Draft Screening Assessment

Cyanides

Environment and Climate Change Canada
Health Canada

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Synopsis

Pursuant to sections 68 and 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 cyanides. Ten of these substances were identified as priorities for assessment as they met categorization criteria under subsection 73(1) of CEPA or were considered a priority based on other human health concerns. 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.

Cyanides identified as priorities for assessment under subsection 73(1) of CEPA

CAS RN	**DSL name**	**Common name**
74-90-8	Hydrocyanic acid	Hydrogen Cyanide
143-33-9	Sodium cyanide	Sodium cyanide
506-61-6	Argentate(1-), bis(cyano-c)-, potassium	Potassium dicyanoargentate
13601-19-9	Ferrate(4-), hexakis(cyano-c)-, tetrasodium, (oc-6-11)	Tetrasodium ferrocyanide (yellow prussiate of soda)
13746-66-2	Ferrate(3-), hexakis(cyano-c)-, tripotassium, (oc-6-11)-	Tripotassium ferricyanide
13943-58-3	Ferrate(4-), hexakis(cyano-c)-, tetrapotassium, (oc-6-11)-	Tetrapotassium ferrocyanide
13967-50-5	Aurate(1-), bis(cyano-c)-, potassium	Potassium dicyanoaurate
14038-43-8	Ferrate(4-), hexakis(cyano-c)-, iron(3+) (3:4), (oc-6-11)-	Ferric ferrocyanide (Prussian blue, insoluble)
25869-00-5	Ferrate(4-), hexakis(cyano-c)-, ammonium iron(3+) (1:1:1),(oc-6-11)-	Ferric ammonium ferrocyanide
25869-98-1	Ferrate(4-), hexakis(cyano-c)-, iron(3+) potassium (1:1:1), (oc-6-11)-	Potassium ferric ferrocyanide (Prussian blue, soluble or Turnbull's blue)

The ecological screening assessment uses a moiety-based approach that focuses on free cyanide (HCN and CN^-),and precursors of free cyanide as the forms of primary ecotoxicological significance, which includes the 10 substances listed above that were

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identified as priorities for assessment. Molecular HCN is considered the moiety of concern for cyanides for the ecological assessment as it is expected to be the dominant free cyanide species under environmentally representative conditions. Precursors of free cyanide relevant to the ecological screening assessment may be classified as "weak acid dissociable" (WAD) cyanide complexes or "strong acid dissociable" (SAD) cyanide complexes. Cyanides may be measured in the environment as free cyanide (CN_{Free}), WAD cyanide (CN_{WAD}) or total cyanide (CN_T), with the latter referring to the sum of CN_{Free} and CN_{WAD} species, and all other remaining strong cyanide complexes (i.e., "strong acid dissociable" CN_{SAD}).

The human health screening assessment focuses on specific substances identified as priorities which are separated into two distinct subgroups: free/simple cyanides (HCN and NaCN) and the metal-cyanide complexes. The human health assessment takes into consideration reported levels of HCN and total cyanide in food and environmental media, as well as exposure of the general population to the 10 cyanides from the use of products available to consumers.

HCN is highly water soluble and highly volatile, while metal-cyanide complexes are generally water soluble but are not considered volatile. If released to air, HCN will rapidly disperse and is unlikely to accumulate near the point of release; however, HCN is considered persistent in air due to an estimated atmospheric lifetime of approximately six months. HCN and other cyanides are not considered persistent in water as they may biodegrade or undergo a variety of other transformation processes (e.g., transformation to thiocyanate, complexation with iron). HCN and other precursors of free cyanide are not considered bioaccumulative.

The presence of free cyanide in environmental media, food or products may result from natural or anthropogenic sources. A number of cyanides are naturally occurring substances that may be produced in the environment by abiotic processes (e.g., combustion) and by biota (e.g., cyanogenic glycosides in plants from the Brassica genus). There are also many natural and anthropogenic point and diffuse sources for release of free cyanide to air and water, including industrial facilities, forest and house fires, and vehicle emissions. Cyanides are manufactured incidentally by many industries, including iron and steel manufacturing.

Results from a regulatory survey for the 10 substances identified as priorities for assessment indicate that 7 substances were imported into Canada in 2011. Cyanides are imported into Canada for use by many sectors for a variety of applications, including analytical reagents for plating and surface finishing or as chemical intermediates. Sodium cyanide (NaCN) is the most commercially important cyanide substance with an import volume in 2011 of 10 000 000–50 000 000 kg. NaCN is mainly used as an extraction agent for precious metals (e.g., gold), and to a lesser degree base metals, and may be released in the effluent of metal mining facilities. Another substance of interest is tetrasodium ferrocyanide, with an import volume in 2011 of 10 000–100 000 kg, which is used mainly as an anticaking agent in road salts. Hydrogen cyanide is incidentally produced in Canada (at a volume of 1 000 000–10 000 000 kg in 2011) by a few sectors where high temperature and pressure processes are used, such as iron and steel manufacturing (from coke ovens and blast furnaces at integrated steel mills), where releases of cyanides to air and surface water may occur.

HCN disrupts energy metabolism in organisms and it is highly toxic to aquatic organisms. This is evident from the predicted no-effect concentration (PNEC) of 1.7 µg/L for freshwater that was derived through a species sensitivity distribution approach using chronic toxicity endpoints for 12 aquatic species. The ecotoxicity of metal-cyano complexes is largely driven by their ability to dissociate and release free cyanide.

The ecological exposure assessment for cyanides focuses on potential releases of free cyanide from three main sectors of activity: metal mining, iron and steel manufacturing, and application of ferrocyanide-containing road salts. When available, measurements of CN_{WAD} and CN_{Free} were considered in addition to measurements of CN_T for the ecological exposure characterization. Approximately 40% of measured concentrations of total cyanide (CN_T) in samples collected in areas receiving metal mining effluent exceeded the PNEC. Average yearly releases of cyanides from integrated steel mills were calculated using loadings reported to a provincial government and it was determined that releases from two facilities could exceed the PNEC. Finally, concentrations of CN_T and CN_{WAD} in the environment receiving runoff from parking lots and highways where ferrocyanide-containing road salts were applied were determined to be sufficiently elevated to have the potential to cause chronic adverse effects to organisms.

Considering all available lines of evidence presented in this draft screening assessment, there is risk of harm to organisms, but not to the broader integrity of the environment from cyanides which include free cyanide and precursors of free cyanide. It is proposed to conclude that free cyanide and precursors of free cyanide meet the criteria under paragraph 64(a) of CEPA as they are entering or may enter 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. However, it is proposed to conclude that free cyanide and precursors of free cyanide do not meet the criteria under paragraph 64(b) of CEPA as they are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger to the environment on which life depends.

For the assessment of risk to human health, the metal-cyanide complexes were addressed in a qualitative manner. For the single-iron cyanide complexes (CAS RNs 13601-19-9, 13746-66-2, 13943-58-3), tetrasodium ferrocyanide and tetrapotassium ferrocyanide are approved food additives with a limited number of permitted uses in a small number of food categories. Tetrasodium ferrocyanide and its decahydrate salt are listed in the Natural Health Products Ingredients Database (NHPID) with a non-medicinal role for use as an anticaking agent in natural health products (NHPs) up to 0.025 mg/kg-bw/day. Tetrasodium ferrocyanide is an ingredient present in two dermally applied cosmetic products in Canada. The anticipated exposure to the general population from single-iron cyanide complexes is negligible due to their low concentration as food additives and in products, low dermal absorption and known product use patterns. Therefore, the risk is considered to be low.

The risk is considered to be low for the multi-iron cyanide complexes (CAS RNs 14038-43-8, 25869-98-1, 25869-00-5). Adverse health effects are not expected for these substances. Furthermore, there is minimal exposure due to their low bioavailability and high stability.

The gold- and silver-cyanide complexes (CAS RNs 13967-50-5 and 506-61-6) were addressed in a qualitative manner as exposure of the general population is not expected based on current uses and the risk is considered to be low.

The risk is considered to be low for the free/simple cyanides subgroup (CAS RNs 74-90-8, 143-33-9). Following inhalation exposure, the critical health effects were effects on the thyroid. A comparison of levels in ambient air with critical health effect levels resulted in margins of exposure that are considered adequate to account for uncertainties in the health effects and exposure databases. For oral exposure, the critical effects were effects on the male reproductive system. A comparison of levels of dietary exposure to the free/simple cyanides with critical health effect levels resulted in margins of exposure which are considered adequate to account for uncertainties in the health effects and exposure databases.

On the basis of the information presented in this draft screening assessment, it is proposed to conclude that the 10 cyanides identified as priorities for assessment 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 free cyanide and precursors of free cyanide meet one or more of the criteria set out in section 64 of CEPA.

Free cyanide and precursors of free cyanide are proposed to meet the persistence criteria but not the bioaccumulation criteria as set out in the Persistence and Bioaccumulation Regulations of CEPA.

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List of Tables and Figures

1. Introduction

Pursuant to sections 68 and 74 of the Canadian Environmental Protection Act, 1999 (CEPA) (Canada 1999), the Ministers of Environment and of Health have conducted a screening assessment of cyanides to determine whether these substances present or may present a risk to the environment or to human health; these were moiety- and substance-based assessments, respectively. Ten of these substances were identified as priorities for assessment as they met categorization criteria under subsection 73(1) of CEPA (ECCC, HC [modified 2007]).

The focus of the ecological assessment is on free cyanide, consisting of the cyanide anion (CN^-) and molecular hydrogen cyanide (HCN), and on precursors of free cyanide. Because molecular HCN is expected to be the dominant free cyanide species under environmentally representative conditions, it is considered the moiety of concern for cyanides for the ecological assessment. Precursors of free cyanide have the potential to release free cyanide under environmentally relevant conditions (i.e., pH, temperature) and transformation processes (e.g., dissociation, degradation or photolysis); all 10 of the substances identified as priorities for assessment are considered precursors of free cyanide from an ecological perspective. It is recognized that combined exposure of organisms to free cyanide may occur from different pathways and sources. Exposure to free cyanide may occur due to anthropogenic activities involving cyanides, including incidental production, and background concentrations of cyanides.

For the human health risk assessment, the 10 substances identified as priorities for assessment were divided into two subgroups based on differences in their structure, properties, stability, bioavailability, sources and uses: the free/simple cyanides and the metal-cyanide complexes. The free/simple cyanides subgroup includes hydrogen cyanide and the simple salt NaCN, and the metal-cyanide complexes subgroup includes eight metal-cyanide complexes. The metal-cyanide complexes subgroup was further divided into the gold- or silver-cyanide complexes, the single-iron-cyanide complexes, and the multi-iron-cyanide complexes. The available data for the free/simple cyanides and metal-cyanide complexes indicate that the potential health effects and general population exposure can be substantially different for these subgroups. Thus, this assessment report presents the human health exposure, hazard and risk characterization separately for these subgroups.

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 September 30, 2016. Empirical data from key studies as well as some results from models were used to reach proposed conclusions. When available and relevant, information presented in assessments from other jurisdictions was considered.

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 ecological and human health portions of this assessment have undergone external peer review and/or consultation. Comments on the technical portions relevant to the environment were received from Andrew Jaques from the Cyanide Council. Comments on the technical portions relevant to human health were received from Lynne Haber, Department of Environmental Health, College of Medicine, University of Cincinnati; Michael Jayjock, Jayjock Associates; and Susan Griffin, US Environmental Protection Agency. Comments were compiled by scientists at the Toxicology Excellence for Risk Assessment (TERA), Department of Environmental Health, College of Medicine, University of Cincinnati. 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[2]. This draft screening assessment presents the critical information and considerations upon which the proposed conclusions are made.

2. Identity of Substances and Scope of the Assessment

Cyanides contain the cyano functional group (-CN), consisting of a carbon atom triple bonded to a nitrogen atom. The cyanide anion (CN^-) reacts with many elements to form simple cyanide salts which have the general chemical formula $M(CN)_x$ and include, for example, sodium cyanide (NaCN) (Ghosh et al. 2006a). The cyanide anion (CN^-) also readily forms metal-cyanide complexes in solution with a reported 28 elements over 68 oxidation states (Broderius 1973). Metal-cyanide complexes have the general chemical formula ($M(CN)_x^{n-}$) (Ghosh et al. 2006a) and are generally classified as “weak” or “strong” metal complexes depending on their stability constants and their ability to release free cyanide. Weak complexes release free cyanide under slightly acidic conditions (approximately pH 4) and are referred to as “weak acid dissociable” (WAD) cyanides, while strong complexes require strong acidic conditions to dissociate and are referred to as “strong acid dissociable” (SAD) cyanides (CCME 1997a,c; Ghosh et al. 2006a,b). Metal-cyanide complexes may also bond with other metal cations to form

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[2] 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 used by 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.

metal-metal cyanide solids of the general formula $A_x[M(CN)_y]$ (where A is an alkali or alkaline earth metal) or $M_x[M(CN)_y]$ (where M is a transition metal) (Ghosh et al. 2006a).

The Chemical Abstracts Service Registry Numbers (CAS RN[3]), Domestic Substances List (DSL) names and common names for the 10 cyanides that met subsection 73(1) of CEPA in the Cyanides assessment are presented in the Synopsis (page i). For the purpose of the human health risk assessment, the 10 cyanide substances identified as priorities for assessment were divided into two sub-groups: the free and simple cyanides (74-90-8, 143-33-9) and the metal-cyanide complexes. The latter subgroup was further divided into the gold- or silver-cyanide complexes (13967-50-5, 506-61-6), the single-iron cyanide complexes (13601-19-9, 13746-66-2, 13943-58-3), and the multi-iron cyanide complexes (14038-43-8, 25869-00-5, 25869-98-1).

This assessment addresses key pathways and sources of free cyanide exposure relevant to ecological and human health. This risk assessment only considers effects associated with free cyanide (expressed as concentrations of HCN) and the substances identified as priorities in this assessment, and does not address other elements or moieties that may be present in certain free-cyanide precursors (such as silver or iron). These other elements or moieties may be addressed in upcoming assessments or may have already been addressed via other CMP initiatives.

Many substances release free cyanide as a result of dissociation or other relevant transformation pathways (e.g., hydrolytic, oxidative, photolytic or metabolic) at environmentally or physiologically relevant conditions (i.e., pH and temperature); these are considered precursors of free cyanide. The presence of free cyanide in environmental media, food or products may result from natural or anthropogenic sources.

The ecological screening assessment focuses on free cyanide and on precursors of free cyanide. Inorganic cyanides on the DSL, excluding polymers, were evaluated for their potential to be precursors of free cyanide in the environment, and include free/simple cyanides and complex cyanides (weak and strong metal-cyanide complexes) and cyanogens (ECCC 2016a). Free cyanide may also be released from naturally occurring cyanogenic glycosides in plants. Because HCN is expected to be the dominant species under environmentally representative conditions, it is considered the moiety of concern. Cyanides of commercial significance in Canada were considered in terms of their contribution to the combined ecological exposure of free cyanide. Environmental monitoring data are the primary line of evidence used to develop the ecological exposure characterization of certain sectors or activities that have the potential to release cyanides to the environment, but modelling of releases is also conducted when

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such data are unavailable. The interpretation of cyanide monitoring data considers measurements of total cyanide (CN_T) and of weak-acid dissociable cyanide (CN_{WAD}) and free cyanide (CN_{Free}) when the data for the latter two parameters are available (see Section 7.2.1). Where feasible, background or reference concentrations were differentiated from concentrations attributed to anthropogenic sources.

The human health screening assessment is broken down into two distinct subgroups (free/simple cyanides and the metal-cyanide complexes), based on similarities in their structure, properties, stability, bioavailability, toxicity and uses. The free/simple cyanides subgroup includes HCN and NaCN, while the metal-cyanide complexes subgroup includes eight metal-cyanide complexes identified as priorities in this assessment.

3. Physical and Chemical Properties

A summary of physical and chemical properties of HCN, the moiety of concern from an ecological perspective for this assessment, is presented in Table 3-1, with the range in values indicated for each property. HCN may exist as a gas or liquid at ambient temperature (ECETOC 2007). HCN is highly soluble in water and highly volatile in air. It is a weak acid that dissociates into the cyanide ion (Ghosh et al. 2006a), but HCN will be the dominant species at environmentally relevant pH (5–8) based on a pK_a range of 9.2–9.36.

$$HCN_{(aq)} = H^+ + CN^- \text{ (pKa > 9.2)}$$

Its high Henry's Law Constant (HLC) indicates that it will volatilize from water. It is not expected to partition significantly to lipids (octanol) or to soil based on its low log K_{ow} and log K_{oc}. The log K_{oa} for HCN indicates that it could bind slightly to atmospheric particulate matter.

Table 3-1. Experimental physical and chemical property values for hydrogen cyanide (CAS RN 74-90-8)

Property	Range	Key Reference(s)
Physical state	Liquid or gas	WHO 2004
Melting point (°C)	-13.24 to -13.4	PhysProp 2013; Gail et al. 2012
Boiling point (°C)	25.6 to 25.7	PhysProp 2013; Gail et al. 2012
Vapour pressure (Pa) (at 25°C)	98 900 to 100 000	Chatwin et al. 1987; Daubert and Danner 1985
Henry's law constant ($Pa{\cdot}m^3/mol$) (at 25°C)	13.5 to 5167.6	Gaffney et al. 1987; Yoo et al. 1986
Water solubility (mg/L) (at 25°C)	1 000 000; miscible	Lide 1990; PhysProp 2013
Log K_{ow} (dimensionless)	-0.25 to 0.66	US EPA 1984; Hansch et al. 1995
Log K_{oc} (dimensionless)	0.45 to 1.17	KOCWIN 2010

Property	Range	Key Reference(s)
Log K_{oa} (dimensionless)	2.01	KOAWIN 2010
pK_a (dimensionless) (at 20°C)	9.31 to 9.36	Izatt et al. 1962; AGDH 2010
pK_a (dimensionless) (at 25°C)	9.21 to 9.25	Izatt et al. 1962; Dzomback et al. 2006a

Abbreviations: K_{ow}, octanol–water partition coefficient; K_{oc}, organic carbon–water partition coefficient; K_{oa}, octanol–air partition coefficient; pK_a, acid dissociation constant

CN^- has a high affinity for iron and other transition metals (e.g., cobalt, gold) and forms coordination complexes with these metals in tetrahedral or octahedral forms. The metal-cyanide complexes identified as priorities for assessment are all high molecular weight substances (ranging from 288.1 to 859.3 g/mol) with very low vapour pressures. With the exception of insoluble Prussian blue (14038-43-8), the iron cyanide complexes have one or more alkali (Na, K) or ammonium (NH_4) counter ions and are considered soluble in water (Ghosh et al. 2006a; Karyakin 2001; Lee and Huh 2012)[4]. The iron cyanide complexes identified as priorities for assessment have in common a stable hexacyanoferrate group $[Fe(CN)_6]$. The single iron cyanide complexes are arranged in tetrahedral conformations and the multi-iron complexes in octahedral conformations. With the exception of the silver cyanide complex, which is considered a weak acid dissociable complex, all of the metal-cyanide complexes identified as priorities are considered strong acid dissociable complexes with high equilibrium constants of formation (log K at 25˚C) ranging from 45.61 to 126 (Ghosh et al. 2006a).

4. Sources and Uses

4.1 Natural Sources

A number of cyanides are naturally occurring substances that may be produced in the environment by abiotic processes (e.g., combustion) and by biota. Biomass burning and forest fires are a source of HCN to the atmosphere (Li et al. 2000; Simpson et al. 2011) and may represent more than 90% of all natural or anthropogenic air emissions (ECETOC 2007). Gaseous or particulate cyanide emissions from combustion may enter surface waters by deposition or surface runoff (Barber et al. 2003). Other potential natural sources may include volcanoes or lightning (Cicerone and Zellner 1983).

