Draft Screening Assessment

Copper and Its Compounds

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 copper and its compounds. Twenty-six of these substances were identified as priorities for assessment as they met categorization criteria under subsection 73(1) of CEPA or were considered a priority on the basis of other human health concerns. Eleven additional substances were identified for further consideration following prioritization of the Revised In Commerce List. This draft screening assessment focuses on the copper moiety and therefore considers copper in its elemental form, copper-containing substances, and copper released in dissolved, solid, or particulate form. This screening assessment therefore considers copper-containing substances beyond those identified as priorities for assessment.

Copper is naturally occurring in the environment and moves through various compartments by geochemical and biogeochemical cycling. Anthropogenic activities may contribute copper to the environment during the production of metallic copper or other copper-containing substances (e.g., mining, extracting, processing of ores, and smelting and refining), through other industrial activities (e.g., wastewater treatment), and through the use of products containing copper. This assessment considers combined exposure to the copper moiety from natural or anthropogenic sources, whether it is present in environmental compartments, food, or products. All substances that have the potential to dissolve, dissociate, or degrade to release copper through various transformation pathways can potentially contribute to the exposure of living organisms to bioavailable forms of copper.

Pursuant to CEPA section 71 notices, information was reported for 19 copper substances that were manufactured or imported above the reporting threshold of 100 kg per year in either 2011 or 2012 to 2015. No information above the reporting threshold was received for 15 additional copper substances that were surveyed. A total of over 10 000 000 kg was reported for both manufacturing and imported quantities. These substances are used in a wide variety of products and applications including: arts, crafts and hobby materials; automotive care; building and construction materials; cosmetics; children’s toys; cleaning products; electrical and electronic uses; food packaging; ink, toner and colourants; natural health products and drugs; agricultural products (non-pesticidal); paints and coatings; pest control substances; plastics; textiles; and other industrial and commercial uses.

The ecological exposure assessment focuses on the top sectors of activity as determined by the greatest quantities of copper released to the environment. Specifically, exposure scenarios were developed for the metal mining, base metal smelting, and wastewater treatment sectors.

The ecological effects assessment focuses on the dissolved fraction of copper as this is typically better correlated with ecotoxicity. Where possible, toxicity modifying factors (i.e., hardness, pH, dissolved organic carbon, and temperature) were considered since the portion of dissolved copper is dependent on these water chemistry conditions.

The outcomes of the ecological risk characterization for the metal mining, base metal smelting, and wastewater treatment sectors indicate ecological risks in the aquatic compartment. This was determined by using a weight-of-evidence approach, including a comparison of the predicted environmental concentrations (PECs) to the predicted no-effect concentrations (PNECs) to generate risk quotients (RQs), and by assessing the frequency and magnitude of RQs exceeding a value of one.

Considering all available lines of evidence presented in this draft screening assessment, there is risk of harm to the environment from copper and its compounds. It is proposed to conclude that copper and its compounds meet the criteria under paragraph 64(*a*) of CEPA as they are entering or may enter the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. However, it is proposed to conclude that copper and its compounds 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.

Copper is an essential element for human health, yet elevated intake may result in adverse health effects. In instances of excess chronic oral ingestion of copper, liver damage has been observed as the principal health effect. For that reason, guidelines exist to provide limits against excess copper intake in the general population. In a human volunteer study, no effects were observed up to doses of 10 mg per day for 12 weeks. This study is the basis for the upper tolerable intake level (UL) established by the Institute of Medicine (IOM) for North American populations. The IOM UL is also the basis for limits of copper in multi-vitamin/mineral supplements and supplemented foods as well as the basis for the copper soil quality guideline for copper and the toxicological reference values (TRVs) developed by Health Canada under the Federal Contaminated Site Risk Assessment Program. With respect to exposures via the inhalation route, transient acute respiratory effects were identified in laboratory animals after a single inhaled high dose of copper. Repeat-doses resulted in signs of inflammation of the lungs; however, all effects were reversible once dosing ended.

All Canadians can be exposed to copper through environmental media, food, drinking water and products available to consumers. Food is the main source of intake, and toddlers have the highest intakes when normalized by body weight. To characterize risk, estimates of daily exposure from environmental media, food and drinking water were derived for the general population and for those living near point sources of release (e.g., mines, smelters and refineries). These estimates were compared to the IOM UL and there were no exceedances for either group. Exposure estimates were also derived for the general population from use of products available to consumers. Oral exposure estimates to copper from the use of arts and craft products, children’s toys, cosmetics, and natural health products did not exceed the IOM UL. There is also potential for inhalation exposure to copper in airborne particulate matter for the general population and for those living near point sources of release. Measured air concentrations were compared to the levels at which inhalation-specific health effects were seen, and margins of exposure were considered adequate for copper in particulate matter. Inhalation exposure scenarios from the use of products available to consumers were also derived. Margins of exposure for inhalation of copper from cleaning products, cosmetics, and spray paints were considered adequate to address uncertainties in the health effects and exposure databases. On the basis of the information presented in this draft screening assessment, it is proposed to conclude that copper and its compounds do not meet the criteria under paragraph 64(*c*) of CEPA as they are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health.

It is therefore proposed to conclude that copper and its compounds meet one or more of the criteria set out in section 64 of CEPA. It is also proposed that copper and its compounds meet the persistence criteria but not the bioaccumulation criteria as set out in the *Persistence and Bioaccumulation Regulations* of CEPA.

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List of Tables and Figures

1. Introduction

Pursuant to section 68 or 74 of the *Canadian Environmental Protection Act, 1999* (CEPA) (Canada 1999), the Minister of the Environment and of the Minister of Health have conducted a draft screening assessment of copper and its compounds to determine whether these substances present or may present a risk to the environment or to human health. Twenty-six substances (listed in Appendix A) were identified as priorities for assessment as they met categorization criteria under subsection 73(1) of CEPA or were considered a priority on the basis of other human health concerns (ECCC, HC [modified 2017]). Eleven additional substances were identified for further consideration following prioritization of the Revised In Commerce List (R-ICL)[1] (Health Canada [modified 2017]).

This draft screening assessment focuses on the copper moiety[2] and therefore considers copper in its elemental form, copper-containing substances, and copper released in dissolved, solid, or particulate form. It considers all substances that have the potential to dissolve, dissociate or degrade to release copper through various transformation pathways and that can potentially contribute to the combined exposure of humans and ecological receptors to copper. For simplicity, the copper moiety is referred to as "copper" in the assessment. Specific copper-containing substances will be identified by name or by Chemical Abstracts Service Registry Number (CAS RN) where relevant. The existence of multiple pathways for copper to enter organisms makes all forms of copper potential contributors to exposure, whether they are soluble or not. This screening assessment therefore considers all copper-containing substances and is not limited to the 37 substances listed in Appendix A.

This assessment only considers effects associated with copper and does not address other elements or moieties that may be present in certain copper-containing substances (e.g., cyanide or iodine). Some of these other elements or moieties have been addressed through previous assessments conducted as part of the Priority Substances List program under CEPA or are being addressed via other initiatives of the Chemicals Management Plan (CMP). Engineered nanomaterials containing copper are not explicitly considered in exposure scenarios of this assessment, but measured environmental concentrations of copper could include engineered nanomaterials containing copper or copper from these sources. However, health effects associated with nanoscale copper are not being considered in this screening assessment. Copper

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[1] The Revised In Commerce List (R-ICL) is a list of substances that are known to have been authorized for use in commerce in Canada between 1987 and 2001. As the substances are present in Canada, the government is addressing them for potential impact on human health and the environment in order to risk-manage them, if required.

[2] For the purpose of this document, "moiety" signifies a part of a molecule. A moiety is a discrete chemical entity, identified from a parent compound or its transformation products, that is expected to have toxicological significance.

is an essential nutrient for human health; this assessment evaluates the potential for harm from elevated copper exposure rather than deficiency or essentiality.

This draft screening assessment includes consideration of information on chemical properties, environmental fate, hazards, uses and exposures, including additional information submitted by stakeholders. Relevant data were identified up to January 2018, and additional data were submitted by stakeholders up to February 2018. Empirical data from key studies, as well as results from models, were used to reach proposed conclusions. When available and relevant, information presented in assessments from other jurisdictions was considered.

This draft screening assessment was prepared by staff in the CEPA Risk Assessment Program at Health Canada and Environment and Climate Change Canada and incorporates input from other programs within these departments. The ecological and human health portions of this assessment have undergone external review or consultation. Comments on the technical portions relevant to the environment were received from Dr. Peter Campbell (Institut national de la recherche scientifique, INRS), Dr. James McGeer (Wilfrid Laurier University), and Dr. Kevin Wilkinson (Université de Montréal). Comments on the technical portions relevant to human health were received from Dr. Richard Manderville (University of Guelph), Dr. Bonnie Stern (consultant), and Dr. Carl Keen (University of California). While external comments were taken into consideration, the final content and outcome of the screening assessment remain the responsibility of Health Canada and Environment and Climate Change Canada.

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

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

2. Identity of substances

Copper-containing substances in commerce or incidentally produced belong to various categories, including elemental copper, inorganic metal compounds, organic-metal salts, organometallic compounds, and unknown or variable composition, complex reaction products, or biological materials (UVCBs). Copper-containing organic metal salts or organometallic substances may dissolve, dissociate, or degrade completely or partially to release organic or organometallic transformation products and copper. The Chemical Abstracts Service Registry Numbers (CAS RN[4]), Domestic Substances List (DSL) or R-ICL names, common names, and categories for the 37 substances identified as priorities for assessment are presented in Appendix A.

3. Physical and chemical properties

Copper is a non-magnetic, chalcophilic, soft metal (Reimann and de Caritat 1998). Copper has four main oxidation states including Cu(0) (i.e., elemental copper), Cu (I) (i.e., cuprous ion, Cu^+), Cu (II) (i.e., cupric ion, Cu^{2+}) and Cu (III) (Georgopoulos et al. 2002). It exists naturally in its elemental form and as a constituent of many compounds. Copper (II) is the most stable oxidation state in typical oxic waters (Nordberg et al. 2015). Copper (II) commonly forms salts, most importantly with hydroxide in fresh water (e.g., copper hydroxide, $Cu(OH)_2$) and with chloride in saline water (e.g., copper (II) chloride, $CuCl_2$) (WHO 1998). It can also be a constituent of various organometallics (e.g., copper gluconate) and UVCBs (e.g., Pigment Green 7).

Copper may be released through the dissolution or dissociation of copper-containing substances, which may be characterized using water solubility data of the substances or the acid dissociation constant (K_a) of the organic component of organic-metal salts. Substance-specific values for these properties are presented in Appendix D, Table D-1, where available. The values presented for the molar masses of organometallic and organic-metal salt UVCBs are approximations, based on simple addition of components in the substance name. Certain partition coefficients that pertain to copper as an ion (as compared to bound copper within a substance) are available in Appendix D, Table D-2, and are discussed in the environmental fate section.

The water solubility of copper-containing substances, when available, ranged widely, from very low solubility to very high solubility (i.e., greater than 1.0×10^6 mg/L) (Table D-1). Vapour pressure data were available for two copper-containing substances; volatility

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[4] The Chemical Abstracts Service Registry Number (CAS RN) is the property of the American Chemical Society, and any use or redistribution, except as required in supporting regulatory requirements and/or for reports to the Government of Canada when the information and the reports are required by law or administrative policy, is not permitted without the prior, written permission of the American Chemical Society.

is negligible for copper sulfate, while elemental copper is non-volatile (Boone et al. 2012; CET 2006; ATSDR 2004).

4. Sources and uses

4.1 Natural sources

Copper is a naturally occurring element in the earth’s crust. Copper concentrations in the upper continental crust have been determined to average about 22 mg/kg and to range between 2 and 90 mg/kg (Reimann and de Caritat 1998; Rauch and Pacyna 2009). Copper exists naturally in its elemental (metallic) form and in many minerals, including chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), chalcosite (Cu_2S), malachite ($Cu_2CO_3(OH)_2$), covellite (CuS), digenite (Cu_9S_5) and tetrahedrite ($Cu_{12}Sb_4S_{13}$) (Reimann and de Caritat 1998).

Natural sources of copper emissions to the atmosphere include windblown soil particles, sea salt spray, volcanoes, forest and brush fires, meteoritic dust, and sources from biogenic processes (e.g., volatile plant exudates). Richardson et al. (2001) estimated natural emissions of copper to the atmosphere from the aforementioned sources, except those from biogenic processes due to insufficient data. For Canada, the estimated median natural emission rate was 2600 tonnes (t) of copper per year, representing less than 6% and less than 1% of the fraction of estimated North American (5.0×10^4 t) and global emissions (2.0×10^6 t), respectively. It was found that natural releases largely originate from soil particle flux and, to a lesser extent, from sea salt spray, volcanoes, fires, and negligibly from meteoritic dust. Atmospheric deposition and introduction of copper into surface waters and soils as a result of natural sources are reflected in the geochemical background levels in these environmental compartments. Background levels are considered in the estimation of copper exposure to ecological receptors in Section 7.2.

4.2 Anthropogenic sources

4.2.1 Copper production

Copper can be found in sulfide deposits (e.g., as chalcopyrite), in carbonate deposits (e.g., as azurite), in silicate deposits (e.g., as chrysycolla) and as elemental copper (ICSG 2017). Copper ore was produced in the following provinces and territories in 2015 (from largest to lowest quantities): British Columbia, Ontario, Newfoundland and Labrador, Quebec, Manitoba, Yukon, Saskatchewan, and the Northwest Territories (NRCan 2017). According to the same source, Canada produced 697 322 t of copper in 2015.

In 2016, Canada produced approximately 340 900 t of copper from smelters and approximately 304 300 t of copper and copper-containing compounds from refineries (ICSG 2017). As of 2016, there are seven active smelters and refineries producing copper (as a primary or secondary metal) in Canada. They are located in Newfoundland and Labrador, Quebec, Ontario, Manitoba, and Alberta (MAC 2017).

4.2.2 Manufacture and imports

Of the 37 substances identified as priorities for assessment, 34 copper substances were included in surveys pursuant to a CEPA section 71 notice for the reporting years 2011 and 2012 to 2015 (Canada 2012; Canada 2017). Responses were received for 19 of the substances surveyed (listed in Table B-1, Appendix B). No information above the reporting threshold was received for the other 15 substances. The other three substances (CAS RNs 7440-50-8, 26317-27-1, 28302-36-5) were not surveyed. Results of the survey for the 19 substances with responses indicate that 8 were manufactured in Canada by 6 companies, and 18 copper compounds were imported into Canada by 61 companies (Table B-1, Appendix B) (Environment Canada 2013; ECCC 2017). Out of all the reported manufactured or imported copper substances for the year 2011, six were manufactured or imported in quantities greater than 100 000 kg (Table B-1, Appendix B) (Environment Canada 2013).

4.2.3 Uses

Table B-2 (Appendix B) presents the three activities or uses for which the highest quantities were reported for each substance that was in commerce in 2011 and 2012 to 2015 (Environment Canada 2013; ECCC 2017). Activities or uses reported for substances having the highest quantities in commerce are incidental production as a by-product, laboratory substances, paint additives and coating additives, pigments, and pest control substances. Other activities or uses were reported in quantities on the order of a few tens of tonnes, such as adhesives and sealant substances, processing aids specific to petroleum production, and agricultural substances (non-pesticidal). According to the International Copper Study Group (2017), elemental copper is transported to fabricators mainly as cathode, wire rod, billet, cake (slab) or ingot. Fabricators produce wires, rods, tubes, sheets, plates, strips, castings, powders and other forms of elemental copper through extrusion, drawing, rolling, forging, melting, electrolysis or atomization. More generally, copper is mainly used in electrical cables and wires, water piping, roofing, pigments/dyes, alloys and coins (Reimann and de Caritat 1998; Nordberg et al. 2015; CDA 2017).

The substances for which no information was received above the reporting threshold for the 2011 and 2012 to 2015 reporting years are listed in Table B-3 in Appendix B.

Copper is present in thousands of products available to consumers, including household products, textiles, paints, adhesives and children’s toys (Guney et al. 2014; CPID [modified 2018]). Additional uses of copper in Canada are identified in Table 4-1.

Table 4-1. Additional uses in Canada for copper and its compounds

Use	Copper and its compounds
Food additive [a]	Y
Food packaging materials [a]	Y
Incidental additives [b]	Y
Mineral nutrient added to foods, including supplemented foods [c]	Y
Medicinal or non-medicinal ingredient in disinfectant, human or veterinary drug products [d]	Y
Medicinal or non-medicinal ingredient in licensed natural health products [e]	Y
Notified to be present in cosmetics under the *Cosmetic Regulations* [f]	Y
Active ingredient or formulant in registered pest control products [g]	Y

[a] Health Canada [modified 2017]; sodium copper chlorophyllin as a permitted colouring agent; copper gluconate, copper sulfate, sodium potassium copper chlorophyllin as permitted additives with other accepted uses; personal communications from the Food Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated March 14, 2016; unreferenced.

[b] While not defined under the Food and Drugs Act (FDA), 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). Personal communication, email from the Food Directorate, Health Canada, to the Existing Substances and Risk Assessment Bureau, Health Canada, dated March 14, 2016; unreferenced.

[c] Copper is permitted to be added, as a mineral supplement, to foods in Canada (Health Canada [modified 2016]).

[d] Internal Drug Product Database [modified 2017]; personal communication, email from Therapeutic Products Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated April 28, 2017; unreferenced.

[e] Licensed Natural Health Products Database [modified 2019] and Natural Health Products Ingredients Database [modified 2019]; personal communication, email from Non-prescription and Natural Health Products Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, dated April 10, 2017; unreferenced.

[f] Personal communication, email from Consumer Product Safety Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated May 4, 2017; unreferenced.

[g] Personal communication, email from Pest Management Regulatory Agency, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated March 7, 2017; unreferenced.

5. Releases to the environment

According to Nriagu (1979), the quantity of anthropogenic releases of copper worldwide was almost the same as the quantity of natural releases (ratio of 0.93 to 1). According to Pacyna and Pacyna (2001), non-ferrous metal production is the largest source of copper emitted to the atmosphere worldwide, accounting for 70% of total emissions, while the remaining 30% comes mainly from stationary fossil fuel combustion.

Reporting to the National Pollutant Release Inventory (NPRI) is mandatory for copper and its compounds[5] (ECCC 2016). NPRI data indicate that from 2011 to 2015, total annual releases of copper and its compounds from all Canadian facilities to the three environmental compartments (i.e., air, land, and water) ranged from 450 to 1400 tonnes (Table 5-1).

Table 5-1. Total annual quantity of copper reported to the NPRI in all three environmental compartments (air, water, soil) from 2011 to 2015

Year[a]	Air (t)	Water (t)	Land (t)	All media (< 1 t)	Annual total (t)
2011	330	71	220	1	620
2012	1 100	60	280	15	1400
2013	230	60[b]	280	2	570[b]
2014	250	51[c]	210	9	520[c]
2015	230	33	170	9	450

[a] Data used for this table are current as of September 14, 2017. Facilities may periodically update their information reported to the NPRI. As such, repeated analysis with data extracted at a different time 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 methods and data sources. Therefore, uncertainties exist in the reported quantities (see the NPRI reporting guidance document for more details: ECCC 2016.

[b] The total value omits the spill of 1.0 tonne of copper to water due to the Obed Mountain mine dam failure in 2013.

[c] The total value omits the spill of 20 724 tonnes of copper to water due to the Mount Polley tailings dam failure in 2014.

Releases reported to the NPRI came from a variety of industrial sectors. The sectors with the highest total releases of copper were non-ferrous metal production and processing; metal ore mining; water, sewage and, other systems; pulp, paper and paperboard mills; coal mining; and iron and steel mills and ferro-alloy manufacturing. Information on these sectors is presented in Table C-1, Appendix C.

The sectors that released the most copper to air were non-ferrous metal production and processing; metal ore mining, and pulp, paper and paperboard mills. The sectors that released the most copper to land were metal ore mining, coal mining, and pulp, paper and paperboard mills. The sectors that released the most copper to water were water, sewage and other systems, metal ore mining, non-ferrous metal (except aluminum) production and processing, electric power generation, transmission and distribution, and iron and steel mills and ferro-alloy manufacturing. By far the most significant release of copper (and its compounds) to water during this time period was from the Mount Polley Mine tailings breach in 2014 (BC MOE 2017), with 20 724 tonnes reported.

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[5] 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 by-products and mine tailings) and in a quantity of 10 tonnes or more, and employees worked 20 000 hours or more at a facility.

Releases from other sectors were small compared to the sectors listed above and are therefore not specifically considered further in the ecological assessment. Releases were also reported from foundry operations. The bulk of copper releases from foundries come from the Horne smelting facility and are therefore reported under smelting activities. Therefore, this facility's releases have been considered within the base metal smelting and refining sector (BMS).

Other sources of anthropogenic copper releases to the environment not reported to the NPRI may include releases during the service-life of certain products and use of certain organic or mineral fertilizers and agricultural feeds (ECI 2008). In addition, some important pesticidal uses, such as algaecide for swimming pools and anti-fungal treatment for wood, may lead to copper releases. These pesticidal uses are regulated by the Pest Management Regulatory Agency (PMRA) under the *Pest Control Products Act*.

6. Environmental fate and behaviour

6.1 Environmental distribution

Copper may be present in various forms (e.g., free ion, complexes, colloids, particles, aerosols) in ambient air, surface water, sediments, soils and groundwater. Water solubility greatly influences the fate and partitioning of copper in environmental media. The fate of dissolved copper ions in relation to the aquatic environment may generally be characterized by partition coefficients such as soil-water (K_{sw}), suspended particles-water (K_{spw}) and sediment-water (K_{sdw}) partition coefficients (Appendix D, Table D-2). The fate of particulate forms of copper (e.g., elemental copper and compounds with very low solubility such as copper oxide) may be controlled by their physical properties (e.g., density, particle size) rather than their chemical properties.

