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Draft Screening Assessment

Silver and Its Compounds

**Environment and Climate Change Canada
Health Canada**

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Synopsis

Pursuant to section 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 silver and its compounds. Seven substances in this group were identified as priorities for assessment as they met categorization criteria under subsection 73(1) of CEPA. These seven substances are referred to collectively in this assessment as the Silver and its Compounds Group. The Chemical Abstracts Service Registry Numbers (CAS RN¹), their *Domestic Substances List* (DSL) names, and their common names are listed in the table below.

Substances in the Silver and its Compounds Group

CAS RN	DSL name	Common name
7440-22-4	Silver	Silver
7761-88-8	Nitric acid silver(1+) salt	Silver nitrate
7783-90-6	Silver chloride (AgCl)	Silver chloride
7785-23-1	Silver bromide (AgBr)	Silver bromide
10294-26-5	Sulfuric acid, disilver(1+) salt	Silver sulfate
20667-12-3	Silver oxide (Ag ₂ O)	Silver oxide
21548-73-2	Silver sulfide	Silver sulfide

The draft screening assessment of silver and its compounds focuses on the silver moiety and therefore considers silver in its elemental form, silver-containing substances, and all forms of silver found in the environment. As such, all silver-containing substances beyond the seven substances identified as priorities for assessment are considered. The combined exposure of humans and other living organisms to the silver moiety, whether it is present in environmental compartments (i.e., water, sediment, soil, and air), food, or products, is considered in this assessment.

Canada is the 15th largest producer of silver in the world. According to information submitted pursuant to a CEPA section 71 survey, substances within the Silver and its Compounds Group were manufactured or imported in low to moderate quantities (i.e., less than 1 tonne (t) to less than 10 000 t) by four companies. Silver has a wide variety of uses in Canada, including the manufacturing of bars, coins, jewelry, medals, silverware, silver-containing substances and preparations, glass products, and soap and cleaning compounds. It is also used in brazing and soldering, catalysis, cloud seeding, and electronics. Silver may be used in a range of products in Canada, including drugs, natural health products, cosmetics, pesticides, food additives, food

¹ 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.

packaging, incidental additives (e.g., products used in food processing establishments), and toys.

Silver is naturally released to the environment through weathering of soils and rocks. Anthropogenic releases of silver occur during its production (i.e., mining, processing, smelting, refining), during the manufacturing of silver-containing substances, following product disposal (e.g., batteries, electronics, silver-containing films), and through other activities (e.g., cloud seeding, wastewater treatment). The National Pollutant Release Inventory data from 2012 to 2016 indicate that silver was released to the environment in low quantities (i.e., 4-year total of less than 4 t to air, water, and land combined). Once released into the environment, silver in air and water will migrate to soil and/or sediments where it will persist.

Silver is not an essential nutrient for organism health or human health. Organisms exposed to silver in their habitats rapidly take up silver via their environmental media and accumulate it in internal organs and other tissues. The accumulated silver is mostly bound with sulfur-containing biomolecules and detoxified in aquatic organisms. For sediment or soil-dwelling organisms, the availability of the free silver ion can be reduced by forming inert silver sulfide in these environmental compartments thus decreasing silver bioaccumulation. No evidence of biomagnification across food chains has been found for silver.

Silver causes mortality as well as growth and reproductive effects to aquatic organisms at very low concentrations and to sediment and soil-dwelling organisms at moderate concentrations. The Canadian Water Quality Guideline (CWQG) derived by the Canadian Council of Ministers of the Environment is used as the chronic predicted no-effect concentration (PNEC) for silver for freshwater organisms. The PNECs for silver for marine, sediment and soil-dwelling organisms were derived from reliable ecotoxicity studies.

Ecological exposure to silver was characterized for the following sectors based on their potential to release silver: metal mining, base metal smelting and refining, wastewater treatment (i.e., silver in the final effluent released by wastewater treatment systems, silver in land-applied biosolids), and waste disposal (i.e., landfill leachate). Risk quotient analyses were performed by comparing exposure concentrations in surface water, marine water, sediment and soil compartments to PNECs for aquatic, benthic, and soil-dwelling organisms, respectively. Based on these analyses, there is a moderate potential that silver may cause harm to benthic organisms near some facilities in the metal mining and base metal smelting and refining sectors, but there is low risk to aquatic or soil-dwelling organisms. However, there is a high degree of uncertainty regarding the potential for ecological harm in sediment due to the paucity of data for these sectors and, to a lesser extent, the conservatism incorporated when assessing potential risk in this compartment.

Further analysis of surface water quality monitoring data consulted as part of the Ecological Risk Classification of Inorganic Substances (a classification framework that

classified the silver group as having high potential for ecological concern) indicated that the majority of silver concentrations infrequently exceeded the freshwater PNEC. Exceedances of the PNEC were often associated with high background concentrations of silver, with total concentrations of silver (rather than free ion concentrations), or with the statistical approach taken to address non-detects.

Considering all available lines of evidence presented in this draft screening assessment, there is low risk of harm to the environment from silver and its compounds. It is proposed to conclude that the seven substances in the Silver and its Compounds Group do not meet the criteria under paragraphs 64(a) or (b) of CEPA as they are not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity or that constitute or may constitute a danger to the environment on which life depends.

Silver and its compounds were evaluated using the Biomonitoring-based Approach 2, which compares human biomonitoring data (exposure) against biomonitoring guidance values (health effects), such as biomonitoring equivalents (BEs), to identify substances with low concern for human health. Total silver concentrations were measured in the whole blood of Canadians as part of the Canadian Health Measures Survey and a follow-up study to the Maternal-Infant Research on Environmental Chemicals (MIREC) Study called MIREC-Child Development Plus. Median and 95th percentile blood silver concentrations in Canadians of 0.066 and 0.27 µg/L were lower than the BE of 0.4 µg/L associated with the United States Environmental Protection Agency (U.S. EPA) reference dose for protection against the critical health effect of argyria, characterized by blue or blue-greyish staining of the skin and mucous membrane. Therefore, silver and its compounds are considered to be of low concern for human health at current levels of exposure.

On the basis of the information presented in this draft screening assessment, it is proposed to conclude that silver 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 the seven substances in the Silver and its Compounds Group do not meet any of the criteria set out in section 64 of CEPA.

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1. Introduction

Pursuant to section 68 or 74 of the *Canadian Environmental Protection Act, 1999* (CEPA) (Canada 1999), the Minister of the Environment and the Minister of Health have conducted a screening assessment of silver and its compounds to determine whether these substances present or may present a risk to the environment or to human health. Seven substances in this group were identified as priorities for assessment as they met categorization criteria under subsection 73(1) of CEPA (ECCC, HC [modified 2017]). These seven substances are referred to collectively in this assessment as the Silver and its Compounds Group.

The focus of the draft screening assessment is on the silver moiety² (hereafter referred to as “silver”). Therefore, it considers silver in its elemental form, silver-containing substances, and all forms of silver found in the environment. Some silver-containing substances have the potential to dissolve, dissociate or degrade to release silver through various transformation pathways and therefore contribute to the combined exposure of humans and ecological receptors to silver. The scope of the assessment considers exposure from silver found in environmental compartments (i.e., water, sediment, soil, air) from natural sources and anthropogenic activities including silver production, the manufacture, import, and use of silver-containing substances and products, and the release of silver containing substances. In this sense, the risk assessment is not limited to the seven substances identified as priorities for assessment.

This assessment only considers effects associated with silver. Effects from other elements or moieties that may be present in and released from certain silver-containing substances are not addressed (e.g., chloride, bromide). 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 may be addressed via other initiatives of the Chemicals Management Plan (CMP). Engineered nanomaterials containing silver that may be present in environmental media or in products are not explicitly considered in exposure scenarios of this assessment, but measured concentrations of silver in the environment or human biomonitoring could include engineered silver-containing nanoparticles. Similarly, this assessment does not explicitly consider ecological or health effects associated with nanomaterials containing silver. The Government of Canada’s Proposed Approach to Address Existing Nanomaterials will consider nanoscale forms of substances currently on the *Domestic Substances List* (ECCC, HC [modified 2016]).

This draft screening assessment includes consideration of information on chemical properties, environmental fate, hazards, uses and exposures. Relevant data were

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.

identified up to March 2019. 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 by 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 and/or consultation. Comments on the technical portions relevant to the environment were received from Geoff Granville (GCGranville Consulting Corp.), Dr. Beverly Hale (University of Guelph), and Dr. Jim McGeer (Wilfrid Laurier University). The human health portion of this assessment was based on the Biomonitoring-based Approach 2 science approach document (published December 9, 2016), which was externally peer-reviewed and subjected to a 60-day public comment period. External peer-review comments were received from Lynne Haber and Andrew Maier from Toxicology Excellence for Risk Assessment (TERA) and from Judy LaKind from LaKind Associates. 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 is based.

2. Identity of substances

Silver (Ag) is a natural element. Silver-containing substances in commerce or incidentally produced belong to various substance categories, including elemental silver, inorganic metal compounds, organic-metal salts, and organometallic compounds, represented by either discrete substances or UVCBs (unknown or variable composition, complex reaction products, or biological materials). The seven substances in the Silver and its Compounds Group that were identified as priorities for assessment belong to the inorganic metal compounds group. The Chemical Abstracts Service Registry Numbers

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.

(CAS RN⁴), *Domestic Substances List* (DSL) names, and common names of these substances are presented in Table 2-1.

Table 2-1. Substance identity information for the seven substances in the Silver and its Compounds Group identified as priorities for assessment

CAS RN	DSL name	Common name
7440-22-4	Silver	Silver
7761-88-8	Nitric acid silver(1+) salt	Silver nitrate
7783-90-6	Silver chloride (AgCl)	Silver chloride
7785-23-1	Silver bromide (AgBr)	Silver bromide
10294-26-5	Sulfuric acid, disilver(1+) salt	Silver sulfate
20667-12-3	Silver oxide (Ag ₂ O)	Silver oxide
21548-73-2	Silver sulfide	Silver sulfide

3. Physical and chemical properties

Silver (Ag) is a naturally occurring transition metal. It is soft and malleable and has a white metallic lustre (HSDB 1983-). Pure silver has the highest reflectivity and electrical and thermal conductivity of all metals (Lide 2000). The natural isotopic composition of silver includes two stable isotopes, ¹⁰⁷Ag and ¹⁰⁹Ag, with ¹⁰⁷Ag being slightly more abundant. Silver is one of the least reactive metals and Ag⁺ is the primary oxidation state under natural conditions. Silver oxidation states of +2 are not stable and are easily reducible. Oxidation states of +3 are rare (Greenwood and Earnshaw 1997).

Silver is stable in air and water, except when it reacts with sulfur compounds to form silver sulfide, causing a black tarnish on the surface of the metal (Lide 2000). Silver metal dissolves readily in hot concentrated sulfuric acid, as well as dilute or concentrated nitric acid. In the presence of air, and especially in the presence of hydrogen peroxide, silver dissolves readily in aqueous solutions of cyanide (HSDB 1983-).

Most silver salts are insoluble in water (e.g., silver bromide, 0.14 mg/L; silver chloride, 1.93 mg/L), with some exceptions such as silver nitrate (i.e., 2.16x10⁴ mg/L), perchlorate, and fluoride. Silver halides, especially bromide and iodide, are photosensitive and will decompose to silver metal when exposed to light (WHO 2002).

A summary of physical and chemical property data (Lide 2000, 2005) for the seven substances in the Silver and its Compounds Group is presented in Appendix A.

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4. Sources and uses

4.1 Natural sources

Silver is naturally present in the earth's crust, with average concentrations estimated at 0.07 mg/kg (Yaroshevsky 2006) to 0.1 mg/kg (Purcell and Peters 1998). It predominantly occurs as sulfides and in association with pyrite (i.e., iron disulfide), galena (i.e., lead sulfide), tellurides, and gold (ATSDR 1990; Purcell and Peters 1998). Natural processes responsible for silver mobilization through the environment include weathering and erosion of rocks and soil. As an element, silver does not break down in the environment, but it can change from one geochemical form to another as it moves through various compartments, e.g., from ionic silver in the water column to silver sulfide in sediments (see section 6.1 for a discussion of the environmental fate of silver). Silver is a trace element as it is a minor constituent of the earth's crust, water, and air (see section 7.2.2 for a discussion of background concentrations of silver).

4.2 Anthropogenic sources

4.2.1 Silver production

Silver is sourced from mineral deposits, which are extracted from the earth by the metal mining industry and further processed and refined by the base metal smelting and refining industry. The majority of Canada's mines are polymetallic (NRCan 2018a), and silver is produced mainly as a by-product of mining copper-zinc, copper-nickel, gold, and lead-zinc ores (SAMSSA 2016). Canada's only primary silver mine suspended operations in 2013 with intentions of returning to production in the future (Alexco 2019).

In 2016, world silver production was estimated at approximately 25 100 t; Canada ranked 15th (O'Connell et al. 2017). Natural Resources Canada (NRCan) (2018b) reports that silver production in Canada in 2016 was 385 t, with Ontario being the largest producer (132 t), followed by British Columbia (84 t) and Quebec (83 t). Compared to other metals, metalloids, and non-metals produced in Canada, silver is produced in low quantities.

4.2.2 Manufacture and imports

Information regarding the manufacture and import of silver-containing substances in Canada was acquired through data submitted pursuant to a CEPA section 71 survey (Environment Canada 2013a), through data obtained from the Canadian Border Services Agency (CBSA) (CBSA 2016), and through data available from the Canadian International Merchandise Trade database (CIMI 2017-).

A survey issued pursuant to a CEPA section 71 notice (Canada 2012) (for the reporting year 2011)⁵ included the seven substances of the Silver and its Compounds Group (see section 2) except for silver (CAS RN 7440-22-4). Responses were received for four of these substances: silver nitrate, silver oxide, silver sulfide, and silver sulfate (Environment Canada 2013a). Fewer than four companies reported manufacturing silver nitrate (10 t to less than 100 t) or silver oxide (less than 1.0 t) and four companies reported importing silver nitrate (1.0 t to less than 10 t) or silver sulfide (1 000 t to less than 10 000 t) and/or silver sulfate (less than 1.0 t) (Environment Canada 2013a).

The quantity of silver-containing substances imported into Canada over the period of 2010 to 2013, as reported to the Canadian Border Services Agency (CBSA), for five Harmonized System (HS) codes⁶ related to silver substances, is presented in Appendix B, Table B-1 (CBSA 2016). The HS codes were grouped by category for analysis: silver nitrate, other silver compounds, and silver powder. Only one HS code was related to a discrete substance: silver nitrate. The distribution of import data indicates that many companies imported silver-containing substances related to these HS codes in low to moderate quantities from 2010 to 2013: 150 t for silver nitrate, 150 t for other silver compounds, and 84 000 t for silver powder. Other categories of HS codes include unwrought silver, semi-manufactured silver, and silver ores and concentrates, for which total import quantities were 4200 t, 2500 t, and 1500 t, respectively, over the 2010 to 2013 period. According to the CIMT (2017-), import quantities from 2017 to 2018 were 173 t for silver nitrate, 38 t for other silver compounds, 263 t for silver powder, 3 351 t for unwrought silver, 586 t for semi-manufactured silver, and 11 391 t for silver ores and concentrates.

4.2.3 Uses

Silver-containing substances have a wide variety of uses internationally. Silver is a precious metal of significant economic and aesthetic value and is used in coins, bars, jewelry, and silverware (O'Connell et al. 2017; USGS 2018). Historically, silver was used in the photographic and radiographic film industry (Health Canada 1986; Purcell and Peters 1998; WHO 2002), but this use declined to 20% of its peak worldwide demand in 1999 following changes in imaging technology (O'Connell et al. 2017). Current industrial applications of silver include the manufacture of silver-containing substances and preparations (e.g., silver nitrate is used in the synthesis of potassium dicyanoargentate and silver oxide) and the catalysis of other chemical compounds (e.g., ethylene oxide) (O'Connell et al. 2017; Brumby et al. 2008). Other current industrial

⁵ Values reflect quantities reported in response to the survey conducted under section 71 of CEPA (Canada 2012). See survey for specific inclusions and exclusions (schedules 2 and 3).

