder in asphalt emulsion road maintenance products that are used as dust palliatives or in cold mix surfacing and pothole patching (personal communication, email communication, December 12, 2013, from Pounder Emulsions, Division of Husky Oil Limited, to Ecological Assessment Division, Environment Canada). HFOs may be washed off of roads treated with these products and deposited onto soil adjacent to the road or into roadside surface water.

These HFOs are transported between facilities by pipeline, ship, rail or truck. In general, three operating procedures are involved in the process of transportation: loading, transit and unloading.

The handling of HFOs at petroleum facilities for the purpose of transportation is regulated at both the federal and the provincial levels, with measures covering loading and unloading (SENES 2009). Collectively, these measures establish requirements for the safe handling of petroleum substances and are intended to minimize or prevent potential releases during loading, transport and unloading (SENES 2009).

Releases from washing or cleaning transportation vessels are not considered in this screening assessment, as tanks or containers for transferring petroleum substances are typically dedicated vessels and, therefore, washing or cleaning is not required on a routine basis (US EPA 2008b). Cleaning facilities require processing of greywater to meet local and provincial release standards.

#### 6.1 Release Estimation

With the transport of these substances by ship, train, pipeline or truck, unintentional releases of HFOs will generally enter the air, water or soil depending on the modes of transportation involved. Unintentional spills or leaks during the handling and transit processes were considered in this screening assessment for the potential to cause ecological harm. Due to the low volatility of these HFOs as defined by their physical-chemical properties, evaporative emissions into the air from unintentional spills

would occur in a lower proportion compared to the proportions entering water and/or soil.

Potential releases associated with the transport of HFOs were assessed through an analysis of historical spill data (2002–2012) from Environment Canada's National Enforcement Management Information System and Intelligence System (NEMISIS) database (Environment Canada 2013a). NEMISIS provides national data on releases of substances involving or affecting a federal agency or department, a federal government facility or undertaking, or Aboriginal land; releases that contravene CEPA or the *Fisheries Act*; releases that affect fish, migratory birds or species at risk or that impact an interprovincial or international boundary; and any releases from marine vessels. Other spills may be reported to NEMISIS, but there is no legal requirement to do so. In addition, spills data provided to NEMISIS may vary depending on the provincial reporting requirements, such as spill quantity reporting thresholds.

As there is no spill category for HFOs in general, spills listed as Bunker C fuel oil were used. Releases labelled as Bunker C fuel oil (Fuel Oil No. 6) would also include these Stream 4 HFOs. Many of these releases were generically labelled as "Bunker," and there was no indication as to what specific type of Bunker was released. Thus, all releases labelled as "Bunker" were considered to be Bunker C fuel oil. Bunker C is considered to be a heavy fuel oil and has a wider distribution and volume compared to Stream 4 HFOs. Thus, it is expected that the actual number and volume of Stream 4 HFO spills are considerably lower than those of Bunker C fuel oil spills, but this could not be reliably determined. Of note was the large-volume spill of 734 000 L in 2005. which is known to be a Bunker C fuel oil spill into Lake Wabamun, Alberta; it was not included in the release estimate, as it was definitively known not to be a Stream 4 HFO substance. As well, spills were removed if they were part of environmental emergency training exercises (Environment Canada 2013a). Spills where collisions, poor road conditions and/or adverse weather-related events were listed as a source, reason or cause of spill were not included in the release estimate. Spills to soil within the boundaries of industrial facilities (e.g., refineries and bulk storage terminals) were also not considered within this analysis, as it is expected that spills at these sites undergo immediate remediation that minimizes their entry into the environment. Spills were removed if the notes indicated that no volume was found entering the environment (e.g., spill containment).

Many of the individual reports had no estimate of the volume released into the environment. In order to account for the underestimation of the volume released, the estimated total volumes were extrapolated by assuming that the distribution of reported volumes released was representative of all releases (Table C.1 in Appendix C). From 2002–2012, the extrapolated total volume of spills of HFOs to all media (soil, saltwater and freshwater) was 0.9 million litres from 225 spills (Table C.1 in Appendix C).

The historical spill data were also separated based on the specific compartment affected, so that the estimated average release quantity per spill to each compartment could be determined. Within each compartment, a similar extrapolation was conducted

to account for reported spills with no associated volumes. The estimated average quantities of these HFOs released per spill to freshwater and saltwater are shown in Table 6-1. There is no distinction in the database as to whether the spills occurred during loading, transport or unloading. Thus, the average spill volume was used for each of the scenarios.

Table 6-1. Average release quantities per spill of HFOs to various compartments (kg/spill and L/spill) based on historical Bunker C spill data, 2002–2012 (Environment Canada 2013)

Average release quantities per spilla

Compartment affected	Mass (kg) <sup>b</sup>	Volume (L)	Number of spills
Marine (saltwater)	914	933	76
Freshwater	11 513	11 748	50
Soil	5502	5614	76

Median release quantities per spill<sup>a</sup>

Compartment affected	Mass (kg) <sup>b</sup>	Volume (L)	Number of spills
Marine (saltwater)	25	25	76
Freshwater	112	114	50
Soil	353	360	76

<sup>&</sup>lt;sup>a</sup> Average and median releases of HFOs to each compartment were determined by separating all HFO releases from 2002–2012 into specific compartments (marine, freshwater and soil), determining the extrapolated total released within each compartment (Table C.1 in Appendix C), and then dividing this extrapolated total by the total number of spills affecting that compartment.

The majority of spills of HFO documented by Environment Canada from 2002–2012 affected land (76 incidents), saltwater (76 incidents), and freshwater (50 incidents). For some reported spills, the compartment affected was not documented, whereas for others, multiple compartments were included; thus, this total does not equate to the total reported spills shown in Table C.1 (Appendix C). These numbers are considered to be a low estimate of actual releases due to the limitations in reporting to NEMISIS. Releases to groundwater were not included in the analysis due to insufficient information.

The NEMISIS database provides three columns of data (sources, causes and reasons) for many releases of Bunker C fuel oil. The data in these columns were analyzed to determine how and why the majority of HFO releases occur (Tables C.2a–c in Appendix C).

The industrial areas where the majority of HFO releases occurred (Table C.2a in Appendix C) were other watercraft (34% of the volume), pipelines (33% of the volume) and other, unspecified sources (13% of the volume). Releases at industrial plants and storage facilities accounted for about 10% of the volume, tank trucks accounted for 6%, and refineries accounted for 2%. Other transportation-related sources, each accounting

Determined based on an average density of 0.98 kg/L (Table 3-2).

for less than 1% of releases, included trains, transport trucks, marine tankers, cargo vessels, barges and bulk carriers. The remaining releases were from marine terminals, home heating tanks or electrical equipment, or at production fields.

The NEMISIS data were also analyzed for causes of HFO leaks (Table C.2b in Appendix C). It was found that pipe leaks accounted for 21% of the volume released, which is consistent with pipelines being a major source of release, as noted in Table C.2a. Leaks from containers, tanks and valves accounted for 15% of the volume released, while overflow of tanks, presumably during loading and unloading, accounted for 12%. Discharge accounted for 8% of the total volume, while sinking and grounding of vessels accounted for 2%, and overturn and derailment accounted for 1%. Thirty-eight percent of the volume spilled was due to unknown or otherwise unspecified causes. The remaining causes were well blowouts and process upset.

Analyzing reasons for releases, the data (Table C.2c in Appendix C) identified equipment failure as a major cause of releases, accounting for 43% of the volume released. Unknown reasons accounted for 38% of the volume, human error and negligence accounted for 9%, and material failure accounted for 5%. The remaining 5% was divided among a wide variety of other reasons.

For purposes of assessing the potential exposure of the environment from transport of HFOs, the ecological assessment focuses on unintentional releases to water and soil due to spills, and considers exposure due to dust suppressants and potash to soil. In comparison, assessment of potential exposure of the general population from transport of HFOs focuses on evaporative emission, which occurs during regular operation activities. Although spills occur during transit and in loading or unloading operations, such releases are considered to occur on a non-routine or unpredictable basis in distinct locations and are therefore not considered in the assessment of exposure of the general population.

## 7. Environmental Fate

When petroleum substances are released into the environment, four major fate processes will take place: dissolution in water, volatilization, biodegradation and adsorption. These processes will cause changes in the composition of these UVCB substances. In the case of spills on land or water surfaces, photodegradation—another fate process—can also be significant.

As noted previously, the solubility and vapour pressure of components within a mixture will differ from those of the component alone. These interactions are complex for complex UVCBs such as petroleum hydrocarbons.

Each of the fate processes affects hydrocarbon families differently. Aromatics tend to be more water-soluble than aliphatics of the same carbon number, whereas aliphatics tend to be more volatile (Potter and Simmons 1998). Thus, when a petroleum mixture is released into the environment, the principal water contaminants are likely to be aromatics, whereas aliphatics will be the principal air contaminants (Potter and Simmons 1998). The volatilities of alkenes and alkanes are similar and they are more volatile than aromatics and cycloalkanes. Aromatics and cycloalkanes have similar volatility. The most soluble and volatile components have the lowest molecular weight; thus, there is a general shift to higher molecular weight components in residual materials. Following an initial loss due to volatilization and solubilization, the remaining degradative pathway is biodegradation, usually by bacteria.

Biodegradation is almost always operative when petroleum mixtures are released into the environment. It has been widely demonstrated that nearly all soils and sediments have populations of bacteria and other organisms capable of degrading petroleum hydrocarbons (Pancirov and Brown 1975). Degradation occurs both in the presence and absence of oxygen. Two key factors that determine degradation rates are oxygen supply and molecular structure. In general, degradation is more rapid under aerobic conditions. Decreasing trends in degradation rates according to structure are as follows (Potter and Simons 1998):

- (1) *n*-alkanes, especially in the  $C_{10}$ – $C_{25}$  range which are degraded readily:
- (2) isoalkanes;
- (3) alkenes:
- (4) benzene, toluene, ethylbenzene and xylenes (BTEX) (when present in concentrations that are not toxic to microorganisms);
- (5) monoaromatics;
- (6) polynuclear (polycyclic) aromatic hydrocarbons (PAHs); and
- (7) higher molecular weight cycloalkanes (which may degrade very slowly (Pancirov and Brown 1975)).

Three weathering processes—dissolution in water, volatilization and biodegradation—typically result in the depletion of the more readily soluble, volatile and degradable

compounds and the accumulation of those most resistant to these processes in residues.

No empirical data on the environmental fate of Stream 4 HFOs were found. Due to the complex interaction of components within a mixture that impact their physical-chemical properties and behaviour, it is difficult to predict the fate of a complex mixture. Therefore, as a general indication of the fate of these HFOs, the physical-chemical properties of representative structures (Table B.3 in Appendix B) were examined.

Based on the vapour pressure of the representative structures of HFOs, it is expected that, if released to air, components less than  $C_{20}$  are likely to remain in air, while the heavier structures will partition out of air.

If released to water, based on their aqueous solubility, most  $C_{10}$ – $C_{12}$  components will remain in water. The components greater than  $C_{12}$  will typically settle in the sediment due to low aqueous solubilities and high log  $K_{oc}$ . Volatilization from water surfaces is not expected to be an important fate process despite the presence of some representative structures with moderate to very high estimated Henry's Law constants. The tendencies for evaporation and sorption are competing and the exact nature of the release would dictate how the HFO behaves.

If released to soil, most representative structures of HFOs are expected to sorb to soil due to their high log  $K_{oc}$  (3.2 to 14; Table B.3 in Appendix B). Competing with this tendency are evaporative forces. Some of the smaller structures, such as decane (a  $C_{10}$  hydrocarbon), might volatize into the air due to their high vapour pressures. Volatilization from moist soil surfaces may be an important fate process based on estimated Henry's Law constant values of  $5 \times 10^{-5}$  to  $2 \times 10^{9}$  Pa·m³/mol. Lower molecular weight representative structures of HFOs ( $C_{10}$ – $C_{11}$  alkanes, isoalkanes, cycloalkanes and monoaromatics) may slightly to substantially volatilize from dry soil surfaces based on their moderate vapour pressures.

When large quantities of a hydrocarbon mixture enter the soil compartment, soil organic matter and other sorption sites in soil are fully saturated and the hydrocarbons will begin to form a separate phase (a non-aqueous phase liquid or NAPL) in the soil. At concentrations below the retention capacity for the hydrocarbon in the soil, the NAPL will be immobile (Arthurs et al. 1995); this is referred to as residual NAPL (Brost and DeVaull 2000). Above the retention capacity, the NAPL becomes mobile and will move within the soil (Arthurs et al. 1995; Brost and DeVaull 2000).

