Draft Screening Assessment

Petroleum Coke Group

Chemical Abstracts Service Registry Numbers
64741-79-3
64743-05-1

Environment and Climate Change Canada
Health Canada

September 2020

Synopsis

Pursuant to section 74 of the *Canadian Environmental Protection Act, 1999* (CEPA), the Minister of the Environment and the Minister of Health have conducted a screening assessment of two substances referred to collectively under the Chemicals Management Plan as the Petroleum Coke Group. Substances in this group were identified as priorities for assessment as they met categorization criteria under subsection 73(1) of CEPA. The Chemical Abstracts Service Registry Numbers (CAS RN[1]), their *Domestic Substances List* (DSL) names and their common names are listed in the table below.

Substances in the Petroleum Coke Group

CAS RN	DSL name	Common name
64741-79-3	Coke (petroleum)	green coke
64743-05-1	Coke (petroleum), calcined	calcined coke

Coke (petroleum), hereinafter referred to as green coke, is a carbon-rich solid residue obtained as a by-product during the thermal conversion process of refining crude oil and oil sands upgrading. Further heating of green coke to remove the volatiles produces coke (petroleum), calcined, hereinafter referred to as calcined coke. The carbon content for green and calcined coke ranges from 84-97% (CONCAWE 1993). Both green coke and calcined coke are of Unknown or Variable composition, Complex reaction products or Biological material (UVCB). Calcined coke is more refined than green coke from a chemical standpoint and it contains less volatile substances or other impurities. For the purpose of this assessment, the two substances are grouped together and are referred to as the Petroleum Coke Group.

In Canada, some of the green coke that is produced is used onsite at refineries or upgraders as fuel, but most is stockpiled (such as in the Athabasca Oil Sands Region (AOSR)) for future use. Green coke from Canadian or imported sources is also calcined and then used in aluminium and steel plants.

Since the substances in the Petroleum Coke Group are UVCBs, information on environmental concentrations and toxicity to the environment of the actual petroleum coke substances themselves is often limited. As such, components of petroleum coke such as polycyclic aromatic hydrocarbons (PAHs), nickel and vanadium are used as surrogates for environmental exposure, hazard and risk, when applicable.

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It is assumed that substances in the petroleum coke group have low bioavailability based on physical-chemical properties, such as low water solubility and high molecular weight of the UVCB components, as well as the limited observed adverse effects at high concentrations in aquatic, terrestrial, and mammalian laboratory toxicity tests.

The presence of polycyclic aromatic hydrocarbons (PAHs) and metal impurities associated with petroleum coke have been identified in leaching and field studies performed under specific experimental conditions. However, these components are not considered to be readily bioavailable under standard environmental conditions of petroleum coke storage in stockpiles because of the insolubility, the high carbon content, large particle size of petroleum coke.

To address concerns regarding leaching of embedded substances from stockpiles of petroleum coke near rivers, analysis of available surface water and sediment monitoring data for areas of the Athabasca River surrounding petroleum coke stockpiles in the Athabasca Oil Sands Region (AOSR) was carried out. The measurements did not indicate increased aquatic risk from PAH and metal (Ni and V) components of petroleum coke downstream of the outdoor stockpiles.

Considering all available lines of evidence presented in this draft screening assessment, there is low risk of harm to the environment from green and calcined petroleum coke. It is proposed to conclude that green coke and calcined coke 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.

The United States Environmental Protection Agency performed a screening level hazard characterization for green petroleum coke and calcined coke dust. Hazard assessments on petroleum coke have also been performed by the Agency for Toxic Substances and Disease Registry (ATSDR). There was no evidence of in vivo or in vitro genotoxicity, carcinogenicity or reproductive or developmental toxicity following particulate matter (dust) inhalation or dermal exposure to these substances. However, two-year repeat-dose inhalation exposure to green coke resulted in accumulation of coke dust particles and pulmonary inflammation in rats.

Measurements of particulates released from petroleum coke into the air from stockpiles in the AOSR, near urban petroleum coke production and transport facilities, near iron and aluminum mills, and near coke calcining plants did not indicate increased risk associated with the inhalation exposure to petroleum coke. There are also low concerns from exposure to petroleum coke in soil and water.

On the basis of the information presented in this draft screening assessment, it is proposed to conclude that green coke and calcined coke 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.

Therefore, it is proposed to conclude that green coke and calcined coke do not meet any of the criteria set out in section 64 of CEPA.

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1. Introduction

Pursuant to section 74 of the *Canadian Environmental Protection Act, 1999* (CEPA) (Canada 1999), the Minister of the Environment and the Minister of Health have conducted a screening assessment of two substances, coke (petroleum) (CAS RN[2] 64741-79-3) and coke (petroleum), calcined (CAS RN 64741-05-1), referred to collectively under the Chemicals Management Plan as the Petroleum Coke Group to determine whether these substances present or may present a risk to the environment or to human health. The substances in this group were identified as priorities for assessment as they met categorization criteria under subsection 73(1) of CEPA (ECCC, HC [modified 2017]).

Substances in the Petroleum Coke Group are of Unknown or Variable composition, Complex reaction products or Biological material (UVCB), information on environmental concentrations and toxicity to human health and the environment of the actual substances themselves is limited. As such, components of petroleum coke such as polycyclic aromatic hydrocarbons (PAHs), nickel and vanadium are used as surrogates for exposure, hazard and risk, when applicable.

Releases of or exposures to certain chemical components from petroleum coke substances are considered in this assessment. Components considered are certain PAHs, vanadium and nickel. Existing risk assessment for these components inform this assessment. These include:

- Vanadium and nickel are considered in past moiety assessments for inorganic compounds (Environment Canada, Health Canada 1996; HC 2016b) and are listed on Schedule 1 of CEPA.
- Polycyclic aromatic hydrocarbons (PAHs), including those from the use of petroleum coke, released from the metallurgical sector (metals and coking plants), aluminum smelters, and wastes containing PAHs have been assessed (Environment Canada, Health Canada 1994) and are listed on Schedule 1 of CEPA.
- Health effects associated with coarse and fine particulate matter have been assessed by Health Canada (Health Canada 2013, Health Canada 2016a) and Canadian Ambient Air Quality Standards for $PM_{2.5}$ have been established (CCME 2019). Guidance for $PM_{2.5}$ in indoor air has also been established (Health Canada 2012).

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The substances in the Petroleum Coke Group have been reviewed internationally by the United States Environmental Protection Agency (US EPA 2011, MDEQ 2014, ATSDR 2016). These assessments were used to inform the health effects characterization in this screening assessment.

This draft screening assessment includes consideration of information on chemical properties, environmental fate, hazards, uses and exposures, including additional information submitted by stakeholders. Relevant data were identified up to March, 2019. Targeted literature searches were conducted up to January 2020. When available and relevant, information presented in assessments from other jurisdictions was considered. Empirical data from key studies as well as results from models were used to reach proposed conclusions.

This draft screening assessment was prepared by staff in the CEPA Risk Assessment Program at Health Canada and Environment and Climate Change Canada and incorporates input from other programs within these departments. The assessment has undergone external written peer review and/or consultation. Comments on the technical portions relevant to the environment were received from Mr. Geoff Granville (GCGranville Consulting Corp), and Dr. Connie Gaudet while comments on the technical portions relevant to human health were received from Dr. J. A. Caruso (Wayne State University), Dr. G. T. Johnson (University of South Florida), and Dr. D. Singh (University of South Florida). While external comments were taken into consideration, the final content and outcome of the screening assessment remain the responsibility of Health Canada and Environment and Climate Change Canada.

This draft screening assessment focuses on information critical to determining whether substances meet the criteria as set out in section 64 of CEPA by examining scientific information and incorporating a weight of evidence approach and precaution.[3] This draft screening assessment presents the critical information and considerations on which the proposed conclusions are based.

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

2. Identity of substances

The CAS RN, *Domestic Substances List* (DSL) names and common names for the individual substances in the Petroleum Coke Group are presented in **Error! Reference source not found.**.

Coke (petroleum), hereinafter referred to as ‘green coke’, is a carbon-rich solid residue obtained as a by-product during the thermal conversion process of refining crude oil and, in Canada, oil sands upgrading. Further heating of green coke to release the volatiles produces the solid coke (petroleum), calcined (hereinafter referred to as ‘calcined coke’). When referring to the group properties of green and calcined petroleum coke, the term Petroleum Coke Group is used. The term ‘petroleum coke’ is used when referring to non-specified mixtures of petroleum coke (such as outdoor stockpiles).

Table 2-1. Substance identities for the two petroleum coke substances

CAS RN	DSL name	Common Name
64741-79-3	Coke (petroleum)	Green coke
64743-05-1	Coke (petroleum, calcined)	Calcined coke

Green coke contains higher volatile matter and residual impurities as compared to calcined coke which contains significantly less volatile matter and other impurities. Green coke is used as a fuel whereas calcined coke has a range of uses including aluminum and steel production.

The substances in the Petroleum Coke Group are UVCBs. These substances are derived from natural sources or complex reactions and cannot practicably be synthesized by simply combining individual components. The characteristics of any batch of petroleum coke are determined by the feedstock composition and type of coking process and conditions (Hill et al. 2014).

Green coke is a black, polycrystalline carbonaceous solid material produced as a by-product of the crude oil coking process, and oil sands upgrading (Hill et al. 2014). Petroleum vacuum distillates or heavy distillates are heated to thermal cracking temperatures (415°C - 505°C) at high pressures (90 psi) to convert these materials to petroleum vapours and remaining solid coke (Ellis and Paul 1998, API 2008, USEPA 2011, McKee et al. 2014, Speight 2014). Major coking technologies include delayed coking (a semi-batch process) and fluid coking (a continuous process performed at higher temperatures) (Hill et al. 2014). The residual green coke contains the heaviest hydrogen-poor portions of petroleum feedstock (i.e., asphaltenes and resins), essentially all the feed metals and ash, and large portions of the feedstock sulphur and nitrogen (Parkash 2010). Green coke has low density and contains typically 2 to 15 wt% volatile matter, but can contain up to 21 wt % (Al-Haj-Ibrahim and Morsi 1992; CONCAWE 1993).

The volatile matter contained within the carbonaceous matrix of green coke consists mostly of hydrocarbons, including some PAHs (CONCAWE 1993). Analyses of green coke have detected polycyclic aromatic compounds, including parent and alkylated PAHs: naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, benzo[a]pyrene, benzo[e]pyrene, benzo[g,h,i]perylene, benzo[a]anthracene, benzo[a,b]anthracene, dibenzo[a,h]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, phenanthrene, methyl benzo[a]pyrene, fluorine and indeno(1,2,3-cd)pyrene and methylbenzo[g,h,i]perylene (CONCAWE 1993; Dalbey et al. 1998; API 2008; Jongeneelen et al. 1989; Predel 2014; Chibwe et al. 2019).

