



**Screening Assessment** 

Silver and its Compounds

# Environment and Climate Change Canada Health Canada

August 2022

Cat. No.: En84-302/2022E-PDF ISBN 978-0-660-44697-4

Information contained in this publication or product may be reproduced, in part or in whole, and by any means, for personal or public non-commercial purposes, without charge or further permission, unless otherwise specified.

You are asked to:

- Exercise due diligence in ensuring the accuracy of the materials reproduced;
- Indicate both the complete title of the materials reproduced, as well as the author organization; and
- Indicate that the reproduction is a copy of an official work that is published by the Government of Canada and that the reproduction has not been produced in affiliation with or with the endorsement of the Government of Canada.

Commercial reproduction and distribution is prohibited except with written permission from the author. For more information, please contact Environment and Climate Change Canada's Inquiry Centre at 1-800-668-6767 (in Canada only) or 819-997-2800 or email to <u>enviroinfo@ec.gc.ca</u>.

© Her Majesty the Queen in Right of Canada, represented by the Minister of the Environment and Climate Change, 2022.

Aussi disponible en français

## 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 of these substances 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 RN<sup>1</sup>), *Domestic Substances List* (DSL) names, and common names of these substances are listed in the table below.

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 <sub>2</sub> O)	Silver oxide
21548-73-2	Silver sulfide (Ag <sub>2</sub> S)	Silver sulfide

#### Substances in the Silver and its Compounds Group

The 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 screening assessment.

Canada is the 14<sup>th</sup> largest producer of silver in the world. According to information submitted in response to a CEPA section 71 survey, substances within the Silver and its Compounds Group that were included in the survey 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, as a formulant in registered pest control products, and toys. It is a permitted food additive and may be

<sup>&</sup>lt;sup>1</sup> 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.

used as a component in the manufacture of food packaging materials and as a component in an incidental additive used in food processing establishments.

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). The National Pollutant Release Inventory data from 2012 to 2017 indicate that silver and its compounds were released to the environment from public and industrial activities in low quantities (i.e., yearly average of 0.027 t for all media 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. In aquatic organisms, the accumulated silver is mostly bound with sulfur-containing biomolecules and detoxified. Bioaccumulation of silver in benthic and soil-dwelling organisms may be reduced by the formation of inert silver sulfide in these environmental compartments. Currently, there is no indication of biomagnification of silver across food chains.

Silver causes mortality as well as growth and reproductive effects to aquatic organisms at very low concentrations and to benthic 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. Ecotoxicity studies were used to derive chronic PNECs for silver for organisms in the marine water, freshwater sediment, and soil compartments.

Ecological exposure to silver was characterized for the following sources based on their potential to release silver: metal mining, base metal smelting and refining, wastewaters (i.e., silver in the final effluent released by wastewater systems and silver in land-applied biosolids), and waste disposal (i.e., landfill leachate). Risk quotient analyses were performed by comparing measured and modelled exposure concentrations in fresh waters, marine waters, freshwater sediments and soils to chronic PNECs for freshwater and marine water aquatic, freshwater 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 potential to cause harm to aquatic or soil-dwelling organisms. However, there is uncertainty regarding the potential for ecological harm in sediment due to the paucity of ecotoxicity studies and uncertainties around the bioavailability of sediment-bound silver.

Considering all available lines of evidence presented in this screening assessment, there is low risk of harm to the environment from silver and its compounds. It is concluded 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 95<sup>th</sup> percentile blood silver concentrations in Canadians of 0.066  $\mu$ g/L and 0.27  $\mu$ g/L were lower than the BE of 0.4  $\mu$ g/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 membranes. 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 screening assessment, it is concluded 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 concluded 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.

# **Table of Contents**

Synopsis	ii
1. Introduction	8
2. Substance identity	9
3. Physical and chemical properties	10
4. Sources and uses	11
4.1 Natural sources	11
4.2 Anthropogenic sources	11
5. Releases to the environment	14
6. Environmental fate and behaviour	15
6.1 Environmental distribution	
6.2 Environmental persistence	16
6.3 Potential for bioaccumulation	
7. Potential to cause ecological harm	18
7.1 Ecological effects assessment	18
7.2 Ecological exposure assessment	27
7.3 Characterization of ecological risk	
8. Potential to cause harm to human health	
8.1 Uncertainties in evaluation of risk to human health	
9. Conclusion	
References	
Appendix A. Physical and chemical properties	
Appendix B. Canadian Border Services Agency import data	
Appendix C. National Pollutant Release Inventory data	
Appendix D. Background concentrations	
Appendix E. Silver sediment toxicity dataset	
Appendix F. Silver soil toxicity dataset	73

# List of Tables and Figures

Table 2-1.	Substance identity information for the seven substances in the Silver and its Compounds Group identified as priorities for assessment
Table 7-1.	Summary of available silver toxicity data to freshwater organisms
	Summary of available silver toxicity data to marine water organisms
	Key soil toxicity studies considered in determining a critical toxicity value for soil
Table 7-4.	Silver freshwater concentrations in exposure and reference areas of metal
	mines subject to the Metal and Diamond Mining Effluent Regulations <sup>a</sup> 30
Table 7-5.	Silver sediment concentrations in exposure and reference areas of metal
	mines subject to the Metal and Diamond Mining Effluent Regulations <sup>a</sup> 31
Table 7-6.	Silver freshwater exposure and reference areas of base metal smelting
	activities subject to the Metal and Diamond Mining Effluent Regulations <sup>a</sup> 32
Table 7-7.	Silver sediment concentrations in exposure and reference areas of base
	metal smelting and refining activities subject to the Metal and Diamond
	Mining Effluent Regulations <sup>a</sup>
Table 7-8.	Silver freshwater and sediment concentrations in exposure and reference
	areas of one base metal smelting facility not subject to the Metal and
	Diamond Mining Effluent Regulations (EEC Ltd and LAC Ltd 2014)
Table 7-9.	Landfill leachate predicted environmental concentrations 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) and in 2020 (ECCC 2020) 39
Table 7-10	D. Summary of risk quotients obtained for different environmental
	compartments and exposure scenarios for silver and its compounds 40
Table 7-12	1. Weighted lines of key evidence used for the ecological assessment of silver
	and its compounds
Table 8-1.	Concentrations of total silver in whole blood (µg/L) in Canadians50
Table A-1.	Physical and chemical properties for the seven substances in the Silver and
	its Compounds Group65
Table B-1.	Annual aggregate quantities of silver-containing substances imported into
	Canada from 2010 to 2013 (CBSA 2016)
	. Estimated uses of silver-containing substances summarized from import data
	over 2010 to 2013 in tonnes by independently assigned NAICS6 codes
	(CBSA 2016)
Table C-1	. Total quantities of silver released to air, water, and land by industrial and
	public sources from 2012 to 2017 (NPRI 2019)69
Table D-1	. Statistics describing background concentrations of total silver in Canada's
	ecozones, Great Lakes, and the North Atlantic and North Pacific oceans70
	Ag toxicity on sediment-dwelling organisms
	Ag toxicity on soil-dwelling organisms
Figure 7-1	. Species sensitivity distribution for long-term silver soil toxicity. The averaged
	model fit to data is shown on the graph, along with the 95% confidence
	interval and 5th percentile of the distribution (HC5)27

## 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 of these substances 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 screening assessment as the Silver and its Compounds Group.

The focus of the screening assessment is on the silver moiety<sup>2</sup> (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 screening assessment considers exposure from silver found in environmental media (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. Therefore, the risk assessment is not limited to the seven substances identified as priorities for assessment.

This screening 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 the exposure scenarios of this screening assessment, but measured concentrations of silver in the environment or human biomonitoring could include silver from these sources. Similarly, this screening 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* (DSL) (ECCC, HC [modified 2016]).

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

<sup>&</sup>lt;sup>2</sup> 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 December 2020. Empirical data from key studies as well as results from models were used to reach the conclusion. When available and relevant, information presented in assessments by other jurisdictions was considered.

This screening assessment was prepared by staff in the CEPA Risk Assessment Program at Health Canada and Environment and Climate Change Canada and incorporates input from other programs within these departments. The ecological and human health portions of this screening assessment have undergone external review and 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 screening assessment was based on the Biomonitoring-based Approach 2 science approach document (Health Canada, 2016), which was externally peer-reviewed and subject 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 and from Judy LaKind from LaKind Associates. Additionally, the draft of this screening assessment (published August 2020) was subject to a 60-day public comment period. 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 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.<sup>3</sup> This screening assessment presents the critical information and considerations on which the conclusion is based.

# 2. Substance identity

Silver (Ag) is a natural element. Silver-containing substances belong to various substance categories, including elemental silver, inorganic compounds, organic-metal salts, and organometallic compounds, represented by either discrete substances or UVCBs (unknown or variable composition, complex reaction products, or biological

<sup>&</sup>lt;sup>3</sup> 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.

materials). The Chemical Abstracts Service Registry Numbers (CAS RN<sup>4</sup>), DSL names, and common names of these substances are presented in Table 2-1.

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 <sub>2</sub> O)	Silver oxide
21548-73-2	Silver sulfide (Ag <sub>2</sub> S)	Silver sulfide

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

## 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, <sup>107</sup>Ag and <sup>109</sup>Ag, with <sup>107</sup>Ag being slightly more abundant. Silver is one of the least reactive metals and Ag<sup>+</sup> 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 have limited water solubility (e.g., silver bromide, 0.14 mg/L; silver chloride, 1.93 mg/L), with some exceptions such as silver nitrate (i.e., 2.16 x  $10^4$  mg/L), silver perchlorate, and silver fluoride. Silver halides, especially silver bromide and silver 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.

<sup>&</sup>lt;sup>4</sup> 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.

# 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 2018), and silver is produced mainly as a by-product of mining copper-zinc, copper-nickel, gold, and lead-zinc ores. Canada's only primary silver mine suspended operations in 2013 with intentions of returning to production in the future (Alexco 2019).

In 2018, global silver production was estimated at approximately 26 000 tonnes (t), and Canada ranked 14<sup>th</sup> out of the top 20 producing countries (Newman et al. 2020). Natural Resources Canada (NRCan 2020) reports that silver production in Canada in 2018 was 392 t, with Ontario being the largest producer (113 t), followed by British Columbia (84 t) and Quebec (83 t).

#### 4.2.2 Manufacture and imports

Information regarding the manufacture and import of silver-containing substances in Canada was acquired through data submitted in response 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 (CIMT) database (CIMT 2017-2021). A survey issued pursuant to section 71 of CEPA (Canada 2012) (for the reporting year 2011)<sup>5</sup> included six of the seven substances in the Silver and its Compounds Group. 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), silver sulfide (1 000 t to less than 10 000 t), and 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 by the Canadian Border Services Agency (CBSA), for five Harmonized System (HS) codes<sup>6</sup> 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. Many companies imported silver-containing substances related to these HS codes in low to moderate quantities with the following averages from 2010 to 2013: 0.45 t/y for silver nitrate, 0.45 t/y for other silver compounds, and 0.41 t/y for silver powder. Other categories of HS codes include unwrought silver, semi-manufactured silver, and silver ores and concentrates, for which average import quantities were 3.1t/y, 0.82t/y, and 29 t/y, respectively, over the 2010 to 2013 period. According to the CIMT database (2017-2021), average import quantities from 2017 to 2019 were 1.6 t/y for silver nitrate, 0.40 t/y for other silver compounds, 3.0 t/y for silver powder, 20 t/y for unwrought silver, 4.0 t/y for semi-manufactured silver, and 110 t/y 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; Newman et al. 2020). Historically, silver was used in the photographic and radiographic film industry (Health Canada 1986; Purcell and Peters 1998; WHO 2002). This use accounted for 26% of the total global demand for silver in 1999 but only 3% in 2019 due to changes in imaging technology, such as the emergence of digital photography (Newman et al. 2020). Current industrial applications of silver documented internationally 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

<sup>&</sup>lt;sup>5</sup> Values reflect quantities reported in response to the CEPA section 71 survey (Canada 2012). See survey for specific inclusions and exclusions (schedules 2 and 3).

<sup>&</sup>lt;sup>6</sup> 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 (<u>http://www.cbsa-asfc.gc.ca/trade-commerce/tariff-tarif/hcdcs-hsdcm/menu-eng.html</u>).

other chemical compounds (e.g., ethylene oxide) (Brumby et al. 2008; O'Connell et al. 2017; Newman et al. 2020). Other industrial 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; Newman et al. 2020), as well as the use of silver iodide for cloud seeding (WHO 2002).

According to information submitted in response to a CEPA section 71 survey, uses of silver-containing substances in Canada 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; Newman et al. 2020). 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 include use information. Therefore, a subset of imports representing substantial quantities (those greater than 500 kg) was identified and NAICS6 codes<sup>7</sup> were used 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 2021]; NHPID [modified 2021]), 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), a formulant in registered pest control products (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), and toys (Health Canada 2016). It is a permitted food additive (Health Canada [modified 2006]) and may be used as a component in the manufacture of food packaging materials, and as a component in an incidental additive used in food processing establishments (personal communication, emails from the

<sup>&</sup>lt;sup>7</sup> North American Industry Classification System (NAICS) codes have a hierarchical structure composed of five levels. The fifth level, represented by six digits (NAICS6), correspond to Canadian industries.

Foods Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated March 14, 2016; unreferenced).

## 5. Releases to the environment

Canada's National Pollutant Release Inventory (NPRI) estimates annual releases of silver and its compounds to the environment, annual quantities recycled, and annual quantities disposed. 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 2018a).

Submissions to the NPRI from 2012 to 2017 indicate that in Canada, 37 facilities across 10 sectors and sources reported releases of silver to air, water or all media less than one tonne (NPRI 2019; Appendix C, Table C-1). Releases to land were not reported during the 6-year period but may be captured within the category of "all media less than one tonne." The total release of silver to air from 2012 to 2017 from six reporting sources was low (1.8 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 sources reported negligible releases to air (less than or equal to 0.045 t). The total release of silver to water during the same 6-year period from five reporting sources was also low (0.74 t). The metal mining sector released 0.35 t of silver to water from eight facilities. Submissions to the "all media less than one tonne" category from 2012 to 2017 indicate that the total release of silver was also low (2.2 t) and mostly attributable to the base metal smelting and refining sector, while other sources released negligible quantities (less than or equal to 0.100 t). Therefore, the NPRI data indicates that silver was released to the environment in low quantities from public and industrial activities meeting the reporting threshold from 2012 to 2017.

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). Freshwater monitoring data collected in proximity to one photographic manufacturing plant indicate concentrations of silver decreased to below the detection limit (<10  $\mu$ 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 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.

Furthermore, effluents from these industries typically undergo municipal wastewater treatment where removal of silver is effective.

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 AgCl complexes due to high concentrations of chloride ions, and complexes of AgCl, AgCl<sub>2</sub><sup>-</sup>, or AgCl<sub>3</sub><sup>2-</sup> progressively predominate as water salinity increases (Miller and Bruland 1995; Ward and Kramer 2002; Wood et al. 2004; Wood 2012). When industrial and domestic wastewaters containing silver are treated at wastewater treatment systems , 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 through adsorption to clay minerals and hydrous metal oxides, e.g., manganese and iron hydroxides, and through precipitation of insoluble compounds, e.g., silver sulfide (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 and are unlikely to remobilize (Callahan et al. 1979; Donner et al. 2015). 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 remobilize silver ions from the 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 high adsorption (log  $K_{sw}$  of approximately 8.8 to 14.2) (Wood 2012). Volatilization from 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. Silver is considered persistent because it cannot degrade through processes such as photodegradation or biodegradation. However, silver can transform into different chemical species, e.g., by forming complexes with chlorides, sulfides, and biomolecules when entering the environment and organisms (Wood 2012), and it can 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 has been the subject of much debate and criticism because these factors are considered of little use in predicting metal hazards (McGeer et al. 2003; Schlekat et al. 2007). An inverse relationship between aquatic silver concentrations and BCFs and BAFs has been demonstrated (as exposure concentrations increased, BCFs and BAFs decreased) (McGeer et al. 2003; Lopez-Serrano et al. 2014). Therefore, BCF and BAF values were not the sole focus of the CWQG. Instead, silver bioavailability, bioaccumulation, and biomagnification via food chains were considered as overall lines of evidence in

determining the bioaccumulation potential of silver. The silver CWQG report (CCME 2015a) determined that no evidence of silver biomagnification was found. Additional information not reviewed in the silver CWQG is summarized below.