Higher plants produce small amounts of HCN as part of certain metabolic processes (Lechtenberg and Nahrstedt 1999), and cyanogenic glucosides (CGs) are known to be produced in at least 2000 plant species (Speijers 1993). Many edible plant-based foods naturally contain CGs, which have the potential to release free cyanide. There are numerous types of CGs (e.g., linamarin, amygdalin, dhurrin) that exist and the degree to which a particular glycoside is present varies depending on the given plant (FSANZ

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4. The solubility of ferric ammonium ferrocyanide and potassium ferric ferrocyanide refers to the ease with which the coordinated ammonium and potassium ions can be peptized (i.e., form stable dispersions of colloidal particles) rather than the real solubility of ferric ferrocyanide (Karyakin 2001).

2014). Examples of foods that contain CGs include lima beans, apple seeds, cassava, bamboo, stone fruit pits (e.g., apricot, peach, cherry) and flaxseed. The leaching and subsequent hydrolysis of CGs from plant matter may release free cyanide to the environment (Bjarnholt et al. 2008). Aquatic microorganisms such as green algae (Chlorella sp.) and particularly the blue-green algae (Anacystis nidulans) can produce HCN (Gewitz et al. 1976; Pistorius et al. 1979). A review by NICNAS determined that cyanides may be produced by other microorganisms (i.e., bacteria and fungi) as well as a small number of invertebrates (e.g., arthropods) (AGDH 2010).

4.2 Anthropogenic Sources

4.2.1 Manufacture and incidental production

Information regarding the manufacture of the 10 substances identified as priorities for assessment for the year 2011 was acquired through a notice issued pursuant to section 71 of CEPA (Canada 2012). For the purpose of the notice, “manufacture” is defined as the production or the preparation of a substance, including when the substance is produced incidentally (Environment Canada 2012).

Cyanides do not appear to be intentionally manufactured in Canada for commercial purposes (Environment Canada 2013; ICMC 2015). While not purposely manufactured in Canada, results of the survey indicate that 1 000 000–10 000 000 kg of HCN (CAS RN 74-90-8) was incidentally manufactured by fewer than four companies in iron and steel mills and ferro-alloy manufacturing (NAICS 33111) or all other basic inorganic chemical manufacturing (NAICS 325189) sectors (Environment Canada 2013). Cyanides are manufactured during iron and steel manufacturing in coke ovens and blast furnaces in integrated mills (Environment Canada 2001). The pulp and paper sector may incidentally manufacture cyanides, but there were uncertainties with respect to the accuracy of the analytical method used to measure cyanides and the quantity manufactured was unknown (Environment Canada 2013). The cyanide ion (CN^-) (CAS RN 57-12-5) was also reported to be manufactured or imported whether in a mixture or product at a concentration of less than 0.1% by weight as a contaminant, byproduct and waste by less than four companies within the aluminum smelting sector, and by fewer than four companies within the iron and steel manufacturing sector (Environment Canada 2013). In the aluminum smelting sector, cyanides are mainly found in spent potliners (SPL) of electrolytic cells, and SPLs are considered hazardous waste (Environment Canada 2015; Freitas et al. 2016; Silveira et al. 2002).

Other documented anthropogenic sources of cyanides include electroplating factories (Kjeldsen 1999), organic and inorganic chemical manufacturing (Ontario 2016), synthetic gas (syngas) manufacturing (e.g., coal gasification) and manufactured gas plants (Luthy et al. 1979; Kapusta et al. 2013; Broer 2015; Shifrin et al. 1996), petroleum refining (Sheu and Weng 2000) and oil sands extraction or processing (Boerger and Aleksiuk 1987), the use of road salts containing ferrocyanides (EC, HC

2001), wastewater treatment systems[5], including some potentially receiving wastewater from integrated steel mills that contains cyanides (HH RAP TT 2010), landfill sites (Conestoga-Rovers and Associates 2013) and fuel combustion from vehicles (Moussa et al. 2016a).

4.2.2 Import

Information regarding the import of the 10 substances identified as priorities for assessment for 2011 was also acquired through the same notice issued pursuant to section 71 of CEPA (Canada 2012). Table 4-1 presents a summary of the total import quantities for seven cyanides (Environment Canada 2013). Results indicate that sodium cyanide (CAS RN 143-33-9) is the most important substance commercially with quantities imported ranging from 10 000 000–50 000 000 kg, or representing 97% of total quantities of the substances imported according to responses received (based on the upper ranges).

Table 4-1. Summary of information on Canadian imports for the 10 substances identified as priorities for this assessment submitted pursuant to a CEPA section 71 survey for 2011 (Environment Canada 2013)

CAS RN	Common Name	Total Imports[a] (kg)
74-90-8	Hydrogen cyanide	N/A
143-33-9	Sodium cyanide	10 000 000–50 000 000
506-61-6	Potassium dicyanoargentate	100–1000
13601-19-9	Tetrasodium ferrocyanide	10 000–100 000
13746-66-2	Tripotassium ferricyanide	100–1000
13943-58-3	Tetrapotassium ferrocyanide (Yellow prussiate of potash)	100–1000
13967-50-5	Potassium dicyanoaurate	N/A
14038-43-8	Ferric ferrocyanide (Prussian blue insoluble)	100–10 000
25869-00-5	Ferric ammonium ferrocyanide	1000–10 000
25869-98-1	Potassium ferric ferrocyanide (Prussian blue, soluble or Turnbull's blue)	N/A

Abbreviations: N/A, Not Applicable

[a] Values reflect quantities reported in response to the survey conducted under section 71 of CEPA (Environment Canada 2013). See survey for specific inclusions and exclusions (schedules 2 and 3).

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[5] In this assessment, the term "wastewater treatment system" refers to a system that collects domestic, commercial and/or institutional household sewage and possibly industrial wastewater (following discharge to the sewer), typically for treatment and eventual discharge to the environment. Unless otherwise stated, the term wastewater treatment system makes no distinction as to ownership or operator type (municipal, provincial, federal, Indigenous, private, partnerships). Systems located at industrial operations and specifically designed to treat industrial effluents will be identified by the terms "on-site wastewater treatment systems" and/or "industrial wastewater treatment systems."

Additional information regarding the import of a number of 10-digit Harmonized System (HS) codes corresponding to cyanides was acquired through data obtained from the Canada Border Services Agency (CBSA) for 2012–2013 (CBSA 2015). Imported quantities of sodium cyanides (i.e., “Cyanides and cyanide oxides of sodium”; HS code 2837110000) accounted for the majority of the total quantity of cyanides imported to Canada with over 30 000 000 kilograms in both 2012 and 2013.

4.3 Uses

Uses of the substance in the free/simple cyanides subgroup according to non-confidential business information reported pursuant to the section 71 survey (Environment Canada 2013) are limited to industrial applications, which include extraction of gold from ore/mining applications; oil and natural gas extraction; and as solid separation agents (Environment Canada 2013). Uses of the metal-cyanide complexes according to non-confidential business information reported pursuant to the section 71 survey (Environment Canada 2013) include uses in both industrial applications and products available to consumers, including corrosion inhibitors and anti-scaling agents, dyes, oil and natural gas extraction, paints and coatings, personal care products,[6] and solid separation agents (Environment Canada 2013).

Results from CBSA data for 2012 and 2013 (CBSA 2015) show that companies importing cyanides and cyanide oxides of sodium were principally involved in chemical distribution or chemical manufacturing. The substance NaCN may be used for the synthesis of chemical and pharmaceutical intermediates; the formulation of chemical products, cleaning and degreasing in the metal finishing industry; and as an extraction agent for precious metals and electroplating (Cyanco 2016; DuPont 2012). The import of “complex cyanides of metals” into Canada (CBSA 2015) may refer to use of iron-cyanide complexes in Canada as anticaking agents in road salts (EC, HC 2001; Exall et al. 2011). Some iron-cyanides such as sodium ferrocyanide were also used in forest-fire retardants; however their use in forest-fire retardants has been phased out in the United States and Canada due to toxicity concerns related to these substances dissociating and releasing free cyanide in the environment (personal communication from Canadian Interagency Forest Fire Centre 2016; USDA 2011). Table 4-2 includes additional information on current uses of the 10 substances identified as priorities for this assessment.

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[6] For the purpose of this document, a personal care product is a product that is generally recognized by the public for use in daily cleansing or grooming. Depending on how the product is represented for sale and its composition, personal care products may fall into one of three regulatory categories in Canada: cosmetics, drugs or natural health products.

Table 4-2. Additional uses in Canada for the 10 substances identified as priorities for this assessment

CAS RN **Use**	74-90-8	143-33-9	506-61-6	13967-50-5	13601-19-9	13746-66-2	13943-58-3	14038-43-8	25869-00-5	25869-98-1
Food packaging materials / incidental additives[a]	N	N	N	N	Y	N	N	Y	Y	N
Food additive[a]	N	N	N	N	Y[e]	N	Y[e]	N	N	N
Drug Product Database[a]	N	N	N	N	N	N	N	N	N	N
Natural Health Products Ingredients Database[a]	Y[f]	N	N	N	Y[g]	N	Y[f,g]	Y[f,g]	Y[g]	N
Licensed Natural Health Products Database as being present as a medicinal or non-medicinal ingredient in natural health products in Canada[a]	Y	N	N	N	Y	N	Y	Y	Y	N
List of Prohibited and Restricted Cosmetic Ingredients[b]	Y	Y	N	N	N	N	N	N	N	N
Notified to be present in cosmetics, based on notifications submitted under the Cosmetic Regulations to Health Canada[c]	N	N	N	N	Y	N	N	Y	Y	N
Formulant in pest control products registered in Canada[d]	N	N	N	N	Y	N	N	N	N	N
Active ingredient in pest control products registered in Canada[d]	N	Y	N	N	N	N	N	N	N	N

a Personal communication, emails from the Health Products and Food Branch, Health Canada, to the Existing Substances Risk Assessment Bureau, dated March 2016; unreferenced.

b Health Canada [amended on Dec. 14, 2015], Cosmetic Ingredient Hotlist: List of Ingredients that are Prohibited for Use in Cosmetic Products. Ottawa, ON: Health Canada, Consumer Product Safety Directorate (CPSD) [accessed April 28, 2016]. http://www.hc-sc.gc.ca/cps-spc/cosmet-person/hot-list-critique/hotlist-liste-eng.php

c Personal communication, emails from the CPSD, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated Jan. 11, 2016; unreferenced.

d Personal communication, emails from the Pest Management Regulatory Agency, Health Canada to ESRAB, Health Canada, date November 2015; unreferenced.

e Tetrasodium ferrocyanide (13601-19-9) and tetrapotassium ferrocyanide (13943-58-3) are associated with an acceptable daily intake of 0.025 mg/kg-bw/day.

f Homeopathic role.

g Non-medicinal role.

Identified uses in Canada carried forward for human health exposure characterization are outlined in Section 8.1. Briefly, exposures to the substances in the free/simple cyanide subgroup were characterized for ambient air and foods.

5. Releases to the Environment

Reporting to the National Pollutant Release Inventory (NPRI) is mandatory for hydrogen cyanide (CAS RN 74-90-8) (HCN) and cyanides (ionic) (NA-07)[7] (ECCC 2016b). The category cyanides (ionic) is defined by the NPRI as including the salts of hydrogen cyanides, but excluding organo-cyanides, nitriles and organometallic cyanide compounds (ECCC 2016c). Results for 2010–2014 show that releases were principally to air and water (Table 5-1).

Table 5-1. Summary of releases of hydrogen cyanide and cyanides (ionic) in tonnes reported to the NPRI per year from 2010–2015 (ECCC 2016b)

Substance	Air	Water	Land	Category "Total All Media < 1 Tonne"[a]
Cyanides (ionic)	1.5–22.5	0.6–2.2	0–4.6 x 10^{-2}	0–1.6
Hydrogen cyanide (CAS RN 74-90-8)	0–117.8	0–3.8 x 10^{-3}	0	0–0.16

[a] Refers to companies that released < 1 tonne of a substance and reported total release to all media combined.

All releases of cyanides (ionic) or hydrogen cyanide to water as well as all releases of cyanides (ionic) to soil were reported to the NPRI from the metal ore mining sector. This sector also accounted for most releases of cyanides (ionic) to air (i.e., 1.5–22.5 tonnes), with the chemical/product distribution and waste management sector reporting small quantities (i.e., 6x10^{-4}–4.6 x 10^{-2} tonnes). Releases of hydrogen cyanide to air were reported by petroleum refiners (i.e., 0–75.2 tonnes), metal ore mining (i.e., 0–42.6 tonnes) and chemical manufacturing (i.e., 0–13.3 tonnes) between 2010 and 2015 (ECCC 2016b). Releases for "total all media < 1 tonne" also shows releases of hydrogen cyanide from the "electronics and electrical equipment" sector (i.e., 0–0.16 tonne) and releases of cyanides (ionic) from the medical, health products and veterinary sector (i.e., 0–0.49 tonne), waste management (i.e., 0–6.0 x 10^{-2} tonnes) and metal ore mining (i.e., 1.6 x 10^{-2}–1.5 tonnes) from 2010–2015 (ECCC 2016b).

Other documented sources of cyanides to water include the release of effluent from iron and steel manufacturing plants (and especially integrated mills) (Ontario 2016) and urban snow melt and runoff where road salts containing ferrocyanides were used (Exall et al. 2011; 2013). HCN releases from fuel combustion in vehicles are also considered a major source of release of cyanide to air, representing 90% of the total atmospheric load in the United States by some estimates (Hagelstein and Mudder 1997). US EPA 1981 reported average emission rates of HCN in automobiles equipped with catalytic

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[7] Reporting to the NPRI is mandatory for these substances if they are manufactured, processed or otherwise used at a facility at a concentration greater than 1% by weight (except for byproducts and mine tailings) and in a quantity of 10 tonnes or more, and employees worked 20 000 hours or more at a facility.

converters (under optimum operating conditions) as 1 mg/mile (0.6 mg/km; ATSDR 2006). Data from more modern in-use vehicle fleets show mean idle HCN emissions at 39 µg/min from cold start and 21 µg/min from warm start (Baum et. al. 2007). More recent Canadian data for light-duty vehicles for 2008–2011 show average emission factors of 1.4 mg/km for HCN (Moussa et al. 2016a).

6. Environmental Fate and Behaviour

6.1 Environmental Distribution

The fate of cyanides in the environment is complex and depends on their speciation and on a variety of processes that influence their partitioning to all media. Key processes in the environment, as summarized by AGDH (2010) and Kjeldsen (1999) (Figure 6-1), include

- volatilization of HCN;
- complexation of CN^- with metals;
- biodegradation of cyanides;
- decomposition (e.g., photolysis of complex cyanides such as ferrocyanide);
- precipitation and dissolution of cyanide salts;
- redox reactions (e.g., ferrocyanide to ferricyanide);
- formation of thiocyanate and thiocyanate complexes; and
- oxidation and hydrolysis of HCN.

In air, cyanides exist primarily as gaseous HCN and, to a lesser extent, as fine particulates (ATSDR 2006). The solubility of HCN in water decreases significantly at low partial pressures (e.g., <1 torr) of HCN, and so removal of atmospheric HCN via precipitation (e.g., rainfall) is expected to be negligible despite its high water solubility (Cicerone and Zellner 1983). A relative vapour density of 0.94 compared to 1 for air (CDC 2005) indicates that HCN is lighter than air, and gaseous HCN emitted to the troposphere will rise from its immediate point of release and is expected to mix well with air (Cicerone and Zellner 1983; AGDH 2010). Therefore, HCN emissions from point or diffuse sources are quickly diluted and undergo atmospheric transportation (ECETOC 2007). HCN is subject to long-range transport, and in fact is used as a tracer to track forest-fire generated plumes. Long-range transport of HCN emitted from biomass burning from mid-latitude to the Arctic has been documented (Rinsland et al. 2002; Viatte et al. 2015).

HCN is the dominant free cyanide species in water under environmentally relevant conditions (Section 3). HCN may adsorb weakly to sediment of particulate matter but it is highly soluble and expected to remain in solution (Dzombak et al. 2006a). Volatilization of HCN from water has been identified as an important removal process of free cyanide from tailings ponds (Botz and Mudder 2000; Simovic and Snodgrass 1985, 1989) and a similar behaviour would be expected for HCN in natural waters considering its high HLC (Section 3.1). Volatilization rates of free cyanide increase with lower pH where HCN dominates, higher temperature, water column agitation and greater surface area to volume of solution (Johnson 2015). However, the cyanide ion (CN^-) forms complexes with other metals in solution (e.g., copper, zinc, nickel or iron) which are not expected to volatilize from solution, and the dissociation of these metal complexes is an important mechanism limiting the natural removal of free cyanide from water via volatilization of HCN (Simovic 1984; Simovic and Snodgrass 1985, 1989; Botz and Mudder 2000). Due to the ubiquity of iron in the environment, the most important cyanide complexation reactions generally occur with this metal to produce ferricyanide ($Fe(CN)_6^{3-}$) or ferrocyanide ($Fe(CN)_6^{4-}$ (Johnson 2015). While iron-cyanide complexes are highly stable under neutral conditions, they can undergo rapid photolysis and fully dissociate to release CN^- ions (Broderius and Smith 1980; Exall et al. 2011; Kuhn and Young 2005; Young et al. 2006). Hexacyanoferrate ($Fe(CN)_6^{4-}$) photolysis half-lives ranging from 7.5 to 23 min were calculated for deionized water and for three natural waters at 20^oC–21^oC exposed to a light intensity of 110 $\mu mol/m^2$ s ultraviolet (UV) photons (Kuhn and Young 2005). The rate of free cyanide formation was approximately three times slower because of the temporary accumulation of undefined intermediate cyanoferrate species (Kuhn and Young 2005). Kuhn and Young (2005) determined that photolysis rates are positively correlated with UV intensity and short wavelengths, but inversely correlated with concentrations of dissolved organic matter (colour) in solution. The removal of cyanide from ice-covered tailings ponds has been observed to stagnate, presumably due to a decrease in light intensity preventing the photo-dissociation of metal-cyanide complexes and volatilization of HCN (Simovic and Snodgrass 1989; Botz and Mudder 2000). Metal-cyanide compounds with transition, alkali or alkaline earth metals (e.g., Prussian blue $Fe_4(Fe(CN)_6)_3$) often have low water solubility and may accumulate in sediments (Jambor et al. 2009).The cyanide anion (CN^-) can react with sulphur species (e.g., polysulphides S_xS^{2-} or thiosulphate $S_2O_3^{2-}$) to form the much less toxic thiocyanate species (SCN^-) (Smith and Mudder 1991; Dzombak et al. 2006a). HCN may also oxidize into hydrogen cyanate (HCNO) and the cyanate anion (CNO^-) in the presence of strong oxidizers such as ozone, hydrogen peroxide or hypochlorite (AGDH 2010) during water treatment; however, this reaction is not expected in the natural environment. Hydrolysis of HCN may not occur under environmental conditions (Section 6.3) (ECETOC 2007).