Green coke also contains inorganic components within the carbon matrix. Sulphur mainly exists as organic sulphur bound to the carbon matrix, while iron, silicon, and ash exist as particulates (Al-Haj-Ibrahim and Morsi 1992; API 2008; Ellis and Paul 1998). Other metals such as vanadium and nickel exist as chelates or porphyrins in the asphaltene fraction, or as part of the ash and particulates when not chemically bonded to the coke structure (Ellis and Paul 2000a; 2000b).

The composition of the substances in the Petroleum Coke Group vary based on the feedstock and the coking process used (CONCAWE 1993). Typical compositional ranges of Petroleum Coke Group are provided in Table 2-2. In addition, other elements have also been reported as components of petroleum coke such as silicon, aluminum and boron while heavy metals may be found at low concentrations as components of the ash (API 2008).

Table 2-2. Typical ranges for compositional characteristics of petroleum coke

Property	Range	Unit[a]	References
Carbon	84 – 97	%	CONCAWE 1993
Hydrogen	Up to 5	%	CONCAWE 1993
Ash	0.03 – 7	wt %	Lee et al. 1997; Government of Alberta 2018
Volatile matter	2 – 15	%	CONCAWE 1993
PAH	100 –250	mg/kg	Jongeneelen et al. 1989; Predel 2014
Sulfur	0.2 – 6	%	CONCAWE 1993
Nickel	10 – 3000	mg/kg	CONCAWE 1993
Vanadium	5 – 5000	mg/kg	CONCAWE 1993
Iron	50 – 2000	mg/kg	CONCAWE 1993

[a] Units are as reported by the authors.

Further heating of green coke to high temperatures (1200 °C -1350 °C) to release the volatiles produces calcined coke (API 2008). Calcined coke has higher density, mechanical strength, and electrical conductivity than the green coke feedstock (Parkash 2010). The green coke carbon matrix pores are filled with a hardened hydrocarbon residuum, which distills off during calcination to produce calcined coke (Al-Haj-Ibrahim and Morsi 1992; API 2008). The calcination process removes moisture and reduces volatile matter to less than 0.25% by weight (Lee et al. 1997), while increasing physical strength and electrical conductivity (Ellis and Paul 2000a). As a result, calcination also increases the percentage of elemental carbon (API 2008) and metal concentrations in calcined coke relative to green coke (Sun et al. 2009).

A summary of the characteristics of calcined coke used in metallurgical operations is presented in Table 2-3. It should be noted that despite being calcinated (which increases the relative proportion of metals), the maximum concentrations of metal reported are lower than those in Table 2-2 due to the practice of selecting low-metal green coke feedstocks for calcination (Lee et al. 1997).

Table 2-3. Typical ranges for compositional characteristics of metallurgical anode grade calcined coke (from Lee et al. 1997)

Property	Range	Unit[a]
Ash	0.1-0.3	wt %
Volatile matter	<0.25	wt %
Sulfur	1.7-3.0	wt %
Nickel	120-350	mg/kg
Vanadium	165-350	mg/kg

[a] Units converted as required for ease of reporting.

3. Physical and chemical properties

Typical physical-chemical properties of the Petroleum Coke Group are difficult to determine as the melting and boiling points are high, and vapour pressures are very low and cannot be measured or estimated accurately under ambient environmental conditions (API 2008; USEPA 2011). The Petroleum Coke Group are also insufficiently soluble in water to determine an octanol-water partition coefficient (API 2008). Measurements of the hydrocarbon and inorganic components of green coke in water extracts are typically below detectable levels: 5 µg/L for the organic fraction, 0.4 µg/L to 200 µg/L for metals, and 5.1 mg/L for sulphur (Wildlife International Ltd. 2007a; 2007b; 2007c). It is expected that the vapour pressure and water solubility of the Petroleum Coke Group are negligible (USEPA 2011). The bulk density for green coke and calcined coke is 0.8-1.4 g/cm^3 and 0.80-0.88 g/cm^3, respectively (Lee et al. 1997).

4. Sources and uses

Tables 4.1 and 4.2 summarize the supply and disposition information for petroleum coke from refineries in Canada for 2012 and 2016, as reported by Statistics Canada (2020). Petroleum coke is mostly produced and stockpiled in Alberta where there is a trend of rising stockpile inventories. Petroleum coke production rates in Alberta ranged from 8.6 million tonnes to 10.1 million tonnes per year (~11x10^6 m^3 – 13x10^6 m^3) between 2013 and 2017 (AER 2013, 2014, 2015, 2016, 2017a). At the same time, the total inventory of petroleum coke increased from 84 million tonnes (~11x10^7 m^3) in 2013, to 113 million tonnes (~14x10^7 m^3) in 2017 (AER 2018).

Table 4-1. Supply and disposition of petroleum coke in Canada in 2012 in thousands of cubic metres (Statistics Canada 2020)[a]

Parameter	Quebec	Ontario	Alberta	Other provinces and territories	Total for Canada
Refinery production	NA	435.2	344.9	NA	1272.0
Exports	NA	26.3	0	NA	85.9
Imports	NA	302.4	4.6	NA	1678.5
Inter-regional transfers [b]	NA	-28.6	0	NA	0
Total domestic sales	805.0	470.2	230.9	668.9	2175.0

Abbreviations: NA, data not available.

[a] Data reported from refining companies in Canada and major wholesalers/distributors (Statistics Canada 2013).

[b] Negative values (–) denote an out-of-province transfer. Positive values denote transfers into a province.

Table 4-2. Supply and disposition of petroleum coke in 2016 in thousands of cubic metres (Statistics Canada 2020)[a]

Parameter	Atlantic	Quebec	Ontario	Alberta	Total for Canada
Refinery production	NA	NA	>82[b]	>147[b]	1020 [b]
Exports	NA	0	>15[b]	0	32[b]
Imports	>335[b]	532	>771[b]	0.745	>2028[b]
Inter-regional transfers [b]	0	42[b]	-48[c]	0	48

Abbreviations: NA, data not available.

[a] Data reported from refining companies in Canada and major wholesalers/distributors (Statistics Canada 2017).

[b] Annual data with “>” indicate data was not available for certain months

[c] Negative values (–) denote an out-of-province transfer. Positive values denote transfers into a province.

Up to 60% (by weight) of feedstock in petroleum streams may be converted to green coke (Speight 2014). Alberta oil sands operators had produced 60 million tonnes (~8×10^7 m^3) of green coke by 2008 (Baker et al. 2012). In 2011, production at upgraders only in Alberta and Saskatchewan was nearly 9 million tonnes (~1x10^7 m^3) (Stockman 2013). Fedorak and Coy (2006) estimate that over the lifetime of oil sands extraction operations, 1 billion m^3 of green coke will be produced.

Between January 2011 to September 2012, Canada imported almost 3.4 million tonnes of green coke (~4x10^6 m^3) from the United States for fuel and manufacturing uses (Stockman 2013). From 2013 to 2016, Canada’s annual import of petroleum coke from the US decreased from approximately 1.9 million tonnes to 1.3 million tonnes annually (~24x10^5 m^3 to 16x10^5 m^3) (EIA 2017). Globally, about 80% of petroleum coke produced is used as a fuel (in power generation, cement kilns, and other industries). It is also used in manufacturing products such as aluminum, paints, coatings, colourings, steel, paper and fertilizer (National Association of Manufacturers 2015).

A survey issued pursuant to a CEPA section 71 notice (ECCC 2016a) was conducted for both substances in the petroleum coke group, and a search for information in the public domain was performed. In addition to general uses such as production of aluminum, nickel, copper and steels, and in carbon electrodes, information received in response to a CEPA section 71 survey indicated that petroleum coke is used in a number of other industries, see Table 4.3 (ECCC 2016a). In Canada, some petroleum coke produced is used on site at mine extraction and upgrading facilities and refineries as fuel or is sold; however, most is stockpiled (ERCB 2011) for future use. According to Alberta Energy and Utilities Board regulations, coke must be stored onsite for future recovery, as it is a potential fuel (Puttaswamy et al. 2010; Fedorak and Coy 2006). In 2016, about 10% of green coke produced by the upgraders in Alberta was used as fuel on site, while approximately 90% was stockpiled (AER 2017b). Since 2000, the amount of green coke used in Canadian manufacturing (including refineries and upgraders) has averaged about 2 million tonnes per year (Stockman 2013).

Table 4-3. Uses of petroleum coke in Canada according to information received in response to a CEPA section 71 survey (Environment Canada 2016a) and other sources.

Substance [CAS RN]	**Uses**
Coke (petroleum) [64741-79-3]	-Primary production of alumina and aluminum -Iron and steel mills and ferro-alloy manufacturing -Petroleum refineries -Clay building material and refractory manufacturing -Fuels and fuel additives -Filler for carbon electrodes
Coke (petroleum), calcined [64743-05-1]	-Primary production of alumina and aluminum -Iron and steel mills and ferro-alloy manufacturing -Abrasive product manufacturing -Non-ferrous metal (except aluminum) smelting and refining -Intermediates -Production of carbon steel billets and coil rod -Reducing agent during pyrometallurgical smelting for the production of crude lead bullion -Batteries -Filler for carbon electrodes used in aluminum smelting; -Manufacture of anodes -Abrasive grain which is the main component in grinding wheels -Nickel and copper smelting intermediates and refined nickel

In addition, green coke may be combined with oil sands process water (Jensen-Fontaine et al. 2014; Fedorak and Coy 2006), as a potential medium for reclamation of tailings ponds (Hill et al. 2014). Most oil sands mine operators intend to use the stockpiled coke in reclamation processes (AER 2017b). In 2009, a pilot project was initiated to manage the tailings at Wapisiw Lookout (Suncor Pond 1) using petroleum coke caps. As of 2018, this project had expanded to include additional sites (Suncor Pond 5) (Suncor 2018). Additionally, research has been initiated in the Mildred Lake oil sands site to evaluate the use of petroleum coke to filter and detoxify tailings water (COSIA 2017). There are research studies on potential uses of petroleum coke including use as a material in the construction of reclaimed wetlands (Baker et al. 2012), and for integration into terrestrial and aquatic landscapes as part of oil sands closure plans, long term storage, and future recovery (Puttaswamy et al. 2010).