6.1.1 Air

Copper is a non-gaseous element with a negligible vapour pressure and is emitted to air principally in the form of fine particulate matter (PM). Depending on the size of the PM to which copper is associated, it will travel for a certain distance in air before being deposited to aquatic or terrestrial environments. Long-range transport potential (LRTP) was not quantified in this screening assessment, as copper-containing substances or incidental releases are not expected to travel over very long distances to contribute significantly to environmental concentrations in remote areas (e.g., arctic). The environmental concentrations (in water, soil or sediments) near the major sources of releases were considered and could include copper deposited from air releases (see the Ecological Exposure Assessment section).

6.1.2 Freshwaters and sediments

The water solubility of copper-containing substances ranges widely (Appendix D, Table D-1). Therefore, if released to water bodies, some substances will release copper ions more readily than others. Under typical environmental pH and E_h (oxido-reduction potential) conditions, the copper (II) oxidation state is more stable than copper (I) or copper (III) (Nordberg et al. 2015). However, copper (I) may be more thermodynamically stable under some environmental conditions, such as high pH and low E_h (Brookins 1988) or in suboxic zones, including sediments. Under conditions commonly found in oxic freshwaters (i.e., pH between 5 and 9; E_h between 0.5 and 1 V), copper is predominantly in the form of Cu^{2+}, CuO^0, or $CuOH^+$ (Brookins 1988; Takeno 2005).

Copper is expected to be more mobile under oxidizing conditions than under reducing conditions (Garrett 2005), where it is mainly associated with the solid phase including particulates. In addition, environmental mobility will be higher under acidic conditions (Reimann and de Caritat 1998; Garrett 2005) because copper tends to desorb from the particulate phase at acidic pH values, due to competition with hydronium ions.

In aquatic media, copper tends to sorb preferably to solid particles, and a significant proportion of dissolved copper forms will end up in sediments through adsorption to settling suspended particles (Harvey et al. 2007). Copper is expected to stay primarily in the bottom sediments, but the particles may become re-suspended through bioturbation, dredging, seasonal floods or mixing by turnover events. In addition, the partitioning of copper is greatly dependent on the conditions of the system. Variations in pH or reduction-oxidation condition may also cause remobilization (Heijerick et al. 2005).

Large particles of elemental copper and compounds with very low solubility (e.g., copper oxide) are not expected to be found in significant amounts in the water column. A portion of these compounds may be found in sediments, or in soil if released to this compartment, in a non-dissolved, solid form.

Sediments act as sinks for trace metals in aquatic systems (Horowitz 1981). Copper may be found in a variety of fractions in the sediment compartment: dissolved in porewater; present in exchangeable fractions of clays, hydrated oxides of iron and manganese and humic acids; bound to carbonates; bound to iron and manganese oxides; bound to particulate organic matter; complexed with sulfides including acid volatile forms; and in the crystal lattice of primary and secondary minerals (Tessier et al. 1979; Förstner and Wittmann 1981; Di Toro et al. 1992). Copper can be periodically redistributed in the water column during episodes of spring and fall mixing (e.g., in lakes) and may be remobilized under different physicochemical conditions, such as during decreases in dissolved oxygen, pH, and redox-potential and increases in mineralization and dissolved organic matter (Linnik and Zubenko 2000).

6.1.3 Soils

Similar to sediments, soils are major sinks for metals released to air from natural and anthropogenic sources. The behaviour of copper in soils is linked to chemical and physical properties of both the soil (e.g., pH, cationic exchange capacity (CEC), soil organic matter, clay content) (ARCHE Consulting 2017) and the particular copper-containing compound (e.g., water solubility) entering this compartment. Higher solubility in porewater is associated with a greater potential for mobility and bioaccessibility. An increase in the factors mentioned above (except soil organic matter) will tend to decrease the porewater concentration. In addition, given the occurrence of ageing, which commonly refers to reactions transferring metals from labile pools to relatively insoluble pools over time (Smolders et al. 2007), the amount of copper in mobile and bioaccessible forms will tend to decrease over time.

6.2 Environmental persistence

Copper is considered persistent because it cannot be degraded through any processes (e.g., photodegradation, biodegradation), although it can transform into different chemical species or partition among different phases within an environmental medium. Certain organic metal salts and organometallics may photodegrade or biodegrade under certain conditions (OECD 2014). The persistence of the parent organic metal salts and organometallics and their possible organic counter-ions or organic transformation products is not evaluated individually in the present assessment.

6.3 Potential for bioaccumulation

Studies that investigate the bioavailability and bioaccumulation of copper are usually conducted with a variety of inorganic soluble copper-containing substances that readily dissociate to release the copper moiety. For exposure in water, bioavailability, uptake, and bioaccumulation of copper is related to the free copper ion activity (e.g., concentration of Cu^{2+} at a specific ionic strength), which is a fraction of the total copper in water (Campbell 1995; Kim et al. 1999). The amount of free copper depends on the complexation capacity of the water, which is driven by hardness, pH, and especially the amount of dissolved organic carbon (DOC) (ECI 2008). The biotic ligand model (BLM) was developed for copper to predict metal bio-uptake in recognition that the bioavailability and bioreactivity of metals control their potential to cause adverse effects in organisms (ECCC 2019b). See section 7 (Potential to Cause Ecological Harm) and ECCC (2017b) for more details.

Copper may be found in a variety of forms in sediments, ranging from weakly bound (e.g., to exchangeable fractions of clays) to strongly bound (e.g., complexed with sulfides). The bioavailability of copper to benthic organisms is controlled by various key factors, including pH, organic carbon, sulfides, and clay concentrations (CCME 1999a). It has been shown that by taking into account pH and copper binding to amorphous iron oxides, the concentration of dissolved copper in porewater can be estimated (Campbell and Tessier 1996) and the bioavailable fraction can be evaluated.

For soils, the predicted no-effect concentration (PNEC) calculator, an Excel-based software developed by ARCHE Consulting (2017), suggests that the most influential factors affecting the behaviour and bioavailability of copper in soils included the CEC, pH, organic carbon content, and clay content. An increase in one or more of these values will generally decrease the bioavailability of copper by decreasing the concentration of free copper in porewater.

The bioconcentration factor (BCF) and bioaccumulation factor (BAF) approaches for metals have been contested because these ratios are considered of limited usefulness in predicting metal accumulation (McGeer et al. 2003; Schlekat et al. 2007). An inverse relationship between copper concentrations in water and copper BCFs/BAFs in aquatic biota has been demonstrated (DeForest et al. 2007). Thus, BCF/BAF values were not reported in this assessment as they are less meaningful for copper, which is physiologically regulated and nutritionally required (Couillard et al. 2008; Norwood et al. 2007). ECI (2008) concluded that copper does not biomagnify through the trophic chain. The absence of copper biomagnification has been demonstrated in field studies of food chains and terrestrial food webs (Barwick and Maher 2003; Farag et al. 1998; Hunter and Johnson 1982, cited in ECI 2008; Laskowski 1991; Quinn et al. 2003; Wang 2002).

Copper is well-regulated in both aquatic and terrestrial organisms, and there is an absence of biomagnification through food chains.

7. Potential to cause ecological harm

7.1 Ecological effects assessment

7.1.1 Essentiality

Copper is an essential element necessary for optimal growth and the development of micro-organisms, plants, and animals. It is involved in numerous physiological and enzymatic processes in animals and copper deficiency has been observed in fish, crops, and farm animals (WHO 1998). Copper uptake is mainly through facilitated transport systems and is generally restricted to specialized organs, such as the gills for waterborne uptake and the digestive tract for dietary uptake (ECI 2008). It is regulated internally by all living organisms through homeostatic mechanisms to maintain appropriate levels in tissues to meet metabolic needs (ECI 2008).

7.1.2 Mechanisms of toxic action

Copper is necessary for the normal functioning of enzymes and proteins required for a range of metabolic processes (ECCC 2019b). However, copper that is in excess of an optimal range defined by essentiality can be detrimental to organisms. For plants and algae, copper exposure may adversely affect growth/cell division, photosynthesis, respiration, and nitrogen fixation depending on the species involved (Foster 1977; Rosko and Rachlin 1977; Laube et al. 1980; Stauber and Florence 1987). For fish, the effect of copper on sodium uptake is associated with inhibition of the basolateral Na^+/K^+-ATPase, leading to a disruption in the ionic balance in the organism, which can cause toxicity (Grosell and Wood 2002; Morgan et al. 2004). For soil microbial life, excess copper is associated with adverse effects on biomass, diversity, and organic matter decomposition, in addition to a disruption of the carbon cycle via inhibition of dehydrogenase enzyme activity (Princz et al. 2016).

7.1.3 Effects on aquatic organisms

Many empirical studies are available on the chronic toxicity of copper and its compounds to aquatic organisms such as algae, plants, invertebrates and fish. A draft federal water quality guideline (FWQG) for copper (ECCC 2019b) was derived from data evaluating the toxicological effects of copper on aquatic organisms using the protocol described by the Canadian Council of Ministers of the Environment (CCME 2007). In this assessment, the FWQG was selected as the freshwater PNEC for copper and its compounds because it is based on recent scientific studies, integrates toxicity modifying factors (TMFs), and uses chronic toxicity data that are an indicator of potential for harm from a long-term exposure to copper. Details on the derivation of the FWQG are available in ECCC (2017b).

The FWQG is based on toxicity data published up to January 2017 and includes datasets from the European Union (ECI 2008), the U.S. EPA (unpublished 2015) and the BC Ministry of Environment (unpublished 2017). Of the 422 toxicity endpoints in the dataset, 98 endpoints for 46 species met criteria outlined in CCME (2007). The acceptable toxicity dataset included 22 endpoints for 19 fish species, 44 endpoints for 22 invertebrate species and 32 endpoints for 5 species of plants or algae.

A geometric mean was calculated for species with multiple endpoints of similar effect and duration, and the most sensitive endpoint was selected for each species for inclusion in the species sensitivity distribution (SSD). The 5th percentile of the normalized SSD was then defined as the FWQG. Site-specific PNECs are generated in this assessment with considerations of key TMFs, including DOC, pH, hardness, and temperature. Notably, the PNEC is most sensitive to the concentration of DOC. Using the central tendencies of TMFs for all eco-regions and Great Lakes (see Section 7.2 and Table D-2), the aquatic PNEC for copper ranges from 0.6 to 18.8 µg/L. On average, plants and algae were the most sensitive group of aquatic organisms, followed by invertebrates and fish.

7.1.4 Effects on benthic organisms

A review of the toxicity of copper to benthic organisms was conducted (CCME 1999a; Environment Canada 1999) to derive an interim sediment quality guideline (ISQG) and a probable effects level (PEL) for freshwater and estuarine/marine environments. Copper is associated with different sediment fractions of varying bioavailability, and changes in ambient environmental conditions (e.g., sediment perturbation, decrease in pH, etc.) can increase the bioavailability of copper associated with some of these fractions (CCME 1999a). Benthic organisms are exposed to particulate and dissolved copper in interstitial and overlying waters, as well as to sediment-bound copper through surface contact and sediment ingestion (CCME 1999a). The majority of the data used to derive ISQGs and PELs come from the Biological Effects Database for Sediments (BEDS) (Environment Canada 1999). Adverse biological effects for copper in the BEDS include decreased benthic invertebrate diversity, reduced abundance, increased mortality, and behavioural changes (Environment Canada 1999). The freshwater ISQG and the probable effect level (PEL) were determined to be 35.7 mg Cu/kg and 197 mg Cu/kg dry weight (dw), respectively (CCME 1999a).

7.1.5 Effects on soil-dwelling organisms

Empirical studies are available on the chronic toxicity of copper and its compounds to soil-dwelling organisms such as plants and invertebrates. Canadian soil quality guidelines for copper were derived for different land uses using different receptors and exposure scenarios for each type of use: agricultural, residential/parkland, commercial and industrial (CCME 1999b; CCME 1997). The derivation of the soil quality guideline for soil contact is based on toxicological data for 19 vascular plant species and 7 invertebrate species (CCME 1997). It was calculated to be 63 mg Cu/kg of soil (dry weight) and was adopted as the soil quality guideline for agricultural and residential/parkland uses. However, the CCME guideline does not consider bioavailability differences due to varying soil conditions (i.e., TMFs).

The soil PNEC calculator, an Excel-based software developed by ARCHE Consulting (2017), considers TMFs and laboratory-to-field factors that account for both ageing and leaching processes to determine copper PNECs in diverse types of soils. TMFs for copper include effective cation exchange capacity, percent organic carbon, percent clay and pH. Using the European Chemicals Agency registration dossiers for copper-containing substances, data from 9 plant species, 10 invertebrate species, and 9 microbial processes were considered, including 67, 108, and 77 toxicity values, respectively. The calculated PNECs (based on total copper) for six standard European soil types range from 25.7 mg Cu/kg for the acid sandy arable soil (highest bioavailability) to 176.4 mg Cu/kg for the peaty soil (lowest bioavailability).

7.2 Ecological exposure assessment

7.2.1 Background concentrations and toxicity modifying factors

Copper is ubiquitous in the environment, and in some areas of Canada not impacted by anthropogenic activities (i.e., areas representative of background conditions), concentrations of copper may be naturally elevated. In other areas, anthropogenic activities cause copper concentrations to be higher than background concentrations.

Background concentration medians for total copper (Cu_T) in surface waters for Canadian ecozones were estimated by Kilgour & Associates Ltd. (2016). Samples considered to be in reference condition, deemed as such using the approach outlined in Kilgour & Associates Ltd. (2016) and Proulx et al. (2018), were used to calculate the medians. Data from a variety of federal and provincial surface water quality monitoring programs and other repositories were used for these calculations (Table E-1 in Appendix E).[6] Median concentrations of Cu_T were also calculated for Lake Erie, Lake Ontario, and Lake Superior using measurements taken during the period of 2005 to 2015.[7] In all cases, non-detects were substituted with one-half the reported detection limit.

The chronic BLM-based FWQG for dissolved copper requires data for four main TMFs: total hardness, pH, DOC, and temperature. Representative TMF data were therefore derived for Canadian ecozones and Great Lakes (Table E-2 in Appendix E). Central tendencies of the TMFs developed for the ecozones were based on data identified as being in reference condition, as defined by the approach in Proulx et al. (2018). The datasets were obtained from a variety of federal and provincial surface water quality monitoring programs and data repositories covering the period of 2005 to 2015.[8] Geometric means for total hardness and DOC were preferred since these parameters typically follow a log-normal distribution in the environment, whereas averages were used for pH. Central tendencies of the TMFs were also developed for certain Great

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[6] BQMA 2015; FQMS 2014; FQMS 2016; NLTWQM 2016; PWQMN 2015; RAMP 2016; personal communication, data prepared by the Water Stewardship Division, Province of Manitoba, for the Ecological Assessment Division, Environment and Climate Change Canada, dated February 24, 2016; unreferenced; personal communication, data prepared by the Environmental and Municipal Management Services, Saskatchewan Water Security Agency, for the Ecological Assessment Division, Environment and Climate Change Canada, dated February 25, 2016; unreferenced.

[7] Personal communication, data provided by the Water Quality Monitoring and Surveillance Division, Environment and Climate Change Canada (ECCC) to the Ecological Assessment Division, ECCC, dated June 20, 2017; unreferenced.

[8] BQMA 2015; FQMS 2016; NLTWQM 2016; PWQMN 2015; RAMP 2016; personal communication, data prepared by the Water Stewardship Division, Province of Manitoba, for the Ecological Assessment Division, Environment and Climate Change Canada, dated February 24, 2016; unreferenced; personal communication, data prepared by the Environmental and Municipal Management Services, Saskatchewan Water Security Agency, for the Ecological Assessment Division, Environment and Climate Change Canada, dated February 25, 2016; unreferenced.

Lakes using data collected during the period of 2005 to 2015.[9] Hardness geometric means were calculated using dissolved measurements of calcium and magnesium (U.S. EPA 2015) as direct measurements were unavailable.[10] In all cases, non-detects were substituted with one-half the reported detection limit. Where measured TMF data were unavailable for the effluent receiving environment, the central tendencies for the TMFs were used as a substitute.

For soils, McKeague et al. 1979 reported a mean of 22 mg Cu/kg in Canadian soils. By region, the mean soil copper concentrations are 11 mg/kg for the Canadian Shield, 17 mg/kg for the Appalachians, 19 mg/kg for the St. Lawrence Lowlands, 21 mg/kg for the Interior Plains, and 46 mg/kg for the Cordilleran Region. CCME (1997) reported that the average copper concentration in Canadian soils is estimated to be 20 mg/kg, with a range between 2 and 100 mg/kg. Other publications report copper concentrations in soil for Manitoba and Ottawa that are within this range (Rasmussen et al. 2001; Haluschak et al. 1998).

7.2.2 Approach for the exposure characterization

Detailed exposure scenarios were developed for three industrial activities reporting the largest releases of copper to all media—metal mining, base metals smelting and refining, and wastewater treatment—as determined from NPRI data (Section 5). It is noted that other sectors of activity may be sources of copper to the environment. However, preliminary exposure scenarios conducted using environmental concentrations or effluent concentrations, when available, indicated that some of these other activities would be of lower concern.

For each scenario, predicted environmental concentrations (PECs), expressed as concentrations of elemental copper, were estimated for the aquatic environment using measured concentrations of copper in surface freshwater when available (preferably dissolved copper, $Cu_{D,}$ otherwise total copper, Cu_T). Although based on measured concentrations, these concentrations are considered predictive due to the extent of their spatial and temporal variation.

When environmental measured concentrations were unavailable, PECs were estimated by adding the appropriate median background concentration of Cu_T (Table E-1 in Appendix E) to the estimated aquatic concentrations (EAC) of copper in the receiving environment (i.e., PEC = EAC + median background concentration). The EACs were

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[9] Personal communication, data provided by the Water Quality Monitoring and Surveillance Division, Environment and Climate Change Canada (ECCC), to the Ecological Assessment Division, ECCC, dated June 20, 2017; unreferenced.

[10] Personal communication, data provided by the Water Quality Monitoring and Surveillance Division, Environment and Climate Change Canada (ECCC), to the Ecological Assessment Division, ECCC, dated July 27, 2017; unreferenced.

determined by applying a dilution factor of 10 to effluent concentrations to reflect conditions near the discharge point.

In this assessment, the exposure characterization of copper in the aquatic environment requires, at a minimum, data for four main TMFs (i.e., total hardness, pH, DOC, and temperature) to derive site-specific PNECs (Section 7.3.1). Certain sectors provide measured data for the TMFs in their receiving environment (e.g., *Metal and Diamond Mining Effluent Regulations* (MDMER) environmental effects monitoring (EEM) for metal mining). For sectors where no receiving environment data are available, representative data for TMFs were derived for applicable ecozones and Great Lakes (Table E-2 in Appendix E).

Tukey box plots were generated for each facility of a given sector to display the distribution of copper concentrations (Cu_D or Cu_T). They are interpreted as follows: the lower and upper hinges (edges) of the box represent the first and third quantiles (Q1 and Q3), which are the 25th and 75th percentiles, respectively, while the black horizontal line within the box represents the second quantile, or the 50th percentile (median). The distance between the 25th and 75th percentile is called the interquartile range (IQR). The lower whisker represents the lowest data that are within the Q1 – 1.5 x IQR threshold, and the upper whisker represents the highest data that are within the Q3 + 1.5 x IQR threshold. Data exceeding these thresholds appear as circles. However, if the minimum and maximum are within these thresholds, they represent the lower and upper whiskers and no outliers are present. The 95th percentile was also indicated (blue line). The sample size (n) and detection frequency (i.e., percentage of samples above the method detection limit) are also displayed above each box plot.

7.2.3 Metal mining

In Canada, copper-containing ores are extracted from underground and above-ground mines (Environment Canada 2009). The extracted ores are crushed, ground in mills, and concentrated by differential flotation to produce copper concentrates (Environment Canada 2009). Ore extraction and concentration operations generate dust, which may escape and deposit nearby, and effluents, which may be stored in tailings ponds or treated and released to surface waters. The generated dusts, potential leachates from tailings ponds, and effluent releases to surface waters are all pathways from which copper may be released into the surrounding environment (Rashed 2010). From 2011 to 2015, annual releases of copper and its compounds to water reported to the NPRI by the metal mining sector ranged from 5 to 11 t (or 20 724 t when considering the Mount Polley spill in 2014, Section 5.0).

Canadian metal mines that discharge effluent at any time into any water at a flow rate exceeding 50 m^3/day are subject to the MDMER (formerly known as the *Metal Mining and Effluent Regulations)* (Canada 2018) under the *Fisheries Act*. Schedule 4 of the MDMER prescribes concentration limits in effluents for certain parameters, including copper. The maximum authorized monthly mean concentration of total copper (Cu_T) in effluent is 0.30 mg/L. In addition, the maximum authorized concentration is 0.45 mg/L Cu_T in a composite sample and 0.60 mg/L Cu_T in a grab sample. The analytical requirements for metal mining effluent under Schedule 3 of the MDMER (with respect to data submitted under Section 12, Effluent Monitoring Conditions) prescribe a maximum method detection limit (MDL) of 0.0010 mg Cu_T/L (as of June 2018; previously 0.010 mg Cu_T/L). Facilities are also required to conduct environmental effects monitoring (EEM) as per Schedule 5, under which water quality monitoring, including analysis for total copper, must be completed in the exposure areas surrounding the point of entry of effluents into waterbodies from each final discharge point and from the related reference areas. Concentrations of Cu_T measured in surface water samples from exposure and reference areas, as submitted to Environment and Climate Change Canada under the MDMER and EEM program between 2011 and 2015, were analyzed. During this period, 124 metal mining facilities submitted copper data at least once for the exposure and reference areas corresponding to surface freshwaters (EEM 2016). Non-detects were replaced with one-half the corresponding method detection limit (MDL), and blanks and zero values without reported MDLs were removed. The MDLs ranged from 0.002 to 2000 µg Cu_T/L.

Box plots of Cu_T concentrations for the exposure and reference areas of 10 facilities are presented in Figure 7-1. These 10 facilities were selected from the 124 facilities on the basis of their current operational status (open), magnitude of copper enrichment in the exposure area(s), and sample size (n equal to or greater than 8). Within the selected 10-facility subset, certain facilities have more than one reference area, as indicated in the box plot (e.g., Facility 3: Reference 1, Reference 2). Facilities 6 and 7 combine their effluents with base metals smelters (i.e., BMS Facilities 4 and 5, respectively, see Section 7.2.4).