# 8. Persistence and Bioaccumulation

Due to the complex nature of petroleum substances such as HFOs, the persistence and bioaccumulation potential of components of these substances is characterized based on empirical and/or modelled data for a suite of petroleum hydrocarbons structures.

#### 8.1 Environmental Persistence

Persistence was characterized based on empirical and/or modelled data for a suite of petroleum hydrocarbons expected to occur in petroleum substances.

Model results and the weighing of information are reported in the supporting documentation on petroleum substance persistence and bioaccumulation (Environment Canada 2014). These data are summarized in Table D.2 (Appendix D).

Empirical and modelled half-lives in the atmosphere for many components of these HFOs are less than two days (Environment Canada 2014). However, some components, such as the C<sub>13</sub> cycloalkane diaromatics, can have half-lives greater than two days; they are thus considered persistent in air and may therefore undergo long-range transport. In addition, a number of three- to six-ring PAHs can undergo long-range transport to remote regions due to sorption to particulate matter (Environment Canada 2014).

Considering biodegradation in water, soil and sediment, the following components are expected to have half-lives greater than 6 months in water and soils and greater than 1 year in sediments:  $C_{30}$  isoalkanes,  $C_{50}$  monocycloalkanes,  $C_{15}$ – $C_{50}$  dicycloalkanes,  $C_{18}$ – $C_{22}$  polycycloalkanes,  $C_{12}$  monoaromatics,  $C_{10}$ – $C_{20}$  cycloalkane monoaromatics,  $C_{10}$ – $C_{50}$  diaromatics,  $C_{12}$  cycloalkane diaromatics,  $C_{14}$ , and  $C_{30}$ – $C_{50}$  three-ring aromatics,  $C_{16}$ – $C_{20}$  four-ring aromatics,  $C_{20}$ – $C_{30}$  five-ring aromatics and  $C_{22}$  six-ring aromatics. The  $C_{30}$  monocycloalkanes,  $C_{12}$ dicycloalkanes,  $C_{14}$ polycycloalkanes, and  $C_{11}$ ,  $C_{15}$ , and  $C_{30}$ – $C_{50}$  monoaromatics have half-lives greater than 1 year in sediments (Table D.2 in Appendix D).

#### 8.2 Potential for Bioaccumulation

Bioaccumulation potential was characterized based on empirical and/or modelled data for a suite of petroleum hydrocarbons expected to occur in petroleum substances. Bioaccumulation factors (BAFs) are the preferred metric for assessing the bioaccumulation potential of substances, as the bioconcentration factor (BCF) may not adequately account for the bioaccumulation potential of substances via the diet, which predominates for substances with log K<sub>ow</sub> greater than approximately 4.5 (Arnot and Gobas 2003).

In addition to fish BCF and BAF data, bioaccumulation data for aquatic invertebrate species were also considered. Biota-sediment/soil accumulation factors (BSAFs),

trophic magnification factors and biomagnification factors were also considered in characterizing bioaccumulation potential.

Empirical and modelled bioaccumulation data for petroleum hydrocarbons, as well as the weighing of information, can be found in the supporting document (Environment Canada 2014). A summary of the results for bioaccumulation potential is presented below and in Table D.3 (Appendix D).

Overall, there is consistent empirical and predicted evidence to suggest that the following components have the potential for high bioaccumulation with BAF/BCF values greater than 5000: C<sub>13</sub>–C<sub>15</sub> isoalkanes, C<sub>12</sub>–C<sub>15</sub> monocycloalkanes, C<sub>12</sub> and C<sub>15</sub> dicycloalkanes, C<sub>14</sub> and C<sub>22</sub> polycycloalkanes, C<sub>15</sub> monoaromatics, C<sub>15</sub>–C<sub>20</sub> cycloalkane monoaromatics, C<sub>12</sub>-C<sub>13</sub> diaromatics, C<sub>20</sub> cycloalkane diaromatics, C<sub>14</sub> and C<sub>20</sub> threering aromatics, C<sub>16</sub>–C<sub>20</sub> four-ring aromatics, C<sub>20</sub>–C<sub>22</sub> five-ring aromatics, and C<sub>22</sub> six-ring aromatics. These components are associated with a slow rate of metabolism and are highly lipophilic. Exposures from water and diet, when combined, suggest that the rate of uptake would exceed that of the total elimination rate. Most of these components are not expected to biomagnify in aquatic or terrestrial food webs, largely because a combination of metabolism, low dietary assimilation efficiency and growth dilution allows the elimination rate to exceed the uptake rate from the diet (Environment Canada 2014); however, one study (Harris et al. 2011) suggests that some alkyl-PAHs may biomagnify. While only BSAFs were found for some PAHs, it is possible that BSAFs will be greater than 1 for invertebrates, given that they do not have the same metabolic competency as fish. BSAFs will likely decrease beyond C<sub>22</sub> due to reduced bioavailability of the higher boiling point fractions (Muijs and Jonker 2010).

# 9. Potential to Cause Ecological Harm

Toxicity data have been reviewed in previous assessments of site- and industry-restricted HFOs and HFO fuels and are summarized in Environment Canada, Health Canada (2011, 2013, 2014). The following values were chosen for toxicity endpoints.

# 9.1 Ecological Effects Assessment

## 9.1.1 Aquatic compartment

No experimental data were available for the aquatic toxicity of these Stream 4 HFOs; therefore, data from Fuel Oil No. 6 were used in a read-across approach to estimate the potential for aquatic toxicity (Environment Canada, Health Canada 2013b). Other studies have shown that, with HFOs, variations in aquatic toxicity exist in part due to differences in boiling point ranges determining the composition of the HFOs (ECB 2000a). For marine scenarios, a critical toxicity value (CTV) of 0.9 mg/L is selected based on the 48-hour acute LC<sub>50</sub> value with *Mysidopsis almyra* (Neff and Anderson 1981). For freshwater exposure scenarios for ship loading/unloading and transport, the selected CTV is the 96-hour acute EC<sub>50</sub> (immobilization) of 4.1 mg/L with *Daphnia magna* (MacLean and Doe 1989).

#### 9.1.2 Avian effects

HFOs can be toxic to aquatic birds through ingestion (CONCAWE 1998; Environment Canada 2011b; Michigan 2010), contact with feathers (Environment Canada 2011b) and contact with eggs (Albers and Szaro 1978; Coon et al. 1979; CONCAWE 1998). More detailed information is provided in Environment Canada (2011b).

# 9.1.3 Terrestrial compartment

The Canada-Wide Standards for Petroleum Hydrocarbons in Soil (CCME 2008) were used as a data source for effects of HFOs on terrestrial ecosystems. These standards were developed based on consideration of four fractions of total petroleum hydrocarbons (TPHs): Fraction 1 (F1;  $C_6$ – $C_{10}$ ), Fraction 2 (F2; greater than  $C_{10}$ – $C_{16}$ ), Fraction 3 (F3; greater than  $C_{16}$ – $C_{34}$ ) and Fraction 4 (F4; greater than  $C_{34}$ ). Depending on the HFO, the carbon ranges may cover both F2 and F3 (e.g., CAS RN 64741-67-9 which is  $C_{10}$ – $C_{25}$ ), or both F3 and F4. Standards were developed for four land-use classes (agricultural, residential, commercial and industrial) and two soil types (coarse grained and fine grained), and assumed a 20:80 ratio of aromatics to aliphatics. The land-use and soil type with the lowest standard is typically agricultural/residential/grassland coarse-grained soils. The standards for soil contact by non-human organisms for agricultural coarse-grained soils are 150, 300 and 2800 mg/kg dw for F2, F3 and F4, respectively (CCME 2008). As most HFOs are mainly

F3 and F4 and there are no soil exposure scenarios specific to CAS RN 64741-67-9, the standard of 300 mg/kg dw will be used for HFOs in general.

# 9.2 Ecological Exposure Assessment

## 9.2.1 Aquatic

To determine the predicted environmental concentration (PEC) arising from ship transport, the volume of water predicted to be in contact with spilled oil was determined using a study conducted by the Risk Management Research Institute (RMRI) (2007). This work was originally developed for crude oil but can be applied to HFOs, as they have a similar density. The area of a slick created within Hazard Zones around Newfoundland was estimated for specific volume ranges of oil using ocean spill dispersion models. The volume of contacted water was then estimated by multiplying the area by 10 to represent the top 10 metres of water. This becomes a conservative estimate, as it assumes that all of the water is equally contacted by the petroleum substances spilled.

For loading and unloading scenarios for ships, the volume of water in contact with oil from Hazard Zone 1 was used, as this region includes loading and unloading operations at Whiffen Head and the Come-by-Chance refinery. For ship transport scenarios, the estimated volume of water in contact with HFOs is the volume of water averaged over Hazard Zones 2 to 5 (the average volume of water for summer and winter for Hazard Zone 2 was used in this calculation). Density of Stream 4 HFOs varied considerably from 0.85 to 1.1 g/cm³ (Table 3-2); therefore, an average density of 0.98 kg/L was chosen to represent all Stream 4 HFOs. However, some Stream 4 HFOs will have lower densities and thus be in contact with less water, while some will have higher densities and be in contact with more water.

In the case of loading and unloading of HFOs by ship in marine water, an estimated median volume of 25 L of HFOs are released in one event (Table 5). At an average density of 0.98kg/L (Environment Canada 2010), this is equivalent to 0.2 barrels of HFOs and is therefore expected to be in contact with  $6\times10^{10}$  L of water (Table D.1 in Appendix D). This volume is estimated from the enclosed waters found at wharves and loading terminals. The resulting concentration in water would be 0.0004 mg/L ( $2.5\times10^7$  mg /  $6\times10^{10}$  L), which is considered the marine PEC for ship loading and unloading.

In the case of transport of HFOs by ship in marine water, an estimated median volume of 25 L of HFOs are released in one event (Table 5). At an average density of 0.98 kg/L (Environment Canada 2010), this is equivalent to 0.2 barrels of HFOs and is therefore expected to be in contact with  $5.8\times10^{12}$  L of water (Table D.1 in Appendix D). The resulting concentration in water would be  $4.3\times10^{-6}$  mg/L ( $2.5\times10^{7}$  mg /  $5.8\times10^{12}$  L), which is considered the marine PEC for ship transport.

In the case of loading and unloading of HFOs by ship in freshwater, an estimated median volume of 114 L of HFOs are released in one event (Table 5). At an average

density of 0.98 kg/L (Environment Canada 2010), this is equivalent to 0.7 barrels of HFOs and is therefore expected to be in contact with  $6\times10^{10}$  L of water (Table D.1in Appendix D). This volume is estimated from the enclosed waters found at wharves and loading terminals. The resulting concentration in water would be 0.002 mg/L  $(1.1\times10^8$  mg /  $6\times10^{10}$  L), which is considered the freshwater PEC for ship loading and unloading.

In the case of transport of HFOs by ship in freshwater, an estimated median volume of 114 L of HFOs are released in one event (Table 5). At an average density of 0.98 kg/L (Environment Canada 2010), this is equivalent to 0.7 barrels of HFOs and is therefore expected to be in contact with  $5.8\times10^{12}$  L of water (Table D.1in Appendix D). The resulting concentration in water would be  $1.9\times10^{-5}$  mg/L ( $1.1\times10^{8}$  mg /  $5.8\times10^{12}$  L), which is considered the freshwater PEC for ship transport.

HFOs can be used to adjust the viscosity of the asphalt binder in asphalt emulsion road maintenance products, such as dust palliatives used on gravel or dirt roads, and in cold mix asphalt emulsions used for the surfacing of some roads and pothole repair. Only one CAS RN from Stream 4 HFOs, CAS RN 68955-27-1, was identified as being present in these road maintenance products (Environment Canada 2011a); however, it is acknowledged that other HFOs could be used in the dust palliative (personal communication, email communication, December 12, 2013, from Pounder Emulsions, Division of Husky Oil Limited, to Ecological Assessment Division, Environment Canada) and presumably in the cold mix asphalt emulsion as well.

It is possible that HFOs, or components of HFOs, used in asphalt emulsion road maintenance products might be washed from roadways treated with these products into surface water (e.g., ditches and nearby streams) or onto soil adjacent to treated roads. Studies indicate that this occurs with oil-based products. For example, a previous assessment of used crankcase oil found that use of such oil as a dust palliative on roads posed a risk to aquatic environments (Environment Canada 2005). Additionally, Metzler et al. (1984) reviewed studies on the impact to the environment of using waste oils as dust palliatives, and modelled runoff from treated roads. It was concluded that there might be a risk due to significant runoff of oil components (e.g., heavy metals and PAHs) during heavy rainfalls following the application of oil (Metzler et al. 1984), as the majority of runoff from treated roads is expected to occur during the first few rainfall events following oil application (Freestone 1972). Later runoff contains lower levels of oil (Freestone 1972).