No uses of petroleum coke in foods, natural health products, cosmetics, veterinary medicines, or as active ingredients or formulants in pest control products have been reported [Personal communication, email from Food Directorate, Health Canada, to Existing Substances Risk Assessment Bureau, Health Canada, dated July 10, 2018; unreferenced; Natural Health Products Ingredients Database. 2018, Ottawa (ON): Health Canada; Licensed Natural Health Products Database. 2016, Ottawa (ON): Health Canada; Health Canada. Personal communication, email from the Natural and Non-prescriptive Health Products Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated July 11 2018; unreferenced; Personal communication, email from the Consumer Product Safety Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated June 29, 2018; unreferenced; Health Canada's Pest Management Regulatory Agency. List of formulants. Published 31 August 2010.]

5. Releases to the environment

Petroleum coke may be released to the environment during storage, transportation, and as a result of commercial or industrial use. However, it has negligible water solubility and vapour pressure, and is not expected to be readily bioavailable to organisms.

In Canadian industrial and commercial settings (other than oil and gas production), significant releases of petroleum coke to the environment are not expected. In these settings, petroleum coke is used as processing intermediates, incorporated directly into products or burned as fuel. As a result, the petroleum coke is either consumed on site or processed as a constituent of products from which environmental releases are expected to be lower due to their expected uses. Quantities for industrial or commercial uses are also expected to be minor in comparison to the large quantities stockpiled outdoors as a by-product of oil and gas production.

In Alberta, the majority of green coke produced from the processing of bitumen is stockpiled on-site in large containment cells or as outdoor piles exposed to the natural environment (Puttaswamy et al. 2010; Fedorak and Coy 2006), potentially subject to release via runoff or as fugitive dust emissions to air, where it may be carried by wind and settle to land or water. To control potential petroleum coke emissions to air as fugitive dust, the API (2014) suggests practices to maintain optimal moisture content through water wetting or application of anti-dust chemical agents, in addition to enclosures and wind screens in storage.

Petroleum coke is transported via ocean freight, barges, rail and truck, where there is potential for fugitive dust emissions to air. Suggested steps to minimize these emissions include wetting, application of anti-dust agents, covering of loading areas, and truck washing with management of resulting water (API 2014).

Trace concentrations of hazardous components in petroleum coke such as heavy metals and PAHs have the potential to be released to the environment. Trace heavy metal components may be released to air during its combustion, to water and soil through stockpile leachate or if used in remediation projects (Puttaswamy et al. 2010). PAH components may be released to air during the combustion of petroleum coke, further calcination, use in the metallurgical sector, or through wind-blown particles of petroleum coke from stockpiles (Zhang et al. 2016a). Fugitive dusts from petroleum coke stockpiles in the ASOR have also been identified as main contributors of elements through air deposition, particularly in the winter months (Gopalapillai et al. 2019).

6. Environmental fate and behaviour

Environmental distribution and transport will depend on particle size and density of the petroleum coke material released (API 2008). If released to water, petroleum coke is expected to either incorporate into sediment or float on the surface (API 2008), given its insolubility in water. If terrestrial releases occur, the petroleum coke substances are expected to be incorporated into the soil with little mobility (USEPA 2011) or become transported via wind or surface water flow. As petroleum coke is a solid, the carbonaceous components of the particles are not expected to volatilize to air. However, if released to air as fugitive dust emissions (API 2014), it is likely to be transported via wind and settle to land or water.

The hydrocarbon content of green coke is unlikely to engage in direct or indirect photochemical reactions, undergo hydrolysis, or be subject to degradation by microorganisms (API 2008). High stability in the environment is expected on the carbonized and compact nature of petroleum coke (USEPA 2011). Given its composition and physical chemical properties, abiotic degradation and biodegradation are unlikely. With the assumed high molecular weight of the carbonaceous matrix (USEPA 2011), the bioaccumulation potential of the Petroleum Coke Group is expected to be very low. Additionally, the components of petroleum coke embedded in the carbon matrix are also expected to have lowered bioavailability relative to unbound forms.

7. Potential to cause ecological harm

7.1 Ecological effects assessment

7.1.1 Effects on aquatic organisms

Due to the limited water solubility of petroleum coke, reported laboratory aquatic testing was conducted using water accommodated fractions (WAFs). Limit tests using 1000 mg/L green coke were conducted using algae, aquatic invertebrates and fish. Table 7-1 summarizes the key aquatic toxicity studies for green coke. No effects were reported for invertebrates or fish, but the 96-hour No Observable Effect Loading Rate (NOELR) for the algal species *Raphidocelis subcapitata (*formerly *Selenastrum capricornutum)* was reported as <1000 mg/L, where slight growth inhibition was observed in the single 1000 mg/L treatment, although a similar effect was not observed in prior range finding testing (Wildlife International Ltd 2007a).

Table 7-1. Key aquatic toxicity studies for green coke

Common name	Test organism	Endpoint	Value (mg/L)	Reference
Algae	*Raphidocelis subcapitata* (formerly *Selenastrum capricornutum*)	96 h NOELR Cell density, biomass, growth rate	<1000	Wildlife International, Ltd. 2007a
Cladoceran	*Daphnia magna*	48 h NOELR immobilization	1000	Wildlife International, Ltd. 2007b
Fathead minnow	*Pimephales promelas*	96 h NOELR	1000	Wildlife International, Ltd. 2007c

Puttaswamy et al. (2010) reported that exposure from petroleum coke leachates collected from field lysimeters in outdoor stockpiles resulted in observed acute adverse effects to *Ceriodaphnia dubia*. Two lysimeters were placed in excavated areas of a coke deposit. Leachate samples were collected periodically from a shallow lysimeter (overlain with 50 cm of glacial till and mineral peat topsoil) and a deep lysimeter (overlain with 100 cm of till and peat soil) for toxicity testing. Acute adverse effects were observed when *C. dubia* were exposed to undiluted leachate samples. The 7-day lethal concentration to 50% of a population (LC_{50}) for survival fell between 12.5% and 21.8% v/v for the shallow lysimeter leachates and 7.2%-14.4% v/v for the deep lysimeter leachates. An analysis of the leachate attributed the adverse effects at lower leachate concentrations (<25% v/v) to nickel and vanadium, which had been released from the petroleum coke. In a subsequent laboratory chronic toxicity study (Puttaswamy 2011), it was determined that nickel and vanadium were both the cause of the adverse effect response of *C. dubia*. Leachate pH also was a factor influencing observed toxicity, as vanadium was the primary cause of toxicity at pH 9.5, while both nickel and vanadium were identified as the primary toxicants at pH 5.5.

Embryonic fathead minnows (*Pimephales promelas*) experienced reduced survival when exposed to melted snow samples collected from sites greater than 7 km from mining operations and petroleum coke stockpiles along the Athabasca river (Parrot et al. 2018). Snow samples contained the atmospheric deposition of fugitive dusts which had accumulated over winter seasons (4-5 month durations). The snow samples were melted and embryos and hatched minnows were exposed for 12-21 days to the ion adjusted snowmelt water. Reductions in larval minnow survival of the exposed organisms were correlated to the sum of the concentration of alkylated PAHs, with adverse effects occurring in the 2-20 mg/L range. It should be noted that survival effects were not noted in spring melt water that was also collected from the same areas. The contaminants in snow appear to be sufficiently diluted by the Athabasca River during the spring melt period that they are no longer eliciting adverse effects.

Physical effects such as clogging gills or burying of sediment-dwelling organisms have been identified as potential concerns in aquatic environments (Dimond 2013).

7.1.2 Effects on Terrestrial Organisms

Table 7-2 summarizes the key soil toxicity studies for the petroleum coke substances. Laboratory studies on terrestrial organisms were conducted with green coke incorporated directly into artificial soil at a concentration of 1000 mg/kg (nominal). No effects were observed for any of the tested plant or earthworm species.

Table 7-2. Key soil toxicity for the green coke

Common name	Test organism	Endpoint	Value (mg/kg)	Reference
Compost worm	*Eisenia fetida*	14 d NOEC	1000	Wildlife International, Ltd. 2007d
Corn	*Zea mays*	21 d NOEC Seedling emergence, growth	1000	Wildlife International, Ltd. 2007e
Radish	*Raphanaus sativus*	21 d NOEC Seedling emergence, growth	1000	Wildlife International, Ltd. 2007e
Soybean	*Glycine max*	21 d NOEC Seedling emergence, growth	1000	Wildlife International, Ltd. 2007e

Abbreviation: NOEC, no observed effect concentration

In field studies, Nakata et al. (2011), found select plants were able to survive in petroleum coke, however, symptoms of stress were exhibited. In addition, potentially phytotoxic concentrations of nickel and vanadium were found in some plant tissues, while the heavy metal molybdenum accumulated in shoots at concentrations previously reported to cause molybdenosis in ruminants.

7.2 Ecological exposure assessment

UVCB substances such as petroleum coke cannot be accurately measured in environmental media. Components of the substance, such as PAHs and metals, are frequently measured as they are environmentally relevant components of petroleum coke. Though petroleum coke group substances are used manufacturing products such as aluminum, the outdoor petroleum coke stockpiles are the primary concern for ecological exposure. Petroleum coke stockpiles were identified as the major source (contribution of 45-95%) for atmospheric deposition of PAHs in living moss of the Alberta Oil Sands Region (AOSR) (Zhang et al. 2016a). The total concentration of 13 parent (lacking any alkyl side chains) PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k+j]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, dibenz[a,h]anthracene) ranged from 28.7 ng/g to 389 ng/g dry weight in moss samples and from 0.036 µg/m^2 to 76.9 µg/m^2 in snow. The total concentration of 13 parent PAHs reached 260 to 370 ng/g dry weight. in the top 6 cm of peat cores (Zhang et al. 2016a; 2016b). Concentrations of the 16 priority PAHs listed by the US EPA were all less than 0.05 ug/L in petroleum coke leachates collected in field lysimeters in the AOSR (Puttaswamy et al. 2011).

Exposure to PAH components in air that are released during petroleum coke combustion, further calcination, or use in the metallurgical sector have been previously assessed (Environment Canada, Health Canada 1994). Petroleum coke fine particles that are derived from the delayed coking process can contain up to 80 µg/g of the EPA 16 priority PAHs (Jautzy et al. 2015). Isotopic analysis of PAHs in lake sediments has shown petroleum coke is capable of long range transport via air; it was found to be a contributing source of PAH contamination as far as 150 km away from the source (Jautzy et al. 2015). Additionally, a study of metal and PAH concentrations in air samples collected around the AOSR identified delayed petroleum coke dust as a source of atmospheric benzo[a] pyrene and vanadium (Xu 2018). This is discussed further in section 8.1.1.1.

