Screening Assessment

Cyanides

Environment and Climate Change Canada
Health Canada

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Synopsis

Pursuant to sections 68 or 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. The Chemical Abstracts Service Registry Number (CAS RN[1]), *Domestic Substances List* (DSL) name and common name(s) of the ten prioritized substances are listed in the table below.

Substances in the Cyanides Group

CAS RN[a]	DSL name	Common name(s)
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 (Yellow prussiate of potash)
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)

[a] These substances were identified as a priority for assessment as they met the categorization criteria under subsection 73(1) of CEPA.

The ecological portion of this 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 include the 10 substances listed above. Precursors to free cyanide are substances that contain the cyanide moiety and that can degrade to free cyanide through any transformation pathway (e.g., hydrolytic, redox, or

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metabolic) at environmentally, industrially or physiologically relevant conditions. These substances consist of cyanide salts, and cyanide complexes. Precursors of free cyanide relevant to the ecological 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 (CNFree), WAD cyanide (CNWAD), or total cyanide (CNT). CNWAD measured in the environment includes CNFree and CNWAD. CNT refers to the sum of CNFree and CNWAD species, and all other remaining CNSAD. The ecological assessment focuses on CNFree and CNWAD data where available, as these are the most relevant measures for ecological effects. Measurements of CNT, which represent the sum of cyanide compounds in a sample (including CNSAD), are also used as a line of evidence in the ecological portion of this screening assessment as a supplement to, or in the absence of, CNFree and CNWAD. Characterizing ecological exposure using CNT is potentially conservative; however, there is evidence that CNSAD species can transform in the environment to CNFree.

The human health portion of this screening assessment focuses on the specific substances identified as priorities which are separated into two distinct subgroups: free/simple cyanides and the metal-cyanide complexes. The human health assessment takes into consideration reported levels of HCN and CNT 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 water soluble and 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. HCN is considered persistent in air due to an estimated atmospheric lifetime of approximately one to six months. Free cyanide and precursors of free cyanide 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). However, ferrocyanides are considered persistent in soils and sediments. Free cyanide and precursors of free cyanide are not considered bioaccumulative.

The presence of free cyanide in environmental media, food or products available to consumers 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 some industries.

According to information submitted in response to a CEPA section 71 survey, 7 of the 10 substances were imported into Canada in 2011 above the reporting threshold of 100 kg. 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) had the highest import quantity of 10 000 tonnes to 50 000 tonnes in 2011. 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 quantity in 2011 of 10 tonnes to 100 tonnes, which is used mainly as an anticaking agent in road salts. HCN is incidentally produced in Canada (at quantities of 1 000 tonnes to 10 000 tonnes 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) and chemical manufacturing, where releases of cyanides to air and surface water may occur.

Free cyanide is generally the more hazardous cyanide species. HCN disrupts energy metabolism and is highly toxic to aquatic organisms. The predicted no-effect concentration (PNEC) of 1.7 µg/L for free cyanide in fresh water was derived through a species sensitivity distribution approach using chronic toxicity endpoints for 12 aquatic species. The ecotoxicity of cyanide complexes is largely driven by their ability to dissociate and release free cyanide.

The ecological exposure assessment for cyanides focuses on potential releases of cyanide from three main sectors of activity: metal mining, iron and steel manufacturing, and application of ferrocyanide-containing road salts. When available, measurements of CNWAD and CNFree were considered in addition to measurements of CNT for the ecological exposure characterization. Risk quotient analyses were conducted to compare the measured or estimated concentrations in the aquatic compartments to the PNEC for free cyanide in aquatic organisms. Exposure scenarios for metal mining, integrated steel mills, and runoff from parking lots and highways where ferrocyanide-containing road salts were applied indicate that releases of free cyanide and precursors of free cyanide may pose a risk to aquatic organisms.

Considering all available lines of evidence presented in this screening assessment, there is risk of harm to the environment from free cyanide and precursors of free cyanide. It is concluded that free cyanide and precursors of free cyanide meet the criterion 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 concluded that free cyanide and precursors of free cyanide do not meet the criterion 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, and 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 is present as a non-medicinal ingredient in a limited number of oral and topical natural health products (NHPs), while tetrapotassium ferrocyanide is present as a medicinal ingredient in a limited number of oral NHPs licensed as homeopathic medicines. Tetrasodium ferrocyanide is an ingredient present in a limited number of dermally applied cosmetics 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 available to consumers, low dermal absorption and known product-use patterns. Therefore, the risk is considered to be low.

The risk to human health is also considered to be low for the multi-iron cyanide complexes (CAS RNs 14038-43-8, 25869-98-1, and 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 to human health is considered to be low for the free/simple cyanides subgroup (CAS RNs 74-90-8 and 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.

Considering all the information presented in this screening assessment, it is concluded that the 10 cyanides identified as priorities for assessment do not meet the criterion under paragraph 64(c) of CEPA as they are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health. It is therefore concluded that free cyanide and precursors of free cyanide meet one or more of the criteria set out in section 64 of CEPA. It has also been determined that free cyanide and precursors of free cyanide meet the persistence criteria but not the bioaccumulation criteria as set out in the *Persistence and Bioaccumulation Regulations* of CEPA.

Table of Contents

List of Tables and Figures

1. Introduction

Pursuant to sections 68 or 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 2017]).

The focus of the ecological assessment is on free cyanide, consisting of the cyanide anion (CN^-) and hydrogen cyanide (HCN), as these are the most relevant for ecological effects, and on precursors of free cyanide. Precursors of free cyanide have the potential to release free cyanide under environmentally relevant conditions (e.g., pH, temperature) and transformation processes (e.g., dissociation, degradation, or photolysis). The 10 substances identified as priorities for assessment are considered precursors of free cyanide from an ecological perspective. Exposure to free cyanide from anthropogenic activities may occur from different pathways and sources, which encompass incidental production.

For the human health risk assessment, a moiety approach was considered based on biomonitoring data of urinary thiocyanate (SCN), the primary metabolite of cyanide in humans (CDC 2015). However, this approach was not considered appropriate because SCN was not considered suitable as a biomarker of free cyanide exposure due to high dietary levels of SCN and/or its precursors (Kirman et al. 2018). 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 HCN and sodium cyanide (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 screening assessment presents the human health exposure, hazard and risk characterization separately for these subgroups.

This screening assessment includes consideration of information on chemical properties, environmental fate, hazards, uses and exposures, including additional information submitted by stakeholders. Relevant data were identified up to December 2021. Empirical data from key studies as well as some results from models were used to reach the conclusions. When available and relevant, information presented in assessments from other jurisdictions was considered. This 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 screening 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, United States Environmental Protection Agency. Comments were compiled by scientists at the Toxicology Excellence for Risk Assessment, Department of Environmental Health, College of Medicine, University of Cincinnati. Additionally, the draft of this screening assessment (published February 10, 2018) was subject to a 60-day public comment period. While external comments were taken into consideration, the final content and outcome of this screening assessment remain the responsibility of Health Canada and Environment and Climate Change Canada.

This 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 screening assessment presents the critical information and considerations on which the conclusions are based.

2. Identity of substances and scope of the assessment

Cyanides are a large family of inorganic chemicals that contain the cyano functional group (-CN), consisting of a carbon atom triple bonded to a nitrogen atom. Precursors to free cyanide are substances that contain the cyanide moiety and that can degrade to free cyanide through any transformation pathway (e.g., hydrolytic, redox, or metabolic) at environmentally, industrially or physiologically relevant conditions. These substances contain the cyanide moiety bonded to any chemical group through ionic bonds (i.e., “cyanide salts”) or through co-ordinate bonds (i.e., “cyanide complexes”).

The Chemical Abstracts Service Registry Number (CAS RN[3]), *Domestic Substances List* (DSL) name and common name(s) of the 10 cyanides that met subsection 73(1) of CEPA are presented in Table 2.

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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.

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Table 2. Identity of substances identified as priorities for assessment under subsection 73(1) of CEPA

CAS RN	DSL name	Common name (s)[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)	$Na_4Fe(CN)_6$	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)	$K_4Fe(CN)_6$	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
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

CAS RN	DSL name	Common name (s)[b]	Molecular formula	Molecular weight (g/mol)	Subgroup
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 and aqueous HCN (HSDB 1983-).

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

Free cyanides (CN_{Free}) are cyanide compounds present in the form of the cyanide anion (CN^-) or hydrogen cyanide (HCN). CN^- reacts with many elements to form simple cyanide salts which have the general chemical formula $M(CN)_x$ and include, for example, NaCN (Ghosh et al. 2006a). 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 ability to release free cyanide. Weak complexes release free cyanide under slightly acidic conditions (pH 4 to 6) and are referred to as “weak acid dissociable” (WAD) cyanides, while strong complexes require strong acidic conditions ($pH < 2$) to dissociate in the absence of light, 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 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 ecological portion of this screening assessment focuses on CN_{Free} or CN_{WAD} as these measured analytes are the most relevant for ecological effects. Measurements of CN_T, which represents the sum of cyanide compounds in water (including CN_{SAD}), is a line of evidence in the assessment as a supplement to, or in the absence of, CN_{Free} and CN_{WAD}. It is noted, however, that CN_T measurements may overestimate the potential for toxicity (Redman and Santore 2012). Inorganic cyanides on the DSL 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 2020). Free cyanide may also be released from naturally occurring cyanogenic glycosides (CGs) in plants. Environmental monitoring data were 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. Modelling of exposure concentrations from release data was also conducted when receiving environment data were unavailable. Where feasible, background or reference concentrations were differentiated from concentrations attributed to anthropogenic sources.

The human health portion of this 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 for assessment. The latter subgroup was further divided into the gold- or silver-cyanide complexes (CAS RNs 13967-50-5 and 506-61-6), the single-iron cyanide complexes (CAS RNs 13601-19-9, 13746-66-2, and 13943-58-3), and the multi-iron cyanide complexes (CAS RNs 14038-43-8, 25869-00-5, and 25869-98-1).

3. Physical and chemical properties

A summary of physical and chemical properties of HCN, the dominant free cyanide species at most environmentally relevant conditions, 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). As indicated, HCN should be the dominant free cyanide species at environmentally relevant pH (e.g., 5 to 8) based on a pK_a range of 9.21 to 9.36.

$$HCN_{(aq)} = H^+ + CN^- \text{ (pKa > 9.21)}$$

A high Henry’s law constant indicates that HCN will volatilize from water. The volatilization rate of HCN is a direct function of temperature, turbulence, surface area of the solvent medium, level of agitation, initial concentration, and an indirect function of pH (Fuller 1984; Johnson 2015).

HCN is not expected to partition significantly to lipids (octanol) or to soil based on its low K_{ow} and low K_{oc}. The K_{oa} for HCN indicates that it could bind slightly to atmospheric particulate matter.

Table 3-1. Experimental physical and chemical property values for HCN

Property	Range	Key reference(s)
Physical state	Liquid or gas	IPCS 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 as cited in AGDH 2010; Daubert and Danner 1985
Henry’s law constant (Pa·m^3/mol) (at 25°C)	13.5 to 5167.6	Gaffney et al. 1987; Yoo et al. 1986 as cited in ATSDR 2006

Property	Range	Key reference(s)
Water solubility (mg/L) (at 25°C)	miscible	Lide 1990 as cited in ATSDR 2006; PhysProp 2013
log K_{ow} (dimensionless)	-0.25 to 0.66	US EPA 1984 as cited in ATSDR 2006; Hansch et al. 1995
log K_{oc} (dimensionless)	0.45 to 1.2	KOCWIN 2010
log K_{oa} (dimensionless)	2.0	KOAWIN 2010
pK_a (dimensionless) (at 20°C)	9.31 to 9.36	Izatt et al. 1962 as cited in ECETOC 2007; AGDH 2010
pK_a (dimensionless) (at 25°C)	9.21 to 9.25	Izatt et al. 1962 as cited in ECETOC 2007; 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 (CAS RN 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 (Karyakin 2001; Ghosh et al. 2006a; Lee and Huh 2012)[4]. The iron cyanide complexes identified as priorities for assessment have a hexacyanoferrate group $[Fe(CN)_6]$ in common. 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 WAD complex, all of the metal-cyanide complexes identified as priorities are considered SAD complexes with high formation constants (log K at 25˚C) ranging from 18.9 to 64.0 (Beck 1987).

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

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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).

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 as cited in Wong-Chong et al. 2006a), and 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 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 the National Industrial Chemicals Notification and Assessment Scheme 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 survey issued pursuant to section 71 of CEPA (Canada 2012). For the purpose of the survey, “manufacture” is defined as the production or the preparation of a substance, including when the substance is produced incidentally (Environment Canada 2012). These 10 substances were not reported to be intentionally manufactured in Canada (Environment Canada 2013; ICMC 2015).