The studies by Environment Canada (2005) and Metzler et al. (1984) were on used or waste oil-based products (e.g., lubricating oils), which are sprayed onto roads, and not asphalt emulsions that contain HFOs. This is an important distinction because oil-based sprays are different in chemical composition and function than the asphalt emulsions containing HFOs. The HFOs will dissolve into the asphalt, a highly viscous petroleum fraction containing very high molecular weight components, which may impede the loss of HFO components. Leaching studies with asphalt indicate a very low release of PAHs, with most below detection limit (Kriech 1990, Brandt and De Groot 2001,Legret et al. 2005). Unlike oil-based sprays, which are applied 1–3 times per year to a road due to

loss of the product with time (Metzler et al. 1984), the asphalt emulsion products are applied much less frequently. The asphalt emulsion dust palliative identified as containing HFO requires re-application only once every 4–6 years (personal communication, email communication, December 12, 2013, from Pounder Emulsions, Division of Husky Oil Limited, to Ecological Assessment Division, Environment Canada), while asphalt emulsion containing HFO used for cold mix surfacing is only applied once to a road, with patch repairs made as needed thereafter (personal communication, January 8, 2014, telephone conversation between Pounder Emulsions, Division of Husky Oil Limited, and Ecological Assessment Division, Environment Canada). The loss of material from the asphalt emulsion is less frequent and likely much lower than that from oil-based products.

#### 9.2.2 Terrestrial

Stream 4 HFOs are also used as floatation oils in the production of potash. Trace amounts of HFOs may remain in potash prior to its application to agricultural soils as a commercial fertilizer. The concentration of HFOs in potash products is estimated between 0.001 and 0.1%, with the high-end concentration value used for a conservative estimate. An estimate was made of the concentration of HFOs in soil after 50 years of application of potash, assuming no degradation or loss of HFO (Environment Canada 2013b), which resulted in a PEC<sub>soil</sub> for this scenario of 0.4 mg/kg dw.

The majority of HFO spills from 2002–2012 that affect soil occur at refineries (17 spills), at storage facilities (15 spills) or from other, unknown sources (23 spills). Of the unknown sources, the majority of these appear to be linked with storage tanks or vehicle overflow. It was assumed that spills that occurred at refineries and storage facilities are subject to some degree of containment and rapid remediation that minimizes their entry into the environment. Of the remaining 21 spills, 9 are from trucks or other motor vehicles, 7 are from pipelines, 3 are from watercraft and 2 are from trains. It is thus estimated that there will be ≤ 1 release event per year in total for truck loading, unloading and transport, and approximately 1 release event per year in total for truck loading, unloading and transport based on historical release information from the NEMISIS database (2002–2012; Environment Canada 2013a). For pipeline transport of these HFOs, it is expected that there would be approximately one release event per year based on historical release information from the NEMISIS database (2002–2012; Environment Canada 2013a).

#### 9.2.3 Air

Releases to air were not considered in the ecological portion of this assessment, as the volatility of HFO components greater than  $C_{20}$  is low. A headspace analysis and microextraction procedure using a ratio of 50 mL oil per litre of water (1:20) determined that Bunker C contributed very little, if any, volatile material to the water soluble fraction (0 mg/L for headspace extraction and 1.7 mg/L for microextraction) (Murray et al. 1984). Similar results are expected for the HFOs in this assessment. Thus, the concentrations of volatile components expected to be lost to the atmosphere are small.

# 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. For each endpoint organism, an estimate of the potential to cause adverse effects and a predicted no-effect concentration (PNEC) was determined. Also, a PEC was determined from the aquatic exposure scenario. The PNEC is the critical toxicity value (CTV) for the organism of interest divided by an appropriate assessment factor. A risk quotient (RQ = PEC/PNEC) was calculated for each endpoint organism and is an important line of evidence in evaluating the potential risk to the environment. From this, a minimum spill volume required to obtain a risk quotient of one was also determined in order to evaluate the number of spills that might exceed that threshold in a given year.

For HFOs, the PNEC for freshwater scenarios was determined based on the CTV, which is a 96-hour acute  $EC_{50}$  (immobilization) of 4.1 mg/L Fuel Oil No. 6 for *Daphnia magna*. An assessment factor of 10 was applied to the CTV to account for laboratory-to-field extrapolations and inter- and intra-species variability, resulting in a freshwater PNEC of 0.4 mg/L. For the marine scenarios, the PNEC was determined based on the 48-hour acute  $LC_{50}$  value of 0.9 mg/L Fuel Oil No. 6 for *Mysidopsis almyra*. An assessment factor of 10 was applied to the CTV to account for laboratory-to-field extrapolations and inter- and intra-species variability, resulting in a marine PNEC of 0.09 mg/L.

Table 9-1 is the summary of the risk quotients for Stream 4 HFOs.

Table 9-1. Risk quotients calculated for aquatic transport of Stream 4 HFOs

Compartment affected	Organism	PEC	СТУ	Assess- ment factor	PNEC	Risk quotient
Freshwater (loading/ unloading)	Daphnia magna	0.002 mg/L	4.1 mg/L	10	0.4 mg/L	0.005
Freshwater (transport)	Daphnia magna	1.9×10 <sup>-5</sup> mg/L	4.1 mg/L	10	0.4 mg/L	4.8×10 <sup>-5</sup>
Marine (loading/ unloading)	Mysidopsis almyra	0.0004 mg/L	0.9 mg/L	10	0.09 mg/L	0.004
Marine (transport)	Mysidopsis almyra	4.3×10 <sup>-6</sup> mg/L	0.9 mg/L	10	0.09 mg/L	4.8×10 <sup>-5</sup>

For all aquatic spill scenarios, the critical spill volume for HFOs required to create harmful conditions to aquatic organisms (i.e., to obtain an RQ = 1) was determined. The frequency of spills above that threshold was determined from the NEMISIS database (2002–2012; Environment Canada 2013a) (Table 9-2).

Table 9-2. Spill volumes required to create harmful conditions to aquatic organisms and the proportion of reported spills of HFOs above this threshold volume based on spill data from the NEMISIS database, 2002–2012 (Environment Canada 2013a)<sup>a</sup>

Compartment affected	Critical spill volume required to obtain risk quotient = 1 (L)	Proportion of reported spills above the threshold volume	Number of spills per year expected to be above the threshold volume	
Freshwater (loading/unloading)	61 500	1%	Less than 1	
Freshwater (transport)	7 100 000	0%	0	
Marine (loading/unloading)	13 800	4%	Less than 1	
Marine (transport)	575 000	0%	0	

<sup>&</sup>lt;sup>a</sup> HFO spills were assumed to be equal to Bunker C spills due to the inability of the dataset to distinguish between these different HFOs. Actual number and volume of Stream 4 HFO spills are expected to be less than reported here.

For marine and freshwater scenarios during ship transport, critical spill volumes of 575 000 L and 7 100 000 L of HFOs, respectively, are needed to obtain an RQ of 1 for aquatic organisms (Table 9) based on toxicity estimations and spill dispersion models of the volume of water affected. None of the reported spills from 2002–2012 were greater than these threshold volumes during ship transport. The expected number of spills per year above this volume is therefore zero.

For ship loading/unloading scenarios, spill volumes of 13 800 L and 61 500 L of HFOs are needed to obtain an RQ of 1 for aquatic organisms in marine and freshwaters, respectively (Table 9). There are some reported spills above these threshold volumes during the loading/unloading of ships in marine water (4% of spills) and freshwater (1% of spills). However, these frequencies equate to, on average, less than one spill per year above the threshold volume in marine waters or freshwaters.

These frequencies for marine and freshwater releases during transport and loading/unloading are based on spill data from NEMISIS. The narrow scope of the reporting requirements to NEMISIS may lead to a low estimation of the frequency of spills. However, this is not as great a concern for spills to water, as NEMISIS does require the reporting of marine spills or those that contravene the *Fisheries Act*. In addition, the frequencies determined are based on the entire dataset from NEMISIS for spills of Bunker C, which are expected to be more frequent than spills of Stream 4 HFOs. Thus, based on the relatively low number of spills per year above the threshold volumes required for an RQ greater than 1, spills of these HFOs to water during loading and unloading are considered to be infrequent and pose a low risk of harm to aquatic organisms.

These spill volumes were calculated based on models developed by RMRI (2007), relating the volume spilled and concentration of petroleum substance in the water. Since these models take into consideration dispersion of the petroleum substance spilled, the calculated spill volume relating to a risk quotient of 1 is not for the acute, initial exposure to the spilled material. It is recognized that local, acute effects may occur during the initial phase of a spill before significant dispersion occurs.

Both field reports and experiments have shown that commercial blends of HFOs can be toxic to aquatic birds through ingestion (CONCAWE 1998; Environment Canada 2011b; Michigan 2010), contact with feathers (Environment Canada 2011b) and contact with eggs (Albers and Szaro 1978; Coon et al. 1979; CONCAWE 1998). The negative effects of oil on feathers, however, are not specific to HFOs and are primarily based on Bunker C fuel oil. Indeed, average spills to marine water for these Stream 4 HFOs are based on the NEMISIS data for Bunker C fuel oil (Environment Canada 2013a), and reporting requirements for NEMISIS include spills from marine vessels. Use of these data overestimates the number of spills of the HFOs considered in this assessment. Thus, there is a low frequency of releases of these Stream 4 HFOs to marine waters, and thus a low risk to sea birds through direct toxicity and indirect effects.

Comparing the concentration of HFOs expected in soil from the application of potash (PEC = 0.4 mg/kg) to the Canada-Wide Standard (CWS) for eco-soil contact for Fraction 3 in coarse-grained soil of 300 mg/kg (the CTV for soil exposure), little risk to soil organisms is anticipated.

As noted in the Ecological Exposure Assessment section, if HFOs or their components are released from road maintenance products, this will likely occur to the greatest extent during the first few rainfall events following application of the product (Freestone 1972). Indeed, for asphalt emulsions, the risk of release is greatest following application and before it is fully cured, when the emulsion is still in a water-based state (personal communication, email communication, December 12, 2013, from Pounder Emulsions, Division of Husky Oil Limited, to Ecological Assessment Division, Environment Canada). The majority (80%) of HFO (CAS RN 68955-27-1) reported in road maintenance products is in the cold mix asphalt emulsion, which is applied only once to a road, with the remainder used in the dust palliative that is applied every 4 to 6 years. Additionally, exposure to these components in surface water is expected to be transient, as HFO components  $> C_{12}$  are expected to sorb to particulate matter due to low water solubilities and high partition coefficients (log K<sub>oc</sub>) (see Environmental Fate section). Based on the infrequent application of these road maintenance products containing HFOs and the expected short-term environmental exposure following a rain event shortly after application, their use is expected to result in a low risk to the environment.

The NEMISIS database reports small numbers of transport-related Bunker C spills to soil via train (2 spills), truck (9 spills) and pipelines (7 spills) between 2002 and 2012. Considering the cause and reason of spill, it was determined that for loading, transport and unloading of trains, less than 1 spill per year is expected. By the same analysis, less than 1 spill per year to soil for loading, transport and unloading by truck or by

pipeline is expected. Thus, terrestrial spills from train, truck and pipeline transport of HFOs are unlikely to cause harm due to their low frequency. It is acknowledged that the narrow scope of the reporting requirements to NEMISIS also results in the low estimation of frequency of some spills, especially those to land. However, this is offset by the fact that the spill frequency determined from NEMISIS is based on release data listed as "Bunker" or "Bunker C" and, therefore, includes HFOs other than those considered within this assessment.

Based on the available information, these HFOs contain components that might persist in soil, water and/or sediment, thus increasing the duration of exposure to organisms. The HFOs assessed in this report are also expected to contain components that are highly bioaccumulative. Studies suggest that most components will not likely biomagnify in food webs; however, there is some indication that alkylated PAHs might.

In general, fish can efficiently metabolize aromatic compounds. There is some evidence that alkylation increases the bioaccumulation of naphthalene (Neff et al. 1976; Lampi et al. 2010), but it is not known if this can be generalized to larger PAHs or if any potential increase in bioaccumulation due to alkylation will be sufficient to exceed a BAF/BCF of 5000 thus being considered highly bioaccumulative.

Some lower trophic level organisms (i.e., invertebrates) appear to lack the capacity to efficiently metabolize aromatic compounds, resulting in high bioaccumulation potential for some aromatic components as compared to fish. This is the case for some three-, four-, five- and six-ring PAHs, which were bioconcentrated to high levels (BCF >5000) by invertebrates (e.g., *Daphnia* and molluscs) but not by fish. There is potential for such bioaccumulative components to reach toxic levels in organisms if exposure is continuous and of sufficient magnitude, though this is unlikely in the water column following a spill scenario due to relatively rapid dispersal. However, some of these components can also persist in sediments for long periods of time, which can increase the exposure duration of benthic invertebrates to these components.