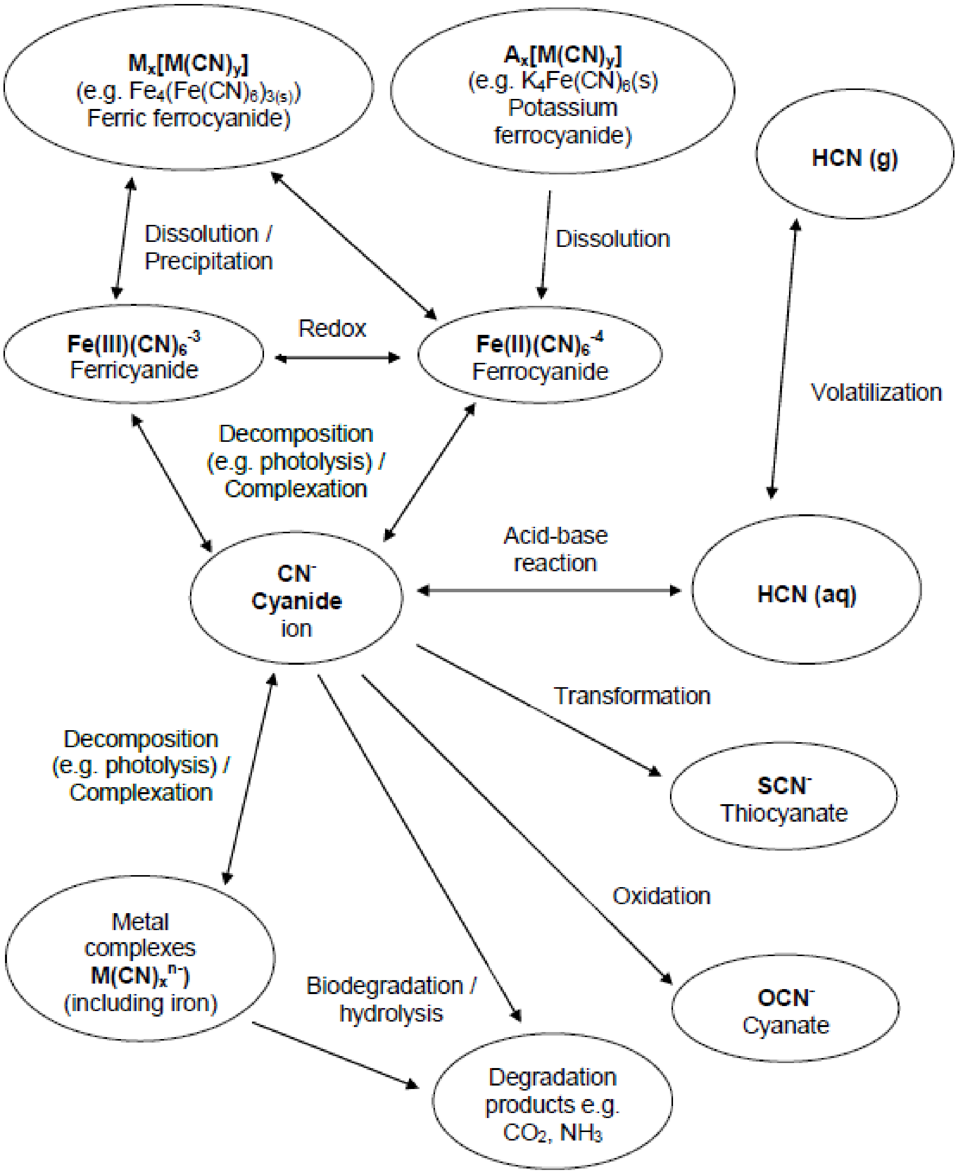

Figure 6-1. Key cyanide species and transformation processes (adapted from Kjeldsen 1999)

A review of the behaviour of free cyanide in soil was conducted by the CCME (1997a). Volatilization of HCN and biodegradation of free cyanide were identified as the two major processes affecting the transport and distribution of cyanides in soils. Free cyanide may form complexes with metals (e.g., iron) and precipitate out of solution, and such complexes may undergo photolysis at the soil surface. While adsorption of cyanides to clays and biological solids may occur, these rates are not significant compared to volatilization and biodegradation rates. A review of the behaviour of iron-cyanides in soils by EC and HC (2001) indicate that ferrocyanides have low mobility in soil due to the presence of sulphur and transition metals in soil, which may produce sparingly soluble complexes (e.g., ferric ferrocyanide, known as Prussian blue). Retention and immobilization in soils (e.g., particle adsorption) is a major attenuation pathway for metal-cyanide complexes.

6.2 Environmental Persistence

The persistence of cyanides and their degradation via abiotic or biotic processes varies depending on the species (e.g., free or complex cyanides).

In air, the residence time of HCN based solely on reactions with hydroxyl radicals ($OH^{.}$) and photolysis is estimated to range from to 1 to 2.5 years, depending on the OH concentration and rate (K_{OH}) (Cicerone and Zellner 1983; Fritz et al. 1982). However, shorter lifetimes of 5.3 months in the troposphere and from 5.0 to 6.2 months in the whole atmosphere (Li et al. 2003; Singh et al. 2003), corresponding to half-lives of 3.6 and 3.5 to 4.3 months, respectively (ECETOC 2007), have been calculated when also considering ocean uptake, which has been determined to be the principal sink of atmospheric HCN (Singh et al. 2003). It is hypothesized that HCN is subsequently degraded in oceans, presumably by microorganisms (Singh et al. 2003). The tropospheric lifetime of HCN was recently estimated to range from 30–180 days (Viatte et al. 2015). Therefore HCN may be considered persistent in air.

In water, cyanides are not expected to hydrolyze under environmentally relevant conditions because HCN hydrolysis is slow under acidic conditions or requires high temperatures under alkaline conditions (Dzombak et al. 2006a; Smith and Mudder 1991). Free cyanide may react with sulphur species (e.g., polysulphides S_xS^{2-} or thiosulphate $S_2O_3^{2-}$) and yield thiocyanate species (SCN^-) (Smith and Mudder 1991; Dzombak et al. 2006a). No biodegradability data derived using standard OECD protocols (e.g., OECD 301 Ready Biodegradability) are available for HCN or other cyanides for the aquatic environment. However, the biodegradation of HCN and other cyanide complexes has been extensively studied for the treatment of cyanide-containing industrial effluents since it is often less costly than other physical or chemical methods and faster than natural attenuation (Dash et al. 2009). A review by Ebbs et al. (2006) identified many species of bacteria or fungi isolated from sewage sludge, waste streams or soil that were able capable of metabolizing HCN and other cyanides, and confirms that free cyanide is biodegradable under certain conditions. Factors affecting the biodegradation of cyanides include cyanide concentrations, the presence of acclimatized microorganisms, low availability of nutrients, low temperature, and low or high pH depending on the microorganisms (Dash et al. 2009). A high concentration of free cyanide is considered the principal factor affecting biodegradation in wastewater treatment systems (Strotmann and Pagga 1995; Wild et al. 1994). The same controlling factors may apply to natural waters where biodegradation is expected to be an important removal process (CCME 1997a). In conclusion, free cyanide and other cyanides can biodegrade in water, but the rates will vary with environmental conditions and are unknown.

A review by the CCME (1997a) concluded that biodegradation in soils, and especially under aerobic conditions, is an important removal process for cyanides, but as with the aquatic environment, rates are unknown. Factors cited as limiting biodegradation rates include microorganisms' acclimatization, the availability of oxygen, free cyanide concentrations and nutrient availability (e.g., phosphorus).

6.3 Potential for Bioaccumulation

Free cyanide is not expected to bioconcentrate in aquatic organisms due to the low log K_{ow} value ranging from -0.25 to 0.66 (Table 3-1). Empirical bioconcentration factor (BCF) values between 1.7 and 170 L/kg have been reported for rainbow trout (Oncorhynchus mykiss) when exposed to sublethal concentrations of cyanides for 15 days to 16 weeks (Bois and Leduc 1988; Lanno and Dixon 1996).

Bioaccumulation of cyanides in the aquatic and terrestrial organisms, and biomagnification in food webs has not been observed. This may be due to the lethal effects of cyanides at high doses and rapid detoxification of cyanide to less toxic metabolites by most species at sublethal concentrations (Eisler 1991; ATSDR 2006; AGDH 2010).

7. Potential to Cause Ecological Harm

7.1 Ecological Effects Assessment

7.1.1 Mode of action

The principal mode of action of free cyanide toxicity and its main toxic effect in short-term exposures is to inhibit cellular electron transport via the inhibition of oxidative phosphorylation causing a disruption of energy metabolism (AGDH 2010; Barron et al. 2015). Once absorbed, CN^- rapidly reacts with cytochrome c oxidase to form stable cyanide complexes that inhibit the transfer of electrons in the mitochondria of cells causing cytotoxic hypoxia or cellular asphyxiation. The lack of available oxygen causes a shift from aerobic to anaerobic metabolism, resulting in the reduction of energy-rich compounds and the accumulation of lactate (lactate acidosis) in the bloodstream. The combination of cytotoxic hypoxia with lactate acidosis depresses the central nervous system, resulting in respiratory arrest and death (Eisler 1991; ICMC 2015). HCN also disrupts the activities of other enzymes, including catalase, various peroxidases, myoglobin, nitrite and nitrate reductase and nitrogenase (Solomonson 1981), and CO_2 reductase (Eisler 1991).

HCN is highly water soluble and is readily taken up by aquatic organisms via contact with skin and mucous membranes (e.g., gills) and absorbed in the bloodstream (Eisler 1991; Gensemer et al. 2006). In fish, HCN can cause sublethal effects by passing through the gill membrane, causing biochemical disturbances and resulting in tissue damage and nervous system effects (Murgatroyd et al. 1998). Common carp exposed to sublethal concentrations of sodium cyanide (100 µg/L of NaCN equivalent to approximately 67 µg/L HCN) for a duration of 10 or 20 days showed reduced enzymatic activity in the liver and irreversible oxidative damage to kidney and liver cells (David and Kartheek 2016). African catfish exposed to 50 µg/L of KCN (equivalent to 20 µg/L HCN) for four weeks experienced liver and reproductive system damage (Authman et al. 2013). Additionally, vitellogenin (Vtg) levels in serum, vitellogenin gene expression (Vtg mRNA) and estrogen receptors (ER mRNA) were decreased in female fish, but Vtg levels increased in the liver of male fish, possibly because of the stimulation of estrogen receptors (Authman et al. 2013). HCN may be considered an endocrine-active compound that may mimic the action of hormones in fish. HCN was observed to reduce fish reproduction at sublethal concentrations of 10 µg/L over a period of 12 days by increasing dopamine levels in fish brains that inhibit gonadotropin production, thereby affecting gonadal development in male and female fish (Szabo et al. 1991).

A review by the CCME (1997a) determined that the main effect of free cyanide in plants was related to its complexation with metal ions, which inhibits the action of various metalloenzymes. In addition to inhibiting aerobic respiration, CN^- also removes copper from plastocyanin inhibiting the electron transport to the photosystem (Berg and Krogman 1975).

Detoxification of free cyanide and other cyanides is mainly conducted by a mitochondrial or bacterial enzyme known as rhodanese that converts HCN to less toxic thiocyanate, which is excreted in urine (Solomonson 1981). Volatilization of HCN, or urine excretion of other metabolites produced by oxidative metabolism, are other minor detoxification processes (Eisler 1991; AGDH 2010).

7.1.2 Aquatic toxicity

The aquatic environment is considered the most important medium for cyanides due to the high solubility of free cyanide and many precursors of free cyanide. Literature reviews on the aquatic toxicity of cyanides were recently completed for Environment and Climate Change Canada (Nautilus Environmental 2009; Aquaterra Environmental Consulting Inc. 2016), or conducted as part of other international assessments (AGDH 2010; ECETOC 2007). No studies on the ecotoxicity of cyanides in sediment were identified. However, exposure from sediment may be relatively minor compared to exposure from water (Gensemer et al. 2006) and the focus is therefore on effects related to organisms in the water column.

Toxicity data are available for CN^- and HCN, simple salts (e.g., NaCN), metal complexes (e.g., sodium ferrocyanide $Na_4Fe(CN)_6$), as well as a few other cyanide species (e.g., cyanogen chloride) for many aquatic species of algae, aquatic plants, invertebrates and fish. Some aquatic species (e.g., ceriodaphnids) have been observed to be as sensitive to simple salts as to complex cyanides (Manar et al. 2011). However, the toxicity of metal-cyanide complexes is usually lower than simple salts that are capable of rapid and full dissociation to free cyanide (Gensemer et al. 2006). For example, the acute 96-hr EC_{50} for the freshwater rainbow mussel (Villosa iris) is greater than 100 mg/L and 1000 mg/L for ferric ferrocyanide and sodium ferrocyanide respectively, several orders of magnitude greater than the 96-hr EC_{50} of 1.1 mg/L for sodium cyanide for the same species (Pandolfo et al. 2012). Also, Little et al. (2007) observed that the 96-hr LC_{50} for rainbow trout (Oncorhynchus mykiss) decreased from 112.9 mg/L to 0.38 mg/L when test solutions using a stable cyanide complex potassium hexacyanocobaltate were exposed to UV radiation to cause photolysis and dissociation of the metal-cyanide complex. The selection of toxicity endpoints considered relevant for the ecological effects assessment of cyanides therefore focuses on studies conducted using free cyanide species or other simple cyanide salts such as NaCN or KCN that fully dissociate to free cyanide in solution, and whose counter ions do not cause added adverse effects.

The toxicity of HCN may be modified by a number of abiotic factors, such as temperature, water pH or oxygen content (Alabaster et al. 1983; Cairns et al. 1978; Eisler 1991; Smith and Heath 1978), but the correlation between water quality variables and HCN toxicity is not significant enough to be systematically incorporated in the calculation of a predicted-no-effect-concentration (PNEC) (Nautilus Environmental 2009).

A total of 31 toxicity studies conducted with HCN or other simple salts were reviewed and yielded acute toxicity data for 1 species of algae, 5 species of amphibians, 1 species of protozoa, 15 species of invertebrates (including 1 unionidae species) and 11 species of fish. Toxicity values for LC/EC_{50}s ranged from a low 48-hr LC_{50} of 1 µg/L HCN for the common water flea (Daphnia pulex) to a high 48-hr LC_{50} of 160 000 µg/L HCN for an annelid (Aeolosoma headleyi) (Cairns et al. 1978). In general, fish appear to exhibit a higher degree of sensitivity to free cyanide (Nautilus Environmental 2009) with the majority of LC_{50} values lower than 1 mg/L of HCN, whereas invertebrates, algae and plants had multiple LC_{50} values exceeding 1 mg/L.

Chronic toxicity data were identified from 17 studies for three species of algae, two species of aquatic plants, five species of invertebrates and six species of fish. Toxicity values (i.e., EC_{10}, EC/IC_{50}, MATC, NOEC, LOEC) ranged from a low 289-d NOEC value for reproduction of 5.2 µg/L HCN for the bluegill (Lepomis macrochirus) to a 32-d IC_{50} of 29 800 µg/L HCN for the Eurasian Watermilfoil (Myriophyllum spicatum) (Kimball et al. 1978; Stanley 1974). Fish are more sensitive to chronic exposure to free cyanide than most other organisms (Eisler 1991; AGDH 2010).

Chronic toxicity data are a more sensitive indicator of potential for harm from long-term exposure. Considering the persistence of free cyanide, chronic toxicity data were used to derive a chronic critical toxicity value (CTV), which is a quantitative expression of a low toxic effect (e.g., EC_{10}) that relates to the most sensitive toxicity endpoint for receptor organisms in the medium of interest.

Long-term exposure PNEC derivation

The chronic toxicity data set available for hydrogen cyanide meets the minimum species data requirements as outlined by the CCME (2007) allowing for the derivation of a chronic CTV using a species sensitivity distribution (SSD). Endpoints from reliable studies were selected following guidance from the CCME for the derivation of WQGs (CCME 2007). The software SSD Master v3.0 (SSD Master 2010) was used to plot the SSD (Figure 7-1). Several cumulative distribution functions (normal, logistic, extreme value and Gumbel) were fit to the data using regression methods. Model fit and assumptions were assessed using statistical and graphical techniques and the preferred model was selected based on consideration of goodness-of-fit and model feasibility.

Long-term exposure (chronic) toxicity endpoints from reliable studies were selected for 12 species, including 1 aquatic plant, 3 algae, 4 invertebrates and 4 fish species, to derive the chronic toxicity SSD (Figure 7-1) for HCN (See Table B-1 Appendix B). The endpoints represent the low-effects threshold (i.e., EC_{10}, MATC or NOEC) and were selected through consideration of several criteria, including test duration, effects observed (i.e., growth, mortality or reproduction) and their magnitude (i.e., preference was given to lowest reliable values), and species type (i.e., Canadian or surrogate species). EC_{10} values used in the SSD were calculated by Nautilus Environmental (2009). When fitting a model to the SSD, the extreme value model provided the best fit of the models tested upon visual inspection, the lowest levels of statistical variability (residuals), even distribution of the residuals, and lowest confidence interval spread. The extreme value model had the lowest Anderson-Darling statistic test value (A^2) = 0.249 ($p < 0.05$). The CTV is derived using the 5th percentile of the SSD, and is referred to as the hazardous concentration at the 5th percentile protection level (HC_5). The HC_5 of the SSD plot is 1.7 µg HCN/L with lower and upper confidence limits of 1.14 and 2.49 µg HCN/L, respectively.

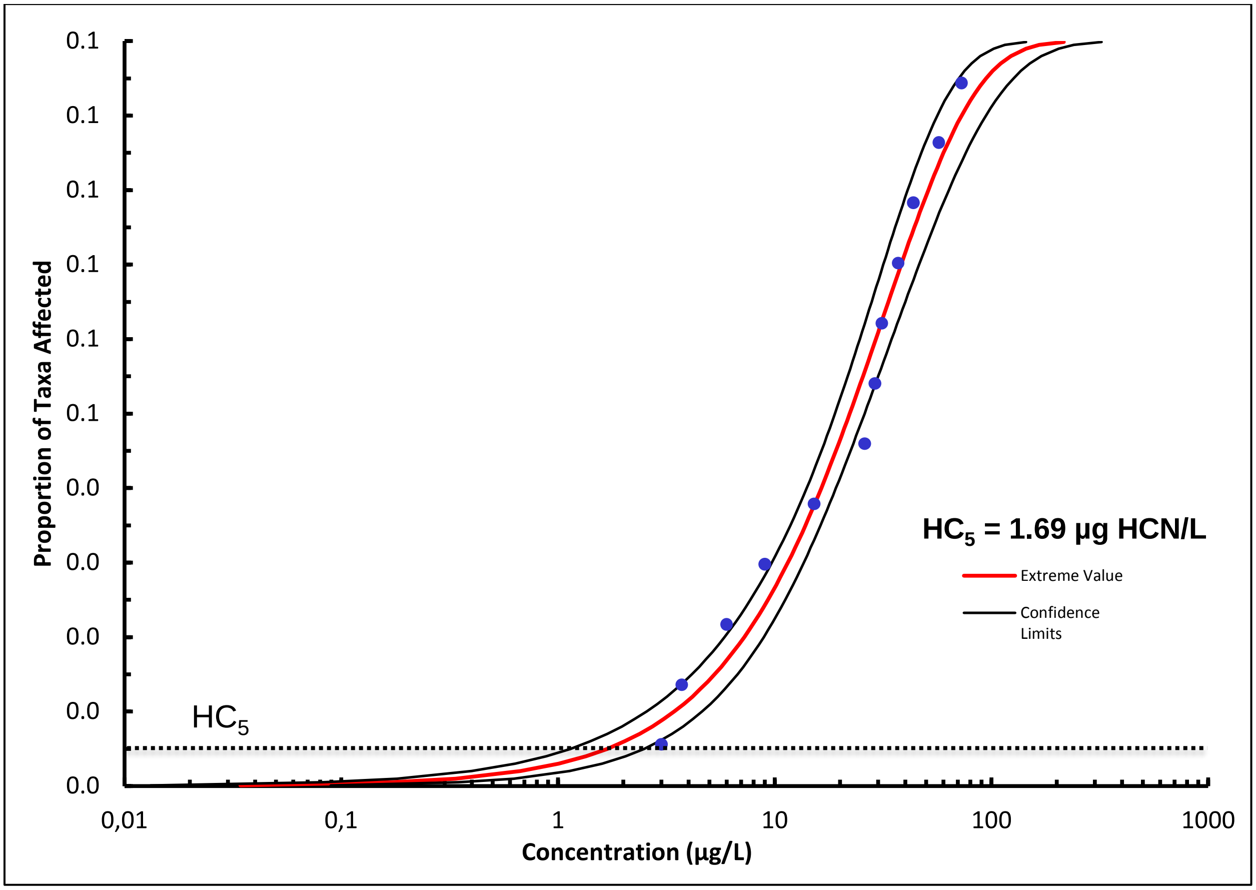

Figure 7-1. Species sensitivity distribution (SSD) for HCN based on chronic toxicity study endpoints. The extreme value model fit to data is shown on the graph, along with the 95% confidence interval and the 5th percentile of the distribution

The HC_5 of 1.7 µg HCN/L calculated from the SSD is selected as the CTV for aquatic organisms for free cyanide. According to the CCME (2007), long-term exposure guidelines identify maximum concentrations that are intended to protect all forms of aquatic life (all species and all life stages) for indefinite exposure periods and this value is therefore used to derive the PNEC for aquatic organisms. Because the HC_5 is based on a chronic SSD that covers multiple species and taxa, no additional assessment factor is needed and the PNEC for aquatic organisms is 1.7 µg HCN/L.