While not reported to be manufactured for commercial purposes in Canada, results of the survey indicate that 1 000 to 10 000 tonnes of HCN (CAS RN 74-90-8) were incidentally manufactured by fewer than four companies belonging to the 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 incidentally 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 anion (CN^-) 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, by-product and waste by fewer 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 of electrolytic cells, which are considered hazardous waste (Silveira et al. 2002; Environment Canada 2015; Freitas et al. 2016).

Other documented anthropogenic sources of cyanides include electroplating facilities (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; Shifrin et al. 1996; Kapusta et al. 2013; Broer 2015), petroleum refining (Sheu and Weng 2000), 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 reported in response to a CEPA section 71 survey (Canada 2012). Table 4-1 presents a summary of the total import quantities for seven cyanides (Environment Canada 2013). Results indicate that NaCN imports ranged from 10 000 to 50 000 tonnes, representing the vast majority of total quantities of the substances imported according to responses received.

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

CAS RN	Common name(s)	Total imports[a] (t)
74-90-8	Hydrogen cyanide	N/A
143-33-9	Sodium cyanide	10 000 to 50 000
506-61-6	Potassium dicyanoargentate	0.1 to 1
13601-19-9	Tetrasodium ferrocyanide	10 to 100
13746-66-2	Tripotassium ferricyanide	0.1 to 1
13943-58-3	Tetrapotassium ferrocyanide (Yellow prussiate of potash)	0.1 to 1
13967-50-5	Potassium dicyanoaurate	N/A

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[5] In this screening 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.”

CAS RN	Common name(s)	Total imports[a] (t)
14038-43-8	Ferric ferrocyanide (Prussian blue insoluble)	1 to 10
25869-00-5	Ferric ammonium ferrocyanide	1 to 10
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).

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

4.3 Uses

Uses of the substances in the free/simple cyanides subgroup according to non-confidential business information reported in response to a CEPA section 71 survey (Canada 2012) were limited to industrial applications. These 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 include both industrial applications and uses in 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 (SDS 2012). Tobacco smoke may be a potential source of HCN (personal communication, emails from the Tobacco Control Directorate, Health Canada (HC), to the Existing Substances Risk Assessment Bureau (ESRAB), dated November 2021; unreferenced). The import of "complex cyanides of metals" into Canada (CBSA 2015) may include the use of iron-cyanide complexes in Canada as anticaking agents in road salts (EC, HC 2001; Exall et al. 2011). Some iron-

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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, natural health products, or non-prescription drugs.

cyanides such as sodium ferrocyanide were also historically 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.

Table 4-2. Additional uses in Canada for each of the substances in the Cyanides Group[a]

Substance code [a] **Use**	1	2	3	4	5	6	7	8	9	10
Food additive[b]	N	N	N	N	Y[i]	N	Y[i]	N	N	N
Incidental additives[b,c]	N	N	N	N	Y	N	N	N	N	N
Food packaging materials[b]	N	N	N	N	N	N	N	Y	Y	N
Medicinal or non-medicinal ingredients in natural health products (NHPs)[d]	Y[j]	N	N	N	Y[k]	N	Y[j,k]	Y[j,k]	Y[i]	N
List of Prohibited and Restricted Cosmetic Ingredients[e]	Y	Y	N	N	N	N	N	N	N	N
Notified to be present in cosmetics under the *Cosmetic Regulations*[f]	N	N	N	N	Y	N	N	Y	Y	N
Formulant in registered pest control products[g]	N	N	N	N	Y	N	N	N	N	N
Active ingredient in registered pest control products registered in Canada[h]	N	Y	N	N	N	N	N	N	N	N

[a] Substance codes 1 to 10 represent CAS RNs 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, and 25869-98-1, respectively.

[b] Personal communication, emails from the Health Products and Food Branch (HPFB), Health Canada (HC), to the Existing Substances Risk Assessment Bureau (ESRAB), dated March 2016; unreferenced.

[c] While not defined under the *Food and Drugs Act*, incidental additives may be regarded for administrative purposes, as those substances which are used in food processing plants and which may potentially become adventitious residues in foods (e.g., cleaners, sanitizers).

[d] Substance is listed in the Natural Health Products Ingredients Database (NHPID) and in the Licensed Natural Health Products Database (LNHPD). Personal communication, emails from the HPFB, HC, to the ESRAB, dated March 2016; unreferenced.

[e] Health Canada [amended on Dec. 3, 2019], Cosmetic Ingredient Hotlist: List of Ingredients that are Prohibited for Use in Cosmetic Products. Ottawa, ON: Health Canada, Consumer Hazardous Products Safety Directorate (CHPSD) [accessed July 21, 2021]. http://www.hc-sc.gc.ca/cps-spc/cosmet-person/hot-list-critique/hotlist-liste-eng.php

[f] Personal communication, emails from the CHPSD, HC, to the ESRAB, HC, dated January 11, 2016; unreferenced.

[g] Personal communication, emails from the Pest Management Regulatory Agency (PMRA), HC to ESRAB, HC, dated November 2015; unreferenced.

[h] Personal communication, emails from the PMRA, HC to ESRAB, HC, dated November 2015; unreferenced; Sodium cyanide use in pesticides as the active registration will be discontinued as of Dec 31, 2021 (personal communication, email from PMRA to HC RA Nov 24, 2021;unreferenced).

[i] Tetrasodium ferrocyanide (CAS RN 13601-19-9) and tetrapotassium ferrocyanide (CAS RN 13943-58-3) are associated with an acceptable daily intake (ADI) of up to 0.025 mg/kg bw/day.

[j] Homeopathic role.

[k] 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 cyanides subgroup were characterized for ambient air and foods.

5. Releases to the environment

Reporting to the National Pollutant Release Inventory (NPRI) is mandatory for HCN and cyanides (ionic) (NA-07)[7] (NPRI 2020). The category cyanides (ionic) is defined by the NPRI as including the salts of HCNs, but excluding organo-cyanides, nitriles and organometallic cyanide compounds (ECCC 2016a). Results for 2010 to 2017 show that releases were principally to air and water (Table 5-1).

Table 5-1. Summary of releases of HCN and cyanides (ionic) in tonnes (t) reported to the NPRI per year from 2010 to 2017 (NPRI 2020)[a]

Substance	Air (t)	Water (t)	Land (t)	Total (per year)[b] (t)
Cyanides (ionic)	1.5 to 22.5	0.1 to 13.7	0 to 0.07	2.1 to 24.2
HCN	15.6 to 168.2	0 to 3.8×10^{-3}	0	15.6 to 168.2

[a] Data used for this table is current as of July 16, 2020. Facilities can and do update their information reported to the NPRI at any time. As a result, similar analysis done with different versions of the data may produce different results. There is a degree of complexity surrounding NPRI data reporting, such as meeting reporting thresholds and the use of various acceptable estimation or measurement methods and data sources. Therefore, uncertainties exist in the reported quantities. See the NPRI reporting guidance document for more details NPRI 2020). Releases reported in the table are rounded to the nearest 0.1 t.

[b] The total release in this column also captures reported releases to all media <1 t.

From 2010 to 2017, all releases of cyanides (ionic) to land reported to the NPRI were from the metal ore mining sector (i.e., 0 to 0.07 tonnes per year). Releases to water were reported by the metal mining (i.e., 0.1 to 1.7 tonnes per year) and water, sewage and other systems sectors (i.e., 0 to 13.4 tonnes per year). The metal mining sector also accounted for most releases of cyanides (ionic) to air (i.e., a range of 1.5 to 22.5 tonnes per year), with the chemical/product distribution and waste management sectors reporting smaller quantities (0.001 tonnes and 0.05 tonnes per year, respectively). Releases of cyanide (ionic) for “total all media < 1 tonne” were reported from the medical, health products and veterinary sector (i.e., 0 to 0.49 tonnes per year), waste management (i.e., 0 to 0.06 tonnes per year) and metal ore mining sectors (i.e., 0.016 to 1.5 tonnes per year). Releases of HCN to air were reported by petroleum refiners (i.e., 0 to 125.8 tonnes per year), metal ore mining (i.e., 0 to 42.6 tonnes per year), and chemical manufacturing (i.e., 0 to 13.3 tonnes per year) between 2010 and 2017 (NPRI 2020). Releases of HCN to air from the chemical manufacturing sector in this dataset relate to HCN incidentally produced during the manufacture of carbon black. Other sources of information, namely surveys issued pursuant to section 71 of CEPA and reports prepared for provincial authorities, suggest that the incidental manufacture of HCN from this activity may be ongoing in Canada and that releases may be ecologically

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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.

relevant (US EPA 2000; Environment Canada 2013; Lehder 2015; Trinity Consultants 2020). Releases of HCN to water were reported by the metal ore mining sector (i.e., 0 to 0.004 tonnes per year). There were no HCN releases reported to land in the same time frame. Releases for “total all media < 1 tonne” also shows releases of HCN from the electronics and electrical equipment sector (i.e., 0 to 0.16 tonnes per year) (NPRI 2020).

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 as cited in AGDH 2010). US EPA (1981) reported average emission rates of HCN in automobiles equipped with catalytic 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 to 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 partitioning to all environmental compartments. 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 (SCN) and SCN 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., < 133.3 Pa) 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 (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 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. HCN is water soluble, though it may adsorb weakly to sediment or particulate matter or form complexes of variable stability with transition metals in solution (Dzombak et al. 2006a). Photolysis is not expected to be a major loss process for free cyanide in the environment based on two studies that observed minimal degradation of free cyanide (Ostathaphan et al. 2013) and CN_{WAD} (Rader et al. 1995) without a catalyst following continuous irradiation for 180 minutes (at pH 9.5) and 17 days (at pH 11), respectively.

However, an important loss process identified for free cyanide from water is volatilization. Volatilization of HCN from water has been identified as an important removal process of free cyanide from tailings ponds (Simovic and Snodgrass 1985, 1989; Botz and Mudder 2000) and a similar behaviour would be expected in natural waters considering its high Henry's law constant. Volatilization rates of free cyanide increase with lower pH, where HCN dominates, higher temperature, greater water column agitation, and greater surface area to volume of solution (Johnson 2015; Brüger et al. 2018). For example, Broderius and Smith (1980) estimated volatilization rates of HCN across a range of free cyanide concentrations (i.e., 25, 50, 100, and 200 µg CN/L) and temperatures (i.e., 10, 15, 20, and 25°C), under laboratory conditions. The rate of HCN volatilization was approximately first-order, indicating that the initial cyanide concentration in solution affected the rate of HCN volatilization. Half-lives ranged from 111 hours (25 µg/L CN and 10°C) to 22 hours (200 µg/L CN and 25°C). Outdoor experiments conducted in the same study showed that the rate of HCN volatilization increased two-fold compared to the indoor laboratory results. This observation was thought to be due to wind agitation.

While volatilization may be an important loss process for HCN, the cyanide anion (CN^-) forms complexes with transition metals in solution (e.g., copper, zinc, nickel or iron) which are not expected to volatilize from solution. The formation 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). The most important cyanide complexation reactions generally occur with iron due to its ubiquity in the environment, which produces ferricyanide ($Fe(CN)_6^{3-}$) or ferrocyanide ($Fe(CN)_6^{4-}$; also called hexacyanoferrate(II)) (Johnson 2015).