Bioaccumulation of aromatic compounds might be lower in natural environments than what is observed in the laboratory. PAHs may sorb to organic material suspended in the water column (dissolved humic material) which decreases their overall bioavailability primarily due to an increase in size. This has been observed with fish (Weinstein and Oris 1999) and *Daphnia* (McCarthy et al. 1985).

Considering all available lines of evidence presented in this screening assessment, there is a low risk of harm to organisms and the broader integrity of the environment from these substances. It is therefore concluded that Stream 4 HFOs (CAS RNs 64741-57-7, 64741-62-4, 64741-67-9, 64741-81-7, 64742-59-2, 64742-90-1 and 68955-27-1) do not meet the criteria under paragraphs 64(a) or (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.

# 9.4 Uncertainties in Evaluation of Ecological Risk

All modelling of the substances' physical-chemical properties, as well as persistence, bioaccumulation and toxicity characteristics, is based on chemical structures. As these HFOs are UVCBs, they cannot be represented by a single, discrete chemical structure. The specific chemical compositions of these HFOs are not well defined. HFO streams under the same CAS RNs can vary significantly in the number, identity and proportion of constituent compounds, depending on operating conditions, feedstocks and processing units. Therefore, for the purposes of modelling, a suite of representative structures that provide average estimates for the entire range of components likely present was identified. Specifically, these structures were used to assess the fate and hazard properties of HFOs. Given that more than one representative structure may be used for the same carbon range and type of component, it is recognized that structure-related uncertainties exist for these substances. The physical-chemical properties of 48 representative structures were used to estimate the overall behaviour of these HFOs in order to represent the expected range in physical-chemical characteristics. Given the large number of potential permutations of the type and percentages of the structures in HFOs, there is uncertainty in the results associated with modelling.

The fate and toxicity of petroleum hydrocarbons depend to a large extent on their chemical form. As such, conservative assumptions about chemical form, bioavailability and absorption through the digestive tract were generally carried forward in the screening assessment. HFO representative structures were assessed with the conservative assumption that all of them are bioavailable.

There is uncertainty in the use of historical spill information from the NEMISIS database (Environment Canada 2013a), as spill reports did not distinguish between different forms of HFOs. NEMISIS does not report spills of the specific HFOs assessed here, but rather groups all HFOs under the generic group "Bunker." Thus, the spills reported for Stream 4 HFOs include releases of other HFOs. Additionally, reporting requirements to NEMISIS are limited to releases involving or affecting a federal agency or department, a federal government facility or undertaking, or Aboriginal land; releases that contravene CEPA or the *Fisheries Act*; releases that affect fish, migratory birds or species at risk or that impact an interprovincial or international boundary; and releases from marine vessels. Therefore, NEMISIS likely underreports spills nationally, especially spills to land. These two factors offset each other.

A number of assumptions were made with regard to the location of the spills and, thereby, their environmental significance. There is uncertainty associated with these assumptions. However, due to the small number of spills likely related directly to Stream 4 HFOs, these uncertainties are minimized.

## 10. Potential to Cause Harm to Human Health

# **10.1 Exposure Assessment**

Information obtained under section 71 notices (Environment Canada 2008, 2009, 2011a) indicated that the predominant use of these substances in Canada occurs in industrial settings. This includes manufacturing, followed by consumption or blending (as an intermediate substance) into products that leave the facility under different CAS RNs. Potential exposures from uses by industry as intermediate blending streams were previously considered in the site-restricted (Stream 1) HFO assessment (Environment Canada, Health Canada 2011).

CAS RNs 64741-57-7, 64741-62-4, 64741-67-9, 64741-81-7, 64742-59-2 and 68955-27-1 were identified by section 71 reporting as being transported between petroleum or manufacturing facilities or other industrial settings. Modes of transport between facilities include truck, pipeline, ship and rail car, as previously considered in the industry-restricted (Stream 2) HFO assessment (Environment Canada, Health Canada 2013). Because the modes of transport and the potential evaporative emissions are the same in that report as they are for these six substances, the conclusion for industry-restricted HFOs is considered to apply. Exposure of the general population during transport is expected to be negligible.

No additional information was submitted for CAS RN 64742-90-1 under the *Notice with respect to certain high priority petroleum substances on the* Domestic Substances List (Environment Canada 2011a). However, it was listed in MSDS for industrial/commercial products and so would have exposure associated with industry-restricted HFOs.

Information gathered under a section 71 survey (*Notice with respect to certain high priority petroleum substances on the* Domestic Substances List) on the seven HFO CAS RNs assessed in this report did not reveal any consumer products intended for use by the general population (Environment Canada 2011a). The remaining products that contain the HFO CAS RNs in Canada are limited to industrial or commercial use and are not marketed to the general public. For more information on product searches and the information considered, see the Uses section.

Examples of professional-grade product types containing Stream 4 HFO CAS RNs include road maintenance asphalt emulsions for use in road surfacing and as a dust palliative. These are not intended for use by the general population. Due to the high density of these substances and large aerosol sizes, inhalation exposure at the time of application is not expected. Environmental effects of the use of road maintenance asphalt emulsions containing Stream 4 HFO substances are covered in the Environmental Fate section.

Contributions to environmental media are not expected from professional-grade products containing HFOs as ingredients. Even though the Canadian market

penetration of the products and extent to which they are used are unknown, section 71 survey results indicate that these products would not be used on a scale comparable to HFO fuel and industrial uses (Environment Canada 2011a). Potential general population exposure from environmental media as a result of HFO fuel and industrial uses has been addressed in the previous Stream 1 and Stream 2 (site- and industry-restricted) HFO assessments, and in the Stream 3 Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil assessment (Environment Canada, Health Canada 2011, 2013, 2014). Volatiles from HFOs are not expected due to their low vapour pressure, and exposure to the general population is not expected.

#### 10.2 Health Effects Assessment

Stream 4 HFOs were identified as high priorities for action during DSL categorization because they were determined to present a high potential hazard to human health. A critical effect for their initial categorization was carcinogenicity, based primarily on classifications by international agencies. The International Agency for Research on Cancer (IARC), European Commission and United Nations (UN) have classified Stream 4 HFOs as carcinogens. IARC classified residual (heavy) fuel oils as Group 2B carcinogens ("possibly carcinogenic to humans"), based on sufficient evidence in experimental animals (IARC 1989). The European Commission classified HFOs (CAS RNs 64741-57-7, 64741-62-4, 64741-67-9, 64741-81-7, 64742-59-2, 64742-90-1 and 68955-27-1) as Category 2 carcinogens ("substances which should be regarded as if they are carcinogenic to man"; R45: may cause cancer) (European Commission 1994; ESIS 2008). The UN Globally Harmonized System of Classification and Labelling of Chemicals classified these substances as Category 1B carcinogens ("presumed to have carcinogenic potential for humans, classification is largely based on animal evidence"; H350: may cause cancer) (European Commission 2008).

PAHs are components of HFOs. The proportion of this fraction can vary depending on the nature and extent of feedstock diluents, and whether the residue component is thermally cracked. The Government of Canada has previously completed a human health risk assessment of five PAHs, including critical review of relevant data, under the Priority Substances List Program. Based primarily on the results of carcinogenicity bioassays in animal models, these PAHs were classified as "probably carcinogenic to humans": substances for which there is believed to be some chance of adverse effects at any level of exposure (Canada 1994). PAHs are on the List of Toxic Substances in Schedule 1 of CEPA (Environment Canada 2013c).

The studies listed below are considered to describe the most relevant and critical health effect endpoints. These studies are described in detail in Table E.1 (Appendix E).

Median lethal dose (LD<sub>50</sub>) animal studies reported results of post-mortem examinations. Dermal exposure of rabbits and rats to 2000 mg/kg-bw of CAS RN 64741-57-7, 64741-62-4, 64741-81-7 or 64742-90-1 with occlusion on abraded or intact skin lead to subtle or no systemic effects after 24 hours. Localized skin effects, including erythema and edema, were the only clinical effects observed. Lethalities were not observed,

meaning that dermal LD<sub>50</sub> values were not established in these studies (LD<sub>50</sub> more than 2000 mg/kg-bw) (API 2004; ECB 2000b).

A number of skin-painting assays were conducted in laboratory animals to investigate the dermal carcinogenicity of HFOs. The majority of these studies followed a chronic skin painting exposure regimen, and significant skin tumour formation was consistently observed. In one chronic study, male mice were dermally exposed to CAS RN 64741-62-4 at doses of 8.4, 16.8, 42.0, 83.8 or 167.6 mg/kg-bw/day, 3 times/week for life. Significant skin tumour formation was observed at all doses, including the lowest dose tested, and the magnitude of induction was dose-dependent (McKee et al. 1990). However, one study was identified that used a short-term exposure initiation protocol; male mice were dermally exposed to CAS RN 64741-62-4 at a dose of 16.8 mg/kg-bw/day for 5 consecutive days (followed by exposure to a promotion agent for 25 weeks) (API 1989). Significant skin tumour formation was observed at this dose with a latency period of 16 weeks. *In vitro* testing by Feuston et al. (1994) indicated high mutagenicity indices for several HFO CAS RNs, including 64741-62-4 and 64741-81-7, showing that, in addition to causing skin tumours in laboratory animals, these substances can also exhibit significant genotoxicity.

Reproductive toxicity in rat dams, namely early and total resorptions, has been demonstrated as a sensitive endpoint and was observed in several studies following short-term exposure to HFOs (Environment Canada, Health Canada 2011, 2013, 2014). Reproductive and maternal dermal NOAELs of 0.05 mg/kg-bw/day were identified in rat dams (22–24 per group) exposed once daily to clarified slurry oil (CAS RN 64741-62-4) from gestational days (GD) 0–19. An increased rate of early and total fetal resorptions was observed at exposure levels of 1, 10, 50 and 250 mg/kg-bw/day (Hoberman et al. 1995). Resorptions exhibited a positive dose-response and were statistically significant (p less than 0.01) at all doses. Exposures were unoccluded, and rats were fitted with collars to prevent ingestion (indicating that some fraction of the test substance was dermally absorbed and available systemically). Resorptions occurred in the presence of maternal toxicity at all dose levels that included dose-dependent, significantly reduced feeding, and reduced body weight gains and body weights (more than 5% reduction at 1 mg/kg-bw/day at study termination). Therefore, the increased early and total resorptions may have been linked to maternal toxicity rather than a targeted toxicological effect. At the highest dose level, the dams did not gain weight but exhibited significant weight loss, and no live fetuses were recorded (compared with 362 live fetuses for the group exposed at the NOAEL of 0.05 mg/kg-bw/day). Multiple studies observed similar adverse maternal and reproductive effects, with significant and dose-related increases in resorptions occurring at 8 or 30 mg/kg-bw/day, after dermal exposure to CAS RNs 64741-62-4 and 64741-81-7 during GD 0-19 (Feuston et al. 1989, 1997; Mobil 1987a, 1990, 1994). Oral gavage exposure to a single dose (125 mg/kg-bw) of CAS RN 64741-62-4 also exhibited maternal toxicity and reproductive and developmental effects (Feuston and Mackerer 1996).

Increased early and total resorptions were also examined in a "pulse" dosing study, whereby rat dams (10 per dose per pulse exposure window) were dermally exposed to

1, 50 or 250 mg/kg-bw/day of CAS RN 64741-62-4, 6 hours/day, for 3-day intervals that spanned GD 0–17, or a 2-day interval on GD 18–19 (Hoberman et al. 1995). A dose-related increased incidence of total and early resorptions was observed during the gestational exposure window of GD 6–8, with exposure to 50 and 250 mg/kg-bw/day. Early resorptions did not occur when the pulse exposure occurred between GD 0–5 or GD 9–19, suggesting a specific toxicological response during the period of early organogenesis. Additionally, 250 mg/kg-bw/day also caused increased resorptions when exposure occurred during GD 9–11, corresponding with the period of late organogenesis.

#### 10.3 Characterization of Risk to Human Health

Stream 4 HFOs were identified as priorities for assessment as they met the categorization criteria under subsection 73(1) of CEPA and were considered a priority based on other human health concerns.

A critical effect for the initial categorization of HFO substances was carcinogenicity, based primarily on classifications by international agencies. These substances are classified as Group 2B carcinogens by IARC (1989), Category 2 carcinogens by the European Commission (European Commission 1994; ESIS 2008), and Category 1B carcinogens using the Globally Harmonized System (European Commission 2008).