This PNEC value is lower than the current CCME- and US EPA-recommended Water Quality Guidelines for free cyanide of 5 µg CN/L or 5.2 µg HCN/L (CCME 1997b; US EPA 2016) or the ANZECC- recommended value of 7 µg CN/L (ANZECC 2000), which both use the acute to chronic ratio (ACR) applied to short-term LC_{50}s in lieu of chronic endpoints. However, it is comparable to the more recently derived PNEC value of 1.1 µg CN^-/L calculated by ECETOC (2007). This PNEC is based on an SSD-calculated HC_5 value of 1.1 µg CN^-/L (90% confidence interval from 0.4 to 2.3µg/L) or 1.14 µg HCN/L calculated using a chronic toxicity data set (NOECs) from freshwater and saltwater species. It is noted that a HC_5 value of 1.4 µg CN^-/L (90% confidence interval from 0.4 to 2.8 µg/L) was also calculated using freshwater species only (ECETOC 2007).

7.1.3 Terrestrial toxicity

Data on the ecotoxicity of free cyanide in soil are limited and restricted to plants and invertebrates. Information on the acute and chronic toxicity of free cyanide in soil organisms was reviewed by the CCME (1997a,c) to derive a soil quality guideline for the protection of environmental and human health for free cyanide.

The derivation of the Canadian Soil Quality Guideline for Soil Contact (SQGSC) is based on ecotoxicological data for three vascular plant species and one soil invertebrate species (earthworm). A value of 0.9 mg/kg (i.e., 900 µg/kg) of HCN was selected as the Soil Quality Guideline (SQG) for the protection of environmental health for agricultural or residential/parkland land use. A more recent soil toxicity test conducted with E. fetida using KCN yielded a 14-d EC_{50} and EC_{10} of 74 and 56 µg/kg of CN^- (equivalent to 76.8 and 58.2 µg/kg of HCN) respectively (Manar et al. 2011). This EC_{10} value is lower than two 14-d NOEC values of 1200 and 3000 µg/kg CN^- observed for the same species during the development of the SQG.

7.2 Ecological Exposure Assessment

7.2.1 Approach for the exposure characterization

Exposure scenarios have been developed for three activities that may release free cyanide and precursors of free cyanide to surface water: metal mining, iron and steel manufacturing, and cyanide-containing road salt application. Exposure scenarios were developed for these three activities since they use or manufacture large quantities of cyanides (i.e., metal mining or iron and steel manufacturing) and they may release cyanides to the aquatic environment through effluent (i.e., metal mining and iron and steel) or through the application of cyanide-containing commercial products (i.e., the application of cyanide-containing road salts). For each exposure scenario, predicted environmental concentrations (PECs) expressed as molecular hydrogen cyanide (HCN) are estimated in order to assess exposure to ecological receptors in surface water. PECs consist of ranges of concentrations for individual or multiple sites, or of arithmetic means or medians for individual sites. PECs were primarily estimated using measured concentrations of cyanides when available. Those concentrations provide evidence for exposure to organisms in Canada from specific activity sectors. The adequacy of measured environmental concentrations was assessed considering factors such as distance between sampling sites and source of release, the year and seasons the samples were collected, analytical method used, and number of available measurements. Although based on measured concentrations, PECs are labelled as “predicted” because measurements taken from specific sites for an activity sector are used to represent the sector as a whole. When measured concentrations were unavailable, PECs were estimated using facility-specific yearly average loadings of cyanide in effluent.

It is noted that other activity sectors, such as oil refining, chemical manufacturing or aluminum manufacturing, may also be sources of cyanides to the environment (Section 5.0). However, internal analyses determined that potential releases would be of lower concern. For example, releases reported by the oil refining sector to the NPRI are mainly to air, which are of lesser concern than releases to the aquatic environment due to atmospheric dispersion and diffusion (Section 6).

7.2.2 Environmental monitoring

Environmental samples (i.e., water, soil, sediment, biota) generally comprise many chemical species of cyanide and analytical methods for the different species differ according to their properties, including their capacity for dissociation. Environmental measurements of free cyanide (CN_{Free}) refer to the concentration of HCN/CN^- in a sample, measurements of “weak acid dissociable” cyanide (CN_{WAD}) refer to the concentration of free cyanide and weak cyanide complexes in a sample, and measurements of total cyanide (CN_T) refer to the sum of CN_{Free}, CN_{WAD} and all other cyanide complexes (i.e., “strong acid dissociable” CN_{SAD}) in a sample (Ghosh et al. 2006b). CN_{WAD} complexes include cyanide complexes with cadmium, zinc, silver, copper, nickel and mercury that release free cyanide under slightly acidic conditions (approximately pH 4) (CCME 1997a; Ghosh et al. 2006a,b). CN_{SAD} complexes include cyanide complexes with gold, platinum, iron and cobalt that require strong acidic conditions to dissociate (CCME 1997c; Ghosh et al. 2006a,b). The fraction of CN_{SAD} in a total cyanide measurement may be calculated by subtracting the concentration of CN_{WAD} from its corresponding CN_T concentration. Because CN_T measurements are usually obtained by acidifying the sample with a strong acid and by irradiating the sample to fully dissociate the strong complexes, CN_T may sometimes be referred to as CN_{SAD} by laboratories, even though CN_T measurements quantify both free and WAD cyanide species. Reviews of available analytical methods for each fraction in environmental media are discussed in Ghosh et al. (2006b) and AGDH (2010). A number of chemical species, including sulphide, sulphur, sulphite, oxidants such as chlorine, thiocyanate, thiosulphate, aldehydes, fatty acids, carbonate, nitrate and nitrite, may cause interference if present in solution when cyanide analysis is being conducted in water (Ghosh et al. 2006b; OI Analytical 2012; US EPA 2007). Sulphite, thiocyanate, thiosulphate and oxidizing agents may cause false negatives, while sulphide, nitrate and nitrite may cause false positive measurements (OI Analytical 2012). Additionally, exposure of the sample to sunlight may cause photolysis of metal-cyanide complexes in solution and loss of HCN due to volatilization resulting in lower measured concentrations.

While toxicity of cyanides is driven by free cyanide (CN_{Free}), measuring CN_{Free} only underestimates the potential for toxicity and most standard analytical methods, with the exception of the US EPA Method 9213 (US EPA 1996), also measure weakly bound metal complexes that dissociate at pH 6 (e.g., zinc cyanide complexes) (AGDH 2010). Therefore, CN_{WAD} measurements are widely used to measure “biologically available” cyanides (AGDH 2010) since it considers both free cyanide (HCN/CN^-) and weak complexes that may dissociate and release the moiety of concern (AGDH 2010). For example, the BC water quality criteria for cyanides in freshwater is based on CN_{WAD} and stipulates that the average concentration of CN_{WAD} (based on a minimum of five weekly samples) over a 30-day period in unfiltered samples should not exceed 5 µg CN/L (BC MOE 1986). However, CN_{WAD} measurements do not quantify strong cyanide complexes (CN_{SAD}) that have the potential to photo-dissociate to release free cyanide. Therefore, when confirming that the criterion is met, the BC MOE also recommends measuring CN_T (referred to as CN_{SAD} in the guideline). In the event where CN_T measurements exceed the criterion, additional sampling should be carried out hourly and during bright sunlight (between 11 a.m. and 2 p.m.) even if the criterion for CN_{WAD} is met, to determine whether the photolysis of iron-cyanide complexes produced unacceptable free cyanide concentrations (BC MOE 1986).

The interpretation of cyanide monitoring data should ideally consider both CN_T and CN_{WAD} concentrations when available to more accurately assess the potential for adverse effects associated with cyanides in the environment. However, environmental monitoring of cyanides by regulatory bodies or industry is most often reported as total cyanide (CN_T). While it is noted that CN_T measurements may sometimes overestimate the potential for toxicity (Redman and Santore 2012), particularly in settings where ratios of CN_{WAD}/CN_{SAD} cyanide species are low and the potential for photolysis is negligible, CN_T concentrations will be used as the primary line of evidence of the presence of cyanide in the Canadian environment due to the greater availability of the data. When available, CN_{WAD} and CN_{Free} concentrations will also be used as secondary lines of evidence of the presence of cyanides in the environment and their potential to cause adverse effects.

7.2.3 Cyanide concentrations in Canadian surface water

7.2.3.1 Natural background

Cyanides are naturally produced by many organisms or other natural abiotic processes (Section 4) which may result in detectable natural levels of cyanide in the environment (CCME 1997a). However, the availability of monitoring data (i.e., CN_{Free}, CN_{WAD} or CN_T concentrations) representative of background levels of cyanides in the aquatic environment is low, since cyanides tend to be measured close to anthropogenic sources (BC MOE 1986). Natural concentrations of cyanides are expected to be low due to removal processes such as volatilization or biodegradation, which can prevent long-term accumulation of cyanide in the water column or in sediments (BC MOE 1986). However, concentrations of CN_T in rural watersheds in Germany have been observed to fluctuate with the seasons, possibly as a result of algal blooms in the spring and decomposing organic matter in autumn and winter (ECETOC 2007; Krutz 1981). In one natural stream, normal CN_T levels of 0.7–2.1 µg/L increased to a maximum of 5 µg/L in the spring and 10 µg/L in autumn (ECETOC 2007; Krutz 1981).

7.2.3.2 Provincial water quality monitoring data

Concentrations of cyanides in surface waters are routinely monitored in three provinces: Alberta, British Columbia and Saskatchewan. Monitoring data in freshwater for relevant cyanide species for these three provinces were queried for the 2005–2015 period from Alberta Environment and Parks (AEP) (personal communication, Excel spreadsheets prepared by the Water Policy Branch, AEP, for the Ecological Assessment Division, Environment and Climate Change Canada, dated October 2, 2015; unreferenced), the British Columbia Ministry of the Environment (BC MOE) (EMSWR 2016) and the Saskatchewan Water Security Agency (SWSA) (personal communication, Excel spreadsheets prepared by the Environmental and Municipal Management Services, SWSA, for the Ecological Assessment Division, Environment and Climate Change Canada, dated February 25, 2016; unreferenced). The data sets were analyzed to define cyanide concentrations in Canadian surface waters and to identify potential sources. Statistical summaries were generated for each data set, including the total number of measurements, the number of detects, and other descriptive statistics (Table 7-1). For samples with non-detected measurements, a concentration of half the detection limit was assumed and used for the statistical analyses.

Median concentrations of CN_T from the Alberta and Saskatchewan data sets were low (1 and 0.5 µg/L) and the percentage of detected measurements (detects) was less than 10%. No notable anthropogenic sources were identified next to sites where higher concentrations were observed, with the exception of urbanization, indicating that some exceedances might be the result of releases from wastewater treatment systems, road salt applications (if measured in the winter or spring) or other unidentified sources. For example, the highest CN_T measurements for the Alberta data set (i.e., 66 µg/L) was measured in the North Saskatchewan River near the Pakan Bridge in April 2011, when road salt applications could have occurred.

In British Columbia, monitoring data in surface water were available for the parameters CN_T and CN_{WAD} (EMSWR 2016). The statistical analysis of two data sets appears to show a greater percentage of detects and higher concentrations of both CN_{WAD} and CN_T in surface waters than in Alberta or Saskatchewan. However, a high percentage of detects (including concentrations in exceedance of the PNEC of 1.7µg HCN/L) were measured at monitoring sites in the vicinity of the former Nickel Plate Mine site, near the town of Hedley, which closed in 1998. Indeed, 86% of all CN_T detects (n=3268) and 53% of all CN_{WAD} detects (n=521) were measured at 18 monitoring stations located at or in the vicinity of the Nickel Plate Mine site, including Cahill, Hedley, Red Top Gulch and Sunset creeks. Those measurements accounted for 99.2% and 92.9% of all CN_T and CN_{WAD} concentrations found to exceed the PNEC. In 2006, the BC MOE observed that the water quality objective for CN_{WAD} was not met consistently in the Cahill Creek watershed (BC MOE 2008); however, this site is closed and considered managed and is not further considered in this analysis. Other CN_T and CN_{WAD} concentrations were detected at monitoring stations located close to five mining sites (active or inactive), one former pulp and paper mill, one municipal wastewater treatment system and one site receiving runoff from a parking lot. Another 32% of detected CN_{WAD} concentrations were measured at monitoring stations that do not appear to be located directly next to point sources, but are located in watersheds where anthropogenic activities take place (e.g., mining, urbanization, agriculture, logging) (BC MOE 2017).

Table 7-1. Cyanide monitoring data from Alberta, Saskatchewan and British Columbia (2005–2015)

Province	**Alberta**	**Sask.**	**BC**	**BC**
Data set label	CN_T	CN_T	Cyanide	Cyanide (WAD)
Parameters	CN_T	CN_T	CN_T	CN_{WAD}
Number of sites	116	48	60	81
Total number of measurements (% of detects)	1424 (9%)	818 (6%)	8486 (45%)	8744 (11%)
MDLs range (µg/L)	2 - 10	1	0.5 - 100	0.5 - 100
Min – Max (µg/L)	<2 - 66	<1 - 5	<0.5 – 2477	<0.5 – 2477
Arithmetic mean (µg/L)	1.28	0.56	6.8	4.1
Geometric mean (µg/L)	1.13	0.53	2.2	1.6
Median (µg/L)	1	0.5	2.5	2.5
95th percentile (µg/L)	2.5	1	12	5

7.2.4 Metal mining

Information regarding imports of a number of cyanides for 2011 show that 10 000 000 to 50 000 000 kg of sodium cyanide (NaCN) were imported into Canada that year for use by the metal mining sector (Environment Canada 2013). The cyanide anion (CN^-) is the main reagent used to extract gold and other precious metals efficiently from ore (Johnson et al. 2002). Once ore has been extracted from a mine, it is processed to recover the valuable minerals. Major steps in ore processing include grinding and crushing, chemical/physical separation and dewatering (Environment Canada 2009). Cyanides (e.g., NaCN) may be added in the grinding circuit or during ore separation processes involving flotation or cyanide leaching, which is the dominant process for the recovery of metallic gold or silver (Environment Canada 2009). In the leaching process, cyanide solutions prepared using cyanide salts (e.g., NaCN or KCN) are used to dissolve and to extract precious metals present in the ore (Johnson 2015). Approximately 1–2.5 kg of NaCN may be used per tonne of ore (Wong-Chong et al. 2006b). Leaching is conducted at higher pHs (i.e., 9.5–11) to reduce losses of free cyanide due to hydrolysis, reaction with carbon dioxide or volatilization of HCN (US EPA 1994). A portion of cyanides may be reused in processing but some is discarded in tailings and, as a result, wastewater from cyanide-using facilities may contain cyanides (Environment Canada 2009). Mines that use cyanides often use treatment technologies to destroy the cyanide in effluent, though some operations rely solely on natural degradation of cyanide (HATCH 2014). In Canada, common technologies used for the removal of cyanides from mining wastes (e.g., effluent and tailings) are the SO_2-air process and the hydrogen peroxide process. Natural degradation is often used as a polishing step.

Canadian metal mines that deposit effluent into any water at a flow rate exceeding $50 m^3$/day are subject to the Metal Mining Effluent Regulations (MMER 2002) under the Fisheries Act. Schedule 4 of the MMER prescribes concentration limits in effluent for certain parameters, including cyanide. The maximum authorized monthly mean concentration of cyanides in effluent is 1.0 mg/L CN_T and the analytical requirements for metal mining effluent under Schedule 3 of the MMER recommend a maximum MDL of 10 µg/L CN_T. Facilities are also required to conduct Environmental Effects Monitoring (EEM) programs under which water quality monitoring must be completed in the exposure area surrounding the point of entry of effluent into water from each discharge point and from the related reference areas. Concentrations of CN_T are measured in the exposed and reference areas if the substance is used as a process reagent within the operation.

The concentration and availability of cyanides in leaching wastes (i.e., tailings and effluent) may decrease over time due to changes in cyanide speciation and removal pathways (e.g., volatilization and degradation), but recently deposited tailings may contain significant concentrations of CN_{Free} and CN_{WAD} species. For example, average CN_T and CN_{WAD} concentrations (i.e., 19.5 mg CN_T/kg and 2.95 mg CN_{WAD}/kg) measured in tailings recently deposited in a tailings pond (i.e., less than three months prior) were greater than concentrations (i.e., 3.2 mg CN_T/kg and <0.5 mg CN_{WAD}/kg) measured in “aged” tailings deposited six to nine years prior (Zagury et al. 2004). In terms of speciation, cyanide species in fresh tailings were more soluble and available than species in old tailings. Zagury et al. (2004) determined that 45%–53% of the cyanides in fresh tailings were free, readily soluble cyanides and weak to moderately strong complexes compared with 15%–33% in old tailings (Zagury et al. 2004). Similar findings were observed in effluent, where the concentrations of CN_T and CN_{WAD} measured at one heap leach operation one week after leaching (i.e., CN_{WAD} 4.84 mg/L; CN_T 6.99 mg/L) were much greater than concentrations measured in effluent eight months after leaching (i.e., CN_{WAD} 0.18 mg/L; CN_T 1.05 mg/L) and CN_{WAD} species represented a greater percentage of the CN_T concentrations (Johnson et al. 2008). Prior to the closure of the Nickel Plate Mine in British Columbia, concentrations of CN_T (2–7 mg/L) and CN_{WAD} concentrations (0.2–3.0 mg/L) were measured in the reclaim water from the tailings area used in milling (Given and Meyer 1998), indicating that CN_{Free} and CN_{WAD} species were present in solution, but in lower concentrations than CN_{SAD} species. In another example, the sampling of a creek receiving cyanide-contaminated exfiltration water from the tailings pond of an active gold and silver mine and mill facility determined that CN_T and CN_{WAD} concentrations were virtually identical and that CN_{WAD} species represented on average 90% of the cyanide species measured in the creek (BC MOEP 1986). These findings suggest that in the absence of prolonged natural attenuation or additional treatment, a significant portion of the cyanides in effluent from active sites may be the more available and more hazardous CN_{WAD} species.

Photolysis and dissociation of strong metal-cyanide complexes was observed in the effluent of a former gold mine. CN_{WAD} concentrations in samples collected from an open channel receiving effluent from an inactive ore heap were observed to rapidly increase during daytime to 0.7 mg/L CN_{WAD} and to decrease to 0.2 mg/L at night, while concentrations of CN_{SAD} complexes (i.e., $Fe(CN)_6^{4-}$ complex) showed the opposite behaviour (Johnson et al. 2002). The rapid photodissociation rate of cyano-complexes was estimated at 0.9 mg CN/L/hr with a water temperature ranging from 14.6°C–28.2°C (Johnson et al. 2002). The design of channel used in the study, which was approximately 0.5 metres wide and a few centimetres deep, may have favoured the dissociation of metal-cyanide complexes as photo dissociation rates vary with sunlight intensity, light, light absorption in the water column and temperature (Johnson et al. 2015). In alignment with the BC WQC for cyanide (BC MOE 1986), these results suggest the presence of a regular diurnal cycle for the speciation of cyanides, indicating that CN_{SAD} species measured in CN_T measurements can photo-dissociate and be a source of CN_{Free} in gold mine effluent and possibly in the receiving environment. Therefore, dissociation of CN_{SAD} species in the receiving environment could lead to potentially harmful HCN concentrations in the environment, especially in areas where concentrations of CN_{WAD} or CN_{Free} were already measured.