While iron-cyanide complexes can be stable under neutral conditions (Meeussen et al. 1992; Wild et al. 1994), several studies reported that they can undergo photolysis and fully dissociate to release CN^- depending on environmental conditions (Broderius and Smith 1980; Little and Calfee 2000, 2002, 2003; Kuhn and Young 2005; Young et al. 2005; Exall et al. 2011). Yu et al. (2011) reported conversion of ferri- and ferrocyanides to free cyanide under alkaline conditions (0.1% NaOH) in the presence of 20 000 lux of artificial light (sunlight may be as intense as 100 000 lux (Spitschan et al. 2016). Little and Calfee (2000, 2002, 2003) also found that ferrocyanide compounds, used as forest fire retardants in the past, release free cyanide when exposed to ultraviolet (UV) light. The researchers also observed a significant increase in toxicity associated with the formation of free cyanide from ferrocyanide and UV radiation. Ferrocyanide photolysis half-lives ranging from 7.5 minutes to 23 minutes were calculated for deionized water and for three natural waters at 20°C to 21°C exposed to a light intensity of 110 µmol/m^2/s UV photons (midwinter UV light intensity ranges up to approximately this amount) (Kuhn and Young 2005). The rate of free cyanide formation was approximately three times slower than the loss of ferrocyanide because of the temporary accumulation of intermediate cyanoferrate species ($Fe(CN)_x^{n-}$) (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. Photolysis and dissociation of strong metal-cyanide complexes were also observed in the effluent of a former gold mine. Concentrations of CN_{WAD} in samples collected from an open channel receiving effluent from an inactive ore heap of a former gold mine, 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/hour with a water temperature ranging from 14.6 to 28.2°C (Johnson et al. 2002). The characteristics of the channel used in this study, which was approximately 0.5 metres wide and a few centimetres deep (Johnson et al. 2002), may have favoured the dissociation of metal-cyanide complexes as photodissociation rates vary with sunlight intensity, light absorption in the water column, and temperature (Johnson et al. 2015). In alignment with the British Columbia water quality criteria 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 photodissociate and be a source of CN_{Free} in gold mine effluent and possibly in the environment. Additionally, the removal of cyanide from ice-covered tailings ponds has been observed to stagnate, presumably due to a decrease in light intensity preventing the photodissociation of metal-cyanide complexes and volatilization of HCN (Simovic and Snodgrass 1989; Botz and Mudder 2000).

Therefore, dissociation of CN_{SAD} species in the receiving environment could potentially lead to increased HCN concentrations in the environment. However, the rates of photodissociation would be expected to vary across environmental conditions, with factors such as depth playing an important role, as releases of HCN resulting from photolysis of ferrocyanides have been characterized to be negligible below depths of approximately 50 to 100 cm in most well-mixed natural waters (Broderius and Smith 1980).

Metal-cyanide compounds with transition or alkaline earth metals (e.g., Prussian blue, $Fe_4(Fe(CN)_6)_3$), may accumulate in sediments (Jambor et al. 2009). The CN^- can react with sulphur species (e.g., polysulphides S_xS^{2-} or thiosulphate $S_2O_3^{2-}$) to form the much less hazardous SCN^- species (Smith and Mudder 1991 as cited in Dzombak et al. 2006c; Dzombak et al. 2006a). HCN may also oxidize to 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 (ECETOC 2007).

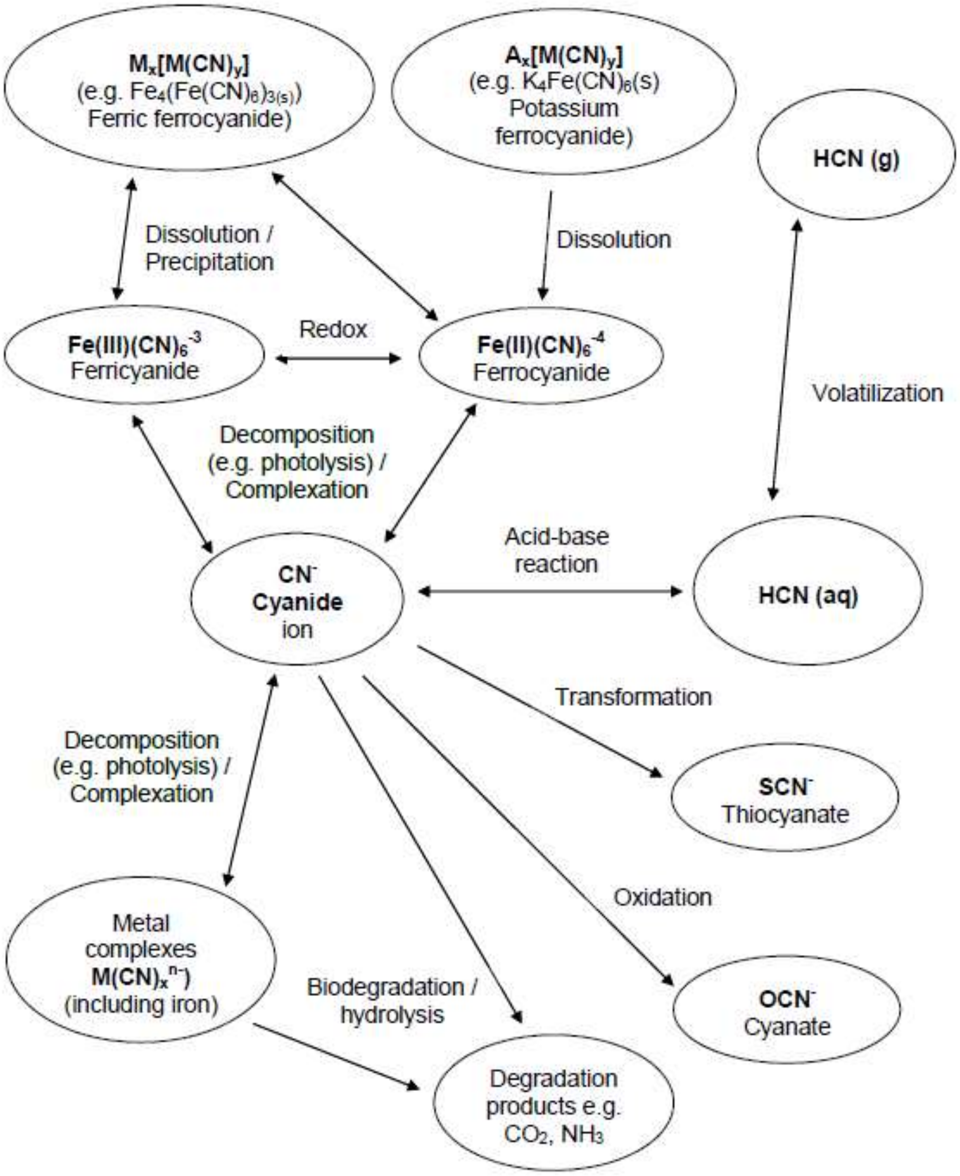

Figure 6-1. Key cyanide species and transformation processes (adapted from Kjeldsen 1999)

A review of the behaviour of free cyanide in soil was conducted by the Canadian Council of Ministers of the Environment (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. Much like the aquatic compartment, free cyanide may form complexes with metals (e.g., iron) and precipitate out of the soil 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 behaviour in soils by EC and HC (2001) indicates 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 ($OH_{\cdot}$) and photolysis is estimated to range from 1 to 2.5 years, depending on the OH concentration and rate (k_{OH}) (Cicerone and Zellner 1983; Fritz et al. 1982 as cited in ECETOC 2007). 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 months 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 to 180 days (Viatte et al. 2015). Therefore HCN may be considered persistent in air.

In water, free cyanide is not expected to hydrolyze under environmentally relevant conditions and HCN hydrolysis is either slow under acidic conditions or requires high temperatures under alkaline conditions (Dzombak et al. 2006a; Smith and Mudder 1991 as cited in Dzombak et al. 2006c). 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 as cited in Dzombak et al. 2006c; Dzombak et al. 2006a). No biodegradability data derived using standard Organisation for Economic Co-operation and Development (OECD) protocols (e.g., OECD 301 Ready Biodegradability) are available for HCN or other cyanide complexes that could inform their persistence in 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 capable of metabolizing HCN and other cyanides, and confirms that free cyanide is biodegradable under certain conditions. Factors affecting the biodegradation of cyanides include initial concentrations, the presence of acclimatized microorganisms, availability of nutrients, temperature, and pH depending on the microorganisms present (Dash et al. 2009). A high concentration of free cyanide is considered the principal factor affecting biodegradation in wastewater treatment systems (Wild et al. 1994; Strotmann and Pagga 1996). The same controlling factors may apply to natural waters where biodegradation is expected to be an important removal process (CCME 1997a). Studies support that 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 microorganism acclimatization, the availability of oxygen, free cyanide concentrations and nutrient availability (e.g., phosphorus).

Meeussen et al. (1992) used a decomposition model to estimate the half-life of iron cyanide complexes in soil solutions at 15 ^{o}C at varying pH and reduction potential (pE) levels. Assuming a total hexacyanoferrate(II) concentration of 1 mM and an ionic strength of 0.03 M, the results show that the half-life varied from 1 year at pH 4 in reduced soil (i.e., pE = 5) to 1 000 years at the same pH in oxidized soil (i.e., pE = 10). The findings also indicate that when pE levels are kept constant, the half-life would significantly increase as the soil becomes more alkaline. The study supports that ferrocyanides may be considered persistent in both soil and in sediments.

6.3 Potential for bioaccumulation

Free cyanide is not expected to bioconcentrate in aquatic organisms due to low log K_{ow} values, ranging from -0.25 to 0.66 (Table 3-1). Empirical bioconcentration factor (BCF) values for HCN between 1.7 L/kg and 6.3 L/kg have been reported for rainbow trout (*Oncorhynchus mykiss*) when exposed to sublethal concentrations for up to 15 days (Bois and Leduc 1988). However, significant accumulation of the metabolite SCN was demonstrated by BCF values, calculated as SCN plasma concentrations divided by HCN exposure concentrations, ranging from 39 to 170 L/kg for exposure periods of 15 days to 16 weeks, respectively (Bois and Leduc 1988; Lanno and Dixon 1996).

Bioaccumulation of free cyanide in 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 disrupt cellular electron transport and energy metabolism via the inhibition of oxidative phosphorylation (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 (CNS), 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 as cited in Eisler 1991), and CO_2 reductase (Eisler 1991).

HCN is water soluble and is readily taken up and absorbed in the bloodstream of aquatic organisms via contact with skin and mucous membranes (e.g., gills) (Eisler 1991; Gensemer et al. 2006). In fish, HCN can cause sublethal effects and biochemical disturbances, tissue damage and nervous system effects (Murgatroyd et al. 1998 as cited in ECETOC 2007). Common carp exposed to sublethal concentrations of NaCN (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 potassium cyanide (KCN; equivalent to approximately 20 µg/L HCN) for four weeks experienced liver and reproductive system damage (Authman et al. 2013). Additionally, vitellogenin (Vtg) levels in serum, vitellogenin (Vtg mRNA) and estrogen receptor (ER mRNA) gene expression 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 was observed to reduce fish reproduction at sublethal concentrations of 10 µg/L over a period of 12 days by increasing dopamine to levels in fish brains that may 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, inhibiting the action of various metalloenzymes. In addition to inhibiting aerobic respiration, CN^- also removes copper from plastocyanin inhibiting 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

SCN, which is generally excreted in urine (Solomonson 1981 as cited in Eisler 1991). 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 Effects on aquatic organisms

The aquatic compartment is considered an important source of exposure for cyanides owing to the high solubility of free cyanide and many precursors of free cyanide. Literature reviews on the aquatic toxicity of cyanides were completed for Environment and Climate Change Canada (Nautilus Environmental 2009; Aquaterra Environmental Consulting Inc. 2016), or conducted as part of other international assessments (ECETOC 2007; AGDH 2010). 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 free cyanide, 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 that of simple salts capable of rapid and full dissociation to free cyanide (Gensemer et al. 2006). For example, the acute 96-hour EC_{50} for the freshwater rainbow mussel (*Villosa iris*) is greater than 100 mg/L and 1 000 mg/L for ferric ferrocyanide and sodium ferrocyanide, respectively -- several orders of magnitude greater than the 96-hour EC_{50} of 1.1 mg/L for NaCN for the same species (Pandolfo et al. 2012). Also, Little et al. (2007) observed that the 96-hour 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 (Cairns et al. 1978; Smith and Heath 1978; Alabaster et al. 1983; Eisler 1991), 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 48 toxicity studies conducted with HCN or other simple salts were reviewed, yielding data addressing both acute and chronic effects.

Acute toxicity data were identified from 31 studies, which included 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} ranged from a 48-hour LC_{50} of 1 µg/L HCN for the common water flea (*Daphnia pulex*) to a 48-hour LC_{50} of 160 000 µg/L HCN for an annelid (*Aeolosoma headleyi*) (Cairns et al. 1978). Although invertebrates appear to have the greatest range of individual acute sensitivities, in general, fish appear to exhibit a higher degree of acute sensitivity to free cyanide (Nautilus Environmental 2009) with the majority of LC_{50} values lower than 1 000 µg/L of HCN.

Chronic toxicity data were identified from 17 studies, which included 3 species of algae, 2 species of aquatic plants, 5 species of invertebrates, and 6 species of fish. Toxicity values [i.e., EC_{10}, EC/IC_{50}, maximum acceptable toxicant concentration (MATC), no-observed-effect concentration (NOEC), lowest-observed-effect concentration (LOEC)] ranged from a 289-day NOEC value for reproduction of 5.2 µg/L HCN for the bluegill (*Lepomis macrochirus*) to a 32-day IC_{50} of 29 800 µg/L HCN for the Eurasian watermilfoil (*Myriophyllum spicatum*) (Stanley 1974; Kimball et al. 1978). Fish are also generally more sensitive to chronic exposure to free cyanide than most other organisms (Eisler 1991; AGDH 2010).