Concentrations of PAHs associated with delayed petroleum coke measured in mosses were found to be at significantly higher concentrations at sites closest to bitumen upgrading activity, than at sites located further away (Zhang et al. 2016a). Releases of components from petroleum coke to air will not be further considered in the ecological portion of the screening assessment. However, information on the human health impacts of releases to air are further considered in section 8.3.

Studies have also provided evidence that metals can leach from petroleum coke (Squires 2005; Kessler and Hendry 2006; Puttaswamy et al. 2010; Puttaswamy et al. 2011), particularly vanadium and nickel (Nesbitt et al. 2017). An *in situ* microcosm study (Baker et al. 2012) evaluating the potential effect of petroleum coke as a material for the construction of reclaimed wetlands, found that increased concentrations of trace metals (vanadium, nickel, lanthanum and yttrium) were present in tissues of aquatic macrophytic algae (*Chara spp*.) grown in association with petroleum coke, and bitumen production tailings. It was noted that nickel was measured at 1.5 times higher concentrations in petroleum coke treatments relative to native sediment treatments.

Environmental concentrations of priority PAHs (PAHs identified in Canadian Council of Ministers of the Environment (CCME) guidelines), nickel and vanadium near petroleum coke processing facilities and stockpiles along the Athabasca River from Regional Aquatics Monitoring Program (RAMP 2019a) and Joint Canada-Alberta Implementation Plan for Oil Sands Monitoring (JOSM 2019) programs in the AOSR are summarized in Table 7-3 and Table 7-4. Concentrations in surface water and sediments from three areas of the Athabasca River were monitored: upstream of, downstream of, and adjacent to the Tar Island fuel grade (green coke) stockpile (Suncor 2019). The distances of the monitoring stations from the stockpile vary depending on the dataset and the matrix analyzed (see Appendix A. Summary of Athabasca River Environmental Monitoring Station Information). Given the large size of the Tar Island petroleum coke stockpiles and the close proximity to the Athabasca River, the analysis using Athabasca River monitoring data from the AOSR was considered to have the highest potential of environmental releases of petroleum coke components (PAHs, Ni and V) to the environment in Canada. Additionally, the environmental concentrations of the metal components in this assessment are presented as measured total metal concentrations, instead of dissolved metal. This approach is considered more conservative as some of the non-dissolved metals would not be bioavailable.

Following the approach outlined in Environment Canada, Health Canada (2016), the PAHs analyzed were limited to those outlined in Table 7-6 The PAHs were selected for analysis based on presence in petroleum coke, availability of monitoring data, and associated environmental guideline values. Although Table 7-3 and Table 7-4 present ranges of total concentrations of PAHs, data was available for the selected individual PAHs for different sites and different sampling dates and this data was used in the subsequent analyses. Note that all individual PAH measurements were not necessarily available for each sampling site and date. Sampling sites and dates with no reported data were excluded from the analysis.

Table 7-3. Concentrations of PAHs and metals in surface waters near petroleum coke processing facilities and stockpiles

Analyte	Location	Concentration (ng/L)
PAH	Upstream	0.05-2250
PAH	Adjacent	0.08-273

PAH	Downstream	0.08-316
Ni (total)	Upstream	0.01-19.7
Ni (total)	Adjacent	0.01-13.7
Ni (total)	Downstream	0.16-16.8
V (total)	Upstream	0.20-23.2
V (total)	Adjacent	0.24-17.8
V (total)	Downstream	0.19-23.4

Table 7-4. Concentrations of PAHs and metals in sediments near petroleum coke processing facilities and stockpiles

Analyte	**Location**	**Concentration (µg/kg)**
PAH	Upstream	0.02-665
PAH	Adjacent	0.02-92
PAH	Downstream	0.05-36
Ni (total)	Upstream	5.0-27.7
Ni (total)	Adjacent	3.9-27.2
Ni (total)	Downstream	4.0-32.6
V (total)	Upstream	5.0-28.0
V (total)	Adjacent	4.2-31.0
V (total)	Downstream	4.0-42.1

Monitored PAH concentrations in both surface water and sediment were highest at the upstream monitoring sites. Naphthalene in surface water was measured upstream at a maximum concentration of 2250 ng/L, which is significantly higher than other PAHs. It was measured in concentrations higher than 100 ng/L several times between 2012 and 2014. It was also the PAH found in the highest concentration at adjacent (273 ng/L) and downstream (316 ng/L) sites. In sediments, chrysene was found in the highest maximum concentration upstream (665 µg/kg), while dibenz[a,h]anthracene was the PAH with the highest maximum concentration adjacent (92 µg/kg) and downstream (36 µg/kg).

For metals, the maximum concentrations of total nickel and vanadium measured in surface water were lowest at monitoring sites closest in proximity to the petroleum coke stockpiles, with downstream measured concentrations being comparable to, or lower than, those upstream. In sediment, maximum nickel concentrations ranged from 27.2-32.6 µg/kg at all 3 locations, while maximum vanadium concentrations ranged from 28.0 to 42.1 µg/kg. Minimum sediment concentrations of nickel and vanadium are lower than upstream concentrations, while maximum concentrations were found downstream.

7.1 Characterization of ecological risk

The approach taken in this ecological screening assessment was to examine available information and develop proposed conclusions using a weight -of- evidence approach and precaution. Evidence was gathered to determine the potential for substances in the Petroleum Coke Group to cause harm in the Canadian environment. Lines of evidence considered include those evaluated in this assessment that support the characterization of ecological risk in the Canadian environment. Secondary or indirect lines of evidence are considered when available, including but not limited to regulatory decisions and classification of hazard or fate characteristics made by other regulatory agencies.

Substances in the Petroleum Coke Group are generally considered to be non-reactive solids composed primarily of elemental carbon, with negligible water solubility and vapour pressure. As a result, the particles, as well as the PAH and metal components within the carbon matrix are expected to have low bioavailability to organisms if released to the environment. Water accommodated fraction (WAF) based laboratory studies suggest that selected PAHs in petroleum coke do not leach into water or soil at harmful level as no toxicity was observed in aquatic and terrestrial tests in general; furthermore, there was a lack of detection in the WAF of components of green coke for aquatic toxicity tests or in test soil samples for terrestrial tests (API 2008; McKee et al. 2014). Terrestrial toxicity tests on green coke in earth worms and plant species all showed no effects at 1000 mg/kg (Table 7-2). Overall, available laboratory evidence indicates petroleum coke has a low potential to cause adverse effects in aquatic and terrestrial organisms under laboratory conditions.

However, field studies conducted with petroleum coke have found evidence of presence and potential toxic effects of PAH and metal components in areas close to petroleum coke production and stockpiling. Air born dust from petroleum coke stockpiles was identified as the major source of the atmospheric deposition of PAHs (Zhang et al. 2016a). Additionally, PAHs in meltwater from field collected snow have been shown to cause toxic effects in fish in laboratory tests (Parrot et al. 2018). Vanadium and nickel are among the most abundant metals in petroleum coke, and they have been identified as the probable cause of petroleum coke related adverse effects in aquatic organisms (Puttaswamy et al. 2010; 2011) in field studies. Measured concentrations of metals in leachates by lysimeter studies within outdoor stockpiles showed concentrations high enough to result in adverse effects to aquatic invertebrates (*Ceriodaphnia dubia*). Toxicological testing was based on samples were collected from the lysimeters every 3-6 months. Vanadium in petroleum coke is most mobile and susceptible to leaching when exposed to oxygen and meteoric waters, conditions which occur during outdoor stockpiling and storage (Nesbitt and Lindsay, 2017). A screening assessment report conducted on vanadium (vanadium pentoxide, vanadium oxide) concluded that it was not posing a risk to the environment but was a concern for human health (Environment Canada, Health Canada 2010, ECCC 2016b, Health Canada 2016b). In a separate assessment, it was concluded that nickel and its compounds represents a concern for human health and the environment (Environment Canada, Health Canada 1994). It should be noted that no unacceptable risks to the environment from these metals, as components of petroleum coke, were identified in either the nickel or vanadium screening assessments.

To assess the potential ecological risk of the PAH and metal components potentially released from petroleum coke, environmental guidelines and scientific literature were used to identify predicted no-effect concentrations (PNECs) (Table 7-5 and Table 7-6).

Table 7-5. Metal PNECs for water, sediment and soil organisms

Metal	Surface water (µg/L)	Soil (mg/kg dw)	Sediment (mg/kg dw)
Nickel	25[a]	45[c]	16[d]
Vanadium	120[b]	130[c]	90[b]

[a] Guideline value for nickel in water with hardness values of 0-60 mg/L (CCME, 1999)
[b] Federal Environmental Quality Guideline for vanadium in freshwater (Environment Canada, 2016)
[c] Conservative (agricultural/residential) guideline value for nickel in soil (CCME, 1999)
[d] Ontario Ministry of the Environment guideline value nickel in sediment (Ontario, 2011)

Table 7-6. PAH PNECs for water, sediment and soil organisms

PAH	Surface water (µg/L)[c]	Sediment (µg/kg dw)[a]	Soil (mg/kg dw)[a,b]
Acenaphthene	59	6.71	0.28[c]
Acenaphthylene	N/A	5.87	320[c]
Anthracene	0.06	46.9	2.5
Benz(a)anthracene	0.09	31.7	0.1
Benzo[a]pyrene	0.07	31.9	0.7
Benzo[b]fluoranthene	N/A	N/A	0.1
Benzo[k]fluoranthene	N/A	N/A	0.1
Chrysene	N/A	57.1	6.2
Dibenz[a,h]anthracene	N/A	6.22	0.1
Fluoranthene	0.20	111	50
Fluorene	125	21.2	0.25[c]
Indeno[1,2,3-cd]pyrene	N/A	N/A	0.1
Naphthalene	2.2	34.6	0.013[c]
Phenanthrene	0.80	41.9	0.046[c]
Pyrene	0.40	53.0	0.1

N/A, no guideline value available
[a] CEQG values for the protection environmental and human health (CCME, 2010).
[b] CEQG for the protection of soil. The most protective guideline was selected from those for the various land-use types (CCME, 2010).
[c] Guideline value for protection of freshwater life (CCME, 1999)

Risk quotient (RQ) analyses were performed by comparing the monitored concentrations of PAHs, nickel and vanadium (Table 7-3 and Table 7-4) to respective environmental quality guidelines for these substances (**Error! Reference source not found.** and Table 7-6) for relevant environmental compartments to determine whether there is potential for ecological harm in Canada. The surface water PNEC for nickel was also adjusted to correct for water hardness, as outlined in CCME 1999.