⁶ The Harmonized Commodity Description and Coding System is an international goods classification system developed by the Customs Co-operation Council (now the World Customs Organization) and used by Canada to classify imported and exported goods (<http://www.cbsa-asfc.gc.ca/trade-commerce/tariff-tarif/hcdcs-hsdcm/menu-eng.html>).

applications of silver include batteries, brazing and soldering, catalytic converters, circuit boards, electronics, electroplating, hardening bearings, inks, mirrors, and solar cells (O'Connell et al. 2017; USGS 2018), as well as the use of silver iodide for cloud seeding (WHO 2002).

According to information reported pursuant to a CEPA section 71 survey, uses of silver-containing substances include laboratory uses and distribution of silver nitrate (CAS RN 7761-88-8) and silver sulfate (CAS RN 10294-26-5) (Canada 2012). Additional use information from this source cannot be disclosed due to confidentiality requests. Other uses of silver-containing substances in Canada include the fabrication of coins, jewelry, medals, and silverware; brazing and soldering; and ethylene oxide catalysis (O'Connell et al. 2017). Silver iodide is used for cloud seeding activities in Alberta (personal communication, email from the Alberta Severe Weather Management Society, to the Ecological Assessment Division, Environment and Climate Change Canada, dated March 21, 2019; unreferenced). The CBSA (2016) import data for various silver-containing substances does not contain use information. Therefore, a subset of imports was identified and NAICS6 codes⁷ were assigned for analysis to garner further insight on silver uses in Canada. Total quantities imported were tallied by the assigned NAICS6 code descriptions for three categories: silver nitrate, other silver compounds, and silver powder (Appendix B, Table B-2). The inferred uses of silver nitrate, other silver compounds, and silver powder in Canada includes those related to various manufacturing processes, namely: manufacturing of inorganic chemicals, glass products, electronic parts and equipment, and soap and cleaning compounds (silver nitrate); other miscellaneous chemical product and preparation manufacturing; manufacturing of other miscellaneous silver compounds; and switchgear and switchboard apparatus manufacturing (silver powder).

Silver may be used in a range of products in Canada which are available to consumers, including: drugs (DPD [modified 2018]), natural health products (LNHPD [modified 2018]; NHPID [modified 2019]), cosmetics (Health Canada [modified 2018]; personal communication, emails from the Consumer and Hazardous Products Safety Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated February 24, 2016; unreferenced), pesticides (personal communication, emails from the Pesticide Management Regulatory Agency, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated March 1, 2016; unreferenced), food additives (Health Canada [modified 2006]), food packaging, incidental additives (e.g., products used in food processing establishments) (personal communication, emails from the Foods Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated March 14, 2016; unreferenced), and toys (Health Canada 2016).

⁷ North American Industry Classification System (NAICS) codes have a hierarchical structure composed of five levels. The fifth level, represented by six digits, correspond to Canadian industries.

5. Releases to the environment

Canada's National Pollutant Reporting Inventory (NPRI) estimates annual releases of silver and its compounds to the environment, annual quantities recycled, and annual quantities disposed of. Reporting is mandatory for facilities meeting the reporting threshold, which includes facilities that manufacture, process, or otherwise use silver and its compounds at a concentration (of elemental silver) greater than or equal to 1% by weight (except for by-products and mine tailings) and in a quantity of 10 t or more, and where employees work 20,000 hours per year (ECCC 2016a).

Submissions to the NPRI during the 2012 to 2016 reporting period indicate that in Canada, 32 facilities across 10 sectors reported releases of silver to air, water or all media less than one tonne (Appendix C, Table C-1). Releases to land were not reported during the 5-year period but may be captured within the category of "all media less than one tonne." The total release of silver to air during the 2012 to 2016 period from six reporting sectors was low (2.0 t) and largely attributable to the base metal smelting and refining sector (1.3 t) and the non-conventional oil extraction sector (0.41 t). The other four sectors reported negligible releases to air (less than or equal to 0.040 t). The total release of silver to water during the same 5-year period from five reporting sectors was also low (0.70 t). The metal mining sector released 0.3 t of silver to water from eight facilities. Submissions to the "all media less than one tonne" category from 2012 to 2016 indicate that the total release of silver was also low (1.0 t) and mostly attributable to the base metal smelting and refining sector, while other sectors released negligible quantities (less than or equal to 0.090 t). Therefore, the NPRI data indicates that silver was released to the environment in low quantities from industrial activities meeting the reporting threshold during the 2012 to 2016 period.

Releases of silver to the environment may also occur from the manufacture, use, and disposal of silver-containing substances and products (e.g., batteries, electronics, silver-containing films), and from other activities (e.g., cloud seeding) (ATSDR 1990; Purcell and Peters 1998; WHO 2002; USGS 2018).

Historically, the photographic and radiographic film industries in Canada and other countries used silver extensively and were a significant source of silver releases to the environment (Health Canada 1986; Purcell and Peters 1998; WHO 2002). Surface water monitoring data collected in proximity to one photographic manufacturing plant indicate concentrations of silver decreased to below the detection limit ($<10 \mu\text{g/L}$) from the 1970s to the 1990s (WHO 2002). Since silver's peak use in these industries in 1999, uses declined due to changes in imaging technologies (section 4.2.3) and consequently, releases to the environment decreased (USGS 2018; Metcalfe et al. 2018). Therefore, considering the decline in silver use by the photographic and radiographic industries, it is expected that releases of silver to the Canadian environment from these sources are low. Further, effluents from these industries typically undergo municipal wastewater treatment where removal of silver is effective (section 7.2.5).

Disposal of consumer, commercial, and industrial silver-containing products may also release silver to the environment. Products such as various electronics (e.g., cell phones, circuit boards, etc.) and batteries are either recycled or ultimately disposed of in landfills.

Cloud seeding is another source of release of silver to the Canadian environment. Currently, there is one hail suppression program operating in Alberta, conducted by Weather Modification Inc. Since 1996, in an attempt to reduce damage caused by hail, the company has seeded a number of developing thunderstorms in the Calgary Red Deer area between May and September of each year. It uses silver iodide as a seeding agent, and releases to the environment from this activity are low (average of 0.221 t of silver iodide per year and range of 0.0484 to 0.400 t of silver iodide from 1996 to 2018) (personal communication, email from the Alberta Severe Weather Management Society, to the Ecological Assessment Division, Environment and Climate Change Canada, dated March 21, 2019; unreferenced).

6. Environmental fate and behaviour

6.1 Environmental distribution

In the ambient atmosphere, silver and its compounds are expected to exist solely in the particulate phase and may be removed from the atmosphere via wet or dry deposition (HSDB 1983-).

In the freshwater compartment, silver primarily exists as silver complexes (CCME 2015a; Kramer et al. 2007; Shafer et al. 1996; Wen et al. 1997). Free silver ions will rapidly complex with ligands in water such as sulfides, chlorides, natural organic matter (NOM), and suspended particles (Andren and Bober 2002; Bodek et al. 1988; CCME 2015a; Kramer et al. 2007; Ratte 1999; Shafer et al. 1996; Wen et al. 1997; Wood 2012). In estuarine and marine water, silver mainly forms Ag-Cl complexes due to high concentrations of chloride ions, and complexes of AgCl , AgCl_2^- , or AgCl_3^{2-} progressively predominate as water salinity increases (Miller and Bruland 1995; Ward and Kramer 2002; Wood et al. 2004; Wood 2012). When silver-containing industrial and domestic wastewaters are treated at sewage treatment plants, approximately 75% to 94% of silver will be transformed to insoluble silver sulfides and remain in the sludge (Bard et al. 1976; CCME 2015a; Lytle 1984; NAPM 1974; Pavlostathis and Maeng 1998; Shafer et al. 1998).

Silver may partition from water to sediment and adsorb onto clay minerals and hydrous metal oxides, e.g., manganese and iron hydroxides (Bodek et al. 1988). The precipitation of silver sulfide (Ag_2S) may be another effective mechanism of removing silver from water (Bodek et al. 1988; Shafer et al. 1996). The partition coefficients ($\log K_d$) for silver range from 1.20 to 6.32 (Flegal et al. 1997; HSDB 1983- ; Mueller-Harvey et al. 2007), indicating that silver compounds have a range of adsorption affinities to suspended solids and sediments under various environmental conditions. Silver adsorbed to suspended solids settles to sediments and may accumulate over time, and

thus sediments may act as an active sink for silver in the aquatic environment (Callahan et al. 1979). However, adsorbed silver ions may desorb and re-enter the water column upon contact with seawater (Bodek et al. 1988). It has also been suggested that the relatively large amounts of organic colloids in sea water will lower the K_d of silver and remobilize a free silver ion from a particulate phase into the overlying waters (Bodek et al. 1988; Flegal et al. 1997). Volatilization from water surfaces is not expected to be an important fate process for silver (HSDB 1983-).

Upon entering soil, silver will adsorb onto organic colloids, clay minerals, hydrous metal oxides, and sulfides (notably, acid-volatile sulfide or iron sulfide) (Bodek et al. 1988; Mueller-Harvey et al. 2007). The soil-water partition coefficient ($\log K_{sw}$) of 2.79 summarized by Mueller-Harvey et al. (2007) indicates that silver will be moderately adsorbent to soil particles. Silver complexes with sulfides and dissolved organic carbon in soil and will remain in soil due to extremely high adsorption ($\log K_{sw}$ of ~ 8.8 to 14.2) (Wood 2012). Volatilization from moist and dry soil surfaces is not expected to be an important fate process for silver compounds based on their ionic nature and low vapour pressure values (HSDB 1983-).

6.2 Environmental persistence

Silver generally exists as elemental silver and silver complexes in the environment. There is no evidence for the biotransformation of Ag^0 , but silver will complex with chlorides, sulfides, and biomolecules when entering the environment and organisms (Wood 2012). Silver is considered persistent because it cannot degrade through processes such as photodegradation or biodegradation, though it can transform into different chemical species or partition among different phases within environmental compartments.

6.3 Potential for bioaccumulation

Silver is not an essential element for organisms. The assessment of silver bioaccumulation takes into account the speciation and bioavailability of silver in the environment. Bioavailability is discussed below with a focus on the silver moiety.

Silver bioaccumulation has been extensively reviewed in the Canadian water quality guideline (CWQG) (CCME 2015a). It is recognized that the bioconcentration and bioaccumulation factor (BCF and BAF) approach for metals is currently the subject of much debate and criticism because these factors are considered of little use in predicting metal hazards (McGeer et al. 2003; Schlegel et al. 2007). Therefore, BCF and BAF values are not the focus of the CWQG document or this screening assessment. Instead, silver bioavailability, bioaccumulation, and biomagnification via food chains will be considered as overall lines of evidence in determining the bioaccumulation potential of silver. No evidence of silver biomagnification was found, and an inverse relationship between the uptake rate constant for silver and its concentrations in water was demonstrated for the silver BCFs and BAFs (McGeer et al.

2003; López-Serrano et al. 2014). Therefore, only new information will be further discussed in this screening assessment.

The bioavailability and bioaccumulation of silver in the aquatic environment is mostly driven by the free silver ion (Ag^+) – the form that is toxic to all aquatic organisms (Rodgers et al. 1997a, b). The silver ion has the tendency to bioaccumulate in organisms because it is compatible for uptake via cell membrane ion transporters (Fabrega et al. 2011; Luoma 2008). The uptake and accumulation of waterborne Ag in aquatic organisms are proportional to aqueous Ag concentrations and, to a lesser degree, exposure duration (Brown et al. 2003; Bury et al. 2002; Carvalho et al. 1999; Couillard et al. 2008; Guevara et al. 2005; Lam and Wang 2006; Martin et al. 2017; Roditi and Fisher 1996; Rodgers et al. 1997b; Wood et al. 1996;). Dietary exposure of Ag is not considered a significant concern (CCME 2015a). The understanding of Ag detoxification mechanisms in aquatic organisms is limited. Zimmermann et al. (2017) suggested that zebra mussels possess regulatory mechanisms to restrict Ag bioaccumulation, with excess Ag eliminated only after all binding sites are occupied. Martin et al. (2017) demonstrated that rapid binding with the cysteine-rich protein metallothionein (MT) in fish is the main pathway for detoxification of Ag^+ due to the high affinity of Ag for the thiol groups in MT.

In the natural sediment environment, silver sulfide is considered the predominant form, with high levels of iron sulfides in sediments favouring the formation of silver sulfide (Hirsch 1998b). The low Ag levels accumulated in tissues of sediment-dwelling organisms and the lack of effects observed when the organisms were exposed to silver sulfide at concentrations of 444 to 920 mg Ag/kg dw indicate that Ag-sulfide complexes in sediments may not be bioavailable to organisms (Hirsch 1998b).

Limited data were available on silver uptake and bioaccumulation in terrestrial animals and plants. The predominant factor affecting the behaviour and bioavailability of silver in soils are sulfides, or acid-volatile sulfides, which complex with the free silver ion to form less bioavailable silver sulfides. Velicogna et al. (2017) investigated earthworm Ag bioaccumulation in AgNO_3 -spiked field soil. The reported kinetic BAF was 0.74, which is in agreement with other studies conducted with terrestrial oligochaetes (Schlich et al. 2013). BAF values of similar range (1.12 to 6.40) were observed for other soil invertebrate species (Tourinho et al. 2016; Waalewijn-Kool et al. 2014). Ag uptake routes seem to be species-specific among soil organisms, with oral uptake being the primary route for earthworms compared to dermal uptake for soil isopods (Diez-Ortiz et al. 2015; Tourinho et al. 2016).

Plants accumulate silver primarily in the root systems, as demonstrated by the investigation of Ag bioavailability in biosolids-amended soil to lettuce at environmentally relevant Ag concentrations (Doolette 2015). Ag accumulation in shoots was not significant compared to roots. Cl^- was found to react with Ag^+ forming soluble/bioavailable Ag-chloro complexes until over-saturation occurred and AgCl precipitated (Doolette 2015).

A recent study by Yoo-iam et al. (2014) on Ag biomagnification potential through a tropical freshwater food chain with green alga (*Chlorella* sp.), water flea (*Moina macrocopa*), silver barb (*Barbonymus gonionotus*), and blood worm (*Chironomus* spp.) further supported the CCME (2015) conclusion that Ag does not biomagnify. The calculated biotransference factor (BTF), or biomagnification factor (BMF) were within 0.02 to 0.46 from predators to prey, suggesting no biomagnification.

The present weight of evidence indicates that silver is rapidly taken up and accumulated in organs and other tissues by organisms. The accumulated silver is shown to be mostly bound to biomolecules such as MT or detoxified in aquatic organisms. The Ag regulation or detoxification mechanisms in sediment or soil-swelling organisms is unclear; the availability of the free Ag⁺ could be reduced by forming inert silver sulfide in these environmental compartments, thus decreasing Ag bioaccumulation by organisms. No evidence of biomagnification across food chains has been found for silver (CCME 2015a; McGeer et al. 2003; Ratte 1999; Terhaar et al. 1977; Yoo-iam et al. 2014).

7. Potential to cause ecological harm

7.1 Ecological effects assessment

7.1.1 Essentiality

There is no evidence that silver is an essential element for living organisms (CCME 2015a).

7.1.2 Mode/Mechanisms of Toxic Action

Silver generally exists as silver complexes (e.g., colloids and particulates) in most natural environments (CCME 2015a; Kramer et al. 2007; Shafer et al. 1996; Wen et al. 1997).

The well-known mechanism of silver toxicity to freshwater organisms is related to its interference with the vital Na⁺/Cl⁻ uptake process (McGeer and Wood 1998; Morgan et al. 1997; Wood 2012). The Ag toxic mode of action in both fresh and marine water fish has been discussed in detail in the CWQG for silver (CCME 2015a). The primary mechanism of silver toxicity in freshwater fish is an almost total inhibition of Na⁺/K⁺-ATPase activity, resulting in the disruption of the functions of two key gill enzymes that are essential for ionoregulation (CCME 2015a; Hogstrand and Wood 1998; Webb and Wood 1998; Wood 2012). The main toxicity mechanism in marine fish appears to involve osmoregulatory failure, as seen in freshwater fish, although marine fish have two possible target organs (gills and gut) and two possible target functions (branchial ionoregulation and gastrointestinal ionoregulation) (CCME 2015a; Wood 2012). It is shown that long-term exposure to silver in juvenile rainbow trout induced the production of the detoxifying protein metallothionein (MT), suggesting fish liver offers inherent protection against chronic Ag toxicity (Hogstrand et al. 1996).