Chronic toxicity data are generally a more relevant indicator of potential for harm from long-term exposure. Therefore, chronic toxicity data were used to derive a 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 dataset available for HCN meets the minimum species data requirements as outlined by the CCME (2007) 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 water quality guidelines for the protection of aquatic life (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.

Chronic toxicity endpoints from reliable studies were selected to derive the chronic toxicity SSD (Figure 7-1) for HCN, and included data for 12 species, including 1 aquatic plant, 3 algae, 4 invertebrates, and 4 fish species (see Table A-1 Appendix A). The endpoints represent low-effects (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 the most sensitive endpoint for a given species), 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 also had the lowest Anderson-Darling statistic test value (A^2) = 0.249 ($p < 0.05$). The CTV was derived using the 5th percentile of the SSD, also referred to as the HC_5 (i.e., the 5th percentile of the hazard concentration distribution). The HC_5 of the SSD plot is 1.7 µg HCN/L, with lower and upper confidence limits of 1.1 µg HCN/L and 2.5 µg HCN/L, respectively.

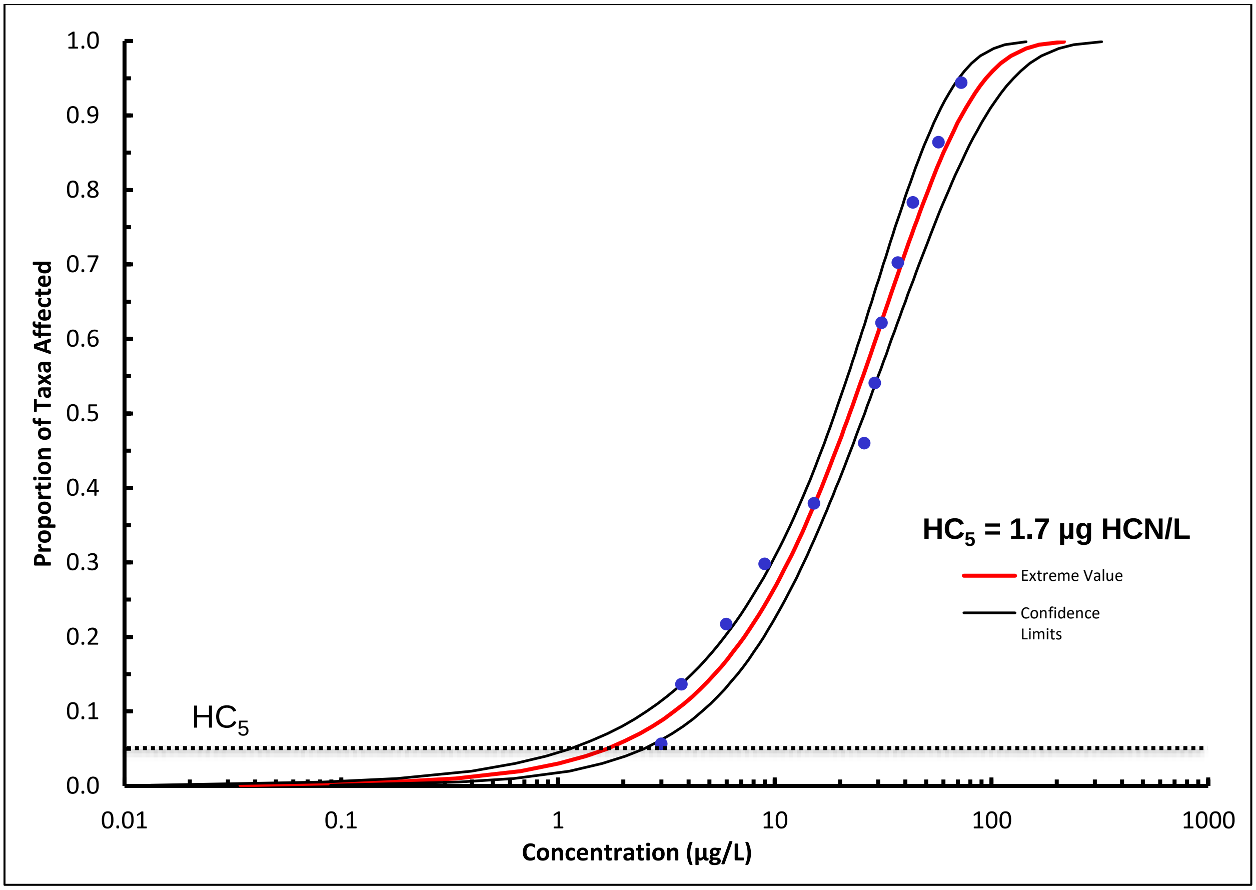

Figure 7-1. Species sensitivity distribution (SSD) for HCN based on chronic toxicity study endpoints. The extreme value model fit to data is shown on the graph, along with the 95% confidence interval and the 5th percentile of the distribution

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 SSD approach with a chronic toxicity dataset covering multiple species and taxa, no additional assessment factor was applied and the PNEC for aquatic organisms is 1.7 µg HCN/L.

This PNEC value is lower than the current CCME and United States Environmental Protection Agency (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) and the Australian and New Zealand Environment and Conservation Council recommended value of 7 µg CN/L (ANZECC 2000), all of which use an acute to chronic ratio (ACR) applied to short-term LC_{50}s in lieu of chronic endpoints. However, it is comparable to the derived value of 1.1 µg CN^-/L calculated by ECETOC (2007). The ECETOC (2007) value is based on a SSD-calculated HC_5 of 1.1 µg CN^-/L (90% confidence interval from 0.4 to 2.3 µg CN^-/L) or 1.14 µg HCN/L, calculated using a chronic toxicity dataset (NOECs) from freshwater and saltwater species with no assessment factors applied. ECETOC (2007) also calculated an HC_5 value of 1.45 µg HCN/L (90% confidence interval from 0.42 to 2.9 µg/L) using only freshwater species (ECETOC 2007).

7.1.3 Effects on terrestrial organisms

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 is based on ecotoxicological data for three vascular plant species and one soil invertebrate species (earthworm). A value of 0.9 mg HCN/kg (i.e., 900 µg HCN/kg) 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 *Eisenia fetida* using KCN yielded a 14-day EC_{50} and EC_{10} of 74 µg/kg and 56 µg/kg of CN^- (equivalent to 77 µg HCN/kg and 58 µg HCN/kg), respectively (Manar et al. 2011). This EC_{10} value is lower than two 14-day NOEC values of 1 200 µg CN^-/kg and 3 000 µg CN^-/kg available for the same species when the SQG was developed.

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 HCN are estimated in order to assess exposure to ecological receptors in surface water. PECs were estimated using measured concentrations when available. When measured concentrations were unavailable, PECs were estimated using facility-specific yearly average loadings of cyanide in effluent.

It is noted that other sectors, such as oil refining, chemical manufacturing or aluminum manufacturing, may also be sources of cyanides to the environment. However, preliminary exposure information available at the time of assessment indicated their releases may be of lesser concern or that data were lacking.

7.2.2 Environmental monitoring

Environmental samples (i.e., water, soil, sediment, and 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 CN_{Free} refer to the concentration of HCN and CN^- in a sample, measurements of CN_{WAD} refer to the concentration of free cyanide and weak cyanide complexes, and measurements of CN_T refer to the sum of CN_{Free}, CN_{WAD}, and all other cyanide complexes (i.e., CN_{SAD}) (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 (pH 4 to 6) (CCME 1997a; Ghosh et al. 2006a,b). CN_{SAD} complexes include cyanide complexes with gold, platinum, iron, and cobalt that require strong acidic conditions, or exposure to sunlight, to dissociate (CCME 1997c; Ghosh et al. 2006a,b). 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. 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, SCN, thiosulphate, aldehydes, fatty acids, carbonate, nitrate and nitrite, may cause interference if present in solution when cyanide analysis is conducted in water (Ghosh et al. 2006b; US EPA 2007; OI Analytical 2012). Sulphite, SCN, thiosulphate, and oxidizing agents may cause negative bias, while sulphide, nitrate and nitrite may cause positive bias in 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 only CN_{Free} 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 and CN^-) and weak complexes that may dissociate and release CN^- (AGDH 2010). For example, the BC water quality criteria for cyanides in fresh water 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 photodissociate to release free cyanide. Therefore, when confirming that the criterion is met, the British Columbia Ministry of the Environment (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 conducted as total cyanide (CN_T) [e.g., *Metal and Diamond Mining Effluent Regulations* (MDMER)].

7.2.3 Ambient concentrations

Cyanides are naturally produced by many organisms and other natural abiotic processes which may result in detectable ambient 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 limited, since cyanides tend to be measured close to anthropogenic sources (BC MOE 1986). Ambient 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). 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 (Krutz 1981; ECETOC 2007). In one natural stream, normal CN_T levels of 0.7 µg/L to 2.1 µg/L increased to a maximum of 5 µg/L in the spring and 10 µg/L in autumn (Krutz 1981; ECETOC 2007).

Provincial water quality monitoring data

Concentrations of cyanides in surface waters are routinely monitored in three provinces: Alberta, British Columbia and Saskatchewan. Monitoring data for relevant cyanide species for these three provinces were queried for the 2005 to 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 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). Statistical summaries were generated for each dataset, 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 datasets were low (< 2 µg /L and < 1 µg/L, respectively), and the percentage of detected concentrations 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 higher CN_T concentrations 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 measurement for the Alberta dataset (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.

For British Columbia, monitoring data in surface water were available for CN_T and CN_{WAD} (EMSWR 2016; Table 7-1). However, these parameters were not measured simultaneously, and variation in sampling location, time, and sample size precluded calculating a speciation ratio between CN_T and CN_{WAD}. The dataset was processed to include only concentrations reported for sites labelled as background in an effort to represent minimally impacted sites or sites upstream of an emission source or discharge point. Samples taken on the same day, at the same site, with the same method were considered replicates and averaged.

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

Province	Alberta	Sask.	BC	BC
Parameter	CN_T	CN_T	CN_T	CN_{WAD}
Number of sites	116	48	16	27
Number of measurements (% of detects)	1424 (9%)	818 (6%)	1656 (38%)	1663 (15%)
MDLs (µg/L)	2 to 10	1	0.5 to 100[a]	0.5 to 100[a]
Range (µg/L)	<2 to 66	<1 to 5	<0.5 to <100	0.5 to <100
Arithmetic mean (µg/L)	1.28	0.56	4.1	2.8
Geometric mean (µg/L)	1.13	0.53	3.07	5.6
Median (µg/L)	<2	<1	<5	<5
95th percentile (µg/L)	2.5	1	10	6

Abbreviations: MDL, method detection limit; Sask., Saskatchewan; BC, British Columbia

[a] The MDL for 2 sampling points in the dataset were unusually high (100 µg/L), but there was no indication of an error.

7.2.4 Metal mining

Information regarding imports of a number of cyanides for 2011 show that 10 000 to 50 000 tonnes of NaCN were imported into Canada for use by the metal mining sector (Environment Canada 2013). Once ore has been extracted from a mine, it is processed to recover the valuable minerals. The CN^- is the main reagent used to extract gold and other precious metals efficiently from ore (Johnson et al. 2002). Major steps in ore processing include grinding and crushing, physical and chemical separation, and dewatering (Environment Canada 2009). Cyanides (e.g., NaCN) may be added in the grinding circuit or during ore separation processes. Cyanide leaching is the dominant process for the recovery of metallic gold or silver (Environment Canada 2009). In the cyanide leaching process, solutions prepared using cyanide salts (e.g., NaCN or KCN) are used to dissolve and extract precious metals present in the ore (Johnson 2015). Approximately 1 to 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 to 11) to reduce losses of free cyanide due to hydrolysis, reaction with carbon dioxide or volatilization of HCN (US EPA 1994b). 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.

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% to 53% of the cyanides in fresh tailings were free, readily soluble cyanides and weak to moderately strong complexes, compared with 15% to 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 in 1998 of the Nickel Plate Mine in British Columbia, concentrations of CN_T (2 to 7 mg/L) and CN_{WAD} concentrations (0.2 to 3.0 mg/L) were measured in reclaimed 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.