The bioavailability and bioaccumulation of silver in the aquatic environment is mostly driven by the free silver ion (Ag<sup>+</sup>) which is the form that is ecotoxic to all aquatic organisms (Rodgers et al. 1997a, b). The silver ion may accumulate 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 silver in aquatic organisms increases with elevated aqueous silver 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. 1997a; Wood et al. 1996). Dietary exposure of silver is not considered a significant concern (CCME 2015a). The understanding of silver detoxification mechanisms in aquatic organisms is limited. Zimmermann et al. (2017) suggested that zebra mussels possess regulatory mechanisms to restrict silver bioaccumulation, with excess silver eliminated only after all binding sites are occupied. Martin et al. (2017) demonstrated that rapid binding with the cysteine-rich protein metallothionein in fish is the main pathway for detoxification due to the high affinity of silver for the thiol groups in metallothionein.

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 silver 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 silver-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 silver bioaccumulation in AgNO<sub>3</sub>-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). Silver 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 silver bioavailability in biosolids-amended soil to lettuce at environmentally relevant silver concentrations (Doolette 2015). Silver accumulation in shoots was not significant compared to roots. Cl<sup>-</sup> was found to react with Ag<sup>+</sup> 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 silver 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 (2015a) determination that silver 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 metallothionein or detoxified in aquatic organisms. Silver regulation or detoxification mechanisms in sediment or soil-swelling organisms is unclear; the availability of free Ag<sup>+</sup> could be reduced by forming inert silver sulfide in these environmental compartments, thus decreasing silver 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 Mode/mechanism of toxic action

The well-known mechanism of silver toxicity to freshwater organisms is related to its interference with the vital Na<sup>+</sup> and Cl<sup>-</sup> uptake process (McGeer and Wood 1998; Morgan et al. 1997; Wood 2012). The mode of action of silver in both fresh and marine water fish has been discussed in detail in the CWQG (CCME 2015a). The primary mechanism of silver toxicity in freshwater fish is an almost total inhibition of Na<sup>+</sup>/K<sup>+</sup>-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 mode of toxicity 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 , suggesting fish liver offers some inherent protection against chronic silver 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<sup>+</sup>/K<sup>+</sup>-ATPase inhibition in *D. magna* was directly related to silver hindering the whole body sodium uptake of the organism. However, the nature of the sodium uptake inhibition in *D. 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 (Hook and Fisher 2001; Wood 2012).

In marine invertebrates, however, the exact mode 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 the gills, hepatopancreas, or both, causing significant changes in Na<sup>+</sup>/K<sup>+</sup>-ATPase activity. Changes also occurred in both total and intracellular ion (Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) concentrations in different tissues of 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<sup>+</sup>, K<sup>+</sup>, or Cu<sup>+</sup>); 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 interfere with the expression of proteins in ATP-synthesis and photosynthesis and can replace Cu<sup>+</sup> in key proteins involved in those processes (Pillai et al. 2014). Leonardo et al. (2016) demonstrated that silver bound with molecules containing sulfur and was effectively detoxified upon entering the cytosol in the green microalga *Coccomyxa actinabiotis* at low concentrations (e.g.,  $10^{-5}$  mol/L). However, silver may enter the cytosol and chloroplasts at higher concentrations (e.g.,  $> 10^{-4}$  mol/L), 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<sup>+</sup> of thiol, P (phosphatase), S (arylsulfatase), and N (urease) enzymes (Domsch 1984; Falbe and Regitz 1992; NAPM 1974).

## 7.1.2 Toxicity-modifying factors (TMF)

The CCME reviewed potential toxicity-modifying factors for silver in accordance with their 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<sup>+</sup>; and therefore, factors affecting the free Ag<sup>+</sup> 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<sup>+</sup> (CCME 2015a; Erickson et al. 1998; Wood 2012).

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

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

The protective effects of Cl<sup>-</sup> could be species-specific for freshwater organisms and is an 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.,  $H_3O^+$ ) on silver toxicity is unclear. It has been speculated that the effects caused by pH were due to its interaction with DOC, which reduced H<sup>+</sup> leaving increased DOC for silver 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 silver have been reviewed in the recent CWQG for silver (CCME 2015a). These models were considered useful candidates in generating short-term toxicity estimates under site-specific conditions. However, no BLM is available for predicting the chronic toxicity of silver to freshwater organisms (CCME 2015a; Wood 2012).

## 7.1.3 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<sup>+</sup> 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<sup>+</sup> 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 (LeBlanc et al. 1984; Hogstrand et al. 1996; Rodgers et al. 1997a,b). This is likely due to the proportion of total silver in the exposure medium that is the free Ag<sup>+</sup> 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 from 2014 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 (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 at the early larvae and juvenile life stages are more sensitive to silver toxicity than adult fish, particularly the rainbow trout (*Oncorhynchus mykiss*) and fathead minnow (*Pimephales promelas*) (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  $\mu$ g/L to 23  $\mu$ g/L, with the exception of the most tolerant invertebrate species, midge (*Chironomus tentans*), with a 10-day no effect concentration for reproduction at 125  $\mu$ g/L (Table 7-1) (CCME 2015b; Rodgers et al. 1997b). 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).

Group	Effect	Acute or chronic	Effect concentratio n range (µg/L) <sup>a</sup>	Reference <sup>b</sup>
Fish	Mortality	Acute	1.48 to 280	Auffan et al. 2014; Asmonaite et al. 2016; CCME 2015b; Ribeiro et al. 2014
Invertebrates	Mortality	Acute	0.11 to 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 to 248.2	CCME 2015b; Li et al. 2015; Navarro et al. 2015; Sorensen and Baun 2015
Protozoan	Mortality	Acute	8.8	CCME 2015b
Fish	Growth/mo rtality	Chronic	0.24 to 23	CCME 2015b
Invertebrates	Reproducti on/growth	Chronic	0.78 to 125	CCME 2015b; Ribeiro et al. 2014
Algae/plants	Growth	Chronic	0.63 to 6	CCME 2015b; Sekine et al. 2015; Sorensen and Baun 2015

Table 7-1. Summary of available silver toxicity data to fre	eshwater organisms
---	--------------------

<sup>a</sup> The effect concentrations included are for toxicity tests performed using AgNO<sub>3</sub>.

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

The long-term CWQG for silver for the protection of freshwater organisms (CCME 2015a) is 0.25  $\mu$ g/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 (5<sup>th</sup> 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  $\mu$ g/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; Sorensen and Baun 2015; Xin et al. 2015; Yoo-iam et al. 2014; Zhang et al. 2015). Therefore, a freshwater predicted no-effect concentration (PNEC<sub>freshwater</sub>) of 0.25  $\mu$ g/L (total silver) will be used for the risk characterization.

#### 7.1.4 Effects on marine organisms

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

The data on silver toxicity to marine organisms available in the silver 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).

Group	Effect	Acute or chronic	Effect concentratio n range (µg/L) <sup>a</sup>	Reference <sup>b</sup>
Fish	Mortality/ embryo development	Acute	100 to 1876	Auffan et al. 2014; CCME 2015b; Matson et al. 2016
Invertebrates	Mortality/ embryo development	Acute	5.8 to 647	CCME 2015b; Khodaparast 2015; Martin et al. 1981
Algae/plants Fish	Growth Growth/ mortality	Acute Chronic	21 to 86 <sup>c</sup> 19 to 1000	CCME 2015b CCME 2015b
Invertebrates	Reproduction /growth	Chronic	3.9 to 100	Chan and Chiu 2015; CCME 2015b
Algae	Growth/yield	Chronic	2.5 to > 20	Steele and Thursby 1995; Sanders and Abbe 1989

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

<sup>a</sup> Unless otherwise mentioned, the effect concentrations included are for toxicity tests performed using AgNO<sub>3</sub>.

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

<sup>c</sup> The effect concentrations included are for toxicity tests performed using metallic silver and reported as lethal effect, LC<sub>50</sub>.

A short-term CWQG for the protection of marine water organisms (CCME 2015a) of 7.5  $\mu$ g/L (total silver) is available, but there were insufficient data to derive a long-term marine guideline (CCME 2015a). Acute toxicity studies on saltwater organisms published after the data collection period of the CWQG were collected and reviewed (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 were consistent with the short-term CWQG. Additional chronic toxicity data found for marine algae (Sanders and Abbe 1989) are not enough for an SSD approach for deriving a chronic marine PNEC due to lack of long-term toxicity data for marine fish (CCME 2007).

An assessment factor (AF) approach (Okonski et al. 2021) was used in this screening assessment to derive a long-term PNEC for marine organisms. Short- and long-term silver toxicity data in estuarine and marine water were standardized (Okonski et al. 2021). The lowest standardized value was used as the critical toxicity value (CTV). The 48-hour LC<sub>50</sub> of 5.8  $\mu$ g/L in Eastern oyster (*Crassostrea virginica*) at 25 ppt salinity (Calabrese et al. 1977) was the selected CTV. An AF of 10 was applied, which considers an endpoint standardization factor of 10 to extrapolate from an acute median lethal effect to a long-term sub-lethal no effect concentration. A factor of 1 each was also applied to account for species variation and mode of action, respectively, because data were available for a large number of species representing multiple categories of organisms. These result in a chronic PNECmarine water of 0.58  $\mu$ g/L.

#### 7.1.5 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 acid volatile sulfides) (Call et al. 2006; Rodgers et al. 1995; Hirsch 1998a; Yoo et al. 2004). In studies of silver bioavailability to *Hyalella azteca* in AgNO<sub>3</sub>-spiked field sediments, the 10-day LC<sub>50</sub> based on total acid-extractable silver ranged from 1.62 mg/kg dw to 2980 mg/kg dw, and 10-day no observed effect (NOEC) and lowest observed effect concentration (LOEC) for reduced growth ranged from 12 to 2150 mg/kg dw, and 31 to 4310 mg/kg dw, respectively (Appendix E) (Call et al. 2006; Rodgers et al. 1997a). Lower silver toxicity was found in sediments having higher pH and greater amounts of organic matter, clay, cation-exchange capacity, and acid-volatile sulfides (Call et al. 2006; Rodgers et al. 1997a). This large difference in toxicity indicates major impacts of differential adsorption and subsequent bioavailability.

Ligand complexation significantly affects silver bioavailability and toxicity (Call et al. 2006; Hirsch 1998a; Rodgers et al. 1997a). In experiments with the freshwater amphipod *H. azteca*, field sediments were enriched with AgNO<sub>3</sub>, AgCl, Ag<sub>2</sub>S, and silver thiosulfate complex [Ag(S<sub>2</sub>O<sub>3</sub>)<sub>n</sub> (69% Ag)]. Effects on amphipods exposed to AgNO<sub>3</sub>-

spiked sediments occurred at much lower concentrations, with 10-day  $LC_{50}$  values between 1.62 and 2980 mg/kg dw. In comparison, no adverse effects were observed in sediments spiked with AgCl, Ag<sub>2</sub>S, and Ag(S<sub>2</sub>O<sub>3</sub>)<sub>n</sub> at maximum test concentrations ranging from 753 to 2560 mg/kg dw (Hirsch 1998a; Rodgers et al. 1997a). The considerably reduced toxicity of the latter three silver-containing substances is likely due to ligand complexation leading to reduced bioavailability.

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).

Rajala et al. (2016) investigated exposure of blackworms (*Lumbriculus variegatus*) to AgNO<sub>3</sub>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<sub>50</sub>) (reproduction) of 23.9 mg/kg dw and a 28-day median effect concentration (EC<sub>50</sub>) (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 silver complexation, as well as a direct spike method to avoid Ag<sup>+</sup> complexation with Cl<sup>-</sup> in overlying water.

The sediment PNEC derivation followed an AF approach (Okonski et al. 2021). The lowest toxicity value after standardization was a 10-day LC<sub>50</sub> of 1.62 mg/kg with *H. azteca* (Rodgers et al. 1997a) obtained with sediments of extremely low silver complexing ligands. In this study, the silver concentration in overlying water reached 9.7 µg/L on day 10, comparable to the water-only 96-hour LC<sub>50</sub> of 6.8 µg/L for the same organism (Rodgers et al. 1997b). It is possible that water exposure was the primary route of silver toxicity observed in *H. azteca*, and this data point is therefore inappropriate for use as the CTV. The second lowest toxicity value after standardization, the chronic 28-day IC<sub>50</sub> (reproduction) of 23.9 mg/kg dw in blackworms (Rajala et al. 2016), was chosen as the CTV for silver 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 and 1 to account for variation in species sensitivity and mode of action, respectively, resulting in an overall AF of 25. Therefore,

Chronic PNEC<sub>sediments</sub>= 23.9 / (5 x 5 x 1) = 1.0 mg Ag<sub>Total</sub>/kg (or  $\mu$ g/g, dw)

## 7.1.6 Effects on soil-dwelling organisms

AgNO<sub>3</sub> is the silver salt most commonly used in laboratory soil toxicity tests due to its high water solubility and ready dissociation to release the Ag<sup>+</sup> ion. Ag<sub>2</sub>S is considered the predominant silver species in soil and biosolids (Doolette 2015; Jesmer et al. 2016).

Soil toxicity studies on silver 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 F). 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 F).

Mixed factors in soil physical-chemical properties (e.g., pH, organic carbon, cation exchange capacity, and the amounts of silt and clay) affect silver bioavailability and toxicity to soil organisms and plants (Appendix F). 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 with varying properties including sand and clay contents, percent organic matter, pH, and cation exchange capacity. Reported EC<sub>10</sub> for barley root length and tomato emergence varied up to about 13-fold. Silver toxicity to soil invertebrates was less variable with changing soil properties compared to plants, with median effect endpoints (E(L)C<sub>50</sub>) 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 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 2006a). Toxicity endpoints considered reliable are summarized in Appendix F. Table 7-3 lists the dataset that was used for a long-term SSD using the software ssdtools version 0.3.3 (Dalgarno 2018) (Figure 7-1). When more than one acceptable endpoint of comparable test condition and effect 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 F). Growth endpoints for plants and reproduction endpoints for soil invertebrates are more sensitive to survival.

Table 7-3. Key	soil toxicity	studies c	onsidered in de	etermining a	critical toxicity
value for soil					

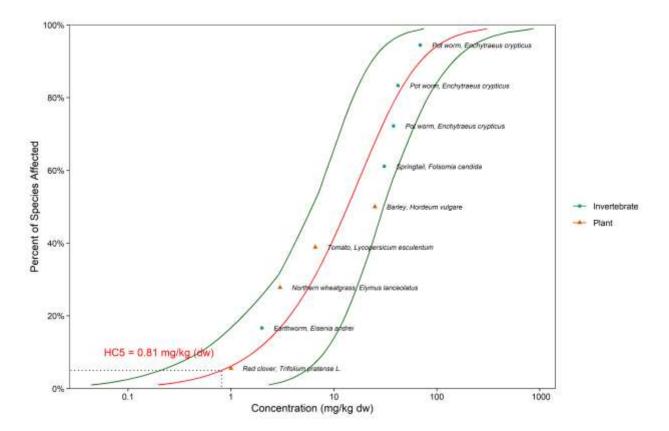
Group	Test organism	Endpoint	Value <sup>a</sup> (mg/kg dw)	Reference
Plant	Barley ( <i>Hordeum vulgare</i> )	5-day EC <sub>10</sub> , root length	25	Langdon et al. 2015
Plant	Northern wheatgrass ( <i>Elymus</i> <i>lanceolatus</i> )	21-day EC <sub>10</sub> , root/shoot dry mass	3	ECSTL 2011

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

Abbreviations: dw = dry weight; EC<sub>10</sub> = 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.