Concentrations of CN_T measured in surface water samples collected from exposed and reference areas between 2003 and 2015 submitted to Environment and Climate Change Canada under the MMER and EEM program were analyzed (Table 7-2) (EEM 2016). Reported MDLs for the whole data set ranged from 1.0×10^{-3}–100 µg/L CN_T and were often above the PNEC value of 1.7 µg/L for HCN. Measurements that fell below the MDL were retained in the exposure analysis but were transformed to half of the specific MDL.

Results of the analysis generally show higher CN_T concentrations in water samples collected in exposed areas compared to samples collected in reference areas. Detected concentrations of CN_T exceeded the PNEC more regularly in the exposure areas (i.e., 39%) compared with the reference areas (i.e., 23%). The maximum concentration reported, the geometric mean and the arithmetic mean were also greater than those of the reference areas. The medians for the exposure and reference data sets are comparable, and are explained by the number of non-detects subsequently transformed to half of the MDL. Because MDLs (e.g., 0.1 mg/L CN_T) were often higher than the PNEC, a non-detect does not signify the absence of cyanides in a sample and cyanide concentrations exceeding the PNEC may be more numerous than the proportion of detects would suggest.

Table 7-2. Summary of monitoring results for CN_T measured under the MMER from 2003–2015 (EEM 2016)

Parameter	Exposure Area	Reference Area
Total number of measurements (% of detects)	2501 (41%)	2405 (23%)
Number of facilities	85	84
Number of detects[a] exceeding the PNEC[b] (% of exceedances)	970 (39%)	553 (23%)
Number of facilities with detects exceeding the PNEC	70	64
Min – Max (µg/L)	$<1.0 \times 10^{-3}$ – 926	$<1.0 \times 10^{-3}$ – 420
Arithmetic mean (µg/L)	13.9	3.9
Geometric mean (µg/L)	3.2	2.0
Median (µg/L)[c]	2.5	2.5
95th percentile (µg/L)	39	11.3

a Measurements exceeding the analytical Method Detection Limit (MDL).
b Chronic PNEC = 1.7 µg HCN/L.
c Median values are equal for both areas because of the large percentage of measured values under the MDL.

Data for 10 mining facilities (gold mines or milling facilities) identified as having more than 50% of detected measurements in the exposed areas exceeding PNEC, and a large data set were analyzed (Table 7-3). CN_T concentrations were reported in the effluent of all facilities, confirming that cyanides are used in their processes. Results confirm that CN_T concentrations in exposed areas were greater than the reference area and could be positively linked to mining activity and were not significantly impacted by other sources (e.g., forest fires).

Table 7-3. Site-specific analysis for CN_T measurements (EEM 2016)

Site	Sampling Period	Type of Area	Sample Size	Detects > PNEC	Median (µg/L)	Geo-mean (µg/L)	Aver-age (µg/L)
1[a]	2004–2015	Exposed	120	90%	7	6.8	10.7
1[a]	2004–2015	Reference	108	18.5%	1	1.4	2.0
2	2004–2015	Exposed	47	74.5%	3	3.0	3.9
2	2004–2015	Reference	46	13%	1	1.2	1.2
3	2004–2015	Exposed	35	74%	4	5.0	14
3	2004–2015	Reference	34	3%	1	0.9	1
4	2003–2015	Exposed	44	70%	9.6	8.2	11.5
4	2003–2015	Reference	44	48%	3.8	4.6	5.9

Site	Sampling Period	Type of Area	Sample Size	Detects > PNEC	Median (µg/L)	Geo-mean (µg/L)	Aver-age (µg/L)
5[b]	2004–2015	Exposed	13	92%	313	206.9	336.7
5[b]	2004–2015	Reference	16	87.5%	7.9	6.7	7.5
6	2004–2015	Exposed	50	62%	8.3	6.3	30.6
6	2004–2015	Reference	49	45%	1	2.9	8.2
7	2009–2015	Exposed	25	92%	14	15.1	32.9
7	2009–2015	Reference	26	50%	5	5.8	9.5
8	2009–2015	Exposed	25	88%	20	17.5	43.4
8	2009–2015	Reference	26	50%	2.5	2.5	5.1
9	2005–2015	Exposed	41	78%	13	10	18.0
9	2005–2015	Reference	41	46%	5	4.7	6.4
10	2004–2015	Exposed	221	65%	10.2	9.4	17
10	2004–2015	Reference	149	45%	2.5	4.5	5.7

a Site 1 comprises one milling facility and one mine that conduct joint “Environmental Effects Monitoring” but that submit separate water concentration data sets to the MMER reporting system. The information was analyzed jointly.

b Site 5 ceased operation in 2008 but continued to release effluent to the receiving environment.

Concentrations of CN_{Free} and preferably CN_{WAD} in the receiving environment of the same 10 sites were extracted and analyzed (Table 7-4) to clarify the speciation of cyanides in the receiving environment from metal mining facilities. The availability of monitoring data for these two parameters was generally low. Additionally, CN_{Free} and CN_{WAD} were not systematically analyzed at all sampling sites used to characterize “exposed” or “reference” areas used in environmental effects monitoring (i.e., sites in Table 7-2 & Table 7-3) and data were sometimes available for other sampling sites (e.g., site 1 – Exposed creek near field). The data presented in Table 7-4 consist of already calculated statistics obtained from Environmental Effects Monitoring (EEM) reports (e.g., Site 6), or of statistics (median, geomean and arithmetic mean) calculated from the raw data in the reports (ECCC 2016d). Values below the detection limit were converted to half the detection limit. CN_{WAD} and CN_{Free} were detected in the receiving environment of all facilities where it was measured, but median concentrations are generally low since many measurements were below the MDLs. CN_T concentrations above CN_{WAD} and CN_{Free} concentrations were systematically measured at all sites indicating that a fraction of CN_T species are CN_{SAD} species.

Table 7-4. Site-specific analysis for CN_{Free} and CN_{WAD} and corresponding CN_T concentrations (EMSWR 2016; ECCC 2016d)

Sites	Sampling Period	Type of Area	Para-meter	Sample Size	Median (µg/L)	Geo-mean (µg/L)	Aver-age (µg/L)
1	2011–2012	Exposed (lake)	CN_{WAD}	5	1	1.2	1.4
1	2011–2012	Exposed (lake)	CN_T	6	8	7.3	7.7
1	2011–2012	Reference (lake)	CN_{WAD}	7	1	1	1
1	2011–2012	Reference (lake)	CN_T	7	1	1	1
1[a]	2008–2010	Exposed (creek n.f.)	CN_{WAD}	34	-	-	2 - 4
1[a]	2008–2010	Exposed (creek n.f.)	CN_T	52	-	-	5 - 11
1	2008–2010	Reference (creek)	CN_{WAD}	33	-	-	2 - 4
1	2008–2010	Reference (creek)	CN_T	37	-	-	2 - 4
2	2014–2015	Exposed	CN_{WAD}	14	1	1.4	1.6
2	2014–2015	Exposed	CN_T	14	2.5	2.2	2.8
2	2014–2015	Reference	CN_{WAD}	8	1	1	1
2	2014–2015	Reference	CN_T	8	1	1	1
6	2005–2012	Exposed	CN_{Free}	-	1	-	4.3
6	2005–2012	Exposed	CN_T	-	6.2	-	20
6	2005–2012	Reference	CN_{Free}	-	1	-	3
6	2005–2012	Reference	CN_T	-	5	-	14
6	2012–2014	Exposed	CN_{Free}	94	-	-	2
6	2012–2014	Exposed	CN_T	94	-	-	18
6	2012–2014	Reference	CN_{Free}	75	-	-	2.1
6	2012–2014	Reference	CN_T	75	-	-	8
7	2009–2015	Exposed	CN_{WAD}	12	2.5	4.5	6.7
7	2009–2015	Exposed	CN_T	15	8	8.8	12
7	2009–2015	Reference	CN_{WAD}	9	2.5	4.6	6
7	2009–2015	Reference	CN_T	13	7	5.8	8.6
8	2015	Exposed	CN_{WAD}	3	5	6.8	11

Sites	Sampling Period	Type of Area	Para-meter	Sample Size	Median (µg/L)	Geo-mean (µg/L)	Aver-age (µg/L)
8	2015	Reference	CN_{WAD}	3	1	1.7	2.3
10[b]	2012–2015	Exposed	CN_{WAD}	181	2.5	2.8	3
10[b]	2012–2015	Reference	CN_{WAD}	35	2.5	2.5	2.5

a n.f = near field

b Data from EMSWR (2016): 15% of measurements in the exposed area were above the PNEC (1.7 µg/L) and DL.

The concentrations of monitoring data suggest that the metal mining sector is a source of cyanides, and CN_T were often above PNEC values. While the speciation of the cyanides measured in CN_T is unknown, some occurrences of measured CN_{WAD} or CN_{Free} concentrations were reported at all sites where these measurements were taken. It is unknown whether the presence of these species in the receiving environment is due to direct releases from mining effluent of CN_{WAD} or due to the photolysis of stable complexes. While many occurrences of CN_{WAD} or CN_{Free} measurements were below detection limits, it is unknown whether the samples were collected during maximal sun exposure, when photolysis of the complex cyanides would have led to the formation of free cyanide, or whether there was sufficient light penetration in the water body. Samples collected early in the morning or late in the afternoon could be underrepresenting the presence of those species in the environment.

The existence of CN_T measurements above the PNEC and MDL for the whole data set (i.e., 23% of all measurements) in reference areas is seldom explained in the EEM reports. The presence of cyanides in the reference samples may be due to confounding factors such as releases from former mining sites or tailings areas, from natural sources such as decaying plant matter or forest fires.

7.2.5 Iron and steel manufacturing

Free cyanide and other species may be found in gas and in wastewater from coke plants and blast furnaces at integrated mills (Luzin et al. 2012; Petelin et al. 2008; Yu et al. 2016). Metallurgical coke is prepared by heating coke in an oxygen-free atmosphere, and metallurgical coke is used in blast furnaces to reduce iron ore to iron (US EPA 2008). Cyanides are produced by the reaction between carbon and nitrogen under reducing conditions and high temperatures (>1000°C), conditions that are found during coking and blast furnace operations (Wong-Chong et al. 2006c; Petelin et al. 2008). Cyanides may be found in coke oven gas (COG) and blast furnace gas, or in cooling water that has been in contact with COG, in flushing liquor resulting from the cleaning of coke oven gas to remove contaminants (also referred to as waste ammonia liquor, [WAL]) or in blast furnace gas scrubber effluent (Wong-Chong et al. 2006b; US EPA 2008). In addition to free cyanide, other cyanides formed during blast furnace operations are the simple cyanides KCN and NaCN or cyanogen (CN_2) (Luzin et al. 2012; Petelin et al. 2008), which readily dissociate in water to form free cyanide. Iron-cyanide complexes have been identified in blast furnace sludge resulting from gas cleaning (Rennert and Mansfeldt 2002).

Elevated concentrations of cyanides have been reported in blast furnace gas scrubber effluent and coke oven effluent, as illustrated by concentrations (presumably CN_T) of 5.7 and 80 mg/L respectively (Ellis et al. 1976), but the speciation is not always specified. Concentrations of 2.1 mg/L CN_T, 0.3 mg/L of dissociable cyanides and 0.8 mg/L of complex cyanides have been reported in untreated wastewater from a coking operation (Kelada 1989). There is uncertainty with the accuracy of the 0.3 mg/L dissociable cyanides reported since, by definition, the sum of dissociable cyanides and complex cyanides should equal the concentration of CN_T and the actual measurement of dissociable cyanides may instead be 1.3 mg/L. CN_{Free} and CN_T concentrations of 430 and 833 µg/L were measured in blast furnace effluent in Australia (Pablo et al. 1997), indicating that a significant fraction of cyanides released to the environment (i.e., > 50%) may be the more available CN_{Free} form. Integrated mills were identified as sources of cyanides to Hamilton Harbour from 1997 to 2007 through the release of process and cooling waters during steel production (HH RAP TT 2010), but releases from these facilities have decreased significantly since 2002.

Under the Effluent Monitoring and Effluent Limits – Iron and Steel Manufacturing Sector Regulations (O. Reg 214/95) (Ontario 1990) certain facilities from the iron and steel sector are required to report monthly releases of cyanides (as loadings of CN_T) to the receiving environment to the Ontario Ministry of the Environment and Climate Change (ONT MOECC). Cyanide loadings may be reported for “process effluent”, “once-through-cooling-water (OTCW) effluent” and “combined effluent” (Ontario 2016). Predicted environmental concentrations (PECs) based on CN_T were derived using average yearly concentrations calculated for each effluent stream and using data submitted quarterly by industry for 2012–2014 (Table 7-5) (Ontario 2016) and by applying a dilution factor of 10 to estimate concentrations in the aquatic environment. The natural concentration of cyanides in the environment is assumed to be negligible and no default “background” value was added to the PEC values.

Results indicate that two facilities (Site 1 and Site 4) have PECs greater than the PNEC value of 1.7 µg/L for CN_{Free} as a result of releases from their process effluent and the combined effluent.

Table 7-5. PECs based on CN_T for the iron and steel sector 2012–2014 (Ontario 2016)

Sites	Year	Total Yearly Loading (kg)[a]	PEC (Process Effluent) (µg/L)	PEC (OTCW Effluent) (µg/L)	PEC (Combined Effluent) (µg/L)
1	2014	2125	1.82	0.38	-
1	2013	3034	3.20	0.23	-
1	2012	2142	2.54	-	-

Sites	Year	Total Yearly Loading (kg)[a]	PEC (Process Effluent) (µg/L)	PEC (OTCW Effluent) (µg/L)	PEC (Combined Effluent) (µg/L)
2	2014	352	5.60×10^{-2}	0	0.38
2	2013	297	0.31	0	0.27
2	2012	303	0.46	-	0.27
3	2014	76	0.15	0.20	-
3	2013	158	0.26	0.28	-
3	2012	31	0.26	-	-
4	2014	924	7.74	-	3.42
4	2013	596	5.82	-	2.83
4	2012	855	8.28	-	2.19

[a] Loading calculated using average yearly loading based on monthly loadings reported to the Ontario MOECC.

7.2.6 Road salts

Ferrocyanides may be used as anticaking agents in road salts to prevent clumping (EC, HC 2001). Road salts containing ferrocyanide anticaking agents are applied as de-icing agents on roads and parking lots in many Canadian provinces (EC & HC 2001; Exall et al. 2013) during the late fall, winter and spring seasons. The four most commonly used anticaking cyanides are tetrasodium ferrocyanide (YPS; CAS RN 13601-19-9), sodium ferrocyanide (CAS RN 14217-21-1), potassium ferrocyanide (YPP; CAS RN 13943-58-3) and ferric ferrocyanide (Prussian blue; CAS RN 14038-43-8) (EC & HC 2001; Exall et al. 2011; Levelton Consultants 2007). Content of YPS per kilogram of road salt was reported to range from 30–124 mg/kg of NaCl (EC, HC 2001). More recent data show the negligible presence of YPS (i.e., negligible to 0.045 mg YPS/kg of NaCl) in samples collected from provincial road authorities in BC, Alberta and Manitoba, but greater concentrations ranging from 17–102 mg YPS/kg of NaCl in samples collected from Ontario, Quebec, New Brunswick and Newfoundland and Labrador provincial authorities (Exall et al. 2013).

Sodium ferrocyanide dissolves in water and releases the ferrocyanide anion $Fe(CN)_6^{4-}$ (EC, HC 2001). While the ferrocyanide anion is stable and exhibits low toxicity to organisms, in solution it can fully dissociate due to photolysis to produce free cyanide (HCN/CN^-) (EC, HC 2001; Exall et al. 2011). Photolysis experiments were conducted on three highway runoff samples collected in 2012 which were exposed to sunlight for a period of six hours daily under winter conditions (e.g., light intensity) and temperatures ranging from -5°C to -2°C (Exall et al. 2013). Results determined that the ferrocyanide anion was rapidly converted to free cyanide (expressed as CN_{WAD} measurements) based on half-lives ranging from 2.2–3.9 hours (Exall et al. 2013). Therefore, free cyanide may be released into the environment due to the use of ferrocyanides as anticaking agents in road salts during the late fall, winter and spring seasons when de-icing agents are applied to roads and parking lots.

The use of ferrocyanides as anticaking agents was investigated under the Priority Substances List (PSL) assessment of road salts in 2001 (EC, HC 2001). Because measured environmental concentrations were limited, concentrations of free cyanide in runoff were modelled and estimated to range from 0.0039–39 µg CN^-/L after one hour (EC, HC 2001). The assessment determined that sensitive species of aquatic microorganisms, aquatic plants, aquatic invertebrates and aquatic vertebrates in roadside ditches and watercourses in areas of road salt use could experience potential adverse effects at those levels of salt use (EC, HC 2001). The modelled scenario assumed incomplete dissociation of the $Fe(CN)_6^{4-}$ anion (i.e., maximum 85% dissociation) based on the findings of Broderius and Smith (1980), but a more recent study by Kuhn and Young (2005) observed full dissociation of the ferrocyanide anion and partial dissociation of $Fe(CN)_6^{4-}$ was deemed inconsistent with other photolytic reaction models by Young et al. (2005).

Cyanide concentrations have been measured in the United States in snow (CN_T Non-detected – 270 µg/L), in an urban stream modified for stormwater conveyance (CN_T Non-detected – 45 µg/L) and in surface waters of four different sites receiving runoff from salt storage facilities (CN_T Non-detected – 200 µg/L; CN_{Free} Non-detected – 96 µg/L) (Novotny et al. 1998; Ohno 1989).

In Canada, CN_T and CN_{WAD} concentrations have been measured in storm sewers; in runoff from highways, parking lots or snow storage facilities; and in stormwater ponds (Table 7-6). Measured CN_T and CN_{WAD} concentrations depended on a variety of factors, including the salt content of the anti-skidding product used on roads, MDLs, the period between road salt application and sample collection, and sampling methods. In all studies, significant CN_T concentrations were measured. The City of Edmonton uses an abrasive-salt mixture with a low salt content (7%) as anti-skidding product, which may have contributed to the low CN_T concentrations measured in storm water at that location (Novotny et al. 1998).

Table 7-6. Concentrations of CN_{WAD} and CN_T in storm sewer and runoff in Canada

Sample Type (date)	Location (sample size n)	CN_T Median[a] (range) (µg/L)	CN_{WAD} Median[a] (range) (µg/L)	Reference
Storm sewer outfall[b]	Edmonton (n=5)	3–7	-	Novotny et al. 1998
Parking lot runoff (alternative de-icer)[c] (2009)	Mississauga (n=21)	55 (ND–847)	5 (ND–444)	Exall et al. 2011
Parking lot runoff[c] (2009)	Mississauga (n=46)	45.5 (ND–415)	5 (ND–80)	Exall et al. 2011
Snowmelt snow storage facility[d] (2007–2008)	Richmond Hill (n=61)	30 (ND–551)	10 (ND–29)	Exall et al. 2011
Stormwater ponds[e] (2008–2009)	Peterborough, Richmond Hill, Toronto (n=65)	3 (ND–49)	3 (ND–36)	Exall et al. 2011
Bridge deck highway runoff (2010–2012)[f]	Burlington (n=24)	77 (28–245)	4 (ND–17)	Exall et al. 2013
Parking lot runoff (2010–2012)[f]	Burlington (n=34)	92 (35–483)	<2 (2–24)	Exall et al. 2013

Abbreviations: ND means non-detected.

a The median for Exall et al. (2011) was calculated by converting non-detects to half the detection limit.

b Edmonton used a mixture of abrasive-salt mixture and salt (content 7% salt by weight) (Novotny et al. 1998).

c Parking lot runoff samples were collected on the first snowmelt/runoff event after salt application (Exall et al. 2011) from November 2008–April 2009; the MDL equalled 10 µg/L for the CN_T and CN_{WAD}.

d Snow storage runoff samples were collected when melting occurred days or weeks after road salt application (Exall et al. 2011) from January 2007 to April 2008; the MDL equalled 20 µg/L for the CN_T and CN_{WAD}.

e Stormwater pond samples were generally collected in the spring and summer, months after road salt application (Exall et al. 2011), the MDL for the CN_T and CN_{WAD} equalled 17 µg/L and was lowered to 6 µg/L during the study.

f Highway bridge deck and parking lot runoff samples collected from December 2010 to April 2011 and from December 2011 to April 2012 (Exall et al. 2013).