Exposure to the general population to Stream 4 HFOs is not expected, as consumer products containing these substances were not identified. Exposures to site-restricted HFOs (Stream 1) and industry-restricted HFOs (Stream 2) have been previously assessed under the PSSA (Environment Canada, Health Canada 2011; Environment Canada, Health Canada 2013). It is noted that HFOs are considered to be of high hazard, as they can contain a high proportion of potentially carcinogenic PAHs, and some have been classified by various international organizations (e.g., IARC and European Commission) as dermal carcinogens. Additionally, reproductive toxicity is a critical effect for dermal exposure to HFOs. However, since general population exposure to these substances is not expected, the risk is low.

#### 10.4 Uncertainties in Evaluation of Human Health Risk

The PSSA screening assessments evaluate substances that are complex mixtures (UVCBs) composed of a number of components in various proportions due to the source of the crude oil or bitumen and its subsequent processing.

Given that HFOs are UVCBs, their specific compositions are not well defined. HFO streams under the same CAS RN can vary significantly in the number, identity and proportion of components. Consequently, it is difficult to obtain a representative toxicological dataset for these specific HFO CAS RNs. As a result, one HFO substance,

namely 64741-62-4, is often used to represent the health effects for all Stream 4 HFO CAS RNs.

## 11. Conclusion

Considering all available lines of evidence presented in this screening assessment, there is a low risk of harm to organisms and the broader integrity of the environment from these substances. It is therefore concluded that Stream 4 HFOs (CAS RNs 64741-57-7, 64741-62-4, 64741-67-9, 64741-81-7, 64742-59-2, 64742-90-1 and 68955-27-1) do not meet the criteria under paragraphs 64(a) or (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.

Products that contain Stream 4 HFO CAS RNs are limited to industrial or commercial use. Exposure to the general population is not expected and risk is low.

Based on the information presented in this screening assessment, it is concluded that Stream 4 HFOs (CAS RNs 64741-57-7, 64741-62-4, 64741-67-9, 64741-81-7, 64742-59-2, 64742-90-1 and 68955-27-1) do not meet the criteria under paragraph 64(c) of CEPA as they are not 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.

It is concluded that Stream 4 HFOs (CAS RNs 64741-57-7, 64741-62-4, 64741-67-9, 64741-81-7, 64742-59-2, 64742-90-1 and 68955-27-1) do not meet any of the criteria set out in section 64 of CEPA.

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# **Appendices**

## **Appendix A. Petroleum Substance Groupings**

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

Group <sup>a</sup>	Description	Example
Crude oils	Complex combinations of aliphatic and aromatic hydrocarbons and small amounts of inorganic compounds, naturally occurring under the Earth's surface or under the seafloor	Crude oil
Petroleum and refinery gases	Complex combinations of light hydrocarbons primarily from C <sub>1</sub> to C <sub>5</sub>	Propane
Low boiling point naphthas	Complex combinations of hydrocarbons primarily from C <sub>4</sub> to C <sub>12</sub>	Gasoline
Gas oils	Complex combinations of hydrocarbons primarily from $C_9$ to $C_{25}$	Diesel fuel
Heavy fuel oils	Complex combinations of heavy hydrocarbons primarily from C <sub>11</sub> to C <sub>50</sub>	Fuel Oil No. 6
Base oils	Complex combinations of hydrocarbons primarily from C <sub>15</sub> to C <sub>50</sub>	Lubricating oils
Aromatic extracts	Complex combinations of primarily aromatic hydrocarbons from C <sub>15</sub> to C <sub>50</sub>	Feedstock for benzene production
Waxes, slack waxes and petrolatum	Complex combinations of primarily aliphatic hydrocarbons from C <sub>12</sub> to C <sub>85</sub>	Petrolatum
Bitumen or vacuum residues	Complex combinations of heavy hydrocarbons having carbon numbers greater than C <sub>25</sub>	Asphalt

<sup>&</sup>lt;sup>a</sup> These groupings were based on classifications developed by Conservation of Clean Air and Water in Europe (CONCAWE) and a contractor's report presented to the Canadian Petroleum Products Institute (Simpson 2005).

# **Appendix B. Physical and Chemical Data Tables for HFOs**

Table B.1. Substance identity of HFOs

CAS RN and DSL name	Major components and carbon range	Approximate ratio of aromatics to non-aromatics	4- 7-ring PAHs (wt%)
64741-57-7 Gas oils (petroleum), heavy vacuum	Aliphatic and aromatic hydrocarbons; $C_{20}$ – $C_{50}$ <sup>a</sup>	50:50 to 40:60 <sup>b</sup>	more than 5% <sup>c</sup>
64741-62-4 Clarified oils (petroleum), catalytic cracked	Aliphatic and aromatic hydrocarbons; more than $C_{20}^{a}$	50:50 to 40:60 <sup>b</sup>	more than 5% <sup>c</sup>
64741-67-9 Residues (petroleum), catalytic reformer fractionator	Aliphatic and aromatic hydrocarbons; $C_{10}$ – $C_{25}$ <sup>c</sup>	50:50 to 40:60 <sup>b</sup>	more than 5% <sup>c</sup>
64741-81-7 Distillates (petroleum), heavy thermal cracked	Aliphatic and aromatic hydrocarbons; $C_{15}$ – $C_{36}$ <sup>c</sup>	50:50 to 40:60 <sup>b</sup>	more than 5% <sup>c</sup>
64742-59-2 Gas oils (petroleum), hydrotreated vacuum	Aliphatic and aromatic hydrocarbons; $C_{13}$ – $C_{50}$ <sup>c</sup>	50:50 to 40:60 <sup>b</sup>	more than 5% <sup>c</sup>
64742-90-1 Residues (petroleum), steam-cracked	Aliphatic and aromatic hydrocarbons; more than C <sub>14</sub>	50:50 to 40:60 <sup>b</sup>	more than 5% <sup>c</sup>
68955-27-1 Distillates (petroleum), petroleum residues vacuum	Aliphatic and aromatic hydrocarbons; $C_{20}$ – $C_{50}$ <sup>d</sup>	50:50 to 40:60 <sup>b</sup>	more than 5% <sup>c</sup>

<sup>&</sup>lt;sup>a</sup> API 2011 <sup>b</sup> API 2004

<sup>&</sup>lt;sup>c</sup> CONCAWE 1998 <sup>d</sup> Based on similarity to CAS RN 64741-57-7

Table B.2. Boiling point ranges for HFOs (CONCAWE 1998)

CAS RN	Boiling point range (°C)	Carbon range	Reference
64741-57-7	350-600	C <sub>20</sub> –C <sub>50</sub>	CONCAWE 1998
64741-62-4	more than 350	more than C <sub>20</sub>	CONCAWE 1998
64741-67-9	160-400	C <sub>10</sub> -C <sub>25</sub>	CONCAWE 1998
64741-81-7	260-480	C <sub>15</sub> –C <sub>36</sub>	CONCAWE 1998
64742-59-2	244–570	C <sub>13</sub> –C <sub>50</sub>	CONCAWE 2010
64742-90-1	more than 260	more than C <sub>14</sub>	CONCAWE 1998
68955-27-1	262 (350–600) <sup>a</sup>	C <sub>20</sub> –C <sub>50</sub>	CONCAWE 2010; API 2004

<sup>&</sup>lt;sup>a</sup> Based on similarity to CAS RN 64741-57-7.

Table B.3. Physical-chemical properties for representative structures of HFOs<sup>a</sup>

## Alkanes

Carbon number, name (CAS RN)	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa) <sup>b</sup>
C <sub>10</sub> n-decane (124-18-5)	174.1 (expt.)	29.7 (expt.)	191.0 (expt.)
C <sub>12</sub> dodecane (112-40-3)	216.3 (expt.)	9.6 (expt.)	18.0 (expt.)
C <sub>15</sub> pentadecane (629-62-9)	270.6 (expt.)	9.9 (expt.)	0.457 (expt.)
C <sub>20</sub> eicosane (112-95-8)	343 (expt.)	36.8 (expt.)	6.2×10 <sup>-4</sup> (expt.)

## Isoalkanes

Carbon number, name (CAS RN)	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa) <sup>b</sup>	
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C <sub>10</sub> 4-methylnonane (17301-94-9)	165.7 (expt.)	-99 (expt.)	339
C <sub>12</sub> 2,3-dimethyldecane (17312-44-6)	181.4	43.0	165.0
C <sub>15</sub> 2-methyltetra-decane (1560-95-8)	250.2	1.5	5.8
C <sub>20</sub> 3-methyl-nonadecane (6418-45-7)	326.3	39.5	0.092
C <sub>30</sub> hexamethyl-tetracosane (111-01-3)	408.5	74.7	0.037

# Monocycloalkanes

Carbon number, name (CAS RN)	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa) <sup>b</sup>
C <sub>10</sub> butylcyclohexane (1678-93-9)	180.9 (expt.)	-74.7 (expt.)	175 (expt.)
C <sub>12</sub> n-hexylcyclohexane (4292-75-5)	224 (expt.)	43 (expt.)	15.2 (expt.)
C <sub>15</sub> nonylcyclohexane (2883-02-5)	282 (expt.)	-10 (expt.)	0.331 (expt.)
C <sub>20</sub> tetradecylcyclohexane (1795-18-2)	360 (expt.)	24 (expt.)	0.02
C <sub>30</sub> 1,5-dimethyl-1-(3,7,11,15-tetramethyl	421	103	1.5×10 <sup>-4</sup>

octadecyl) cyclohexane			
C <sub>50</sub>	674.2	294.0	5.6×10 <sup>-13</sup>

# Dicycloalkanes

Carbon number, name (CAS RN)	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa) <sup>b</sup>
C <sub>12</sub> dicyclohexyl (1,1'-bicyclohexyl) (92-51-3)	238 (expt.)	4 (expt.)	14.4 (expt.)
C <sub>15</sub> pentamethyldecalin (91-17-8)	187.3 (expt.)	30.3 (expt.)	163 (expt.)
C <sub>20</sub> 2,4-dimethyloctyl-2-decalin	323	41	0.1
C <sub>30</sub> 2,4,6,10,14-pentamethyldodecyl-2-decalin	420.3	105.9	0.0001
C <sub>50</sub>	663.8	289.1	1.2×10 <sup>-12</sup>

# Polycycloalkanes

Carbon number, name (CAS RN)	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa) <sup>b</sup>
C <sub>14</sub> hydrophenanthrene	255	21	4.5
C <sub>18</sub> hydrochrysene	353 (expt.)	115 (expt.)	0.004
C <sub>22</sub> hydropicene	365	108.1	0.003

## **Monoaromatics**

Carbon number, name (CAS RN)	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa) <sup>b</sup>
C <sub>12</sub> 1,2,3-triethylbenzene (42205-08-3)	229.59	11.85	10.6
C <sub>15</sub> 2-nonylbenzene (1081-77-2)	281 (expt.)	-24 (expt.)	0.76 (expt.)
C <sub>20</sub> Tetradecylbenzene (1459-10-5)	359 (expt.)	16 (expt.)	0.0038 (expt.)
C <sub>30</sub> 1-benzyl-4,8,12,16 tetramethyl eicosane	437	131	1.1×10 <sup>-5</sup>
C <sub>50</sub>	697	304	2.0×10 <sup>-14</sup>

## **Cycloalkane monoaromatics**

Carbon number, name (CAS RN)	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa) <sup>b</sup>
C <sub>10</sub> tetralin (tetrahydronaphthalene) 119-64-2	102-104 (expt.)	-35.7 (expt.)	49.1 (expt.)
C <sub>15</sub> methyloctahydro-phenanthrene	267.11	27.85	2.34
C <sub>20</sub> ethyl dodecahydrochyrsene	338.41	81.93	0.0191

## **Diaromatics**

Carbon number, name (CAS RN)	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa) <sup>b</sup>
C <sub>12</sub> biphenyl (92-52-4)	256.1 (expt.)	69 (expt.)	1.2 (expt.)
C <sub>15</sub> 4-isopropylbiphenyl (7116-95-2)	308	43.7	0.109
C <sub>20</sub> 2-isodecylnaphthalene	366.4	99.5	0.0014
C <sub>30</sub> 2-(4,8,14,18-tetramethyl hexadecyl)naphthalene	469	170.6	7.1×10 <sup>-7</sup>
C <sub>50</sub>	722	316	3.1×10 <sup>-15</sup>

# **Cycloalkane diaromatics**

Carbon number, name (CAS RN)	Boiling	Melting	Vapour
	point	point	pressure
	(°C)	(°C)	(Pa) <sup>b</sup>
C <sub>12</sub> acenaphthene (83-32-9)	279	93.4	0.287
	(expt.)	(expt.)	(expt.)
C <sub>15</sub> Ethylfluorene (65319-49-5)	337.6	94.6	0.0073
C <sub>20</sub> Isoheptylfluorene	380	126.3	0.00032

# Three-ring aromatics

Carbon number, name (CAS RN)	Boiling point	Melting point	Vapour pressure	
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	(°C)	(°C)	(Pa) <sup>b</sup>
C <sub>15</sub> 2-methylphenanthrene (2531-84-2)	155–160 (expt.)	57–59 (expt.)	0.009
C <sub>20</sub> 2-isohexylphenanthrene	331	67.3	0.039
C <sub>30</sub> 2-(2,4,10-trimethyl tridecyl) phenanthrene	493	191.6	9.8×10 <sup>-8</sup>
C <sub>50</sub>	746	327.5	4.9×10 <sup>-13</sup>

# **Four-ring PAHs**

Carbon number, name (CAS RN)	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa) <sup>b</sup>
C <sub>16</sub> fluoranthene (206-44-0)	384 (expt.)	107.8 (expt.)	1.2×10 <sup>-3</sup> (expt.)
C <sub>20</sub> benzo[ <i>k</i> ]fluoranthene (207-08-9)	480 (expt.)	217 (expt.)	1.3×10 <sup>-7</sup> (expt.)