Like fish, freshwater invertebrates (e.g., *Daphnia magna*) exposed to silver also exhibited ionoregulatory disturbance (Bianchini and Wood 2003). The Na⁺/K⁺-ATPase inhibition in *Daphnia magna* was directly related to silver hindering the whole body sodium uptake of the organism. However, the nature of the sodium uptake inhibition in *Daphnia magna* was different from that in fish (competitive versus non-competitive in fish) (Bianchini and Wood 2003). Silver may also inhibit the reproduction of some invertebrate species by disrupting the synthesis of vitellogenin (Wood 2012).

In marine invertebrates, however, the exact mechanism of toxic action is unclear. Marine invertebrates did not exhibit osmoregulatory failure or ionoregulation impairment at the hemolymph level when exposed to silver. Instead, silver induced significant changes in the water content in gills and/or hepatopancreas, causing significant changes in Na⁺/K⁺-ATPase activity. Changes also occurred in both total and intracellular ion (Cl⁻, Na⁺, K⁺, Mg²⁺, and Ca²⁺) concentrations in different tissues of the marine invertebrates (Bianchini et al. 2005). It has been suggested that other mechanisms are involved in water and ion transport at the cell membrane that induces impairments in water and ion regulation at the cellular level in different tissues of marine invertebrates (Bianchini et al. 2005).

Silver uptake by freshwater algae has been suggested to occur via three mechanisms: (1) accidental cation transport; (2) transport through a system used for the uptake of other essential cations (e.g., Na⁺, K⁺, or Cu⁺); and (3) transport across cell membranes to the cytosol via passive diffusion directly through the lipid bilayer as a neutral AgCl complex (Lee et al. 2004). Once entering the algae cell, silver interferes specifically with sulfur-containing molecules (Leonardo et al. 2016; Ratte 1999), causing misfolding and damage of proteins by binding to thiol groups (Pillai et al. 2014). Silver can also regulate the expression of proteins in ATP-synthesis and photosynthesis and can replace Cu⁺ in key proteins involved in those processes (Pillai et al. 2014). Leonardo et al. (2016) demonstrated that silver bound with molecules containing sulfur and effectively detoxified upon entering the cytosol in the green microalga *Coccomyxa actinabiotis* at low concentrations (e.g., 10⁻⁵M). However, silver may enter the cytosol and chloroplasts at higher concentrations (e.g., > 10⁻⁴ M), causing damage to the photosystem and inhibiting photosynthesis and growth (Leonardo et al. 2016).

Silver is considered to have strong fungicidal, algicidal, and bactericidal properties due to inhibition by Ag⁺ of thiol, P (phosphatase), S (arylsulfatase), and N (urease) enzymes (Domsch 1984; Falbe and Regitz 1992; NAPM 1974).

7.1.3 Toxicity-modifying factors (TMF)

The CCME reviewed potential toxicity-modifying factors for silver in accordance with the CCME protocol for the derivation of water quality guidelines (CCME 2007) when developing the silver water quality guideline (CCME 2015a). The review determined that silver toxicity is correlated with concentrations of the free silver ion, Ag⁺, and therefore factors affecting the free Ag⁺ availability are expected to modify its toxicity. Silver toxicity decreases considerably in natural water compared to tests with laboratory water. The

complexation with various ligands and adsorption on fine suspended solids in natural waters reduce the availability of the free Ag^+ (CCME 2015a; Erickson et al. 1998; Wood 2012).

Sulfide complexation and, to a lesser degree, thiosulfate complexation are the predominant factors influencing Ag speciation in the environment and can mitigate Ag toxicity (Bianchini and Bowles 2002; Bianchini and Wood 2008; CCME 2015a).

Natural organic matter (NOM) in natural water is another important ligand that can form large Ag-NOM complexes, rendering the silver non-bioavailable (CCME 2015a; Erickson et al. 1998). When studying Ag effects on three species of microorganisms, González et al. (2015) found that silver complexation with dissolved NOM was most pronounced at low concentrations, long exposure time, and high DOC, illustrating the strong protective role of NOM.

The protective effects of Cl^- could be species-specific for freshwater organisms and is an extremely important factor in reducing silver toxicity to marine organisms, as high chloride concentrations favours the formation of less toxic Ag-chloro complexes (Bury and Wood 1999; CCME 2015a; Galvez and Wood 1997; Hogstrand et al. 1996; McGeer and Wood 1998; Ratte 1999).

The effect of pH (i.e., H^+) on Ag toxicity is unclear. It has been speculated that the effects caused by pH were due to its interaction with DOC, which reduced H^+ leaving increased DOC for Ag complexation (CCME 2015a).

Several biotic ligand models (BLMs) have been developed to predict the acute toxicity of silver to freshwater organisms. The merit of three such models for Ag have been reviewed in the recent Canadian water quality guideline for silver (CCME 2015a). These models were considered useful candidates in generating short-term toxicity estimates under site-specific conditions. Unfortunately, no BLM is available for predicting the chronic toxicity of Ag to freshwater organisms (CCME 2015a; Wood 2012).

7.1.4 Effects on aquatic organisms

The speciation of silver is a crucial factor in its potential to cause aquatic toxicity. While insoluble or complexed silver compounds have low toxicity to aquatic organisms, the high toxicity of silver has long been known to be due to the free Ag^+ ion (Bury and Wood 1999; Hogstrand et al. 1996; Karen et al. 1999; Leblanc et al. 1984; Ratte 1999; Rodgers et al. 1997a, b). Readily soluble salts such as silver nitrate are used in laboratory toxicity studies and produce effects in freshwater organisms at low concentrations due to the release of free Ag^+ ions (Hogstrand et al. 1996; Rodgers et al. 1997a, b). Other silver salts (e.g., thiosulfate, sulfide, chloride, etc.) were found to be much less toxic than silver nitrate, and AgCl is essentially nontoxic (LeBlanc et al. 1984; Hogstrand et al. 1996; Rodgers et al. 1997a,b). This is likely due to the proportion of total Ag in the exposure medium that is the free Ag^+ ion.

Data on the toxicity of silver to freshwater organisms are summarized in Table 7-1. This dataset includes data collected from the literature up to 2013 for the derivation of the CWQG (CCME 2015b). An additional literature search on silver toxicity data published post-2013 up to 2017 was conducted for the purpose of this screening assessment. The updated literature search retrieved approximately 100 additional journal articles on silver toxicity and bioaccumulation studies (in various environmental media). All studies were critically reviewed, and only data from high-quality studies were considered.

In acute toxicity tests, cladocerans and green algae are among the most sensitive species to silver compared to fish and aquatic insects or other invertebrate groups (CCME 2015a). Fish, particularly rainbow trout (*Oncorhynchus mykiss*) and fathead minnows (*Pimephales promelas*), at the early larvae and juvenile life-stages, are more sensitive to silver toxicity than adult fish (Table 7-1) (CCME 2015b). In chronic toxicity tests, fish, invertebrates and aquatic plants displayed similar sensitivity to silver in the range of 0.32 to 23 µg/L, with the exception of the most tolerant invertebrate species, midge (*Chironomus tentans*), with a 10-day no effect concentration for reproduction at 125 µg/L (Table 7-1) (CCME 2015b; Rodgers et al. 1997a). It was hypothesized that the complexation of silver by food particles in long-term toxicity tests of invertebrates reduced silver bioavailability (Wood et al. 2002).

Table 7-1. Summary of available Ag toxicity data to freshwater organisms

Group	Test Types/ Endpoints	Acute/ chronic	Toxicity range (µg/L) ^a	Reference ^b
Fish	Mortality	Acute	1.48 – 280	Auffan et al. 2014; Asmonaite et al. 2016; CCME 2015b; Lacave et al. 2016; Ribeiro et al. 2014
Invertebrates	Mortality	Acute	0.11 – 5030	Banumathi et al. 2017; CCME 2015b; Domingues 2016; Khan et al. 2015; Mackevica et al. 2015; Mehennaoui et al. 2016; Rainville et al. 2014; Ribeiro et al. 2015; Seitz et al. 2015
Algae/plants	Growth	Acute	1.29 – 248.2	CCME 2015b; Li et al. 2015; Navarro et al. 2015; Sørensen and Baun 2015
Protozoan	Mortality	Acute	8.8	CCME 2015b
Fish	Growth/mortality	Chronic	0.24 – 23	CCME 2015b
Invertebrates	Reproduction/growth	Chronic	0.78 – 125	CCME 2015b; Ribeiro et al. 2014
Algae/plants	Growth	Chronic	0.63 – 6	CCME 2015b; Sekine et al. 2015; Sørensen and Baun 2015

^a The effect concentrations included are for toxicity tests performed using AgNO₃.

^b Unless otherwise listed, references cited as CCME 2015b refer to the dataset presented in Appendix A of the CWQG (CCME 2015b).

The current long-term CWQG for silver for the protection of freshwater organisms (CCME 2015a) is 0.25 µg/L. This guideline value is based on a species sensitivity distribution (SSD) approach using chronic toxicity data for 9 aquatic species (i.e., 4 fish, 4 invertebrates, and 1 aquatic plant), and the guideline represents the HC5 (5th percentile) of the distribution.

New toxicity data for freshwater organisms obtained since the publication of the silver long-term (chronic) CWQG support the value of 0.25 µg/L as protective of freshwater aquatic organisms (Asmonaite et al. 2016; Call et al. 1997, 1999, 2006; Domingues 2016; Khan et al. 2015; Li et al. 2015; Mackevica et al. 2015; Mehennaoui et al. 2016; Navarro et al. 2015; Rainville et al. 2014; Ribeiro et al. 2015; Seitz et al. 2015; Sekine et al. 2015; Shen et al. 2015; Sørensen and Baun 2015; Xin et al. 2015; Yoo-iam et al. 2014; Zhang et al. 2015). Therefore, a freshwater predicted no effect concentration (PNEC_{freshwater}) of 0.25 µg/L (total silver) will be used for the risk characterization.

7.1.5 Effects on marine organisms

The high chloride content in seawater reduces silver toxicity to marine organisms by forming less soluble/bioavailable and less toxic Ag-chloro complexes (Ferguson and Hogstrand 1998; Ratte 1999).

The data on Ag toxicity to marine organisms available in the current Ag CWQG (CCME 2015b) are summarized in Table 7-2. In acute toxicity tests with marine water, invertebrates and algae are more sensitive to silver than fish (CCME 2015b). In chronic toxicity tests, the red alga *Champia parvula* was found to be the most sensitive species to silver toxicity, while fish species were the least sensitive (CCME 2015b).

Table 7-2. Summary of available Ag toxicity data to marine water organisms

Group	Test Types/ Endpoints	Acute/ chronic	Toxicity range (µg/L) ^a	Reference ^b
Fish	Mortality/ embryo development	Acute	100 – 1876	Auffan et al. 2014; CCME 2015b; Matson et al. 2016
Invertebrates	Mortality/ embryo development	Acute	5.8 – 647	CCME 2015b; Khodaparast 2015; Martin et al. 1981
Algae/plants	Growth	Acute	21 – 86 ^c	CCME 2015b
Fish	Growth/ mortality	Chronic	19 – 1000	CCME 2015b
Invertebrates	Reproduction /growth	Chronic	3.9 – 100	Chan and Chiu 2015; CCME 2015b

Group	Test Types/ Endpoints	Acute/ chronic	Toxicity range (µg/L) ^a	Reference ^b
Algae	Growth/yield	Chronic	2.5 – > 20	Steele and Thursby 1983; Sanders and Abbe 1989

^a Unless otherwise mentioned, the effect concentrations included are for toxicity tests performed using AgNO₃.

^b Unless otherwise listed, references cited as CCME 2015b refer to the dataset presented in Appendix A of the CWQG (CCME 2015b).

^c The effect concentrations included are for toxicity tests performed using metallic Ag and reported as lethal effect, LC₅₀.

A short-term CWQG for the protection of marine-water organisms (CCME 2015a) of 7.5 µg/L (total silver) is available, but there were insufficient data to derive a long-term marine guideline (CCME 2015a). Additional data on silver acute toxicity to saltwater organisms were collected and reviewed during the previously mentioned literature search post-2013 (Auffan et al. 2014; Berry et al. 1999; Magesky and Pelletier 2015; Martin et al. 1981; Matson et al. 2016). The new toxicity data for saltwater organisms would not result in any change to the short-term CWQG, and while additional chronic toxicity data were found for marine algae (Sanders and Abbe 1989), a SSD approach for deriving a chronic marine PNEC is not feasible due to lack of long-term toxicity data for marine fish (CCME 2007).

An assessment factor approach was used in this screening assessment to derive a long-term PNEC for marine organisms. Short- and long-term Ag toxicity data in estuarine and marine water were standardized by extrapolating the endpoints to long-term lowest observed effect concentrations (LOECs) or no observed effect concentrations (NOECs). The lowest standardized value was used as the critical toxicity value (CTV). The 48 h LC₅₀ of 5.8 µg/L in Eastern oyster (*Crassostrea virginica*) at 25 ppt salinity (Calabrese et al. 1977) was the selected CTV. An assessment factor of 10 was applied, which considers an endpoint standardization factor of 10 to extrapolate from an acute median effect to a long-term sub-lethal no effect concentration. A factor of 1 was also applied to account for species variation because data were available for a large number of species representing multiple categories of organisms. These result in a chronic PNEC_{marine water} of 0.58 µg/L.

7.1.6 Effects on sediment organisms

Bioavailability and toxicity of silver to benthic organisms in freshwater sediments depend strongly on the physical-chemical properties of the sediments (e.g., pH, organic carbon, cation exchange capacity, the amounts of silt and clay) and the test conditions, and they are species-dependent (Call et al. 2006; Rodgers et al. 1995; Hirsch 1998a; Yoo et al. 2004). In a tiered study of Ag bioavailability to *Hyalella azteca* in four AgNO₃-spiked field sediments, the 10-day LC₅₀ based on total acid-extractable silver ranged from 1.6 to approximately 380 mg/kg dw. Lower Ag toxicity was found in sediments having higher pH and greater amounts of organic matter, clay, cation-exchange

capacity, and acid-volatile sulfides (Rodgers et al. 1997b). This large difference in toxicity indicates major impacts of differential adsorption and subsequent bioavailability.

Complexation of ligands significantly affects Ag bioavailability and toxicity (Call et al. 2006; Hirsch 1998a; Rodgers et al. 1997b). In experiments with the freshwater amphipod *Hyalella azteca*, four field sediments were enriched with silver nitrate, silver chloride, silver sulfide, and silver thiosulfate complex $[\text{Ag}(\text{S}_2\text{O}_3)_n]$ (69% Ag). The 10-day LC_{50} values were between 1.62 and 2980 mg/kg dw in AgNO_3 -spiked sediments, again demonstrating that differences in adsorption to sediments have an impact on Ag bioavailability. NOECs determined for sediments spiked with AgCl, Ag_2S , and silver thiosulfate ranged from 753 to 2560 mg/kg dw (Hirsch 1998a; Rodgers et al. 1995).

Silver toxicity to sediment organisms is also species-dependent. *Chironomus* sp. larvae and *C. tentans* were much less sensitive to silver toxicity than *Hyalella* sp. (Call et al. 1997, 1999, 2006; Ewell et al. 1993).

Call et al. (2006) conducted sediment toxicity tests with *Hyalella azteca* on two lake sediment samples. One sandy loam sediment contained low concentrations of complexation ligands for Ag binding. The observed toxicity test resulted in a 10-day LC_{50} of 84 mg/kg dw. Compared to mortality, growth was the more sensitive endpoint, with a 10-day NOEC and LOEC of 12 mg/kg dw and 31 mg/kg dw, respectively. The silt loam sediment had a higher potential for Ag binding and greater protection from Ag toxicity. The observed toxicity was a 10-day LC_{50} at 2980 mg/kg dw, and a NOEC and LOEC for reduced growth of 2150 and 4310 mg/kg dw, respectively.

Rajala et al. (2016) investigated exposure of blackworms (*Lumbriculus variegatus*) to silver nitrate in an artificial sediment and two samples of natural sediments. Adverse effects on blackworm reproduction and number of worms at the end of 28-day tests were observed in artificial sediments with a 28-day median inhibition concentration (IC_{50}) (reproduction) of 23.9 mg/kg dw and a 28-day median effect concentration (EC_{50}) (number of worms) of 38 mg/kg dw. The higher silver toxicity in the artificial sediments, compared to the natural sediments, was attributed to the lower organic carbon and sulfide levels resulting in lower Ag complexation, as well as direct spike method to avoid Ag^+ complexation with Cl^- in overlying water.