In the Exall et al. (2011) study, a colorimetric method was used to analyze CN_{WAD} concentrations and the MDL ranged from 6–20 µg/L over the course of the study. Approximately 40% of parking lot runoff samples showed CN_{WAD} concentrations greater than the MDL of 10 µg/L, and since runoff from the parking lots was discharged directly to an adjacent creek, it is a direct source of free cyanide to the environment. The lower percentage of snowmelt samples (11%) and stormwater pond samples (6%) exceeding CN_{WAD} MDL compared to parking lot runoff could be explained by the longer period between road salt application and sampling (weeks to months) or dilution. The longer period could have allowed for greater photolysis of the ferrocyanides and subsequent volatilization of HCN, thereby decreasing overall CN_{WAD} measurements (Exall et al. 2011).

Median CN_{WAD} concentrations of 4 and < 2 µg/L measured in runoff collected from a highway bridge and a parking lot in Burlington from 2010–2012 (Exall et al. 2013) suggest lower CN_{WAD} concentrations than previously measured in the Mississauga parking lot runoff (Exall et al. 2011). However, based on CN_T concentrations in the runoff (i.e., median of 92 µg/L), the authors suggested that the sampling procedure used during the 2010–2012 study was inadequate for the collection of samples for CN_{WAD} analyses and likely explained the lower CN_{WAD} concentrations measured in parking lot runoff in this study (Exall et al. 2013).

Recent results from both Exall et al. studies (2011, 2013) are considered realistic worst-case exposure scenarios for the release of free cyanide to the environment from parking lot and highway runoff as a result of road salt application in the winter and spring seasons. PECs in the receiving aquatic environment were derived by applying a dilution factor of 10 to concentrations of cyanide (i.e., median and range) measured in parking lot runoff in Mississauga and Burlington and to concentrations measured in highway runoff. The natural concentration of cyanides in the environment is assumed to be negligible and no default “background” value was added to the PEC values.

7.3 Characterization of Ecological Risk

This ecological screening assessment focuses on cyanides and, more specifically, on free cyanide and the moiety of concern HCN, as well as other substances that are considered precursors of free cyanide, including the 10 cyanide substances identified as priorities for assessment. Various lines of evidence are considered and conclusions are developed based on a weight-of-evidence approach and using precaution as required under CEPA. Lines of evidence include results from risk quotient calculations for key exposure scenarios; information on fate, persistence and toxicity; and sources of cyanides in the Canadian environment.

7.3.1 Risk quotient analysis

A risk quotient analysis, integrating measured concentrations and realistic worst-case estimates of exposure with chronic toxicity information, was performed for aquatic environments to determine whether there is potential for ecological harm in Canada. Risk quotients (RQs) for three exposure scenarios described in Section 7.2 are presented in Table 7-7. RQs were calculated by comparing PECs, derived for the metal mining and iron and steel sectors and for runoff (from parking lots and highways) from the application of ferrocyanide-containing road salts (runoff from parking lots and highways), with the long-term PNEC for aquatic organisms. The long-term PNEC was used for the risk quotient analysis since releases from all three exposure scenarios are expected to either be continuous (i.e., precious metals mining and integrated steel mills) or to occur over consecutive days or weeks leading to exposure of aquatic organisms to free cyanide over periods representative of chronic exposure.

PECs were based on CN_T measured concentrations or loadings. RQs calculated using PECs based on CN_{WAD} concentrations are also presented for the exposure characterization for parking lot runoff as an additional line of evidence, since both CN_{WAD} and CN_T were analyzed simultaneously from the same samples and can be correlated. The availability of CN_{WAD} measurements for the metal mining sector was insufficient to characterize the whole sector.

Table 7-7. Risk quotient (RQ) calculations in surface water based on a PNEC of 1.7 µg/L HCN for exposures scenarios within three activity sectors

Sector	Details	PEC Range (µg/L)	RQ Range	PEC Median(s) (µg/L)	RQ Median(s)	PEC Geo-mean (µg/L)	RQ Geo-mean
Metal mining	All sites (n=85) CN_T	<MDL–926	Negl.–548	2.5	1.5	3.2	1.9
Metal mining	10 sites specific analysis CN_T[a]	0.5–926	0.3–548	3–313	1.8–185	3–207	1.8–122
Iron and steel	All sites (n=4) CN_T	-	-	Negl.–8.28	Negl.–4.9	-	-
Runoff road salts (parking lots)	3 sites CN_T	0.5–84.7	0.3–50.1	4.5–9.2	2.7–5.4	-	-
Runoff road salts (parking lots)	2 sites CN_{WAD}	0.5–44.4	0.3–26.3	0.5	0.3	-	-
Runoff road salts (highway runoff)	1 site CN_T	0.3–24.5	0.16–14.5	7.7	4.5	-	-

Abbreviations: “Negl.” negligible; “-” not applicable.

a These 10 sites are included within the 85 mining sites.

7.3.2 Consideration of the lines of evidence and uncertainties

7.3.2.1 Consideration of the lines of evidence

Once released in the aquatic environment, cyanides may dissociate and release free cyanide and the toxic moiety of concern HCN. HCN may then volatilize, biodegrade or create complexes of variable stability with many metals, among a series of other transformation processes. HCN is not persistent in water and does not bioaccumulate. However it is highly toxic to aquatic organisms, and chronic exposure to low concentrations of HCN (i.e., as low as 1.7 µg HCN/L) may cause adverse effects to aquatic organisms. Measured CN_T concentrations include CN_{Free} and CN_{WAD} species, but also CN_{SAD} species that exhibit lower toxicity than HCN and basing PECs on CN_T

measurements is potentially conservative. However, there is ample evidence that CN_{SAD} species can rapidly photodissociate in the environment, and therefore constitute a potential reservoir of free cyanide. Hence, releases of cyanides to the aquatic environment from certain industries or other activities such as road salt application may generate concentrations of free cyanide near point sources that may be causing harm to organisms in Canada, particularly fish.

The metal mining sector, and more specifically gold and precious metals mining, uses large quantities of sodium cyanide for metal recovery. Facilities that use cyanides in their process report effluent concentrations to ECCC under the MMER and monitor CN_T concentrations in the receiving environment as part of EEM studies. Cyanides in effluent may be treated using passive attenuation or active treatment systems (e.g., biodegradation or oxidation) prior to discharge. However, monitoring data gathered under the MMER indicate that CN_T is measured in the receiving environment in a constant manner, as illustrated by 40% of detects exceeding PNEC from 2003–2015, and chronic effects on aquatic organisms may be occurring.

Cyanides are incidentally manufactured by integrated steel mills during coking and smelting activities. Loadings of CN_T released to effluent by integrated steel mills are reported to the ONT MOECC monthly and indicate that concentrations of cyanides near the point of discharge of various continuous effluent streams by certain facilities may exceed the PNEC and cause chronic effects in aquatic organisms.

A number of iron cyanides and, most importantly, ferrocyanides are used as anticaking agents in de-icing products applied to roads and parking lots in a number of Canadian provinces. Recent studies conducted in Canada (Exall et al. 2011; 2013) confirm that ferrocyanides can rapidly dissociate to free cyanide once de-icing products are applied to roads and parking lots. PECs based on measured CN_T or CN_{WAD} concentrations in parking lot and highway runoff in Canada indicate that this activity may cause adverse effects in certain aquatic organisms if runoff is released directly to surface waters over the late fall, winter and spring months. These results support the findings of the 2001 road salt assessment based on modelled releases, which determined that at current levels of salt use, sensitive species of aquatic microorganisms, aquatic plants, aquatic invertebrates and aquatic vertebrates in roadside ditches and watercourses in areas of road salt use could experience potential adverse effects (EC, HC 2001).

The information indicates that free cyanide and precursors of free cyanide have the potential to cause ecological harm in Canada. Free cyanide and precursors of free cyanide are proposed to meet the persistence criteria but not the bioaccumulation criteria as set out in the Persistence and Bioaccumulation Regulations of CEPA.

Considering all the lines of evidence presented in this screening assessment, there is risk of harm to organisms and biodiversity, but not to the broader integrity of the environment, from free cyanide and precursors of free cyanide.

7.3.2.2 Uncertainties

The speciation of cyanides is complex and cyanide species exhibit different behaviours and properties in the environment. Proper timing and sampling methods are therefore important, particularly important when determining the concentration of CN_{WAD} and CN_{Free} in solution. Indeed, with HCN being volatile, it may volatilize from samples if the collection methods are inappropriate, as hypothesized by Exall et al. (2013), which could underestimate environmental concentrations. Additionally, the timing of the sample collection is important for measuring CN_{WAD} or CN_{Free} as photolysis of the CN_{SAD} species, and therefore concentrations of CN_{Free} or CN_{WAD}, will be greatest mid-day when sun exposure is maximal. Hence, while CN_{WAD} and CN_{Free} concentrations were considered as a line of evidence when available, PECs were ultimately based on CN_T measurements.

Another source of uncertainty with regard to cyanide analysis is the often high detection limits reported that often exceeded the long-term PNEC for surface water. Measurements considered non-detects were transformed to half DLs, and in some cases those values exceeded the PNEC value of 1.7 µg HCN/L. A non-detect does not signify that free cyanide or other cyanides were completely absent from a sample, so it is therefore difficult to accurately determine how many water samples exceeded the PNEC. This method adequately addresses some uncertainties with non-detects.

The chronic (long-term) toxicity data set for the aquatic environment was suitable to derive a PNEC using an SSD in accordance with CCME protocol (CCME 2007). However, the interpretation of certain endpoints differed from the ECETOC (2007) report. While concentrations reported in the Bringmann and Kuhn (1978) studies were interpreted as being for KCN and subsequently converted to CN^- in the ECETOC (2007) document, in this report these concentrations were interpreted as already reported in CN^- and only corrected to HCN. Also, a low 48-hr LC_{50} reported for Daphnia pulex in Cairns et al. (1978) was much lower than other values reported for the species and considered an outlier. These adjustments may contribute to the differences between the chronic PNEC obtained by ECETOC and the one used in this assessment.

There are uncertainties with regard to potential background levels of cyanides in Canadian surface waters and whether CN_T concentrations fluctuate with seasons. Cyanides are generally monitored close to anthropogenic sources and results for pristine areas are seldom available. Based on results from provincial water quality monitoring programs, natural concentrations of cyanides in the environment are anticipated to be low. However, a high number of detected CN_T measurements (23%) in samples collected from reference areas as part of the EEM program were above the PNEC. These elevated concentrations could be explained by confounding factors such as historical contamination, algal blooms or forest fires or due to issues with sampling and analysis. For example, sulphides, nitrate and nitrite may give positive interference and should be removed from a sample before analysis (BC MOE 1986; OI Analytical 2012).

8. Potential to Cause Harm to Human Health

For the human health risk assessment, the 10 substances identified as priorities for assessment were divided into two subgroups: the free/simple cyanides (hydrogen cyanide, sodium cyanide) and the metal-cyanide complexes. The latter were further divided into the gold- or silver-cyanide complexes (potassium dicyanoargentate, potassium dicyanoaurate); the single-iron cyanide complexes (tetrasodium ferrocyanide, tripotassium ferricyanide, tetrapotassium ferrocyanide); and the multi-iron cyanide complexes (ferric ferrocyanide, ferric ammonium ferrocyanide, potassium ferric ferrocyanide).

8.1 Exposure Assessment

Potential exposures to free/simple cyanides and certain metal-cyanide complexes from environmental media, food and use of products are discussed in this section. Free cyanide and precursors of free cyanide are released from natural and anthropogenic sources into environmental media. Some cyanides are present in products available to consumers, including natural health products, cosmetics, pesticides, food additives and food packaging materials. The non-CBI uses reported in the DSL Inventory Update (Environment Canada 2013) are provided in section 4.3. There are limited CAS RN-specific exposure data. Environment and Climate Change Canada research has measured hydrogen cyanide (HCN; 74-90-8) in ambient air, and Health Canada has quantified total cyanide (CN_T) in drinking water distribution systems and the Canadian diet.

US NHANES biomonitoring data on thiocyanate (SCN), the primary metabolite of cyanide in humans, in urine were considered as a biomarker of free/simple cyanide exposure for this assessment (CDC 2015). An important criterion for determining the adequacy of a biomarker for risk assessment is the specificity of the marker for the chemical of interest (Aylward et al. 2008; Hays et al. 2008). Upon further evaluation, urinary SCN was determined to be an inadequate biomarker of free cyanide exposure because of the relatively high levels of SCN and/or SCN precursors in the North American diet (Kirman et al. in prep).

For the free/simple cyanide subgroup, refined estimates of potential exposure to free cyanide for the relevant routes of exposure are presented.

Metal-cyanide complexes – single-iron cyanide complexes (tetrasodium ferrocyanide, tripotassium ferricyanide, tetrapotassium ferrocyanide)

Environmental media and food
Cyanide levels in environmental media and food are typically reported as total cyanide or HCN. There are no studies with measured levels of tetrasodium ferrocyanide (13601-19-9), tripotassium ferricyanide (13746-66-2) or tetrapotassium ferrocyanide (13943-58-3) in environmental media in Canada. Metal-cyanide complexes in this assessment are of negligible volatility, so do not occur in air in the gas phase.

Particulate metal-cyanide complexes may occur in air, but measured concentrations in ambient air, indoor air and household dust relevant to the general population are not available.

Iron-cyanide complexes may potentially be present in drinking water and soil. Where free cyanide is introduced to water and soil, the formation of iron-cyanide complexes is favoured because of the abundance of iron in the environment and the high affinity of iron to the cyanide anion (Dzombak et al. 2006a). High amounts of ferrocyanides are found in the soils surrounding US superfund sites and former manufactured gas plants where cyanide was released (ATSDR 2006). Ferrocyanide salts, of which tetrasodium ferrocyanide is the most predominant, are used in road salts in Canada as anticaking agents, so soil and surface water levels may be higher around roadways (EC, HC 2001; Exall et al. 2011; 2013; See section 7.2.6). Predicted Environmental Concentration in soil (PECsoil) values for cyanide, assumed to be liberated from ferrocyanide by photodegradation, are presented in the EC, HC 2001 PSL assessment of road salts. Based on the assumptions in the PSL Tier 1 worst case PECsoil and default soil ingestion rates for a child (0.5–4 years), intakes of tetrasodium ferrocyanide from soil are expected to be minimal.

In Canada, tetrasodium ferrocyanide and tetrapotassium ferrocyanide are approved food additives with a limited number of permitted uses in a small number of food categories (i.e., in salt, dentritic salt and wine), as proscribed in the List of Permitted Anticaking Agents and the List of Permitted Food Additives with Other Generally Accepted Uses, which are incorporated by reference, respectively, in the Marketing Authorization for Food Additives That May Be Used as Anticaking Agents and the Marketing Authorization for Food Additives with Other Generally Accepted Uses, issued under the authority of the Food and Drugs Act (Canada 1985). Dietary exposure to tetrapotassium ferrocyanide (13943-58-3) from its use as a fining agent in wine is expected to be negligible and given the manner in which it is used, it would not be expected to be present in the final product as consumed; the exposure from the other approved additive uses is expected to be minimal (personal communication, emails from the HPFB, HC, to the ESRAB, HC, dated March 2016; unreferenced).

Products available to consumers

Tetrasodium ferrocyanide and its decahydrate salt are listed in the Natural Health Products Ingredients Database (NHPID) with a non-medicinal role for use as an anticaking agent in natural health products (NHPs) up to 0.025 mg/kg-bw/day. Tetrasodium ferrocyanide is listed as being present as a non-medicinal ingredient in a single licensed oral NHP in the Licensed Natural Health Products Database (LNHPD) (personal communication, emails from the HPFB, HC, to the ESRAB, dated March 2016; unreferenced).

Tetrasodium ferrocyanide is used in two cosmetic products, for online purchase only, in Canada: a bath salt product with a concentration not exceeding 0.10% and an anti-wrinkle cream with a concentration of 0.0001% (personal communication, emails from the CPSD, HC, to the ESRAB, HC, dated April 12 2017; unreferenced). Dermal absorption data are not available for ferrocyanides; however, oral absorption studies using radiolabelled compound indicates minimal intestinal absorption (Nielsen et al. 1990a). It is anticipated that dermal absorption will be substantially less than oral absorption (based on physical chemical properties and molecular weight). Given the low concentrations of tetrasodium ferrocyanide in these products, the low anticipated dermal absorption of the substance and the use patterns of these two products, the Canadian general population's exposure to tetrasodium ferrocyanide from cosmetics is expected to be negligible.

Tetrapotassium ferrocyanide is listed in the NHPID with a non-medicinal role for use as an anticaking agent in NHPs up to 0.025 mg/kg-bw/day; however, it is not listed as being present as such in licensed NHPs in the LNHPD. Tetrapotassium ferrocyanide, as kali ferrocyanatum, is also listed in the NHPID with a homeopathic role for use as a medicinal ingredient in homeopathic medicines at the minimum homeopathic potency of 3X (corresponding to a maximum concentration of 10^{-3}); it is listed as being present as such in a limited number of licensed oral NHPs in the LNHPD.

No evidence of exposure of the Canadian general population to tripotassium ferricyanide through the use of products available to consumers was found. Dermal exposure to tripotassium ferricyanide may occur from the use of farmer's reducer for retouching photographs, but is limited to hobbyists with specialized skills; thus, general population exposure is not expected.

Metal-cyanide complexes – Multi-iron cyanide complexes (ferric ferrocyanide, ferric ammonium ferrocyanide, potassium ferric ferrocyanide**)**

Environmental media and food

Cyanide levels in environmental media and food are typically reported as total cyanide or HCN. There are no studies with measured levels of ferric ferrocyanide (14038-43-8), ferric ammonium ferrocyanide (25869-00-5) or potassium ferric ferrocyanide (25869-98-1) in environmental media in Canada. Metal-cyanide complexes in this assessment are of negligible volatility, so do not occur in air in the gas phase. Particulate metal-cyanide complexes may occur in air, but measured concentrations in ambient air, indoor air and household dust relevant to the general population are not available.

Iron-cyanide complexes may potentially be present in drinking water and soil. Where free cyanide is introduced to water and soil, the formation of iron-cyanide complexes is favoured because of the abundance of iron in the environment and the high affinity of iron to the cyanide anion (Dzombak et al. 2006a). High amounts of ferrocyanides are found in the soils surrounding US superfund sites and former manufactured gas plants where cyanide was released (ATSDR 2006). Ferric ferrocyanide is used in road salts in Canada as an anticaking agent, so soil and surface water levels may be higher around roadways where road salt is applied (EC, HC 2001; Exall et al. 2011; 2013; See Section 7.2.6).

In Canada, ferric ferrocyanide and ferric ammonium ferrocyanide have also been identified for use in some food packaging applications, for which there is no direct contact with the food (personal communication, emails from the HPFB, HC, to the ESRAB, dated March 2016; unreferenced).

Products available to consumers

Ferric ferrocyanide is listed in the NHPID with a non-medicinal role for topical use as a colour additive in NHPs and is listed as being present as a non-medicinal ingredient in a limited number of licensed topical NHPs in the LNHPD. Ferric ferrocyanide, as ferrum cyanatum, is also listed in the NHPID with a homeopathic role for use as a medicinal ingredient in homeopathic medicines at a minimum homeopathic potency of 1X (corresponding to a maximum concentration of 10^{-1}). However, it is not listed as being present as such in licensed NHPs in the LNHPD. Ferric ammonium ferrocyanide is listed in the NHPID with a non-medicinal role for topical use as a colour additive and is listed as being present as such in a limited number of licensed topical NHPs in the LNHPD.