<sup>a</sup> The toxicity endpoints listed are for soil toxicity tests performed with AgNO<sub>3</sub> and are used in the SSD approach in deriving a silver soil PNEC. The full dataset of soil toxicity studies found to be reliable is summarized in Appendix F.

<sup>b</sup> Geometric means calculated for the SSD data points.



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

Model averaged (i.e., normal, logistic, gamma) SSDs and associated statistics including the HC5 (5<sup>th</sup> percentile, representing the hazardous concentration to 5% of soil-dwelling organisms) were generated using the ssdtools software (Dalgarno 2018). The estimated HC5 of the average distribution is 0.81 mg/kg (Figure 7-1). A factor of 1 each was applied to account for endpoint standardization, species variation, and mode of action, respectively, because data were available for a large number of species representing multiple categories of organisms. This value is selected as the PNEC for long-term silver soil toxicity.

Chronic PNEC<sub>soil</sub> = 0.81 mg Ag<sub>Total</sub>/kg (or  $\mu$ 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 sources: (1) metal mining; (2) base metals smelting and refining (BMS); (3)

wastewater; and (4) waste disposal. The metal mining and BMS sectors are implicated in the production of silver. Wastewater systems (WWS) receive consumer, commercial, and industrial effluents that may contain silver, and therefore, treated effluents from WWSs may release silver to the environment.<sup>8</sup> Finally, silver-containing products may be disposed of in landfills and silver may 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 and base metal smelting and refining sectors. Where measured concentration data were not available, PECs were modeled from other types of data.

PECs for wastewater effluents and leachate concentrations were calculated from effluent/leachate concentrations (C<sub>a</sub>), as described in the equation below. Median background concentrations (C<sub>b</sub>) for silver were derived for corresponding ecozones and the Great Lakes (Table D-1, Appendix D). A dilution factor appropriate for the given waterbody was applied to reflect conditions near the discharge point and capped at a maximum of 10. Background concentrations were accounted for to reflect the natural presence of silver at the discharge point.

$$\textit{PEC} (\mu g/L) = C_b (\mu g/L) + \left(\frac{C_a (\mu g/L)}{DF}\right)$$

The exposure characterization considers dissolved silver concentrations, where available, and total 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 with estimated concentrations ranging from 0.07 mg/kg (Yaroshevsky 2006) to 0.1 mg/kg (Purcell and Peters 1998). Ambient concentrations of silver in the atmosphere are unavailable, but WHO (2002) has

<sup>&</sup>lt;sup>8</sup> In this assessment, the term "wastewater 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 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 systems" and/or "industrial wastewater systems."

estimated that typical urban air concentrations of silver would be less than 0.00005 mg/m<sup>3</sup>. Background concentrations of silver in fresh waters vary; they are the highest near mineral deposits (Purcell and Peters 1998), but are generally in the sub- $\mu$ g/L range.

Background concentration ranges (expressed as normal ranges) and medians of total silver (Ag<sub>T</sub>) in fresh waters were estimated by Kilgour & Associates Ltd. (2016) for Canadian ecozones using water quality monitoring data from various federal and provincial sources.<sup>9</sup> Only samples considered to be in reference condition, according to the approach outlined in Proulx et al. (2018), were included in the derivation of these statistics (see Appendix D). Median background concentrations of Ag<sub>T</sub> 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. In all cases, non-detect measurements were treated prior to analysis by substituting with one-half the reported MDL. Background median concentrations were highest in the Mixedwood Plains ecozone. Concentrations in the Great Lakes were especially low (medians of 0.0005 µg Ag<sub>T</sub>/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) (i.e., the maximum expected background concentration in this assessment). 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  $\mu$ g/L).

Background concentrations of silver in the marine environment are 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<sub>D</sub>) in the North Pacific Ocean and total silver in the North Atlantic Ocean are 0.0011  $\mu$ g Ag<sub>D</sub>/L (n=22) (Kramer et al. 2011) and 0.00032  $\mu$ g Ag<sub>T</sub>/L (n=9) (Rivera-Duarte et al. 1999), respectively.

## 7.2.3 Metal mining

Exposure of ecological receptors to silver may occur through metal mining activities that release effluents into surface waters. The *Metal and Diamond Mining Effluent Regulations* (MDMER) prescribe the maximum authorized concentration limits for deleterious substances in mine effluent. Environmental effects monitoring (EEM) is also required by the MDMER, which includes analyzing certain water quality and sediment parameters in exposure and reference areas. Silver is not a parameter monitored under

<sup>&</sup>lt;sup>9</sup> The references cannot be provided because the identities of the WWSs cited here are confidential.

the MDMER; however, EEM studies submitted to ECCC may contain additional information, including data for Ag<sub>T</sub> and Ag<sub>D</sub> concentrations in effluents, exposure areas, and reference areas. According to the most recent status report on the performance of metal mines subject to the Regulations, at least 22 sites involving metal mining activities were associated with silver production in 2017 (ECCC 2018b). Between these sites there are 18 sites which have EEM studies providing freshwater concentrations of silver.

Silver freshwater data were systematically extracted from the EEM studies (up to 2018) available for 18 of the sites that are involved in silver production. For each site, the most recent report was investigated first. If the most recent report did not contain silver data, the next most recent report was investigated and so on. If the most recent report contained freshwater concentrations of silver that were in excess of the freshwater PNEC (0.25  $\mu$ g AgT/L), all data from previous reports, if any, were also extracted for analysis. If the most recent report did not contain freshwater concentrations of silver in excess of the freshwater PNEC, previous reports were not investigated. Overall, 3 of the 18 sites have silver concentrations above the freshwater PNEC. Data for two of the sites are presented in Table 7-4 (one of the sites was excluded, as the corresponding mine has been closed for over 5 years). It is important to note that MDLs across the EEM studies investigated here (i.e., 0.005 to 0.20  $\mu$ g/L) were below the freshwater PNEC of 0.25  $\mu$ g AgT/L. Silver was not detected in the majority of freshwater samples.

Site	Area type	Period	Fractio	Sampl	Percen	PEC	PEC
			n	e size	tage of	range	median
					detects	(µg/L)	(µg/L)
Site 1	Exposure	2010 to	Т	82	65%	<0.01 to	0.02
		2012;				9.94	
		2015 to					
		2018					
Site 1	Exposure	2015 to	D	46	9%	<0.01 to	<0.10
		2018				0.035	
Site 1	Reference	2010 to	Т	116	29%	<0.01 to	<0.10
		2012;				0.231	
		2015 to					
		2018					
Site 1	Reference	2015 to	D	70	7%	<0.01 to	<0.10
		2018				0.075	
Site 2 <sup>b</sup>	Exposure	2004,	Т	19	10%	<0.02 to	<0.10
		2007,				<10	
		2011					
Site 2 <sup>b</sup>	Exposure	2004,	D	13	23%	<0.01 to	<0.10
		2011				0.2	
Site 2 <sup>b</sup>	Reference	2004,	Т	13	7.7%	<0.10 to	<0.10
		2007,				0.30	
		2009					

Table 7-4. Silver freshw	ater concer	ntrations	in expos	ure and re	eference ai	reas of
metal mines subject to	the Metal a	nd Diamo	nd Minin	g Effluen	t Regulatio	ons <sup>a</sup>

Site	Area type	Period	Fractio n	Sampl e size	Percen tage of detects	PEC range (μg/L)	PEC median (μg/L)
Site 2 <sup>b</sup>	Reference	2004, 2007	D	10	0%	<0.10	<0.10

Abbreviations: T, total; D, dissolved.

<sup>a</sup> Data were extracted from EEM studies (EEM 2021)

<sup>b</sup> Site 2 activities includes those from base metal smelting and refining (i.e., Site 2 in section 7.2.5).

Silver concentrations in sediments were extracted from the most recent EEM studies (up to 2020). Exposure and reference area data were available for 12 silver producers. Table 7-5 presents data for the sites where concentrations in the exposure area exceed the sediment PNEC of 1.0  $\mu$ g/g dw. Concentrations of silver in Site 2 exposure area sediments may have increased up to 2011 and remained comparable in 2018 (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; range of 4.13 to 12.5 mg/kg, average of 8.4 mg/kg in 2018).

Table 7-5. Silver sediment concentrations in exposure and reference areas of	
metal mines subject to the Metal and Diamond Mining Effluent Regulations <sup>a</sup>	

Site	Area	Period	Sample	Sample	Percen-	PEC	PEC
	type		depth	size	tage of	range	median
			(cm)		detects	(µg/g dw)	(µg/g dw)
Site 2 <sup>b</sup>	Exposure	2004,	0 to	29	93%	<0.20 to	6.0
		2007,	approx.			21	
		2011,	10 <sup>c</sup>				
		2018					
Site 2 <sup>b</sup>	Referenc	2004,	0 to	10	70%	< 0.20 to	0.90
	е	2007,	approx.			1.25	
		2009	10 °				
Site 3	Exposure	2018	NR	5	100%	0.691 to	2.18
	-					6.05	
Site 3	Referenc	2018	NR	2	100%	0.294 to	0.322
	е					0.350	
Site 4	Exposure	2005,	NR	10	100%	0.46 to	1.95
		2019				8.4	
Site 4	Referenc	2005,	NR	10	90%	<0.2 to	1.05
	е	2019				2.5	
Site 5	Exposure	2017	NR	4	100	1.44 to	2.28
						2.53	
Site 5	Referenc	2017	NR	4	100	1.40 to	1.29
	е					1.35	

Abbreviations: NR, not reported.

<sup>a</sup> Data were extracted from EEM studies (EEM 2021)

<sup>b</sup> Site 2 activities include those from base metal smelting and refining (i.e., also Site 2 in section 7.2.5).

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

#### 7.2.4 Base metal smelting and refining

Currently, there are 10 base metal 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. Information on freshwater concentrations of silver was extracted from the associated EEM studies (up to 2018), where available (Table 7-6). Similar to the metal mining facilities, MDLs across the EEM studies investigated here were below the freshwater PNEC (0.25  $\mu$ g AgT/L) and the majority of the silver freshwater concentration data were non-detects (i.e., below the MDL).

 Table 7-6. Silver freshwater exposure and reference areas of base metal smelting activities subject to the Metal and Diamond Mining Effluent Regulations <sup>a</sup>

Site	Area type	Period	Fraction	Sample	Percen	PEC	PEC
				size	tage of detects	range (µg/L)	Median (µg/L)
Site 1	Exposure	2008, 2010	Т	7	14%	<0.10 to 0.16	<0.10
Site 1	Reference	2008, 2010	Т	11	9%	<0.10 to 0.18	<0.10
Site 2 <sup>b</sup>	Exposure	2004, 2007, 2011	Т	19	10%	<0.02 to <10	<0.10
Site 2 <sup>b</sup>	Exposure	2004, 2011	D	13	23%	<0.01 to 0.2	<0.10
Site 2 <sup>b</sup>	Reference	2004, 2007, 2009	Т	13	7.7%	<0.10 to 0.30	<0.10
Site 2 <sup>b</sup>	Reference	2004, 2007	D	10	0%	<0.10	<0.10
Site 3	Exposure	2005, 2008, 2012	Т	12	50%	<0.010 to 0.50	<0.10
Site 3	Reference	2005, 2008, 2012	Т	12	50%	<0.010 to 0.50	<0.10
Site 4	Exposure	2015	Т	6	17%	<0.010 to 0.016	<0.010
Site 4	Exposure	2015	D	6	0%	<0.010	<0.010
Site 4	Reference	2015	Т	5	20%	<0.010 to 0.011	<0.010
Site 4	Reference	2015	D	5	0%	<0.010	<0.010

Abbreviations: T, total; D, dissolved.

<sup>a</sup> Data were extracted from EEM studies (EEM 2021)

<sup>b</sup> Site 2 represents releases of BMS and metal mining effluent (i.e., Site 2 in section 7.2.4).

Silver concentrations in sediments were extracted from the most recent EEM studies (up to 2020). Exposure and reference area concentrations were available for four BMS associated with silver producers (Table 7-7). The data for Site 2, which represents releases of BMS and metal mining effluent, is in excess of the sediment PNEC derived for this assessment. As noted in section 7.2.4, concentrations of silver in the exposure area sediments of Site 2 appear to have increased up to 2011 and remained comparable in 2018.

Table 7-7. Silver sediment concentrations in exposure and reference areas of
base metal smelting and refining activities subject to the Metal and Diamond
Mining Effluent Regulations <sup>a</sup>

Site	Area type	Period	Sample depth (cm)	Sampl e size	Percenta ge of detects	PEC range (µg/g dw)	PEC median (μg/g dw)
Site 1	Exposure	2013, 2018	NA	10	0%	<0.5	<0.5
Site 1	Reference	2013, 2018	NA	12	0%	<0.5	<0.5
Site 2 <sup>b</sup>	Exposure	2004, 2007, 2011, 2018	0 to approx. 10 <sup>c</sup>	29	93%	<0.20 to 21	6.0
Site 2 <sup>b</sup>	Reference	2004, 2007, 2009	0 to approx. 10 <sup>c</sup>	10	70%	<0.20 to 1.25	0.90
Site 3	Exposure 1	2008, 2012	NA	13	100%	0.06 to 0.476	0.23
Site 3	Reference	2008, 2012	NA	8	62%	<0.05 to 0.201	0.07
Site 4	Exposure	2011, 2015	0 to 4.0	20	100%	0.12 to 0.26	0.18
Site 4	Reference	2011, 2015	0 to 4.0	20	90%	<0.10 to 0.25	0.20

Abbreviations: NA, not available.

<sup>a</sup> Data were extracted from EEM studies (EEM 2021).

<sup>b</sup> Site 2 activities includes those from metal mining activities (i.e., Site 2 in section 7.2.4).

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

Data for one facility not subject to the MDMER were extracted from a comprehensive monitoring report (EEC Ltd and LAC Ltd 2014). Freshwater concentrations of Ag<sub>T</sub> and Ag<sub>D</sub> at two locations upstream and at three locations downstream of the site were measured (Table 7-8). All concentrations were below MDL (0.02  $\mu$ g/L or 0.05  $\mu$ g/L).

Sediment data were also available in this report for three upstream reference areas and five downstream exposure areas for October 2012 (Table 7-8). 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 7-8. Silver freshwater and sediment concentrations in exposure and
reference areas of one base metal smelting facility not subject to the Metal and
Diamond Mining Effluent Regulations (EEC Ltd and LAC Ltd 2014)

Compart ment	Area type	Period	Fraction	Sample size	Percenta ge of detects	PEC range (μg/L or μg/g dw)	PEC median (μg/L or μg/g dw)
Freshwate r	Exposure	2012- 2016	Т	337	0%	<0.005 to <0.02	<0.005
Freshwate r	Exposure	2012- 2016	D	337	0%	<0.005 to <0.02	<0.005
Freshwate r	Referenc e	2012- 2016	Т	71	0%	<0.005 to <0.02	<0.005
Freshwate r	Referenc e	2012- 2016	D	71	0%	<0.005 to <0.02	<0.005
Sediment	Exposure	2012	E	7	100%	0.6 to 5.7	1.4
Sediment <sup>a</sup>	Referenc e	2012	E	3	0%	<0.2	0.1

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

<sup>a</sup> Concentrations reflect the first 0 to 15 cm of homogenized cores.

## 7.2.5 Wastewater

Silver may be present in wastewaters generated from consumer, commercial, and industrial sources and therefore may be a constituent of the influent received by WWSs. Municipal by-laws concerning the discharge of wastewater (i.e., influents) to WWSs 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 to 5.0 mg Ag<sub>T</sub>/L.<sup>10</sup> Because WWS processes do not use silver compounds, the treatment processes do not contribute to the silver content of the effluents released into the environment. The federal *Wastewater System Effluent Regulations* (Canada [modified 2015]) do not prescribe final effluent limits for silver.