Canadian metal mines that deposit deleterious substances into water frequented by fish at a flow rate exceeding 50 m^3/day are subject to the MDMER (Canada 2002). Under Schedule 5, facilities are required to conduct water quality monitoring 4 times per calendar year and at least one month apart in the exposure area (EXP) surrounding the point of entry of effluent into water from each discharge point and from the related reference areas (REF). Facilities are also required to conduct water quality monitoring at the same time that the biological monitoring studies are conducted. Water quality monitoring includes recording the concentration of cyanide if it is used as a process reagent at the mine.

Total cyanide concentrations collected under water quality monitoring provisions required by the MDMER are presented in Figures 7-2 and 7-3, for the years 2009 to 2018 (EEM 2019). Mining sites were separated into CN users[8] and non-CN users in order to depict potential releases from sites frequently or recently using cyanide. CN_T concentrations are presented using a combined box-and-whisker and split violin plot. The whiskers of the box-and-whisker plot represent the 95th and 5th percentile of the whole dataset, and the split violin plot is scaled proportionally to the number of observations and illustrates the distribution and density of detect and non-detect measurements. Method detection limits (MDLs) for the whole dataset ranged from 0.001 to 5 000 µg CN_T/L. Measurements that fell below the MDL were retained in the exposure analysis but transformed to half of the detection limit.

Figure 7-2 generally shows higher CN_T concentrations in water samples collected by CN users in exposure (EXP) areas. The EXP (CN user) group had the highest median and 95th percentile CN_T concentrations; however, the medians of all groups are comparable and are likely explained by the high number of non-detects present in the dataset. The EXP (CN user) group had a detection frequency of 44% while the EXP (non-CN user), REF (CN user) and REF (non-CN user) groups had lower detection frequencies of 16%, 21%, and 15%, respectively. The exposure area CN_T data for non-cyanide users and the reference area CN_T data for cyanide-users and non-cyanide

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[8] For the purpose of this analysis, a facility was considered a cyanide user if: (1) it reported using cyanide for at least 12 months consecutively within a given year between 2009 and 2018 or (2) it reported using cyanide for at least one month in 2017 and 2018.

users appear to have comparable distributions. The peaks expressed in the split violin plots for non-detects represent one-half of multiple MDLs in the dataset.

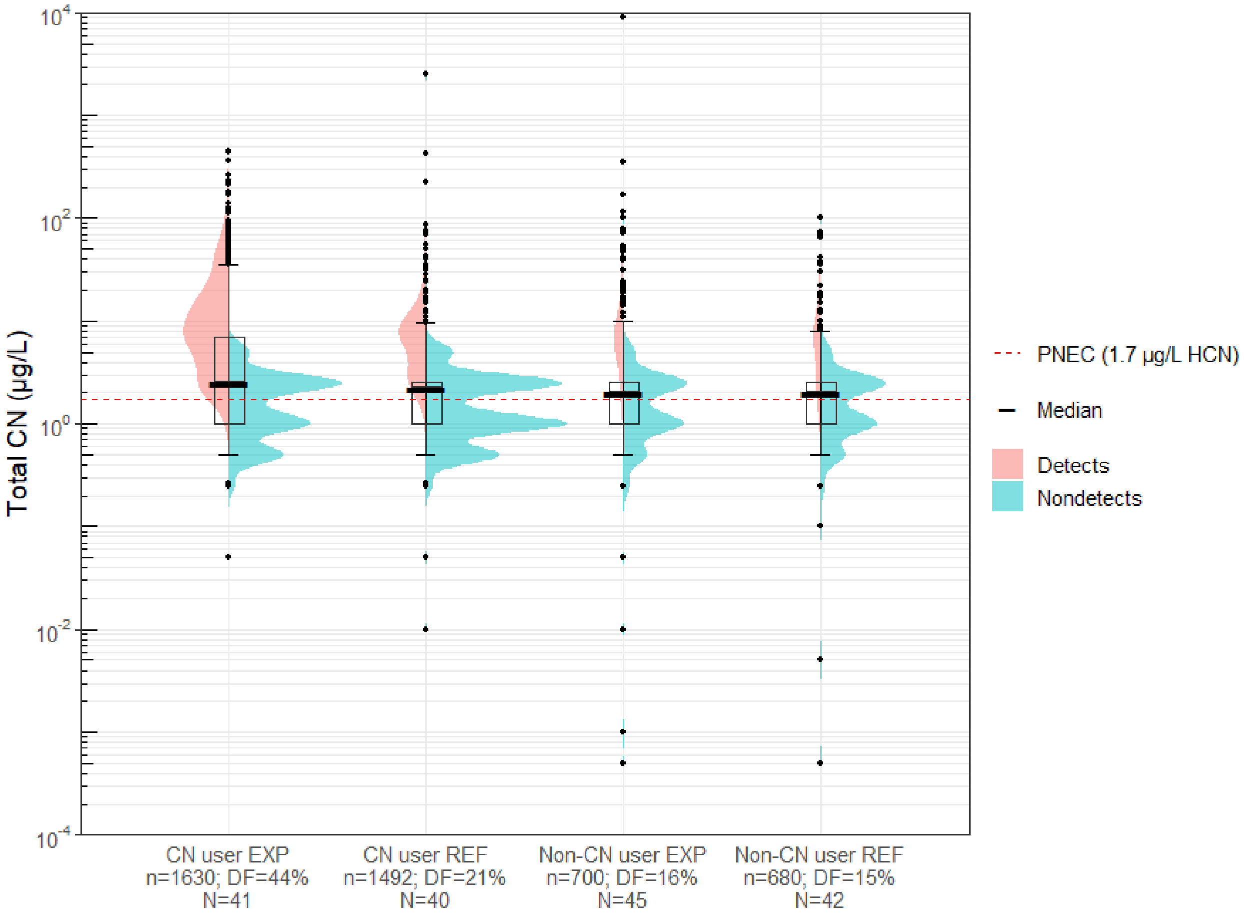

Figure 7-2. Combined box-and-whisker and split violin plot summarizing total cyanide concentrations (µg/L) collected from exposure (EXP) and reference (REF) monitoring sites between 2009 and 2018 by cyanide (CN) and non-cyanide (non-CN) users under the MDMER (EEM 2019)

Nine mining facilities (gold mines or milling facilities) considered cyanide users as per the definition introduced above with the largest datasets and highest detection frequencies (i.e., greater than approximately 50%) were selected for closer analysis of CN_T measurements (Figure 7-3). All samples were collected between 2009 and 2018. The data in Figure 7-3 show similar tendencies to Figure 7-2. Observations of the median and 95th percentile (top whisker of the box plot) show that CN_T concentrations were higher in EXP areas than in corresponding REF areas. Analytical methods used for measurements of cyanide included CAM SOP-00457 and MA.300-CN 1.2 (Center of Expertise in Environmental Analysis of Quebec 2016).

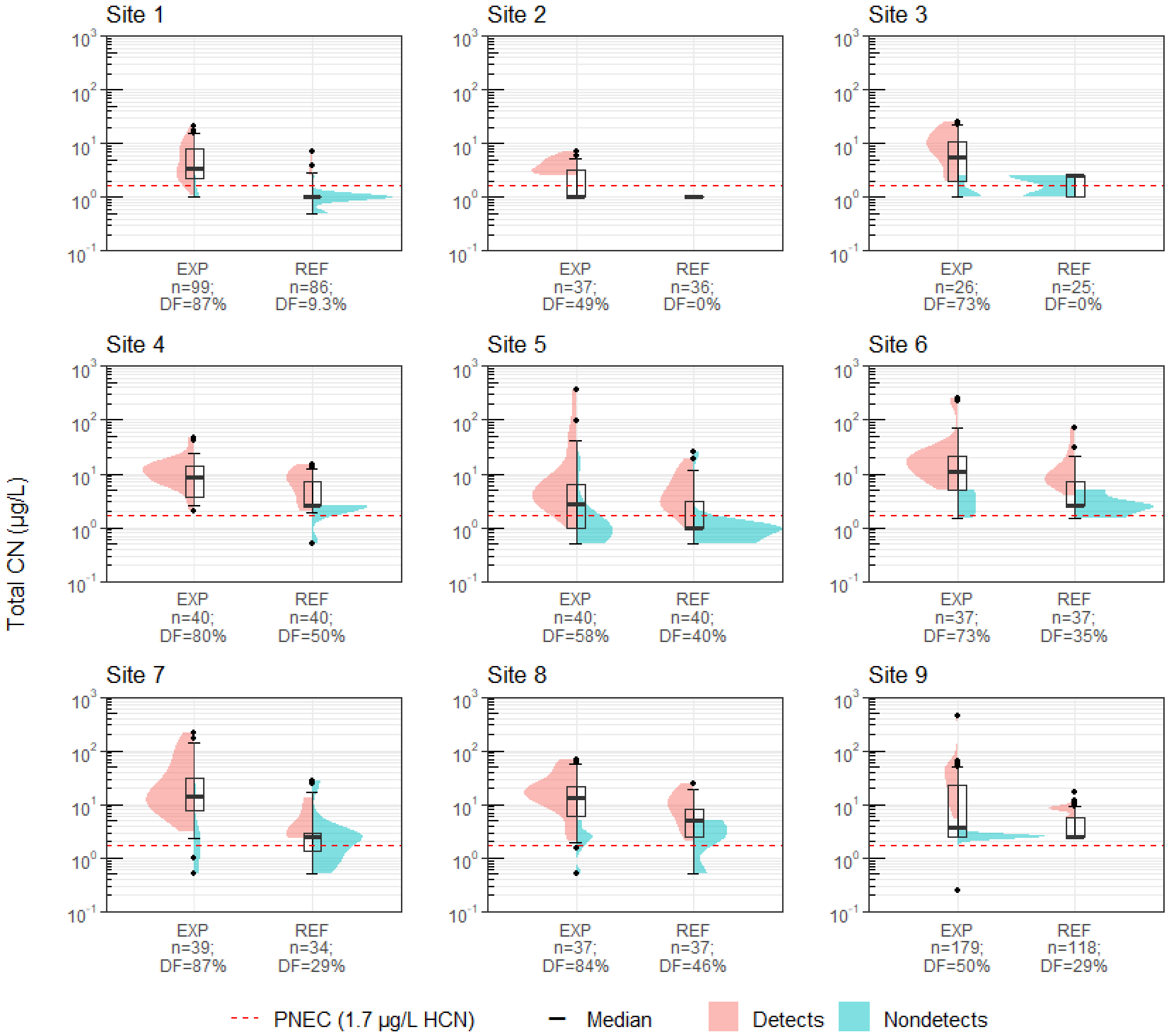

Figure 7-3. Combined box-and-whisker and split violin plot summarizing site-specific analysis of CN_T measurements in surface water samples collected from exposure (EXP) and reference (REF) areas of cyanide users subject to the MDMER from 2009 to 2018 (EEM 2019)

Of the 9 cyanide users reporting the highest release of CN_T, some sites also reported concentrations of CN_{WAD} and CN_{Free} (Table 7-2). Monitoring data of CN_{WAD} from one site were collected from the BC MOE environmental monitoring system (EMSWR 2019), and are also shown in Table 7-2. 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 EXP or REF areas used in environmental effects monitoring (i.e., sites in Figures 7-2 and 7-3)Error! Reference source not found.. The data presented in Error! Reference source not found.2 consist of summary statistics obtained from Environmental Effects Monitoring (EEM) reports when raw data were not included in the reports (e.g., Site 6), or consist of summary statistics calculated using the raw data when they were included (EEM 2019). 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.