According to the MDMER, “exposure area” means all fish habitat and waters frequented by fish that are exposed to metal mining effluent, whereas “reference area” means waters frequented by fish that are not exposed to metal mining effluent and that have fish habitat similar to that of the exposure area (Canada 2018). Therefore, exposure and reference areas may be located on the same waterbodies (Facilities 5, 8, 9, and 10) or on different waterbodies (Facilities 1, 2, 3, 4, 6, and 7). Facilities 3 and 4 discharge into the same waterbody and use the same reference data (i.e., Facility 3 Reference 1, Reference 2 and Facility 4 Reference 1, Reference 2 are the same data, respectively).

All 10 facilities show evidence of copper enrichment in the exposure areas, where copper concentrations were 5.0 to 66 times higher than in the reference areas, as based on a comparison of median concentrations. The observation of copper enrichment is corroborated by the effluent concentration data for these facilities, which all reported concentrations for Cu_T during the 2011 to 2015 period. All facilities have high detection frequencies (i.e., low frequencies of non-detects) in the exposure areas (equal to or greater than 95%) except for Facility 10 Exposure (69%), which also has a low detection frequency in the corresponding reference area (i.e., 7.7%).

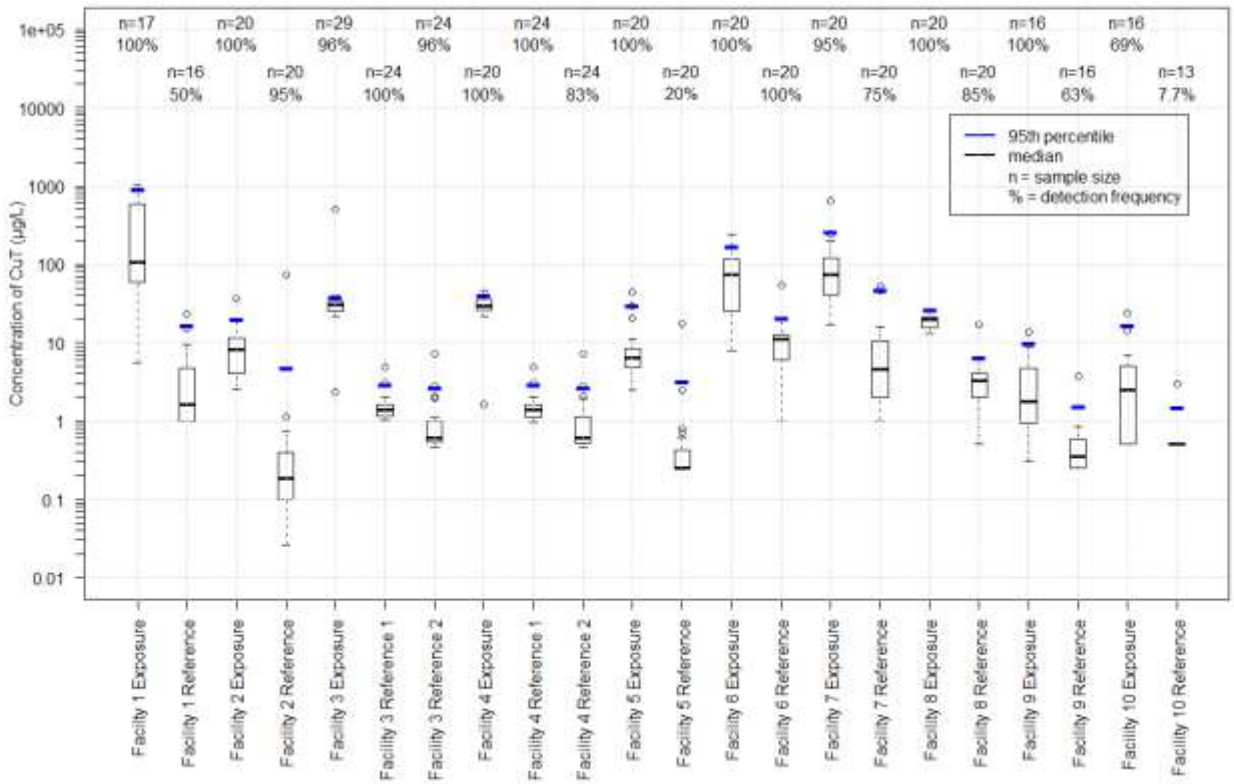

Figure 7-1. Box plots for Cu$_T$ in surface waters from exposure and reference areas reported by 10 selected facilities subject to the MDMER from 2011 to 2015 (EEM 2016)

In addition to the analysis of Cu$_T$ required for the MDMER EEM program, pH, total hardness, and temperature measurements in the exposure areas and reference areas are also required. Monitoring of DOC is not required; however, some facilities provided data. Site-specific PNECs were calculated for the facilities' exposure and reference areas on the basis of measured TMF data, where available, or estimated TMF data (Table E-3 in Appendix E). In the absence of measured data for total hardness, pH, DOC, or temperature for a particular sample, the geometric means (total hardness, DOC) or averages (pH, temperature) of pooled data from all samples for the corresponding exposure or reference areas were applied. Monthly averages were calculated for temperature. The calculated PNECs for the exposure and reference areas ranged from 0.20 to 72 µg/L and from 0.20 to 33 µg/L, respectively (Table E-3 in Appendix E).

For some facilities, the TMF levels in the exposure areas differed from those in the reference areas, notably for total hardness. Hardness levels may be higher in the exposed areas compared to reference areas because of the addition of lime during effluent treatment in order to precipitate dissolved metals and to control pH (Lane and Associates Limited. 1990). As a result, the site-specific median PNECs in exposure areas are generally greater than the site-specific median PNECs calculated in reference areas.

7.2.4 Base metals smelting and refining

Canada is a producer of refined copper and other copper compounds (Section 4.2.1). There are currently 12 major base metals smelting and refining (BMS) facilities in Canada (Cheminfo 2013). The BMS sector processes concentrates from metal mines and mills as well as other feedstocks (i.e., recycled materials such as electronics and batteries) to produce metals (Environment Canada 2006), including copper. From 2011 to 2015, total annual releases of copper and its compounds to water reported to the NPRI by BMS facilities ranged from 2.4 to 3.3 t (Table C-1, Appendix C) (NPRI 2015).

Releases from primary and secondary copper smelters and copper refineries and releases from primary and secondary zinc smelters and zinc refineries were assessed under the Priority Substances List (PSL) (EC, HC 2001). Air emissions from these facilities were concluded to be toxic under CEPA (EC, HC 2001), and “particulate matter containing metals that is released to the atmosphere from copper smelters or refineries, or from both”, as well as “particulate matter containing metals that is released in emissions from zinc plants” were listed on Schedule 1 in 2001. All BMS facilities in Canada were subsequently subject to a Pollution Prevention Planning Notice published in the *Canada Gazette* in 2006. Based on these previous risk assessment and risk management activities, air emissions of copper from these sources are not considered. However, this current assessment does consider releases of copper to the aquatic environment as a result of effluent discharges from these sources as they were not specifically considered in the previous assessment.

From 2011 to 2015, five BMS facilities were subject to the MDMER under the *Fisheries Act* (Section 7.2.3). Concentrations of Cu_T measured in surface waters downstream of effluent discharges (i.e., exposed areas) and in corresponding reference areas are therefore available under the MDMER EEM program. Surface water monitoring data for these facilities from 2011 to 2015 are summarized in Figure 7-2 (Facility 1, 2, 3, 4, and 5). There is evidence of copper enrichment for Facility 4 in both exposure areas (i.e., Exposure 1 and Exposure 2) compared to the corresponding reference areas (i.e., Reference 1 and Reference 2). Facility 1 shows slight enrichment in Exposure 1, while Facilities 2, 3, and 5, show exposure areas with lower concentrations of Cu_T compared to the reference areas. As discussed in Section 7.2.3, the MDMER definitions of exposure and reference have a specific definition relating to fish habitat and effluent exposure. Further investigation into the exposure and reference areas of these facilities revealed that all paired exposure and reference areas are located on different waterbodies.

Exposure data were available for two additional facilities not subject to the MDMER—one in British Columbia represented as Facility 6 in Figure 7-2 and one in Ontario.

For Facility 6 located in B.C., Cu_T and Cu_D surface water concentrations were measured at two upstream reference sites (1.9 and 9.7 km) and at three downstream exposure sites (0.2, 1.1 and 15.8 km) from 2011 to 2013 (EEC Ltd & LAC Ltd 2014). For the purposes of exposure characterization, Cu_D concentrations from the closest upstream reference site (Reference 1) and the two closest downstream exposure sites (Exposure 1, Exposure 2) were analyzed. Cu_T concentrations were also measured for the sediment compartment in 2012 at three upstream reference areas and at seven downstream exposure areas. Average dry weight concentrations were 5.4 mg/kg (n = 3) and 287 mg/kg (n = 7) for the reference and exposure sites, respectively, showing an enrichment of copper in sediments in the exposure area.

Additionally, PECs were modeled from effluent concentrations available for the facility in Ontario. Under the Ontario *Effluent Monitoring and Effluent Limits – Metal Mining Sector Regulations* (O. Reg 560/94; Government of Ontario [modified 2017]), certain BMS facilities discharging effluents to the environment are required to report monthly releases of copper (as loadings of Cu_T) to the receiving environment to the Ministry of the Environment, Conservation and Parks (Government of Ontario [modified 2017]). Copper loadings are reported for process effluent (Government of Ontario [modified 2017]). Estimated aquatic concentrations (EAC) for Cu_T were derived for the facility by calculating average annual effluent concentrations using data submitted quarterly from 2012 to 2014 (Government of Ontario [modified 2017]) and then applying a dilution factor of 10. PECs were then derived by summing the EACs and the median background concentration of Cu_T for Lake Erie (Table E-1). PECs were determined to range from 2.14 to 2.80 µg Cu/L (n = 3).

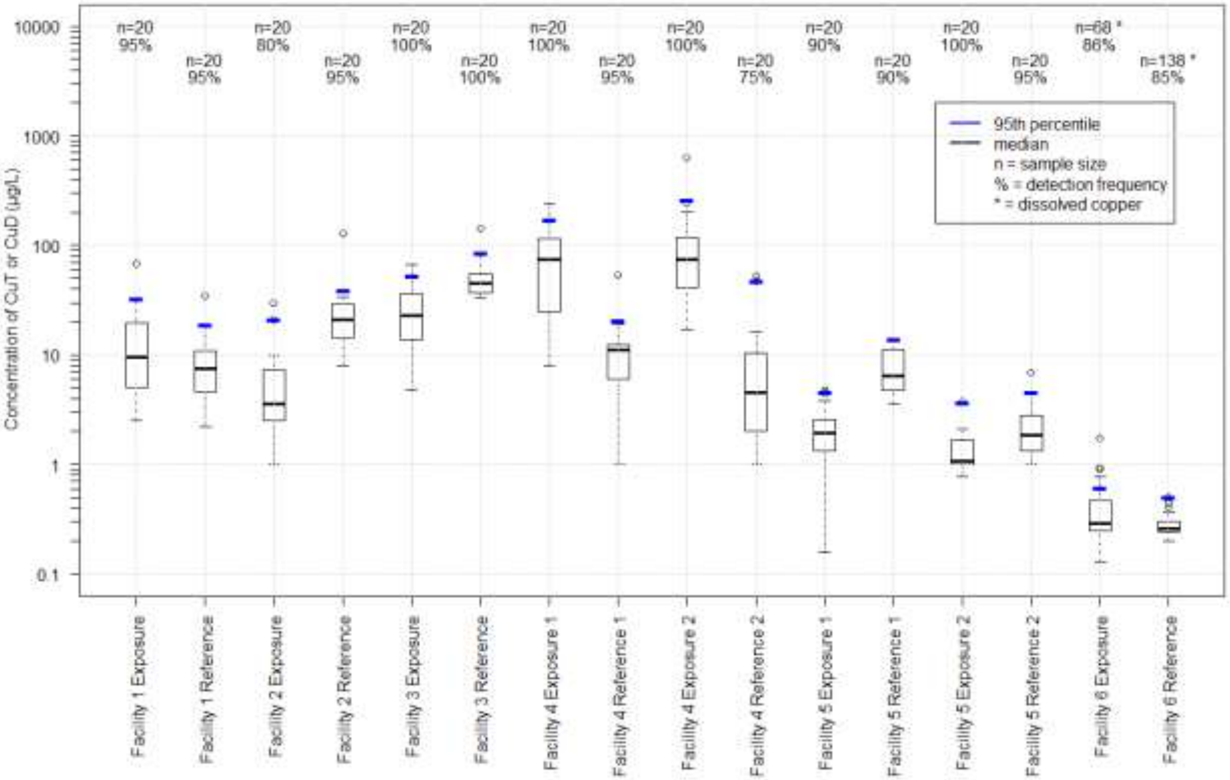

Figure 7-2. Box plots of Cu_T in surface waters from exposure and reference areas reported by base metal smelters subject to the MDMER from 2011 to 2015 and Cu_D for one smelter not subject to the MDMER from 2011 to 2013 (EEM 2016; EEC Ltd & LAC Ltd 2014)

The TMF values used and the calculated PNECs for this sector are presented in Table E-4 in Appendix E. The calculated PNECs for the exposure and reference areas for Facilities 1 through 6 range from 0.58 to 53 µg/L and from 0.72 to 40 µg/L, respectively.

7.2.5 Wastewater treatment

Effluent discharges to surface waters from wastewater treatment systems (WWTS) may contain copper. The copper in WWTS influent, and therefore in effluent, originates from consumer, commercial, or industrial uses. Releases of copper to surface waters reported to the NPRI from 12 WWTSs during the period of 2011 to 2015 ranged from 25 to 51 t (Table C-1, Appendix C).

Empirical monitoring data were collected under the Chemicals Management Plan (CMP) Environmental Monitoring and Surveillance Program from 25 municipal WWTS located across Canada from February 2009 to March 2012 (Environment Canada 2013). A total of 191 influent, 90 primary effluent, and 191 final effluent 24-hour composite samples were collected and analyzed for total copper. Copper was above detection limits in all samples, with median concentrations of 63.5 µg Cu/L for influent, 69.0 µg Cu/L for primary effluent and 17.6 µg Cu/L for final effluent. The median removal value of copper from influent to final effluent was 75.3% (n = 191 paired influent and effluent samples) (Environment Canada 2013). Although influent and effluent samples were collected as 24-hour composites, they may not accurately represent the removal value for copper since the hydraulic retention times of the facilities were not accounted for during sampling (i.e., the amount of time it takes water to pass through a given WWTS).

PECs for the wastewater treatment sector were derived for 21 WWTS facilities that release to freshwater (Table 7-5). PECs were calculated by applying a dilution factor of 10 to final effluent concentrations and adding the median background copper concentrations corresponding to the ecozone where the facility is located (Table 7-8). The TMF values used for each facility and resulting PNECs are presented in Table E-5 of Appendix E. The calculated PNECs for the exposure areas range from 0.86 to 40 µg/L.

Table 7-5. Calculated PECs of Cu_T for the wastewater treatment sector based on effluent concentrations from 21 WWTS across Canada from 2009 to 2012 (EC 2013)

Facility	Sample size	Diluted effluent range (µg Cu_T/L)	Median background concentration (µgCu_T/L)	PEC range (µgCu_T/L)	PEC median (µgCu_T/L)
1	5	3.09–3.80	1.05	4.1–4.8	4.7
2	12	0.275–2.42	0.82	1.1–3.2	1.5
3	6	0.761–1.25	0.50	1.3–1.8	1.3
4	6	0.195–2.26	0.82	1.0–3.1	1.9
5	12	0.112–7.04	1.9	2.0–9.0	2.7
6	6	0.277–1.76	0.82	1.1–2.6	1.8
7	6	0.387–1.59	1.0	1.4–2.6	1.9
8	6	0.470–4.11	1.1	1.6–5.2	1.9
9	6	1.48–6.61	0.82	2.3–7.4	2.8
10	12	2.34–4.88	0.82	3.2–5.7	3.5
11	6	3.05–5.35	0.79	3.8–6.1	4.4
12	6	2.25–9.69	0.50	2.8–10	3.7
13	12	0.570–5.70	0.76	1.3–6.5	2.5
14	6	1.55–4.35	0.80	2.4–5.2	3.1
15	6	1.37–4.78	0.82	2.2–5.6	2.5
16	6	0.178–2.17	0.80	1.0–3.0	1.7
17	12	0.805–4.15	0.80	1.6–5.0	2.4
18	6	0.894–3.07	0.80	1.7–3.9	2.6
19	6	1.07–2.78	1.9	3.0–4.7	4.2
20	12	0.327–3.22	1.9	2.3–5.2	2.8

21	6	1.37–3.00	0.51	1.9–3.5	2.3

7.3 Characterization of ecological risk

The approach taken in this ecological screening assessment was to examine assessment information and develop proposed conclusions using a weight-of-evidence approach and precaution. Evidence was gathered to determine the potential for copper to cause harm in the Canadian environment. Lines of evidence considered include those evaluated in this assessment that support the characterization of ecological risk in the Canadian environment. Secondary or indirect lines of evidence are considered when available, including regulatory decisions and classification of hazard or fate characteristics made by other regulatory agencies. This ecological screening assessment of copper and its compounds focuses on the copper moiety.

7.3.1 Risk quotient analyses

Risk quotient analyses were performed by comparing the various estimates of exposure (PECs; see the Ecological Exposure Assessment section) with ecotoxicity information (PNECs; see the Ecological Effects Assessment and the Ecological Exposure Assessment sections) to determine whether there is potential for ecological harm in Canada. Risk quotients (RQs) were calculated by dividing the PEC by the PNEC for the relevant environmental compartments and associated exposure scenarios. Specifically, RQs were calculated for the aquatic compartment (i.e., surface freshwaters) in the exposure scenarios described in Section 7.2 for three sectors: metal mining, base metals smelting, and wastewater treatment. PECs were primarily estimated using recent measured concentrations of copper in surface water (preferably Cu_D where available, otherwise Cu_T) or were estimated. PNECs were calculated using the chronic BLM-based dissolved copper FWQG for aquatic organisms (ECCC 2019b) with facility-specific toxicity modifying factor (TMF) data from the exposure and reference waterbodies, where available, or by using ecozone or Great Lakes TMF data.

As in the case of the ecological exposure characterization (Section 7.2.2), box plots were generated for each facility of a given sector to display the distribution of RQs. Section 7.2.2 explains how the box plots are constructed. An additional red line was added to indicate where the RQ is equal to 1.

The metal mining sector ecological risk characterization utilized raw surface freshwater data submitted to the MDMER EEM program for the period of 2011 to 2015 (EEM 2016). Therefore, the PECs consisted of measured data for Cu_T from the effluent receiving environments (i.e., exposure areas) and corresponding reference areas of metal mining facilities. The PNECs were modeled with the BLM using the exposure and reference area measured data for total hardness, pH, dissolved organic carbon (DOC) and temperature. The MDMER EEM program does not require measuring DOC and therefore limited data were submitted. In many instances, the ecozone geometric means of DOC were used. RQs that were generated for the 10 selected facilities chosen for ecological exposure assessment in Section 7.2.3 are presented here for ecological risk characterization (Figure 7-3). Several of these facilities show evidence of ecological risk due to metal mining effluent releases of copper.

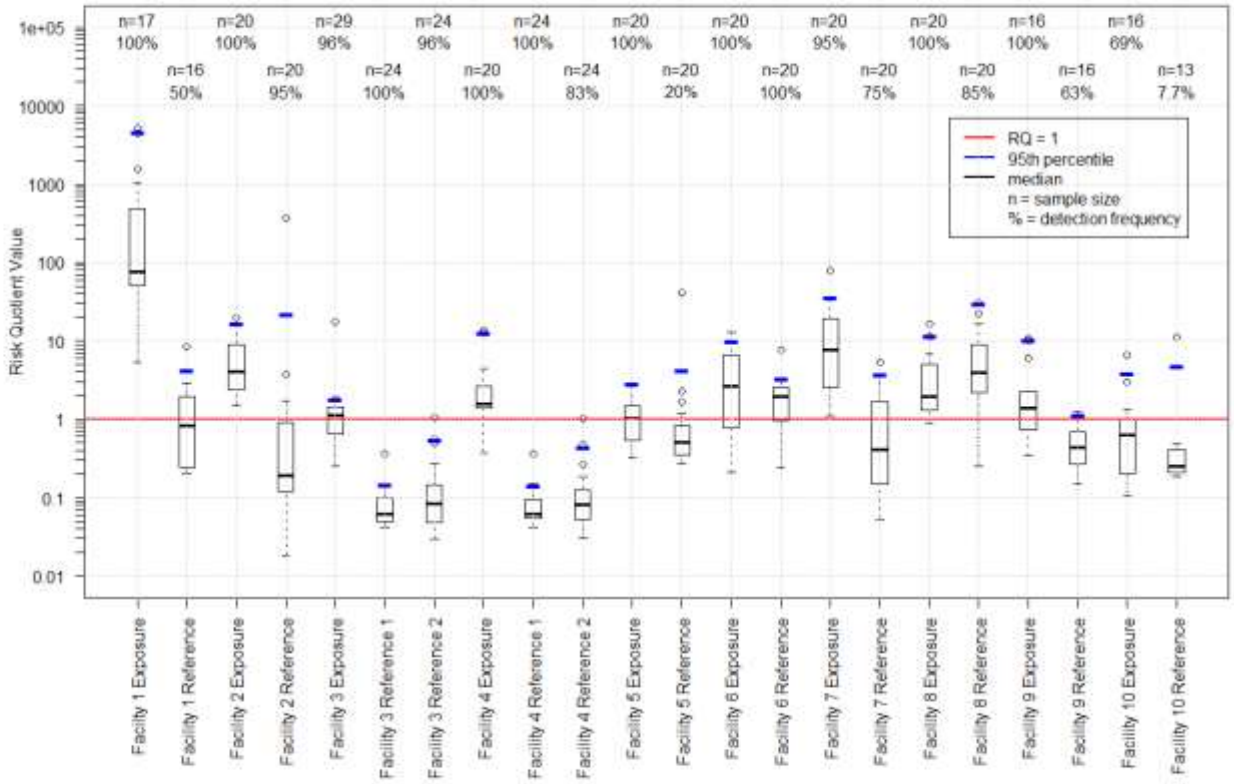

Figure 7-3. Metal mining sector box plots of risk quotients for 10 selected facilities subject to the MDMER from 2011 to 2015 (EEM 2016)

Some of the box plots in Figure 7-3 indicate clear instances of ecological risk through the frequency and magnitude of RQs greater than 1 in the exposure areas, especially when compared to the corresponding reference areas. Further, the detection frequencies of Cu_T in exposure areas are high (equal to or greater than 95%) for most facilities.