<sup>&</sup>lt;sup>10</sup> The references cannot be provided because the identities of the WWSs cited here are confidential.

Empirical monitoring data for silver in influents, effluents, and biosolids were collected under the CMP Environmental Monitoring and Surveillance Program from 36 WWSs located across Canada from February 2009 to 2014 and 2018 to 2019 (Environment Canada 2013b; Environment Canada 2015; ECCC 2019). Results from this initiative show that influent concentrations of total silver (Ag<sub>T</sub>) are low and that there is a high degree of partitioning to solids (Environment Canada 2013b). Total silver concentrations (Ag<sub>T</sub>) were detected in 64 of 191 influent samples and in 30 of 191 final effluent samples, with maximums of 6.55 and 2.55 µg/L, respectively, of the 25 WWSs sampled from 2009 to 2012. The median removal value for Ag<sub>T</sub> was 88.6% (N = 64 paired influent and effluent samples). The biosolid samples contained Ag<sub>T</sub> in the range of  $\mu g/g$ , 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 WWS). Final effluent concentrations of Ag<sub>T</sub> were low and frequently below detection limits. Unfiltered samples were digested and analyzed for total silver using inductively coupled plasma methods as per standard methods (APHA et al. 2005). The MDLs for effluent quantitation were 0.0005  $\mu$ g/L, 0.005  $\mu$ g/L or 0.02  $\mu$ g/L for Ag<sub>D</sub> and Ag⊤.

Figures 7-2 and 7-3 present dissolved and total silver PECs for 21 and 36 WWSs that release effluent to either the freshwater (FW) or the marine water (MW) environment (see section 7.2.6 for more details on the PEC calculations). Effluent non-detect data were substituted with one-half MDL.

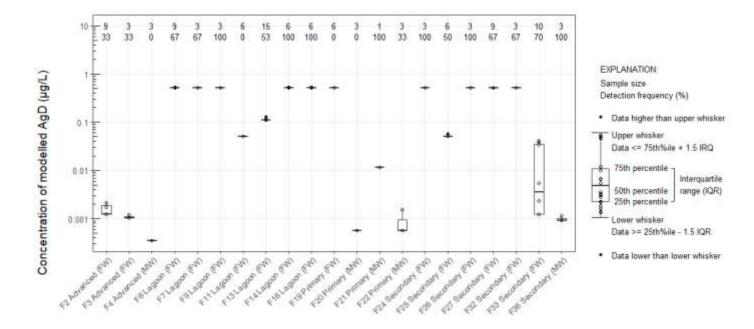
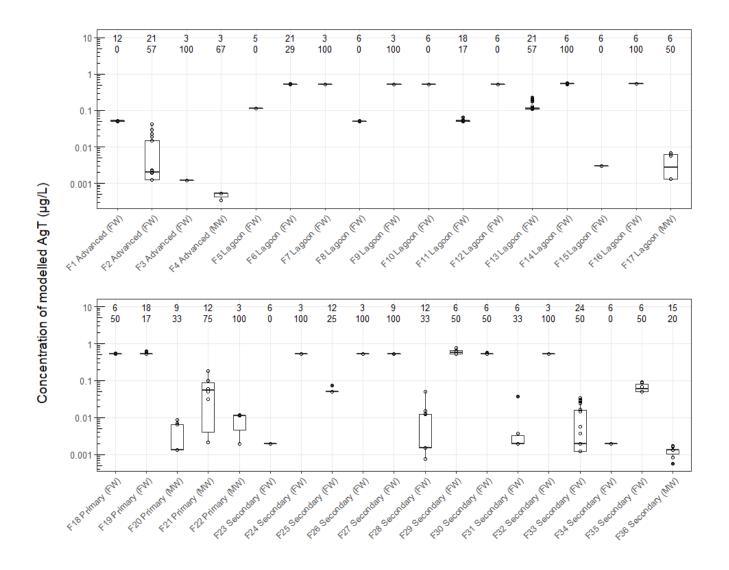


Figure 7-2. Box plots of modelled aquatic dissolved silver concentrations for 22 wastewater systems from 2013 to 2014 and 2018 (Environment Canada 2015, ECCC 2019).



## Figure 7-3. Box plots of modelled aquatic total silver concentrations for 36 wastewater systems from 201309 to 2014 and 2018 (Environment Canada 2013b, Environment Canada 2015, ECCC 2019).

See Figure 7-2 for an explanation of the data presentation in the box plots.

Silver was not detected in the final effluents of the majority of WWSs. In some cases, silver was detected in the final effluents less than 50% of the time. WWSs within the Mixedwood Plains ecozone have the highest PECs possibly related to the relatively high median background concentration of silver (i.e., 0.52  $\mu$ g Ag<sub>T</sub>/L) compared to other ecozones.

Total silver was detected in most solid samples (307 of 325) collected at the 25 WWSs (Environment Canada 2013b). Concentrations of Ag<sub>T</sub> in primary sludge, secondary sludge, and biosolids ranged from <0.0005 to 18.3  $\mu$ g/g, from <0.0005 to 8.19  $\mu$ g/g, and from <0.0002 to 16.4  $\mu$ g/g, respectively. Biosolids from WWSs 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.

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

To simulate a conservative 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/m<sup>3</sup> were used (Williams 1999), along with the highest concentration of silver measured in biosolids (16.4 mg/kg dw) from WWSs 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  $\mu$ g/g) dw.

### 7.2.6 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 14 larger landfills across Canada between 2008 and 2014 (Conestoga-Rovers and Associates 2015) and in 2020 (ECCC 2020) under the CMP monitoring program. Total and dissolved silver concentrations were measured in leachates before treatment, and for some landfills, after treatment. MDLs ranged from 0.001 to 10  $\mu$ g Ag/L.

Prior to treatment, concentrations in leachates ranged from <0.005 to 3.00  $\mu$ g AgT/L<sup>11</sup> (median of <1  $\mu$ g AgT/L; n=116; N=14)<sup>12</sup> and from <0.005 to 1.21  $\mu$ g AgD/L (median of 0.011  $\mu$ g AgD/L; n=47; N=5). Post-treatment concentrations ranged from <0.005 to 0.547  $\mu$ g AgT/L (median of <1  $\mu$ g AgT/L; n=26; N=5) and from <0.005 to 0.182  $\mu$ g AgD/L (median of <0.005  $\mu$ g AgD/L; n=1). Twelve landfills send their leachates to WWSs while three landfills release their leachates, treated (N=2) or untreated (N=1), directly to the environment. Concentrations of silver were not detected in leachates released directly to the environment, possibly due to high MDLs (<1 to <10  $\mu$ g AgT/L, median of <1  $\mu$ g AgT/L; n=26). Table 7-9 presents the PECs generated for these three landfills (see section 7.2.6 for more details on the PEC calculations).

<sup>&</sup>lt;sup>11</sup> The maximum is the highest detected value reported.

<sup>&</sup>lt;sup>12</sup> The symbols "n" and "N" represent the sample size and number of facilities, respectively.

Table 7-9. Landfill leachate predicted environmental concentrations based on preor 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) and in 2020 (ECCC 2020)

Land fill site	Measure- ment type	Sampl e size (% detect s)	Pre- treatme nt range (µg /L)	Post- treatment range (µg/L)	Median backgrou nd concen- tration (μg/L)	PEC range (µg/L)	PEC media n (μg/L)
1	Total	6 (0%)	<0.10 to <10	NR	0.11	0.12 to 0.61	0.16
2	Total	6 (0%); 6 (0%)	<0.10 to <10	<0.10 to <10	0.050	0.055 to 0.55	0.10
3	Total	6 (0%); 3 (0%)	<0.10 to <10	<0.10 to <10	0.52	0.52 to 1.0	0.57

Abbreviations: NR: not reported.

## 7.3 Characterization of ecological risk

The approach taken in this characterization of ecological risk involved the examination of assessment information and development of 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 screening assessment that support the characterization of ecological risk in the Canadian environment.

### 7.3.1 Risk quotient analysis

Risk quotient (RQ) analyses involved comparing estimates of exposure, with ecotoxicity information to determine whether there is potential for ecological harm in the Canadian environment. RQs were derived by dividing the predicted environmental concentrations (PECs) from the exposure scenarios by the predicted no-effect concentrations (PNECs) for the appropriate environmental compartments. RQs for metal mining, base metal smelting and refining, wastewater, and landfill disposal are presented below (Table 7-10). Non-detect concentrations (i.e., PECs below the method detection limit (MDL)) were substituted with one-half the MDL before calculating RQs.

 Table 7-10. Summary of risk quotients obtained for different environmental compartments and exposure scenarios for silver and its compounds

Sector Source (number of facilities or sites)	Compart- ment	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) <sup>a</sup>	Water	Т	<0.003- 9.94 <sup>b</sup>	0.02 to 0.05	0.0006 to 40 <sup>b</sup>	0.04 to 0.2
Metal mining (N=2) <sup>a</sup>	Water	D	<0.01 to 0.20	0.05	0.02 to 0.8	0.2
Metal mining (N=4) <sup>c</sup>	Sediment	Е	<0.20 to 21	1.95 to 6.0	0.1 to 21	1.95 to 6.0
Base metal smelting and refining (N=4) <sup>d</sup>	Water	Т	<0.01 to 0.5	0.005 to 0.05	0.02 to 2	0.02 to 0.2
Base metal smelting and refining (N=4) <sup>d</sup>	Water	D	<0.01 to 0.2	0.005 to 0.05	0.02 to 0.8	0.02 to 0.2
Base metal smelting and refining (N=4) <sup>d</sup>	Sediment	Τ, Ε	0.06 to 21	0.18 to 6.0	0.06 to 21	0.18 to 6.0
Base metal smelting and refining (N=1) <sup>e</sup>	Water	Т	<0.005 to <0.02	0.0025	0.01 to 0.04	0.01
Base metal smelting and refining (N=1) <sup>e</sup>	Water	D	<0.005 to <0.02	0.0025	0.01 to 0.04	0.01
Base metal smelting and refining (N=1) <sup>e</sup>	Sediment	Е	0.6 to 5.7	1.4	0.6 to 5.7	1.4
Wastewater treatment (biosolids land- application) (N=1) <sup>f</sup>	Soil	т	0.6	N/A	0.7	N/A
Waste disposal (N=3) <sup>g</sup>	Water	Т	0.055 to 1.0	0.10 to 0.57	0.22 to 4.1	0.40 to 2.3

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

<sup>a</sup> One of these sites (Site 2) includes base metal smelting activities.

<sup>b</sup> The highest detect value is reported.

<sup>c</sup> This site includes metal mining activities.

<sup>d</sup> These BMS activities are subject to the MDMER because their effluents are combined with those from metal mining activities; upper end of the range is based on non-detect values.

<sup>e</sup> This BMS facility is not subject to the MDMER.

<sup>f</sup> 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<sub>T</sub>/g dw).

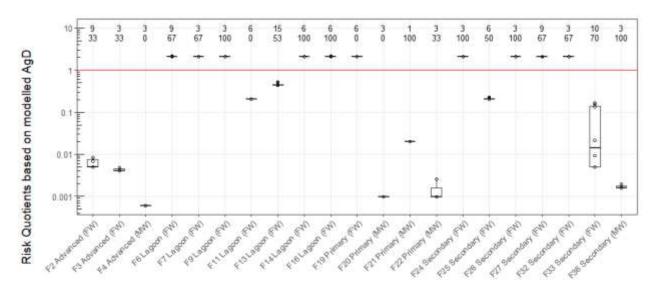
<sup>9</sup> These three landfills release directly to the environment (i.e., do not pass through a WWS first); all of the PECs were derived from non-detect concentrations.

Regarding the metal mining sector (data were available for 18 sites that produce silver) and the base metal smelters subject to the MDMER (four sites), the RQs developed for exposure of ecological receptors to silver in the freshwater compartment suggest low potential for ecological harm. For the analyses using total silver concentrations, RQs greater than 1 are infrequent and of low magnitude (5 of 43 for metal mining Site 1; 2 of 19 for metal mining and base metal smelting Site 2: 2 of 12 for base metal smelting Site 3) and if accompanied by corresponding dissolved silver concentrations, the RQs for dissolved silver are less than 1. Further, the majority of the water concentration data collected from the EEM studies of the 18 sites 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<sub>T</sub>/kg dw), potential ecological harm is found for two sites (metal mining and BMS Site 2 and metal mining Site 3). The exposure concentrations for these sites are also elevated (e.g., Site 2; n=29; median PEC=6.0 mg/kg) compared to upstream reference area concentrations (e.g., Site 2; n=10; median PEC=0.9 mg/kg). Potential for ecological harm in sediments is also observed at metal mining sites 4 and 5; however, reference sediments have comparable silver concentrations.

The RQ analysis of one base metal smelter not subject to the MDMER indicates low potential ecological harm in the freshwater compartment. However, it indicates potential ecological harm 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).

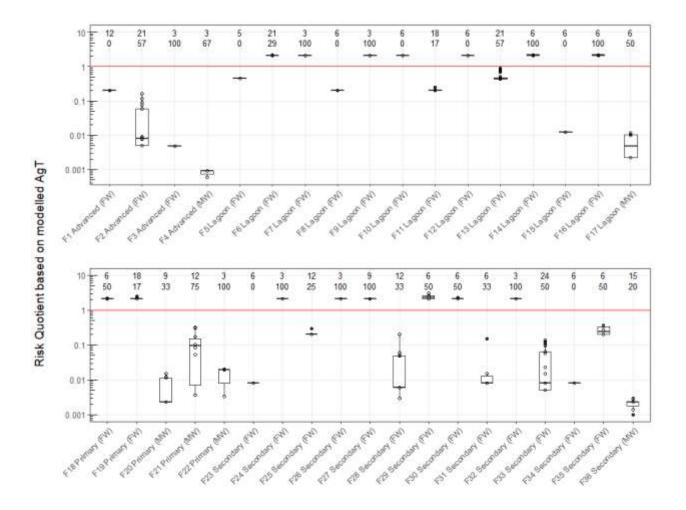
For wastewaters, 10 of 22 wastewater systems (WWSs) and 15 of 36 WWSs with Ag<sub>D</sub> and Ag<sub>T</sub> effluent concentrations, respectively, have RQs greater than 1 in the freshwater compartment (Figures 7-4 and 7-5). All of these facilities are located in the Mixedwood Plains ecozone, which has naturally elevated background concentrations of silver (the maximum expected background concentration of Ag<sub>T</sub> is 2.1 µg/L). The median background concentration of Ag<sub>T</sub> used to model the PECs for facilities in this ecozone (0.52 Ag<sub>T</sub>/L) 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<sub>T</sub> and that effluent concentrations are generally low (range of <0.005 to 0.420 µg Ag<sub>D</sub>/L, <0.005 to 2.52 µg Ag<sub>T</sub>/L), the risk characterization of wastewaters indicates low potential for ecological harm in the freshwater compartment. No data are available for the sediment compartment downstream of WWSs. A conservative exposure scenario for concentrations of silver in soil following the

application of silver-containing biosolids to land (0.6  $\mu$ g Ag<sub>T</sub>/g, dw) resulted in an RQ below 1 when comparing it to the chronic PNEC generated for soil organisms (0.81  $\mu$ g Ag<sub>T</sub>/g,dw). Therefore, ecological risk in the soil compartment is not expected following land application of silver-containing biosolids from WWSs.



## Figure 7-4. Box plots of risk quotients based on modelled aquatic dissolved silver concentrations for 22 wastewater systems from 2013 to 2014 and 2018 (Environment Canada 2015, ECCC 2019).

See Figure 7-2 for an explanation of the data presentation in the box plots.