Table 7-2. Site-specific analysis of CN_{Free} and CN_{WAD} concentrations extracted from EEM reports (EEM 2019) and a BC MOE environmental monitoring database (EMSWR 2019)

Site key[a]	Sampling period	Type of area	Parameter	Sample size (detection frequency, %)	Median (µg/L)	Geometric mean (µg/L)	Arithmetic mean (µg/L)
1[b,c]	2011 to 2016	EXP (lake)	CN_{WAD}	39 (5%)	1[e]	1[e]	1[e]
1 [b,c]	2011 to 2016	REF (lake)	CN_{WAD}	18 (0%)	1[e]	1[e]	1[e]
1[b,c]	2008 to 2010	EXP (creek n.f.)	CN_{WAD}	34 (unknown)	NA	NA	2 to 4
1 [b,c]	2008 to 2010	REF (creek)	CN_{WAD}	33 (unknown)	NA	NA	2 to 4
2[c]	2014 to 2016	EXP	CN_{WAD}	20 (20%)	1	1.2	1.3
2[c]	2014 to 2016	REF	CN_{WAD}	12 (0%)	1[e]	1[e]	1[e]
6[c]	2005 to 2012	EXP	CN_{Free}	NA	1	NA	4.3
6[c]	2005 to 2012	REF	CN_{Free}	NA	1	NA	3
6[c]	2012 to 2014	EXP	CN_{Free}	94 (unknown)	NA	NA	2
6[c]	2012 to 2014	REF	CN_{Free}	75 (unknown)	NA	NA	2.1
7[c]	2009 to 2015	EXP	CN_{WAD}	12 (33%)	2.5[e]	4.5	6.7
7[c]	2009 to 2015	REF	CN_{WAD}	9 (44%)	2.5[e]	4.6	6
8[c]	2015 to 2016	EXP	CN_{Free}	7 (86%)	4.8	6.1	14

Site key[a]	Sampling period	Type of area	Parameter	Sample size (detection frequency, %)	Median (µg/L)	Geometric mean (µg/L)	Arithmetic mean (µg/L)
8[c]	2015 to 2016	REF	CN_{Free}	7 (14%)	1[e]	0.8	0.9
A[d]	2012 to 2018	EXP	CN_{WAD}	350 (14%)	2.5[e]	2.9	3.1
A[d]	2012 to 2018	REF	CN_{WAD}	66 (0%)	2.5[e]	2.5	2.5

Abbreviations: EXP, exposure area; REF, reference area; n.f., near field; NA, not applicable

[a] Site numbers correspond with site numbers in Figure 7-3 where CN_{Free} and CN_{WAD} data were available.

[b] Site 1 comprises one milling facility and one mine that conduct joint EEM but submit separate water concentration datasets to the MDMER reporting system. The information was analyzed collectively.

[c] Data for this site were extracted from EEM reports (ECCC 2019).

[d] Data for this mine site were extracted from a BC MOE environmental monitoring database (EMSWR 2019).

[e] This is a non-detect represented by a one half MDL substitution.

The environmental measurements of cyanides presented above suggest that some facilities in the metal mining sector are a source of cyanides into the environment. The majority of available data are for CN_T, and it was not possible to estimate the cyanide speciation (i.e., the proportion of CN_{WAD} or CN_{Free}) in these samples. The existence of cyanide measurements in reference areas is seldom explained in the EEM reports. The presence of cyanides in the reference samples may be due to natural sources such as decaying plant matter or forest fires.

7.2.5 Iron and steel manufacturing

Free cyanide and other cyanide species may be found in gas and in wastewater from coke plants and blast furnaces at integrated mills (Petelin et al. 2008; Luzin et al. 2012; 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 (greater than 1 000°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 COG to remove contaminants (also referred to as waste ammonia liquor) 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 $(CN)_2$ (Petelin et al. 2008; Luzin et al. 2012), 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

mg/L and 80 mg/L, respectively (Ellis et al. 1976), but the speciation is not always given. 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). Analytical method details and operational definitions of dissociable and complex cyanides for this particular study were not available; and therefore, there is some uncertainty in the proportions reported. CN_{Free} and CN_T concentrations of 430 µg/L 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., more than half) 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, Conservation and Parks (MECP). Cyanide loadings may be reported for “process effluent”, “once-through-cooling-water (OTCW) effluent” and “combined effluent” (Ontario 2020). 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 to 2016 (**Error! Reference source not found.**3) (Ontario 2020) and by applying a dilution factor of 10 to estimate concentrations in the aquatic environment. The ambient concentration of cyanides in the environment was assumed to be negligible and no default “background” value was incorporated in the PEC calculation. No CN_{WAD} or CN_{Free} measurements were available for the iron and steel manufacturing sectors.

Table 7-3. PECs based on CN_T for the iron and steel manufacturing sector from 2012 to 2016 (Ontario 2020)

Sites	Year	Total yearly loading (kg)[a]	PEC (Process effluent) (µg/L)	PEC (OTCW effluent) (µg/L)	PEC (Combined effluent) (µg/L)
1	2016	1135	1.12	0.12	NR
1	2015	5180	4.33	1.18	NR
1	2014	2125	1.82	0.38	NR
1	2013	3034	3.20	0.23	NR
1	2012	2142	2.54	NR	NR
2	2016	199	0.23	NR	0.18
2	2015	185	0.09	NR	0.19
2	2014	352	5.60×10^{-2}	0	0.38

Sites	Year	Total yearly loading (kg)[a]	PEC (Process effluent) (µg/L)	PEC (OTCW effluent) (µg/L)	PEC (Combined effluent) (µg/L)
2	2013	297	0.31	0	0.27
2	2012	303	0.46	NR	0.27
3	2016	52	0.09	NR	NR
3	2015	107	0.21	NR	NR
3	2014	76	0.15	0.20	NR
3	2013	158	0.26	0.28	NR
3	2012	31	0.26	NR	NR
4	2016	1370	16.20	NR	2.25
4	2015	1633	18.04	NR	3.81
4	2014	924	7.74	NR	3.42
4	2013	596	5.82	NR	2.83
4	2012	855	8.28	NR	2.19

Abbreviations: OTCW, once-through cooling water; NR, not reported.

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

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 three most commonly used anticaking cyanides are tetrasodium ferrocyanide and its decahydrate (CAS RN 13601-19-9), potassium ferrocyanide (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 as cited in Exall et al. 2011). The content of tetrasodium ferrocyanide per kilogram of road salt was reported to range from 30 to 124 mg/kg of NaCl (EC, HC 2001). More recent data show a lower concentration of tetrasodium ferrocyanide (i.e., from negligible to 0.045 mg tetrasodium ferrocyanide/kg of NaCl) in samples collected from provincial road authorities in British Columbia, Alberta, and Manitoba, but greater concentrations ranging from 17 to 102 mg tetrasodium ferrocyanide/kg of NaCl in samples collected from provincial road authorities in Ontario, Quebec, New Brunswick, and Newfoundland and Labrador (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

(EC, HC 2001; Exall et al. 2011). Photolysis experiments were conducted on three highway runoff samples collected in 2012. The samples 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 converted to free cyanide (expressed as CN_{WAD} measurements) with half-lives ranging from 2.2 to 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 to 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, not-detected to 270 µg/L), in an urban stream modified for stormwater conveyance (CN_T, not-detected to 45 µg/L) and in surface waters of four different sites receiving runoff from salt storage facilities (CN_T, not-detected to 200 µg/L; CN_{Free}, not-detected to 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 (**Error! Reference source not found.**4). Measured CN_T and CN_{WAD} concentrations depend 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. High CN_T concentrations were measured at locations studied in Ontario. However, low CN_T concentrations were measured in storm water at one location in the city of Edmonton, where an abrasive-salt mixture with a low salt content (7%) was used as an anti-skidding product (Novotny et al. 1998).

Table 7-4. 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	Edmonton[b] (n=5)	3 to 7	NA	Novotny et al. 1998
Parking lot runoff (alternative de-icer)[c] (2009)	Mississauga (n=21)	55 (ND to 847)	5 (ND to 444)	Exall et al. 2011
Parking lot runoff[c] (2009)	Mississauga (n=46)	45.5 (ND to 415)	5 (ND to 80)	Exall et al. 2011
Snowmelt snow storage facility[d] (2007 to 2008)	Richmond Hill (n=61)	30 (ND to 551)	10 (ND to 29)	Exall et al. 2011
Stormwater ponds[e] (2008 to 2009)	Peterborough, Richmond Hill, Toronto (n=65)	3 (ND to 49)	3 (ND to 36)	Exall et al. 2011
Bridge deck highway runoff (2010 to 2012)[f]	Burlington (n=24)	77 (28 to 245)	4 (ND to 17)	Exall et al. 2013
Parking lot runoff (2010 to 2012)[f]	Burlington (n=34)	92 (35 to 483)	<2 (2 to 24)	Exall et al. 2013

Abbreviations: ND, not-detected; NA, not available.

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

[b] The city of 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 to April 2009; the MDL was 10 µg/L for CN_T and CN_{WAD} in parking lot runoff.

[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 was 20 µg/L for CN_T and CN_{WAD} in snowmelts.

[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} in stormwater ponds was 17 µg/L and was lowered to 6 µg/L over the course of 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 to 20 µg/L over the course of the study in the different sample matrices. Approximately 40% of parking lot runoff samples showed CN_{WAD} concentrations greater than the parking lot runoff MDL of 10 µg/L, and since parking lot runoff 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 different MDLs, or 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 µg/L and less than 2 µg/L measured in runoff collected from a highway bridge and a parking lot in Burlington from 2010 to 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 to 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 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 ambient concentration of cyanides in the environment was assumed to be negligible and no default “background” value was incorporated in the calculation of PECs.

7.3 Characterization of ecological risk

The ecological portion of this screening assessment focuses on free cyanide, consisting of the cyanide anion (CN^-) and hydrogen cyanide (HCN), as well as precursors of free cyanide, including the 10 cyanide substances identified as priorities for assessment. Various lines of evidence to determine the potential for cyanides to cause harm in the Canadian environment were considered and conclusions were developed using a weight-of-evidence approach and precaution. Lines of evidence considered include those that support the characterization of ecological risk in the Canadian environment, including sources of cyanide exposure; results from risk quotient (RQ) calculations for key exposure scenarios; and information on fate, persistence and toxicity.

7.3.1 Risk quotient analysis

A RQ analysis, integrating measured concentrations and estimates of exposure with chronic toxicity information, was performed for the aquatic compartment to determine whether there is potential for ecological harm in Canada. RQs for the three exposure scenarios described in Section 7.3 are presented in **Error! Reference source not found.**5. RQs were calculated by comparing PECs, derived for the metal mining and iron and steel sectors and from the application of ferrocyanide-containing road salts (i.e., runoff from parking lots and highways), with the long-term PNEC (1.7 µg/L HCN) for aquatic organisms. The long-term PNEC was used for the RQ 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 to free cyanide over periods more representative of chronic exposure.

Where possible, PECs based on CN_{Free} and CN_{WAD} were used to calculate RQs. However, consistent with data availability, most RQs were calculated using PECs based on CN_T. Although use of CN_T concentrations may overestimate exposure to free cyanide, this approach was taken given the uncertainties in the data.

Table 7-5. Risk quotient (RQ) calculations in surface water based on a PNEC of 1.7 µg/L HCN for exposure scenarios within three sectors of activity

Sector	Details	PEC (µg/L; range)	RQ range	Range of PEC medians (µg/L)	Range of RQ medians
Metal mining	1 site[a] (CN_{WAD})	NA	NA	4.8	2.82
Metal mining	41 sites (cyanide users only; exposure sites only; CN_T)[b]	<MDL to 447	0.03 to 265	0.5 to 14	0.3 to 8.3
Metal mining	9 sites (cyanide users only; exposure sites only; CN_T)[c]	<MDL to 439	0.15 to 259.8	1-14	0.6 to 8.3
Iron and steel manufacturing	4 sites (process effluent only; CN_T)	0.06 to 18.0	0.03 to 10.6	0.21 to 8.28	0.13 to 4.9
Road salt runoff (parking lots)	3 sites (CN_T)	0.5 to 84.7	0.3 to 50.1	4.5 to 9.2	2.7 to 5.4
Road salt runoff (parking lots)	2 sites (CN_{WAD})	0.5 to 44.4	0.3 to 26.3	0.5	0.3
Road salt runoff (highway)	1 site (CN_T)	0.3 to 24.5	0.16 to 14.5	7.7	4.5

Abbreviations: MDL, method detection limit; NA, not applicable; PEC, predicted environment concentration; CN_T, total cyanide; CN_{WAD}, weak acid dissociable cyanide.

[a] This site corresponds to site 8 in Table 7-2.

[b] These sites correspond to CN users in Figure 7-2.

[c] These sites correspond to Figure 7-3 and are included within the 41 mining sites in Figure 7-2.

7.3.2 Consideration of the lines of evidence

The environmental fate and behaviour of cyanides are complex. Once released to the aquatic environment, cyanides may dissociate and release free cyanide (HCN and CN^-). HCN may then volatilize, biodegrade or form complexes of variable stability with many metals, among a series of other transformation processes. On the basis of the information available, HCN is not persistent in water; however, it is considered persistent in air. Ferrocyanides are considered persistent in soil and sediment. Free cyanide and precursors to free cyanide are not considered bioaccumulative.

Free cyanide is highly hazardous to aquatic organisms, and chronic exposure to low concentrations may cause adverse effects (PNEC = 1.7 µg HCN/L).