The sediment PNEC selection followed an assessment factor (AF) approach. The lowest toxicity value was a 10-day LC_{50} of 1.62 mg/kg with *Hyalella azteca* (Rodgers et al. 1997b) obtained with sediments of extremely low Ag complexing ligands. In this study, the Ag concentration in overlying water reached 9.7 $\mu\text{g/L}$ on day 10, comparable to the water-only 96 h LC_{50} of 6.8 $\mu\text{g/L}$ for the same organism (Rodgers et al. 1997a). It is possible that water exposure was the primary Ag toxicity observed in *Hyalella azteca*, and this data point is therefore inappropriate for use as the basis for a sediment PNEC. The second lowest toxicity value, the chronic 28-day IC_{50} (reproduction) of 23.9 mg/kg dw in blackworms (Rajala et al. 2016), was chosen as the CTV for Ag toxicity to sediment-dwelling organisms. The CTV is divided by a factor of 5 to extrapolate from a median effects level concentration to a lowest or no observed effect concentration, and

it is further divided by another factor of 5 to account for variation in species sensitivity, resulting in an overall assessment factor of 25. Therefore,

Chronic PNEC_{sediments} = $23.9 / (5 \times 5) = 1.0 \text{ mg Ag}_{\text{Total}}/\text{kg}$ (or $\mu\text{g/g}$, dw)

7.1.7 Effects on soil-dwelling organisms

AgNO₃ is the Ag salt most commonly used in laboratory soil toxicity tests due to its high water solubility and ready dissociation to release the Ag⁺ ion. Ag₂S is considered the predominant Ag form in soil and biosolids (Doolette 2015; Jesmer et al. 2016).

Soil toxicity studies on Ag with plants (red clover, *Trifolium pratense* L., and northern wheatgrass, *Elymus lanceolatus*), and terrestrial invertebrates (earthworm, *Eisenia andrei*, and springtail, *Folsomia candida*) were performed by the Environment Canada Soil Toxicology Lab (ECSTL 2011). All tests were conducted in a sandy-loam soil following ECCC biological test methods (Environment Canada 2004, 2005, 2007). For the plants, growth (i.e., root/shoot dry mass, length) was the most sensitive endpoint (Appendix E). Plant emergence was not a sensitive endpoint with both plants showing no effect at the highest concentration tested (3014 mg/kg dw). For both invertebrates, reproduction and growth were the more sensitive endpoints relative to survival (Appendix E).

Mixed factors in soil geo-properties affect silver bioavailability and toxicity to soil organisms and plants (Appendix E). Velicogna et al. (2016) reported that the highest toxicity for clover dry mass was observed in a sandy-loam soil, while the highest toxicity for plant emergence and plant length were observed in a silt loam soil. Similar trends were evident for wheatgrass dry mass and emergence. Langdon et al. (2015) investigated barley (*Hordeum vulgare*) and tomato (*Lycopersicum esculentum*) growth on eight field soils of varied sand/clay contents, percent organic matter, pH, cation exchange capacity, etc. Reported EC₁₀ for barley root length and tomato emergence varied up to about 13-fold. Soil invertebrates were less sensitive to soil properties compared to plants, with median effect endpoints (E(L)C₅₀) varying approximately 2- to 4-fold in sandy- and silt loam soils (ECSTL 2011; Mendes et al. 2015; Novo et al. 2015; Schlich et al. 2013; Velicogna et al. 2016; Waalewijn-Kool et al. 2014).

Chronic toxicity data for silver to soil organisms were compiled and evaluated. The dataset is adequate for a long-term species sensitivity distribution (SSD) approach as specified in the CCME protocol on deriving a soil quality guideline for soil contact (i.e., for the protection of plants and invertebrates) (CCME 2006). Toxicity endpoints considered reliable are summarized in Appendix E. Table 7-3 lists the dataset that was used for a long-term SSD using the software SSD Master Version 3.0 (SSD Master 2013) (Figure 7-1). When more than one acceptable endpoint was available for an individual species, the geometric mean was calculated. Plants are more sensitive to silver than soil invertebrates, with the exception of earthworms (Table 7-3, Appendix E). Growth endpoints for plants and reproduction endpoints for soil invertebrates are more sensitive endpoints relative to survival.

Table 7-3. Key soil toxicity studies considered in determining a critical toxicity value for soil

Group	Test organism	Endpoint	Value ^a (mg/kg dw)	Reference
Plant	Barley (<i>Hordeum vulgare</i>)	5-d EC ₁₀ , root length	25	Langdon et al. 2015
Plant	Northern wheatgrass (<i>Elymus lanceolatus</i>)	21-d EC ₁₀ , root/shoot dry mass	3	ECSTL 2011
Plant	Red clover (<i>Trifolium pratense</i> L.)	14-d EC ₁₀ , root/shoot dry mass	1	ECSTL 2011
Plant	Tomato (<i>Lycopersicum esculentum</i>)	21-d EC ₁₀ , emergence	6.6	Langdon et al. 2015
Invertebrates	Earthworm (<i>Eisenia andrei</i>)	56-d EC ₁₀ , reproduction	2	ECSTL 2011
Invertebrates	Earthworm (<i>Eisenia andrei</i>)	56-d EC ₁₀ , dry mass	11	ECSTL 2011
Invertebrates	Pot worm (<i>Enchytraeus crypticus</i>)	21-d EC ₁₀ , reproduction	38	Bicho et al. 2016
Invertebrates	Pot worm (<i>Enchytraeus crypticus</i>)	11-d EC ₁₀ , hatching	42	Bicho et al. 2016
Invertebrates	Pot worm (<i>Enchytraeus crypticus</i>)	25-d EC ₁₀ , growth	69	Bicho et al. 2016
Invertebrates	Springtail (<i>Folsomia candida</i>)	28-d EC ₁₀ , reproduction	20 ^b	ECSTL 2011
Invertebrates	Springtail (<i>Folsomia candida</i>)	28-d EC ₁₀ , reproduction	31 ^b	Mendes et al. 2015
Invertebrates	Springtail (<i>Folsomia candida</i>)	28-d EC ₁₀ , reproduction	47.6 ^b	Waalewijn-Kool et al. 2014

Abbreviations: dw = dry weight; EC₁₀ = the concentration of a stressor that is estimated to be effective in producing a biological response, other than mortality, in 10% of the test organisms over a specific time interval.

^a The toxicity endpoints listed are for soil toxicity tests performed with AgNO₃ and are used in the SSD approach in deriving a Ag soil PNEC. The full reliable Ag soil toxicity dataset is summarized in Appendix E of this screening assessment.

^b Geometric means applied for the SSD data points.

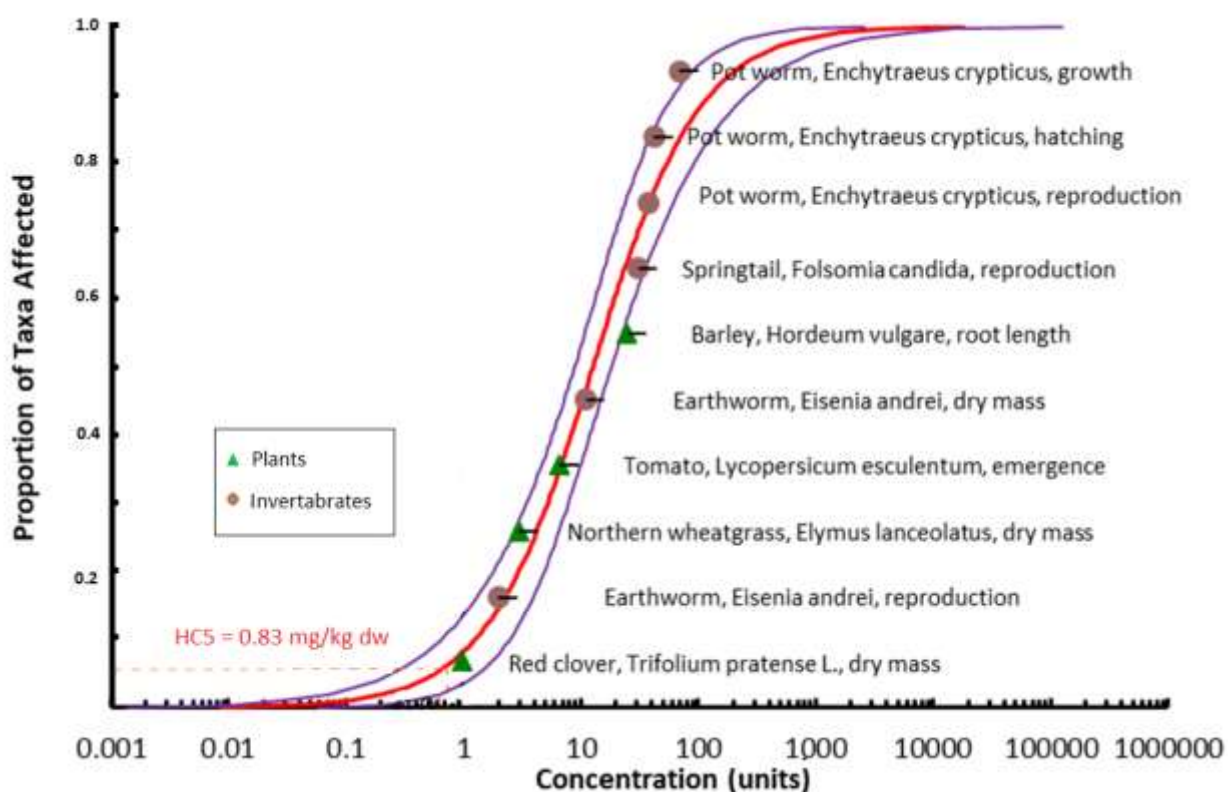


Figure 7-1. Species sensitivity distribution (SSD) for long-term silver soil toxicity. The normal model fit to data is shown on the graph, along with the 95% confidence interval and 5th percentile of the distribution (HC5).

Model assumptions and fit were verified with statistical tests for deriving the SSD. The normal model provided the best fit of the models tested. The HC5 (5th percentile, representing the hazardous concentration to 5% of soil-dwelling organisms) of the distribution is at 0.83 mg/kg (Figure 7-1), and this value is selected as the PNEC for long-term silver soil toxicity.

Chronic $PNEC_{soil} = 0.83 \text{ mg Ag}_{Total}/\text{kg}$ (or $\mu\text{g/g}$, dw)

7.2 Ecological exposure assessment

7.2.1 Approach for exposure characterization

Considering the analyses of sources, uses and releases of silver to the Canadian environment (sections 4.2 and 5), exposure scenarios were developed for the following four sectors: (1) metal mining; (2) base metals smelting and refining, (3) wastewater

treatment systems;⁸ and (4) waste disposal. The metal mining and base metals smelting and refining sectors are implicated in the production of silver. Wastewater treatment systems (WWTS) receive consumer, commercial, and industrial effluents that may contain silver, and therefore treated effluents from WWTSs may release silver to the environment. Finally, silver-containing products may be disposed of in landfills and enter the environment through leachates. Exposure scenarios were not developed for other activities as the information available at the time of the development of this screening assessment indicates that releases of silver to the environment from other activities are negligible.

Measured concentration data were the preferred choice to represent predicted environmental concentrations (PECs) of silver in various environmental compartments. This type of data was available for the receiving environments of the metal mining sector and base metal smelting and refining sector. Where measured concentration data were not available, PECs were modeled from other types of data. Specifically, PECs for the wastewater treatment sector and waste disposal sector were derived by applying a default dilution factor of 10 to final effluent or leachate concentrations, respectively, to which background concentrations of silver, represented by median concentrations associated with ecozones or Great Lakes, were added. The default dilution factor was chosen to reflect conditions near the discharge point under the assumption that full dilution does not occur immediately upon effluent release to large waterbodies. The exposure characterization considers both total and dissolved silver concentrations. Non-detects were substituted with one-half method detection limit (MDL).

7.2.2 Background concentrations of silver

Silver is a trace element in the earth's crust. It has been estimated at concentrations ranging from 0.07 mg/kg (Yaroshevsky 2006) to 0.1 mg/kg (Purcell and Peters 1998), and environmental background concentrations (i.e., naturally occurring concentrations) are low. Ambient concentrations of silver in the atmosphere are unavailable, but WHO (2002) has estimated that, in typical urban air, silver concentrations would be less than 0.00005 mg/m³. Background concentrations of silver in surface waters vary; they are

⁸ In this assessment, the term "wastewater treatment system" refers to a system that collects domestic, commercial and/or institutional household sewage and possibly industrial wastewater (following discharge to the sewer), typically for treatment and eventual discharge to the environment. Unless otherwise stated, the term wastewater treatment system makes no distinction of ownership or operator type (municipal, provincial, federal, indigenous, private, partnerships). Systems located at industrial operations and specifically designed to treat industrial effluents will be identified by the terms "on-site wastewater treatment systems" and/or "industrial wastewater treatment systems."

the highest near mineral deposits (Purcell and Peters 1998), but are generally in the sub- $\mu\text{g/L}$ range.

Background concentration ranges (expressed as normal ranges) and medians of total silver (Ag_T) in surface waters were recently estimated by Kilgour & Associates Ltd. (2016) for Canadian ecozones using water quality monitoring data from various federal and provincial sources.⁹ Only samples considered to be in reference condition, according to the approach outlined in Kilgour & Associates Ltd. (2016) and Proulx et al. (2018), were included in the derivation of these statistics (see Appendix D). Median background concentrations of Ag_T were also estimated for an additional ecozone, the Taiga Shield, following the same approach (Kilgour & Associates Ltd. 2016; Proulx et al. 2018) and using federal water quality monitoring data (NLTWQM 2016) as well as for Lake Erie, Lake Ontario, and Lake Superior using samples taken during the period of 2005 to 2015.¹⁰ In all cases, non-detect measurements were treated prior to analysis by substituting with one-half the reported method detection limit (i.e., $1/2\text{MDL}$). Background median concentrations were highest in the Mixedwood Plains ecozone. Concentrations in the Great Lakes were especially low (medians of $0.0005 \mu\text{g Ag}_\text{T}/\text{L}$, which are non-detects substituted by one-half MDL).

The normal ranges estimated by Kilgour & Associates Ltd. (2016) include the upper inner tolerance limit (ITL) (referred to as maximum expected background concentration in this assessment), representing the highest concentration of total silver associated with background concentrations. The ITLs for various ecozones are presented in Appendix D. The ITLs for four ecozones (i.e., Boreal Plains, Boreal Shield, Mixedwood Plains, and Prairies) exceed the freshwater PNEC ($0.25 \mu\text{g/L}$).

Background concentrations of silver in the marine environment are also anticipated to be low. Median background concentrations of silver in the North Pacific and North Atlantic oceans were estimated using data collected at depths of up to 50 m from sampling sites in proximity to Canada's Pacific and Atlantic coasts. The median background concentrations for dissolved silver (Ag_D) in the North Pacific Ocean and total silver in the North Atlantic Ocean are $0.0011 \mu\text{g Ag}_\text{D}/\text{L}$ ($n=22$) (Kramer et al. 2011) and $0.00032 \mu\text{g Ag}_\text{T}/\text{L}$ ($n=9$) (Rivera-Duarte et al. 1999), respectively.

⁹ BQMA 2015; FQMS 2014; FQMS 2016; PWQMN [modified 2018]; 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.

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 June 20, 2017; unreferenced.

7.2.3 Canadian surface water quality monitoring data

Canadian surface water monitoring data were analyzed through the Ecological Risk Classification of Inorganics (ERC-I) at the onset of the third phase of the CMP. The ERC-I is a classification framework that uses measured and modelled data to classify inorganic substances or groups as low, moderate, or high ecological concern (ECCC 2018b). The silver group was classified as having high potential for ecological concern based on its high hazard (i.e., freshwater guideline of 0.25 µg/L) and on the results of the surface water monitoring data analyses. Specifically, seven datasets (dissolved and total data are separate) from six monitoring programs individually scored moderate ecological concern. Therefore, monitoring data from those datasets were subjected to further analysis. Table 7-4 summarizes the PECs from these monitoring datasets.