# Figure 7-5. Box plots of risk quotients based on modelled aquatic total silver concentrations for 36 wastewater systems from 2009 to 2014 and 2018 (Environment Canada 2013b, Environment Canada 2015, ECCC 2019).

See Figure 7-2 for an explanation of the data presentation in the box plots.

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

### 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

screening assessment) and qualitatively weighted. The key lines of evidence supporting the assessment conclusion are presented in Table 7-11, 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.

Line of evidence	Level of confidence <sup>a</sup>	Relevance in assessment <sup>b</sup>	Weight assigned <sup>c</sup>
Persistence	High	High	High
Bioaccumulation in aquatic and/or terrestrial organisms	High	High	High
PNEC for aquatic organisms in freshwater	High	High	High
PNEC for aquatic organisms in marine water	Moderate	Moderate	Moderate
PNEC for benthic organisms in sediment	Moderate	Moderate	Moderate
PNEC for organisms in soil	High	High	High
PECs based on measurements in freshwater – metal mining	High	High	High
PECs based on measurements in freshwater – base metal smelting and refining	High	High	High
PECs modelled for freshwater – wastewaters	Moderate	Moderate	Moderate
PECs modelled for freshwater – waste disposal	Low	Moderate	Low to moderate
PECs based on measurements in sediment – metal mining	Moderate	Moderate	Moderate
PECs based on measurements in sediment – base metal smelting and refining	Moderate	Moderate	Moderate
PEC modelled for soil – land application of biosolids	Moderate	Moderate	Moderate
RQs for freshwater – metal mining	High	High	High

 Table 7-11. Weighted lines of key evidence used for the ecological assessment of silver and its compounds

Line of evidence	Level of confidence <sup>a</sup>	Relevance in assessment <sup>b</sup>	Weight assigned <sup>c</sup>
RQs for freshwater – base metal smelting and refining	High	High	High
RQs for freshwater – wastewaters	Moderate	Moderate	Moderate
RQs for freshwater – waste disposal	Low	Moderate	Low to 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 (wastewaters )	Moderate	Moderate	Moderate

Abbreviations: PNEC, predicted no-effect concentration; PEC, predicted environmental concentration; RQ, risk quotient.

<sup>a</sup> Level of confidence is determined according to data quality, data variability, and data gaps (i.e., are the data fit for purpose).

<sup>b</sup> Relevance refers to the impact of the evidence in the assessment.

<sup>c</sup> 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 silver in tissues and internal organs, but they have mechanisms to regulate concentrations and detoxify. 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 fresh waters or land. Following release to the freshwater 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 less likely to resupply free 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 sediments.

It was determined that there is low potential for ecological harm from the release of silver to fresh water from metal mining, base metal smelting and refining (BMS), wastewaters, and waste disposal. Instances of PNEC exceedances were either infrequent or associated with non-detects.

There may be moderate ecological harm caused by silver in sediment. Sediment data are available for four of five BMS sites subject to the MDMER, of which only one site (Site 2) has downstream sediment concentrations of silver in excess of the sediment PNEC (n=29, median=6.0 µg/g). This site also represents metal mining activities. It is unclear whether these concentrations increased from 2004 to 2011 and remained stable to 2018, or if they represent variability in the exposure area, because the sediment cores were not obtained in the same locations between years. Some reference area concentrations also exceed the sediment PNEC, but at a lower frequency (median=0.9µg/g). Some concentrations of silver in the sediments downstream of the BMS facility not subject to the MDMER are also slightly above the sediment PNEC. Sediment data for four sites associated with mining activity also show elevated downstream concentrations (compared to reference concentrations) that exceed the PNEC, but are based on limited datasets. The median silver sediment concentration downstream from the BMS facility not subject to the MDMER was 1.4 µg/g, which is in exceedance of the sediment PNEC. Low amounts of complexing ligands (e.g., low organic carbon and clay contents) reported at the sampling location may suggest higher potential for silver bioavailability to benthic organisms at the vicinity of the exposure area. Considering the datasets are small and either have weak temporal and spatial correlations or are limited to one year, the weight assigned is moderate. Furthermore, 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 Site 2 but considered relevant for the BMS facility not subject to the MDMER.

Given silver's high affinity for binding to particles, WWSs have high removal values. A conservative risk characterization scenario for the land application of silver-containing biosolids indicates low potential for ecological harm in the soil compartment.

This information indicates that silver and its compounds have low potential to cause ecological harm in the freshwater and soil compartments in Canada. Silver and its compounds have a moderate potential to cause ecological harm in the sediment compartment, but confidence in this line of evidence is reduced due to uncertainties around the sediment PNEC and 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, silver may have an environmental effect of concern given its potential to cause adverse effects on sediment-dwelling 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, and their impact on the 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 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 2017, releases are low.

The data used in the exposure scenarios for the four sources examined in this screening assessment are not comprehensive. Only about one-fifth of the over 100 metal mines in Canada (ECCC 2018b) and about one-third of the 13 active BMS facilities had data to consider in this assessment. However, given that silver is a precious metal, there is incentive to limit releases into the environment. The exposure scenarios for wastewaters and waste disposal included relatively small subsets of Canada's many WWSs and landfills. For wastewater systems (WWSs), the subset of systems was selected to be representative of Canadian wastewater treatment types and of different locations around the country (e.g., Atlantic, Central, and Western Canada). The majority of Canada's wastewater (by volume) receives secondary level of treatment, and the most prevalent method of wastewater treatment by number of systems is lagoons, which is reflected by the WWSs included in the exposure assessment (personal communication, email from the Emerging Priorities Division, Environment and Climate Change Canada, to the Ecological Assessment Division, Environment and Climate Change Canada, dated January 16, 2020; unreferenced). The subset of sites for landfills is also considered representative because it includes some of the largest landfills in Canada.

#### **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 AgNO<sub>3</sub>) that readily dissociate and release the free Ag<sup>+</sup> ion, which is the most bioavailable and toxic form of silver. Typically, toxicity test media 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 them 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 silver to freshwater organisms is not available at this time (CCME 2015a; Wood 2012).

The 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  $\mu$ m) and colloids (>0.45  $\mu$ m) in fresh waters (Andren and Bober 2002; Shafer et al. 1996; Wen et al. 1997). Thus, free ionic silver 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, this conservatism was considered in the ecological risk characterization of silver, where potential for ecological harm in the water and sediment was interpreted to be low under current levels of exposure.

#### Freshwater compartment

Non-detect data were prevalent in the aquatic datasets analyzed in this screening assessment. Their presence was inconsequential for the metal mining and BMS sectors since MDLs were below the PNEC. PECs modeled from non-detects for wastewaters were not the drivers behind instances of RQs greater than 1. However, the waste disposal dataset contained non-detect PECs higher than the freshwater PNEC due to high MDLs (e.g.,  $10 \mu g/L$ ). This leaves uncertainty as to whether or not potential for ecological harm is present at the sampling sites. As mentioned, it is predicted that only a very small fraction of total silver concentrations is bioavailable (WHO 2002). Therefore, the conclusion considers these uncertainties for waste disposal.

#### Sediment compartment

Sediment data are limited for the sectors and sources investigated. The NPRI analysis indicates that releases of silver to water from 2012 to 2017 are low. While releases may be low, silver is expected to partition to sediment rapidly (Andren and Bober 2002). Sediment concentrations of silver associated with wastewaters and waste disposals are unavailable.

The silver sediment PNEC was derived from a study in which silver bioavailability was likely high due to a low amount of silver complexing ligands. The site-specific sediment characteristics can influence the bioavailability and toxicity of silver to sediment organisms. Therefore, the PNEC may be considered conservative in some cases, such as for the BMS facility subject to the MDMER (Site 2). For the BMS facility not subject to the MDMER, the sediment PNEC may not necessarily be conservative because the sediment composition downstream is likely more susceptible to be available for benthic organisms with low amounts of silver complexing ligands at the exposure area of the

facility. 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 possible that silver will be mostly bound to sulfides, where they are not bioavailable but may be ingested by benthic organisms.

#### Soil compartment

Soil data are not available for the sectors and sources investigated. The NPRI analysis indicates that releases of silver to air and land from 2012 to 2017 are low or negligible, respectively, and given this, it is unlikely that silver deposition or release to land from the sectors and sources investigated is occurring in concerning amounts. Further, the conservative risk characterization for the land-application of silver-containing biosolids indicates low potential for ecological harm in the soil compartment. Therefore, the 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 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 2011). While some recent reviews have focused mainly on nanosilver, the focus of this screening 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 United States Environmental Protection Agency (U.S. EPA) derived a reference dose (RfD) 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 screening 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 Maternal-Infant Research on Environmental Chemicals (MIREC) Child Development (CD) Plus study, a MIREC follow-up study (Table 8-1).

A BE of 0.4 µg/L for ionic silver associated with the U.S. EPA 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 95<sup>th</sup> percentile of blood concentrations from the biomonitoring data are presented in Table 8-1 below.

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

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

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

<sup>a</sup> Health Canada 2013, n=6070.

<sup>b</sup> 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 screening assessment, there is low risk of harm to the environment from silver and its compounds. It is concluded 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 screening assessment, it is concluded 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 concluded 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.

## References

[Alexco] Alexco Resource Corp. 2019. <u>Alexco</u>. Vancouver (BC): Alexco Resource Corp. [accessed 2019 Feb 4]. Bellekeno project.

Andren AW, Bober TW, editors. 2002. Silver in the environment: transport, fate, and effects. Pensacola (FL): Society of Environmental Toxicology and Chemistry. 192 p.

[APHA] American Public Health Association, Eaton AD, American Water Works Association, and Water Environment Federation. 2005. Standard Methods for the Examination of Water and Wastewater. 21st ed. Washington (DC): APHA-AWWA-WEF.

Arbuckle TE, Fraser WD, Fisher M, Davis K, Liang CL, Lupien N, Bastien S, Velez MP, von Dadelszen P, Hemmings DG, et al. 2013. Cohort profile: the maternal-infant research on environmental chemicals research platform. Paediatr Perinat Epidemiol. 27(4):415-425.

Asmonaite G, Boyer S, de Souza KB, Wassmur B, Sturve J. 2016. Behavioural toxicity assessment of silver ions and nanoparticles on zebrafish using a locomotion profiling approach. Aquat Toxicol. 173:143-153.

[ATSDR] Agency for Toxic Substances and Disease Registry. 1990. <u>Toxicological Profile for Silver [PDF]</u>. Atlanta (GA): U.S. Department of Health and Human Services, Public Health Service.

Auffan M, Matson CW, Rose J, Arnold M, Proux O, Fayard B, Liu W, Chaurand P, Wiesner MR, Rottero JY, et al. 2014. Salinity-dependent silver nanoparticle uptake and transformation by Atlantic killifish (*Fundulus heteroclitus*) embryos. Nanotoxicology. 8(S1):167-176.

Aylward LL, Bachler G, von Goetz N, Poddalgoda D, Hays AM, Nong A. 2016. Biomonitoring equivalents for interpretation of silver biomonitoring data in a risk assessment context. Int J of Hyg Environ Health. 219(6):521-526.

Banumathi B, Vaseeharan B, Suganya P, Citarasu T, Govindarajan M, Alharbi N, Kadaikunnan S, Khaled JM, Benelli G. 2017. Toxicity of *Camellia sinensis*-fabricated silver nanoparticles on invertebrate and vertebrate organisms: morphological abnormalities and DNA damages. J Clust Sci. 28:2027-2040.

Bard CC, Murphy JJ, Stone DL, Terhaar CJ. 1976. Silver in photoprocessing effluents. J Water Pollut Control Fed. 48(2):389-394.

Bell RA, Kramer JR. 1999. Structural chemistry and geochemistry of silver-sulfur compounds: critical review. Environ Toxicol Chem. 18(1):9-22.

Berry WJ, Cantwell MG, Edwards PA, Serbst JR, Hansen DJ. 1999. Predicting toxicity of sediments spiked with silver. Environ Toxicol Chem. 18(1):40-48.

Bianchini A, Bowles KC. 2002. Metal sulfides in oxygenated aquatic systems. Implications for the biotic ligand model. Comp Biochem Physiol C Toxicol Pharmacol. 133(1-2):51-64.

Bianchini A, Playle RC, Wood CM, Walsh PJ. 2005. Mechanism of acute silver toxicity in marine invertebrates. Aquat Toxicol. 72(1-2):67-82.

Bianchini A, Wood CM. 2003. Mechanism of acute silver toxicity in *Daphnia magna*. Environ Toxicol Chem. 22(6):1361-1367.

Bianchini A, Wood CM. 2008. Does sulfide or water hardness protect against silver toxicity in *Daphnia magna*? A critical assessment of the acute-to-chronic toxicity ratio for silver. Ecotoxicol Environ Saf. 71(1):32-40.

Bicho RC, Ribeiro T, Rodrigues NP, Scott-Fordsmand JJ, Amorim MJB. 2016. Effects of Ag nanomaterials (NM300K) and Ag salt (AgNO<sub>3</sub>) can be discriminated in a full life cycle long term test with *Enchytraeus crypticus*. J Hazard Mater. 318:608-614.

Bodek I, Lyman WJ, Reehl WF, Rosenblatt DH, editors. 1988. Environmental inorganic chemistry. Properties, processes, and estimation methods. New York (NY): Pergamon Press. p. 7.13-1 to 7.13-3.

Brown CL, Parchaso F, Thompson JK, Luoma SN. 2003. Assessing toxicant effects in a complex estuary: A case study of effects of silver on reproduction in the bivalve, *Potamocorbula amurensis*, in San Francisco Bay. Hum Ecol Risk Assess. 9(1):95-119.

Brumby A, Braumann P, Zimmermann K, Van Den Broeck F, Vandevelde T, Goia D, Renner H, Schlamp G, Zimmermann K, Weise W, et al. 2008. <u>Silver, silver compounds, and silver alloys</u>. In: Ullman's Encyclopedia of Industrial Chemistry. 6th ed., vol. 33. Weinheim: Wiley. p. 15-94.

Bury NR, Shaw J, Glover C, Hogstrand C. 2002. Derivation of a toxicity-based model to predict how water chemistry influences silver toxicity to invertebrates. Comp Biochem Physiol C. 133(1-2):259-270.

Bury NR, Wood CM. 1999. Mechanism of branchial apical silver uptake by rainbow trout is via the protoncoupled Na<sup>+</sup> channel. Am J Physiol. 277:R1385-R1391.

Caires AM, Chandra S. 2011. Conversion factors as determined by relative macroinvertebrate sampling efficiencies of four common benthic grab samplers. J Freshw Ecol. 27(1):97-109.

Calabrese A, MacInnes JR, Nelson DA, Miller JE. 1977. Survival and growth of bivalve larvae under heavy metal stress. J Mar Biol. 41(2):179-184.

Call DJ, Markee TP, Brooke LT, Polkinghorne CN, Geiger DL. 1997. Bioavailability and toxicity of silver to *Chironomus tentans* in water and sediments. Proceedings of the 5th Argentum International Conference on the Transport, Fate, and Effects of Silver in the Environment; 1997 Sep 28-Oct 1; Hamilton (ON). p. 245-248.

Call DJ, Polkinghorne CN, Markee TP, Brooke LT, Geiger DL, Gorsuch JW, Robillard KA. 1999. Silver toxicity to Chironomus tentans in two freshwater sediments. Environ Toxicol Chem. 18(1):30-39.

Call DJ, Polkinghorne CN, Markee TP, Brooke LT, Geiger DL, Gorsuch JW, Robillard KA. 2006. Toxicity of silver in water and sediment to the freshwater amphipod Hyalella azteca. Environ Toxicol Chem. 25(7):1802-1808.

Callahan MA, Slimak MW, Gabel NW, May IP, Fowler CF, Freed JR, Jennings P, Durfee RL, Whitmore FC, Maestri B, et al. 1979. <u>Water-related environmental fate of 129 priority pollutants [PDF]</u>. Volume I: Introduction and technical background, metals and inorganics, pesticides and PCBs. Washington (DC): U.S. Environmental Protection Agency. p. 171. EPA-440/4 79-029a.