Facilities 3 and 4 have high frequencies of RQs exceeding 1 in the exposure areas and no RQs exceeding 1 in the corresponding reference areas. Other instances of ecological risk are shown in the relative magnitudes of the RQs of the exposure and reference area(s), despite varying portions of reference area RQs exceeding 1. Notably, while approximately 50% of the RQs for the Facility 1 Reference area exceed 1, 100% of the Facility 1 Exposure area RQs exceed 1 and are of much higher magnitude (e.g., the median RQ for the exposure area is approximately 100 fold higher than that of the reference area).

Despite the evidence of copper enrichment in the receiving environment for Facility 8 (Figure 7-1), the distribution of RQs for the reference area span and exceed the distribution of RQs for the exposure area. It is important to note that Facility 8 has high concentrations of total hardness in the exposure area due to effluent inputs (the reference area is upstream of the discharge point, where total hardness measurements were much lower). Since high hardness mitigates copper bioavailability, the modeled PNECs for the exposure area were approximately 2 to 10 times higher than those for the reference area (total hardness and PNEC ranges are presented in Table E-3).

The base metals smelting and refining sector ecological risk characterization also utilized raw surface freshwater data, including MDMER EEM program data for the five facilities that combine their effluent with those of metal mines for the period of 2011 to 2015 (EEM 2016) as well as data from a report for one facility that is not subject to the MDMER (EEC Ltd & LAC Ltd 2014). For another facility, PECs were modeled from effluent concentrations reported under the Ontario Regulation 560/94, *Effluent Monitoring and Effluent Limits – Metal Mining Sector* (Government of Ontario [modified 2017]).The EEC Ltd & LAC Ltd 2014 report did not provide DOC data and therefore the ecozone geometric mean was used. Figure 7-4 presents the RQs calculated for six of seven facilities. The sample size for Facility 7 was too small to create a box plot (n = 3) and is discussed below. Only one facility shows evidence of ecological risk due to either base metals smelting or mining effluent inputs of copper, as these activities combine their effluent at this site. No evidence of ecological risk was observed from the two facilities that do not combine their effluent with that of a metal mine in the aquatic compartment (Facility 6 and Facility 7). However, the average sediment concentration (287 mg/kg dw, n=7) for the exposure areas of Facility 6 (Teck, see section 7.2.4) exceed the freshwater ISQG (35.7 mg/kg dw) and the PEL (197 mg Cu/kg dw), indicating the potential for ecological risk in the sediment compartment.

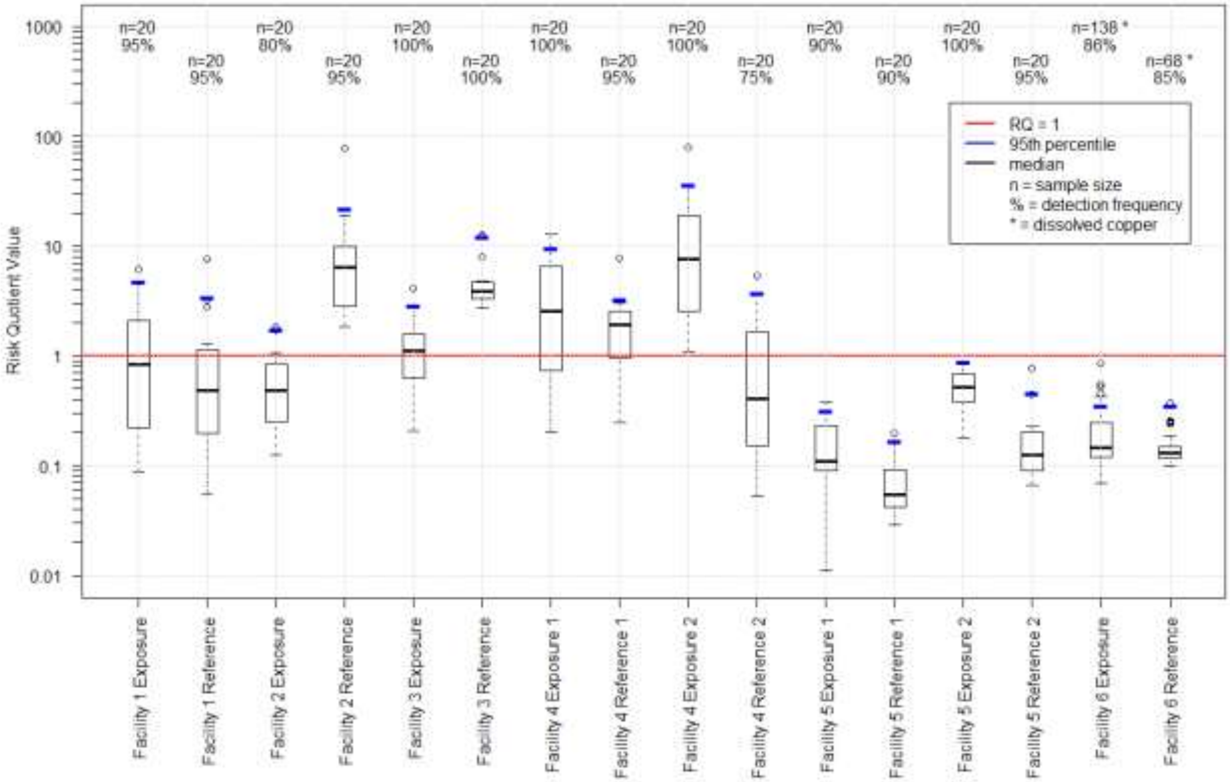

Figure 7-4. Base metal smelting sector box plots of risk quotients for five facilities subject to the MDMER from 2011 to 2015 and one smelter not subject to the MDMER from 2011 to 2013 (EEM 2016; EEC Ltd & LAC Ltd 2014)

As can be seen from the box plots in Figure 7-4, Facility 4 is the only facility demonstrating the potential for ecological risk due to effluent inputs. The contrary is apparent for Facilities 2 and 3: the exposure areas show less frequent and lower magnitudes of ecological risk. As explained in Section 7.2.4, all of these facilities, except Facility 1, have their exposure and reference areas located on different waterbodies that may have different Cu_T concentrations and water chemistry (i.e., TMFs). Facility 1 shows minimally elevated ecological risk in the exposure area. In this case, the exposure and reference areas are located downstream and upstream, respectively, of the effluent discharge point.

Facility 6 and Facility 7 are the two facilities not subject to the MDMER. Low ecological risk is observed for these facilities. The RQs for Facility 7 (not included in Figure 7-4) ranged from 0.43 to 0.56 (n = 3).

The wastewater treatment sector ecological risk characterization relied on PECs modeled from the effluent concentrations of 21 WWTSs releasing to freshwaters collected from 2009 to 2012 by the CMP Environmental Monitoring and Surveillance program (EC 2013) and on PNECs generated from ecozone or Great Lakes central tendencies of TMFs (Table E-2 in Appendix E), depending on the location of the WWTS. The box plots of RQs generated for the 21 WWTSs are presented in Figure 7-5.

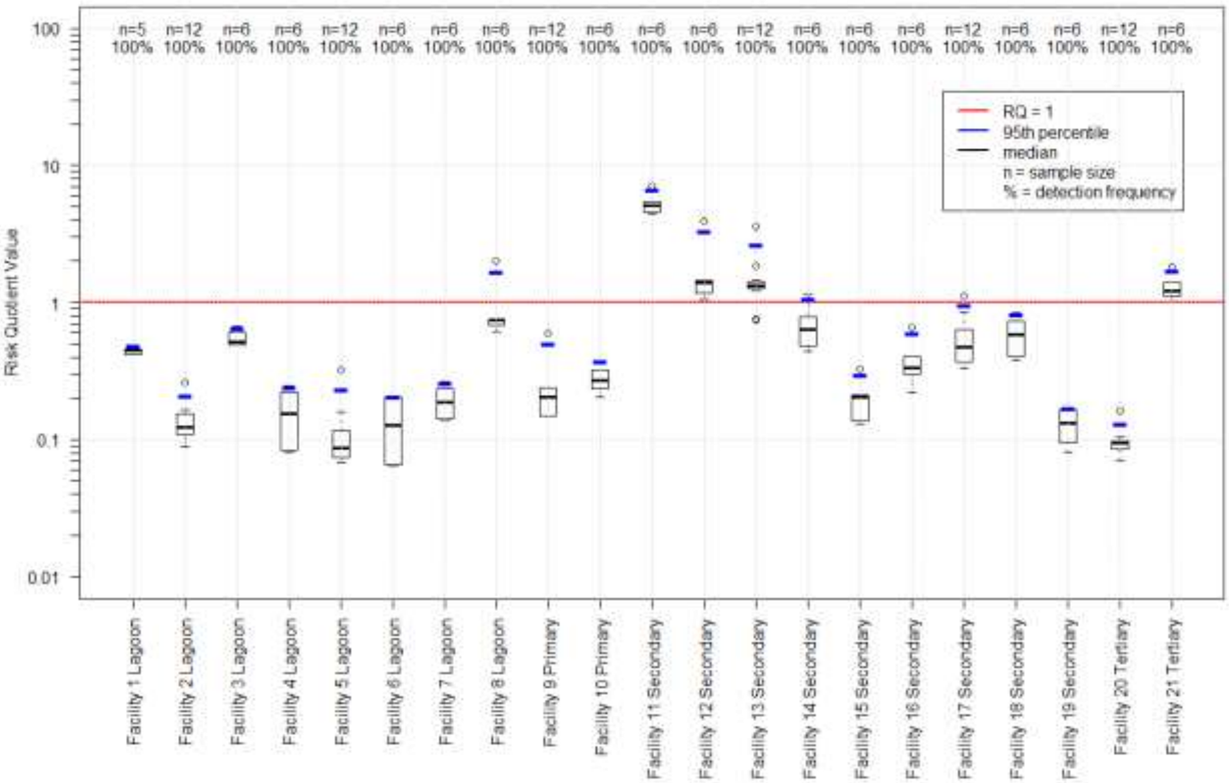

Figure 7-5. Wastewater treatment sector box plots of risk quotients for 21 facilities releasing to surface freshwaters from 2009 to 2012 (EC 2013)

The box plots in Figure 7-5 indicate that about 20% of the WWTSs show evidence of ecological risk through the frequency and magnitude of RQs greater than 1. Three WWTSs using secondary treatment and one WWTS using tertiary treatment have median RQs greater than 1 (i.e., more than 50% of their RQs are greater than 1). Notably, Facility 11 has a high frequency and high magnitude of RQs greater than 1.

As mentioned in Section 7.2.2, additional preliminary exposure scenarios for other sectors were further characterized for ecological risk. None of the information available for these sectors (i.e., pulp, paper and paperboard mills; electric power generation (from coal); landfill leachates; and oil sands mining) indicated ecological risk.

7.3.2 Consideration of the lines of evidence

To characterize the ecological risk of copper and its compounds, technical information for various lines of evidence were considered (as discussed in the relevant sections of this report) and qualitatively weighted. The key lines of evidence supporting the assessment conclusion are presented in Table 7-6, with an overall discussion of the weight of evidence provided in Section 7.3.3. The level of confidence refers to the combined influence of data quality and variability, data gaps, causality, plausibility and any extrapolation required within the line of evidence. The relevance refers to the impact the line of evidence has when determining the potential to cause harm in the Canadian environment. Qualifiers used in the analysis ranged from low to high, with the assigned weight having five possible outcomes (i.e., low; low to moderate; moderate; moderate to high; high).

Table 7-6. Weighted lines of key evidence considered to determine the potential for copper and its compounds to cause harm in the Canadian environment

Line of evidence	Level of confidence[a]	Relevance in assessment[b]	Weight assigned[c]
Persistence in the environment	High	Moderate	Moderate to high
Bioaccumulation in aquatic and/or terrestrial organisms	High	Low	Moderate
PNEC for aquatic organisms in surface water	High	High	High
PNEC for benthic organisms in sediment	Moderate	Low	Low to moderate
Toxicity modifying factors (sample-specific measured data)	High	High	High
Toxicity modifying factors (ecozone and Great Lakes central tendencies)	Moderate	High	Moderate to high
Monitoring data for concentrations of copper in surface freshwater (PECs for metal mining, base metal smelting)	High	High	High
Monitoring data for concentrations of copper in effluents (modeled PECs for base metal smelting, wastewater treatment)	Moderate	High	Moderate to High
RQ(s) for surface freshwater	High	High	High

[a] Level of confidence is determined according to data quality, data variability, data gaps (i.e., are the data fit for purpose).
[b] Relevance refers to the impact of the evidence in the assessment.
[c] Weight is assigned to each line of evidence according to the overall combined weights for level of confidence and relevance in the assessment.

7.3.3 Weight of evidence for determining potential to cause harm to the Canadian environment

Once released in the environment, copper and its compounds may dissolve, dissociate, or degrade to release bioavailable forms of copper that may contribute to the total exposure of organisms to copper. The copper moiety is persistent and can therefore accumulate in the environment and result in long-term exposure to organisms. Copper is also an essential element and may accumulate in certain organisms; however, there is no evidence of biomagnification in ecosystems.

In the aquatic compartment, copper partitions between the water column and sediments and may be found in particulate and dissolved forms. The speciation of copper in surface waters depends on the composition and quality of the given waterbody. The concentrations of Cu^{2+} and certain carbonate and hydroxides forms (i.e., $Cu(OH)^{+}$; $Cu(OH)_2$; $Cu(CO_3)_2^{-2}$) are predominant under conditions of low pH, low alkalinity, and absence of DOC (dissolved organic carbon) (ECCC 2019b). Bioavailability, uptake, and bioaccumulation of copper in aquatic organisms are dependent on the free copper ion activity (e.g., concentration of Cu^{2+} at a specific ionic strength), which is a fraction of the total copper in water. Four main copper TMFs in surface water, which influence the speciation of copper and its competition for binding to biotic sites on organisms, were considered when deriving PNECs: hardness, pH, DOC, and temperature. As hardness and DOC concentrations increase, copper bioavailability and chronic toxicity to aquatic organisms decrease. For pH, there are competing effects: as pH increases, copper complexation increases, but since the concentration of hydronium ions decreases, there is less competition for binding (protective effect). The PNEC increases only minimally as temperature increases.

Copper is released to the aquatic compartment from many industries. The three sectors with the highest reported releases are metal mining, base metal smelting, and wastewater treatment. As discussed in Section 7.3.1, there is evidence for ecological risk due to effluent releases to surface waters from all three sectors. Specifically, the data available for some metal mining facilities shown here (notably, Facilities 1, 2, 3, 4 and 7) and one BMS facility which combines its effluent with a metal mining facility (BMS Facility 4) strongly suggest ecological risk due to the frequency and magnitude of PNEC exceedances in the exposure areas. Monitoring data downstream of base metals smelting and refining facilities that do not combine their effluent with metal mining facilities do not indicate potential for ecological risk for the aquatic environment. However, average concentrations of copper in exposure area sediments downstream of Facility 7 exceeded the freshwater ISGQ and PEL, indicating potential ecological risk in the sediment compartment from this activity. About 20% of the 21 WWTSs had modelled aquatic concentrations in the receiving environment showing evidence of ecological risk.

7.3.4 Sensitivity of conclusion to key uncertainties

Exposure and risk characterization scenarios for surface water were developed for three sectors: metal mining, base metals smelting and refining, and wastewater treatment. Many other uses or sectors may release copper to the environment. However, the aforementioned sectors reported direct releases of copper and its compounds to surface waters to the NPRI and were the primary sectors of interest based on the magnitude of the releases reported. The key uncertainties associated with PECs, PNECs, RQs, non-detect treatment, and sectors are discussed below.

Most PECs originated from copper concentrations measured in the exposure areas of effluent releases. However, the PECs for the wastewater treatment sector, and in one case, the base metals smelting sector (i.e., Facility 7), were modelled from effluent concentrations, which may or may not be a representative dilution factor, depending on the depth, rapidity of mixing, or other factors relating to the receiving environment. This could lead to a potential overestimation of ecological risk for the wastewater treatment sector and the BMS facility. However, low ecological risk was found at BMS Facility 7 in the aquatic compartment. Some datasets of measured PECs contained non-detects and these were replaced with one-half the reported detection limit (DL). A sensitivity analysis was conducted to determine whether the replacement choice (one-half the DL) produced false positives in the ecological risk outcome. However, using a zero value instead of one-half the DL yielded similar results meaning that this approach was unlikely to affect the conclusion of the assessment.

The majority of the PECs were total copper, and few sources provided dissolved copper data, which is the preferred measurement since the chronic BLM calculated PNECs for dissolved copper and in surface waters dissolved copper is always some fraction of the total concentration. Therefore, in some instances, RQs may be overestimated. However, where RQs calculated using total copper are very high, the analyses with dissolved copper may also result in a conclusion of ecological risk.

Exposure and reference areas may be downstream and upstream, respectively, on the same waterbody, or may be located on different waterbodies (i.e., not upstream and downstream paired). It follows that in some cases the copper concentrations in the reference area may be influenced by natural or historical anthropogenic factors that lead to higher values than in the designated exposure area. While potentially observed for some facilities, this potential confounding factor was not important enough to influence the weight of evidence in the risk characterization because the EEM program is based on no effect in reference sites (even if Cu concentrations are elevated), and exposure sites may also be influenced by historical inputs.

PNECs for surface water were calculated using the chronic BLM-based dissolved copper FWQG for aquatic organisms and incorporating hardness, pH, DOC, and temperature data in water for specific sites or monitoring stations. Measured TMF data were not always available and needed to be estimated. Geometric means and averages were chosen since these statistics do not represent extreme values and therefore provide realistic values for the TMFs that are unlikely to under- or overestimate ecological risk.

The copper biotic ligand model (BLM) predicts metal bio-uptake in recognition that the bioavailability and bioreactivity of metals control their potential to cause adverse effects in organisms (ECCC 2019b). However, organisms can be exposed to other forms of copper through other pathways, such as ingestion or maternal transfer, which can also contribute to adverse effects (Smith et al. 2015) not accounted for in the copper BLM. However, this could be partially offset by the conservatism of using total concentrations to characterize these sectors in the absence of dissolved concentrations.

Finally, certain metal mining facilities and BMS facilities combine their effluent for treatment, rendering certain BMS facilities subject to the MDMER. Specifically, facilities combining their effluents include metal mining Facilities 6 and 7 (which combine effluent with that of BMS Facility 4) and BMS Facilities 1 through 5. Since metal mining and BMS effluents are combined, it is impossible to determine if the observed ecological risk comes from the metal mining activities, BMS activities, or both. However, BMS facilities that do not combine their effluent with metal mining facilities (i.e., BMS Facilities 6 and 7) indicated some potential for ecological risk for the aquatic compartment, but with a high level of uncertainty. Potential ecological concern was also identified in the sediment compartment downstream of BMS Facility 6 with a high degree of uncertainty due to a relatively small sample size.

8. Potential to cause harm to human health

8.1 Essentiality

Copper is an essential element for human health and is necessary for many biochemical processes including hemoglobin formation, iron metabolism, carbohydrate metabolism, connective tissue biosynthesis, neutrophil maturation, neurotransmission, and antioxidant defense (ATSDR 2004; WHO 1998; SARA 2008). Copper is also necessary for the maturation of neutrophils and plays an important role in the regulation of gene transcription (SARA 2008). Copper ions are important catalytic co-factors for enzymatic redox reactions. Copper-zinc superoxide dismutase plays an essential role in the cellular defence against reactive oxygen species (ROS), which are normally formed during cellular metabolism (WHO 1998). As with other essential nutrients, levels of copper in the body are homeostatically regulated to ensure sufficient uptake of copper to meet physiological requirements and to avoid excessive copper accumulation that might lead to toxicity (WHO 2004).

Overall, the World Health Organization (WHO) has concluded from available data on human exposure worldwide that there is a greater risk of health effects from deficiency of copper intake than from excess copper intake (WHO 1996, 1998). The Institute of Medicine (IOM) has established dietary reference intakes for copper to ensure nutritional adequacy for the U.S. and Canadian populations (IOM 2001). The estimated average requirement (EAR) is the amount of nutrient intake required to ensure nutritional adequacy for 50% of the general population. The recommended dietary allowance (RDA) is derived from the EAR to ensure average daily dietary intakes sufficient for 97% to 98% of individuals. The EAR and RDA for adults are set at 0.7 and 0.9 mg/day, respectively. The EAR and RDA for pregnant and lactating women are slightly higher at 0.8 to 1 mg/day (pregnant women) and 1 to 1.3 mg/day (lactating women) in order to provide sufficient copper to the developing fetus and growing infant. The upper tolerable intake level (UL), which is the highest level of daily nutrient intake that is likely to pose no risk of adverse health effects for almost all individuals, is set at 10 mg/day for adults (IOM 2001).

8.2 Health effects assessment

Several international organizations have reviewed copper. WHO (2004) has derived a health-based drinking water guideline of 2 mg/L on the basis of studies by Araya et al. (2001, 2003), Olivares et al. (1998, 2001), Pizarro et al (1999a, 1999b, 2001) and Zeitz et al. (2003). The U.S. EPA has set a maximum contaminant level goal (MCLG) and maximum contaminant level (MCL) for copper in drinking water of 1.3 mg/L on the basis of a 1957 study by Wyllie (Wyllie 1957; U.S. EPA 1994). The IOM (2001) has set an upper tolerable intake level (UL) of 10 mg/day for adults based on a volunteer study in humans (Pratt et al. 1985).