Table 7-4. Silver surface water concentration datasets from Canadian water quality monitoring programs subject to further analysis following the ERC-I

Program abbreviation (number of sampling sites)	Period	Fraction	Sample size (percentage of detects)	PEC range (µg/L)	Range of median PECs (µg/L)	Range of 95 th percentile PECs µg/L)
EMS ^a (N=1717)	2005-2015	T	22 086 (31%)	0.00050–50	0.00050–14	0.001–50
EMS ^a (N=780)	2005-2015	D	11 010 (8.0%)	0.00050–12	0.00050–12	0.001–12
BEMLOSS ^b (N=2955)	2005-2015	T	2 964 (4.5%)	0.0050–12	0.0050–2.6	0.0050–7.6
BEMLOSS ^b (N=5)	2005-2015	D	52 (1.9%)	0.0050–0.50	0.0050–0.50	0.0050–0.50
PWQMN ^c (N=324)	2012-2016	T	8 243 (34%)	0.25–21	0.25–2.6	0.25–9.0
BQMA ^d (N=101)	2008-2014	E	1 045 (65%)	0.0015–19	0.00050–0.046	0.0015–0.070
NLTWQM ^e (PEI data) (N=3)	2007-2008	D	12 (0%)	0.050–0.28	0.050–0.16	0.23–0.28

Abbreviations: T, total; D, dissolved; E, extractable.

^a EMSWR 2016.

^b 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.

^c PWQMN [modified 2018].

^d BQMA 2015.

^e Personal communication, data prepared by the Water Quality Monitoring and Surveillance Division, Environment and Climate Change Canada (ECCC), for the Ecological Assessment Division, ECCC, dated September 13, 2016; unreferenced. (PEI data).

7.2.4 Metal mining

Exposure of ecological receptors to silver may occur through metal mining activities that release effluents into surface waters. Canadian metal mines that deposit effluent at any time into any water at a flow rate exceeding 50 m³/day are subject to *the Metal and Diamond Mining Effluent Regulations* (Canada [modified 2018]) under the *Fisheries Act*. Schedule 4 of the MDMER sets concentration limits in effluent for certain parameters, and the MDMER implements Environmental Effects Monitoring (EEM) studies under Schedule 5, requiring monitoring of certain parameters in effluent and surface waters (i.e., the exposure and reference areas). Silver is not a parameter monitored under Schedule 4 or 5 of the MDMER; however, EEM cycle reports submitted to ECCC may contain additional information, including data for total and dissolved silver concentrations in effluents, exposure areas, and reference areas. According to the most recent status report on the performance of metal mines subject to the MDMER, 21 metal mining facilities were associated with silver production in 2016 (ECCC 2018a). Of these facilities, 16 provided surface water concentrations of silver in one or more EEM cycle reports.

Silver data were systematically extracted from the EEM cycle reports of the 16 facilities that reported silver data and that are involved in silver production. The most recent reports were investigated first. If the most recent reports did not contain data, the next most recent reports were investigated and so on. If the most recent reports contained surface water concentrations of silver that were in excess of the freshwater PNEC (0.25 µg Ag/L), all data from previous reports were also extracted for analysis. Overall, 3 out of 16 facilities reported silver data in the most recent report that were above the freshwater PNEC. Data from these facilities are presented in Table 7-5 (one of the facilities was excluded since it has been closed for over 5 years). Non-detect concentrations were substituted with one-half method detection limit (MDL) for the generation of descriptive statistics. It is important to note that MDLs across the EEM cycle reports investigated here (i.e., 0.005 µg/L to 0.20 µg/L) were below the freshwater PNEC of 0.25 µg Ag_T/L. The majority of silver surface water concentration data collected from the 16 facilities for Ag_T and dissolved fractions were non-detects (i.e., below the MDL).

Table 7-5. Metal mining sector PECs for surface water exposure and reference areas of metal mining facilities^a

Facility	Area type	Period	Fraction	Sample size	Percentage of detects	PEC range (µg/L)	PEC median (µg/L)
Facility 1	Exposure	2010-2012; 2015	T	43	60%	<0.01-0.611	0.02
Facility 1	Exposure	2015	D	7	0%	<0.01	0.05

Facility	Area type	Period	Fraction	Sample size	Percentage of detects	PEC range (µg/L)	PEC median (µg/L)
Facility 1	Reference ^b	2010-2012; 2015	T	60	32%	<0.01-0.096	0.005
Facility 1	Reference ^b	2015	D	14	0%	<0.01	0.05
Facility 2 ^c	Exposure	2004, 2007, 2011	T	19	10%	<0.02- <10	0.05
Facility 2 ^c	Exposure	2004, 2011	D	13	23%	<0.01-0.2	0.05
Facility 2 ^c	Reference	2004, 2007, 2009	T	13	7.7%	<0.10-0.30	0.05
Facility 2 ^c	Reference	2004, 2007	D	10	0%	<0.10	0.05

Abbreviations: T, total; D, dissolved.

^a Confidential unpublished reports prepared for the Environmental Effects Monitoring program of the *Metal and Diamond Mining Effluent Regulations*.

^b Represents pooled data from multiple reference areas occurring on the same waterbody.

^c Facility 2 combines its effluent with base metal smelting effluent (i.e., BMS Facility 2 in section 7.2.5).

Sediment data were available in the EEM reports for metal mining Facility 2, which is co-located with Facility 2 of the base metal smelting and refining sector (section 7.2.5) (Table 7-6). Concentrations of silver in sediments measured in the exposure area of Facility 2 appear to increase over time (range of < 0.2 to 6.4 mg/kg, average of 2.6 mg/kg in 2004; range of 0.3 to 8.8 mg/kg, average of 3.6 mg/kg in 2007, range of 0.45 to 21 mg/kg, average of 13 mg/kg in 2011).

Table 7-6. Silver sediment concentrations in exposure and reference areas of base metal smelting facilities subject to the MDMER^a

Facility	Area type	Period	Sample depth (cm)	Sample size	Percentage of detects	PEC range (µg/g dw)	PEC median (µg/g dw)
Facility 2 ^b	Exposure	2004, 2007, 2011	0~10 ^c	21	90%	<0.20 - 21	5.9
Facility 2 ^b	Reference	2004, 2007, 2009	0~10 ^c	10	70%	<0.20 - 1.25	0.90

^a Confidential unpublished reports prepared for the EEM program of the MDMER.

^b Facility 2 combines its effluent with base metal smelting effluent (i.e., BMS Facility 2 in section 7.2.5).

^c Estimated based on the maximum bite depth of the Petite Ponar Grab sampler (Caires and Chandra 2011).

7.2.5 Base metal smelting and refining

Currently, there are 11 base metals smelting and refining (BMS) facilities in Canada, some of which produce pure silver and silver-containing products. Five BMS facilities are subject to the MDMER because they combine their effluents with those of metal mines (section 7.2.4). Information on concentrations of silver was extracted from the associated EEM cycle reports, where available (Table 7-7). Non-detect data were substituted with one-half the method detection limit (MDL) for the generation of descriptive statistics. Similar to the metal mining facilities, MDLs across the EEM cycle reports investigated here were below the freshwater PNEC ($0.25 \mu\text{g Ag}_T/\text{L}$) and the majority of the silver surface water concentration data were non-detects (i.e., below the MDL).

Table 7-7. Base metal smelting and refining sector PECs for surface water exposure and reference areas of base metal smelting facilities subject to the MDMER^a

Facility	Area type	Period	Fraction	Sample size	Percentage of detects	PEC range ($\mu\text{g/L}$)	PEC Median ($\mu\text{g/L}$)
Facility 1	Exposure	2008, 2010	T	7	14%	<0.10 – 0.16	0.05
Facility 1	Reference	2008, 2010	T	11	9%	<0.10 – 0.18	0.05
Facility 2 ^b	Exposure	2004, 2007, 2011	T	19	10%	<0.02 – <10	0.05
Facility 2 ^b	Exposure	2004, 2011	D	13	23%	<0.01 – 0.2	0.05
Facility 2 ^b	Reference	2004, 2007, 2009	T	13	7.7%	<0.10 – 0.30	0.05
Facility 2	Reference	2004, 2007	D	10	0%	<0.10	0.05
Facility 3	Exposure ^{c, d}	2005, 2008, 2012	T	12	50%	<0.010 – 0.50	0.05
Facility 3	Reference ^{c, d}	2005, 2008, 2012	T	12	50%	<0.010 – 0.50	0.05
Facility 4	Exposure	2015	T	6	17%	<0.010 – 0.016	0.005
Facility 4	Exposure	2015	D	6	0%	<0.010	0.005
Facility 4	Reference	2015	T	5	20%	<0.010 – 0.011	0.005
Facility 4	Reference	2015	D	5	0%	<0.010	0.005

Abbreviations: T, total; D, dissolved

^a Confidential unpublished reports prepared for the Environmental Effects Monitoring program of the *Metal and Diamond Mining Effluent Regulations*.

^b Facility 2 combines its effluent with metal mining effluent (i.e., metal mining Facility 2 in section 7.2.4).

^c Represents pooled data from multiple exposure or reference areas from the same waterbody

^d Represents pooled data from multiple exposure or reference areas from different waterbodies

Silver concentration data in sediments were also extracted from the associated EEM cycle reports for the four facilities, when available (Table 7-8). The data for Facility 2 is in excess of the sediment PNEC derived for this assessment (Facility 2 is co-located with metal mining Facility 2). As noted in section 7.2.4, concentrations of silver in sediments measured in the exposure area of Facility 2 appear to increase over time (range of < 0.2 to 6.4 mg/kg, average of 2.6 mg/kg in 2004; range of 0.3 to 8.8 mg/kg, average of 3.6 mg/kg in 2007, range of 0.45 to 21 mg/kg, average of 13 mg/kg in 2011).

Table 7-8. Silver sediment concentrations in exposure and reference areas of base metal smelting facilities subject to the MDMER^a

Facility	Area type	Period	Sample depth (cm)	Sample size	Percentage of detects	PEC range (µg/g dw)	PEC median (µg/g dw)
Facility 1	Exposure	2013, 2018	NA	10	0%	< 0.5	0.25
Facility 1	Reference	2013, 2018	NA	12	0%	< 0.5	0.25
Facility 2 ^b	Exposure	2004, 2007, 2011	0~10 ^c	21	90%	< 0.20–21	5.9
Facility 2 ^b	Reference	2004, 2007, 2009	0~10 ^c	10	70%	< 0.20–1.25	0.90
Facility 3	Exposure _{1d,e}	2008, 2012	NA	13	100%	0.06–0.476	0.23
Facility 3	Reference ^d	2008, 2012	NA	8	62%	< 0.05–0.201	0.07
Facility 4	Exposure	2011, 2015	0–4.0	20	100%	0.12–0.26	0.18
Facility 4	Reference	2011, 2015	0–4.0	20	90%	< 0.10–0.25	0.20

Abbreviations: NA, not available

^a Confidential unpublished reports prepared for the EEM program of the MDMER.

^b Facility 2 combines its effluent with metal mining effluent (i.e., metal mining Facility 2 in section 7.2.4).

^c Estimated based on the maximum bite depth of the Petite Ponar Grab sampler (Caires and Chandra 2011).

^d Represents pooled data from multiple exposure or reference areas from the same waterbody.

^e Represents pooled data from multiple exposure or reference areas from different waterbodies.

Data for one facility not subject to the MDMER were extracted from a comprehensive monitoring report (EEC Ltd and LAC Ltd 2014). Surface water concentrations of Ag⁺

and Ag₀ upstream of the facility at two locations and downstream at three locations were measured (Table 7-9). All concentrations were below MDL (0.02 or 0.05 µg/L). Sediment data were also available in this report for three upstream reference areas and five downstream exposure areas for October 2012 (Table 7-9). Concentrations of silver in the exposure area sediments are elevated (0.6 to 5.7 mg/kg) compared to those in the reference areas (< 0.2 mg/kg).

Table 7-9. Silver surface water and sediment concentrations in exposure and reference areas of one base metal smelting facility not subject to the MDMR (EEC Ltd and LAC Ltd 2014)

Compartment	Area type	Period	Fraction	Sample size	Percentage of detects	PEC range (µg/L or µg/g dw)	PEC median (µg/L or µg/g dw)
Surface water	Exposure	2012-2016	T	337	0%	<0.005- <0.02	0.0025
Surface water	Exposure	2012-2016	D	337	0%	<0.005- <0.02	0.0025
Surface water	Reference	2012-2016	T	71	0%	<0.005- <0.02	0.0025
Surface water	Reference	2012-2016	D	71	0%	<0.005- <0.02	0.0025
Sediment ^a	Exposure	2012	E	7	100%	0.6-5.7	1.4
Sediment ^a	Reference	2012	E	3	0%	<0.2	0.1

Abbreviations: T, Total; D, dissolved; E, strong acid extractable.

^a Concentrations reflect the first 0-15 cm of homogenized cores.

7.2.6 Wastewater treatment

Silver may be present in wastewaters generated from consumer, commercial, and industrial sources and therefore may be a constituent of the influent received by wastewater treatment systems (WWTS). Municipal by-laws concerning the discharge of wastewater (i.e., influents) to WWTSs may prescribe limits for silver concentrations in influents entering storm, sanitary, and combined sewers. For some major Canadian cities, these limits range from 0.05 mg Ag_T/L to 5.0 mg Ag_T/L.¹¹ Because WWTS effluent treatment processes do not use silver compounds, the treatment processes do not contribute to the silver content of the effluents released into the environment. The

¹¹ The references cannot be provided because the identities of the WWTSs cited here are confidential.

federal *Wastewater System Effluent Regulations* (Canada [modified 2015]) do not prescribe final effluent limits for silver.

Effluent monitoring data were collected under the CMP Environmental Monitoring and Surveillance Program (EMSP) from 25 WWTS located across Canada from February 2009 to March 2012 (Environment Canada 2013b). Results from this initiative show that influent concentrations of total silver (Ag_T) are low and that there is a high degree of partitioning to solids (Environment Canada 2013b). Total silver concentrations (Ag_T) were detected in 64 of 191 influent samples and in 30 of 191 final effluent samples, with maximums of 6.55 $\mu\text{g/L}$ and 2.55 $\mu\text{g/L}$ respectively, of the 25 WWTSs sampled. The median removal value for Ag_T was 88.6% ($N = 64$ paired influent and effluent samples). The biosolid samples contained Ag_T in the range of $\mu\text{g/g}$, indicating high removal during treatment processes. Although influent and effluent samples were collected as 24 hour composites, they may not accurately represent the removal value for silver 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). However, this estimated median removal value is in agreement with estimates summarized by the CCME (2006), where the estimated removal efficiencies for most treatment types is between 75% and 95%. Final effluent concentrations of Ag_T were low and frequently below detection limits. Unfiltered samples were digested and analyzed for total silver using inductively coupled plasma (ICP) methods as per standard methods (APHA et al. 2005). The method detection limits (MDLs) for both influent and effluent quantitation were 0.005 $\mu\text{g/L}$ or 0.02 $\mu\text{g/L}$.

PECs for the wastewater sector were derived for 25 WWTS facilities that release effluent to either the freshwater or the marine environment (Table 7-10). PECs were calculated by applying a default dilution factor of 10 to final effluent concentrations and adding the median background silver concentrations (Appendix D) corresponding to the location of the WWTS. Effluent non-detect data were substituted with one-half MDL.