The toxicity of PAHs and other non-polar narcotic substances is additive (DiToro et al. 2000; DiToro and McGrath 2000). A narcotic mode of action (MoA) is associated non-specific interference with cell membranes and usually referred to as baseline toxicity. A non-narcotic MoA is referred to as excess toxicity (reactive and specifically-acting) and generally associated with the potential for long-term effects to occur at lower tissue concentrations.

A toxic units (TU) approach, as described in Appendix 4 of Environment Canada (2015), was employed to determine the risk of total PAHs to aquatic (surface water) organisms. The toxic unit contribution for each PAH in the substance was determined by dividing its concentration at a sampling point on a given date by a PNEC (in this case the environmental quality guideline values). These individual PAH RQ (or toxic units for the individual PAHs) for a given location and date were then summed to obtain the overall toxic units for all PAHs considered for the given sampling site and date. In cases where the measured environmental concentration was below analytical detection limits, a value of one-half of the detection limit was used in calculating risk quotients and toxic units.

Unlike the CCME PAH guideline values for water, which were derived from a single critical toxicity value, CCME PAH guideline values for sediment organisms were based on field samples and therefore consider the presence of other PAHs in the sample. For this reason, a toxic units approach was not used for these scenarios as the guidelines are already reflective of PAHs present in a mixture. Table 7-7 and Table 7-8 present RQs and TUs calculated from the Athabasca River monitoring data.

Table 7-7. Summary of toxic units (PAHs) and risk quotients (metals) for surface water obtained from monitoring stations along the Athabasca River for components of substances in the Petroleum Coke Group.

Analyte	Location	Mean (Max) TU/RQ	% Exceedances (>1)
PAH[a]	Upstream	0.2 (1.2)	4
PAH[a]	Adjacent	0.2 (0.6)	0
PAH[a]	Downstream	0.1 (0.6)	0
Ni (total)	Upstream	0.1 (0.8)	0
Ni (total)	Adjacent	0.1 (0.6)	0
Ni (total)	Downstream	0.1 (0.7)	0
V (total)	Upstream	<0.1(0.2)	0
V (total)	Adjacent	<0.1(0.2)	0
V (total)	Downstream	<0.1(0.2)	0

[a] Sum of toxic unit (TU) approach used for PAHs in surface water.

Table 7-8. Summary of risk quotients for sediments obtained from monitoring stations along the Athabasca River for components of substances in the Petroleum Coke Group.

Analyte	Location	Mean (Max) RQ	% Exceedances (RQ>1)
PAH[a]	Upstream	4.3 (11.7)	18
PAH[a]	Adjacent	0.8 (2.6)	6
PAH[a]	Downstream	0.3 (0.7)	0
Ni (total)	Upstream	1.3 (1.7)	73
Ni (total)	Adjacent	1.2 (1.7)	67
Ni (total)	Downstream	1.3 (2.0)	87
V (total)	Upstream	0.2 (0.3)	0
V (total)	Adjacent	0.3 (0.5)	0
V (total)	Downstream	0.2 (0.5)	0

[a] Risk quotient reported for the PAH with highest monitored concentration. Exceedance calculations are for all PAHs reported in Table 7-6

Exceedances of PAHs in surface water were noted in 4% of upstream measurements. Analysis of the monitoring data found no adjacent or downstream exceedances. A small downward trend was observed in the mean RQs, with the upstream RQ (0.2) decreasing to 0.1 at the downstream location (Table 7-7). Analysis of sediment PAH monitoring data show a downward trend in exceedances of environment quality guideline values moving from upstream to downstream of petroleum coke stockpiles (Table 7-8). At the upstream monitoring site, exceedances make up 18% of all PAH measurements. Chrysene had the highest calculated upstream RQ (mean = 4.3, maximum = 11.7). Adjacent to the stockpile, 6% of monitored values exceeded PAH guideline values, with dibenz[a,h]anthracene having the highest RQ (mean = 0.8, maximum = 2.6). No exceedances were noted downstream, which suggests that additional factors (e.g. additional natural or anthropogenic sources) may be influencing PAH concentrations upstream of the stockpile, as well as concentrations being diluted by the flow of the Athabasca River. As with the adjacent sites, dibenz[a,h]anthracene had the highest RQ downstream (mean = 0.3, max = 0.7). Given the downward trend in mean RQs and guideline value exceedances, it is unlikely that the stockpile is contributing significantly to the PAH concentrations in the Athabasca River.

Analysis of total nickel and vanadium data generated no environmental quality guideline exceedances (RQs ≥1) in Athabasca River surface water (Table 7-7). Vanadium RQs were consistently well below 1 at all monitoring locations, with no apparent trend based on sampling location and time of year. Maximum RQs for nickel approached, but did not exceed 1, and were lowest at the adjacent monitoring site. Expanded analysis of all Athabasca River monitoring data also showed no RQ≥1 (data not shown).

Low risk quotients for sediment were calculated for vanadium (Table 7-8). The mean RQs were similar from upstream to downstream of the stockpile. Vanadium did show increases in both mean and maximum concentrations adjacent to the stockpile and downstream, however; the magnitude of the increase was small and did not exceed the environmental quality guideline for sediment. Guideline exceedances were noted for nickel in sediment at all monitoring locations. Mean exceedances ranged from 1.2 (adjacent) to 1.3 upstream and downstream, with the highest maximum exceedance occurring downstream (2.0). The frequency of exceedances was highest downstream from the stockpile (87% of measurements) and lowest adjacent to the stockpile (67% of measurements). In an expanded analysis of all sediment monitoring data, the JOSM dataset had a 100% exceedance rate, while the RAMP dataset had a 32% exceedance rate (data not shown), which suggests elevated concentrations are due in part from natural background or historical anthropogenic contributions and not solely due to releases from petroleum coke stockpiles. This is interpreted as an indication that the stockpile is not contributing significantly to the nickel concentrations in sediment of the Athabasca River.

Considering all available lines of evidence presented in this screening assessment, green coke and calcined coke are unlikely to be causing ecological harm in Canada.

7.1.1 Sensitivity of conclusion to key uncertainties

Laboratory toxicity data for green coke used in this assessment is based on water accommodated fractions (aquatic tests) or incorporation of coke into soil (terrestrial tests). Chemical analysis of the WAFs used for testing did not measure PAH or metals in the water soluble fraction, and the tests did not observe significant toxic responses. In contrast, leaching experiments on petroleum coke, or using field collected samples indicated that, in certain circumstances, both metal and PAH components could elicit toxic responses in test organisms. The impacts of weathering of petroleum coke and the release of vanadium have been investigated by Nesbitt and Lindsay (2017). However, the high potential for local distribution of petroleum coke via wind-blown fugitive dusts and changes in bioavailability produced by weathering processes may result in increased estimates of environmental presence of metals and PAHs from petroleum coke. The potential for fugitive dusts and leached petroleum coke impurities is unknown. Local impacts on surrounding sensitive ecosystems such as wetlands are not well studied in published literature.

Given the large size of the Tar Island petroleum coke stockpiles and the close proximity to the Athabasca River, the risk quotients calculated using Athabasca River monitoring data were used as a worst case scenario for assessing trends of guideline exceedances of petroleum coke components (PAHs, Ni and V) to the environment. There are several limitations to this approach. The location of some monitoring stations were quite distant from the stockpiles, such as station M9 (Appendix A), making source attribution more difficult. Limited monitoring data created gaps in analysis, particularly for PAHs. Many of the sampling sites did not have measurements on all sampling dates, and not all PAHs measured for each sample This could potentially lead to underestimation of the total toxic units in some cases. Measurements in sediment were limited in most cases to only 2-5 measurements over time per PAH and matrix at each location. No monitoring data for ground water, soil or air were available for petroleum coke components. However, particulate matter in air is further examined in section 8.3, The lack of monitoring information on PAHs and metals limited the evaluation of risk to only surface water and sediment, and no monitoring data for areas surrounding petroleum coke stockpiles outside the AOSR were available.

There is no Canadian federal guideline value for nickel in sediment. A review of guidelines from other jurisdictions was conducted to select an appropriate value for use in this screening assessment. The Ontario sediment quality guideline (Ontario 2011) was selected as it is from a Canadian jurisdiction and was among the lowest at 16 mg/kg; therefore, it is one of the most protective values for estimation of risk.

It cannot be assumed that the petroleum coke stockpile contributed to all of the petroleum coke component concentrations measured in surface water and sediments. The stockpile is situated among other petroleum extraction upgrading facilities, which may also contribute metals and PAHs to water and sediment.

Some proposed uses for petroleum coke such as for capping tailings ponds (Suncor 2018) or as a surface sediment amendment for artificial wetlands have been identified as potential areas of environmental risk in scientific literature (Puttaswamy et al. 2011; Baker et al. 2012). These uses have the potential to create conditions favourable for leaching of metals (Puttaswamy et al. 2011), but they were not further investigated in this assessment.

8. Potential to cause harm to human health

8.1 Exposure assessment

Petroleum coke is not present in prescription and non-prescription drugs, natural health products, cosmetics, pesticides, products available to consumers, food additives, or food packaging in Canada. Therefore, exposure to the general population in Canada from products available to consumers is not expected.

Green coke is produced in large quantities in oil sands operations in AOSR in Alberta and in small quantities in refineries in other regions in Canada. Calcined petroleum coke is produced in coke ovens in calcining plants which use externally sourced green coke as starting material and are often associated with aluminum smelting facilities. Calcined coke is imported into Canada by some facilities (Canada 2017b). Potential exposure to the general population from these sources is through environmental media.

Petroleum coke will not vaporize into the atmosphere or react chemically in the presence of water or light. Based on particle size, petroleum coke released into the environment could be incorporated into soils and sediments, or be transported by wind or surface water (CRS 2013).

8.1.1 Environmental Media

General population exposure to petroleum coke can potentially occur through environmental media such as air, soil, and water from industrial activities related to production, storage, and transportation. Each of these exposure sources is discussed separately below.

Inhalation of petroleum coke dust during the production, storage, or transport of this product from different sources is a potential pathway for human exposure. For this route of exposure, particulate matter originating from petroleum coke is of primary concern. Incidental ingestion or dermal exposure to fugitive dust in soil and water generated from petroleum coke processing can also potentially occur (Caruso 2015).