Existing assessments by Health Canada were used to inform the health effects section for this assessment. Health Canada has reviewed copper as part of the recommended Dietary Reference Intake guidelines for Canadians (Health Canada [modified 2006]) and in order to set limits on the amount of copper permitted in multi-vitamin/mineral supplements (Health Canada [modified 2018b]) and in supplemented foods (Health Canada [modified 2016]). In each of the above cases, Health Canada has selected the IOM UL as the basis for their guidelines. Health Canada has also used the IOM UL as the basis for deriving soil quality guidelines (CCME 1997) and toxicological reference values (TRVs) for copper under the Federal Contaminated Site Risk Assessment Program (Health Canada [modified 2013]). Health Canada’s guideline technical document on copper in drinking water (Health Canada [modified 2018a]) proposed a maximum acceptable concentration (MAC) of 2 mg/L on the basis of an infant study by Olivares et al. (1998).The following human health effects section describes the toxicokinetics of copper and the critical health effects related to excess exposure to copper. This assessment does not assess the risk of adverse health effects associated with copper deficiency. A literature search was conducted from the year prior to the IOM 2001 report until January 1, 2018.

8.2.1 Toxicokinetics

Copper is absorbed mainly in the upper gastrointestinal (GI) tract (primarily the duodenum). The rate of absorption is influenced by several factors, including the individual’s nutritional copper status, age, amount of copper in the diet, presence of other dietary metals (such as zinc) and solubility of the ingested copper compounds (IOM 2006; Turnlund et al. 1989). In two studies in adults, Harvey et al. (2003, 2005) showed that when corrected for fecal excretion of absorbed copper, true absorption ranged from 45% to 49% for dietary copper intakes in the range of 0.6 to 6 mg/day. The IOM (2006) reported 35% absorption from a diet containing 2 mg of copper per day, which is considered to be the average dietary intake for Canadians. It has been demonstrated that much less copper is absorbed than is ingested (Turnlund et al. 1989, 2005; OECD 2014).

Dermal absorption for soluble and insoluble copper is considered to be ≤0.3% (OECD 2014). There are no human studies that examined the rate and extent of absorption following inhalation exposure to copper (ATSDR 2004).

Once orally absorbed, copper is transported to the liver and kidney (ATSDR 2004). About 40% of copper is taken up by the liver in the first pass. In the liver, copper is stored bound to metallothionein or incorporated into ceruloplasmin (a plasma protein) and released into the blood system for distribution to other organs and tissues or excreted in the bile (EFSA 2015). Approximately two thirds of total copper in the body is found in the bones and muscle; the brain is also an important site of copper storage (IOM 2006).

Approximately, 95% of copper in plasma is bound to ceruloplasmin, which can function as a ferroxidase (Danzeisen et al. 2007). The remaining 5% of copper in plasma is predominantly found as histidine-bound or albumin-bound copper (EFSA 2015). The concentration of copper in the plasma is tightly regulated through homeostatic mechanisms that involve GI absorption and biliary excretion (Danzeisen et al. 2007; ATSDR 2004; EFSA 2015).

During pregnancy, copper is transferred to the fetus via the placenta (EFSA 2015). Approximately one-half of the copper in a developing fetus is stored in the liver, mostly bound to metallothionein.

Metabolism of copper consists mainly of its transfer to and from various organic ligands and into various organs where it performs a number of metabolic functions (ATSDR 2004). Copper is primarily removed from the body by fecal excretion. Biliary excretion is the main mechanism of copper homeostasis (EFSA 2015; Harvey and McArdle 2008). Approximately 72% to 98% of absorbed copper is excreted through bile in the feces of healthy humans (ATSDR 2004; Health Canada [modified 2018a]). Urinary excretion is reported to be as little as 0.5% to 3% (Turnlund et al. 2005; ATSDR 2004). To a lesser extent, copper is excreted through sweat, menses, breast milk and hair (Turnlund et al. 1990; Wijmenga and Klomp 2004; Stern et al. 2007; Mauceri and Mishra 2014; all cited by Health Canada [modified 2018a]).

Copper elimination in most organs and tissues is biphasic (ATSDR 2004). In plasma, the half-lives of the first and second components are 2.5 and 69 days, respectively. It is likely that ceruloplasmin-associated copper has the shorter half-life (i.e., 2.5 days). The estimated copper half-lives for other tissues are 3.9 and 21 days for the liver, 5.4 and 35 days for the kidney, and 23 and 662 days for the heart. Copper elimination in the brain appears to be monophasic, with a half-life of 457 days (ATSDR 2004).

Plasma/serum copper and ceruloplasmin concentrations are commonly measured biomarkers in clinical settings (Harvey and McArdle 2008; Bertinato and Zouzoulas 2009). Population level biomonitoring data (i.e., the Canadian Health Measures Study) are available for blood copper and urinary copper. Blood (plasma) copper levels are tightly regulated through homeostasis and do not correlate to modest changes in dietary copper intake or copper status (Danzeisen et al. 2007; Bertinato and Zouzoulas 2009). In healthy adults, excess copper intake results in downregulation of copper absorption and upregulation of biliary excretion through homeostatic processes. Thus, blood copper levels do not reflect changes in exposure levels (Danzeisen et al. 2007; IOM 2001). Plasma copper is primarily bound to ceruloplasmin and its regulation may reflect regulation of the protein, not the copper levels (Danzeisen et al. 2007). In a human metabolic study, Turnlund et al. (2005) demonstrated that plasma copper and ceruloplasmin concentrations did not change with copper supplementation over typical dietary intakes. In addition, ceruloplasmin levels change for factors not related to copper levels, such as changes in estrogen levels, pregnancy, use of contraceptive pills, illness, age and seasonal changes (Danzeisen et al. 2007; Bertinato and Zouzoulas 2009). These limitations also apply to plasma copper, as it is a reflection of ceruloplasmin levels (Danzeisen et al. 2007). As a result, blood copper or ceruloplasmin levels are not suitable biomarkers to quantify excess exposure for this assessment.

Copper excretion in urine is low (0.5% to 3%) and does not change with dietary intake levels (ATSDR 2004; IOM 2001). Thus, urinary copper is also not a reliable quantitative biomarker of excess copper exposure.

8.2.2 Health effects

Acute health effects

Acute intake of copper can cause reversible GI symptoms in humans, such as nausea, epigastric pain, vomiting, or diarrhea (Pizarro et al. 1999a, 1999b; Araya et al. 2001; Olivares et al. 1998, 2001; all cited in Health Canada [modified 2018a]). These effects have been observed in multiple studies following ingestion of bolus doses of copper in drinking water and are attributed to direct irritation of the stomach (Araya et al. 2003, as cited in Health Canada [modified 2018a]). They are not associated with systemic toxicity (U.S. EPA 2009).

Inhalation of copper as dust or mist is likely to be irritating to the respiratory system. An acute inhalation endpoint was established by the OECD on the basis of an acute inhalation study (Wesson 2003 unpublished, as cited in ECI 2008). Recoverable respiratory effects (i.e., increased respiration rate, laboured breathing) were noted following a 4 hour exposure at a lowest observed adverse effect concentration (LOAEC) of 1140 mg/m^3 (equivalent to 653 mg/m^3 elemental copper). A study was available in which mice and hamsters were give a single 3-hour exposure of copper sulfate (Drummond et al. 1986), but it was not considered appropriate for risk assessment because of concerns regarding animal health and the limited number of endpoints examined (Drummond et al. 1986, as cited in ATSDR 2004).

Dermal exposure to copper tends to cause moderate to low skin irritation. Copper is generally non-sensitizing in animals, and since copper powders have low solubility and bioaccessibility, they do not present a hazard by the dermal route (OECD 2014).

Repeat-dose health effects

As previously noted, Health Canada and several international organizations have established exposure guidance values to protect against copper toxicity.

In a double-blind study by Pratt et al. (1985), there was an absence of indicators of adverse liver effects or GI damage in healthy human adults given a 10 mg capsule of copper gluconate daily over a 12-week period. As there was no indication of adverse effects, the IOM derived ULs for different age groups based on 10 mg in adults (see Table 8-1) (IOM 2001). It should be noted that the IOM ULs established for the younger age groups were not based on empirical data or studies, but derived by relative body weight adjustments to the UL for adults. The IOM endpoints do not account for the dietary intakes of the individuals in the study (approximately 2 mg/day). Chronic exposure for the general population to very high levels (≥ 30 mg/day), may lead to liver and renal damage (O'Donohue et al. 1993; IPCS 1998; O'Donohue et al. 1999; Stern et al. 2007; all cited in Health Canada [modified 2018a]). It is expected that at the first signs of reversible GI effects (i.e., nausea, epigastric pain, vomiting, or diarrhea), which may occur between doses of 10 to 30 mg Cu/day, copper supplementation would cease prior to developing liver toxicity.

Table 8-1. IOM tolerable upper intake levels (UL) for different age groups (IOM 2001)

Age group (years)	UL (mg/day)
0–1	NA[a]
1–3	1
4–8	3
9–13	5
14–18 (including lactating and pregnant women)	8
19–50 (including lactating and pregnant women)	10

[a] The IOM did not derive a UL for infants 0–1 year old (not possible to establish; source of intake should be from food and formula only)

The WHO (2004) based their drinking water guideline (2 mg/L) on several repeat-dose studies ranging from 2 weeks to 9 months, with copper concentrations from 0 to 6 mg/L. The conclusion from the studies is that although there were incidences of GI symptoms (diarrhea, nausea, abdominal pain, or vomiting), there were no significant changes in indicators of liver function or biomarkers of liver toxicity (WHO 2004). Similarly, Health Canada (modified 2018a) derived a maximum acceptable concentration (MAC) of 2 mg/L from a study by Olivares et al. (1998), in which infants continuously received 2 mg/L of Cu(II) from ages 3 to 12 months and showed no effects (Health Canada [modified 2018a]).

In a non-guideline 12-day dermal toxicity study, rats were treated topically with 100 or 1000 mg/kg bw/day of an 8% elemental copper mixture. Although dose-related increases in dermal irritation were observed, no systemic toxicity was noted. A systemic no observed adverse effect level (NOAEL) of 1000 mg/kg bw/day, the highest dose tested, was established (Kiplinger 1996, as cited in U.S. EPA 2009). In a guideline 90-day dermal toxicity study, albino rats were dermally exposed to copper naphthenate at doses of 0, 100, 300, or 1000 mg/kg bw/day for 13 weeks. No adverse systemic effects were noted. The dermal toxicity NOAEL was 100 mg/kg bw/day on the basis of lesions related to dermal irritation at the site of dosing with 300 mg/kg bw/day and above, and the systemic NOAEL was 1000 mg/kg bw/day, the highest dose tested (Tompkins 1990, as cited in U.S. EPA 2007). A lack of systemic toxicity following dermal dosing, along with the physical-chemical properties (i.e., low solubility and low bioaccessibility), further demonstrates that the dermal toxicity of copper is limited. This is consistent with the approaches of the U.S. EPA and PMRA, which did not establish endpoints to quantify dermal exposure to copper given the lack of systemic toxicity (U.S. EPA 2009; Health Canada 2009).

In a study reviewed by OECD’s Cooperative Chemicals Assessment Programme (OECD 2014), cuprous oxide was administered to Sprague Dawley Crl:CD (SD) rats by whole-body inhalation exposure for 6 hours/day over 4 weeks (5 days/week) at exposure levels of 0.2, 0.4, 0.8 and 2.0 mg/m^3. After 4 weeks of exposure, signs of acute inflammation, along with increased lung, bronchial and mediastinal lymph node weights were observed. Alveolar histiocytosis and a slight increase in collagen deposition were observed, along with minimal olfactory epithelium degeneration in a few animals. These effects were reversible and no systemic effects were noted in animals administered 2 mg/m^3 (the highest dose tested) for 4 weeks, followed by a 13-week recovery period (Kirkpatrick 2010, as cited in OECD 2014). On the basis of these results, a no observed adverse effect concentration (NOAEC) of 2 mg/m^3 (equivalent to 1.77 mg/m^3 elemental copper) was established for this study, as doses higher than this were not tested. This value was brought forward for risk characterization with repeat inhalation exposures. Other studies with repeat dosing via inhalation were conducted on mice and rabbits; however, these studies were limited in the number of endpoints examined, had poor exposure characterization, had concerns about animal health and/or lacked controls (ATSDR 2004). Therefore, they were not used to derive inhalation endpoints.

The currently available evidence on copper and its compounds does not cause concern for oral repeat dose toxicity, genotoxicity, neurotoxicity, reproductive and developmental toxicity, or carcinogenicity (OECD 2014; Health Canada [modified 2018a]).

8.3 Exposure assessment

8.3.1 Daily exposure from environmental media, food and drinking water

Copper occurs naturally in the Earth’s crust and anthropogenically in environmental releases from human activities. This assessment considers combined exposure to the copper moiety from natural and anthropogenic sources, whether it is present in environmental compartments, food, or products available to consumers. All substances that have the potential to dissolve, dissociate, and/or degrade to release copper through various transformation pathways can potentially contribute to the exposure of living organisms to bioavailable forms of copper. Total copper (total amount of copper from all sources) has been measured in food, breast milk, air, household dust and soil, drinking water distribution systems and tap water, including in areas close to point sources of exposure such as copper mines and refineries.

Food is considered to be the primary source of copper exposure from natural sources (ATSDR 2004). Copper enters the food chain through natural uptake by plants from soil. It may also be present in foods through its use as a food additive, in supplemented foods, as an incidental additive during food processing, and from food packaging (email from the Food Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated March 14, 2016; unreferenced). Copper cookware can leach small amounts of copper into food during preparation, and for this reason, copper pots and pans are usually coated with another metal that prevents the copper from coming into contact with food (Health Canada [modified 2015]). The Health Canada Total Diet Study (TDS) captures copper concentrations in foods from both natural and anthropogenic sources by preparing and processing food samples as they would be consumed in an average household (Health Canada 2011).

In Canada and the United States, foods that contribute substantial amounts of copper in the diet are those with high concentrations of copper generally consumed in small quantities (such as organ meats and seeds), along with those of lower concentrations that are typically consumed in higher quantities (such as potatoes and cereal-based foods) (IOM 2001). Based on copper measurements in the TDS from 1993 to 1999 and 2007, high concentrations of copper were found in organ meats, shelled seeds, nuts, mushrooms and some herbs and spices (Health Canada 2011). Dairy products and vegetables are some examples of foods that typically have low levels of copper. Copper concentrations measured in food commodities as part of the TDS were used to derive average dietary intakes of copper for Canadians from 1993 to 2007 (Health Canada 2011). A 5-year average dietary intake estimate was derived from the years 2003 to 2007 and results ranged from 0.8 mg/day (0.052 mg/kg bw/day) in infants up to 1.9 mg/day (0.026 mg/kg bw/day) in adults (Table F-2, Appendix F).

Dietary intake estimates are also available for Indigenous people in Canada and take into account the consumption of traditional foods (Chan et al. 2016; Gagné et al. 2012; Kuhnlein et al. 2004, 2007, 2008). Traditional foods include wild game and berries, and contribute to higher intakes of copper in both adults and children. In Alberta, mean dietary intake of copper was 1.6 mg/day on days when traditional foods were included in the diet, as compared to 1.1 mg/day on days when traditional foods were not included (Chan et al. 2016). Similarly, children in the Northwest Territories and the Yukon also experienced higher intakes of copper on days that included traditional foods in the diet (Kuhnlein and Receveur 2007). With the consumption of traditional foods, intake estimates for Indigenous people are similar to intake estimates for the general population in Canada, but are lower when traditional foods are not consumed.

Copper is present in breast milk, which is a source of dietary intake for nursing infants. The average daily intake of copper by infants from breast milk is 0.042 mg/kg bw/day (equivalent to 0.3 mg/day, based on 7.5 kg bw), derived on the basis of breast milk values collected from 847 participating mothers from the Maternal-Infant Research on Environmental Chemicals (MIREC) study from 2008 to 2010 (email from the Food Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated March 3, 2016; unreferenced).

Copper is commonly measured at water treatment facilities and distribution systems across the provinces and territories, and the results are presented in the *Copper in Drinking Water* guideline technical document for public consultation (Health Canada [modified 2018a]). In drinking water, concentrations of copper at the tap may be higher than in distribution systems because of potential leaching from copper pipes used in indoor plumbing (Health Canada 1992). The highest median copper concentration reported in Canadian tap water samples was 0.035 mg/L, which is well below the proposed drinking water guideline of 2 mg/L (Health Canada [modified 2018a]). There are cases where high levels of copper release have been observed. In 1985, a study found that 50% of rural Nova Scotia homes served by private wells had copper levels that exceeded 1 mg/L (Health Canada [modified 2018a]). However, across the provinces and territories, median copper levels at the tap were found to be low (below 1 mg/L). Drinking water data were also available from Indigenous communities in British Columbia, Manitoba, Ontario and Alberta (Chan et al. 2011, 2012, 2014, 2016). After flushing for 5 minutes, copper levels in all four provinces were below 2 mg/L, the proposed drinking water guideline (Chan et al. 2012).

Airborne copper in particulate matter (PM) can originate from both natural and anthropogenic sources. In 2011, total copper was measured in PM in 910 samples from 9 different sites across Canada as part of the National Air Pollution Surveillance (NAPS) Program. The median concentration of total copper in $PM_{2.5}$ outdoor air was 1.14 ng/m^3, ranging from 0.14 to 28.22 ng/m^3, with a 95th percentile of 3.44 ng/m^3 (NAPS [modified 2013]). Matched indoor, outdoor and personal monitoring air data ($PM_{2.5}$ samples) were collected from Windsor, Ontario, in the years 2005 to 2006 (Rasmussen et al. 2016). The highest median copper concentration was measured in personal air samples (5.15 ng/m^3), followed by outdoor and indoor air concentrations (median of 4.15 and 3.99 ng/m^3 respectively) while the 95th percentiles displayed a different trend, with indoor air (24.9 ng/m^3) being higher than personal air (19.3 ng/m^3), which was higher than outdoor air (14.8 ng/m^3) (Rasmussen et al. 2016). This data suggests that at median copper concentrations, outdoor air had a higher influence on personal air concentrations, whereas at the 95th percentile, indoor air had a greater influence. Exposure to copper in PM was also measured in metro systems in Vancouver, Toronto and Montreal (van Ryswyk et al. 2017). Median concentrations of copper were higher in metro systems, ranging from 40 to 1646 ng/m^3, when compared to outdoor air measurements in either the NAPS program or the data from Windsor, Ontario (median of 1.14 and 4.15 ng/m^3 respectively).

Nationally representative copper concentrations in dust from Canadian homes were available from the Canadian House Dust Study (CHDS) (Rasmussen et al. 2013). The CHDS includes measurements of total copper from 1025 homes and is statistically representative of urban residential homes in Canada. Median and 95th percentile concentrations of total copper in fresh vacuum dust were 199 mg/kg and 660 mg/kg, respectively (Rasmussen et al. 2013). These results are similar to an earlier study of 48 homes in Ottawa, Ontario, where the median and 95th percentile total copper concentrations in house dust were 157 mg/kg and 489 mg/kg, respectively (Rasmussen et al. 2001). The copper concentrations in urban house dust are an order of magnitude higher than the natural background, suggesting that anthropogenic sources dominate in indoor urban environments (Rasmussen et al. 2013). Bioaccessibility values (in simulated stomach fluids) for copper in dust were available from several studies; median bioaccessibility values have been reported to range from 30.5% to 49% (SARA 2008; Boros et al. 2017; Rasmussen et al. 2008).

Copper concentrations in Canadian soil are well described in the Canadian Soil Quality Guideline for Copper (CCME 1997). They range from 2 to 100 mg/kg and the average copper concentration in Canadian soil is estimated to be approximately 20 mg/kg (CCME 1997; McKeague et al. 1979). More recent publications report copper concentrations in Manitoba and Ottawa, Ontario, within this same range (Rasmussen et al. 2001; Haluschak et al. 1998). The Ontario Ministry of Environment (ON MOE 2004) derived background levels of contaminants in soil that were deemed to represent typical upper limits across Ontario. The typical upper limit background concentration of copper was estimated to be 85 mg/kg (ON MOE 2004). Bioaccessibility values (in simulated stomach fluids) have been reported to range from 30% to 74% (Rasmussen et al. 2008; SARA 2008). There is a soil quality guideline for human health of 1100 mg/kg (CCME 1997). Exceedances of the soil quality guideline have been found around point sources such as mines and smelters; concentrations up to 9700 mg/kg were reported within 1 kilometre of a copper smelter in Canada (CCME 1997).

Average intake estimates were derived for the general Canadian population on the basis of copper concentrations measured in food, drinking water, air, dust and soil. Daily intake of copper for the general public ranges from 0.32 to 1.9 mg/day in infants and adults, respectively. Intakes normalized by body weight are highest in infants (0.042 to 0.082 mg/kg bw/d) and toddlers (0.042 mg/kg bw/d) and decline in the elderly (0.018 mg/kg bw/d) (Table F-1, Appendix F). Food is the primary source of total daily intake for the general public, accounting for approximately 95% to 99% of intake depending on the age group. Meat, cereals, nuts and vegetables such as potatoes are key sources of dietary intake. Drinking water accounts for 2% to 5% of daily copper intake, while air, soil and dust account for less than 2%. Dietary intake is also the primary source of exposure for intake among Indigenous people living in northern Canada, particularly when the diet includes traditional foods, such as fish (Kuhnlein et al. 2002).