Environmental measurements of CN_{Free} and CN_{WAD} constitute the most direct line of evidence for evaluating potential ecological harm from the use, incidental manufacture, and release of cyanides. However, these measurements are not widely available, particularly compared to CN_T, which is more commonly measured. Measured CN_T concentrations include CN_{Free} and CN_{WAD} species, but also CN_{SAD} species that exhibit lower toxicity than HCN. Basing PECs on CN_T measurements is potentially conservative as it may overestimate the potential for toxicity (Redman and Santore 2012). However, there is evidence that CN_{SAD} species can transform in the environment and therefore may constitute a potential reservoir of free cyanide that could contribute to ecological harm from free cyanide near point sources.

In the metal mining sector, and more specifically gold and precious metals mining, some facilities use large quantities of NaCN for metal recovery. Facilities that use cyanides in their process report effluent concentrations under the MDMER and monitor CN_T concentrations in the receiving environment as part of EEM studies. In some cases, CN_{WAD} and CN_{Free} are also reported. Cyanides in effluent may be treated using passive attenuation or active treatment systems (e.g., biodegradation or oxidation) prior to discharge. At 6 sites, average or median concentrations of CN_{WAD} and CN_{Free} in areas receiving effluent appear to exceed the PNEC (Table 7-2). However, the dataset has several uncertainties such as small sample sizes, and, with the exception of one site, low detection frequency, and the concentrations in corresponding reference areas were comparable and also exceeded the PNEC. Monitoring data for CN_T was, by comparison, more readily available, and CN_T was frequently detected in the receiving environment in concentrations exceeding the PNEC. These data tend to show higher cyanide concentrations (CN_{Free}/CN_{WAD} and CN_T) in water samples receiving effluent from mining activities and in concentrations that suggest there is potential for ecological harm with releases of cyanides from certain facilities in this sector.

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 Ontario MECP and indicate that predicted concentrations of cyanides near the point of discharge of various continuous effluent streams by certain facilities may exceed the PNEC that suggest there is potential for ecological harm with releases of cyanides from certain facilities in this sector.

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 aquatic organisms if runoff is released directly to surface waters. These results support the findings of the 2001 road salt assessment based on modelled releases, which determined that at the 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).

7.3.3 Sensitivity of conclusion to key uncertainties

Most environmental measurements of cyanides available for this ecological assessment were for $CN_{T.}$ It was not possible to reliably estimate the content of CN_{WAD} and CN_{Free} within a given measurement of CN_T. Depending on the local environmental conditions, CN_T may provide a conservative measure of CN_{Free} in the environment and an overestimation of risk. However, as the fate of cyanides in the environment is complex and depends on a variety of site-specific processes that influence partitioning, the degree to which this uncertainty may cause over estimation of potential risk is undetermined.

Where CN_{WAD} and CN_{Free} were measured, proper timing and sampling methods were important. Indeed, HCN may volatilize from samples if the collection methods are inappropriate, as hypothesized by Exall et al. (2013). This could lead to an underestimation of environmental concentrations, and subsequently an underestimation of ecological risk. Additionally, the timing of the sample collection is important for measuring CN_{WAD} or CN_{Free} as the photolysis rate can vary throughout the day.

Another source of uncertainty with regard to cyanide analysis is the often high detection limits that frequently exceeded the long-term PNEC for surface water. Measurements considered non-detects were transformed to half detection limits, and in some cases those values exceeded the PNEC of 1.7 µg HCN/L. A non-detect does not signify that free cyanide or other cyanides were absent from a sample, so it is therefore difficult to accurately determine how many water samples exceeded the PNEC. The half detection limit approach is commonly used to address non- detects. Alternative methods for generating descriptive statistics for datasets containing non-detect measurements described by Helsel (2012) and Bolks et al. (2014) were explored. For datasets with less than 80% non-detects, estimates of the mean and median PECs were generated either using the Kaplan-Meier, Maximum Likelihood Estimation, or robust Regression on Order Statistics methods depending on their distributions, sample sizes, proportions of non-detect data, and number of MDLs. Results from alternative methods tended to show a greater difference in mean and median PECs between exposure and corresponding reference areas.

The chronic (long-term) toxicity dataset for the aquatic environment was suitable to derive a PNEC using an SSD approach 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 converted to HCN.

There are uncertainties with regard to potential background concentrations of cyanides in Canadian surface waters and whether CN_T concentrations fluctuate seasonally. Cyanides are generally monitored close to anthropogenic sources and results for pristine areas were seldom available. A number of detected CN_T measurements (20%) collected from reference areas by cyanide users as part of the EEM provisions were above the PNEC. These elevated reference area concentrations could be explained by confounding factors such as algal blooms or forest fires, or 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 (HCN and NaCN) and the metal-cyanide complexes. The latter were further divided into the gold- or silver-cyanide complexes (potassium dicyanoargentate, and potassium dicyanoaurate); the single-iron cyanide complexes (tetrasodium ferrocyanide, tripotassium ferricyanide, and tetrapotassium ferrocyanide); and the multi-iron cyanide complexes (ferric ferrocyanide, ferric ammonium ferrocyanide, and 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 NHPs, cosmetics and pesticides. Some are also approved food additives with limited permitted uses, may be used as a component in the manufacture of food packaging materials, and may be used as a component in an incidental additive used in food processing establishments. The non-confidential uses reported in response to a notice issued under CEPA section 71 (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 HCN in ambient air, and Health Canada has quantified total cyanide (CN_T) in drinking water distribution systems and the Canadian diet.

The United States National Health and Nutrition Examination Survey 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 exposure 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. 2018).

For the free/simple cyanides subgroup, refined estimates of potential exposure to free cyanide for the relevant routes of exposure are presented. For the single iron-cyanide complexes, upper-bounding estimates of potential exposure from products available to consumers for the relevant routes of exposure are presented.

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

Environmental media and food

Cyanide levels in environmental media and food are typically reported as total cyanide or HCN. Due to the photodissociation of ferri- and ferrocyanides when exposed to UV light, there are no studies with measured levels of tetrasodium ferrocyanide, tripotassium ferricyanide or tetrapotassium ferrocyanide in environmental media in Canada. Metal-cyanide complexes in this screening 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 CN^- (Dzombak et al. 2006a). However, due to the photolysis of ferri- and ferrocyanides when exposed to UV light, ferrocyanides in water depths above 50 to 100 cm, and surface layers of soil are likely to dissociate and release CN^- (Broderius and Smith 1980; Little and Calfee 2000; 2002, 2003; Johnson et al. 2015). High amounts of ferrocyanides are found in the soils surrounding United States 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). Predicted environmental concentration in soil (PECsoil) values for cyanide, assumed to be liberated from ferrocyanide by photodegradation, are presented in the PSL assessment of road salts (EC, HC 2001). Based on the assumptions in the PSL Tier 1 worst case PECsoil and default soil ingestion rates for a child (0.5 year to 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, dendritic salt and wine), as proscribed in the *List of Permitted Anticaking Agents* and the *List of Permitted Food Additives with Other 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 1978, 1985). Dietary exposure to tetrapotassium ferrocyanide 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. Tetrasodium ferrocyanide may be used as a component in an incidental additive used in food processing establishments, with no exposure expected (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 anticaking agent in NHPs, as well as with an ADI of up to 0.025 mg/kg bw/day. Tetrasodium ferrocyanide is listed as being present as a non-medicinal ingredient in a limited number of oral and topical NHPs in the Licensed Natural Health Products Database (LNHPD) (personal communication, emails from the HPFB, HC, to the ESRAB, HC, dated March 2016; unreferenced).

Tetrasodium ferrocyanide is used in a limited number of cosmetics, 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 Consumer Hazardous Products Safety Directorate (CHPSD), 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 anticaking agent in NHPs, as well as with an ADI of up to 0.025 mg/kg bw/day calculated as sodium ferrocyanide; however, it is not listed as being present as such in 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 oral

NHPs licensed as homeopathic medicines in the LNHPD (personal communication, emails from the HPFB, HC, to the ESRAB, HC, dated March 2016; unreferenced).

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 (MSDS 2009), 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, and potassium ferric ferrocyanide)

Environmental media and food

Cyanide levels in environmental media and food are typically reported as total cyanide or HCN. Due to the photodissociation of ferri- and ferrocyanides when exposed to UV light, there are no studies with measured levels of ferric ferrocyanide, ferric ammonium ferrocyanide or potassium ferric ferrocyanide in environmental media in Canada. Metal-cyanide complexes in this screening 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 CN^-(Dzombak et al. 2006a). However, due to the photolysis of ferri- and ferrocyanides when exposed to UV light, ferrocyanides in water depths above 50 to 100 cm, and surface layers of soil are likely to dissociate and release CN^- (Broderius and Smith 1980; Little and Calfee 2000, 2002, 2003; Johnson et al. 2015). 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 as a component in the manufacture of some food packaging materials, for which there is no direct contact with the food (personal communication, emails from the HPFB, HC, to the ESRAB, HC, dated March 2016; unreferenced).

Products available to consumers

Ferric ferrocyanide is listed in the NHPID with a non-medicinal role for topical (external) use only as a colour additive in NHPs and is listed as being present as a non-medicinal ingredient in a limited number of 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 NHPs in the LNHPD. Ferric ammonium ferrocyanide is listed in the NHPID with a non-medicinal role for topical use only as a colour additive and is listed as being present as such in a limited number of topical NHPs in the LNHPD (personal communication, emails from the HPFB, HC, to the ESRAB, HC, dated March 2016; unreferenced).

Ferric ferrocyanide and ferric ammonium ferrocyanide are widely used as pigments/colourants in personal care products (Environment Canada 2013; personal communication, emails from the CHPSD, 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 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 (potassium dicyanoargentate and potassium dicyanoaurate)

There are no studies with measured levels of potassium dicyanoargentate or potassium dicyanoaurate in environmental media in Canada, likely due to the photodissociation of these substances to CN^- when exposed to UV light. 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, during which they are reduced to positively charged cations deposited onto the base metal (Kohl 2010; Schlesinger 2010; Brumby et al. 2012; Renner et al. 2012). As such, the use of these substances as electroplating reagents is not expected to be a source of exposure to the general population.

Free/simple cyanides subgroup (hydrogen cyanide and sodium cyanide)

Environmental media and food

NaCN 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. 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)[9].

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. 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 0.0008 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 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

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[9] 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).

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 screening 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

An important process for free cyanide loss from water is volatization, resulting in a decrease of free cyanide concentrations in water. In addition, most free cyanide released to soil will form ferrocyanides due to the strong affinity of CN^- for iron and the high abundance of iron in soils (Dzombak et al. 2006a). However, due to the photolysis of ferri- and ferrocyanides when exposed to UV light, ferrocyanides in surface layers of water and soil are likely to dissociate and release CN^- (Broderius and Smith 1980; Little and Calfee 2000, 2002, 2003; Johnson et al. 2015). CN_T has been measured in drinking water in Canada for six provinces (personal communication, emails from the Water and Air Quality Bureau, HC, to the ESRAB, HC, dated October 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 to 0.19 mg/L, with an average of 94.3% of samples at or below the detection limit (0.001 to 0.02 mg/L). The Canadian guideline for CN_T in drinking water is a maximum acceptable concentration of 0.2 mg/L (Health Canada 2014).

Food and beverages

Many plant-based foods contain low levels of naturally occurring CGs (e.g., linamarin, amygdalin and dhurrin), which have the potential to release HCN (FSANZ 2014). Examples of foods or components of foods that contain CGs include lima beans, apple seeds, cassava, bamboo, stone fruit pits and flaxseed. Raw apricot kernels, which are the seeds found inside the pits of apricots, may contain higher levels of cyanogenic glycosides. As a result, Health Canada has established a maximum level of 20 ppm total extractable cyanide in apricot kernels in the *List of Contaminants and Other Adulterating Substances in Foods,* even though they are not a food that is commonly consumed (Canada 1978).

Estimates of dietary exposure to total HCN[10], converted to a total CN basis, from CGs in foods for the general Canadian population were derived by Health Canada's Food Directorate. Detailed dietary intakes by food type and age-sex group are provided in Table B-1 of Appendix B. 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 (Honig et al. 1983; Gupta 1987). 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 to 178 mg HCN/kg), apple sauce (n = 3; mean of 3.9 mg HCN/kg; range of 3.6 to 4.1 mg HCN/kg) and green peas (n = 1; 20 mg HCN/kg).

Food consumption data from the Canadian Community Health Survey – 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 to 0.00379 mg/kg bw/day and from 0.00091 to 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 to 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% to 70% and 11% to 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 for CN established by the FAO/WHO Expert

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[10] 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 CGs followed by basification to release HCN/CN^- (FAO/WHO 2012).