Canada. 1999. *Canadian Environmental Protection Act, 1999.* S.C. 1999, c.33. Canada Gazette Part III, vol. 22, no. 3.

Canada. 2012. <u>Canadian Environmental Protection Act, 1999</u>: <u>Notice with respect to certain substances</u> <u>on the Domestic Substances List [PDF]</u>. Canada Gazette, Part I, vol. 146, no. 48, Supplement.

Canada. [modified 2015 Jan 1]. *Fisheries Act: Wastewater System Effluent Regulations* [PDF]. P.C. 2012-942. 28 June, 2012, SOR/2012-139.

Carvalho RA, Benfield MC, Santschi PH. 1999. Comparative bioaccumulation studies of colloidally complexed and free-ionic heavy metals in juvenile brown shrimp *Penaeus aztecus* (Crustacea: Decapoda: Penaeidae). Limnol Oceanogr. 44(2):403-414.

[CBSA] Canada Border Services Agency. 2016. Information on imports corresponding to the HS Codes 2608.00.0081, 2616.10.0081, 2843.21.0000, 2843.29.0000, 7106.10.0000, 7106.10.0010, 7106.10.0020, 7106.91.0011, 7106.91.0019, 7106.91.0020, 7106.91.0021, 7106.91.0029, 7106.92.0011, 7106.92.0019, 7106.92.0090, 7106.92.1100, 7106.92.1900, 7106.92.2100, 7106.92.2210, and 7106.92.2290. Ottawa (ON): CBSA, Commercial and Trade Operations Division. Confidential information received by Environment and Climate Change Canada for calendar years 2010-2013.

[CCME] Canadian Council of Ministers of the Environment. 2006a. A protocol for the derivation of environmental and human health soil quality guidelines [ODF]. Winnipeg (MB): Canadian Council of Ministers of the Environment. 186 p.

[CCME] Canadian Council of Ministers of the Environment. 2007. <u>Canadian water quality guidelines for</u> <u>the protection of aquatic life [PDF]</u>. Winnipeg (MB): Canadian Council of Ministers of the Environment.

[CCME] Canadian Council of Ministers of the Environment. 2015a. <u>Scientific Criteria Document for the</u> <u>Development of the Canadian Water Quality Guidelines for the Protection of Aquatic Life: Silver [PDF]</u>. Scientific Criteria Document. Winnipeg (MB): Canadian Council of Ministers of the Environment. 73 p. PN 1539. ISBN 978-1-77202-018-2.

[CCME] Canadian Council of Ministers of the Environment. 2015b. <u>Appendix A: Summary of toxicity data</u> <u>evaluated for short-term benchmark concentration and long-term Canadian Water Quality Guideline</u> <u>derivation [XLSX Spreadsheet]</u>. Winnipeg (MB): Canadian Council of Ministers of the Environment.

Chan CYS, Chiu JMY. 2015. Chronic effects of coated silver nanoparticles on marine invertebrate larvae: a proof of concept study. PLoS ONE 10(7): e0132457.

[CIMT] <u>Canadian International Merchandise Trade Database</u>. 2017-2021. Canada: Statistics Canada. [updated 2020 June 6; accessed 2020 Dec 7].

Conestoga-Rovers and Associates. 2015. Compiling and Interpreting Chemical Data from Municipal Solid Waste Landfill Leachate. Unpublished report prepared for Environment Canada. Report No.: 10. 318 p.

Couillard Y, Grapentine LC, Borgmann U, Doyle P, and Masson S. 2008. The amphipod *Hyalella azteca* as a biomonitor in field deployment studies for metal mining. Environ Pollut. 156(3):1314-1324

Diez-Ortiz M, Lahive E, George S, Ter Schure A, van Gestel CAM, Jurkschat K, Svendsen C, Spurgeon DJ. 2015. Short-term soil bioassays may not reveal the full toxicity potential for nanomaterials;

bioavailability and toxicity of silver ions (AgNO<sub>3</sub>) and silver nanoparticles to earthworm *Eisenia fetida* in long-term aged soils. Environ Pollut. 203:191-198.

Dalgarno S. 2018. <u>ssdtools: A shiny web app to analyse species sensitivity distributions</u>. Prepared by Poisson Consulting for the Ministry of the Environment, British Columbia. [accessed March 19, 2021]

Domingues VFC. 2016. Toxicity of silver nanoparticles and silver nitrate to the freshwater planarian *Dugesia tigrina* [Master's thesis]. Aveiro (PT): Universidade de Aveiro, Departamento de Biologia. p. 63.

Domsch KH. 1984. Effects of pesticides and heavy metals on biological processes in soil. Plant Soil. 76(1-3):367-378.

Donner E, Scheckel K, Sekine R, Popelka-Filcoff RS, Bennett JW, Brunetti G, Naidu R, McGrath SP, Lombi E. 2015. Non-labile silver species in biosolids remain stable throughout 50 years of weathering and ageing. Environ Pollut. 205:78-86.

Doolette CL. 2015. Behaviour of silver and silver sulfide nanoparticles in the environment: Effects on wastewater treatment processes and soil organisms [dissertation]. Adelaide (AU): University of Adelaide, School of Agriculture Food and Wine. p. 142.

[DPD] <u>Drug Product Database [database]</u>. [modified 2018 Dec 14]. Ottawa (ON): Government of Canada. [accessed 2019 Feb].

[ECCC] Environment and Climate Change Canada. 2018a. <u>Guide for to reporting to the National Pollutant</u> <u>Release Inventory: 2018 and 2019 [PDF]</u>. Ottawa (ON): Government of Canada.

[ECCC] Environment and Climate Change Canada. 2018b. <u>Status report on the performance of metal</u> <u>mines subject to the metal mining effluent regulations in 2016 [PDF]</u>. Ottawa (ON): Government of Canada.

[ECCC] Environment and Climate Change Canada. 2019. Wastewater treatment system data collected under the Chemicals Management Plan Environmental Monitoring and Surveillance Program. Data collected in 2018. Unpublished data. Gatineau (QC): Environment Canada.

[ECCC] Environment and Climate Change Canada. 2020. Landfill leachate data collected under the Chemicals Management Plan Environmental Monitoring and Surveillance Program. Unpublished data. Ottawa (ON): Government of Canada. Data collected February 2020.

[ECCC, HC] Environment and Climate Change Canada, Health Canada. [modified 2016 August 10]. <u>Nanomaterials</u>. Ottawa (ON): Government of Canada. [accessed 2019 Jun 25].

[ECCC, HC] Environment and Climate Change Canada, Health Canada. [modified 2017 Mar 12]. <u>Categorization</u>. Ottawa (ON): Government of Canada.

[ECHA] European Chemicals Agency. 2012. <u>Guidance on information requirements and chemical safety</u> <u>assessment [PDF]</u>. Version 2.1. Helsinki (FI): European Chemicals Agency. Chapter R.16: Environmental exposure estimation.

[ECSTL] Environment Canada Soil Toxicology Laboratory. 2011. Evaluation of the ecological effects of silver in soil. Prepared for: Ecological Assessment Division, Environment Canada.

[EEC Ltd and LAC Ltd] Ecoscape Environmental Consultants Ltd. and Larratt Aquatic Consulting Ltd. 2014. Lower Columbia River Aquatic Receiving Environment Monitoring Program for Teck Trail Operations. Annual data collection and interpretation report [PDF]. Kelowna (BC): Ecoscape Environmental Consultants Ltd. p. 449. Ecoscape file No. 12-976.2.

[EEM] <u>Environmental Effects Monitoring</u>. 2021. Gatineau, QC: Environment and Climate Change Canada [accessed 2021 Feb]. [restricted access]. Measured concentrations of silver in exposed and reference waterbodies collected under the Metal and Diamond Mining Effluent Regulations from 2004–2019.

[EFSA] European Food Safety Authority. 2016. <u>Scientific opinion on the re-evaluation of silver (E 174) as</u> <u>food additive</u>. EFSA Panel on Food Additives and Nutrient Sources added to Food (ANS). Parma (IT): EFSA. EFSA Journal 14(1):4364. 64 p.

Environment Canada. 2004. <u>Biological test method: Test for toxicity of contaminated soil to earthworms</u> (*Eisenia andrei, Eisenia fetida*, or *Lumbricus terrestris*) [PDF]. Ottawa (ON): Government of Canada. EPS 1/RM/43.

Environment Canada. 2005. <u>Biological test method: Test for measuring emergence and growth of</u> <u>terrestrial plants exposed to contaminants in soil [PDF]</u>. Ottawa (ON): Government of Canada.\_EPS 1/RM/45.

Environment Canada. 2006. Guidance for conducting ecological assessments under CEPA 1999: Science resource technical series, technical guidance module: Sludge amendment. Working document. Gatineau (QC): Environment Canada, Ecological Assessment Division.

Environment Canada. 2007. <u>Biological test method: Test for measuring survival and reproduction of</u> <u>springtails exposed to contaminants in soil [PDF]</u>. Ottawa (ON): Government of Canada. EPS 1/RM/47.

Environment Canada. 2013a. DSL Inventory Update data collected under the *Canadian Environmental Protection Act, 1999*, section 71: *Notice with respect to certain substances on the Domestic Substances List.* Data prepared by: Environment Canada, Health Canada; Existing Substances Program.

Environment Canada. 2013b. Wastewater treatment system data collected under the Chemicals Management Plan Environmental Monitoring and Surveillance Program. Unpublished data. Ottawa (ON): Government of Canada. Data collected 2009-2012.

Erickson RJ, Brooke LT, Kahl MD, Venter FV, Harting SL, Merkee TP, Spehar RL. 1998. Effects of laboratory test conditions on the toxicity of silver to aquatic organisms. Environ Toxicol Chem. 17(4):572-578.

Ewell WS, Gorsuch JW, Ritter M, Ruffing CJ. 1993. Ecotoxicological effects of silver compounds. Proceedings of the 1st Argentum International Conference on the Transport, Fate, and Effects of Silver in the Environment; 1993 August 8-10; Madison (WI). p. 9.

Fabrega J, Luoma SN, Tyler CR, Galloway TS, Lead JR. 2011. Silver nanoparticles: behavior and effects in the aquatic environment. Environ Int. 37(2):517-531.

Falbe J, Regitz M. 1992. Ro"mpp Chemie Lexikon. Thieme. Stuttgart (DE). [cited in CCME 2015a].

Ferguson EA, Hogstrand C. 1998. Acute silver toxicity to seawater-acclimated rainbow trout: Influence of salinity on toxicity and silver speciation. Environ Toxicol Chem. 17(4):589-593.

Flegal AR, Rivera-Duarte I, Sanudo-Wilhelmy SA. 1997. Silver contamination in aquatic environments. In: Ware GW, Nigg HN, Bevenue A, editors. Reviews of Environmental Contamination and Toxicology. New York (NY): Springer. (Reviews of Environmental Contamination and Toxicology; vol. 148).

Galvez F, Wood CM. 1997. The relative importance of water hardness and chloride levels in modifying the acute toxicity of silver to rainbow trout (*Oncorhynchus mykiss*). Environ Toxicol Chem. 16(11):2363-2368.

Gonzalez AG, Mombo S, Leflaive J, Lamy A, Oleg S, Pokrovsky OS, Rols JL. 2015. Silver nanoparticles impact phototrophic biofilm communities to a considerably higher degree than ionic silver. Environ Sci Pollut Res Int. 22(11):8412-8424.

Greenwood NN, Earnshaw A. 1997. Chemistry of the Elements. 2nd ed. Butterworth-Heinemann. Chapter 28, Copper, Silver and Gold. p. 1173-1200.

Guevara, SR., Arribére, M., Bubach, D., Vigliana, P., Rizzo, A., Alonso, M., and Sanchez, R. 2005. Silver contamination on abiotic and biotic compartments of Nahuel Huapi National Park lakes, Patagonia, Argentina. Sci Total Environ. 336(1-3):119-134.

Health Canada. 1986. <u>Guidelines for Canadian drinking water quality: Guideline technical document -</u> <u>Silver</u>. Ottawa (ON): Health Canada.

Health Canada. [modified 2006 Dec 11]. <u>Food additives permitted for use in Canada</u>. Ottawa (ON): Government of Canada. [accessed 2016 Jan 19].

Health Canada. 2013. <u>Second Report on Human Biomonitoring of Environmental Chemicals in Canada.</u> <u>Results of the Canadian Health Measures Survey cycle 2 (2009-2011)</u>. Ottawa (ON): Health Canada.

Health Canada. 2016. <u>Science Approach Document. Biomonitoring-based Approach 2 for Barium-</u> <u>containing Substances, Molybdenum-containing Substances, Silver-containing Substances, Thallium-</u> <u>containing Substances and Inorganic Tin-containing Substances.</u> Ottawa (ON): Government of Canada. [accessed 2019 Jan 21].

Health Canada. [modified 2018 June 14]. <u>Cosmetic Ingredient Hotlist: list of ingredients that are restricted</u> for use in cosmetic products. Ottawa (ON): Government of Canada. [accessed 2019 Feb].

Hirsch MP. 1998a. Toxicity of silver sulfide-spiked sediments to the freshwater amphipod *Hyalella azteca*. Environ Toxicol Chem. 17(4):601-604.

Hirsch MP. 1998b. Bioaccumulation of silver from laboratory-spiked sediments in the oligochaete (*Lumbriculus variegatus*). Environ Toxicol Chem. 17(4):605-609.

Hogstrand C, Galvez F, Wood CM. 1996. Toxicity, silver accumulation and metallothionein induction in freshwater rainbow trout during exposure to different silver salts. Environ Toxicol Chem. 15(7):1102-1108.

Hogstrand C, Wood CM. 1998. Toward a better understanding of the bioavailability, physiology, and toxicity of silver in fish: Implications for water quality criteria. Environ Toxicol Chem. 17(4):547-561.

Hook S, Fisher N. 2001. Sublethal effects of silver in zooplankton: importance of exposure pathways and implications for toxicity testing. Environ Toxicol Chem. 20(3):568-574.

[HSDB] <u>Hazardous Substances Data Bank [database]</u>. 1983-. Search results for Silver Compounds. Bethesda (MD): National Library of Medicine (US). [updated 2009 Apr 16; accessed 2018 May 1].

[IRIS] Integrated Risk Information System. 1991. <u>Silver CASRN 7440-22-4</u>. U.S. Environmental Protection Agency, National Center for Environmental Assessment. [accessed 2015 Jul 27].

Jesmer AH, Velicogna JR, Schwertfeger DM, Scroggins RP, Princz JI. 2016. The toxicity of silver to soil organisms exposed to silver nanoparticles and silver nitrate in biosolids-amended field soil. Environ Toxicol Chem. 36(10):2756-2765.

Karen DJ, Ownby DR, Forsythe BL, Bills TP, La Point TW, Cobb GB, Klaine SJ. 1999. Influence of water quality on silver toxicity to rainbow trout (*Oncorhynchus mykiss*), fathead minnows (*Pimephales promelas*) and water fleas (*Daphnia magna*). Environ Toxicol Chem. 18(1):63-70.

Khan FR, Paul KB, Dybowska AD, Valsami-Jones E, Lead JR, Stone V, Fernandes TF. 2015. Accumulation dynamics and acute toxicity of silver nanoparticles to *Daphnia magna* and *Lumbriculus variegatus*: implications for metal modeling approaches. Environ Sci Technol. 49(7):4389-4397.

Khodaparast Z. 2015. Toxicity of silver nanoparticles and silver nitrate on *Nassarius recticulatus* larvae [Master's thesis]. Aveiro (PT): Universidade de Aveiro, Departamento de Biologia. p. 62.