There are Canadians with potential for elevated exposure to copper resulting from point sources of release (such as mines, smelters and refineries) to their local environment. In the immediate vicinity of these point sources, copper concentrations in soil, air and dust can be much higher from atmospheric fallout, although in many cases concentrations decrease with distance from the point source (Intrinsik 2010). Estimated daily intake of copper was derived as part of human health risk assessments conducted for residents living near or adjacent to mining, smelting and refining operations in Sudbury, Ontario, and Flin Flon, Manitoba (SARA 2008; Intrinsik 2010). In these assessments, copper concentrations in soil, dust, and air were found to vary greatly across the study area. In some sites, environmental media concentrations were up to 150-fold higher than average values for Canadian environmental media, while environmental media concentrations at other sites were comparable to the average for Canada. Upper 95% confidence intervals on mean air concentrations in the Flin Flon area ranged from 50 to 840 ng/m^3, while typical levels are about 100-fold lower. However, even in areas where environmental media concentrations were elevated, the major contributor of copper intake was still food. For residents in and around the Sudbury area, drinking water was the second highest source of intake, contributing up to 8% of intake in one community and around 1% to 3% of intake in the other study areas. Local foods such as garden food, wild game, local berries and fish contributed up to 4% to 6% of daily intake, while dust, air and soil contributed less than 2% to the estimated total daily intake for all age groups in all communities. Estimated daily intakes (central tendency exposure) ranged from 0.48 to 1.8 mg/day (SARA 2008). When normalized by body weight, intake was lowest in adults and highest in infants (0.021 to 0.079 mg/kg bw/d, respectively). For Canadians living in and around the Flin Flon area, food was the major contributor to copper intake, with drinking water being the second major source. Together, food and drinking water accounted for 90% to 94% of estimated daily intakes for all communities. Estimated daily intakes ranged from 0.58 mg/d in infants to 2.0 mg/day in adults. Estimates normalized by body weight ranged from 0.028 to 0.081 mg/kg bw/d. A route-specific inhalation exposure scenario was derived using the air concentration value of 840 ng/m^3 measured in communities in and around the Flin Flon area (Intrinsik 2010).

In general, food is the predominant contributor to daily intake of copper for Canadians, including Indigenous people and populations near point sources of exposure. Dietary intake estimates for Indigenous people (adults and children) were similar to intake estimates for the general population. Estimated daily intakes derived for people living around point sources of exposure were also similar to estimates derived for the general population (SARA 2008; Intrinsik 2010) except for the toddler age group, which was slightly higher for people living around point sources of exposure (Appendix F, Table F-3). Higher soil ingestion rates for toddlers and higher soil concentrations in these two assessments contributed to the overall higher intake estimate for toddlers in these areas (SARA 2008; Intrinsik 2010).

8.3.2 Products available to consumers

This assessment quantifies exposure from oral and inhalation routes, which are the routes where critical effects have been identified.

No dermal toxicity is expected considering the absence of systemic effects in toxicity studies via the dermal route, as well as the low absorption and bioaccessibility of copper. Dermal exposure was therefore not quantified.

Information submitted to Environment and Climate Change Canada and Health Canada pursuant to CEPA section 71 notices (see Appendix B), notifications submitted under the *Cosmetic Regulations* to Health Canada for copper, the Licensed Natural Health Products Database, the Natural Health Products Ingredients Database, the Drug Product Database, publicly available databases and websites (e.g., CPID [modified 2018]; CPCat 2017; Household Products Database 1993-2017), and material safety and technical datasheets were considered in order to identify products where there is: (a) potential for oral exposure from ingestion or mouthing of products containing copper and; (b) potential for inhalation of copper from aerosols or particulates including powders (non-volatile). As copper is not volatile, the potential for off-gassing and emissions from products is not applicable.

Copper is present in thousands of products available to consumers, including as a medicinal and non-medicinal ingredient in therapeutic drug products and natural health products, cosmetics, household products, textiles, paints, adhesives, and children’s toys (CPID [modified 2018], internal DPD [modified 2017], Guney et al. 2014, NHPID [modified 2019], email from the Consumer Product Safety Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated May 4, 2017; unreferenced). Products such as natural health products, cosmetics, arts and craft materials, cleaning products, paints and lubricants, and toys can all result in direct exposure to consumers during use. Other sources, including copper present in building materials, are more likely to result in exposure through ingestion of house dust or inhalation of indoor air and are captured in the intake estimates from environmental media. Sentinel exposure scenarios (scenarios associated with the highest exposure) were identified to estimate exposure to consumers from the use of products containing copper where oral or inhalation exposure was anticipated.

Oral exposure

Copper was found to be present (including as a dye, pigment or printing ink) in various arts and craft materials, such as children’s paint, glitter glue, play dough, slimy toys, crayons, colouring pencils, markers, and stamp pads (Guney et al. 2014; MSDS 2009a; MSDS 2009b; MSDS 2016). Children can be exposed to copper while playing with these materials, through incidental ingestion from hand-to-mouth contact or object-to-mouth contact. Incidental oral ingestion of wax crayons, modeling clay and craft paint were identified as sentinel exposure scenarios for arts and crafts products. The craft paint scenario would also be applicable to other ink product scenarios, such as hand-to-mouth contact from markers, pens, printing ink or dyes. Wax crayons and modeling clay were chosen as sentinel scenarios for incidental ingestion as these products are used frequently by young children and are easily bitten, chewed or fragmented.

Several recent studies have examined concentrations of copper in children’s products and toys (Guney et al. 2014; Korfali et al. 2013; Stone 2014). Guney et al. (2014) measured total and bioaccessible (via saliva) copper in metallic toys, jewelry, plastic toys, toys with paint or coating, and brittle or pliable toys purchased in North America. Total copper, ranging from 0.38 to 710 000 mg/kg (0.000038 to 71%), was measurable in objects such as metal zippers or buttons present on toys that children might suck on (Guney et al. 2014). Bioaccessible concentrations were used to estimate potential exposure to copper from mouthing of metallic toys, jewellery, plastic toys, toys with paint or coatings, and brittle or pliable toys by toddlers (0.5 to 4 years).

Copper is present as an ingredient in approximately 2000 cosmetic products notified to Health Canada under the *Cosmetic Regulations* (personal communication, email from Consumer Product Safety Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated May 4, 2017; unreferenced). Some of the most common cosmetic products containing copper include moisturizers, nail polish, makeup, shampoo, conditioner and cleansers. Reported concentrations vary from less than 0.1% up to a range of 30% to 100%. Two sentinel scenarios with the potential for oral exposure were identified for cosmetics: oral exposure from lipstick and/or lip balm and oral exposure from toothpaste (without fluoride).

Copper and its compounds are listed as ingredients in approximately 3900 licensed natural health products as both a medicinal and non-medicinal ingredient. The majority of these products contain copper as a medicinal ingredient in multi-vitamin/mineral supplements (LNHPD [modified 2018]). According to Statistics Canada, 44% of Canadians reported taking a multi-vitamin or mineral supplement (Statistics Canada [modified 2017]). This may account for a significant proportion of daily intake in these individuals. Copper is permitted to be present in multi-vitamin/mineral supplements at doses starting at 0.035 to 0.7 mg/day for children aged 1 to 3 years, and ranging up to 8 mg/day in products marketed to adults. It is not permitted in products intended for infants 0 to 12 months of age (Health Canada [modified 2018b]). The top five best-selling multi-vitamin/mineral supplements contain a maximum of 1 mg/day (email from Food Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated January 4, 2018; unreferenced). Copper-containing compounds are also present in natural health products as non-medicinal ingredients, often as a colourant. Examples of some products that contain copper as a non-medicinal ingredient include multi-vitamin/mineral supplements, herbal remedies, tablets for immune support and various creams with SPF.

Oral intake estimates from sentinel scenarios with the highest intakes are presented in Table 8-2 below. Further details on the algorithms and model inputs are presented in Appendix G. Natural health products represent the only product where oral exposure is intended; the other sentinel scenarios represent incidental or unintentional oral exposure.

Table 8-2. Estimated potential intentional and incidental oral exposures to copper from the use of products available to consumers

Product category	Exposure scenario	Age group (years)	Exposure estimate [a] (mg/kg bw/day)	Exposure estimate [a] (mg/day)
Arts and crafts	Using crayons (incidental ingestion)	Toddlers (0.5 to 4)	0.0015	0.023
Arts and crafts	Playing with modeling clay (incidental ingestion)	Toddlers (0.5 to 4)	0.0025	0.039
Arts and crafts	Using craft paint (incidental ingestion)	Toddlers (0.5 to 4)	0.01	0.15
Children’s Toys	Infant; toddler mouthing a toy	Infants; toddler (0 to 0.5; 0.5 to 4)	0.012; 0.0059	0.092
Cosmetics	Wearing lipstick / lip balm	Toddlers (0.5 to 4)	0.038	0.6
Cosmetics	Brushing teeth with toothpaste (without-fluoride)	Toddlers (0.5 to 4)	0.00025	0.0038
Natural health products	Taking oral health supplement containing copper	Children (5 to 11)	0.032	1

[a] See appendix G for further details.

Inhalation

Copper was found in a range of aerosol or spray products whose use may result in inhalation exposure, including cleaning products, cosmetics, paints, sealers and lubricants (CPID [modified 2018], CPISI 2018, email from Therapeutic Products Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated April 28, 2017; unreferenced; MSDS 2015).

Exposure estimates were generated for cosmetic products with the potential for inhalation exposure (i.e., formulated as aerosols), including hair spray and face moisturizer formulated as an aerosol (personal communication from the Consumer Product Safety Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated May 4, 2017; unreferenced). In addition, two scenarios were modeled to represent potential inhalation exposure from use of cleaning products and paints: the use of a spray cleaning product and the use of an aerosol spray paint (CPISI 2018, MSDS 2015).

Air concentrations of copper from use of these products were modeled using the Consumer Exposure Web Model (ConsExpo Web 2016), a computational modeling program intended to estimate exposure of the general population to common products available to consumers. Input values for the model are provided in Appendix E, including any refinements to defaults. A time-weighted air concentration over 4 or 6 hours was calculated on the basis of the duration of the toxicity studies selected for repeat-dose and acute inhalation scenarios (i.e., 6 hours for frequent or repeated exposures and 4 hours for infrequent exposure).

Table 8-3. Estimated potential air concentrations of copper from the use of products

Product category	**Exposure scenario**	**Age group (years)**	**Mean event exposure estimate (mg/m^3)**	**Scenario duration**	**Time-weighted air concentrations (mg/m^3), hours**
Paint	Using spray paint	Adult (20+)	33	Infrequent	2.8, 4 hr
Cleaning products	Using disinfectant spray	Adult (20+)	0.00079 to 0.15	Daily or frequent use	0.00013 to 0.025, 6 hr
Cosmetics	Using spray face moisturizer	Adult (20+)	0.36	Daily or frequent use	0.005, 6 hr

8.4 Characterization of risk to human health

Canadians may be exposed to copper-containing substances from environmental media, food, and drinking water and from their presence in products available to consumers. Critical health effects have been identified following oral and inhalation exposure to copper.

The IOM UL was selected to characterize risk from daily oral intake estimates, which includes exposure from food, drinking water and environmental media (air, soil, dust), as well as from products available to consumers. This is consistent with the endpoint used to set limits by several programs in Health Canada, including for multi-vitamin/mineral supplements (Health Canada 2018b), supplemented food (Health Canada, [modified 2016]), and dietary reference intakes (Health Canada [modified 2006]) and in the derivation of the toxicological reference values (TRVs) and soil quality guidelines for copper (Health Canada [modified 2013]; CCME 1997). The UL for copper is based on a human volunteer study with a NOAEL of 10 mg/day dosing (as a supplement), with no additional adjustment for background dietary intake (Pratt et al. 1985). It is worth noting that the NOAEL would be slightly higher if background dietary exposure was taken into account (i.e., 10 mg/day plus approximately 2 mg/day of dietary exposure).

Average daily intake estimates for the general population from environmental media, food and drinking water are presented in Table 8-4 below. For the general population, total daily intake of copper was less than the IOM UL for each age group. For Canadians living in and around point sources of release (e.g., mines, smelters, refineries), total daily intake estimates (ranging from 0.4 to 2.0 mg/day) were also less than the IOM UL (Table F-3, Appendix F). The primary source of intake of copper for both the general public and those living in communities near point sources of release is food (including breast milk and beverages). Copper from other environmental media (dust, soil, and air) does not contribute more than 10% to the total daily intake in both the general population and those living in the vicinity of point sources of release.

Table 8-4. Average daily intake estimates and risk estimates for Canadians from environmental media, food, and drinking water

Age group	Average daily intake estimate (mg/day) [a]	IOM UL (mg/day) [b]	Exceedances of the IOM UL (Y/N)
0 to 6 months breast fed (formula fed)	0.32 (0.61)	1[c]	**N**
0.5 to 4 years	0.83	1	**N**
5 to 11 years	1.3	3 to 5	**N**
12 to 19 years	1.7	5 to 8	**N**
20 to 59 years	1.9	10	**N**
60 + years	1.2	10	**N**

Abbreviations: Y= yes, N=no

[a] See Table F-1 (Appendix F) for more details.

[b] The IOM UL is based on age groups that vary from Health Canada's standard age groups presented in these risk assessments. When the age groups do not match up, a range is given to encompass both age groups from the IOM.

[c] The IOM did not derive a UL for infants; therefore, a UL was estimated for infants 0 to 6 months of age based on a body weight adjustment (7 kg) from the NOAEL of 10 mg/day for adults.

Copper is present in many products available to consumers, and sentinel exposure scenarios were identified to characterize risk to the general population from the use of products containing copper. Oral exposure estimates to copper from the use of arts and craft products, natural health products, cosmetics, and children's toys were derived. These are considered to be representative of typical daily or frequent use products that could result in direct oral exposure to consumers. The highest oral exposure estimates derived from the sentinel exposure scenarios are presented in Table 8-5. Oral exposure resulting from the use of products available to consumers did not result in exposure estimates exceeding the IOM UL for copper.

Table 8-5. Sentinel oral exposure and risk estimates for copper from products available to consumers

Category	Exposure scenario	Exposure estimates (mg/day)	IOM UL (mg/day)	Exceedances (Y/N)
Arts and crafts	Toddler playing with craft paint (incidental ingestion)	0.15	1	**N**
Children's toys	Infant/ toddler mouthing a toy	0.092	1	**N**
Cosmetics	Toddlers wearing lipstick / lip balm (accidental ingestion)	0.6	1	**N**
Natural health products	Child taking multi-vitamin/mineral supplements	1	3 to 5	**N**

Abbreviations: Y = yes, N = no

Critical health effects were also identified following inhalation exposure to copper-containing substances. For acute scenarios, a LOAEC of 1140 mg/m^3 copper oxychloride (equivalent to 653 mg/m^3 elemental copper) was selected from an acute inhalation study in rats, where transient respiratory effects (i.e., increased respiration rate, laboured breathing) were noted following a 4-hour exposure at this dose. For frequent or repeated exposure scenarios, a NOAEC of 2 mg/m^3 (equivalent to 1.77 mg/m^3 elemental copper) was selected from a 4-week inhalation study in rats (Kirkpatrick 2010, as cited in OECD 2014), in which reversible respiratory effects were seen in the lungs with cuprous oxide administration. These effects and effect levels were used to estimate risk via the inhalation route of exposure, which includes ambient air and products available to consumers (see Table 8-6).

There is potential for inhalation exposures to copper in particulate matter in air for the general population and for those living near point sources of release, such as mines, smelters and refineries. In addition, inhalation exposure scenarios to copper from the use of cleaning products, cosmetics, and paints were identified. These exposure estimates are considered to be conservative as they are based on 100% bioavailability, which is likely not the case for certain copper-containing substances such as phthalocyanine green, a pigment present in cleaning products and copper present in metallic paints. In addition, default values suggested by ConsExpo result in conservatively high air concentration estimates for spray paint (ConsExpo Web 2016). Route-specific margins of exposure (MOEs) were derived for each inhalation scenario by comparing the air concentration with the critical endpoint. The critical endpoint was selected on the basis of the duration of the exposure scenario (i.e., acute or frequent/repeated exposure), and the concentrations were converted to elemental copper equivalents. The sentinel scenarios and MOEs are presented in Table 8-6. Respiratory effects noted are reversible; therefore, the calculated MOEs for inhalation exposure to copper are considered adequate to address any uncertainties in the health effects and exposure databases.

Table 8-6. Relevant inhalation exposure and health effect values for copper, as well as margins of exposure, for determination of risk

Category	**Duration: exposure scenario**	**Air concentration (mg/m^3) [a]**	**Critical effect level (mg/m^3)**	**MOE**
Paints and coating	Acute: adult using spray paint	2.8, 4 hr TWA	653 (LOAEC for respiratory effects)	233
Environmental media (copper in air)	Continuous: Canadians with potential for elevated exposure resulting from point sources of release	0.00084, annual average [b]	1.77 (NOAEC for lung effects)	2107
Cleaning Products	Repeat / frequent: adult using disinfectant spray	0.00013 to 0.025, 6 hr TWA	1.77 (NOAEC for lung effects)	71 to 13615
Cosmetics	Repeat / frequent: adult using spray face moisturizer	0.005, 6 hr TWA	1.77 (NOAEC for lung effects)	354

[a] Exposure estimates for paint, cleaning products and cosmetics are time-weighted averages based on air concentrations predicted by ConsExpo (2016). See Table G-3, Appendix G for further details.
[b] Air concentration is the 95% upper confidence interval of the mean concentration, based on continuous air monitoring sampling for 1 year (0.84 μg/m^3, Intrinsik 2010).

8.5 Uncertainties in evaluation of risk to human health

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

Table 8-7. Sources of uncertainty in the risk characterization

Key source of uncertainty	**Impact**
The health effects noted in inhalation studies at points of departure were localized to the respiratory system and were recoverable; however, a NOAEL was not identified in the acute inhalation study.	+/-

Key source of uncertainty	Impact
The suitability of some inputs to the spray model used to derive air concentrations.	+
The assessment used the highest concentration of copper reported in cleaning products.	+

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

There is uncertainty with respect to the concentration of copper and copper-containing substances in cleaning products. A range of up to 5% copper compound was reported; however, this is likely an overestimate as no aerosol or trigger-spray cleaning products were identified at 5%. With the use of the maximum concentration, the potential risk could be over-estimated.

9. Conclusion

Considering all available lines of evidence presented in this draft screening assessment, there is risk of harm to organisms from copper and its compounds. It is proposed to conclude that copper and its compounds meet the criteria under paragraph 64(*a*) of CEPA as they are entering or may enter the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. However, it is proposed to conclude that copper and its compounds 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.

On the basis of the information presented in this draft screening assessment, it is proposed to conclude that copper and its compounds do not meet the criteria under paragraph 64(*c*) of CEPA as they are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health.

It is therefore proposed to conclude that copper and its compounds meet one or more of the criteria set out in section 64 of CEPA.

It is also proposed that copper and its compounds meet the persistence criteria but not the bioaccumulation criteria as set out in the *Persistence and Bioaccumulation Regulations* of CEPA.

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Appendices

Appendix A. Substance identity information

Table A-1. Substance identity information for copper and its compounds

CAS RN	DSL or R-ICL name	Common name or simplified name[a]	Substance category	Molecular formula[b]	Inventory
137-29-1	Copper, bis(dimethylcarbamodithioato-S,S)-, (SP-4-1)-	Copper dimethyldithiocarbamate	Organometallics	$C_6H_{12}CuN_2S_4$	DSL
142-71-2	Acetic acid, copper(2+) salt	Copper acetate	Organic-metal salt	$C_2H_4O_2.½Cu$	DSL
527-09-3	Copper, bis(D-gluconato-o1,o2)-	Copper gluconate	Organometallics	$C_{12}H_{22}CuO_{14}$	DSL
866-82-0	1,2,3-Propanetricarboxylic acid, 2-hydroxy-, copper (2+) salt (1 :2)	Cupric citrate	Organic-metal salts	$C_6H_4O_7.2Cu$	R-ICL
1111-67-7	Thiocyanic acid, copper(1+) salt	Copper(I) thiocyanate	Inorganics	CuSCN	DSL
1317-38-0	Copper oxide	Copper(II) oxide	Inorganics	CuO	DSL
1317-39-1	Copper oxide	Copper(I) oxide	Inorganics	Cu_2O	DSL
1317-40-4	Copper sulfide	Copper(II) sulfide	Inorganics	CuS	DSL
1319-53-5	Malachite	Malachite	Inorganics	$CH_2Cu_2O_5$	R-ICL
1328-51-4	C.I. Solvent Blue 38	Solvent Blue 38	UVCB-organic-metal salts	$C_{32}H_{12}CuN_8Na_2O_6S_2$	DSL
1328-53-6[c]	C.I. Pigment Green 7	Pigment Green 7	UVCB-organometallic	$C_{32}Cl_{16}CuN_8$	DSL
1337-20-8	Chlorophyllins, copper potassium salt	Chlorophyllins, copper potassium sodium	UVCB-organometallics	NA	R-ICL
1338-02-9	Naphthenic acids, copper salts	Copper naphthenate	UVCB-organic-metal salts	$2(C_{11}H_7O_2)Cu$	DSL
1344-73-6	Sulfuric acid, copper salt, basic	Copper sulfate	UVCB-inorganic	$CuH_2O_8S_2$	DSL
3251-23-8	Nitric acid, copper(2+) salt	Copper nitrate	Inorganics	$Cu(NO_3)_2$	DSL

CAS RN	DSL or R-ICL name	Common name or simplified name[a]	Substance category	Molecular formula[b]	Inventory
7440-50-8	Copper	Elemental copper	Inorganics	Cu	DSL
7447-39-4	Copper chloride	Copper(II) chloride	Inorganics	$CuCl_2$	DSL
7492-68-4	Carbonic acid, copper salt	Carbonic acid, copper salt	Inorganics	CH_2O_3Cu	R-ICL
7681-65-4	Copper iodide	Copper iodide	Inorganics	CuI	DSL
7758-89-6	Copper chloride	Copper(I) chloride	Inorganics	$CuCl$	DSL
7758-98-7	Sulfuric acid copper(2+) salt (1:1)	Copper(II) sulfate	Inorganics	$CuSO_4$	DSL
7798-23-4	Phosphoric acid, copper(2+) salt (2:3)	Copper phosphate	Inorganics	$Cu_3(PO_4)_2$	DSL
11006-34-1	Cuprate(3-), [18-carboxy-20-(carboxymethyl)-8-ethenyl-13-ethyl-2,3-dihydro-3,7,12,17-tetramethyl-21H,23H-porphine-2-propanoato(5-)-N21,N22,N23,N24]-, trisodium, [SP-4-2-(2S-tra*ns)]-	Chlorophyllin	Organometallics	$C_{34}H_{29}CuN_4Na_3O_6$	DSL
12222-04-7	Direct Blue 199	C. I. Direct Blue 199	Organometallics	$C_{32}H_{18}CuN_9NaO_5S_2$	R-ICL
20427-59-2	Copper hydroxide	Copper hydroxide	Inorganics	$Cu(OH)_2$	DSL
22205-45-4	Copper sulfide	Copper(I) sulfide	Inorganics	Cu_2S	DSL
22221-10-9	Hexanoic acid, 2-ethyl-, copper salt	Copper(II) ethylhexanoate	Organic-metal salt	$C_8H_{16}O_2.{}^1/{}_2Cu$	DSL

CAS RN	DSL or R-ICL name	Common name or simplified name[a]	Substance category	Molecular formula[b]	Inventory
26317-27-1	Cuprate(3-), [(7S,8S)-3-carboxy-5-(carboxymethyl)-13-ethenyl-18-ethyl-7,8-dihydro-2,8,12,17-tetramethyl-21H,23H-porphine-7-propanoato(5-)-.kappa.N21,.kappa.N22,.kappa.N23,.kappa.N24]-, trihydrogen, (SP-4-2)-	NA / Copper chlorophyllin	Organometallics	$C_{34}H_{34}CuN_4O_6$	R-ICL
28302-36-5	Cuprate(3-), [(7S,8S)-3-carboxy-5-(carboxymethyl)-13-ethenyl-18-ethyl-17-formyl-7,8-dihydro-2,8,12-trimethyl-21H,23H-porphine-7-propanoato(5-)-.kappa.N21,.kappa.N22,.kappa.N23,.kappa.N24]-, sodium (1:3), (SP-4-2)-	NA / Sodium copper chlorophyllin	Organometallics	$C_{34}H_{29}CuN_4NaO_{7\,(-2)}$	R-ICL
68084-48-0	Neodecanoic acid, copper(2+) salt	Copper neodecanoate	Organic-metal salt	$C_{10}H_{20}O_2.xCu$	DSL
68512-13-0[c]	Copper, [29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]-, brominated chlorinated	Brominated chlorinated copper phthalocyanine	UVCB-organometallic	NA	DSL
68987-63-3[c]	Copper, [29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]-, chlorinated	Chlorinated copper phthalocyanine	UVCB-organometallic	NA	DSL

CAS RN	DSL or R-ICL name	Common name or simplified name[a]	Substance category	Molecular formula[b]	Inventory
105883-51-0	Copper, bis[N-acetyl-.kappa.O)-L-methioninato-.kappa.O]-	Copper acetylmethionate	Organometallics	$Cu(C_7H_{12}NO_3S)_2$	R-ICL
131044-77-4	Copper, N-acetyl-L-tyrosine hydroxy-terminated (S)-[2-(acetylamino)-3-(4-hydroxyphenyl)-1-oxopropoxy] Me siloxanes	NA	UVCB-organometallics	NA	R-ICL
131044-78-5	Copper, hydroxyl-terminated Me (S)-[[5-oxo-2-pyrrolidinyl) carbonyl]oxy] siloxanes 5-oxo-L-proline complexes	Copper PCA methylsilanol	UVCB-organometallics	NA	R-ICL
147550-61-6	Copper carbonate hydroxide	Copper carbonate hydroxide	Inorganics	$CHCuO_4$	R-ICL
CDSL 10024-7[d]	Metal alkyldithiophosphates	NA	UVCB-inorganic	NA	DSL

NA: not available and/or not applicable

[a] A list of additional chemical names (e.g., trade names) is available from the National Chemical Inventories (NCI 2012).