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 NHPs licensed as homeopathic medicines in the LNHPD (personal communication, emails from the HPFB, HC, to the ESRAB, HC, dated March 2016; unreferenced).

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, and 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 minutes to 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, 0.25, 2.5, 25 mg/kg bw/day[11]) 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

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[11] Assumes a bodyweight of 12 kg and a food consumption rate of 300 g/day (as per: Health Canada 1994).

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 (0.05%), which is equivalent to 25 mg/kg bw/day, was used to obtain an ADI of 0.025 mg/kg bw/day (basis for uncertainty factors not given) (FAO/WHO 1975).

Multi-iron cyanide complexes (CAS RNs 14038-43-8, 25869-98-1, and 25869-00-5)

Multi-iron cyanide complexes are very poorly absorbed. Following an oral exposure of 10 mg (36 to 40 mg/kg bw) of ferric ferrocyanide or potassium ferric ferrocyanide in rats (n = 2 to 5), absorption was determined to be 0.21% to 0.49% and whole body retention after seven days was 0.01% to 0.7% (Nielsen et al. 1990a). Likewise, following an oral dose of 500 mg (6.2 to 7.1 mg/kg bw) of potassium ferric ferrocyanide in humans (n = 3, male), absorption was 0.25% to 0.42% and whole body retention after seven days was 0.03% to 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” 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, and 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 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 RfD 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 and 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 sulphur transferase), which is ubiquitously expressed. Catalysis by rhodanese forms 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 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 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).

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 (US EPA 2010; Duarte-Guterman et al. 2014).

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 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 CN^-'s inhibition of ATP synthesis, whereas the latter is caused by the SCN^-'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 as cited in US EPA 2010); 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 as cited in US EPA 2010); a NOAEL and LOAEL of 0.8 mg/kg-bw/day and 1.2 mg/kg bw/day, respectively, for increased triiodothyronine 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 as cited in US EPA 2010). 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 CGs (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. This PoD used in risk characterization 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 mg/kg bw/day and 1.9 mg/kg bw/day, respectively [the BMDL is the 95% lower confidence limit of the BMD; the benchmark response, 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 mg/kg bw/day and 3.2 mg/kg bw/day) are consistent with a more recent gavage study that concluded that male reproductive toxicity occurs in rats at 1.2 mg/kg bw/day 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 HCN and cyanide salts (e.g., NaCN) was conducted by the US EPA (2010). The PoD of 2.5 mg/m^3 used in risk characterization 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 to 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).

NaCN has been previously evaluated in Canada. Health Canada 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 lower PoD of 1.9 mg/kg bw/day selected for use in this screening assessment is based on a more recent drinking water study (NTP 1993). In addition to drinking water, Health Canada also re-evaluated NaCN in pesticides in 2006 (Health Canada 2006), considering information from the US EPA Reregistration Eligibility Decision (US EPA 1994a). As part of the re-evaluation, additional risk reduction measures were proposed for pesticides to further protect handlers and bystanders (Health Canada 2006).

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, and 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, exposure to tetrasodium ferrocyanide from ingestion of soil is expected to be minimal, based on the PSL assessment of road salts in Canada (EC, HC 2001) and the default soil ingestion rates for a child (0.5 to 4 years). Tetrasodium ferrocyanide and tetrapotassium ferrocyanide are approved food additives with a limited number of permitted uses. Exposure from use of tetrasodium ferrocyanide as a non-medicinal ingredient in oral NHPs and of tetrapotasium ferrocyanide as a medicinal ingredient in oral NHPs licensed as homeopathic medicines is not expected to exceed the ADI of up to 0.025 mg/kg bw/day. For the dermal route, tetrasodium ferrocyanide is found in a limited number of cosmetics (bath salts and anti-wrinkle cream) and NHPs (as a non-medicinal ingredient in a limited number of products). Limited data indicated that they have intermittent uses. Limited data also indicate low dermal absorption, and because the cyanides form strong molecular bonds with iron in these complexes, they are highly stable and have low bioavailability. Therefore, exposure to tetrasodium ferrocyanide is not associated with a

risk of the hazardous effects of cyanide. Overall, risk to human health is not expected following exposure to these substances.

Multi-iron cyanide complexes (CAS RNs 14038-43-8, 25869-98-1, and 25869-00-5)
Exposure of the general population of Canada to the ferric ferrocyanide and ferric ammonium ferrocyanide through drinking water, soil and the use of products available to consumers, such as personal care products, paints and coatings, and NHPs, is expected to occur through the oral, dermal and inhalation 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. Potassium ferric ferrocyanide was not identified in environmental media or in products used by the general population in Canada. Based on these considerations, risk to human health is not expected.

Gold- or silver-cyanide complexes (CAS RNs 13967-50-5 and 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 and 143-33-9)
Exposure of the general population of Canada to HCN and NaCN from outdoor and indoor air, drinking water and food is expected to occur through the oral and inhalation routes. 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
Oral exposure: 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; BMDL, benchmark dose lower limit

[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 in the general population using exposure estimates listed in Table B-1 of Appendix B. Flaxseed and apple sauce were identified as the main food sources for children 1 to 3 years of age, and flaxseed and green peas were identified as the main sources for adult males (i.e., 19 years and above) (personal communication, emails from the HPFB, HC, to the ESRAB, HC, dated July 2016; unreferenced). 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, individuals that consume increased amounts of food containing free/simple cyanides may have an elevated exposure potential (Table B-2 Appendix B).

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.

Overall, this information indicates that given the exposure and hazard data for substances in the cyanides group, 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 tables below.

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

Key source of uncertainty	Impact [a]
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.	+
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 has not been the subject of any international assessment; therefore, it is not associated with any previously published critical effect level.	+/-

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

Table 8-3. Sources of uncertainty in the risk characterization of the free/simple cyanides

Key source of uncertainty	Impact [a]
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.	+
There are no chronic animal studies for oral exposure.	+/-
There are no sub-chronic or chronic animal studies for inhalation exposure.	+/-
The 90-day 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.	+/-

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

9. Conclusion

Considering all available lines of evidence presented in this screening assessment, there is risk of harm to the environment from free cyanide and precursors of free cyanide. It is concluded 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 also concluded 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.

Considering all the information presented in this screening assessment, it is concluded that the 10 cyanide substances 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.

It is therefore concluded that free cyanide and precursors of free cyanide meet one or more of the criteria set out in section 64 of CEPA. It has also been determined that free cyanide and precursors of free cyanide meet the persistence criteria but not the bioaccumulation criteria as set out in the *Persistence and Bioaccumulation Regulations* of CEPA.

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Appendix A. Aquatic toxicity tables

Table A-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-day EC_{10} (reproduction, number of eggs per individual)	3	Lind et al. 1977
Aquatic Plant	Gibbous duckweed (*Lemna gibba*)	7-day EC_{10} (growth inhibition)	3.72	ECHA c2007–2015
Invertebrate	Cladocerans (*Moinodaphnia macleayi*)	5-day NOEC (reproduction)	6	Rippon et al. 1992
Fish	Rainbow trout (*Oncorhynchus mykiss*)	20-day EC_{10} (growth at 12°C)	9	Kovacs and Leduc 1982
Invertebrate	Amphipod (*Gammarus pseudolimnaeus*)	83-day MATC (reproduction)	15.2	Oseid 1979
Fish	Brook trout (*Salvelinus fontinalis*)	90-day EC_{10} (growth)	26	Koenst et al. 1977
Invertebrate	Sowbug (*Asellus communis*)	112-day NOEC (growth)	29	Oseid 1979
Algae	*Scenedesmus quadricauda*	8-day NOEC (population)	31.16	Bringmann and Kuhn 1980
Fish	Sheepshead minnow (*Cyprinodon variegatus*)	28-day MATC (growth)	37.1	ECOTOX 2000; Schimmel 1981 as cited in ECOTOX 2000
Invertebrate	*Ceriodaphnia dubia*	7-day EC_{10} (reproduction)	43.6	Manar et al. 2011
Algae	*Pseudokirchneriella subcapitata*	72-hour EC_{10} (growth)	57.1	Manar et al. 2011
Algae	Blue-green algae (*Microcystis aeruginosa*)	8-day NOEC (population)	72.7	Bringmann and Kuhn 1978

Appendix B. Food exposure estimates

Table B-1. Total cyanide exposure (usual intakes) for "all persons". Exposure estimates presented as mean and 90th percentile (p90), with the 95% confidence interval. Estimates marked with "E" have high sampling variability (coefficient of variation from 16.6-33.3%) and should be interpreted with caution.

Age (years) Sex (M=male; F=female)	Number of respondents consuming HCN containing foods	Mean exposure estimate for "all persons" (µg/kg bw/day)	p90 exposure estimate for "all persons" (µg/kg bw/day)
1-3	1409 / 2110 (67%)	3.79 (3.20, 4.55)	11.74E (7.21, 16.42)
4-8	2118 / 3058 (69%)	1.52 (1.34, 1.72)	3.49 (2.94, 4.09)
9-13 (M)	1275 / 2004 (64%)	0.70 (0.63, 0.79)	1.51 (1.36, 1.76)
14-18 (M)	1201 / 2230 (54%)	0.44 (0.38, 0.52)	0.91 (0.75, 1.15)
19-30 (M)	744 / 1766 (42%)	0.62 (0.45, 0.79)	1.43E (1.06, 2.05)
31-50 (M)	973 / 2527 (39%)	0.59E (0.41, 0.84)	1.15 (0.94, 1.56)
51-70 (M)	873 / 2477 (35%)	1.00 (0.82, 1.21)	2.60 (2.06, 2.93)
>70 (M)	520 / 1472 (35%)	1.22 (0.93, 1.54)	3.03E (2.25, 4.44)
9-13 (F)	1229 / 1880 (65%)	0.77 (0.65, 0.90)	1.30 (1.03, 1.62)
14-18 (F)	1241 / 2194 (57%)	0.52 (0.45, 0.59)	1.26 (1.07, 1.49)
19-30 (F)	910 / 1952 (47%)	0.39 (0.34, 0.44)	1.13 (0.93, 1.38)
31-50 (F)	1054 / 2608 (40%)	0.85 (0.64, 1.13)	1.76E (1.14, 2.56)
51-70 (F)	1194 / 3062 (39%)	1.56 (1.23, 1.88)	3.57 (2.90, 3.96)
>70 (F)	913 / 2527 (36%)	1.28 (1.02, 1.62)	2.85E (2.21, 4.43)

Table B-2. Total cyanide exposure (usual intakes) for "eaters only". Exposure estimates presented as mean and 90th percentile (p90), with the 95% confidence interval. Estimates marked with "E" have high sampling variability (coefficient of variation from 16.6-33.3%) and should be interpreted with caution.

Age (years) Sex (M=male; F=female)	Number of respondents consuming HCN containing foods	Mean exposure estimate for "eaters only" (µg/kg bw/day)	p90 exposure estimate for "eaters only" (µg/kg bw/day)
1-3	1409 / 2110 (67%)	6.00 (5.17, 7.06)	18.98 (16.52, 21.40)
4-8	2118 / 3058 (69%)	2.20 (1.95, 2.47)	5.29 (3.94, 6.70)
9-13 (M)	1275 / 2004 (64%)	1.11 (1.01, 1.21)	2.47 (1.80, 3.10)
14-18 (M)	1201 / 2230 (54%)	0.82 (0.70, 0.96)	1.71 (1.38, 2.34)
19-30 (M)	744 / 1766 (42%)	1.47 (1.15, 1.80)	4.25E (2.62, 6.11)
31-50 (M)	973 / 2527 (39%)	1.54E (1.10, 2.22)	2.85 (2.51, 4.03)
51-70 (M)	873 / 2477 (35%)	2.81 (2.38, 3.32)	6.46 (4.67, 7.86)
>70 (M)	520 / 1472 (35%)	3.58 (2.77, 4.43)	8.34E (6.05, 12.67)

9-13 (F)	1229 / 1880 (65%)	1.17 (0.99, 1.37)	2.40E (1.57, 4.87)
14-18 (F)	1241 / 2194 (57%)	0.93 (0.82, 1.05)	2.07 (1.62, 2.37)
19-30 (F)	910 / 1952 (47%)	0.81 (0.74, 0.88)	1.67 (1.45, 1.97)
31-50 (F)	1054 / 2608 (40%)	2.21 (1.66, 2.83)	3.96 (3.32, 5.65)
51-70 (F)	1194 / 3062 (39%)	3.96 (3.19, 4.72)	9.83E (6.26, 13.41)
>70 (F)	913 / 2527 (36%)	3.61 (2.93, 4.47)	12.32 (7.68, 14.83)