## **Five-ring PAHs**

Carbon number, name (CAS RN)	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa) <sup>b</sup>
C <sub>20</sub> benzo[ <i>a</i> ]pyrene (50-32-8)	495 (expt.)	176.5 (expt.)	7.3×10 <sup>-7</sup>
C <sub>30</sub> dimethyloctylbenzo[a]pyrene	544.8 (expt.)	217 (expt.)	1.6×10 <sup>-9</sup>

## Six-ring PAHs

Carbon number, name (CAS RN)	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa) <sup>b</sup>
C <sub>22</sub> benzo[ <i>ghi</i> ]perylene 191-24-2	more than 500 (expt.)	278 (expt.)	1.3×10 <sup>-8</sup> (expt.)

# Table B.3 cont. Physical-chemical properties for representative structures of HFOs<sup>a</sup>

## **Alkanes**

Carbon number, name (CAS RN)	Henry's Law constant (Pa-m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubility (mg/L) <sup>d</sup>
C <sub>10</sub> n-decane (124-18-5)	5.2×10 <sup>5</sup> (expt.)	5.01 (expt.)	4.3	0.05 (expt.)
C <sub>12</sub> dodecane (112-40-3)	829000 (expt.)	6.1 (expt.)	5.3	0.0037 (expt.)
C <sub>15</sub> pentadecane (629-62-9)	1.3×10 <sup>6</sup> (expt.)	7.7	6.7	7.6×10 <sup>-5</sup> (expt.)
C <sub>20</sub> eicosane (112-95-8)	2.2 ×10 <sup>7</sup>	10.2	8.8	0.019 (expt.)
C <sub>30</sub> triacontane (638-68-6)	6.8×10 <sup>8</sup>	15.1	13.1	8.58×10 <sup>-11</sup>

## Isoalkanes

Carbon number, name (CAS RN)	Henry's Law constant (Pa·m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubility (mg/L) <sup>d</sup>
C <sub>10</sub> 4-methylnonane (17301-94-9)	8.2×10 <sup>5</sup>	5.2	4.5	0.97
C <sub>12</sub> 2,3-dimethyldecane (17312-44-6)	2.0×10 <sup>6</sup>	6.1	5.3	0.11
C <sub>15</sub> 2-methyltetradecane (1560-95-8)	4.6×10 <sup>6</sup>	7.6	6.6	3.3×10 <sup>-3</sup>
C <sub>20</sub> 3-methylnonadecane (6418-45-7)	2.6×10 <sup>7</sup>	10.1	8.8	1.1×10 <sup>-5</sup>
C <sub>30</sub> hexamethyltetracosane (111-01-3)	2.1×10 <sup>9</sup>	14.6	12.7	2×10 <sup>-10</sup>

## Monocycloalkanes

Carbon number, name (CAS RN)	Henry's Law constant (Pa·m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubility (mg/L) <sup>d</sup>
C <sub>10</sub> butylcyclohexane (1678-93-9)	9.4×10 <sup>4</sup>	5.1	4.4	1.2
C <sub>12</sub> n-hexylcyclohexane (4292-75-5)	1.9×10 <sup>5</sup>	6.1	5.3	0.14
C <sub>15</sub> nonylcyclohexane (2883-02-5)	5.3×10 <sup>5</sup>	7.5	6.5	0.005
C <sub>20</sub> tetradecylcyclohexane	3.0×10 <sup>6</sup>	10.0	8.7	1.7×10 <sup>-6</sup>

(1795-18-2)				
C <sub>30</sub> 1,5-dimethyl-1-(3,7,11,15- tetramethyloctadecyl) cyclohexane	2.9×10 <sup>8</sup>	14.5	13	4.2×10 <sup>-7</sup>
C <sub>50</sub>	2.0×10 <sup>11</sup>	24.4	21.2	1.4×10 <sup>-20</sup>

## Dicycloalkanes

Carbon number, name (CAS RN)	Henry's Law constant (Pa·m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubility (mg/L) <sup>d</sup>
C <sub>12</sub> Dicyclohexyl (1,1'- bicyclohexyl) (92-51-3)	2.6×10 <sup>4</sup>	5.86	5.08	0.21
C <sub>15</sub> pentamethyldecalin (91-17-8)	4.8×10 <sup>4</sup>	4.2	3.7	0.89
C <sub>20</sub> 2,4-dimethyloctyl-2-decalin	7.2×10 <sup>4</sup>	8.9	7.7	1.2×10 <sup>-4</sup>
C <sub>30</sub> 2,4,6,10,14- pentamethyldodecyl- 2-decalin	3.9×10 <sup>7</sup>	13.6	11.8	1.7×10 <sup>-9</sup>
C <sub>50</sub>	5.7×10 <sup>10</sup>	23.3	20.2	1.4×10 <sup>-19</sup>

## Polycycloalkanes

Carbon number, name (CAS RN)	Henry's Law constant (Pa·m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubility (mg/L) <sup>d</sup>
C <sub>14</sub> hydrophenanthrene	8.6×10 <sup>3</sup>	5.2	4.5	0.49
C <sub>18</sub>	5.7×10 <sup>3</sup>	6.2	5.4	0.011

hydrochrysene				
C <sub>22</sub> hydropicene	3.8×10 <sup>3</sup>	7.3	6.3	0.0022

## **Monoaromatics**

Carbon number, name (CAS RN)	Henry's Law constant (Pa-m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubility (mg/L) <sup>d</sup>
C <sub>12</sub> 1,2,3-triethylbenzene (42205-08-3)	2.5 ×10 <sup>3</sup>	5.1	4.4	2.9
C <sub>15</sub> 2-nonylbenzene (1081-77-2)	1.0×10 <sup>4</sup>	7.1 (expt.)	6.2	0.024
C <sub>20</sub> tetradecylbenzene (1459-10-5)	5.7×10 <sup>4</sup>	10.0	8.6	5.2×10 <sup>-5</sup>
C <sub>20</sub> 1-benzyl-4,8-dimethyl- dodecane	8.2×10 <sup>4</sup>	8.8	7.6	5.5×10 <sup>-5</sup>
C <sub>30</sub> 1-benzyl-4,8,12,16 tetramethyleicosane	3.8×10 <sup>6</sup>	13.5	11.8	6.8×10 <sup>-9</sup>
C <sub>50</sub>	1.0×10 <sup>9</sup>	23.8	20.7	1.7×10 <sup>-19</sup>

## **Cycloalkane monoaromatics**

Carbon number, name (CAS RN)	Henry's Law constant (Pa·m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubility (mg/L) <sup>d</sup>
C <sub>10</sub> tetralin(tetrahydro naphthalene) 119-64-2	138 (expt.)	3.5 (expt.)	3.0	47 (expt.)

C <sub>15</sub> methyloctahydrophenanthrene	1.5×10 <sup>4</sup>	5.6	4.9	0.18
C <sub>20</sub> ethyldodecahydrochyrsene	1.4×10 <sup>4</sup>	7.2	6.2	0.0039

## **Diaromatics**

Carbon number, name (CAS RN)	Henry's Law constant (Pa·m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubility (mg/L) <sup>d</sup>
C <sub>12</sub> biphenyl (92-52-4)	31.2 (expt.)	4.0 (expt.)	3.3 (expt.)	6.94 (expt.)
C <sub>15</sub> 4-isopropylbiphenyl (7116-95-2)	98.7	5.5 (expt.)	4.8	0.90
C <sub>20</sub> 2-isodecylnaphthalene	1190	8.1	7.0	0.0024
C <sub>30</sub> 2-(4,8,14,18-tetramethyl hexadecyl)naphthalene	5.4×10 <sup>4</sup>	12.8	11.1	3×10 <sup>-8</sup>
C <sub>50</sub>	8.6×10 <sup>6</sup>	23.3	20.2	5.6×10 <sup>-19</sup>

# Cycloalkane diaromatics

Carbon number, name (CAS RN)	Henry's Law constant (Pa·m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubility (mg/L) <sup>d</sup>
C <sub>12</sub> acenaphthene (83-32-9)	18.6 (expt.)	3.9 (expt.)	3.6 (expt.)	3.9 (expt.)
C <sub>15</sub> Ethylfluorene (65319-49-5)	5.6	5.1	4.4	0.17
C <sub>20</sub> isoheptylfluorene	32.7	7.5	6.5	5.9×10 <sup>-4</sup>

# Three-ring aromatics

Carbon number, name (CAS RN)	Henry's Law constant (Pa·m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubilit y (mg/L) <sup>d</sup>
C <sub>15</sub> 2- methylphenanthrene (2531-84-2)	2.78	5.2 (expt.) and 4.86 (expt.)	4.2	0.28 (expt.)
C <sub>20</sub> 2-isohexyl- phenanthrene	9.9×10 <sup>4</sup>	8.0	7.0	6.9×10 <sup>-4</sup>
C <sub>30</sub> 2-(2,4,10-trimethyl tridecyl)phenanthrene	942	12.0	10.4	1.2×10 <sup>-8</sup>
C <sub>50</sub>	3.1×10 <sup>5</sup>	23.0	19.3	3.5×10 <sup>-19</sup>

## **Four-ring PAHs**

Carbon number, name (CAS RN)	Henry's Law constant (Pa·m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubility (mg/L) <sup>d</sup>
C <sub>16</sub> fluoranthene (206-44-0)	0.9 (expt.)	5.2 (expt.)	4.8 (expt.)	0.26 (expt.)
C <sub>20</sub> benzo[ <i>k</i> ]fluoranthene (207-08-9)	0.60 (expt.)	6.1 (expt.)	5.6 (expt.)	0.0008 (expt.)

#### **Five-ring PAHs**

Carbon number, name (CAS RN)	Henry's Law constant (Pa·m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubility (mg/L) <sup>d</sup>
C <sub>20</sub> benzo[ <i>a</i> ]pyrene (50-32-8)	0.046 (expt.)	6.1 (expt.)	6.0 (expt.)	0.0016 (expt.)
C <sub>30</sub> dimethyloctylbenzo[ <i>a</i> ] pyrene	0.78	10.9	9.5	1.2×10 <sup>-7</sup>

## **Six-ring PAHs**

Carbon number, name (CAS RN)	Henry's Law constant (Pa·m³/mol) <sup>c</sup>	Log K <sub>ow</sub>	Log K <sub>oc</sub>	Aqueous solubility (mg/L) <sup>d</sup>
C <sub>22</sub> benzo[ <i>ghi</i> ]perylene (191-24-2)	0.033	6.6	5.8	0.00026 (expt.)

<sup>&</sup>lt;sup>a</sup> All values are modelled unless denoted with an (expt.) for experimental data.

b This is the maximum vapour pressure of the surrogate; the actual vapour pressure as a component of a mixture will be lower due to Raoult's Law (the total vapour pressure of an ideal mixture is proportional to the sum of the vapour pressures of the mole fractions of each individual component). The lightest, C<sub>9</sub>, and heaviest, C<sub>50</sub>, representative structures were chosen to estimate a range of vapour pressures from the minimum to the maximum values.
c Henry's Law constants for C<sub>20</sub>–C<sub>30</sub> representative structures were calculated with HENRYWIN Version 3.10 from EPI Suite (2008) using both sub-cooled liquid solubility and sub-cooled liquid vapour pressure. Henry's Law constants

for  $C_{50}$  representative structures were not calculated, as sub-cooled liquid solubility data were not available. Solubility data gave anomalously high values for substances that have negligible solubility and volatility.

d Maximum water solubility was estimated for each surrogate based on its individual physical-chemical properties.