[b] Molecular formula found from NCI (2017) or ChemIDplus (1993-).

[c] The substance bearing the CAS RN did not meet categorization criteria under Section 73(1) of CEPA; they were considered a priority on the basis of other human health concerns.

[d] CDSL (Confidential DSL) accession #10024-7.

Appendix B. Quantities, activities and uses of copper-containing substances for which information was received pursuant to DSL IU Phase II

Table B-1. Summary of information on Canadian manufactured and imported copper substances reported by industries pursuant to the DSL IU Phase 2 (2011) and Phase 3 (2012 to 2015) of CEPA (Environment Canada 2013, ECCC 2017a)

CAS RN	Common name or simplified name	Number of organizations reporting	Total quantity manufactured (kg)	Total quantity imported (kg)
527-09-3	Copper gluconate	<4	0	250
1111-67-7	Copper(I) thiocyanate	<4	0	10 000–100 000
1317-38-0	Copper(II) oxide	15	34 649	10 000–100 000
1317-39-1	Copper(I) oxide	6	>10 000 000	100 000–1 000 000
1317-40-4	Copper(II) sulfide	6	>10 000 000	>10 000 000
1328-53-6	Pigment Green 7	36	0	237 250
1338-02-9	Copper naphthenate	4	100 000–1 000 000	10 000–100 000
1344-73-6	Copper sulfate	<4	1 000 000–10 000 000	0
3251-23-8	Copper nitrate	4	0	2 970
7447-39-4	Copper(II) chloride	<4	0	–154
7681-65-4	Copper iodide	<4	0	1 000–10 000
7758-98-7	Copper(II) sulfate	7	1 000 000–10 000 000	100 000–1 000 000
12222-04-7	C.I. Direct Blue 199	<4	0	160
20427-59-2	Copper hydroxide	<4	100 000 –1 000 000	1 000 000–10 000 000
22205-45-4	Copper(I) sulfide	<4	>10 000 000	1 000 000–10 000 000
68084-48-0	Copper neodecanoate	<4	0	630
68512-13-0	Brominated chlorinated copper phthalocyanine	<4	0	1 000–10 000
68987-63-3	Chlorinated copper phthalocyanine	5	0	1 000–10 000
CDSL[a]	Metal alkyldithiophosphates	<4	0	3 897

[a] CDSL (Confidential DSL) accession #10024-7

Table B-2. Top activities or uses in Canada of copper-containing substances for the 2011 reporting year

CAS RN	Common name or simplified name	First top activity or use (code[a])	Second top activity or use (code[a])	Third top activity or use (code[a])
527-09-3	Copper gluconate	Mineral	-	-
1111-67-7	Copper(I) thiocyanate	CBI[b]	-	-
1317-38-0	Copper(II) oxide	CBI	Agricultural substances (non-pesticidal) (U004)	Processing aids, specific to petroleum production (U025)
1317-39-1	Copper(I) oxide	CBI	CBI	Pigments (U021)
1317-40-4	Copper(II) sulfide	CBI	-	-
1328-53-6	Pigment Green 7	Pigments (U021)	Intermediates (U015)	Paint additives and coating additives (U034)
1338-02-9	Copper naphthenate	Paint additives and coating additives (U034)	Pest control substances (U061)	Adhesives and sealant substances (U002); Lubricants and lubricant additives (U017); pesticide
1344-73-6	Copper sulfate	CBI	-	-
3251-23-8	Copper nitrate	Paint additives and coating additives (U034)	Pest control substances (U061)	CBI
7447-39-4	Copper(II) chloride	Plating agents and surface treating agents (U023)	-	-
7681-65-4	Copper iodide	CBI	-	-
7758-98-7	Copper(II) sulfate	Intermediates (U015)	CBI	Raw material in multi-vitamins / multi-minerals
20427-59-2	Copper hydroxide	CBI	By-product/hazardous waste (-)	-

CAS RN	Common name or simplified name	First top activity or use (code[a])	Second top activity or use (code[a])	Third top activity or use (code[a])
22205-45-4	Copper(I) sulfide	CBI	By-product/hazardous waste (-)	-
68084-48-0	Copper neodecanoate	Processing aids (U026)	-	-
68512-13-0	Brominated chlorinated copper phthalocyanine	Pigments (U021)	-	-
68987-63-3	Chlorinated copper phthalocyanine	Pigments (U021)	Laboratory substances (U033)	Paint additives and coating additives (U034)

[a] Use code, function or product code
[b] CBI = Confidential Business Information

Table B-3. Copper-containing substances for which no information was received for the reporting years 2011 and 2012 to 2015

CAS RN	Common name or simplified name	Substance category	Inventory
137-29-1	Copper dimethyldithiocarbamate	Organometallics	DSL
142-71-2	Copper acetate	Organic-metal salt	DSL
866-82-0	Cupric citrate	Organic-metal salts	R-ICL
1319-53-5	Malachite	Inorganics	R-ICL
1328-51-4	Solvent Blue 38	UVCBs-organic-metal salts	DSL
1337-20-8	Chlorophyllins, copper potassium sodium	UVCBs-organometallic	R-ICL
7492-68-4	Carbonic acid, copper salt	Inorganics	R-ICL
7758-89-6	Copper(I) chloride	Inorganics	DSL
7798-23-4	Copper phosphate	Inorganics	DSL
11006-34-1	Chlorophyllin	Organometallics	DSL
22221-10-9	Copper(II) ethylhexanoate	Organic-metal salt	DSL
105883-51-0	Copper acetylmethionate	Organometallics	R-ICL
131044-77-4	Copper acetyl tyrosinate methylsilanol	UVCBs-organometallic	R-ICL
131044-78-5	Copper PCA methylsilanol	UVCBs-organometallic	R-ICL
147550-61-6	Copper carbonate hydroxide	Inorganics	R-ICL

Appendix C. Releases reported to the NPRI for 2011 to 2015 for copper and its compounds

The top 15 sectors covered by the NPRI (identified by North American Industry Classification System (NAICS) 4-digit codes) are listed in Table C-1 and appear in decreasing order in terms of total on-site releases (i.e., air, land and water). Units are tonnes of copper on an elemental basis.

Table C-1. Top 15 release ranges reported[a] to the National Pollutant Release Inventory for copper and its compounds from 2011 to 2015 (in tonnes)[b]

Industrial sector (NAICS 4)	Air	Land	Water	Total (per year)
Non-Ferrous Metal (except Aluminum) Production and Processing	161.4-211.7[c]	0[d]	2.4-3.3[c]	164.3–214.7[c]
Metal Ore Mining	10.9–57.4	3.4–12.1[e]	4.5–10.5 (20 730)[f]	23.4–73.8 (20 798)[e, f]
Water, Sewage and Other Systems	0–0.2	0	24.8–51.3	25–55.5
Pulp, Paper and Paperboard Mills	4.7–8.7	0–8.8	0.3–0.4	5.1–14
Coal Mining	0	0–12	0.1–0.2 (1.2)[g]	0.1-11.1 (12.1)[g]
Iron and Steel Mills and Ferro-Alloy Manufacturing	1.1–2.1	0	0.6–1.3	2.3–4.6
Electric Power Generation, Transmission and Distribution	0.2–1	0	0–1.6	0.5–2.6
Alumina and Aluminum Production and Processing	0–2.4	0	0	0.3–2.4
Foundries	1.2–1.4[c]	0	0[c]	1.2–1.4[c]
Motor Vehicle Parts Manufacturing	0.2–0.9	0	0	0.3–1
Other Fabricated Metal Product Manufacturing	0	0	0	0–0.9
Defence Services	0.2–0.4	0[h]	0	0.2–0.4[h]
Animal Food Manufacturing	0[i]	0	0	0[i]
Hardware Manufacturing	0[j]	0	0	0[j]
Machine Shops, Turned Product, and Screw, Nut and Bolt Manufacturing	0[j]	0	0	0[j]

[a] There is a degree of complexity in NPRI data reporting, such as meeting reporting thresholds and the use of various acceptable methods and data sources to estimate release, disposal and recycling quantities. Therefore, uncertainties exist in the reported quantities. Quantities for on-site and off-site disposal, as well as for off-site recycling, are not shown. See the NPRI reporting guidance document for more details ECCC (2016).
[b] Values are rounded to 0.1 tonnes. Data used for this table are current as of September 14, 2017. 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.
[c] The bulk of copper releases in "foundries" come from the Horne facility under smelting activities. Therefore, for the purposes of this assessment, this facility's totals were subtracted from foundries and added to the NAICS 4: "Non-Ferrous Metal (except Aluminum) Production and Processing".
[d] With the exception of additional footnotes, a 0 indicates either no reporting from any facility, a quantity of 0 reported by at least one facility or a quantity < 0.050 tonnes that is rounded to 0.
[e] NPRI requires that copper in tailings and by-products be included in the calculation of the reporting threshold regardless of the concentration of copper in these materials (including less than 1%). All releases, disposals and transfers of copper (except for quantities in waste rock at less than 1%) must then be reported to the NPRI if the threshold for reporting was met. The requirement to include all copper in tailings in the calculation of the manufactured, processed or otherwise used threshold may contribute to more extensive reporting from the metal mining sector compared to other sectors. See ECCC (2016b) for more details.
[f] The value in brackets includes 20 724 tonnes, released to water from the spill (dam failure) from Imperial Metals Corporation (Mount Polley Mine) in 2014.
[g] The value in brackets includes 1 tonne, released to water from the spill (dam failure) from Coal Valley Resources Inc. (Obed Mountain mine) in 2013.
[h] 159.4 to 273.7 tonnes are considered temporary releases to land that will eventually be reported as off-site disposal or recycling. The quantity will therefore be updated to 0 to NPRI and is considered to be 0 in this assessment.
[i] According to the NPRI, it may be reasonable to exclude these values (totalling 39.4 tonnes to air) as they are likely reporting errors. The quantity will therefore be updated to 0 by the NPRI and considered as such in this assessment.
[j] Quantities of 857 tonnes (hardware manufacturing) and 56.3 tonnes (machine shops), both to air, were reported by the same facility in 2012 (reports under the two NAICS 4). They are most likely off-site transfers for recycling, but have not been updated yet to 0 by the facility. Values for more recent years (i.e., 2014, 2015) have been corrected to 0. Therefore, the quantity considered in this assessment is 0.

Appendix D. Physical-chemical properties and environmental fate

Table D-1. Physical and chemical properties for copper and its compounds

CAS RN[g]	Common name or simplified name	DSL substance category	Molecular weight (g/mol)	Water solubility ($mg \cdot L^{-1}$ H_2O)	log K_{ow}
137-29-1	Copper dimethyldithiocarbamate	Organometallics	303.98	NA	1.23[d]
142-71-2	Copper acetate	Organic-metal salt	181.64	7.62×10^4; 7.65×10^4; 7.63×10^4 at pH 5.1, 20.0 °C[a]	NA
527-09-3	Copper gluconate	Organometallics	453.84	3.00×10^5 at 25 °C[b]	-7.51[c]
866-82-0	1,2,3-Propanetricarbonxylic acid, 2-hydroxy-, copper (2+) salt (1 :2)	Organic-metal salts	315.18	NA	NA
1111-67-7	Copper(I) thiocyanate	Inorganics	121.63	NA	NA

CAS RN[g]	**Common name or simplified name**	**DSL substance category**	**Molecular weight (g/mol)**	**Water solubility (mg·L^{-1} H_2O)**	**log K_{ow}**
1317-38-0	Copper(II) oxide	Inorganics	79.54	>230 at pH 5.1–5.5, 0.394 at pH 6, 0.01 at pH 9, all at 20 °C[a]	NA
1317-39-1	Copper(I) oxide	Inorganics	143.08	2.86×10^4 at pH 4, 0.639 at pH 6.5–6.6, 0.539 at pH 9.7–9.8 all at 20 °C[a]	NA
1317-40-4	Copper(II) sulfide	Inorganics	95.6	0.33 at 20 °C[c]	NA
1319-53-5	Malachite	Inorganics	221.11	NA	NA
1328-51-4	Solvent Blue 38	UVCBs-organic-metal salts	778.15	4116 at 28 °C[a]	3.86[c,e]
1328-53-6	Pigment Green 7	UVCBs-organometallic	1094.76	0.001–0.003 at 23 °C[a]	-0.4[c,e]
1337-20-8	Chlorophyllins, copper potassium salt	UVCBs-organometallics	NA	NA	NA
1338-02-9	Copper naphthenate	UVCBs-organic-metal salts	405.9	NA	4.1[c]
1344-73-6	Copper sulfate	UVCBs-inorganic	257.69	NA	NA
3251-23-8	Copper nitrate	Inorganics	187.56	1.38×10^6 at 20 °C. 1.45×10^6 at 25 °C[a]	NA
7440-50-8	Elemental copper	Inorganics	63.55	192 at pH 4, 0. 27 at pH 7, 0.13 at pH 9, all at 20 °C[a]	NA
7447-39-4	Copper(II) chloride	Inorganics	134.45	2.57×10^6 at 25 °C[a]	NA
7492-68-4	Carbonic acid, copper salt	Inorganics	125.57	NA	NA
7681-65-4	Copper iodide	Inorganics	190.45	0.2 at 20 °C[a]	NA
7758-89-6	Copper(I) chloride	Inorganics	99.0	47 at 20 °C[a]	NA
7758-98-7	Copper(II) sulfate	Inorganics	159.61	2.2×10^5 at 25 °C[a]	NA
7798-23-4	Copper phosphate	Inorganics	380.58	NA	NA
11006-34-1	Chlorophyllin	Organometallics	722.13	NA	6.14[d]
12222-04-7	Direct Blue 199	Organometallics	NA	NA	NA

CAS RN[g]	Common name or simplified name	DSL substance category	Molecular weight (g/mol)	Water solubility (mg·L^{-1} H_2O)	log K_{ow}
20427-59-2	Copper hydroxide	Inorganics	97.56	3.98×10^4 at pH 4, 0.506 at pH 6.5, 0.25 at pH 10, all at 20 °C[a]	NA
22205-45-4	Copper(I) sulfide	Inorganics	159.16	10 at 20 °C[a]	NA
22221-10-9	Copper(II) ethylhexanoate	Organic-metal salt	349.95	NA	NA
68084-48-0	Copper neodecanoate	Organic-metal salt	406.06	NA	**NA**
68512-13-0	Brominated chlorinated copper phthalocyanine	UVCBs-organometallic	NA	0.001-0.003 at 23 °C[a]	-0.4[c,e]
68987-63-3	Chlorinated copper phthalocyanine	UVCBs-organometallic	NA	0.001-0.003 at 23 °C[a]	-0.4[c,e]
105883-51-0	Copper, bis[N-acetyl-.kappa.O)-L-methioninato-.kappa.O]-	Organometallics	444.03	NA	NA
131044-77-4	Copper, N-acetyl-L-tyrosine hydroxy-terminated (S)- [2-(acetylamino)-3-(4-hydroxyphenyl)-1-oxopropoxy] Me siloxanes	UVCBs-organometallics	NA	NA	NA
131044-78-5	Copper, hydroxyl-terminated Me (S)-[[5-oxo-2-pyrrolidinyl) carbonyl]oxy] siloxanes 5-oxo-L-proline complexes	UVCBs-organometallics	NA	NA	NA
147550-61-6	Copper carbonate hydroxide	Inorganics	140.56 [f]	NA	NA
CDSL#10024-7	Metal alkyldithiophosphates	UVCBs-organometallic	NA	NA	NA

NA: not available and/or not applicable

[a] ECHA (2017)

[b] U.S. EPA (2017)

[c] TOXNET (2017)

[d] Canadian DSL (2017)

[e] log P_{ow} at 23 °C

[f] U.S. EPA (2018)

[g] The Chemical Abstracts Service Registry Number (CAS RN) is the property of the American Chemical Society and any use or redistribution, except as required in supporting regulatory requirements and/or for reports to the Government of Canada when the information and the reports are required by law or

administrative policy, is not permitted without the prior, written permission of the American Chemical Society.

Table D-2. Partition coefficients for copper

Partition coefficient	Value	Reference
Soil-water (log K_{sw})	min, max: 1.924, 3.497 median: 3.08	Allison and Allison 2005; Harvey et al. 2007; Janssen et al. 1997
Sediment-water (log K_{sdw})	min, max: 3.579, 5.532 median: 4.571	Allison and Allison 2005; Besser et al. 2001; Borgmann et al. 2004; Cain et al. 1992; Davis et al. 1996; Harvey et al. 2007; Shutes et al. 1993; Timmermans et al. 1989; van Hattum et al. 1991; Wickham et al. 1987
Suspended particles-water (log K_{spw})	min, max: 4.41, 5.03 median: 4.733	Allison and Allison 2005; Gobeil et al. 2005; Harvey et al. 2007; Lofts and Tipping 2000; Rondeau et al. 2005; Warren and Zimmerman 1994

Appendix E. Background concentrations and toxicity modifying factors

Table E-1. Total copper concentrations for Canadian ecozones and Great Lakes

Region	Sample size	Range (µg Cu_T/L)	Median (µg Cu_T/L)
Atlantic Maritime[a]	12	0.400–0.700	0.500
Boreal Cordillera	302	0.210–45.5	1.09
Boreal Plains	647	0.050–24.3	0.58
Boreal Shield	1970	0.000623–2270	1.05
Mixedwood Plains	5145	0.000145–37.5	0.816
Montane Cordillera	1950	0.0100–32.8	0.51
Pacific Maritime	1468	0.210–19.2	0.79
Prairies	412	0.400–162	1.94
Taiga Cordillera	22	0.930–15.5	1.96
Taiga Shield	162	0.100–1.32	0.450
Lake Erie	106	0.770–4.46	0.995
Lake Ontario	165	0.660–2.85	0.800
Lake Superior	83	0.620–1.65	0.760

[a] Total copper concentrations are unavailable for the Atlantic Maritime ecozone; copper median concentrations are therefore reported.