Ferric ferrocyanide and ferric ammonium ferrocyanide are widely used as pigments/colourants in personal care products (Environment Canada 2013; personal communication, emails from the CPSD, HC, to the ESRAB, HC, dated January 11, 2016; unreferenced) and paints and coatings (Environment Canada 2013). Ferric ferrocyanide and ferric ammonium ferrocyanide were reported in Material Safety Data Sheets (MSDSs) for automotive repair products (fillers, putties, hardeners) available to the Canadian public at concentrations ranging from 1% to 5% (MSDS 2011a; MSDS 2012a,b,c; MSDS 2014).

Based on the use patterns of these products, exposure of the general population to ferric ferrocyanide and ferric ammonium ferrocyanide is expected to predominantly occur through the dermal route. Oral absorption studies using radiolabelled compound indicates minimal intestinal absorption (around 0.5%) for these substances (Nielsen et al. 1990a). It is expected that dermal absorption will be substantially less than oral absorption (based on physical chemical properties and molecular weight).

Potassium ferric ferrocyanide, an analogue of ferric ferrocyanide and ferric ammonium ferrocyanide, was not identified in products used by the general population in Canada. Potassium ferric ferrocyanide was identified in one brand of metal markers available for purchase online in Canada (MSDS 2011b) for industrial/professional use. Exposure to the general population for potassium ferric ferrocyanide is not expected.

Gold- or silver-cyanide complexes subgroup (CAS RNs 506-61-6 and 13967-50-5)

There are no studies with measured levels of potassium dicyanoargentate (506-61-6) or potassium dicyanoaurate (13967-50-5) in environmental media in Canada. Neither dicyanoargentate nor potassium dicyanoaurate have been identified as ingredients in products available to consumers. Potassium dicyanoargentate and potassium dicyanoaurate are widely used as electroplating reagents in the production of silver and gold coatings on jewellery, electrical components, cutlery/tableware and other consumer goods (Brumby et al. 2012; Kohl 2010; Renner et al. 2012; Schlesinger 2010). Electroplating involves careful control of temperature, voltage, pH and plating bath chemistry to reduce potassium dicyanoargentate and potassium dicyanoaurate to positively charged cations (Ag+ and Au+) deposited onto the base metal (e.g., copper or nickel).

Free/simple cyanides subgroup (CAS RNs 74-90-8 and 143-33-9)

Environmental media and food

Sodium cyanide (NaCN; 143-33-9) is a simple cyanide salt that readily dissociates into free cyanide in aqueous solution (ADGH 2010) and becomes protonated at an environmental and physiological pH to become HCN (74-90-8). NaCN is used in large volumes industrially (e.g., gold mining and electroplating) in Canada and to a limited degree in certain pest control products (see Section 4). Human exposure to NaCN may occur occupationally or from accidental/incidental releases during its manufacture, storage, transport or use, or in the disposal of residues remaining after use (ADGH 2010). Levels of cyanide in air are typically reported as HCN and in other environmental media and food as total cyanide (CN_T)[8].

Outdoor air

HCN is released to air from direct volatilization and from incomplete combustion of nitrogen-containing substances/polymers (ATSDR 2006). There are many point and diffuse sources for release of HCN to air, including industrial facilities, forest and house fires, and vehicle emissions (see Section 5). HCN has been reported at mid and upper tropospheric altitudes (ATSDR 2006; LeBreton et al. 2013; Rinsland et al. 2007) and at lower altitudes in suburban (Knighton et al. 2009) and rural (Ambrose et al. 2012) areas. Urban air concentrations can be high, especially in areas dominated by automotive vehicular traffic.

There is no federal air quality standard for HCN in Canada; however, the province of Ontario 24-hour average and half-hour point impingement air quality standards (AAQC) are 0.008 mg/m^3 (approximately 7 ppb) and 0.024 mg/m^3 (approximately 20 ppb), respectively (Moussa et al. 2016a). The 24-hour average air concentrations of HCN in Toronto exceeded the Ontario provincial 24-hour average AAQC on 3 of 16 consecutive weekdays sampled in the summer of 2013 (Moussa et al. 2016a), reaching a peak 24-hour average of 0.0131 mg/m^3 (approximately 11 ppbv) on one of the sampling days (Moussa et al. 2016b), with an average of 0.00411 mg/m^3 (3.45 ppbv) over the study

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[8] These “total cyanide” values include contributions from metal-cyanide complexes. The total cyanide analytical method involves the addition of strong acid with high heat to break up metal-cyanide complexes and conversion to free cyanide prior to measurement. Total cyanide generally includes all free cyanide, all dissociable cyanide complexes and all strong metal cyanide complexes. Cyanates (including thiocyanate), cyanogens (including cyanogen chloride) and certain nitriles (organic cyanide substances) are not included in this analysis or definition (NICNAS 2010).

period (Moussa et al. 2016a). Air HCN concentrations reported in Moussa et al. (2016a,b) were one to two orders of magnitude higher than previous studies (Knighton et al. 2009; Ambrose et al. 2012) reporting ground level ambient air concentrations of HCN, which is likely due to differences in sampling locations in both studies and mass resolution analytical difficulties in the Knighton et al. (2009) study (Moussa et al. 2016a,b). Knighton et al. (2009) reported HCN air concentrations measured continuously over a two-week period near a highway in suburban Boston ranging from <0.0001 to 0.0007 mg/m^3 (<0.1 to 0.6 ppbv) and Ambrose et al. (2012) reported an average of 0.00043 mg/m^3 (0.36 ppbv) HCN in air measured continuously at a 24-metre height in rural New Hampshire near a pine/hardwood forest.

Indoor air

Only one published study reports concentrations of HCN in indoor air, in Hamburg, Germany (Klus et al. 1987). They compared HCN concentrations in indoor air from smoking and non-smoking locations. Concentrations in non-smoker areas (two houses, two restaurants, one car) ranged from non-detect to 0.027 mg/m^3 (22.7 ppb), with an average of 0.0108 mg/m^3 (9.1 ppb). However, due to limitations with this study and a general lack of published indoor air data for HCN, in this assessment, the mean ambient air concentration of 0.0041 mg/m^3 selected from Moussa et al. (2016a) was used for the human health risk characterization.

Soil and drinking water

Most free cyanide released to soil will form ferrocyanides due to the strong affinity of the cyanide anion for iron and the high abundance of iron in soils (Dzombak et al. 2006a). CN_T has been measured in drinking water in Canada for six provinces (personal communication, emails from the WAQB, HC, to the ESRAB, HC, dated Oct 14, 2015; unreferenced). Data for CN_T concentrations in drinking water were only available for Saskatchewan, Quebec and Nova Scotia. Concentrations ranged from 0.001–0.19 mg/L, with 94.3% of samples at or below the detection limit (0.001–0.02 mg/L). The Canadian guideline for CN_T in drinking water is a Maximum Acceptable Concentration (MAC) of 0.2 mg/L (Health Canada 2014).

Food and beverages

Many plant-based foods contain naturally occurring cyanogenic glycosides (CGs; e.g., linamarin, amygdalin and dhurrin), which have the potential to release HCN (FSANZ 2014). Examples of foods that contain CGs include lima beans, apple seeds, cassava, bamboo, stone fruit pits (e.g., apricot, peach and cherry) and flaxseed.

Estimates of dietary exposure to total HCN[9], converted to a total CN basis, from CGs in foods for the general Canadian population were derived by Health Canada’s Food

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[9] Total HCN referred to here is similar to the meaning of CN_T defined earlier in the document as it includes measurement of all releasable cyanide in the sample. In foods, total HCN may be determined by either enzymatic hydrolysis or by the addition of a dilute acid with heating to hydrolyze the cyanogenic glycosides followed by basification to release HCN/CN- (FAO/WHO 2012).

Directorate. Detailed dietary intakes by food type and age-sex group are provided in Table D-1 of Appendix C. Due to a lack of Canadian occurrence data for CGs in food, data were predominantly obtained from the Survey of Cyanogenic Glycosides in Plant-Based Foods in Australia and New Zealand 2010–2013 (FSANZ 2014); this survey aimed to capture most foods known to contain total HCN and was therefore considered reasonably comprehensive. Total HCN data for a limited number of additional foods (i.e., green peas, soy flour, and soy protein isolate) that are known to contain CGs were obtained from the scientific literature (Gupta 1987; Honig et al. 1983). The mean total HCN concentration of a given food type was assumed for foods where multiple data points were available; in cases where multiple samples were not available, the typical total HCN content reported for a given food was employed in the dietary exposure assessment. For foods that were identified as main contributors to total CN dietary exposure, which are discussed further in the paragraph below, the reported concentrations are as follows: flaxseed (n=5; mean of 127 mg HCN/kg; range of 91–178 mg HCN/kg), apple sauce (n=3; mean of 3.9 mg HCN/kg; range of 3.6–4.1 mg HCN/kg) and green peas (n=1; 20 mg HCN/kg).

Food consumption data from the Canadian Community Health Survey (CCHS) – Cycle 2.2 (Statistics Canada 2004) were used to estimate dietary exposure by multiplying the mean concentration of total HCN in each food item by the quantity of that food consumed; when only a single total HCN occurrence value was available for a given food, it was employed rather than the mean. Dietary exposure estimates were expressed on a CN basis using the ratio of the molecular weights of HCN (27.03 g/mol) and CN (26.01 g/mol). For all age-sex groups, mean and 90th percentile “all persons” exposures ranged from 0.00039–0.00379 mg/kg-bw/day and from 0.00091–0.01174 mg/kg-bw/day, respectively. Overall, flaxseed and apple sauce were the main contributors to total dietary exposure, accounting for 42% and 22%, respectively, of exposure for all age-sex groups combined. In the case of children aged 1–3 years, consumption of flaxseed and apple sauce account for 21% and 57%, respectively, of total CN exposure from the diet. For adult males (i.e., 19 years and above), the age-sex group to which the corresponding critical chronic hazard endpoint for CN applies, the main contributors to total dietary exposure were flaxseed and green peas, which accounted for 24%–70% and 11%–34%, respectively, of total CN dietary exposure, depending on the age-sex group within this category (personal communication, email from the Food Directorate, HC to the ESRAB, HC, dated July 19, 2016; unreferenced). The provisional tolerable daily intake (pTDI) for CN established by the FAO/WHO Expert Committee on Food Additives is 0.02 mg/kg-bw/day (20 µg/kg-bw/day) (FAO/WHO 2012).

Products available to consumers

HCN, as hydrocyanicum acidum, is listed in the NHPID with a homeopathic role for use as a medicinal ingredient in homeopathic medicines at a minimum homeopathic potency of 8X (corresponding to a maximum concentration of 10^{-8}); it is listed as being present as such in a limited number of licensed NHPs in the LNHPD.

HCN and NaCN are listed under “Hydrogen cyanide and its salts” on the List of Prohibited Cosmetic Ingredients (more commonly referred to as the Cosmetic Ingredient Hotlist), an administrative tool that Health Canada uses to communicate to manufacturers and others that products containing certain substances, when present in a cosmetic at certain concentrations, may contravene the general prohibition found in section 16 of the Food and Drugs Act, or may contravene one or more provisions of the Cosmetic Regulations (HC [amended 2015]).

8.2 Health Effects Assessment

Metal-cyanide complexes (three subgroups: single-iron cyanide, multi-iron cyanide and gold- or silver-cyanide complexes)

Single-iron cyanide complexes (CAS RNs 13601-19-9, 13746-66-2, 13943-58-3)
The ferrocyanide and ferricyanide salts are poorly absorbed. Intestinal absorption of tetrapotassium ferrocyanide in rats is approximately 2.8%; the whole body retention is 0.09% (seven days post-exposure) (Nielsen et al. 1990a). These substances are not metabolized and only a very small amount of cyanide dissociates from the corresponding complex [dissociation constants are 10^{-47} and 10^{-52} for the ferrocyanide and ferricyanide ions, respectively (Baars et al. 2001)]. These substances do not accumulate in tissues; the half-life is 135 and 40–50 minutes in humans and dogs, respectively (Epstein and Kleeman 1956). Elimination is >94% fecal in rats (Nielsen et al. 1990a).

The toxicity of this subgroup is low because of the strong association between the iron and cyanide. An unpublished study cited by the FAO/WHO (1975) reported no substance-related effects in dogs following a 13-week exposure to 0, 10, 100 and 1000 ppm (or 0, 0.3, 3, 30 mg/kg bw/day[10]) of tetrasodium ferrocyanide (Morgaridge 1970). The previously published critical effect levels for the single-iron cyanide complexes are based on an unpublished, 90-day oral exposure to tetrasodium ferrocyanide (0, 0.05, 0.5 or 5%) in rats (male and female; n=10 per group) by the International Salt Co. (Oser 1959) cited in FAO/WHO (1975). Increased kidney weight (females only) and tubular damage were observed at 0.5% [lowest-observed-adverse effect level (LOAEL); no-observed-adverse effect level (NOAEL)=0.05%]. The NOAEL dose (0.05%), which is equivalent to 25 mg/kg-bw/day, was used to obtain an acceptable daily intake (ADI) of 0.025 mg/kg-bw/day (basis for uncertainty factors not given) (FAO/WHO 1975).

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[10] Assumes a bodyweight of 12 kg and a food consumption rate of 300 g/day (as per: http://www.hc-sc.gc.ca/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/contaminants/approach/approach-eng.pdf).

Multi-iron cyanide complexes (CAS RNs 14038-43-8, 25869-98-1, 25869-00-5)
Multi-iron cyanide complexes are very poorly absorbed. Following an oral exposure of 10 mg (36-40 mg/kg-bw) of ferric ferrocyanide or potassium ferric ferrocyanide in rats (n=2-5), absorption was determined to be 0.21%–0.49% and whole body retention after seven days was 0.01%–0.7% (Nielsen et al. 1990a). Likewise, following an oral dose of 500 mg (6.2–7.1 mg/kg-bw) of potassium ferric ferrocyanide (25869-98-1) in humans (n=3, male), absorption was 0.25%–0.42% and whole body retention after seven days was 0.03%–0.07% (Nielsen et al. 1990b). Elimination is >97% and >99% fecal in rats and humans, respectively. These substances are not distributed or metabolized to any significant degree, nor do they accumulate in tissues.

The multi-iron cyanide complexes do not cause adverse health effects in animals or humans (Pearce, 1994). Indeed, the “NOAEL doses” reported below were always the highest doses administered/tested in each study. For example: (1) no effects were observed up to 6000 mg/kg-bw/day for potassium ferric ferrocyanide in humans (aged 16–70; male and female, one pregnant) being treated for thallium poisoning [(Pai 1987), cited by (Pearce 1994)]; (2) no effects were observed up to 4800 mg/kg-bw/day ferric ferrocyanide in female rats exposed for 4 weeks (Kostial et al. 1981; Beck et al. 2006); and, (3) no effects were observed up to 3200 mg/kg-bw/day in rats exposed to ferric ferrocyanide in drinking water for 12 weeks (Dvorak et al. 1971).

Gold- or silver-cyanide complexes (CAS RNs 13967-50-5, 506-61-6)
This screening assessment does not include a health effects characterization for potassium dicyanoaurate or potassium dicyanoargentate because general population exposure to these substances is not expected. Neither substance has been classified by international agencies for carcinogenicity, mutagenicity or reproductive/ developmental effects. Wu et al. (2001) reported a lowest toxic dose (TDL) of 0.071 mg/kg potassium dicyanoaurate for an adult human. The US EPA (2010) developed a reference dose (Rfd) for potassium dicyanoargentate based on the reference dose for free cyanide, with an adjustment for relative molecular weights (US EPA 2010). However, given the lack of exposure to these substances for the general population of Canada, the health effects have not been extensively investigated at this time.

Free/simple cyanides (CAS RNs 74-90-8, 143-33-9)
Free/simple cyanides are rapidly and extensively absorbed through all routes of exposure. Following oral, inhalation or dermal exposures, absorption occurs through the intestine, alveoli or skin, respectively. In the case of dermal exposure, the slight liposolubility of HCN allows it to pass through the skin, whereas the ionic nature of NaCN slightly impedes absorption. Inside the body, NaCN exists predominantly as HCN because it dissociates and then becomes protonated. Following absorption, HCN is rapidly and extensively distributed. Intestinally absorbed HCN enters circulation through the portal vein and travels to the liver for first-pass metabolism. Inhaled and dermally absorbed HCN bypass first-pass metabolism and directly enter systematic circulation. Metabolism occurs primarily by rhodanese (a thiosulphate sulphurtransferase), which is

ubiquitously expressed. Catalysis by rhodanese forms thiocyanate (SCN), which comprises the majority of cyanide metabolism. While expression levels of rhodanese vary across tissues [highest levels are in the kidney, liver, brain, lung, muscle and stomach (Aminlari et al. 2007)], the rate-limiting step of this reaction is not related to the amount of rhodanese in the tissue; instead, it depends on the amount of endogenous sulphur donors. Therefore, sulphur-deficient individuals are more susceptible to the toxic effects of cyanide. Minor metabolites include 2-aminothiazoline-4-carboxylic acid (ATCA) and various one-carbon molecules (e.g., exhaled HCN and CO_2). Excretion occurs via the urine, and urinary SCN levels are linearly related to exposure concentrations (El Ghawabi et al. 1975). These substances do not bioaccumulate; they are converted to SCN within 3 hours; the SCN is excreted within 30 hours [reviewed in US EPA (2010)].

Acute toxicity, caused by a single high dose of cyanide, causes significant central nervous system (CNS) effects, including CNS depression, convulsions, coma and death. This occurs because metabolic pathways become overwhelmed at high doses and non-metabolized cyanide binds and inhibits cytochrome c oxidase (the final enzyme of the electron transport chain that is required for synthesis of adenosine triphosphate [ATP]), which results in a rapid loss of cellular energy that leads to cell death in extreme cases (Allen et al. 2015; Hawk et al. 2016; Section 7.1.1).

Chronic toxicity, caused by repeated, low-dose exposure, induces thyroid and male reproductive effects. Thyroid dysfunction occurs because SCN competitively inhibits iodine uptake in the thyroid gland, and thereby impairs thyroid hormone synthesis. Impairment of thyroid hormone synthesis can result in hypothyroidism, which is accompanied by goiters and cretinism in extreme cases (Downey et al. 2015). The mechanism for male reproductive dysfunction is not known; however, it may involve crosstalk between the thyroid and gonadal endocrine axes (Duarte-Guterman et al. 2014; US EPA 2010).

Chronic exposures to cyanide that are of moderate dosage (i.e., high enough to overburden, but not overwhelm, the metabolic pathways), or that occur together with a dietary deficiency of sulphur and/or iodine, lead to neuropathies such as Tropical Ataxic Neuropathy (TAN) and Konzo (tropical spastic paraparesis) (Cliff et al. 2015). However, such dietary deficiencies are expected to be less relevant in the Canadian context (due to iodation of salt and adequate levels of protein in North American diets).

Taken together, the difference between the high-dose acute toxicity and low-dose chronic toxicity of these substances is that the former is caused by the cyanide anion's inhibition of ATP synthesis, whereas the latter is caused by the SCN anion's interference with iodine uptake resulting in impaired thyroid hormone synthesis.