Kilgour & Associates Ltd. 2016. Estimating background concentration ranges data to inform ecological chemical risk assessments. Unpublished report. Gatineau (QC): Environment and Climate Change Canada, Ecological Assessment Division.

Kramer D, Cullen JT, Christian JR, Johnson WK, Pedersen TF. 2011. Silver in the subarctic northeast Pacific Ocean: Explaining the basin scale distribution of silver. Mar Chem. 123(1-4):133-142.

Kramer JR, Bell RA, Smith DS. 2007. Determination of sulfide ligands and association with natural organic matter. Appl Geochem. 22(8):1606-1611.

Lam IKS, Wang WX. 2006. Accumulation and elimination of aqueous and dietary silver in *Daphnia magna*. Chemosphere. 64(1):26-35.

Langdon KA, McLaughlin MJ, Kirby JK, Merrington G. 2015. Influence of soil properties and soil leaching on the toxicity of ionic silver to plants. Environ Toxicol Chem. 34(11):2503-2512.

LeBlanc GA, Mastone JD, Paradice AP, Wilson BF, Lockhart HB Jr, Robillard KA. 1984. The influence of speciation on the toxicity of silver to fathead minnow (*Pimephales promelas*). Environ Toxicol Chem. 3(1):37-46.

Lee DY, Fortin C, Campbell PGC. 2004. Influence of chloride on silver uptake by two green algae, *Pseudokirchneriella subcapitata* and *Chlorella pyrenoidosa*. Environ Toxicol Chem. 23(4):1012-1018.

Leonardo T, Farhi E, Pouget S, Motellier S, Boisson AM, Banerjee D, Rébeillé F, den Auwer C, Rivasseau C. 2016. Silver accumulation in the green microalga *Coccomyxa actinabiotis*: toxicity, in situ speciation, and localization investigated using Synchrotron XAS, XRD, and TEM. Environ Sci Technol. 50(1):359–367.

Li X, Schirmer K, Bernard L, Sigg L, Pillai S, Behra R. 2015. Silver nanoparticle toxicity and association with the alga *Euglena gracilis*. Environ Sci Nano. 2(6):594-602.

Liang CL. 2016. Descriptive statistics of metals for MIREC-CD Plus. 28/01/2016. Ottawa (ON): Population Studies Division, Health Canada [personal communication, unpublished data].

Lide DR, editor. 2000. CRC Handbook of chemistry and physics. 81st ed. Boca Raton (FL): CRC Press LLC. p. 4-28.

Lide DR, editor. 2005. CRC Handbook of chemistry and physics. 85th ed. Boca Raton (FL): CRC Press LLC.p. 4-82.

[LNHPD] <u>Licensed Natural Health Products Database</u>. [database]. [modified 2021 Sepy 8]. Ottawa (ON): Government of Canada. [accessed Dec 2021].

Lopez-Serrano A, Muñoz-Olivas R, Sanz-Landaluze J, Olasagasti M, Rainieri S, Cámara C. 2014. Comparison of bioconcentration of ionic silver and silver nanoparticles in zebrafish eleutheroembryos. Environ Pollut. 191:207-214.

Luoma SN. 2008. Silver nanotechnologies and the environment: old problems or new challenges? Project on emerging nanotechnologies. The Pew Charitable Trusts. p. 72.

Lytle PE. 1984. Fate and speciation of silver in publicly owned treatment plants. Environ Toxicol Chem. 3(1):21-30.

Mackevica A, Skjolding LM, Gergs A, Palmqvist A, Baun A. 2015. Chronic toxicity of silver nanoparticles to *Daphnia magna* under different feeding conditions. Aquat Toxicol. 161:10-16.

Magesky A, Pelletier E. 2015. Toxicity mechanisms of ionic silver and polymer-coated silver nanoparticles with interactions of functionalized carbon nanotubes on early development stages of sea urchin. Aquat Toxicol. 167:106-123.

Martin M, Osborn KE, Billig P, Glickstein N. 1981. Toxicities of ten metals to *Crassostrea gigas* and *Mytilus edulis* embryos and *Cancer magister* larvae. Mar Pollut Bull. 12(9):305-308.

Martin JD, Colson TLL, Langlois VS, Metcalfe CD. 2017. Biomarkers of exposure to nanosilver and silver accumulation in Yellow Perch (*Perca Flavescens*). Environ Toxicol Chem. 36(5):1211-1220.

Matson CW, Bone AJ, Auffan M, Lindberg TT, Arnold MC, Hsu-Kim H, Wiesner MR, Di Giulio RT. 2016. Silver toxicity across salinity gradients: the role of dissolved silver chloride species (AgCl<sub>x</sub>) in Atlantic killifish (*Fundulus heteroclitus*) and medaka (*Oryzias latipes*) early life-stage toxicity. Ecotoxicology. 25(6):1105-1118.

McGeer JC, Wood CM. 1998. Protective effects of water Cl<sup>-</sup> on physiological responses to waterborne silver in rainbow trout. Can J Fish Aquat Sci. 55(11):2447-2454.

McGeer JC, Brix KV, Skeaff JM, DeForest DK, Brigham SI, Adams WJ, Green A. 2003. Inverse relationship between bioconcentration factor and exposure concentration for metals: implications for hazard assessment of metals in the aquatic environment. Environ Toxicol Chem. 22(5):1017-1037.

Mehennaoui K, Georgantzopoulou A, Felten V, Andreï J, Garaud M, Cambier S, Serchi T, Pain-Devin S, Guérold F, Audinot JN, Giambérini L, Gutleb AC. 2016. *Gammarus fossarum* (Crustacea, Amphipoda) as a model organism to study the effects of silver nanoparticles. Sci Total Environ. 566-567:1649-1659.

Mendes LA, Maria VL, Scott-Fordsmand JJ, Amorim MJB. 2015. Ag nanoparticles (Ag NM300K) in the terrestrial environment: effects at population and cellular level in *Folsomia candida* (Collembola). Int J Environ Res Public Health. 12(10):12530-12542.

Metcalfe CD, Sultana T, Martin J, Newman K, Helm P, Kleywegt S, Shen L, Yargeau V. 2018. Silver near municipal wastewater discharges into western Lake Ontario, Canada. Environ Monit Assess. 190(9):555.

Miller LA, Bruland KW. 1995. Organic speciation of silver in marine waters. Environ Sci Technol. 29(10):2616-2621.

Morgan IJ, Henry RP, Wood CM. 1997. The mechanism of acute silver nitrate toxicity in freshwater rainbow trout (*Oncorhynchus mykiss*) is inhibition of gill Na<sup>+</sup> and Cl<sup>-</sup> transport. Aquat Toxicol. 38(1-3):145-163.

Mueller-Harvey I, Mlambo V, Sikosana JL, Smith T, Owen E, Brown RH. 2007. Octanol-water partition coefficients for predicting the effects of tannins in ruminant nutrition. J Agric Food Chem. 55(14):5436-5444.

[NAPM] National Association of Photographic Manufacturers. 1974. Environmental Effects of Photoprocessing Chemicals. Vol 1. New York (NY): National Association of Photographic Manufacturers. p. 76-155.

[NAPS] National Air Pollution Surveillance Network. 2011. <u>NAPS Data Products Data Sets</u>: 2011. Ottawa (ON): Government of Canada. [modified 13 Jul 7; accessed 2015 Dec 23].

Navarro E, Wagner B, Odzak N, Sigg L, Behra R. 2015. Effects of differently coated silver nanoparticles on the photosynthesis of *Chlamydomonas reinhardtii*. Environ Sci Technol. 49(13):8041–8047.

[NHPID] <u>Natural Health Products Ingredients Database [database].</u> [modified 2021 Dec 7]. Ottawa (ON): Government of Canada. [accessed Dec 2021].

[NLTWQM] <u>National Long-term Water Quality Monitoring [database]</u>. 2016. Newfoundland and Labrador Long-term Water Quality Monitoring dataset. Ottawa (ON): Government of Canada. [accessed 2017 Nov 12].

Newman P, Meader N, Klapwijk P, Fellows M, Liang J, Chou E, Gao Y, Barot H, Furuno A, Rey F, et al. (The Metals Focus Team at Metals Focus). 2020. <u>World wide silver survey [PDF]</u>. Washington (DC): The Silver Institute.

Novo M, Lahive E, Díez-Ortiz M, Matzke M, Morgan AJ, Spurgeon DJ, Svendsen C, Kille P. 2015. Different routes, same pathways: molecular mechanisms under silver ion and nanoparticle exposures in the soil sentinel *Eisenia fetida*. Environ Pollut. 205:385-393.

[NPRI] <u>National Pollutant Release Inventory</u>. 2019. Ottawa (ON): Government of Canada. Search results for silver and its compounds. [modified 2018 Nov; accessed 2020 July]. NPRI Datasets: Bulk data.

[NRCan] Natural Resources Canada. 2018. <u>Canadian reserves of selected major metals and recent</u> <u>production decisions</u>. Ottawa (ON): Government of Canada. [accessed 2019 Feb 4].

[NRCan] Natural Resources Canada. 2020. <u>Annual statistics of mineral production [PDF]</u>. Ottawa (ON): Government of Canada. [accessed 2020 Dec 7]. Survey year 2018.

Okonski AI, MacDonald DB, Potter K, Bonnell M. 2021. <u>Deriving predicted no-effect concentrations</u> (<u>PNECs</u>) using a novel assessment factor method. Hum Ecol Risk Assess. DOI:10.1080/10807039.2020.1865788.

O'Connell R, Alexander C, Strachan R, Alway B, Nambiath S, Wiebe J, Wong L, Rannestad E, Li S, Aranda D, Scott-Gray N (GFMS team at Thomson Reuters). 2017. <u>World wide silver survey [PDF]</u>. Washington (DC): The Silver Institute.

Pavlostathis SG, Maeng SK. 1998. Aerobic biodegradation of a silver-bearing photoprocessing wastewater. Environ Toxicol Chem. 17(4):617-624.

Pillai S, Behra R, Nestler H, Suter MJF, Sigg L, Schirmer K. 2014. Linking toxicity and adaptive responses across the transcriptome, proteome, and phenotype of *Chlamydomonas reinhardtii* exposed to silver. Proc Natl Acad Sci U S A. 111(9):3490-3495.

Proulx CL, Kilgour BW, Francis AP, Bouwhuis RF, Hill JR. 2018. Using a conductivity-alkalinity relationship as a tool to identify freshwaters in reference condition across Canada. Water Qual Res J Can. 53(4):231-240.

Purcell TW, Peters JJ. 1998. Sources of silver in the environment. Environ Toxicol Chem. 17(4):539-546.

Rainville LC, Carolan D, Varela AC, Doyle H, Sheehan D. 2014. Proteomic evaluation of citrate-coated silver nanoparticles toxicity in *Daphnia magna*. Analyst. 139:1678-1686.

Rajala JE, Maenpaa K, Vehniainen ER, Vaisanen A, Scott-Fordsmand JJ, Akkanen J, Kukkonen JVK. 2016. Toxicity testing of silver nanoparticles in artificial and natural sediments using the benthic organism *Lumbriculus variegatus*. Arch Environ Contam Toxicol. 71(3):405-414.

Ramskov T, Forbes VE, Gilliland D, Selck H. 2015. Accumulation and effects of sediment-associated silver nanoparticles to sediment-dwelling invertebrates. Aqua Toxicol. 166:96-105. Rasmussen et al. 2016. Preliminary Exposure Data for Five Metals from 2014-2017 CMP(3) Research. February 15, 2016. Ottawa (ON): Exposure and Biomonitoring Division, Health Canada [personal communication, unpublished data].

Ratte HT. 1999. Bioaccumulation and toxicity of silver compounds: a review. Environ Sci Tech. 18(1):89-108.

Ribeiro F, Gallego-Urrea JA, Jurkschat K, Crossley A, Hassellöv M, Taylor C, Soares AMVM, Loureiro S. 2014. Silver nanoparticles and silver nitrate induce high toxicity to *Pseudokirchneriella subcapitata*, *Daphnia magna* and *Danio rerio*. Sci Total Environ. 466-467(C):232-241.

Ribeiro F, Gallego-Urrea JA, Goodhead RM, Van Gestel CAM, Moger J, Soares AMVM, Loureiro S. 2015. Uptake and elimination kinetics of silver nanoparticles and silver nitrate by *Raphidocelis subcapitata*: The influence of silver behaviour in solution. Nanotoxicology. 9(6):686-695.

Rivera-Duarte I, Flegal AR, Sanudo-Wilhelmy SA, Veron AJ. 1999. Silver in the far North Atlantic Ocean. Deep-Sea Res II. 46(5):979-990.

Rodgers JH Jr, Deaver E, Rogers PL. 1995. Partitioning and effects of silver in amended freshwater sediments. Proceedings of the 3rd Argentum International Conference on the Transport, Fate, and Effects of Silver in the Environment; 1995 August 6-9; Washington (DC). p. 223-249.

Rodgers JH Jr, Deaver E, Rogers PL. 1997a. Partitioning and effects of silver in amended freshwater sediments. Ecotoxicol Environ Saf. 37(1):1-9.

Rodgers JH Jr, Deaver E, Suedel BC, Rogers PL. 1997b. Comparative aqueous toxicity of silver compounds: Laboratory studies with freshwater species. Bull Environ Contam Toxicol. 58(6):851-858.

Roditi HA, Fisher NS. 1996. Metal assimilation in zebra mussels. The 4th international conference proceedings: transport, fate, and effects of silver in the Environment. Andren AW, Bober TW. (ed.). University of Wisconsin System, Sea Grant Institute, August 1996. p. 241-244.

Sanders JG, Abbe GR. 1989. Silver transport and impact in estuarine and marine systems. In: Suter GW and Lewis MA, editors. Aquatic toxicology and environmental fate. Vol. 11. Philadelphia (PA): American Society for Testing and Materials. p. 5-18.

Schlekat CE, McGeer JC, Blust R, Borgmann U, Brix KV, Bury N, Couillard Y, Dwyer RL, Luoma SN, Robertson S, et al. 2007. Bioaccumulation; hazard identification of metals and inorganic metal substances. In: Adams WJ, Chapman PM, editors. Assessing the hazard of metals and inorganic metal substances in aquatic and terrestrial systems. Pensacola (FL): SETAC Publications, CRC Press. p. 55-87.

Schlich K, Klawonn T, Terytze K, and Hund-Rinke K. 2013. Effects of silver nanoparticles and silver nitrate in the earthworm reproduction test. Environ Toxicol Chem. 32(1):181-188.

Seitz F, Rosenfeldt RR, Storm K, Metreveli G, Schaumann GE, Schulz R, Bundschuh M. 2015. Effects of silver nanoparticle properties, media pH and dissolved organic matter on toxicity to *Daphnia magna*. Ecotoxicol Environ Saf. 111:263-270.

Sekine R, Khurana K, Vasilev K, Lombi E, Donner E. 2015. Quantifying the adsorption of ionic silver and functionalized nanoparticles during ecotoxicity testing: test container effects and recommendations. Nanotoxicology. 9(8):1005-1012.

Shafer MM, Overdier JT, Armstong DE. 1998. Removal, partitioning and fate of silver and other metals in wastewater treatment plants and effluent-receiving streams. Environ Toxicol Chem. 17(4):630-641.

Shafer MM, Overdier JT, Babiarz CL, Hoffman SR, Armstrong DE. 1996. Preliminary observations on the distribution of Ag and other trace metals in the colloidal size fractions of streams and POTW effluents. In: Andren AW, Bober TW, editors. 4th International Conference on Transport, Fate, and Effects of Silver in the Environment (Argentum IV). 1996 Aug 25-28; Madison, Wisconsin, USA. Madison (WI): University of Wisconsin Sea Great Institute. p. 15-22.

Shen MH, Zhou XX, Yang XY, Chao JB, Liu R, Liu JF. 2015. Exposure medium: key in identifying free Ag<sup>+</sup> as the exclusive species of silver nanoparticles with acute toxicity to *Daphnia magna*. Sci Rep. 5:9674.