Table B.4. Representative structures attributed to each CAS RN

#### **Alkanes**

Carbon number	Boiling point (°C)	64741-57-7 / 68955-27-1	64741-62-4	64741-67-9
C <sub>10</sub>	174	-	-	Yes
C <sub>15</sub>	271	-	-	Yes
C <sub>20</sub>	343	-	-	Yes
C <sub>30</sub>	450	Yes	Yes	-
C <sub>50</sub>	548	Yes	Yes	-

#### Isoalkanes

Carbon number	Boiling point (°C)	64741-57-7 / 68955-27-1	64741-62-4	64741-67-9
C <sub>10</sub>	166	-	-	Yes
C <sub>15</sub>	250	-	-	Yes
C <sub>20</sub>	326	-	-	Yes
C <sub>30</sub>	350	Yes	Yes	Yes
C <sub>50</sub>	548	Yes	Yes	-

#### **Monocycloalkanes**

Carbon number	Boiling point (°C)	64741-57-7 / 68955-27-1	64741-62-4	64741-67-9
C <sub>10</sub>	181	-	-	Yes
C <sub>15</sub>	282	-	-	Yes
C <sub>20</sub>	360	Yes	Yes	Yes
C <sub>30</sub>	421	Yes	Yes	-
C <sub>50</sub>	699	-	Yes	-

## **Dicycloalkanes**

Carbon number	Boiling point (°C)	64741-57-7 / 68955-27-1	64741-62-4	64741-67-9
C <sub>12</sub>	256	-	-	Yes
C <sub>15</sub>	244	-	-	Yes
C <sub>20</sub>	339	-	-	Yes
C <sub>30</sub>	420	Yes	Yes	-
C <sub>50</sub>	687	-	Yes	-

## **Polycycloalkanes**

<sup>&</sup>lt;sup>d</sup> Maximum water solubility was estimated for each surrogate based on its individual physical-chemical properties. The actual water solubility of a component in a mixture will be lower, as the total water solubility of an ideal mixture is proportional to the sum of the water solubilities of the mole fractions of each individual component (Banerjee 1984).

Carbon number	Boiling point (°C)	64741-57-7 / 68955-27-1	64741-62-4	64741-67-9
C <sub>14</sub>	255	-	-	Yes
C <sub>18</sub>	316	-	-	Yes
C <sub>22</sub>	365	Yes	Yes	Yes

## **Monoaromatics**

Carbon number	Boiling point (°C)	64741-57-7 / 68955-27-1	64741-62-4	64741-67-9
C <sub>11</sub>	205	-	-	Yes
C <sub>15</sub>	281	-	-	Yes
C <sub>20</sub>	359	Yes	Yes	Yes
C <sub>30</sub>	437	Yes	Yes	-
C <sub>50</sub>	697	-	Yes	-

Cycloalkanes monoaromatics

Carbon number	Boiling point (°C)	64741-57-7 / 68955-27-1	64741-62-4	64741-67-9
C <sub>10</sub>	208	-	-	Yes
C <sub>15</sub>	285	-	-	Yes
C <sub>20</sub>	351	Yes	Yes	Yes

## **Diaromatics**

Carbon number	Boiling point (°C)	64741-57-7 / 68955-27-1	64741-62-4	64741-67-9
C <sub>15</sub>	308	-	-	Yes
C <sub>20</sub>	373	Yes	Yes	Yes
C <sub>30</sub>	469	Yes	Yes	-
C <sub>50</sub>	722	-	Yes	-

**Cycloalkane diaromatics** 

Carbon number	Boiling point (°C)	64741-57-7 <i>/</i> 68955-27-1	64741-62-4	64741-67-9
C <sub>12</sub>	279	-	-	Yes
C <sub>15</sub>	321	-	-	Yes
C <sub>20</sub>	374	Yes	Yes	Yes

Three-ring aromatics

Carbon number	Boiling point (°C)	64741-57-7 <i>/</i> 68955-27-1	64741-62-4	64741-67-9
C <sub>15</sub>	350	Yes	Yes	Yes
C <sub>20</sub>	398	Yes	Yes	Yes
C <sub>30</sub>	493	Yes	Yes	-
C <sub>50</sub>	746	-	Yes	-

**Four-ring aromatics** 

Carbon number	Boiling point (°C)	64741-57-7 / 68955-27-1	64741-62-4	64741-67-9
C <sub>16</sub>	384	Yes	Yes	Yes
C <sub>20</sub>	480	Yes	Yes	-

**Five-ring aromatics** 

Carbon number	Boiling point (°C)	64741-57-7 / 68955-27-1	64741-62-4	64741-67-9
C <sub>20</sub>	495	Yes	Yes	-
C <sub>30</sub>	545	Yes	Yes	-

Six-ring aromatics

Carbon number	Boiling point (°C)	64741-57-7 <i>/</i> 68955-27-1	64741-62-4	64741-67-9
C <sub>22</sub>	more than 500	Yes	Yes	-

## **Alkanes**

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1
C <sub>10</sub>	174	-	-	-
C <sub>15</sub>	271	Yes	Yes	Yes
C <sub>20</sub>	343	Yes	Yes	Yes
C <sub>30</sub>	450	Yes	Yes	Yes
C <sub>50</sub>	548	-	Yes	Yes

#### Isoalkanes

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1
C <sub>10</sub>	166	-	-	-
C <sub>15</sub>	250	-	Yes	-
C <sub>20</sub>	326	Yes	Yes	Yes
C <sub>30</sub>	350	Yes	Yes	Yes
C <sub>50</sub>	548	-	Yes	Yes

One-ring cycloalkanes

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1
C <sub>10</sub>	181	-	-	-
C <sub>15</sub>	282	Yes	Yes	Yes
C <sub>20</sub>	360	Yes	Yes	Yes
C <sub>30</sub>	421	Yes	Yes	Yes
C <sub>50</sub>	699	-	-	Yes

Dicycloalkanes

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1
C <sub>12</sub>	256	-	Yes	-
C <sub>15</sub>	244	-	Yes	-
C <sub>20</sub>	339	Yes	Yes	Yes
C <sub>30</sub>	420	Yes	Yes	Yes
C <sub>50</sub>	687	-	-	Yes

**Polycycloalkanes** 

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1
C <sub>14</sub>	255	-	Yes	-
C <sub>18</sub>	316	Yes	Yes	Yes
C <sub>22</sub>	365	Yes	Yes	Yes

## **Monoaromatics**

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1
C <sub>11</sub>	205	-	-	-
C <sub>15</sub>	281	Yes	Yes	Yes
C <sub>20</sub>	359	Yes	Yes	Yes
C <sub>30</sub>	437	Yes	Yes	Yes
C <sub>50</sub>	697	-	-	Yes

**Cycloalkane monoaromatics** 

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1
C <sub>10</sub>	208	-	-	-
C <sub>15</sub>	285	Yes	Yes	Yes
C <sub>20</sub>	351	Yes	Yes	Yes

## **Diaromatics**

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1
C <sub>15</sub>	308	Yes	Yes	Yes
C <sub>20</sub>	373	Yes	Yes	Yes
C <sub>30</sub>	469	Yes	Yes	Yes
C <sub>50</sub>	722	-	-	Yes

**Cycloalkane diaromatics** 

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1
C <sub>12</sub>	279	Yes	Yes	Yes
C <sub>15</sub>	321	Yes	Yes	Yes

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	163	163	163	J 7	<b>U</b> 20

Three-ring aromatics

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1
C <sub>15</sub>	350	Yes	Yes	Yes
C <sub>20</sub>	398	Yes	Yes	Yes
C <sub>30</sub>	493	-	Yes	Yes
C <sub>50</sub>	746	-	-	Yes

**Four-ring aromatics** 

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1
C <sub>16</sub>	384	Yes	Yes	Yes
C <sub>20</sub>	480	Yes	Yes	Yes

**Five-ring aromatics** 

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1	
C <sub>20</sub>	495	-	Yes	Yes	
C <sub>30</sub>	545	-	Yes	Yes	

Six-ring aromatics

Carbon number	Boiling point (°C)	64741-81-7	64742-59-2	64742-90-1
C <sub>22</sub>	more than 500	-	Yes	Yes

## **Appendix C. Release Estimation**

Table C.1. Reported and extrapolated release volumes and spill numbers of HFO spilled in Canada based on historical Bunker C spill data from the NEMISIS

database, 2002-2012 (Environment Canada 2013a)

Year	Average spill volume (litres)	Maximum single spill volume (litres)	Median spill volume (litres)	Numbe r of spills report ed	% of spills with unknow n volume	Total known volume spilled (litres)	Extrapolated total volume spilled (litres) <sup>a</sup>
2002	1089	11 350	210	43	35	30 490	88 356
2003	1782	19 794	114	35	40	37 432	91 441
2004	2685	35 000	57	28	46	40 276	90 427
2005	2388	18 160	191	32	31	52 536	91 114
2006	1317	15 000	250	24	29	22 391	49 395
2007	135	454	79	15	27	1483	16 914
2008	20 255	178 000	5	11	18	182 296	190 012
2009	1190	5000	200	15	53	8330	39 191
2010	23 369	181 560	145	10	20	186 952	194 667
2011	131	400	107	12	33	1051	16 482
2012	n/a	n/a	n/a	n/a	n/a	n/a	n/a
-	-	-	-	-	Total volume spilled	563 236	868 001

<sup>&</sup>lt;sup>a</sup> The extrapolated total volume was calculated using a proportional estimate of known spills to determine the frequency and volume of unknown spill volumes, assuming that the distribution of reported volumes released was representative of all releases.

Table C.2a. Sources of HFO releases in Canada, 2002–2012 (Environment Canada 2013a)

Source	Total spills	Volume spilled (L)	Proportion of total volume	Average volume spilled (L)
Other watercraft	37	192 733	0.34	8031
Pipeline	9	187 521	0.33	26 789
Other	38	70 801	0.13	2529
Other industrial plant	24	39 115	0.07	1863
Tank truck	13	36 193	0.06	3290
Refinery	15	13 770	0.02	1148
Other storage facilities	11	11 457	0.02	1637
Unknown	27	4911	0.01	702
Storage depot	5	4266	0.01	711
Train	4	945	less than 0.01	473
Marine terminal	13	523	less than 0.01	75

Source	Total spills	Volume spilled (L)	Proportion of total volume	Average volume spilled (L)
Home heating tank	1	250	less than 0.01	250
Electrical equipment	2	227	less than 0.01	114
Bulk carrier	7	205	less than 0.01	103
Transport truck	2	133	less than 0.01	66
Cargo vessel	1	114	less than 0.01	114
Barge	3	50	less than 0.01	50
Marine tanker	4	12	less than 0.01	4
Other motor vehicle	3	9	less than 0.01	9
Production field	2	1	less than 0.01	1
Chemical plant	1	0	0	NA <sup>a</sup>
Municipal sewer	1	0	0	NA
Service station	2	0	0	NA
Total	225	563 236	1	3858

a NA: Data not available

Table C.2b. Causes of HFO releases in Canada, 2002–2012 (Environment Canada 2013a)

Cause	Total spills	Volume spilled (L)	Proportion of volume	Average volume spilled (L)
Pipe leak	47	255 281	0.21	7091
Unknown	46	6659	0.20	370
Other	40	39 436	0.18	1643
Overflow	26	11 736	0.12	533
Discharge	17	5095	0.08	637
Above ground tank leak	14	47 112	0.06	4283
Valve, fitting leak	12	3403	0.05	309
Container leak	10	9503	0.04	1188
Grounding	5	182 450	0.02	91 225
Overturn	3	1592	0.01	796
Well blowout	2	500	0.01	250
Derailment	1	N/A ª	less than 0.01	N/A
Process upset	1	68	less than 0.01	68
Sinking	1	400	less than 0.01	400
Total	225	563 236	1	3858

<sup>a</sup> N/A: Data not available

Table C.2c. Reasons for HFO releases in Canada, 2002–2012 (Environment Canada 2013a)

Reason	Total spills	Volume spilled (L)	Proportion of volume	Average volume spilled (L)
Equipment failure	42	242 132	0.43	8648
Unknown	76	216 767	0.38	5859
Negligence	3	35 000	0.06	35 000
Material failure	27	30 822	0.05	1622
Human error	42	14 584	0.03	417
Gasket, joint	6	9743	0.02	1624
Other	19	5566	0.01	428
Damage by equipment	3	5520	0.01	1840
Power failure	2	2270	less than 0.01	2270
Corrosion	3	650	less than 0.01	325
Intentional	2	182	less than 0.01	182
Total	225	563 236	1	3858

# Appendix D. The Potential for High Environmental Persistence or Bioaccumulation of Components of HFOs

Table D.1. Estimated volume of water in contact with oil ( $m^3 \times 10^6$ ) for loading/unloading and transport processes of oil via ship for various spill sizes (RMRI 2007)