Free/simple cyanides are non-mutagenic in the Ames test (NTP 1993) and are non-carcinogenic (Howard and Hanzal 1955). They are known to be teratogenic, causing reduced birth weight, congenital limb defects and spontaneous abortion. Epigenetic studies for these effects have focused on populations that are exposed to elevated levels of cyanide through improperly prepared cassava or smoking. Studies in experimental animals have used exposures to cassava, HCN or KCN. These studies are extensively reviewed elsewhere (Downey et al. 2015; US EPA 2010). When critical effect levels could be identified in these studies, they were at doses that were similar to or higher than the critical effect level identified herein. For example, a LOAEL of 20 mg/kg-bw/day for decreased body, brain and cerebellar weight, and altered cerebellar dimensions was reported for rats administered KCN in diet (Imosemi et al. 2005); a LOAEL of 20 mg/kg-bw/day for altered maturation of the cerebellum was reported for rats administered KCN in diet (Malomo et al. 2004); a NOAEL and LOAEL of 0.8 mg/kg-bw/day and 1.2 mg/kg-bw/day, respectively, for increased T3 in dams and offspring were reported for goats administered 0, 0.4, 0.8 and 1.2 mg/kg-bw/day KCN by gavage (in water) (Soto-Blanco and Gorniak et al. 2004). However, based on study quality, a study conducted by the National Toxicology Program (NTP 1993; described below) was selected as the most appropriate study for further risk characterization of oral exposure to cyanide, which is consistent with reasoning described elsewhere (US EPA 2010).

Free/simple cyanides are the subject of a number of international assessments, most recently by the US EPA (2010), which evaluated hydrogen cyanide and cyanide salts (various CAS RNs), and FAO/WHO (2012), which evaluated various cyanogenic glycosides (cyanide precursors found in foods). Both reports based their assessments on the same point of departure (PoD) for an oral exposure of 1.9 mg/kg-bw/day, which corresponds to a decrease in cauda epididymis weight. The PoD was taken from a 90-day study in which rats (male and female, n=10 per group) were administered 0, 30, 100 or 300 ppm NaCN in drinking water (NTP 1993). Decreases in cauda epididymis weight were dose-dependent and statistically significant: 0.162 g (± 0.009), 0.150 g (± 0.013), 0.148 g (± 0.013) and 0.141 g (± 0.009). These administered doses (ppm) were converted to 0, 1.4, 4.5 and 12.5 mg/kg-bw/day, and benchmark dose (BMD) modelling of these data produced BMD and BMDL values of 3.5 and 1.9 mg/kg-bw/day, respectively [the BMDL is the 95% lower confidence limit of the BMD; the benchmark response, BMR, was set at 1 standard deviation (SD) from the control mean, which corresponds to a 7% decrease in cauda epididymis weight] (US EPA 2010). These BMDL and BMD values (1.9 and 3.5 mg/kg-bw/day) are consistent with a more recent gavage study that concluded that male reproductive toxicity occurs in rats at 1.2 and 3.2 mg/kg-bw/day (rats exposed to 0, 0.64, 1.2 and 3.2 mg/kg-bw/day NaCN for 90 days) (Shivanoor and David 2015). Specifically, significant changes in testis and prostate weight, sperm count and motility, and levels of testosterone and luteinizing hormone were seen at 1.2 mg/kg-bw/day; in addition to these, sperm abnormalities and significant changes in levels of follicular stimulating hormone were observed at 3.2 mg/kg-bw/day.

The most recent assessment of inhalation exposure for hydrogen cyanide and cyanide salts (e.g., NaCN) was conducted by the US EPA (2010). The PoD of 2.5 mg/m^3 corresponds to thyroid enlargement and altered iodine uptake. This PoD was taken from a study in which employees (n=36) from three factories were exposed to HCN in the air at the following levels for 5–15 years: 10.4 ppm (± 10.9), 8.1 ppm (± 8.2), or 6.4 ppm

(±6.9); mean ppm of n=12 air samples, ± SD (El Ghawabi et al. 1975). The LOAEL (6.4 ppm) was converted to 7.07 mg/m^3, and then adjusted to account for the occupational nature of the exposure to the final PoD value of 2.5 mg/m^3. This endpoint is supported by a more recent study in which levels of thyroxine were decreased following inhalation exposure in cassava processing workers (n=39) (Dhas et al. 2011).

Sodium cyanide has been previously evaluated in Canada. The Water and Air Quality Bureau (WAQB) has published a drinking water guideline of 0.2 mg/L, which is based on the NOAEL of 10.8 mg/kg-bw/day reported in a two-year toxicity study by Howard and Hanzal (1955; Health Canada 1979). The Pest Management Regulatory Agency (PMRA) re-evaluated sodium cyanide in 2006 (Health Canada 2006), considering information from the US EPA Reregistration Eligibility Decision (US EPA 1994). As part of the re-evaluation, the PMRA proposed additional risk reduction measures to further protect handlers and bystanders.

8.3 Characterization of Risk to Human Health

Metal-cyanide complexes (three subgroups: single-iron cyanide complexes, multi-iron cyanide complexes and gold- or silver-cyanide complexes)

Single-iron cyanide complexes (CAS RNs 13601-19-9, 13746-66-2, 13943-58-3)
Exposure of the general population of Canada to the ferrocyanide and ferricyanide salts through environmental media, food and the use of products available to consumers is expected to occur through the oral and dermal routes. For the oral route, tetrasodium ferrocyanide and tetrapotassium ferrocyanide are permitted for use in foods as proscribed in the List of Permitted Anticaking Agents and the List of Permitted Food Additives with Other Generally Accepted Uses, which are incorporated by reference, respectively, in the Marketing Authorization for Food Additives That May Be Used as Anticaking Agents and the Marketing Authorization for Food Additives with Other Generally Accepted Uses, issued under the authority of the Food and Drugs Act (Canada 1985). Exposure from use of tetrasodium ferrocyanide as a non-medicinal ingredient in oral NHPs is not expected to exceed the 0.025 mg/kg bw/day ADI. For the dermal route, tetrasodium ferrocyanide is found in body creams/lotions/moisturizers. Because the cyanides are tightly associated with iron in these complexes, they are highly stable and have low bioavailability; therefore, exposure to these substances is not associated with a risk of the toxic effects of cyanide. Limited data indicate low dermal absorption and intermittent uses of the relevant products (bath salts and anti-aging creams); further, these substances are approved for use in foods. Therefore, risk to human health is not expected.

Multi-iron cyanide complexes (CAS RNs 14038-43-8, 25869-98-1, 25869-00-5)
Exposure of the general population of Canada to the ferric ferrocyanides through the use of products is expected to occur through all routes of exposure. However, due to their low bioavailability and high stability, there are no known adverse health effects from the substances in this subgroup. Further, they have been used to treat

radiocesium and thallium poisoning in humans and animals without producing harmful effects. Based on these considerations, risk to human health is not expected.

Gold- or silver-cyanide complexes (CAS RNs 13967-50-5, 506-61-6)
Exposure of the general population of Canada to potassium dicyanoaurate and potassium dicyanoargentate is not expected. Based on these considerations, risk to human health is accordingly low.

Free/simple cyanides (CAS RNs 74-90-8, 143-33-9)
Margins of Exposure (MOEs) for this subgroup are presented in Table 8-1.

Table 8-1. Relevant exposure and hazard values for free/simple cyanides, and resulting MOEs

Exposure scenario	Exposure concentration (mean)	Critical effect level	Critical hazard endpoint	MOE
Oral exposure				
Children (1–3 years; male and female; “all-persons”)[a]	0.00379 mg/kg-bw/day[a]	1.9 mg/kg-bw/day (BMDL)[b]	Decreased cauda epididymis weight [b]	501
Adult males (19–30 years; “all-persons”)[a]	0.00062 mg/kg-bw/day[a]	1.9 mg/kg-bw/day (BMDL)[b]	Decreased cauda epididymis weight[b]	3065
Inhalation exposure				
Downtown Toronto near major roadway average air concentration[c]	0.00411 mg/m^3 [c]	2.5 mg/m^3 (LOAEL)[d]	Thyroid enlargement and altered iodine uptake[d]	608

Abbreviations: LOAEL, lowest-observed-adverse effect level; M, mean

a Refined intake estimates obtained from the Food Directorate, Health Canada (July 2016); risk characterization based on two age/sex groups: (1) the child group with the highest estimated exposure, and (2) the adult age-sex group most representative of the sub-population most relevant to the corresponding critical hazard endpoint (i.e., male reproductive effects).

b NTP 1993; US EPA 2010.

c Moussa et al. 2016; mean over 16 consecutive weekdays.

d El Ghawabi 1975; US EPA 2010.

MOEs for oral exposure were derived for children and adults using exposure estimates obtained from the Food Directorate (Appendix C), which identified flaxseed and apple sauce as the main food sources for children 1–3 years of age as well as flaxseed and green peas as the main sources for adult males (i.e., 19 years and above). Based on the conservative parameters used in estimating exposure for the general population, the derived MOEs are considered adequate to address uncertainties in the health effects and exposure databases. However, certain groups that could represent the potential for elevated exposure do exist (Appendix C).

An MOE for inhalation exposure was derived for the general population using measured ambient air concentrations reported in a study by Environment and Climate Change Canada (Moussa et al. 2016a), which identified vehicle emissions as the main air source. Based on the conservative parameters used in estimating exposure, the derived MOE is considered adequate to address uncertainties in the health effects and exposure databases. This information indicates that the 10 cyanide substances identified as priorities for assessment have low potential to cause harm to the general population of Canada.

8.3.1 Uncertainties in evaluating risk to human health

The key sources of uncertainty are presented in the table below.

Table 8-2. Sources of uncertainty in the risk characterization

Key source of uncertainty	**Impact** [a]
Metal-cyanide complexes	
Exposure	
The environmental occurrence data were generated using the “total cyanide” method, which includes many cyanide-containing molecules and assumes 100% bioavailability.	+
There is no dermal absorption data for any of the metal-cyanide complexes. Therefore, dermal absorption data were assumed equivalent to empirically derived oral absorption fractions.	+
Hazard	
The previously published critical effect levels for the single-iron cyanide complexes are based on unpublished, sub-chronic studies.	+/-
There are no chronic studies for any of the metal-cyanide complexes.	+/-
Ferric ammonium ferrocyanide (25869-00-5) has not been the subject of any international assessment; therefore, it is not associated with any previously published critical effect level.	+/-
Free/simple cyanides	
Exposure	
There is a lack of Canadian occurrence data for HCN in foods; therefore, values used to derive dietary intakes of HCN were taken almost exclusively from the FSANZ (2014).	+/-
Intakes of free/simple cyanides through diet were generated using “total cyanide” occurrence data, which includes releasable free cyanide occurring from many different possible cyanide-containing molecules, and assumes 100% release and bioavailability in the human body.	+
There is high spatiotemporal variability in air concentrations of HCN due to its high atmospheric mobility. Therefore, the level of inhalation exposure to HCN in air decreases with increasing distance from emission sources.	+

Key source of uncertainty	**Impact** [a]
Hazard	
There are no chronic animal studies for oral exposure.	+/-
There are no sub-chronic or chronic animal studies for inhalation exposure.	+/-
The 90-day National Toxicology Program (NTP 1993) study for oral exposure in rats did not assay for thyroid endpoints.	+/-
The chronic human study used for inhalation exposure (El Ghawabi et al. 1975) did not assay for male reproductive endpoints (focus was on thyroid gland and iodine uptake). Further, there was no temporal correlation between the time of exposure and the degree of thyroid enlargement in this study.	+/-

a "+" Likely to increase conservatism (i.e., likely to be overly-protective); "-" Likely to decrease conservatism; "+/-d" Impact on the assessment not known.

9. Conclusion

Considering all available lines of evidence presented in this draft screening assessment, there is risk of harm to organisms, but not to the broader integrity of the environment from free cyanide and precursors of free cyanide. It is proposed to conclude that free cyanide and precursors of free cyanide meet the criteria under paragraph 64(a) of CEPA as they are entering or may enter 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. However, it is proposed to conclude that free cyanide and precursors of free cyanide do not meet the criteria under paragraph 64(b) of CEPA as they are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger to the environment on which life depends.

Based on the information presented in this draft screening assessment, it is proposed to conclude that the 10 substances identified as priorities for this assessment 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 free cyanide and precursors of free cyanide meet one of the criteria set out in section 64 of CEPA.

Free cyanide and precursors of free cyanide are proposed to meet the persistence criteria but not the bioaccumulation criteria as set out in the Persistence and Bioaccumulation Regulations of CEPA.

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Appendices

Appendix A. Substance Identity Information

Table A-1. Identity of substances identified as priorities for assessment under subsection 73.1 of CEPA

CAS RN	DSL Name	Common Name[b]	Molecular Formula	Molecular Weight (g/mol)	Subgroup
74-90-8[a]	Hydrocyanic acid	Hydrogen cyanide	HCN	27.03	Free and simple cyanides
143-33-9	Sodium cyanide	Sodium cyanide	$NaCN$	49.01	Free and simple cyanides
506-61-6	Argentate(1-), bis(cyano-C)-, potassium	Potassium dicyanoargentate	$KAg(CN)_2$	199.00	Metal cyanide complexes – gold or silver
13967-50-5	Aurate(1-), bis(cyano-c)-, potassium	Potassium dicyanoaurate	$KAu(CN)_2$	288.1	Metal cyanide complexes – gold or silver
13601-19-9	Ferrate(4-), hexakis(cyano-c)-, tetrasodium, (oc-6-11)	Tetrasodium ferrocyanide (Yellow prussiate of soda, YPS)	$Na_4Fe(CN)_6$	303.91	Metal cyanide complexes – single-iron
13746-66-2	Ferrate(3-), hexakis(cyano-c)-, tripotassium, (oc-6-11)-	Tripotassium ferricyanide	$K_3Fe(CN)_6$	329.25	Metal cyanide complexes – single-iron
13943-58-3	Ferrate(4-), hexakis(cyano-c)-, tetrapotassium, (oc-6-11)-	Tetrapotassium ferrocyanide (Yellow prussiate of potash, YPP)	$K_4Fe(CN)_6$	368.35	Metal cyanide complexes – single-iron
14038-43-8	Ferrate(4-), hexakis(cyano-c)-, iron(3+) (3:4), (oc-6-11)-	Ferric ferrocyanide or Prussian blue, insoluble	$Fe_4[Fe(CN)_6]_3$	859.3	Metal cyanide complexes – multiple-iron

CAS RN	DSL Name	Common Name[b]	Molecular Formula	Molecular Weight (g/mol)	Subgroup
25869-00-5	Ferrate(4-), hexakis(cyano-c)-, ammonium iron(3+) (1:1:1),(oc-6-11)-	Ferric ammonium ferrocyanide	$Fe(CN)_6Fe(NH_4)$	291.88	Metal cyanide complexes – multiple-iron
25869-98-1	Ferrate(4-), hexakis(cyano-c)-, iron(3+) potassium (1:1:1), (oc-6-11)-	Potassium ferric ferrocyanide (Turnbull's blue or Prussian blue, soluble)	$Fe(CN)_6FeK$	306.90	Metal cyanide complexes – multiple-iron

[a] CAS RN 74-90-8 refers to both gaseous hydrogen cyanide and aqueous acid hydrocyanic acid (HSDB 1983–2016a).

[b] A list of additional chemical names (e.g., trade names) is available from the National Chemical Inventories (NCI 2016).

Appendix B. Aquatic Toxicity Tables

Table B-1. Key aquatic chronic toxicity studies used in the derivation of the chronic Predicted No Effect Concentration (PNEC)

Organism type	Test Organism	Endpoint (Effect)	Value (µg HCN/L)	Reference
Fish	Fathead minnow (Pimephales promelas)	256-d EC_{10} (reproduction # of eggs per individual)	3	Lind et al. 1977
Aquatic Plant	Gibbous duckweed (Lemna gibba)	7-d EC_{10} (growth inhibition)	3.72	ECHA c2007–2015
Invertebrate	Cladocerans (Moinodaphnia macleayi)	5-d NOEC (reproduction)	6	Rippon et al. 1992
Fish	Rainbow trout (Oncorhynchus mykiss)	20-d EC_{10} (growth at 12°C)	9	Kovacs and Leduc 1982
Invertebrate	Amphipod (Gammarus pseudolimnaeus)	83-d MATC (reproduction)	15.2	Oseid 1979
Fish	Brook trout (Salvelinus fontinalis)	90-d EC_{10} (growth)	26	Koenst et al. 1977
Invertebrate	Sowbug (Asellus communis)	112-d NOEC (growth)	29	Oseid 1979
Algae	Scenedesmus quadricauda	8-d NOEC (population)	31.16	Bringmann and Kuhn 1980
Fish	Sheepshead minnow (Cyprinodon variegatus)	28-d MATC (growth)	37.1	ECOTOX 2000; Schimmel 1981
Invertebrate	Ceriodaphnia dubia	7-d EC_{10} (reproduction)	43.6	Manar et al. 2011
Algae	Pseudokirchneriella subcapitata	72-hr EC_{10} (growth)	57.1	Manar et al. 2011
Algae	Blue-green algae (Microcystis aeruginosa)	8-d NOEC (population)	72.7	Bringmann and Kuhn 1978

Appendix C. Food exposure estimates.

Table C-1. Mean and 90th percentile cyanide dietary exposure estimates for AP and EO consumers (95% confidence interval).

Age-Sex Group	Number of Respondents Consuming Hydrogen Cyanide Containing Foods		Total Cyanide Exposure - Usual Intakes (µg/kgbw·day)			
			All Persons		Eaters Only	
			mean	p90	mean	p90
1-3 yr	1409 / 2110	(67%)	3.79 (3.20, 4.55)	11.74E (7.21, 16.42)	6.00 (5.17, 7.06)	18.98 (16.52, 21.40)
4-8 yr	2118 / 3058	(69%)	1.52 (1.34, 1.72)	3.49 (2.94, 4.09)	2.20 (1.95, 2.47)	5.29 (3.94, 6.70)
9-13 yr M	1275 / 2004	(64%)	0.70 (0.63, 0.79)	1.51 (1.36, 1.76)	1.11 (1.01, 1.21)	2.47 (1.80, 3.10)
14-18 yr M	1201 / 2230	(54%)	0.44 (0.38, 0.52)	0.91 (0.75, 1.15)	0.82 (0.70, 0.96)	1.71 (1.38, 2.34)
19-30 yr M	744 / 1766	(42%)	0.62 (0.45, 0.79)	1.43E (1.06, 2.05)	1.47 (1.15, 1.80)	4.25E (2.62, 6.11)
31-50 yr M	973 / 2527	(39%)	0.59E (0.41, 0.84)	1.15 (0.94, 1.56)	1.54E (1.10, 2.22)	2.85 (2.51, 4.03)
51-70 yr M	873 / 2477	(35%)	1.00 (0.82, 1.21)	2.60 (2.06, 2.93)	2.81 (2.38, 3.32)	6.46 (4.67, 7.86)
71+ yr M	520 / 1472	(35%)	1.22 (0.93, 1.54)	3.03E (2.25, 4.44)	3.58 (2.77, 4.43)	8.34E (6.05, 12.67)
9-13 yr F	1229 / 1880	(65%)	0.77 (0.65, 0.90)	1.30 (1.03, 1.62)	1.17 (0.99, 1.37)	2.40E (1.57, 4.87)
14-18 yr F	1241 / 2194	(57%)	0.52 (0.45, 0.59)	1.26 (1.07, 1.49)	0.93 (0.82, 1.05)	2.07 (1.62, 2.37)
19-30 yr F	910 / 1952	(47%)	0.39 (0.34, 0.44)	1.13 (0.93, 1.38)	0.81 (0.74, 0.88)	1.67 (1.45, 1.97)
31-50 yr F	1054 / 2608	(40%)	0.85 (0.64, 1.13)	1.76E (1.14, 2.56)	2.21 (1.66, 2.83)	3.96 (3.32, 5.65)
51-70 yr F	1194 / 3062	(39%)	1.56 (1.23, 1.88)	3.57 (2.90, 3.96)	3.96 (3.19, 4.72)	9.83E (6.26, 13.41)
71+ yr F	913 / 2527	(36%)	1.28 (1.02, 1.62)	2.85E (2.21, 4.43)	3.61 (2.93, 4.47)	12.32 (7.68, 14.83)

E - Estimates marked with the letter 'E' have high sampling variability (coefficient of variation from 16.6% to 33.3%) and should be interpreted with caution.