8.1.1.1 Air

The release of dust / fine particulates (particle diameters 10 μm or smaller) from petroleum coke stockpiles depends on the grade of the coke produced in the stockpile (physical particle size), the quantity of petroleum coke which is handled, and whether any dust mitigation technologies are employed during the coke production and transportation stages. Pulverizing petroleum coke for use in industry can also generate dust which is released into the air. However, the majority of petroleum coke stockpiles are comprised of granules orders of magnitude larger than this size range (CRS 2013, Caruso et al. 2015, Bari et al. 2016, Landis et al. 2017, Xu 2018). In Canada, release of petroleum coke to air can occur through large petroleum facilities that produce and store petroleum coke in the AOSR, refineries outside of the AOSR that can process heavy crude oil, petroleum coke transport and storage facilities, and coke calcining plants. The production, temporary storage, and transportation of petroleum coke may produce fine particulate matter which may be dispersed in the air.

Other activities in the vicinity of petroleum coke facilities may lead to the release of fine particulates. Chemical profiling of the particulates, in particular, the chemical profile of the embedded PAH mixtures and the ratio of the embedded vanadium (V) to nickel (Ni) concentrations in dust particles differ depending on the source of the dust. Using these chemical profiles, the proportion of dust originating from petroleum coke can be identified in this manner. (Xu 2018, Gopalapillai et al. 2019, Dourson 2016)

<u>Releases into air from green coke production and storage facilities</u>

Releases of green coke near petroleum coke production and storage sites at oil sands and heavy crude oil refineries

Air monitoring for particulate matter with diameter 2.5 µm or smaller at Fort McKay, Patricia McInnes, Athabasca Valley (Fort McMurray region), and Fort Chipewyan locations in or near the AOSR gave annual mean concentrations (three year averages between 1998 to 2012) between 2.4 and 7.7 µg/m^3. No meaningful increasing or decreasing trends in the particulate matter with diameter 2.5 µm or smaller were seen in Fort McKay and Fort McMurray locations during 15 years of air monitoring (between 1998 – 2012) if the effects of regional wildfires are not considered (Bari 2015). If concentrations on days when wildfires affected the particulate concentration are not considered, the maximum daily concentration of particulates 2.5 µm or smaller is 10 µg/m^3.

The large stockpiles of petroleum coke are one of the sources of particle dust emissions in the AOSR (Xing 2017; Zhang et al. 2016a; Manzano 2017). Particle size measurements of wind-blown particulates transferred from green coke stockpiles in the AOSR on to adjacent snow deposits showed that they have effective diameters greater than 10 µm and are therefore not likely respirable and beyond the size range considered for monitoring by most regulatory agencies (Zhang et al. 2016a).

Air monitoring of aerosol dust samples that can be attributed to emissions from the production of petroleum coke was performed at three sites in the AOSR. Chemical profiling shows that as we move farther away from stockpiles, the dust particles can no longer be attributable to petroleum coke stockpiles (Xu 2018, Gopalapillai et al. 2019).

Releases of green coke near urban refineries and storage sites at urban refineries
Outside of the AOSR, refineries capable of processing heavy crude, coke calcining plants in Alberta, British Columbia, and Ontario, and calcined coke import facilities in Quebec and Nova Scotia all require the processing, temporary storage, and transportation of petroleum coke that may potentially contribute to weather-related or activity-related releases of petroleum coke fugitive dust and fine particulates into the atmosphere. Storage and transport amounts of green and calcined coke in some of these facilities are known, but no Canada-specific monitoring data was identified to determine the effect of these petroleum coke transport and storage facilities on the concentration of particulate matter in nearby areas. The National Air Pollution Surveillance Program (NAPS) (Canada 2013) includes data for particulate matter in the 10 µm and smaller range for cities in Ontario which have crude oil refineries with green coke storage facilities and Canadian cities with coke calcining facilities. However, the sites of the monitoring stations are typically 5 km or farther from the coke facilities (typically) and attributing the air quality measurements at the NAPS air monitoring sites to the coke facility is not possible.

A detailed study of fine particulates in the 10 µm or smaller range release at urban green coke and coal transfer facilities in Chicago was undertaken in 2016 and the effect of petroleum coke on the air quality in the surrounding residential areas were investigated (ATSDR 2016). The Chicago green coke storage facilities were significantly larger than similar facilities in Canada and were located near high population density areas in the city. In the absence of Canadian-specific data, the results of these studies were considered as an upper bounding case of similar facilities in Canadian urban or suburban environments. Outside of the AOSR, no coke storage facilities similar to the Chicago facility, in terms of volume of green coke processed, were noted in Canada.

In the study, air monitoring of 10 µm or smaller particulates was carried out at meteorological stations on the fence-line of the two facilities in Chicago. Each station took samples every hour and 24 hr averages were established from data collected during three day intervals. In this study a total of 3313 validated 24 hr average measurements of particulate matter of the size 10 µm or smaller were acquired and provided the basis for the analysis (ATSDR 2016). About 365 of these measurements were taken at a site that is 0.65 miles (1.0 km) from one of the stockpile facilities to provide typical background regional air concentrations for the particulate matter within this size range.

The annual average 10 µm or smaller particulate concentration of the monitoring sites was 25 – 36 µg/m^3 (ATSDR 2016).

Releases of calcined coke into air from industrial facilities near urban areas

Releases from calcining facilities

There are a number of calcining facilities in Canada, namely in Strathcona Alberta, Arvida Quebec, and Kitimat British Columbia (Rain Carbon 2016, Jacobs Consultancy 2019), which convert green coke to calcined coke for use in aluminum manufacturing. There may be exposure to fine particulate matter and gas emissions from the operation of the calcining process. A study by Singh et al. (Singh 2015) used ambient air monitoring at the facility fence-line and AERMOD air dispersion modelling for sites in the vicinity of the factory to study the effect of a calcining facility in a port in eastern Argentina on the air quality of the adjacent city. The production volume of calcined coke in this facility is larger than coke calcining facilities in Canada, but in the absence of information on emissions from similar coke calcining facilities in Canada, this study was used to establish approximate upper bounding exposure values in the Canadian context.

The 10 µm or smaller particulate samples collected at monitoring stations near the calcining facility over a five year period between 2009 to 2014 showed average values below 50 µg/m^3.

In calcining facilities, the green coke is heated to temperatures as high as 1000°C and the volatile organic compounds which constitute a maximum of 21% of the mass in green coke are effectively combusted in the calcining process. It is therefore expected that volatile organic compounds are not significantly released into the atmosphere during the calcination procedure [CONCAWE 1993, Edwards 2015].

Releases from iron and steel mills and aluminum facilities

Iron and steel mill, and aluminum facilities, particularly in the Hamilton, ON, region, use calcined coke as carbon source in their operations. The storage and processing of calcined coke may lead to the release of petroleum coke fine particulate matter into the ambient air. Air monitoring for the 10 µm or smaller particulate fraction is performed by a network of monitoring stations in the greater Hamilton area, one of the contributions of which may be from fine particulates arising from the calcined coke stockpiles used in these facilities. Over the span of 2011 to 2017, the average 24 hr 10 µm or smaller particulate concentration over all Hamilton air monitoring network stations was between 20 – 30 µg/m^3. For the year 2017, only one of the seven stations reporting on 10 µm or smaller fine particulate concentrations had an annual mean greater than 30 µg/m^3 (HAMN 2017). There was no apparent correlation between the 10 µm or smaller particulate concentration reading for the different monitoring stations, and their distances from the steel mill facilities.

8.1.1.2 Soil

Releases into soil from green coke production and storage facilities

Releases of green coke to soil near petroleum coke production and storage sites at oil sands and refinery facilities

Studies were undertaken to determine the presence of petroleum coke particles in samples of snow, peat core, sphagnum moss, and lichen at near- and far-field test sights from green coke stockpiles in the AOSR (Zhang et al. 2016a, Landis 2019, Gopalapillai, et al. 2019). For the testing, the snow/dust samples were melted, then freeze dried, ground and further treated by solvent extraction (hexane / dichloromethane mixture) or digested (H_2O_2/HF/HNO_3 mixture, aqua regia, or 1 M HCl followed by 1 M NaOH at 70°C) and the chemical fingerprints of the green petroleum coke particles were extracted from the resulting solutions with solvents.

At near-field sites (within a range of 20 km of the green coke storage facilities), wind-blown petroleum coke dust particles contribute up to 75% of the chemical signature compounds embedded in the moss and lichen samples (Zhang et al. 2016a, Landis et al. 2019, Gopalapillai et al. 2019) whereas at sites farther than 20 km away (up to 50 km from the coke storage facility), 25% or less of the chemical signatures substance in the moss samples could be attributed to petroleum coke produced by the delayed petroleum coke process in the AOSR coking facilities (Zhang et al. 2016a).

Other studies confirm that signature components embedded in green coke are found in snow, lake sediments, and air in the vicinity of AOSR (Manzano et al. 2017, Landis et al. 2019, Chibwe et al. 2019).

Releases of green coke near urban refineries and storage sites at urban refineries

At urban or suburban coke transportation and storage facilities or coke producing refineries, rainwater wash-off may contribute to the transfer of petroleum coke to soils or surface dust in adjacent areas. No studies were identified regarding the extent of surface wash-off of petroleum coke from storage facilities to the adjacent soil or surface dust in Canada. The possible presence of green petroleum coke in the soil of areas abutting petroleum urban coke transfer facilities in Chicago were studied (Dourson 2016). The results of this study are considered as a possible upper bounding scenario for petroleum coke transfer to soil adjacent to facilities in Canada.

In the Chicago study, there was concern about the potential dispersion of petroleum coke runoff from rain or dispersion of coke particles by strong winds and its settling into soil and surface dust. The composition of soil and surface dust in 43 samples at sites adjacent to petroleum coke facilities (abutting neighbourhoods within roughly two miles) and sites farther away (more than two miles away) were monitored by using chemical markers of petroleum coke (Dourson 2016). Soil and surface dust samples were gathered after a few days of dry weather following a day of rainfall and after periods of strong wind gusts (more than 60 km/hr) which would be expected to disperse the petroleum coke particulates into adjacent areas.

Chemical analysis of soil samples at sites near the stockpile facilities (abutting neighbourhoods within 2 miles or so) and soil samples from sites farther away determined that chemical markers in the two set of samples were similar. As a result, the authors of the study determined that the composition of soil was not affected by the presence of the urban petroleum coke storage and transportation facility. Most of the petroleum coke stayed within the facility and was not dispersed to adjacent areas through seepage following rain runoff or wind gusts (Dourson 2016).

8.1.1.3 Water

There is some evidence that petroleum coke impurities (in particular PAHs, V, and Ni) may leach into water under certain environmental conditions, as outlined in section 7.2.1, in particular when petroleum coke is immersed in water. The conditions under which the leaching was observed involve exposing coke samples immersed in water to freeze / thaw cycle, burying coke samples in soil, and in simulated pond environments with coke in the sediments. There are large stockpiles of green coke near rivers in the AOSR, and therefore there may be a potential for PAHs, V, and Ni to be released into water downstream from the stockpile.