Spill size (barrels)	Loading/unloading	Transport	
1–49	60	5750	
50–999	150	6250	
1000–9999	300	9600	
10 000–99 999	2200	17 350	
100 000–199 999	32 500	49 500	
more than 200 000	35 000	74 100	

Table D.2. An analysis of persistence data for petroleum hydrocarbons representative of heavy fuel oils according to Environment Canada (2014)

# of	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>15</sub>	C <sub>18</sub>	C <sub>20</sub>	C <sub>22</sub>	C <sub>30</sub>	C <sub>50</sub>
carbons		- 10			- 10	- 14	- 10	- 10	- 20		- 00	- 00
<i>n</i> -alkane	-		n/a	n/a	n/a	n/a	-	-	-	n/a	-	-
<i>i</i> -alkane	-	ı	n/a	ı	ı	n/a	ı	n/a	ı	n/a	S, W, Sd	ı
mono- cyclo- alkane	ı	ı	n/a	ı	n/a	n/a	ı	n/a	ı	n/a	Sd	S, V, Sd
dicyclo- alkane	Sd	n/a	n/a	Sd	n/a	n/a	S, W, Sd	n/a	S, W, Sd	n/a	s, Sd	S, V, Sd
poly- cyclo- alkane	n/ a	n/a	n/a	n/a	n/a	Sd	n/a	S, W, Sd	n/a	S, W, Sd	n/a	n/a
mono- aromatic	Sd	n/a	Sd	S, W, Sd	n/a	n/a	Sd	n/a	ı	n/a	Sd	Sd
cyclo- alkane mono- aromatic	S, W, Sd	S, W, Sd	n/a	S, W, Sd	n/a	n/a	S, W, Sd	n/a	S, W, Sd	n/a	n/a	n/a
di- aromatic	n/ a	S, W, Sd	n/a	S, W, Sd	n/a	n/a	S, W, Sd	n/a	S, W, Sd	n/a	S, W, Sd	S, W, Sd
cyclo- alkane	n/ a	-	1	S, W,	Α	n/a	-	n/a	-	n/a	n/a	n/a

di- aromatic				Sd								
3-ring poly- aromatic	n/ a	n/a	n/a	А	n/a	A, S, W, Sd	-	n/a	-	n/a	S, W, Sd	S, W, Sd
4-ring poly- aromatic	n/ a	n/a	n/a	n/a	n/a	n/a	n/a	A, S, V, Sd	S, W, Sd	n/a	n/a	n/a
5-ring poly- aromatic	n/ a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	A, S, V, Sd	n/a	S, W, Sd	n/a
6-ring poly- aromatic	n/ a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	A, S, W, Sd	n/a	n/a

A – Predicted half-life in air of 2 days or greater

S – Predicted half-life in soil of 6 months or greater

W – Predicted half-life in water of 6 months or greater

Sd – Predicted half-life in sediment of 1year or greater

n/a – Indicates that no such carbon numbers exist within the group or the structure was not modelled.

<sup>-</sup> Indicates that these structures are not considered persistent in air, soil, water or sediment.

Table D.3. An analysis of experimental and modelled bioaccumulation data for petroleum hydrocarbons representative of heavy fuel oils according to Environment Canada (2014)

# of	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>15</sub>	C <sub>18</sub>	C <sub>20</sub>	C <sub>22</sub>	C <sub>25</sub>
carbons <sup>a</sup>									10		
<i>n</i> -alkane	-	-	n/a	-	-	-	-	-	•	n/a	n/a
<i>i</i> -alkane	-	-	n/a	-	В	n/a	В	n/a	n/a	n/a	n/a
mono- cycloalka ne	-	-	n/a	В	n/a	n/a	В	n/a	n/a	n/a	n/a
dicyclo- alkane	-	-	n/a	В	-	n/a	В	n/a	n/a	n/a	n/a
polycyclo -alkane	n/a	n/a	n/a	n/a	n/a	В	n/a	ı	n/a	В	n/a
mono- aromatic	-	-	-	-	n/a	n/a	В	n/a	n/a	n/a	n/a
cyclo- alkane mono- aromatic	-	1	n/a	ı	n/a	n/a	В	n/a	В	n/a	n/a
di- aromatic	n/a	ı	-	В	В	-	ı	n/a	n/a	n/a	n/a
cyclo- alkane di- aromatic	n/a	n/a	n/a	-	-	-	-	n/a	В	n/a	n/a
3-ring poly- aromatic	n/a	n/a	n/a	-	n/a	В	-	n/a	В	n/a	n/a
4-ring poly- aromatic	n/a	n/a	n/a	n/a	n/a	n/a	В	В	В	n/a	n/a
5-ring poly- aromatic	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	В	В	n/a
6-ring poly- aromatic	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	В	n/a

<sup>&</sup>lt;sup>a</sup> Structures with carbon number >C<sub>25</sub> are not expected to bioaccumulate.

B – Predicted highly bioaccumulative with a BCF/BAF greater than 5000.

n/a – Indicates that no such carbon numbers exist within the group or the structure was not considered.

<sup>-</sup> Indicates that these structures are not considered highly bioaccumulative.

# **Appendix E. Summary of Health Effects Information**

Table E.1. Critical health effects information on Stream 4 HFO substances

Endpoints	CAS RN	Effect levels <sup>a</sup> /Results
Acute health	64741-57-7	Dermal LD <sub>50</sub> (rabbit): more than 2000 mg/kg-bw
effects	64741-62-4	(both sexes) for four CAS RNs tested (API 2004;
	64741-81-7	ECB 2000b).
	64742-90-1	,
Maternal,	64741-62-4	Critical Effect Level: 50 mg/kg-bw/day for dose-
reproductive		related increases in total and early resorptions, as
and		well as percentage of dead or resorbed
developmental		conceptuses per litter, only after exposure during
health effects		gestation days 6-8 (period of early
		organogenesis). Dose-related decreases in
		maternal food consumption and body weight gain
		were also observed. Doses of 1, 50 or 250 mg/kg-
		bw/day were applied to the shaved skin of
		pregnant CD (Sprague-Dawley) rats (10 animals
		per dose, per group), once daily for 6 hours/day,
		during gestation days 0 through 2, 3 through 5, 6
		through 8, 9 through 11, 12 through 14, 15
		through 17 or 18 through 19 (i.e., "pulse"
		exposures). At 250 mg/kg-bw/day, increased
		resorptions were observed when administered
		during GD 9-11 (period of late organogenesis)
		(Hoberman et al. 1995).
	64741-62-4	Dermal maternal, reproductive and
		developmental LOAEL: 1 mg/kg-bw/day for
		dose-related decreases in maternal food
		consumption, body weight (more than5% at this
		dose), body weight gain and gravid uterine weight,
		as well as the occurrence of red vaginal exudates;
		dose-related increases in total and early
		resorptions, percentage of dead or resorbed
		conceptuses per litter, and decreased number of
		live fetuses; increased incidence of fetal variations
		associated with decreased fetal body weight was
		noted (these effects were noted to be reversible
		delays in development). Doses of 0.05, 1, 10, 50
		or 250 mg/kg-bw/day were applied to the clipped
		skin of pregnant CD (Sprague-Dawley) rats
		(25 animals per dose) continuously during
		gestation days 0-19 (Hoberman et al. 1995).
	64741-62-4	Other dermal study: Doses of 4, 8, 30, 125 or
		500 mg/kg-bw/day were applied to the shaved

	skin of pregnant CD (Sprague-Dawley) rats (10–15 animals per dose) continuously during gestation days 0–19 (4 mg/kg-bw/day dose given as 8 mg/kg-bw every other day). At greater than or equal to 8 mg/kg-bw/day, dose-related aberrant serum chemistry and decreased body weight gain, as well as the occurrence of red vaginal exudates in dams; dose-related increased resorptions and decreased litter size; dose-related decreased fetal body weight. At 125 mg/kg-bw/day, changes in maternal thymus and liver
	weights. At <b>500 mg/kg-bw/day</b> , fetal malformations (Feuston et al. 1997; Mobil 1990).
64741-62-4	Other dermal study: Doses of 4, 8, 30, 125 or 250 mg/kg-bw/day were applied to the shaved skin of pregnant CD (Sprague-Dawley) rats (10 animals per dose) continuously during gestation days 0–19 (4 mg/kg-bw/day dose given as 8 mg/kg-bw every other day). At greater than or equal to 8 mg/kg-bw/day, dose-related decreases in maternal food consumption and body weight; abnormal external development in living and dead fetuses (noted to occur at low incidences). At greater than or equal to 30 mg/kg-bw/day, dose-related increases in resorptions, number of dams with no viable offspring and number of dead/resorbed offspring per litter, as well as decreased number of viable fetuses; dose-related decreases in fetal body weight and crown—rump length, as well as skeletal variations and visceral anomalies. At 250 mg/kg-bw/day, atrophy of the thymus and decreases in thymus and liver weights, as well as increased serum alkaline phosphatase in dams; no viable fetuses (Feuston et al. 1989; Mobil 1987a).
64741-81-7	Other dermal study: Doses of 8, 30, 125 or 250 mg/kg-bw/day were applied to the shaved skin of pregnant Sprague-Dawley rats (15 animals per dose) continuously during gestation days 0–19. At greater than or equal to 8 mg/kg-bw/day, dose-related decreased thymus weight, increased liver weight and skin irritation in dams. At greater than or equal to 30 mg/kg-bw/day, dose-related paleness and emaciation, as well as red vaginal discharge in dams; dose-related increased resorptions. At greater than or equal to

		125 mg/kg-bw/day, dose-related decreased fetal body weight. At 250 mg/kg-bw/day, maternal maribundity (Mobil 1994)
	64741-62-4	Oral study: A single dose of 2000 mg/kg-bw on one of gestation days 11–15 (profile of developmental effects as a function of gestation day) or single doses of 125, 500 or 2000 mg/kg-bw on gestation day 12 (profile of developmental effects as a function of dose) were administered by gavage to pregnant CD (Sprague-Dawley) rats (10 animals per group).  (1) Developmental effects versus gestation day – At 2000 mg/kg-bw, decreases in food consumption, body weight gain and thymus weight, as well as red vaginal discharge, perineal staining and decreased stool in dams (regardless of gestation day); increased resorptions and decreased litter size (greatest on gestation days 11–12); decreased fetal body weights (regardless of gestation day) and increased skeletal anomalies (irreversible) (greatest on gestation days12–14).  (2) Developmental effects versus dose – At greater than or equal to 125 mg/kg-bw/day, dose-related decreases in food consumption, body weight gain and thymus weight in dams; dose-related increased resorptions and decreased litter size; dose-related decreased fetal body weights and increased skeletal anomalies (irreversible) (Feuston and Mackerer 1996).
Carcinogenicity	64741-62-4	Dermal study (chronic): Groups of male C3H mice (50 animals per dose) were treated with 25 μL of catalytically cracked clarified oil at 1%, 2%, 5%, 10% or 20% (8.4, 16.8, 42.0, 83.8 or 167.6 mg/kg-bw) <sup>b,c,d,e</sup> in mineral oil, 3 times per week for life. At 1%, 9/50 exposed mice developed tumours (4 carcinomas, 5 papillomas). At 2%, 34/50 exposed mice developed tumours (30 carcinomas, 4 papillomas with a latency period of 92 weeks). At 5%, 46/50 exposed mice developed tumours (46 carcinomas with a latency period of 61 weeks). At 10%, 48/50 exposed mice developed tumours (47 carcinomas, 1 papilloma with a latency period of 45 weeks). At 20%, all (50/50) exposed mice developed tumours (50 carcinomas with a latency period of 36 weeks). Of

		the 610 mice tested with the negative control (highly refined mineral oil) from this study and two other similar studies conducted by the same author, only two mice developed benign papillomas, and none developed carcinomas (McKee et al. 1990).
64	4741-62-4	Dermal study (initiation): Groups of male CD mice (30 per group) were treated with 50 μL of catalytically cracked clarified oil at 1% (16.8 mg/kg-bw) <sup>b,c,e</sup> in toluene, once per day for 5 consecutive days. After a 2-week rest period, the promoter phorbol-12-myristate-13-acetate was applied 2 times per week for 25 weeks. A significant increase in skin tumour incidence was observed (26/30 exposed mice developed tumours after 16 weeks) (API 1989).

<sup>&</sup>lt;sup>a</sup> LD<sub>50</sub>, median lethal dose; LOAEL, lowest-observed-adverse-effect level.
<sup>b</sup> Body weight not provided; thus, laboratory standards from Salem and Katz (2006) were used.
<sup>c</sup> The following formula was used for conversion of provided values into mg/kg-bw: (% of dilution × *x* mL × ρ) / bw.
<sup>d</sup> Density not provided; thus, a density from CONCAWE (1998) was used.
<sup>e</sup> A volume/volume dilution was assumed.