Table 7-10. Wastewater sector PECs based on final effluent concentrations from 25 WWTSs across Canada sampled during 2009 to 2012 (Environment Canada 2013b)

Facility	Water type	Sample size (% detects)	Effluent range ($\mu\text{g Ag}_T/\text{L}$)	Median back-ground concentration ($\mu\text{g Ag}_T/\text{L}$)	PEC range ($\mu\text{g Ag}_T/\text{L}$)	PEC median ($\mu\text{g Ag}_T/\text{L}$)
1	Fresh	6 (0%)	<0.02	0.001	0.0020	0.0020
2	Fresh	12 (0%)	<0.005– <0.02	0.05	0.050– 0.051	0.051
3	Fresh	5 (0%)	<0.02	0.11	0.11	0.11
4	Fresh	6 (0%)	<0.005– <0.02	0.001	0.0012– 0.0020	0.0016

Facility	Water type	Sample size (% detects)	Effluent range ($\mu\text{g Ag}\tau/\text{L}$)	Median back-ground concentration ($\mu\text{g Ag}\tau/\text{L}$)	PEC range ($\mu\text{g Ag}\tau/\text{L}$)	PEC median ($\mu\text{g Ag}\tau/\text{L}$)
5	Fresh	6 (0%)	<0.02	0.05	0.051	0.051
6	Fresh	12 (0%)	<0.005–<0.02	0.52	0.52	0.52
7	Fresh	12 (33%)	<0.005–0.497	0.11	0.11–0.16	0.11
8	Fresh	6 (0%)	<0.005–<0.02	0.05	0.050–0.051	0.050
9	Fresh	6 (50%)	<0.02–0.322	0.52	0.52–0.55	0.52
10	Fresh	6 (50%)	<0.005–2.52	0.52	0.52–0.77	0.58
11	Fresh	6 (0%)	<0.02	0.52	0.52	0.52
12	Fresh	6 (50%)	<0.005–0.450	0.52	0.52–0.56	0.52
13	Fresh	6 (33%)	<0.02–0.367	0.52	0.52–0.56	0.52
14	Fresh	12 (0%)	<0.005–<0.02	0.52	0.52	0.52
15	Fresh	12 (0%)	<0.005–<0.02	0.05	0.050–0.051	0.051
16	Fresh	6 (0%)	<0.02	0.52	0.52	0.52
17	Fresh	6 (0%)	<0.02	0.52	0.52	0.52
18	Fresh	6 (50%)	<0.005–1.13	0.11	0.11–0.22	0.14
19	Fresh	12 (25%)	<0.005–0.981	0.52	0.52–0.62	0.52
20	Fresh	6 (50%)	<0.02–0.401	0.05	0.051–0.090	0.060
21	Fresh	6 (0%)	<0.02	0.002	0.0030	0.0030
22	Marine	12 (0%)	<0.005–<0.02	0.00032	0.00057–0.0013	0.0013
23	Marine	6 (0%)	<0.02	0.00032	0.0013	0.0013
24	Marine	6 (50%)	<0.02–0.0640	0.00032	0.0013–0.0067	0.0035
25	Marine	6 (50%)	<0.02–1.84	0.0011	0.0021–0.18	0.050

The majority of WWTs did not detect silver in final effluents (i.e., 0% detects) or they detected silver in final effluents less than 50% of the time (e.g., 25%, 33% detects). Facilities within the Mixedwood Plains ecozone have the highest PECs due to the relatively high median background concentration of silver (i.e., 0.52 $\mu\text{g Ag}\tau/\text{L}$) compared to other ecozones.

Total silver was detected in most solid samples (307 of 325) collected at the 25 WWTPs (Environment Canada 2013b). Concentrations of Ag_T in primary sludge, secondary sludge, and biosolids ranged from < 0.0005 to 18.3 µg/g, from < 0.0005 to 8.19 µg/g, and from < 0.0002 to 16.4 µg/g, respectively. Biosolids from WWTSs are sent to landfills, incinerated, or spread on agricultural land. The equation below was used to estimate the input of silver to soils through the land application of biosolids containing silver.

$$PEC = \frac{AgT \text{ concentration in biosolids} \times \text{application rate} \times \text{number of years}}{\text{mixing depth} \times \text{soil density}}$$

To simulate a worst-case exposure scenario for soil-dwelling organisms, a maximum application rate of 8300 kg dw per hectare (dw/ha) per year (based on the highest existing provincial regulatory limit; Environment Canada 2006), a mixing depth of 0.2 m (plough depth; ECHA 2012) and a soil density of 1200 kg/m³ were used (Williams 1999), along with the highest concentration of silver measured in biosolids (16.4 mg/kg dw) from WWTSs in Canada that are not incinerated. A period of 10 consecutive years was chosen as the length of accumulation (ECHA 2012). The cumulative silver concentration in soil at the end of this period is 0.6 mg/kg (or 0.6 µg/g) dw.

7.2.7 Waste disposal

Silver contained in products, manufactured items, or other materials (e.g., contaminated soils) that are disposed of in landfills may leach out and release silver to the environment. Monitoring data were collected at 13 larger landfills across Canada between 2008 and 2014 under the CMP monitoring program. Total and dissolved silver concentrations were measured in leachates before and after treatment. Method detection limits ranged from 0.005 to 10 µg Ag/L.

Prior to treatment, concentrations in leachate ranged from < 0.005 to 3.00 µg Ag_T/L (median of < 1 µg Ag_T/L; n=110) and from < 0.005 to 1.21 µg Ag_D/L (median of 0.0110 µg Ag_D/L; n=47) (Conestoga-Rovers and Associates 2015). Five of the 13 landfills treat their leachate on-site before either sending it to a WWTS or releasing it to the environment. For three of these five landfills, concentrations in leachate after treatment were <1 to 0.547 µg Ag_T/L¹² (median of <1 µg Ag_T/L; n=26). One of these five landfills had post-treatment dissolved silver concentrations ranging from <0.005 to 0.182 µg Ag_D/L (median of <0.005 µg Ag_D/L; n=11) (Conestoga-Rovers and Associates 2015).

Ten of the landfills send their leachate (treated or not) to a WWTS, and removal of silver following wastewater treatment was not accounted for in the generation of PECs. Three landfills, however, release their leachate (treated or not) to the environment, either to wetlands, to a filtering marsh, or directly to a river. In 2008-2011, the total silver

¹² The maximum is the highest detected value reported.

concentrations in the leachate of these three sites (post-treatment if available) were all below detection limits (< 0.1 to $< 10 \mu\text{g Ag}/\text{L}$). PECs for these landfills were estimated using one-half MDL values, a dilution factor of 10, and adding the appropriate ecozone-specific background median concentration.

Table 7-11. Landfill leachate PECs based on pre- or post-treatment leachates measured from larger municipal landfills throughout Canada which release directly to the environment from 2008 to 2014 (Conestoga-Rovers and Associates 2015)

Land-fill site	Measurement type	Sample size (% detects)	Pre-treatment range ($\mu\text{g Ag}/\text{L}$)	Post-treatment range ($\mu\text{g Ag}/\text{L}$)	Median background concentration ($\mu\text{g Ag}/\text{L}$)	PEC range ($\mu\text{g Ag}/\text{L}$)	PEC median ($\mu\text{g Ag}/\text{L}$)
1	Total	6 (0%)	<0.10 – <10	NR	0.11	0.12–0.61	0.16
2	Total	6 (0%); 6 (0%)	<0.10 – <10	<0.10 – <10	0.050	0.055–0.55	0.10
3	Total	6 (0%); 3 (0%)	<0.10 – <10	<0.10 – <10	0.52	0.52–1.0	0.57

7.3 Characterization of ecological risk

The approach taken in this ecological screening assessment involved the examination of assessment information and development of proposed conclusions using a weight-of-evidence approach and precaution. Evidence was gathered to determine the potential for silver and its compounds 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.

7.3.1 Risk quotient analysis

Risk quotient analyses involved comparing estimates of exposure (PECs; see the Ecological Exposure Assessment section), which varied from realistic to worst-case, with ecotoxicity information (PNECs; see the Ecological Effects Assessment section) to determine whether there is potential for ecological harm in the Canadian environment. Risk quotients (RQs) were derived by dividing the PECs from the exposure scenarios by the PNECs for the appropriate environmental compartments. RQs for the metal mining, base metal smelting and refining, wastewater treatment, and landfill disposal sectors are presented below (Table 7-12). RQs generated for further analysis of the Canadian surface water quality monitoring datasets from the ERC-I are also presented below (Table 7-13). Non-detect concentrations (i.e., PECs below MDL) were substituted with one-half the MDL before calculating RQs.

Table 7-12. Summary of risk quotients obtained for different environmental compartments and exposure scenarios for silver and its compounds

Sector (number of facilities)	Compartment	Fraction	PEC range (µg/L or µg/g dw)	Range of median PECs (µg/L or µg/g dw)	RQ range	Range of median RQs
Metal mining (N=2) ^a	Water	T	<0.003- 0.611 ^b	0.02–0.05	0.0006–2.4 _b	0.08–0.2
Metal mining (N=2) ^a	Water	D	<0.01–0.20	0.05	0.02–0.8	0.2
Metal mining (N=1) ^c	Sediment	E	<0.20–21	5.9	0.1–21	5.9
Base metal smelting and refining (N=4) ^d	Water	T	<0.01–0.5	0.005–0.05	0.02–2	0.02–0.2
Base metal smelting and refining (N=4) ^d	Water	D	<0.01–0.2	0.005–0.05	0.02–0.8	0.02–0.2
Base metal smelting and refining (N=4) ^d	Sediment	T, E	0.06–21	0.18–5.9	0.06–21	0.18–5.9
Base metal smelting and refining (N=1) ^d	Water	T	<0.005– <0.02	0.0025	0.01–0.04	0.01
Base metal smelting and refining (N=1) ^e	Water	D	<0.005– <0.02	0.0025	0.01–0.04	0.01
Base metal smelting and refining (N=1) ^e	Sediment	E	0.6–5.7	1.4	0.6–5.7	1.4
Wastewater treatment (N=25)	Water	T	0.00057– 0.77	0.11	0.00098– 3.1	0.0023–2.3
Wastewater treatment (biosolids land- application) (N=1) ^f	Soil	T	0.6	N/A	0.7	N/A

Sector (number of facilities)	Compartment	Fraction	PEC range (µg/L or µg/g dw)	Range of median PECs (µg/L or µg/g dw)	RQ range	Range of median RQs
Waste disposal (N=3) ^g	Water	T	0.055–1.0	0.10–0.57	0.22–4.1	0.40–2.3

Abbreviations: T, Total; D, dissolved; E, strong acid extractable; N/A, not applicable; dw, dry weight.

^a One of these facilities (Facility 2, section 7.2.4) combines its effluent with a BMS facility (Facility 2, section 7.2.5).

^b The highest detect value is reported.

^c This metal mining facility (Facility 2, section 7.2.4) combines its effluent with a BMS facility (Facility 2, section 7.2.5).

^d These BMS facilities are subject to the MDMER and therefore combine their effluents with metal mining facilities; upper end of the range is based on non-detect values.

^e This BMS facility is not subject to the MDMER.

^f One PEC was generated from a conservative land application exposure scenario using the maximum concentration of silver detected in biosolids (i.e., 16.4 µg Ag_T/g dw).

^g These three landfills release directly to the environment (i.e., do not pass through a WWTS first); all values were non-detects.

Regarding the metal mining sector (16 facilities) and the base metal smelters subject to the MDMER (five facilities), the RQs developed for exposure of ecological receptors to silver in the surface water compartment indicate low ecological risk. For the analyses using total silver concentrations, RQs greater than 1 are infrequent and of low magnitude (5 of 43 for metal mining Facility 1; 2 of 19 for metal mining and base metal smelting Facility 2; 2 of 12 for base metal smelting Facility 3) and if accompanied by corresponding dissolved silver concentrations, the RQs for dissolved silver are less than 1. Further, the majority of the data collected from the EEM cycle reports of the 16 facilities were non-detects (for total and dissolved concentrations). However, when comparing concentrations of extractable silver in sediments of the exposure areas to the sediment PNEC (1.0 mg Ag_T/kg dw), potential ecological risk is found for one facility (Facility 2), which belongs to the metal mining sector and the base metal smelting sector. The exposure concentrations are also elevated (n=21; median PEC=5.9 mg/kg) compared to upstream reference area concentrations (n=10; median PEC=0.9 mg/kg).

The RQ analysis of one base metal smelter not subject to the MDMER indicates low ecological risk in the surface water compartment. However, they indicate potential ecological risk in the sediment compartment. These exposure concentrations (n=7; median PEC=1.4 mg/kg) are also elevated compared to upstream reference area concentrations (n=3; median PEC<0.2 mg/kg).

For the wastewater treatment sector, 10 of 25 facilities have RQs greater than 1 (range of 2 to 3) in the surface water compartment. All of these facilities are located in the Mixedwood Plains ecozone, which has naturally elevated background concentrations of silver (the maximum expected background concentration of Ag_T is 2.1 µg/L). The median background concentration of Ag_T used to model the PECs for facilities in this ecozone is already greater than the aquatic PNEC (0.25 µg Ag/L). Given that modeled

PECs are higher than the PNEC due to relatively high background median concentrations of Ag_T and that effluent concentrations are low (range of <0.005 to $2.52 \mu\text{g Ag}_T/\text{L}$), the risk characterization for the wastewater treatment sector indicates low ecological risk in the surface water compartment. No data are available for the sediment compartment for this sector. A conservative exposure scenario for concentrations of silver in soil following the application of silver-containing biosolids to land ($0.6 \mu\text{g Ag}_T/\text{g, dw}$) resulted in an RQ below 1 when comparing it to the chronic PNEC generated for soil organisms ($0.83 \mu\text{g Ag}_T/\text{g, dw}$). Therefore, ecological risk in the soil compartment is not expected following land application of silver-containing biosolids from WWTSSs.

Risk characterization of landfill leachate releases is based on the three landfills that release directly to the surface water compartment (landfill sites 5, 9, 10). The RQ analysis indicates a potential for ecological risk in the surface water compartment, but the PECs were derived using non-detect data, as all measurements of total silver in the leachates of these sites are non-detects (<0.1 to $<10 \mu\text{g/L}$). In addition, one landfill is situated in the Mixedwood Plains ecozone, where the background median and maximum expected background concentrations are greater than the freshwater PNEC. Therefore, the contribution of this sector to the potential ecological risk identified in surface water is expected to be low.

Further analysis of the seven Canadian surface water monitoring datasets from the ERC-I (Table 7-13) indicate that RQs greater than 1 that were associated with detected concentrations occurred infrequently for the BQMA Ag_E and EMS Ag_D datasets and not for any of the BEMLOSS Ag_D or NLTWQM Ag_D PEI datasets.

The EMS Ag_T , BEMLOSS Ag_T , and PWQMN Ag_T datasets showed the highest frequencies of RQs greater than 1 based on detected concentrations. Potential anthropogenic point-sources of silver release to the environment or historical instances of spills were not clearly identified for these sampling sites. The majority of sampling sites from these datasets were within ecozones where the maximum expected background concentrations were already above the freshwater PNEC, namely Pacific Maritime for EMS, Prairies for BEMLOSS, and Mixedwood Plains and Boreal Shield for PWQMN (Appendix D). This suggests that naturally high background concentrations of silver in these areas may be contributing to the elevated RQs in these datasets. Nevertheless, total Ag concentrations in surface waters are mostly associated with the particulate phase (Andren and Bober 2002; WHO 2002) and are therefore much less bioavailable to aquatic organisms. Therefore, elevated Ag_T concentrations in these datasets are not necessarily indicative of ecological risk.

Overall, the further investigation of the seven datasets included in the ERC-I could not link detected concentrations of silver and RQs greater than 1 to specific anthropogenic activities. Given that the maximum expected background concentrations of silver in the corresponding ecozones are high, and given silver's affinity to sorb to particulate matter where its bioavailability is reduced, it is likely that ecological risk in the surface water compartment is low.

Table 7-13. Summary of risk quotients obtained from Canadian surface water quality datasets for silver

Program abbreviation	Fraction	Number of sampling sites	Number of sampling sites with RQs > 1 (detected values)	Range of percent of RQs > 1 (per site, based on detected values)	Range of median RQs ^a	Range of 95 th percentile RQs ^a
EMS ^b	T	1717	36	0–100%	0.0020–58	0.0040–200
EMS ^b	D	781	3	0–100%	0.0020–50	0.0040–50
BEMLOSS ^c	T	294	24	0–100%	0.020–7.6	0.020–30
BEMLOSS ^c	D	5	0	0%	0.02–2	0.02–2
PWQMN ^d	T	324	298	0–100%	1.0–10	1.0–36
BQMA ^e	E	101	1	0–4.3%	0.002–0.19	0.006–0.28
NLTWQM ^f (PEI data)	D	3	0	0%	0.20–0.65	0.92–1.1

Abbreviations: T, total; D, dissolved; E, extractable.

^a Range of the percentage of RQs greater than 1 or the median RQs or the 95th percentile RQs.

^b EMSWR 2016.

^c 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; unreferenceed.

^d PWQMN [modified 2018].

^e BQMA 2015.

^f Personal communication, data prepared by the Water Quality Monitoring and Surveillance Division, Environment and Climate Change Canada (ECCC) for the Ecological Assessment Division, ECCC, dated September 13, 2016; unreferenceed. (PEI data).

7.3.2 Consideration of the lines of evidence

To characterize the ecological risk of silver and its compounds, technical information for various lines of evidence was 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 7-14, 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.