Petroleum coke production and storage at stockpiles and industrial facilities can lead to exposed mounds of petroleum coke which come in contact with runoff from rain or snowmelt. The petroleum coke can thus be transported into storm sewer systems, rivers, lakes, or coastal water (CRS 2013). Petroleum coke in water is not monitored directly (Personal communication, email from Water and Air Quality Bureau, Health Canada, to Risk Management Bureau, Health Canada, dated December 20, 2018; unreferenced, Personal communication, email from Drinking Water and Wastewater/Storm-water Provincial Program, Alberta Environment and Parks, to Risk Management Bureau, Health Canada, dated December 20, 2018; unreferenced). Concentrations of nickel, vanadium, and PAHs near coke processing facilities and stockpiles along the Athabasca River are monitored by the Regional Aquatics

Monitoring Program (RAMP) and the Joint Canada-Alberta Implementation Plan for Oil Sands Monitoring (JOSM) programs in the Alberta Oil Sands Region, and are presented in section 7.2.1. Concentrations in surface water from three areas upstream, downstream, and adjacent to green coke stockpile were measured. Table 7-3 provides a summary of measured values. The maximum concentrations of nickel and vanadium reported at the water monitoring sites closest to the petroleum coke stockpiles were lower than those recorded both upstream or downstream of the stockpile locations. The measured concentrations downstream of the petroleum coke stockpile were similar to, or lower than concentrations recorded upstream. A similar trend was observed with PAH concentrations in the river, where the upstream monitoring sites reported the highest concentrations relative to both adjacent and downstream locations. If there was significant release of these substances from the petroleum coke stockpile, it would be expected that the concentrations downstream of the stockpile would be higher than those upstream of the stockpile.

The observations indicate that there was not an increase in PAHs, nickel, and vanadium concentrations at adjacent and downstream in the river near petroleum coke stockpiles sites in the AOSR compared to concentration values upstream of the stockpiles. Therefore, the concentrations of these substances currently in the surface water cannot be associated with the presence of the petroleum coke stockpiles. As increases of PAHs, nickel, and vanadium concentrations in water near the very large stockpiles in the AOSR were not observed, increases in concentrations of these substances in water near the smaller stockpiles of petroleum coke near urban and suburban industrial facilities (also not immersed in water) in other parts of Canada are not expected.

8.2 Health effects assessment

The two categories of petroleum coke (green coke and calcined coke) have been assessed internationally as a group for their hazard potential, because of their similar physical-chemical properties and similarities in aspects of their manufacturing processes (MDEQ 2014; USEPA 2011).

In most of the cited studies experimental animals were exposed to finely ground green coke particulates of less than 5 µm in diameter (USEPA 2011; API 2008). Chemical analysis showed these coke samples contain typical amounts of impurities, including PAH, V, and Ni as shown in Tables 2-2 and 2-3.

Results of the studies conducted in experimental animals showed that repeated-dose or long-term exposure to petroleum coke did not cause cancer or reproductive or developmental toxicity following dermal or inhalation exposure. The genotoxicity potential of petroleum coke was also negative in standard *in vivo* or *in vitro* assays (Caruso and Stemmer 2018, Caruso 2015; USEPA 2011; API 2008).

Notably, most of the available information about petroleum coke comprises assessment of green coke which has a higher hazard potential because of the higher volatile matter or hydrocarbon content (2-21% by wt) and is considered worst-case as compared to calcined coke. The calcined coke has lower (< 0.25%) volatile matter and is expected to have a lower potential for toxicity (API 2000). In some studies, the American Petroleum Institute (API) used the results of green coke analysis and extrapolated it or used a read-across approach to assess the health effects of calcined coke (API 2008).

In a short-term repeated-dose inhalation (nose-only) study, male F344 rats were exposed to 58 mg/m^3 (0.058 mg/L) of green petroleum coke fine particulates with average diameter of 2.7 µm or 45 mg/m^3 (0.045 mg/L) of calcined coke fine particulates with average diameter size of 2.7 µm for 6 hr/day for 5 days. Rats were examined 7, 28 or 63 days post-exposure. Histological examination of lung tissue was performed only in animals sacrificed at day 63 post-exposure. No mortality or signs of toxicity were observed in treated rats in this study. Similarly, there were no signs of pulmonary toxicity as no gross or histological changes were observed in any treatment group after 7 or 28 days. Evidence of slight pulmonary tract inflammation (increased neutrophils, lymphocytes, total cell count) was observed in bronchoalveolar fluid only after 63 days of exposure (to 58 mg/m^3 or 45 mg/m^3); however, no pulmonary fibrosis was observed and lung weight of coke-exposed rats were comparable to rats in the control group. These effects were reported as not being of toxicological significance by the API (HLS 1999, cited in API 2008; 2000). The highest tested dose of > 50 mg/m^3 was identified as a No Observed Adverse Effect Level (NOAEL) (API 2000).

Similarly, long-term inhalation exposure to 0, 10 or 30 mg/m^3 (USEPA 2011) of finely ground green coke dust particles (approximately 3 µm in diameter) in a glass chamber for 6 hr/day, 5 days/week for 2 years did not cause treatment-related signs of toxicity, mortality or changes in biochemical, haematological or histopathological parameters in male and female SD rats (n = 150 of each sex) or Cynomolgus monkeys (n = 4 of each sex) (Klonne et al. 1987). In both animal species, treatment-related effects were reported as a significant dose-related increase in absolute or relative (to body weight) lung plus trachea weight of male and female rats and monkeys. The absolute lung weights increased 11% and 44% in male rats and 13% and 69% in female rats in 10 or 30 mg/m^3 groups, respectively. In monkeys, the absolute lung plus trachea weight (up to 77% in male and 42% in females) and relative lung plus trachea weight increased in both groups. Alterations in lung weight were accompanied with black pigmentation resulting from phagocytosis of test material by macrophages. In rats, histopathological evaluation of the lung showed inflammatory changes including broncholization, sclerosis, squamous metaplasia and presence of keratin cysts in alveoli (Klonnne et al. 1987). No inflammatory changes were observed in monkeys and no evidence of carcinogenicity was observed by the authors in this study (Klonne et al. 1987). The USEPA reported a LOAEC of 10 mg/m^3 based on pulmonary inflammation and histopathology in monkeys, and did not establish a NOAEC (USEPA 2011). API reported a pulmonary LOAEC of ~10 mg/m^3 and a systemic toxicity NOAEC of > 30 mg/m^3 in both animal species (API 2008). Lung changes similar to that reported by

Klonne et al (1987) have been attributed to an overload of coke fine particulate dust in lungs which would not be relevant to typical human exposure situations (Bevan et al 2018; API 2008; Mauderly and McCunney 1995). This is further supported by the International Life Science Institute (ILSI) workshop (Olin 2000) which stated that: "Since the apparent responsiveness of the rat model at overload is dependent on coexistent chronic active inflammation and cell proliferation, at lower lung doses where chronic active inflammation and cell proliferation are not present, no lung cancer hazard is anticipated."

No evidence of carcinogenicity was seen after long-term repeated-dose application of 100 µL of (250 mg/ml or 25% suspension in mineral oil) green coke (5 µm in diameter) on dorsal skin of C3H/HeJ mice over 3 times/week for 2 years. Histological assessments were performed on all control and treated mice. Some thickening of the skin was observed at the site of application of green coke, but no treatment-related neoplastic effects were noted. Moreover, green coke did not cause neoplasms in chronic inhalation toxicity studies. Mice in positive control group were dermally exposed to benzo[a]pyrene and developed neoplasms of squamous epithelial cells (Wingate and Hepler 1982, cited in Caruso et al 2015, USEPA 2011; API 2008).

Furthermore, genetic toxicity testing showed that green coke was not genotoxic or mutagenic in routine *in vitro* assays (Ames test, Mouse lymphoma cells) and *in vivo* bone marrow chromosomal aberrations assay (API 2000); however, it was reported positive in modified *in vitro* bacterial mutagenicity assay which was developed to optimize certain water-insoluble compounds (ASTM 2004a; Dalbev et al. 1998). (Caruso et al 2018). Collectively, it has been reported that petroleum coke was not genotoxic or mutagenic in standard *in vitro* or *in vivo* assays (CRC 2013; USEPA 2011). (USEPA 2011, API 2008).

In a subchronic combined reproductive/developmental screening test male and female Sprague-Dawley rats (12/sex/group) were exposed (nose-only inhalation) to green coke dust particles (mean diameter 2.3 µm) at 0, 30, 100 or 300 mg/m^3. Male rats were exposed for 2 weeks before mating and then for 28 days (6 hr/day) during and post-mating. Females were exposed for 14 consecutive days (6 hr/day) until pregnancy and then through gestation to postnatal day 4 (USEPA 2011; HLS 2006, cited in API 2008). Standard reproductive (mating indices, pregnancy rates, male fertility indices, gestation length, number of implantation sites and corpora lutea, pre- and post-implantation loss, pups per litter, live born and stillborn pups and incidence of dams with no viable pups) and developmental indices (pup viability, weight, sex ratio and survival) were examined. The only effects were reported as a significant dose-related increase in lung weights of male (37%) and female (58%) rats in 100 mg/m^3 and 300 mg/m^3 dose groups and evidence of pigment deposition, discoloration, and inflammation of lungs in all treated animals. However, no reproductive or developmental effects were observed in this study (Caruso et al. 2015; USEPA 2011). The US EPA suggested the highest dose tested as the NOAEC of 300 mg/m^3 for reproductive or developmental effects and a LOAEC of 30 mg/m^3 for pulmonary effects and histopathology (maternal toxicity) (USEPA 2011).