Table E-2. Canadian ecozones and Great Lakes toxicity modifying factors used for PNEC calculations

Region	Total hardness sample size	Geometric mean of total hardness (mg/L)	pH sample size	Average of pH	DOC sample size	Geometric mean of DOC (mg/L)
Atlantic Maritime	5	32	110	7.2	35	4.4
Boreal Cordillera	305	79	283	8.0	210	1.5
Boreal Plains	643	120	656	8.0	486	19
Boreal Shield	1655	40	1981	7.8	1009	7.4
Mixedwood Plains	4941	150	5154	8.3	1394	5.3
Montane Cordillera	1936	61	1858	7.9	1070	1.2
Pacific Maritime	1490	19	1475	7.3	837	1.4
Prairies	369	260	420	8.2	20	10
Taiga Cordillera	22	110	22	8.0	20	10
Taiga Shield[a]	175	7.4	176	6.9	160	3.6
Lake Erie	362	118	1666	8.03	560	2.5
Lake Ontario	305	125	1990	7.98	260	2.3
Lake Superior	46	45.3	1150	7.60	79	1.6

[a] Metal mining facilities in the Northern Arctic and Southern Arctic ecozones used the DOC data from the Taiga Shield ecozone

Table E-3. Toxicity modifying factors and calculated PNECs for surface waters from exposure and reference areas for 10 facilities subject to the MDMER from 2011 to 2015 (EEM 2016; Table D-2)

Facility	Area type	Range of total hardness (mg/L)	Range of pH	Range of DOC (mg/L)	Range of temperature (ºC)	Range of PNECs[a] (µg/L)	Median PNEC (µg/L)	Type of TMF data[b]
1	Exposure	9.20–610	4.25–7.20	2.6–12	0.900–21.7	0.20–9.4	0.86	S, E
1	Reference	13.0–24.0	6.66–9.22	3.5–9.8	0.50–22.0	0.96–12	3.6	S, E
2	Exposure	31.6–189	6.95–7.89	1.4	2.60–16.4	0.59–2.8	1.8	S, E
2	Reference	6.62–19.2	6.01–8.08	1.4	0.700–14.7	0.20–1.56	0.72	S, E
3	Exposure	261–1930	7.10–8.05	3.7–21	0.400–25.1	9.3–72	26	S, E
3	Reference 1	39.4–58.7	6.70–8.01	14–21	0–25.0	4.6–33	24	S
3	Reference 2	16.5–30.0	6.50–8.30	8.0–12	0–25.1	1.8–17	8.4	S
4	Exposure	227–968	6.40–8.00	7.4	5.40–21.4	2.1–30	15	S, E
4	Reference 1	39.4–58.7	6.70–8.01	13–21	0–25.0	1.9–17	24	S
4	Reference 2	16.6–49.3	6.7–8.2	8.9–12	0–24.5	1.9–17	8.5	S
5	Exposure	108–730	6.60–7.49	7.4	0.06000–21.4	3.2–15	7.3	S, E
5	Reference	8.00–33.0	6.05–6.60	7.4	0.350–20.5	0.39–1.1	0.63	S, E
6	Exposure	35.7–517	6.80–7.85	7.4	0.800–22.6	2.2–20	12	S, E
6	Reference	32.1–178	6.85–7.97	7.4	0.430–24.5	2.4–19	13	S, E
7	Exposure	163–1670	7.03–8.96	7.4	0.610–23.8	6.0–51	26	S, E
7	Reference	62.8–111	6.87–7.68	7.4	0.990–23.0	3.5–10	5.3	S, E
8	Exposure	150–1800	6.22–7.70	7.4	3.90–22.1	1.2–23	9.3	S, E
8	Reference	8.00–36.0	5.02–7.17	7.4	1.30–18.0	0.20–4.3	1.0	S, E

9	Exposure	50.9–130	6.74–8.02	0.50–12	0–6.90	0.20–11	1.4	S
9	Reference	24.9–76.0	7.21–7.94	0.50–9.2	0–6.20	0.25–6.2	0.97	S
10	Exposure	0.370–455	6.90–7.50	2.4–4.2	0.400–20.4	2.1–8.0	4.7	S
10	Reference	12.8–24.1	6.50–7.60	2.3–3.1	0.200–18.4	0.27–2.7	2.0	S

[a] The BLM boundaries are 5.5–8.75 for pH, 7.9–525 mg/L for hardness, and 0.2–33.41 mg/L for DOC, and 8.5 °C–27 °C for temperature. Values outside of this range are replaced with the lower or upper limit as appropriate.

[b] Type of TMF data: S = site-specific data (EEM 2016); E = ecozone geometric mean for hardness and/or DOC and/or average for pH and/or temperature (Table D-2).

Table E-4. Toxicity modifying factors and calculated PNECs for surface waters from exposure areas and reference areas for base metal smelters and refineries (EEM 2016, EEC Ltd & LAC Ltd 2014; Table D-2)

Facility[a]	Area type	Range of total hardness (mg/L)	Range of pH	Range of DOC (mg/L)	Range of tempe-rature (ºC)	Range of PNECs (µg/L)[b]	Type of TMF data[c]
1	Exposure	90.0–517	7.00–9.40	7.4	0.100–23.2	5.2–36	S, E
1	Reference	30.0–484	6.60–9.50	7.4	0.400–22.3	1.2–40	S, E
2	Exposure	275–501	6.40–7.60	7.4	2.00–21.9	2.7–18	S, E
2	Reference	19.2–375	6.41–7.40	7.4	1.00–21.2	1.2–6.8	S, E
3	Exposure	375–1850	6.65–8.71	7.4	1.00–19.9	5.1–36	S, E
3	Reference	33.4–69.9	7.20–8.95	7.4	1.00–18.9	4.8–16	S, E
4	Exposure 1	0.500–1670	7.03–8.96	7.4	0.610–23.8	6.0–53	S, E
4	Reference 1	62.8–111	6.87–7.68	7.4	0.990–23.0	3.5–10	S, E
4	Exposure 2	35.7–517	6.80–7.85	7.4	0.800–22.6	2.2–20	S, E
4	Reference 2	32.1–178	6.85–7.97	7.4	0.430–24.5	2.4–19	S, E

5	Exposure	96.2–232	7.18–8.74	7.4	0.300–23.1	6.6–34	S, E
5	Reference	67.2–223	7.18–8.45	7.4	0.100–23.1	7.1–27	S, E
6	Exposure	54.8–77.9	6.95–8.29	1.2	8.5–15	0.58–2.3	S, E
6	Reference	53.9–74.9	7.10–8.6	1.2	8.5–15	0.72–2.2	S, E
7	Exposure	118	8.03	2.5	9.9	0.45–0.56	GL

[a] Facilities 1 to 5 are subject to the MDMER, and the data presented were collected from the EEM program during the period 2011 to 2015 (EEM 2016).

[b] The BLM boundaries are 5.5–8.75 for pH, 7.9–525 mg/L for hardness, 0.2–33.41 mg/L for DOC, and 8.5 °C–27 °C for temperature. Values outside of this range are replaced with the lower or upper limit as appropriate.

[c] Type of TMF data: S = site-specific data (EEM 2016; EEC Ltd & LAC Ltd 2014); E = ecozone geometric mean for hardness and/or DOC and/or average for pH and/or temperature (Table D-2); GL = Great Lakes geometric mean for hardness and/or DOC and/or average for pH and/or temperature (Table D-2).

Table E-5. Toxicity modifying factors and calculated PNECs for the wastewater treatment sector (Table D-2)

Facility	**Total hardness (mg/L)[a]**	**pH**	**DOC (mg/L)**	**Tempe-rature (ºC)**	**PNEC (µg Cu_T/L)[b]**	**Type of TMF data[c]**
1	40	7.8	7.4	7.8–16	9.9–10	E
2	150	8.3	5.3	5.2–8.2	12	E
3	29	7.2	4.4	0.23–6.9	2.6	E
4	150	8.3	5.3	5.2–11	12–13	E
5	260	8.2	10	0.68–22	28–40	E
6	150	8.3	5.3	1.5–20	12–17	E
7	40	7.8	7.4	0.60–16	9.9–10	E
8	79	8.0	1.5	2.2–9.4	2.6	E
9	150	8.3	5.3	1.5–20	12–17	E
10	150	8.3	5.3	1.3–20	12–15	E
11	19	7.3	1.4	3.1–14	0.86–0.87	E
12	29	7.2	4.4	0.23–18	2.6	E
13	45	7.60	1.6	0.60–20	1.8–1.9	E, GL
14	120	7.98	2.3	1.5–20	4.5–5.3	E, GL
15	150	8.3	5.3	1.5–20	12–17	E
16	120	7.98	2.3	1.5–17	4.6–5.0	E, GL
17	120	7.98	2.3	1.3–22	4.5–5.6	E, GL

18	120	7.98	2.3	1.5–11	4.5–4.6	E, GL
19	260	8.2	10	1.4–20	28–37	E
20	260	8.2	10	0.77–22	28–40	E
21	61	7.9	1.2	1.2–15	1.8–1.9	E

[a] For the ecozone geometric means, measured total hardness values expressed as mg $CaCO_3$/L are reported, whereas for the Great Lakes, calculated values using dissolved calcium and dissolved magnesium measurements are reported.

[b] The BLM boundaries are 8–628.8 mg/L for hardness, 5.5–8.75 for pH, 7.9-525 mg/L for hardness, and 0.2–33.41 mg/L for DOC, and 8.5 °C–27 °C for temperature. Values outside of this range are replaced with the lower or upper limit as appropriate.

[c] Type of TMF data: E = ecozone geometric mean for hardness and/or DOC and/or average for pH and/or temperature (Table D-2); GL = Great Lakes geometric mean for hardness and/or DOC and/or average for pH and/or temperature (Table D-2).

Appendix F. Exposure to environmental media, food and drinking water

Table F-1. Estimated average daily intake of copper by the general population in Canada from environmental media, food and drinking water

Route of exposure	**0–6 months breast fed[a,b] (formula fed)**	**0.5–4 years[c]**	**5–11 years[d]**	**12–19 years[e]**	**20–59 years[f]**	**60+ years[g]**
Personal Air (µg/kg bw/d) [h]	0.0014 (0.0014)	0.0031	0.0024	0.0014	0.0012	0.001
Drinking water (µg/kg bw/d) [i]	NA (3.73)	1.6	1.2	0.71	0.74	0.78
Food and beverages (µg/kg bw/d) [j]	41.8 (77.5)	52	40.6	28.2	26.4	16.8
Household Dust (µg/kg bw/d) [k]	0.49 (0.49)	0.26	0.098	0.0036	0.0034	0.0034
Soil (µg/kg bw/d) [l]	NA (NA)	0.057	0.043	0.002	0.001	0.001
Total intake (µg/kg bw/d)	42 (82)	54	42	29	27	18
Total intake (mg/d)	**0.32 (0.61)**	**0.84**	**1.3**	**1.7**	**1.9**	**1.2**

Abbreviations: NA= not applicable

[a] Assumed to weigh 7.5 kg, to breathe 2.1 m^3 of air per day (Health Canada 1998), and to ingest 38 mg of household dust per day (Wilson et al. 2013). Breastfed infants are assumed to consume solely breast milk for 6 months. Not breastfed infants are assumed to consume formula and food and are assumed to drink 0.8 L of water per day. (Health Canada 1998).

[b] The mean copper concentration in breast milk from MIREC and the average and 95th percentile breast milk

consumption figures for exclusively breastfed infants were employed to derive the estimated daily intake of copper in food and beverages (personal communication, 2016 email from the Bureau of Chemical Safety, Food Directorate, Health Canada to the Existing Substances Risk Assessment Bureau, Health Canada; unreferenced).

[c] Assumed to weigh 15.5 kg, to drink 0.7 L of water, to breathe 9.3 m^3 of air per day (Health Canada 1998), and to ingest 14 mg of soil and 41 mg of household dust per day (Wilson et al. 2013).

[d] Assumed to weigh 31.0 kg, to drink 1.1 L of water, to breathe 14.5 m^3 of air per day (Health Canada 1998), and to ingest 21 mg of soil and 31 mg of household dust per day (Wilson et al. 2013).

[e] Assumed to weigh 59.4 kg, to drink 1.2 L of water, to breathe 15.8 m^3 of air per day (Health Canada 1998).

[f] Assumed to weigh 70.9 kg, to drink 1.5 L of water, to breathe 16.2 m^3 of air per day (Health Canada 1998), and to ingest 1.6 mg of soil and 2.5 mg of household dust per day (Wilson et al. 2013).

[g] Assumed to weigh 72.0 kg, to drink 1.6 L of water, to breathe 14.3 m^3 of air per day (Health Canada 1998), and to ingest 1.5 mg of soil and 2.5 mg of household dust per day (Wilson et al. 2013).

[h] Intake estimated using median 24-hr personal air sample $PM_{2.5}$ of 5.15 ng/m^3 (n= 445) measured in Windsor, Ontario (Rasmussen et al. 2016). Personal air data are considered to be most representative of air concentrations in the breathing zone.

[i] Intake estimated using median concentration in tap water of 0.035 mg/L (n= 1905) measured in Newfoundland and Labrador (Health Canada [modified 2018a]). This value was considered to be sufficient as it was the highest reported median value from tap water.

[j] A five-year average of dietary intake estimates were taken from the TDS over a period from 2003-2007; details in Table F-2.

[k] Intake estimated using the median copper concentration of 199 mg/kg measured in 1025 homes in the Canadian House Dust Study and the 49% bioaccessibility factor (Rasmussen et al. 2013; SARA 2008).

[l] Intake estimated on the basis of the upper limit background level of 85 µg/g in non-contaminated Ontario soil and bioaccessibility of 74% (SARA 2008).

Table F-2. Five-year average dietary intakes from the Total Diet Study (TDS) from the years 2003 to 2007

Average daily intake[a]	0.5–4 years	5–11 years	12–19 years	20–59 years	60 years and older
Intake (ug/kg bw/d)	52.0	40.6	28.2	26.4	16.8
Body weight (kg)	15.5	31	59.4	70.9	72
Average intake (mg/d)	0.8	1.3	1.7	1.9	1.2

[a] Average intakes were estimated over a period of five years from the TDS (Health Canada [modified 2011]). When age groups were not comparable, the highest estimate was taken from the applicable age groups.

Table F-3. Average daily intake estimates for communities of interest from environmental media, food and drinking water

Communities	Infant	Toddler	Child	Teen	Adult
SARA (2008)[a]	0 to < 6 months	6 months to < 5 yrs	5 to 11 yrs	12 to 19 yrs	20 to 70 yrs
Estimated daily intake (mg/d)	0.48	1.2	1.6	1.8	1.5
Estimated daily intake (µg/kg bw/d)	63	79	52	30	21
Intrinsik (2010)[b]	0 to 6 months	7 months to 4 yrs	5 to 11 years	12 to 19 yrs	20 plus yrs
Estimated daily intake (mg/d)	0.58	1.2	1.6	2.0	2.0

Estimated daily intake (µg/kg bw/d)	77	81	52	33	28

[a] Estimated daily intake is highest value among the study areas (from Copper Cliff community).
[b] Estimated daily intake is highest value among the study areas (from West Flin Flon community).

Appendix G. Exposure estimates from use of products

Table G-1. Oral exposure estimates to copper from arts and craft products, cosmetics, and natural health products

Scenario	Form of copper[a]	Conc. of Cu (%)[b]	Amount of product ingested (mg)[c]	Frequency (/day)	Exposure estimate (mg/kg bw/d)[d]	Exposure estimate (mg/day)
Toddler – incidental ingestion of modeling clay	Phthalocyanine green	0.3	100	0.14	0.0025	0.039
Toddler – incidental ingestion of craft paint	Phthalocyanine green	0.3	400	0.14	0.01	0.15
Toddler – incidental ingestion of crayons	Phthalocyanine green	0.3	8	1	0.0015	0.023
Toddler – incidental ingestion while wearing lipstick / lip balm	Copper	10	10	0.6	0.038	0.6
Toddler – incidental ingestion while brushing teeth	Copper chlorophyllin	0.0013	210	1.4	0.00025	0.0038
Child – ingestion from oral health	Copper	100	1	1	0.032	1

Scenario	Form of copper[a]	Conc. of Cu (%)[b]	Amount of product ingested (mg)[c]	Frequency (/day)	Exposure estimate (mg/kg bw/d)[d]	Exposure estimate (mg/day)
supplement						

[a] Concentrations were adjusted on the basis of the form of copper i.e., *Adjusted copper % = Molecular weight of copper / Molecular weight of copper compound * % compound*.

[b] Concentrations of copper for arts and crafts is from < 1 to 5% (MSDS 2009a, MSDS 2016, MSDS 2009b), for cosmetics is up to 10% (email from Consumer Product Safety Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated May 4, 2017; unreferenced) and for oral natural health products is 1 mg/tablet (email from Natural and Non-prescription Health Products Directorate to Existing Substances Risk Assessment Bureau, Health Canada, dated April 10 2017; unreferenced; LNHPD [modified 2018]).

[c] Amount and frequency for arts and crafts (modeling clay, craft paint, crayon) are based on models and default values presented in RIVM (2008); amount and frequency for cosmetics are from Health Canada (2012); amount and frequency for natural health products are from LNHPD [modified 2018] and from personal communications (email from Natural and Non-prescription Health Products Directorate, Health Canada, to Existing Substances Risk Assessment Bureau, Health Canada, dated April 10, 2017).

[d] Estimated daily exposure via oral intake of arts and craft products, cosmetics and health supplements in mg/kg bw/d is calculated by: *Amount of product (mg) * concentration of copper (%) * frequency (/day) / body weight (kg)*. Default mean body weight of toddlers (age 0.5–4 years) is 15.5 kg; for children (age 5–11 years) is 31 kg (Health Canada 1998).

Table G-2. Children's oral exposure to copper through mouthing activities

Scenario	Amount of copper migrated (µg) in 120 min (Guney et al. 2014)	Exposure duration (min/day)[a]	Exposure estimate (mg/kg bw/day)[b]	Exposure estimate (mg/d)
Infant (0–0.5 yrs) mouthing a toy	91.5	120	0.012	0.092
Toddler (0.5–4 yrs) mouthing a toy	91.5	120	0.0059	0.092

[a] Professional judgement for 0–1.5 years.

[b] Estimated daily exposure via mouthing of children's toys and jewellery = *Amount of copper migrated in 120 min (µg/120 mins) * conversion factor (1 mg/1000 µg) / body weight (kg)*. Default body weight for infants (0–0.5 years) is 7.5 kg; toddlers (0.5 – 4 years) is 15.5 kg (Health Canada 1998).

Table G-3. Exposure factors for estimating air concentrations via use of spray products (ConsExpo Web 2016, RIVM [modified 2018])

Product	Exposure factors[a]	Mean event exposure estimate (mg/m^3)	Derived time-weighted amortization (mg/m^3)[b]
All-purpose cleaners	From factsheet “Cleaning and Washing; All-purpose cleaners; all-purpose cleaning spray[c]” Scenario “Application – spraying (non-volatile substances” Exposure model “Exposure to spray – spraying” Concentration: 0.004% copper sulfate, 5% phthalocyanine green (equivalent to 0.0016 and 0.28% Cu) Exposure frequency: 365 / year Spray duration: 0.23 min Exposure duration: 60 min Room volume: 15 m^3 Room height: 2.5 m Ventilation rate: 2.5 per hour Inhalation rate: 25 L/min Mass generation rate: 1.6 g/s Airborne fraction: 0.1 Density non-volatile: 1 g/cm^3 Mean diameter: 2.4 µm Arithmetic coefficient of variation Inhalation cut-off diameter: 10 µm[d] Spraying towards person: No	0.00079–0.15 (0.0016–0.28% Cu)	0.00013–0.025 (based on frequent, repeated exposure, a 6-hr time weighted average (TWA) was derived)
Aerosol face moisturizer	From factsheet “Cosmetics; Hair care cosmetics; hair spray” Scenario “Application” Exposure model “Hair spray, exposure to spray” Concentration: 3%–10% copper PCA (equal to 1.98% Cu) Exposure frequency: 438/year (1.2/day) Room volume: 10 m^3 Spray duration: 0.24 min Exposure duration: 5 min Cloud volume: 0.0625 m^3	0.36	Frequent, repeated exposure, 6-hr TWA 0.005

Product	Exposure factors[a]	Mean event exposure estimate (mg/m^3)	Derived time-weighted amortization (mg/m^3)[b]
	Room height: 2.5 m Ventilation rate: 2 per hour Mass generation rate: 0.4 g/s Airborne fraction: 0.2 Density non-volatile: 1.5 g/cm^3 Inhalation cut-off diameter: 10 μm[d] Spraying towards person: Yes		
Hair spray	From factsheet "Cosmetics; Hair care cosmetics; hair spray" Scenario "Application" Exposure model "Exposure to spray - spraying" Concentration: 0.1% copper saccharomyces ferment Exposure frequency: 438 / year (1.2 / day) Room volume: 10 m^3 Spray duration: 0.24 min Exposure duration: 5 min Cloud volume: 0.0625 m^3 Room height: 2.5 m Ventilation rate: 2 per hour Mass generation rate: 0.4 g/s Airborne fraction: 0.2 Density non-volatile: 1.5 g/cm^3 Median diameter: 46.5 μm Arithmetic coefficient of variation: 2.1 μm Inhalation cut-off diameter: 10 μm[d] Spraying towards person: Yes	0.018	Frequent, repeated exposure, 6-hr TWA 0.00025
Spray paint	From factsheet "Painting products; spray painting; spray can" Scenario "Application" Exposure model "Exposure to spray - spraying" Concentration: 10% copper Exposure frequency: 2 per year Room volume: 90 m^3 (U.S. EPA 2011)[e] Ventilation rate: 1.5 per hour	33	Infrequent exposure, 4-hr TWA 2.8

Product	Exposure factors[a]	Mean event exposure estimate (mg/m^3)	Derived time-weighted amortization (mg/m^3)[b]
	Exposure duration: 20 min Spray duration: 10 min (changed from default on the basis of 300 g used or 1 can of spray paint) Room height: 2.25 m Ventilation rate: 1.5 per hour Mass generation rate: 0.45 g/s Airborne fraction: 0.7 Mass transfer coefficient: 10 m/hr Density non-volatile: 1.5 g/cm^3 Median diameter: 15.1 µm Inhalation cut-off diameter: 10 µm[d] Arithmetic coefficient of variation: 1.2 Spraying toward person: no		

[a] Cleaning product concentrations from email from Therapeutic Products Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated April 28, 2017; unreferenced; CPISI 2018; concentration of copper in cosmetics from email from the Consumer Product Safety Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated May 4, 2017; unreferenced; concentration of copper in spray paint from MSDS 2015.

[b] Time-weighted average (TWA) was calculated using the equation $TWA = T_1 * C_1 / T_{total}$; where T_1 is the exposure duration of the scenario, C_1 is the mean event concentration and the T_{total} is the duration of the toxicity study (i.e., 6 hours for frequent or repeated exposure scenarios and 4 hours for acute scenarios).

[c] Based on the January 2018 update to the cleaning products factsheet (RIVM [modified 2018]).

[d] ConsExpo default for inhalation cut-off diameter is 15 µm; this has been adjusted to 10 µm, which is the default typically used by the Existing Substances Risk Assessment Bureau (Health Canada).

[e] Room volume is based on an average 2-car garage in North America (U.S. EPA 2011).