Table 7-14. Weighted lines of key evidence used for the ecological assessment of silver and its compounds

Line of evidence	Level of confidence^a	Relevance in assessment^b	Weight assigned^c
Persistence	High	Low	Moderate
Bioaccumulation in aquatic and/or terrestrial organisms	High	Low	Moderate
PNEC for aquatic organisms in freshwater	High	High	High
PNEC for aquatic organisms in marine water	Moderate	High	Moderate-high
PNEC for benthic organisms in sediment	Moderate	High	Moderate-high
PNEC for organisms in soil	High	High	High
PECs based on measurements in surface water – metal mining	High	High	High
PECs based on measurements in surface water – base metal smelting and refining	High	High	High
PECs modeled for surface water – wastewater treatment	Moderate	Moderate	Moderate
PECs modeled for surface water – waste disposal	Moderate	Moderate	Moderate
PECs based on measurements in sediment – metal mining	Low	High	Moderate
PECs based on measurements in sediment – base metal smelting and refining	Low	High	Moderate
PEC modeled for soil – land application of biosolids	Moderate	Moderate	Moderate
RQs for surface water – metal mining	High	High	High

Line of evidence	Level of confidence ^a	Relevance in assessment ^b	Weight assigned ^c
RQs for surface water – base metal smelting and refining	High	High	High
RQs for surface water – wastewater treatment	Moderate	High	Moderate-high
RQs for surface water – waste disposal	Low	Moderate	Low-moderate
RQs for sediment – metal mining	Moderate	Moderate	Moderate
RQs for sediment – base metal smelting	Moderate	Moderate	Moderate
RQ for soil – land application of biosolids (wastewater treatment)	Low	Moderate	Low-moderate

^a Level of confidence is determined according to data quality, data variability, and 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 into the environment, substances containing silver may dissolve, dissociate, or degrade to release silver into the environment. Silver is persistent because it is an element and, as such, cannot break down further. It can therefore accumulate in the environment and result in long-term exposure of organisms. Organisms can accumulate substantial amounts of silver in tissues and internal organs at very low environmental concentrations, but they are able to regulate concentrations and detoxify. Therefore, silver does not bioaccumulate in organisms. It also does not biomagnify across trophic levels. Silver is not an essential element for organism health.

When released into the air compartment, silver occurs as a constituent of particulate matter. From there, it is deposited on surface waters or land. Following release to the surface water compartment, silver is mostly associated with particulate forms and is rapidly incorporated into sediments. Resuspension of sediments can resupply total silver to overlying waters but is not likely to resupply dissolved silver concentrations given silver's high affinity to bind to particles. For the same reason, silver deposited to land is not likely to be remobilized into other compartments. Therefore, releases of silver to air and water are anticipated to ultimately accumulate in soils and/or sediments.

It was determined that there is low potential for ecological risk from silver in the surface water compartments of the metal mining, the base metal smelting and refining, the wastewater treatment, and the waste disposal sectors. Further analysis of the ERC-I monitoring datasets indicates PNEC exceedances are associated with high background concentrations and non-detects, and therefore sampling sites within these datasets

show low potential for ecological risk in the aquatic compartment. There may be potential for ecological risk caused by silver in sediment. Facility 2 of the metal mining sector and base metal smelting sector (both combine their effluents and are subject to the MDMER) has elevated concentrations of silver in downstream sediments, but the dataset analyzed is small (n=21) and was collected from different downstream locations during different years (2004, 2007, 2011). Similarly, a small dataset (n=7) collected in 2012 downstream of a BMS facility that is not subject to the MDMER also indicates potential for moderate ecological risk in sediments. Because the datasets are small and either have weak temporal and spatial correlations or are limited to 1 year, and because the silver sediment PNEC assumes high silver bioavailability due to a low amount of silver complexing ligands and may be considered conservative for metal mining and BMS Facility 2, a low weight is assigned to this line of evidence. The sediment PNEC may be considered more relevant for the BMS facility not subject to the MDMER due to the low amounts of complexing ligands in the downstream sampling areas at this location.

Given silver's high affinity for binding to particles, WWTs have high removal values and high concentrations of silver in biosolids. A conservative risk characterization scenario for the land application of silver-containing biosolids indicates low ecological risk in the soil compartment from the wastewater treatment sector.

This information indicates that silver and its compounds have low potential to cause ecological harm in the surface water and soil compartments in Canada. Silver and its compounds have a potential to cause ecological harm in the sediment compartment, but this line of evidence is inconclusive due to the limited dataset and uncertainties around the bioavailability of sediment-bound silver (see section 7.3.4 for further discussion of uncertainties).

While exposure of the environment to silver is not of concern at current levels for the water and soil compartments and is of inconclusive concern for the sediment compartment, silver may have an environmental effect of concern given its potential to cause adverse effects on organisms at low concentrations. Therefore, there may be a concern for the environment if exposures were to increase.

7.3.4 Sensitivity of conclusion to key uncertainties

The key uncertainties associated with the ecological risk characterization, including information gaps, PECs, PNECs, RQs, the further analysis of ERC-I datasets, and their impact on the proposed conclusion, are discussed below.

Identification of key sectors and data availability

While there is a wide variety of known uses of silver and silver-containing substances, relatively little information is available for their manufacture, import, and uses in Canada. However, the proposed conclusion is not sensitive to this because the NPRI is expected to capture significant potential releases of silver to the environment associated

with specific facilities and industrial activities. According to the NPRI data for 2012 to 2016, releases are low, and the exposure scenarios focus on the sectors involved in the production and use of silver and silver-containing substances and products.

The data used in the exposure scenarios for the four sectors considered are not comprehensive. Only about one-fifth of the over 100 metal mines in Canada (ECCC 2018a) and about one-third of the 13 active BMS facilities were analyzed in this assessment. However, given that silver is a precious metal, there is incentive for sectors to limit release into the environment. The exposure scenarios for the wastewater treatment and waste disposal sectors included relatively small subsets of Canada's many WWTSS and landfills. The subsets are considered representative because WWTSS for a variety of municipalities of various sizes located throughout Canada were included, and the landfills included are some of the largest.

Representativeness of PNECs and PECs

The silver PNECs for all environmental compartments derived in this screening assessment are primarily based on laboratory toxicity studies conducted with highly soluble Ag salts (mainly AgNO₃) that readily dissociate and release the free Ag⁺ ion, which is the most bioavailable and toxic form of silver. Typically, toxicity test mediums are also of extremely low ionic strength and have low amounts of organic matter and complexing ligands that mitigate toxicity. In the environment, bioavailable forms of silver are anticipated to be low due to silver's high affinity to complex with sulfides, NOM, chlorides, clay, metal oxides, and various particulates, thus rendering it less bioavailable and less toxic to aquatic and terrestrial organisms. The PNECs do not incorporate toxicity-modifying factors and are therefore conservative and may not provide realistic site-specific ecotoxicity thresholds. This is noticeable when comparing the freshwater PNEC (0.25 µg/L) to PECs in ecozones where expected background concentrations are higher than the PNEC. The use of a BLM, which incorporates bioavailability adjustments, would provide more realistic site-specific ecotoxicity thresholds. However, a BLM that predicts the chronic toxicity of Ag to freshwater organisms is not available at this time (CCME 2015a; Wood 2012).

The silver PECs determined in the exposure scenarios included measured environmental concentrations (total, extractable, dissolved) or modeled concentrations (total) from effluent, leachate, and biosolids data. As previously mentioned, silver has a high affinity for complexing with various ligands. It is associated primarily with macroparticles (< 0.45 µm) and colloids (> 0.45 µm) in fresh waters (Andren and Bober 2002; Shafer et al. 1996; Wen et al. 1997). Thus, truly dissolved silver (i.e., the free ion) is present in very low quantities under natural conditions (Andren and Bober 2002). Once released into the environment from effluents or leachates, free ionic silver, if present, will complex with ligands. These species, along with other silver species that may be present in effluents or leachates, can rapidly incorporate into sediment compared to other metals (Andren and Bober 2002). Silver is unlikely to remobilize once present in sediments and soils, including biosolids (Donner et al. 2015). Thus, the use

of total, extractable, and even dissolved concentrations, produces conservative aquatic PECs.

Comparison of the PECs, which do not represent free ionic silver concentrations, to PNECs, which represent organism exposure to free ionic silver, therefore produce conservative RQs. However, these aspects were considered in the assessment, namely in the ecological risk characterization of silver where indications of possible ecological risk in the water and sediment datasets were lowered.

Surface water compartment

Non-detect data were prevalent in the risk characterization of the sectors and in the seven ERC-I datasets further analyzed in this assessment. Their presence was inconsequential for the metal mining and base metal smelting and refining sectors given that ecological risk was not found for the surface water compartment. PECs modeled from non-detects for the wastewater treatment sector were not the drivers behind instances of RQs greater than 1. However, the waste disposal sector and many of the ERC-I datasets contained non-detect PECs higher than the freshwater PNEC due to high MDLs (e.g., 10 µg/L). This leaves uncertainty as to whether or not ecological risk is present at the sampling sites. For some ecozones, the maximum expected background concentrations of silver (Appendix D) exceeded the freshwater PNEC. Datasets containing data within these ecozones have PECs that are in excess of both the freshwater PNEC and the maximum expected background concentrations (i.e., BEMLOSS, and PWQMN). These PECs could be high due to anthropogenic input, but specific point sources could not be isolated. It is possible that over time, non-point sources have increased concentrations of silver at these sampling sites. However, these PECs are often associated with total data, and corresponding dissolved data are unavailable. As aforementioned, it is predicted that only a very small fraction of total silver concentrations is bioavailable (WHO 2002). Therefore, the proposed conclusion considers these uncertainties for the waste disposal sector and the further analysis of ERC-I datasets.

Sediment compartment

Sediment data are sparse or non-existent for the sectors investigated. The NPRI analysis indicates that releases of silver to water from 2012 to 2016 are low. While releases may be low, silver is expected to partition to sediment rapidly (Andren and Bober 2002). Sediment concentrations of silver in the receiving environments of facilities in the wastewater treatment system and waste disposal sectors are unavailable. They were also unavailable for the sampling locations in the PWQMN and BEMLOSS datasets, where there are high surface water PECs. However, concentrations of silver in sediments downstream of certain facilities in the metal mining and base metal smelting and refining sectors are available. Sediment data are available for four of five BMS facilities subject to the MDMER, of which only one facility, Facility 2, has downstream sediment concentrations of silver in excess of the sediment PNEC. This facility is co-located with Facility 2 of the metal mining sector. It is unclear whether

these concentrations increased from 2004 to 2011 because the sediment cores were not obtained in the same locations between years. Some concentrations of silver in the sediments downstream of the BMS facility not subject to the MDMER are also slightly above the sediment PNEC.

The silver sediment PNEC assumes high silver bioavailability due to a low amount of silver complexing ligands. It may be considered conservative in some cases such as in the case of the facility subject to the MDMER (Facility 2). For the BMS facility not subject to the MDMER, the sediment PNEC may not necessarily be conservative because the sediment composition downstream is similar to conditions used in sediment toxicity testing (e.g., low amounts of silver complexing ligands). However, it is known that silver displaces other metals in metal sulfide compounds (Bell and Kramer 1999), which can increase the bioavailability of other metals through their mobilization into sediment pore waters. Therefore, even when sulfide concentrations in sediments are low or when silver concentrations in sediments are high, it is likely that silver will be mostly bound to sulfides, where they are not bioavailable but may be ingested by benthic organisms.

The proposed conclusion of this assessment is sensitive to these uncertainties. Further investigation of silver in Canadian sediments could influence the proposed conclusion of this assessment.

Soil compartment

Soil data are not available for the sectors investigated. The NPRI analysis indicates that releases of silver to air and land from 2012 to 2016 are low or negligible, respectively, and given this, it is unlikely that silver deposition or release to land from the sectors investigated is occurring in concerning amounts. Further, the conservative risk characterization for the land-application of silver-containing biosolids indicates low ecological risk in the soil compartment. Therefore, the proposed conclusion of this assessment is not sensitive to the lack of data.

8. Potential to cause harm to human health

Silver is a naturally-occurring element that is present in all environmental media in Canada. Total silver has been measured in drinking water distribution systems, household dust, indoor and outdoor air, and breast milk (Arbuckle et al. 2013; NAPS 2011; Rasmussen et al. 2016; Tugulea et al. 2016). Overall, Canadian data demonstrate that concentrations of silver in air, drinking water and dust are low (Health Canada 2016).

The health effects of silver have previously been evaluated by other international organizations (ATSDR 1990; EFSA 2016; IRIS 1991; WHO 2011b). While some recent reviews have focused mainly on nanosilver, the focus of this assessment is on the bulk form of silver. Argyria or argyrosis, characterized by blue or blue-greyish staining of the skin and mucous membranes, is the principle observable change associated with long-

term ingestion or occupational inhalation of high concentrations of metallic silver or ionisable silver compounds (EFSA 2016). Argyria is not associated with pathological damage in any specific target organ (EFSA 2016). The US EPA derived a reference dose of 0.005 mg Ag/kg bw/day for protecting against argyria (IRIS 1991; Health Canada 2016).

The human health risk from exposure to silver and its compounds was characterized using a science approach based on biomonitoring data, as described in the science approach document on Biomonitoring-based Approach 2 (Health Canada 2016). The approach utilizes population-level biomonitoring data from large-scale surveys, such as the Canadian Health Measures Survey (CHMS). The analysis presented in the science approach document focused on the substances in the Silver and its Compounds Group, whereas this assessment focuses on the silver moiety as these surveys measure the concentrations of the moiety in blood (whole blood, serum, plasma) and/or urine. Total silver in blood or urine provides a biologically relevant, integrated measure of exposures that occur across multiple routes (e.g., oral, dermal and inhalation) and sources (including environmental media, diet, and frequent or daily use products to which people were exposed).

In the Biomonitoring-based Approach 2, biomonitoring data are compared with human biomonitoring guidance values, such as a biomonitoring equivalent (BE). BEs are typically derived from existing health-based exposure guidance values, such as a reference dose (RfD) or a tolerable daily intake (TDI). In general, exposure guidance values are converted to BEs using toxicokinetic data or regression correlations between external exposure and the biomarker concentrations (i.e., the chemical concentration in blood or urine). A thorough review of available toxicokinetic data is an integral part of the Biomonitoring-based Approach 2. The approach is only recommended for use if the biomarker (i.e., chemical concentration in whole blood, plasma, serum or urine) is considered adequate to quantify exposure in the general population (Health Canada 2016). If exposures (on the basis of biomonitoring data) are below the human biomonitoring guidance value (i.e., BE), then the substance or metal moiety is considered to be of low concern with respect to human health at current levels of exposure (Health Canada 2016).

Total silver was measured in whole blood in Canadians in both the Canadian Health Measures Survey and the Mother-Infant Research on Environmental Chemicals (MIREC) Child Development Plus study, a MIREC follow-up study (Table 8-1).

A biomonitoring equivalent (BE) of 0.4 µg/L for ionic silver associated with the U.S. EPA reference dose (RfD) of 0.005 mg Ag/kg bw/day for protection against argyria (IRIS 1991; Health Canada 2016) was used to determine potential harm to human health from exposure to silver (Health Canada 2016; Aylward et al. 2016). Argyria is not associated with any systemic health effects and therefore its use as an endpoint for risk characterization is considered conservative. The BE and the median and 95th percentile of blood concentrations from the biomonitoring data are presented in Table 8-1 below.

Table 8-1. Concentrations of total silver in whole blood (µg/L) in Canadians

Survey population	Age (years)	Median (95% CI)	95th percentile (95% CI)	BE (µg/L)	Exceedance
CHMS Cycle 2 ^a Canadian population (2009-11)	3 to 79	0.066 (<LOD to 0.088)	0.27 (0.22–0.31)	0.4	N
MIREC-CD Plus ^b children (2013-14)	1 to ≤3	0.205	0.259	0.4	N

Abbreviations: BE = biomonitoring equivalent, CI = confidence interval, N = no, <LOD = less than the limit of detection where LOD = 0.05 µg/L.

^a Health Canada 2013, n=6070.

^b Liang 2016, n = 214.

The data presented in Table 8-1 demonstrate that whole blood silver concentrations in Canadians are below the BE associated with the U.S. EPA RfD for argyria. Therefore, silver and its compounds are of low concern at the current levels of exposure in the general public. Further details are presented in the Biomonitoring-based Approach 2 science approach document (Health Canada 2016).