Subsequently, McKee et al (2014) followed the same dosing regimen to replicate the reproductive/developmental effects of inhalation exposure to 0, 30, 100 or 300 mg/m^3 of green coke reported in HLS (2006), cited in API (2008). McKee et al. (2014) reported increased lung weight associated with discoloration or black pigmentation of lungs and hyperplasia/hypertrophy of broncho-alveolar epithelium in all exposed rats. The study authors attributed these effects to a high concentration of insoluble coke particles in lungs (Caruso et al. 2015; API 2008). The pulmonary effects of poorly soluble particles (PSP) such as petroleum coke, diesel or shale dusts vary between humans and nonhuman primates versus rodents because of differences in anatomy, morphology or particle distribution patterns (Bevan et al 2018; Clippinger et al. 2018; Warheit et al. 2016). In rats, inhalation overload to PSP has been shown to cause inflammation; however, this response was considered species-specific and regarded as lung particle overload rather than substance-specific effect and unlikely relevant to humans (ECETOC 2013; API 2008). No epidemiology study has shown any association between exposure to PSP and development of lung toxicity in workers following long-term exposure to PSP (Warheit et al. 2016). It has been reported that deposition of fine particulates from petroleum coke results in epithelial hyperplasia, inflammation and fibrotic responses in rats, but not in monkeys suggesting that rats are not good models to predict responses to inhaled levels of PSP in humans and nonhuman primates (Warheit et al. 2016; Nikula et al. 1997). This is in accordance to the studies reported above that short- or long-term exposure to petroleum coke caused pulmonary inflammation only in rats after high-dose exposure, but not in monkeys or humans (HLS 1999, cited in API 2008; Klonne et al 1987). Moreover, rat appears to be the only species that develops lung tumors following long-term inhalation particle overload studies (Mauderly 1995).

Examination of the reproductive endpoints (mating, implantation, pregnancy) showed that 3/12 rats did not become pregnant (1 did not mate, 2 had mated but were not pregnant) and 1/12 dam had no live fetuses in the 300 mg/m^3 dose group. The authors reported that these changes were not statistically significant, but were out of historical control value ranges. These effects were considered treatment-related by the authors who proposed a NOEL of 100 mg/m^3 for reproductive effects. There was no difference in all other reproductive or developmental (litter survival, body weight or size) parameters between treated and control rats and no differences were observed in the survival or body weight of offspring (McKee et al. 2014).

Some studies (Caruso et al. 2015, Hendryx et al. 2016) have found that residents living in the vicinity of green coke facilities (south Chicago) reported chronic bronchitis, emphysema or chronic obstructive pulmonary disease (COPD), chest tightness as well as asthma, chest wheezing and neurological symptoms (headache, migraine, difficulty concentrating/remembering/sleeping, insomnia or anxiety/nervousness). However, the authors cautioned that no clear association could be established between exposure to petroleum coke dust particles and its potential effects due to self-reported nature of surveys, small sample size, location of population near industrial areas and major roads and unequal number of variables including race and ethnicity (Hendryx et al. 2016).

8.3 Characterization of risk to human health

8.3.1 Air

Long-term exposure: For long term inhalation exposure, a LOAEC of 10 mg/m^3 for fine particulates arising from petroleum coke is used from a 2-year SD rat study for increased lung weight and signs of lung inflammation. This is a conservative estimate for humans and primates which do not show the same effects. Using the largest yearly average particulate matter concentrations of 25-36 µg/m^3 near urban petroleum coke facilities and assuming that is comprised of petroleum coke, gives a MOE of approximately 400-280. ~~Given the conservative nature of the assumptions made, t~~The MOEs for urban petroleum coke storage facilities are considered adequate to address uncertainties in the health effects and exposure databases. Long term exposures from petroleum coke stockpiles in the AOSR, steel and aluminum mills in Hamilton, and calcining facilities give lower air-born petroleum coke concentrations and lead to MOEs which are considered adequate to address uncertainties in health effects and exposure databases.

Short-term exposure: The average daily concentrations of 10 µm or smaller particulates measured near the petroleum coke storage and transportation facility in in Chicago (assuming they are entirely attributed to fine particulates arising from petroleum coke), was 100 µg/m^3 or less. Compared to the LOAEC for short-term inhalation exposure to rats of 45 mg/m^3 for lung inflammation from fine particulates arising from petroleum coke, which is conservative as applied to humans and other primates, the worst one-day exposure gives a margin of exposure (MOE) of approximately 450. Based on these toxicological considerations, the estimated MOE is conservative and the calculated margins are adequate to address uncertainties in the health effects and exposure databases.

Studies showed that exposure to green or calcined coke fine particulates did not result in systemic toxicity, carcinogenicity, genotoxicity or significant changes in reproductive or developmental system in animals or *in vitro* (USEPA 2011; API 2008).

Health effects from PAHs, V, and Ni in air borne petroleum coke fine particulates are not characterized since these substances are embedded in the petroleum coke particulates and are not expected to be bioavailable upon uptake of the petroleum coke particulates. Furthermore, no toxic effects associated with the embedded B[a]P, V, and Ni have been seen in the animals exposed to green petroleum coke dust particles.

8.3.2 Soil

Particulates originating from petroleum coke have been observed in soil samples at sites adjacent to the stockpiles in the Athabasca Oil Sands Region (Zhang et al. 2016a). Long term dermal exposure studies to green coke suspended to mineral oil show no treatment related effects (including cancer) on C3H mice (Wingate and Hepler 1982, cited in USEPA 2011, API 2008). It is therefore not expected that incidental dermal contact with petroleum coke from stockpiles dispersed into soil will be of concern to human health.

All health effected following inhalation exposure to petroleum coke are specific to the lung and there are no systemic health effects arising from inhalation exposure. Therefore, indications are that incidental oral exposure to petroleum coke from soil are not expected to be of concern to human health.

Wash-off of petroleum coke to soil and dust in areas adjacent to urban coke storage facilities is determined to be low. Therefore, the likelihood of exposure of the general population to petroleum coke from soil near urban green coke stockpiles is low and risks to human health from this source are considered to be low.

8.3.3 Water

The information presented in section. 7.3 indicates that the runoff from the large petroleum coke stockpiles in the Athabasca Oil Sands region does not increase the downstream PAH, vanadium, and nickel concentrations in surface water. Therefore, the exposure of the general population to these substances in water originating from runoff of AOSR stockpiles, and similarly, the much smaller green or calcined coke stockpiles urban/suburban environments are expected to be low and risks to human health from this source are considered to be low.

8.4 Uncertainties in evaluation of risk to human health

There are no air or soil monitoring measurements at petroleum coke facilities in Canada and therefore there are uncertainties in extending the results of the Chicago study for release of petroleum coke in soil in adjacent sites and PM_{10} measurements from the petroleum coke transport facilities to similar facilities in Canada. Similarly, there is some uncertainty in applying the results of the study of the effect of the coke calcining plant to the air quality of the adjacent city in Argentina to calcining facilities in Canada.

There are uncertainties in the exact amount of petroleum coke that is produced, stockpiled, and transported in transfer facilities and in the AOSR in Alberta and other regions in Canada. A change in the amount of the stockpiles and in the processing and physical state of the stored petroleum coke may affect the size distribution of the particulate matter released into the atmosphere from the stockpiles. There are no studies on the release of PM_{10} for petroleum coke during transportation and storage, specifically during unloading, loading, stockpiling, and shipping.

The key sources of uncertainty are presented in the Table 8-1 below.

Table 8-1 Sources of uncertainty in the risk characterization

Key source of uncertainty	Impact
There are no Canadian air monitoring data on PM_{10} emissions from petroleum coke facilities. NAPS air monitoring data are from stations distant from known petroleum coke facilities.	+/-
There are no Canadian studies on monitoring of the release of petroleum coke to soil and water adjacent to facilities.	+/-
There are no Canadian air monitoring data on fine particulate emissions from coke calcining facilities and only PM_{10} values from far-field monitoring stations are known.	+/-
There are uncertainties in the exact amount of petroleum coke that is produced, stockpiled, and transported in coke transfer facilities and in the Athabasca Oil Sands Region in Alberta and other regions in Canada. If stockpiles increase, there could potentially be changes in regional exposures.	+/-
There is uncertainty with regards to the negative effects of petroleum coke fine particulate matter on susceptible populations including children, elderly or person with chronic disease conditions such as, asthma, bronchitis or cardiovascular conditions.	-

+ = uncertainty with potential to cause over-estimation of exposure/risk; - = uncertainty with potential to cause under-estimation of exposure risk; +/- = unknown potential to cause over or under estimation of risk.

9. Conclusion

Considering all available lines of evidence presented in this draft Screening Assessment, there is a low risk to the environment from green coke and calcined coke. It is proposed to conclude that green coke and calcined coke do not meet the criteria under paragraphs 64(*a*) and 64(*b*) of CEPA 1999 as they are not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity or that constitute or may constitute a danger to the environment on which life depends.

On the basis of the information presented in this draft screening assessment, it is proposed to conclude that green coke and petroleum coke 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 therefore proposed that green coke and calcined coke do not meet any of the criteria set out in section 64 of CEPA.

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Appendix A. Summary of Athabasca River Environmental Monitoring Station Information

Table A-1 and A-2 contain a summary of information related to the monitoring stations used in sections 6.2 and 6.3. The stockpile refers to the Tar Island petroleum coke stockpile (composed primarily of fuel grade,(green) coke) on the Athabasca River. Distances from stockpile were calculated using Google Earth by measuring along the center of the river, between the station and the center of Tar Island.

Table A-1. Summary of relevant Regional Aquatics Monitoring Program monitoring station information (RAMP 2019b)

Location (relative to stockpile)	Station Name	Distance from stockpile (km)	Analytes (Matrix[a])
Upstream	ATR-DC-CC	23	Metals (W,S), PAH (W,S)
Upstream	ATR-DC-E	23	Metals (W,S), PAH (W,S)
Upstream	ATR-DC-W	23	Metals (W,S), PAH (W,S)
Adjacent	ATR-SR-E	0	Metals (W,S), PAH (W,S)
Adjacent	ATR-SR-W	0	Metals (W,S), PAH (W,S)
Downstream	ATR-MR-E	14	Metals (W,S), PAH (W,S)
Downstream	ATR-MR-W	14	Metals (W,S), PAH (W,S)

[a] W=water, S=sediment

Table A-2. Summary of relevant Joint Oil Sands Monitoring Program monitoring station information (JOSM 2018)

Location (relative to stockpile)[a]	Station Name	Distance from stockpile (km)	Analytes (Matrix[b])
Upstream	AL07DD0008	21	Metals (W), PAH (W)
Upstream	M3	22	Metals (S)
Adjacent[b]	AL07DD0004	15 (downstream)	Metals (W), PAH (W)
Adjacent[b]	M4	15 (downstream)	Metals (S)
Downstream	AL07DD0005	18	Metals (W), PAH (W)
Downstream	M9	>100	Metals (S)

[a] Locations were determined using the following criteria; Upstream was identified as the closest monitoring station upstream of the Tar Island petroleum coke stockpile. The adjacent location was identified as the closest monitoring station downstream of the stockpile. Downstream was identified as the next closest downstream monitoring station location. Due to absence of monitoring stations in close proximity to the Tar Island stockpile, this resulted in some cases where adjacent and downstream locations were in closer proximity to each other than the stockpile. ,

[b] W=water, S=sediment