8.1 Uncertainties in evaluation of risk to human health

Uncertainties associated with the biomonitoring approach have been detailed in the science approach document on Biomonitoring-based Approach 2 (Health Canada 2016). The multi-compartment physiologically based pharmacokinetic (PBPK) model used in the derivation of the BE was based on data from both animal and human datasets and validated against other available studies. The PBPK model generally provided reliable predictions of blood concentrations in workers occupationally exposed to silver. However, there are uncertainties regarding the oral absorption fraction assumed, as absorption data are lacking in humans. The available PBPK model is structured for adult physiology only. As a result, predictions relevant for specific sub-populations, such as children or pregnant women, have higher uncertainty than adults in the general population.

9. Conclusion

Considering all available lines of evidence presented in this draft screening assessment, there is low risk of harm to the environment from silver and its compounds. It is proposed to conclude that the seven substances in the Silver and its Compounds Group do not meet the criteria under paragraphs 64(a) or (b) of CEPA as they are not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity or that constitute or may constitute a danger to the environment on which life depends.

On the basis of the information presented in this draft screening assessment, it is proposed to conclude that silver 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 the seven substances in the Silver and its Compounds Group do not meet any of the criteria set out in section 64 of CEPA.

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Appendix A. Physical and chemical properties

Table A-1. Physical and chemical properties for the seven substances in the Silver and its Compounds Group

CAS RN	DSL Name	Molecular formula	Molecular weight (g/mol)	Boiling point (°C)	Density at 20 °C (g/cm ³)	Solubility at 20 °C (mg/L H ₂ O)
7440-22-4	Silver	Ag	107.87	2212 ^a	10.5 ^a	Insoluble ^a
7761-88-8	Nitric acid silver(1++) salt	AgNO ₃	169.87	Decomposes at 440 ^a	4.35 ^a	2.16 x 10 ⁴ ^a
7783-90-6	Silver chloride (AgCl)	AgCl	143.32	1550 ^a	5.56 ^a	1.93 ^a
7785-23-1	Silver bromide (AgBr)	AgBr	187.77	1502 ^a	6.47 ^a	0.14 ^a
10294-26-5	Sulfuric acid, disilver(1++) salt	Ag ₂ SO ₄	311.80	NA	5.45 ^a	8400 ^b
20667-12-3	Silver oxide (Ag ₂ O)	Ag ₂ O	231.74	Decomposes above 100 ^a	NA	Decomposes in aqueous solution ^a
21548-73-2	Silver sulfide (Ag ₂ S)	Ag ₂ S	247.8	Decomposes at 810 ^a	7.33 ^a	0.14 ^a

NA: Not available

^a Lide 2000

^b Lide 2005

Appendix B. Canadian Border Services Agency import data

Table B-1. Annual aggregate quantities of silver-containing substances imported into Canada from 2010 to 2013 (CBSA 2016)

HS code name and number ^a	Number of unique companies importing	Number of individual imports	Median import quantity (t) ^b	90 th percentile import quantity (t) ^b	Quantity imported per year (t) ^c
Silver nitrate ^d	98	336	0.014	0.90	34 – 41
Other silver compounds ^e	100	321	0.0060	0.20	12 – 68
Silver in powder form ^f	89	204	0.50	150	16 – 33

^a The Harmonized Commodity Description and Coding System is an international goods classification system developed by the Customs Co-operation Council (now the World Customs Organization) and used by Canada to classify imported and exported goods (<http://www.cbsa-asfc.gc.ca/trade-commerce/tariff-tarif/hcdcs-hsdcm/menu-eng.html>).

^b Calculated from distribution of individual imports from 2010 to 2013.

^c Note that these quantities do not represent quantities of elemental silver alone but reflect the composition of the substances captured within the HS codes.

^d HS code 2843.21.000.

^e HS code 2843.29.000.

^f Includes the following HS codes: 7106.10.0000 (silver in powder form), 7106.10.0010 (silver powder containing by weight equal to or greater than 92.5% of silver), 7106.10.0020 (silver powder containing by weight less than 92.5% of silver).

Table B-2. Estimated uses of silver-containing substances summarized from import data over 2010 to 2013 in tonnes by independently assigned NAICS6 codes (CBSA 2016)

NAICS6 code description	Silver nitrate^a	Other silver compounds^b	Silver powder^c
Aerospace Product and Parts Manufacturing	NR	2.0	NR
All Other Basic Inorganic Chemical Manufacturing	18	NR	NR
All Other Miscellaneous Chemical Product and Preparation Manufacturing	1.5	63	NR
All Other Miscellaneous Manufacturing	NR	44	NR
Chemical (except Agricultural) and Allied Product Wholesaler-Distributors	2.3	NR	NR
Cutlery and Hand Tool Manufacturing	NR	0.75	NR
Glass Product Manufacturing from Purchased Glass	38	NR	NR
Industrial Machinery and Equipment Merchant Wholesalers	NR	NR	2.0
Office Supplies and Stationery Stores	1.3	NR	NR
Other Electronic Parts and Equipment Merchant Wholesalers	46	3.4	NR
Other Petroleum and Coal Product Manufacturing	NR	2.3	NR
Other Professional Equipment and Supplies Merchant Wholesalers	11	NR	NR
Other Support Activities for Air Transportation	NR	9.5	NR
Professional Machinery, Equipment and Supplies	2.2	NR	NR
Recyclable Metal Wholesaler-Distributors	NR	NR	0.68
Religious Organizations	1.5	NR	NR
Semiconductor and Other Electronic Component Manufacturing	NR	5.5	NR
Soap and cleaning compound manufacturing	19	NR	NR
Switchgear and Switchboard, and Relay and Industrial Control Apparatus Manufacturing	NR	NR	74
Synthetic Dye and Pigment Manufacturing	NR	NR	2.8
Warm Air Heating and Air-Conditioning Equipment and Supplies Merchant Wholesalers	NR	8.3	NR
Total:	140	140	80

NR: not reported.

^a HS code 2843.21.000.

^b HS code 2843.29.000.

^c Includes the following HS codes: 7106.10.0000 (silver in powder form), 7106.10.0010 (silver powder containing by weight equal to or greater than 92.5% of silver), 7106.10.0020 (silver powder containing by weight less than 92.5% of silver).

Appendix C. National Pollutant Release Inventory data

Table C-1. Total quantities of silver released to air, water, and land by industrial sectors from 2012 to 2016 (NPRI 2018)

Sector	Number of reporting facilities ^a	Air (t)	Water (t)	All media <1 t (t)
All Other Miscellaneous Fabricated Metal Product Manufacturing	1	NR	NR	0.06
Base Metal Smelting and Refining ^b	5	1.3	0.002	1
Cement Manufacturing	3	0.006	NR	0.004
Coal mining	1	NR	0.009	NR
Marine Cargo Handling	1	NR	NR	0.003
Metal Mining ^c	12	0.02	0.3	0.07
Non-Conventional Oil Extraction	2	0.41	0.37 ^e	0.0516
Non-Ferrous Metal (except Cu, Al) Rolling, Drawing, Extruding and Alloying	2	0.04	NR	0.02
Pulp and Paper	1	NR	NR	0.09
Waste ^d	4	0.006	0.0021	0.01
Total	32	2	0.7	1

NR: Not reported.

^a Count of facilities which reported releases of silver to air and/or water and/or all media <1 tonne for at least one year during the 2012 to 2016 reporting period.

^b Includes facilities with the following NAICS6 codes: 331410 and, 331529.

^c Includes facilities with the following NAICS6 codes: 212220, 212231, 212232, and 212233.

^d Includes facilities with the following NAICS6 codes: 221320 and 562210.

^e Reporting error, value is 0 t (personal communication, information provided by the Strategy and Operations Services, Suncor Energy Services Inc., to the Ecological Assessment Division, Environment and Climate Change Canada, dated April 4, 2019; unreferenced).

Appendix D. Background concentrations

Table D-1. Statistics describing background concentrations of total silver in Canada's ecozones, Great Lakes, and the North Atlantic and North Pacific oceans.

Ecozone/ waterbody	Sample size	Median (µg Ag_T/L)	Upper inner tolerance limit (µg Ag_T/L)^g
Atlantic Maritime ^{a,b}	3	0.050	0.05
Boreal Cordillera ^b	301	0.0020	0.048
Boreal Plains ^b	644	0.010	0.26
Boreal Shield ^b	486	0.11	1.2
Mixedwood Plains ^b	783	0.52	2.1
Montane Cordillera ^b	1950	0.0010	0.014
Pacific Maritime ^b	1464	0.0010	0.017
Prairies ^b	335	0.050	0.92
Taiga Cordillera ^b	21	0.0040	0.044
Taiga Shield ^c	162	0.00050	NA
Lake Erie ^d	106	0.00050	NA
Lake Ontario ^d	165	0.00050	NA
Lake Superior ^d	83	0.00050	NA
North Atlantic Ocean ^e	9	0.00032	NA
North Pacific Ocean ^{a,f}	22	0.0011	NA

NA: Not available.

^a Dissolved silver concentrations are reported.

^b Kilgour & Associates Ltd. (2016).

^c NLTWQM 2016.

^d 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.

^e Rivera-Duarte et al 1999, median of concentrations measured in multiple locations up to a depth of 50 m.

^f Kramer et al 2011, median of concentrations measured in multiple locations up to a depth of 50 m.

^g Synonymous in this assessment with maximum expected background concentration.

Appendix E. Silver soil toxicity dataset

Table E-1. Ag toxicity data on soil-dwelling organisms

Group	Test organism	Endpoint	Value ^a (mg/kg dw)	Reference
Plant	Barley, <i>Hordeum vulgare</i>	5-d EC ₁₀ , root length	25	Langdon et al. 2015
Plant	Barley, <i>Hordeum vulgare</i>	5-d EC ₅₀ , root length	88	Langdon et al. 2015
Plant	Northern wheatgrass, <i>Elymus lanceolatus</i>	21-d EC ₁₀ , root/shoot dry mass	3 ^b	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus lanceolatus</i>	21-d EC ₅₀ , shoot dry mass	16	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus lanceolatus</i>	21-d EC ₅₀ , shoot dry mass	40, 184	Velicogna et al. 2016
Plant	Northern wheatgrass, <i>Elymus lanceolatus</i>	21-d EC ₅₀ , root dry mass	33	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus lanceolatus</i>	21-d EC ₅₀ , root dry mass	99, 98	Velicogna et al. 2016
Plant	Northern wheatgrass, <i>Elymus lanceolatus</i>	21-d EC ₁₀ , shoot length	7	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus lanceolatus</i>	21-d EC ₁₀ , root length	20	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus lanceolatus</i>	21-d EC ₅₀ , shoot length	68	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus lanceolatus</i>	21-d EC ₅₀ , shoot length	77, 413	Velicogna et al. 2016
Plant	Northern wheatgrass, <i>Elymus lanceolatus</i>	21-d EC ₅₀ , root length	59	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus lanceolatus</i>	21-d EC ₅₀ , root length	45, 106	Velicogna et al. 2016

Group	Test organism	Endpoint	Value ^a (mg/kg dw)	Reference
Plant	Northern wheatgrass, <i>Elymus lanceolatus</i>	21-d EC ₅₀ , emergence	298, 1491	Velicogna et al. 2016
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₁₀ , root/shoot dry mass	1 ^b	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₅₀ , shoot dry mass	4	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₅₀ , shoot dry mass	85, 498	Velicogna et al. 2016
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₅₀ , root dry mass	7	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₅₀ , root dry mass	106, 227	Velicogna et al. 2016
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₁₀ , shoot length	33	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₁₀ , root length	18	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₅₀ , shoot length	1845	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₅₀ , shoot length	54, 304	Velicogna et al. 2016
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₅₀ , root length	336	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₅₀ , root length	75, 172	Velicogna et al. 2016
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₁₀ /EC ₅₀ , emergence	>3014	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense</i> L.	14-d EC ₅₀ , emergence	188, 1047	Velicogna et al. 2016
Plant	Tomato, <i>Lycopersicum esculentum</i>	21-d EC ₁₀ , emergence	6.6	Langdon et al. 2015
Plant	Tomato, <i>Lycopersicum esculentum</i>	21-d EC ₅₀ , emergence	73	Langdon et al. 2015

Group	Test organism	Endpoint	Value ^a (mg/kg dw)	Reference
Invertebrates	Earthworm, <i>Eisenia andrei</i>	56-d EC ₁₀ , reproduction	2	ECSTL 2011
Invertebrates	Earthworm, <i>Eisenia andrei</i>	56-d EC ₅₀ , reproduction	54	ECSTL 2011
Invertebrates	Earthworm, <i>Eisenia andrei</i>	56-d EC ₅₀ , reproduction	46.9	Schlich et al. 2013
Invertebrates	Earthworm, <i>Eisenia andrei</i>	63-d EC ₅₀ , reproduction	29	Velicogna et al. 2016
Invertebrates	Earthworm, <i>Eisenia andrei</i>	56-d EC ₁₀ , dry mass	11	ECSTL 2011
Invertebrates	Earthworm, <i>Eisenia andrei</i>	56-d EC ₅₀ , dry mass	56	ECSTL 2011
Invertebrates	Earthworm, <i>Eisenia andrei</i>	56-d EC ₅₀ , dry mass	42	Schlich et al. 2013
Invertebrates	Earthworm, <i>Eisenia andrei</i>	63-d EC ₅₀ , dry mass	15	Velicogna et al. 2016
Invertebrates	Earthworm, <i>Eisenia andrei</i>	28-d LC ₁₀ , adult	251	ECSTL 2011
Invertebrates	Earthworm, <i>Eisenia andrei</i>	35-d LC ₅₀ , adult	152	Velicogna et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	21-d EC ₁₀ , reproduction	38	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	21-d EC ₂₀ , reproduction	47	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	21-d EC ₅₀ , reproduction	62	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	11-d EC ₁₀ , hatching	42	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	11-d EC ₂₀ , hatching	48	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	11-d EC ₅₀ , hatching	58	Bicho et al. 2016

Group	Test organism	Endpoint	Value ^a (mg/kg dw)	Reference
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	25-d EC ₁₀ , growth	69	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	25-d EC ₂₀ , growth	79	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	25-d EC ₅₀ , growth	98	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	14-d LC ₁₀ , cocoons	41	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	14-d LC ₂₀ , cocoons	47	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	14-d LC ₅₀ , cocoons	57	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	22/25-d LC ₁₀ , cocoons	21, 29	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	22/25-d LC ₂₀ , cocoons	33, 40	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	22/25-d LC ₅₀ , cocoons	54, 62	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	21-d LC ₁₀ , adult	52	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	21-d LC ₂₀ , adult	61	Bicho et al. 2016
Invertebrates	Pot worm, <i>Enchytraeus crypticus</i>	21-d LC ₅₀ , adult	75	Bicho et al. 2016
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d EC ₁₀ , reproduction	20 ^b	ECSTL 2011
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d EC ₁₀ , reproduction	31 ^b	Mendes et al. 2015

Group	Test organism	Endpoint	Value ^a (mg/kg dw)	Reference
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d EC ₁₀ , reproduction	47.6 ^b	Waalewijn-Kool et al. 2014
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d EC ₂₀ , reproduction	76	Mendes et al. 2015
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d EC ₅₀ , reproduction	94	ECSTL 2011
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d EC ₅₀ , reproduction	114, 177	Velicogna et al. 2016
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d EC ₅₀ , reproduction	152	Mendes et al. 2015
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d EC ₅₀ , reproduction	99.5	Waalewijn-Kool et al. 2014
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d LC ₁₀	297	ECSTL 2011
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d LC ₁₀	82	Mendes et al. 2015
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d LC ₂₀	118	Mendes et al. 2015
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d LC ₅₀	785	ECSTL 2011
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d LC ₅₀	216, 356	Velicogna et al. 2016
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d LC ₅₀	284	Waalewijn-Kool et al. 2014
Invertebrates	Springtail, <i>Folsomia candida</i>	28-d LC ₅₀	179	Mendes et al. 2015

Abbreviations: dw = dry weight; EC_{10/20/50} = the concentration of a stressor that is estimated to be effective in producing a biological response, other than mortality, in 10%, 20%, or 50% of the test organisms over a specific time interval; LC_{10/20/50} = the concentration of a stressor that is estimated to be lethal to 10%, 20%, or 50% of the test organisms over a specific time interval.

^a The Ag soil toxicity full dataset. Toxicity tests conducted in soils with pH < 5.5, % OM > 6%, or on microbial are not included in this dataset as per CCME Canadian Soil Quality Guideline (2006). pH > 7, and/or soils with high silt/clay contents are considered case-by-case.

^b Geometric means applied for the species SSD data points.