Sorensen SN and Baun A. 2015. Controlling silver nanoparticle exposure in algal toxicity testing – A matter of timing. Nanotoxicology. 9(2):201-209.

Steele R and Thursby GB. 1995. Sexual reproduction tests with marine seaweeds (Macroalgae). In: Rand GM, editor. Fundamentals of Aquatic Toxicology Effects, Environmental Fate and Risk Assessment. North Palm Beach (FL): Ecological Services Inc. p. 171-188.

Terhaar CJ, Ewell WS, Dziuba SP, White WW, Murphy PJ. 1977. A laboratory model for evaluating the behavior of heavy metals in an aquatic environment. Water Res. 11(1):101-110.

Tourinho PS, van Gestel CAM, Morgan AJ, Kille P, Svendsen C, Jurkschat K, Mosselmans JFW, Soares AMVM, Loureiro S. 2016. Toxicokinetics of Ag in the terrestrial isopod *Porcellionides pruinosus* exposed to Ag NPs and AgNO<sub>3</sub> via soil and food. Ecotoxicology. 25(2):267-278.

Tugulea 2016. A national survey of disinfection by-products and selected drinking water contaminants in Canadian drinking water (2009-2010). Unpublished database. Ottawa (ON): Exposure and Biomonitoring Division, Health Canada.

[USGS] U.S. Geological Survey. 2018. <u>Mineral commodity summaries 2018 [PDF].</u> Reston (VA): U.S. Geological Survey. p. 150-151.

Velicogna JR, Ritchie EE, Scroggins RP, Princz JI. 2016. A comparison of the effects of silver nanoparticles to silver nitrate on a suite of soil dwelling organisms in two field soils. Nanotoxicology. 10(8):1144-1151.

Velicogna JR, Schwertfeger DM, Jesmer AH, Scroggins RP, Princz JI. 2017. The bioaccumulation potential of silver in *Eisenia andrei* exposed to silver nanoparticles and silver nitrate in soil. NanoImpact. 6:11-18.

Waalewijn-Kool PL, Klein K, Forniés RM, van Gestel CAM. 2014. Bioaccumulation and toxicity of silver nanoparticles and silver nitrate to the soil arthropod *Folsomia candida*. Ecotoxicology. 23(9):1629-1637.

Ward TJ, Kramer JR. 2002. Silver speciation during chronic toxicity tests with the mysid, *Americamysis bahia*. Comp Biochem Physiol C Toxicol Pharmacol. 133(1-2):75-86.

Webb NA, Wood CM. 1998. Physiological analysis of the stress response associated with acute silver nitrate exposure in freshwater rainbow trout. Environ Toxicol Chem. 17(4):579-588.

Wen LS, Santschi PH, Gill GA, Paternostro CL, Lehman RD. 1997. Colloids and particulate silver in river an estuarine waters of Texas. Environ Sci Technol. 31(3):723-731.

[WHO] World Health Organization. 2002. <u>Silver and silver compounds: Environmental aspects [PDF]</u>. Concise international chemical assessment document 44. Geneva (CH): World Health Organization. p 42.

[WHO] World Health Organization. 2011. <u>Guidelines for Drinking-water Quality [PDF]. 4th ed</u>. [accessed 2015 Jul 27].

Williams JH. 1999. Regulations on additions of sludge-borne metals to soil and their adaptation to local conditions. In: L'Hermite P, editor. Treatment and use of sewage sludge and liquid agricultural wastes. London (UK): Elsevier Applied Science. p. 243-250.

Wood CM, Hogstrand C, Galvez F, Munger RS. 1996. The physiology of waterborne silver toxicity in freshwater rainbow trout (*Oncorhynchus mykiss*): 1. The effects of ionic Ag<sup>+</sup>. Aquat Toxicol. 35(2):93-109.

Wood CM, McDonald MD, Walker P, Grosell M, Barimo JF, Playle RC, Walsh PJ. 2004. Bioavailability of silver and its relationship to ionoregulation and silver speciation across a range of salinities in the gulf toadfish (*Opsanus beta*). Aquat Toxicol. 70(2):137-157.

Wood CM. 2012. Silver. In: Wood CM, Farrell AP, Brauner CA, editors. Metals: Homeostasis and toxicology: Non-essential metals. Fish Physiology, Vol. 31B. p. 1-65.

Xin Q, Rotchell JM, Cheng J, Yi J, Zhang Q. 2015. Silver nanoparticles affect the neural development of zebrafish embryos. J Appl Toxicol. 35(12):1481-1492.

Yaroshevsky AA. 2006. Abundances of chemical elements in the Earth's crust. Geochem Int. 44(1):48-55.

Yoo H, Lee JS, Lee BG, Lee IT, Schlekat CE, Koh CH, Luoma SN. 2004. Uptake pathway for Ag bioaccumulation in three benthic invertebrates exposed to contaminated sediments. Mar Ecol Prog Ser. 270:141-152.

Yoo-iam M, Chaichana R, Satapanajaru T. 2014. Toxicity, bioaccumulation and biomagnification of silver nanoparticles in green algae (*Chlorella sp.*), water flea (*Moina macrocopa*), blood worm (*Chironomus spp.*) and silver barb (*Barbonymus gonionotus*). Chem Spec Bioavailab. 26(4):257-265.

Zhang Z, Yang X, Shen M, Yin Y, Liu J. 2015. Sunlight-driven reduction of silver ion to silver nanoparticle by organic matter mitigates the acute toxicity of silver to *Daphnia magna*. J Environ Sci. 35:62-68.

Zimmermann S, Ruchter N, Loza K, Epple M, Sures B. 2017. Nanoparticulate versus ionic silver: behavior in the tank water, bioaccumulation, elimination and subcellular distribution in the freshwater mussel *Dreissena polymorpha*. Environ Pollut. 222:251-260.

## 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 <sup>3</sup> )	Solubility at 20 °C (mg/L H <sub>2</sub> O)
7440-22-4	Silver	Ag	107.87	2 212 <sup>a</sup>	10.5 <sup>a</sup>	Insoluble <sup>a</sup>
///////////////////////////////////////	Nitric acid silver(1+) salt	AgNO₃	169.87	Decom- poses at 440 ª	4.35 <sup>a</sup>	$2.16 \times 10^4$
7783-90-6	Silver chloride (AgCl)	AgCl	143.32	1 550 ª	5.56 <sup>a</sup>	1.93 <sup>a</sup>
	Silver bromide (AgBr)	AgBr	187.77	1 502 ª	6.47 <sup>a</sup>	0.14 <sup>a</sup>
	Sulfuric acid, disilver(1+) salt	Ag <sub>2</sub> SO <sub>4</sub>	311.80	NA	5.45 <sup>a</sup>	8 400 <sup>b</sup>
20667-12-3	Silver oxide (Ag <sub>2</sub> O)	Ag <sub>2</sub> O	231.74	Decom- poses above 100 <sup>a</sup>	NA	Decom- poses in aqueous solution <sup>a</sup>
21548-73-2	(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	Ag <sub>2</sub> S	247.8	Decom- poses at 810 <sup>a</sup>	7.33 <sup>a</sup>	0.14 <sup>a</sup>

NA: Not available

<sup>a</sup> Lide 2000

<sup>b</sup> 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 <sup>a</sup>	Number of unique companies importing	Number of individual imports	Average import quantity (t) <sup>b, c</sup>	Median import quantity (t) <sup>b, c</sup>	90 <sup>th</sup> percentile import quantity (t) <sup>b, c</sup>
Silver nitrate <sup>d</sup>	98	336	0.45	0.0090	0.72
Other silver compounds e	99 <sup>f</sup>	321	0.45	0.0030	0.15
Silver in powder form <sup>g</sup>	89	204	0.41	0.46	140
Unwrought silver <sup>h</sup>	307 <sup>f</sup>	1 375	3.1	0.0064	1.8
Semi- manufactur ed silver <sup>i</sup>	852 <sup>f</sup>	3 103	0.82	0.005	0.12
Silver ores and concentrate	5 <sup>f</sup>	51	29	9.0	98

<sup>a</sup> 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 (<u>http://www.cbsa-asfc.gc.ca/trade-</u>commerce/tariff-tarif/hcdcs-hsdcm/menu-eng.html).

<sup>b</sup> Calculated from distribution of individual imports from 2010 to 2013.

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

<sup>d</sup> HS code 2843.21.000.

<sup>e</sup> HS code 2843.29.000.

<sup>f</sup> Some company names were not available, therefore number of unique companies are higher than what is reported here.

<sup>9</sup> 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).

<sup>h</sup> HS codes : 2616.10.0081 (silver ores and concentrates, silver content) and 2608.00.0081 (zinc ores and concentrates, silver content).

<sup>i</sup> HS codes: 7106.91.0011 (silver bullion, unwrought forms, containing by weight>=92.5% of silver), 7106.91.0021 (silver dore, unwrought forms, containing by weight <92.5% of silver), 7106.91.0019 (silver, o/t bullion, unwrought forms, containing by weight >= 92.5% of silver), 7106.91.0029 (silver, o/t dore, unwrought forms, containing by weight < 92.5% of silver), and 7106.91.0020 (silver, unwrought forms, containing by weight <92.5% of silver).

<sup>1</sup> HS codes: 2616.10.0081 (silver ores and concentrates, silver content) and 2608.00.0081 (zinc ores and concentrates, silver content).

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 <sup>a</sup>	Other silver compounds	Silver powder <sup>c</sup>
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

NAICS6 code description	Silver nitrate <sup>a</sup>	Other silver compounds	Silver powder <sup>c</sup>
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.

<sup>a</sup> HS code 2843.21.000.

<sup>b</sup> HS code 2843.29.000.

<sup>c</sup> 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

Source	Number of	Air (t)	Water (t)	All media
	reporting facilities <sup>a</sup>			<1 t (t)
All Other	2	NR	NR	0.11
Miscellaneous				
Fabricated Metal				
Product				
Manufacturing				
Base Metal Smelting	8	1.3	0.0020	1.8
and Refining <sup>b</sup>				
Cement	3	0.0060	NR	0.0043
Manufacturing				
Coal mining	2	NR	0.0090	0.0010
Marine Cargo	1	NR	NR	0.005
Handling				
Metal Mining <sup>c</sup>	12	0.023	0.35	0.067
Non-Conventional Oil	2	0.41	0.37 <sup>e</sup>	0.10
Extraction				
Non-Ferrous Metal	2	0.045	NR	0.015
(except Cu, Al)				
Rolling, Drawing,				
Extruding and				
Alloying				
Pulp and Paper	1	NR	NR	0.090
Waste <sup>d</sup>	4	0.0064	0.0048	0.013
Total	37	1.8	0.74	2.2

Table C-1. Total quantities of silver rele	eased to air, water, and land by industrial
and public sources from 2012 to 2017	NPRI 2019)

NR: Not reported.

<sup>a</sup> 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 2017 reporting period.

<sup>b</sup> Includes facilities with the following NAICS6 codes: 331410 and 331529.

<sup>c</sup> Includes facilities with the following NAICS6 codes: 212220, 212231, 212232, and 212233.

<sup>d</sup> Includes facilities with the following NAICS6 codes: 221320 and 562210.

<sup>e</sup> 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

Ecozone/ waterbody	Sample size	Median (µg Ag⊤/L)	Upper inner tolerance limit (µg Ag⊤/L) <sup>g</sup>
Atlantic Maritime a,b	3	0.050	0.05
Boreal Cordillera <sup>b</sup>	301	0.0020	0.048
Boreal Plains <sup>b</sup>	644	0.010	0.26
Boreal Shield <sup>b</sup>	486	0.11	1.2
Mixedwood Plains <sup>b</sup>	783	0.52	2.1
Montane Cordillera b	1,950	0.0010	0.014
Pacific Maritime <sup>b</sup>	1,464	0.0010	0.017
Prairies <sup>b</sup>	335	0.050	0.92
Taiga Cordillera <sup>b</sup>	21	0.0040	0.044
Taiga Shield <sup>c</sup>	162	0.00050	NA
Lake Erie <sup>d</sup>	106	0.00050	NA
Lake Ontario <sup>d</sup>	165	0.00050	NA
Lake Superior <sup>d</sup>	83	0.00050	NA
North Atlantic Ocean	9	0.00032	NA
North Pacific Ocean	22	0.0011	NA

Table D-1. Statistics de	escribing backgro	ound concentrations	of total silver in			
Canada's ecozones, G	Canada's ecozones, Great Lakes, and the North Atlantic and North Pacific oceans					

NA: Not available.

<sup>a</sup> Dissolved silver concentrations are reported.

<sup>b</sup> Kilgour & Associates Ltd. (2016).

° NLTWQM 2016.

<sup>d</sup> 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.

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

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

<sup>g</sup> Synonymous in this assessment with maximum expected background concentration.

## Appendix E. Silver sediment toxicity dataset

Group	Test organism	Test	Endpoint	Value	Reference
		substance		(mg/kg dw)	
Invertebrate	Hyalella azteca	AgNO₃	10-day LC <sub>50</sub>	60.7	Rodgers et al. 1997a
Invertebrate	Hyalella azteca	AgNO <sub>3</sub>	10-day LC <sub>50</sub>	1.62	Rodgers et al. 1997a
Invertebrate	Hyalella azteca	AgNO₃	10-day LC <sub>50</sub>	45.4	Rodgers et al. 1997a
Invertebrate	Hyalella azteca	AgNO₃	10-day LC <sub>50</sub>	380	Rodgers et al. 1997a
Invertebrate	Hyalella azteca	AgNO <sub>3</sub>	10-day LC <sub>50</sub>	84	Call et al. 2006
Invertebrate	Hyalella azteca	AgNO <sub>3</sub>	10-day NOEC (dry weight)	12	Call et al. 2006
Invertebrate	Hyalella azteca	AgNO₃	10-day LOÉC (dry weight)	31	Call et al. 2006
Invertebrate	Hyalella azteca	AgNO₃	10-day LC <sub>50</sub>	2980	Call et al. 2006
Invertebrate	Hyalella azteca	AgNO <sub>3</sub>	10-day NOEC (dry weight)	2150	Call et al. 2006
Invertebrate	Hyalella azteca	AgNO₃	10-day LOEC (dry weight)	4310	Call et al. 2006
Invertebrate	Hyalella azteca	Ag <sub>2</sub> S	10-day LC50	>753 <sup>a</sup>	Hirsch 1998a
Invertebrate	Hyalella azteca	Ag <sub>2</sub> S	10-day EC <sub>50</sub> (biomass)	>753 <sup>a</sup>	Hirsch 1998a
Invertebrate	Hyalella azteca	AgCl	10-day LC <sub>50</sub>	>2560 <sup>a</sup>	Rodgers et al. 1997a
Invertebrate	Hyalella azteca	Ag <sub>2</sub> (S <sub>2</sub> O <sub>3</sub> ) <sub>n</sub>	10-day LC <sub>50</sub>	>1125 <sup>a</sup>	Rodgers et al. 1997a
Invertebrate	Hyalella azteca	Ag <sub>2</sub> (S <sub>2</sub> O <sub>3</sub> ) <sub>n</sub>	10-day LC <sub>50</sub>	>648 <sup>a</sup>	Rodgers et al. 1997a
Invertebrate	Hyalella azteca	Ag <sub>2</sub> (S <sub>2</sub> O <sub>3</sub> ) <sub>n</sub>	10-day LC <sub>50</sub>	>569 <sup>a</sup>	Rodgers et al. 1997a
Invertebrate	Hyalella azteca	Ag <sub>2</sub> (S <sub>2</sub> O <sub>3</sub> ) <sub>n</sub>	10-day LC <sub>50</sub>	>682 <sup>a</sup>	Rodgers et al. 1997a
Invertebrate	Chironomus tent ans	AgNO₃	10-day LC <sub>50</sub>	2750	Call et al. 1999
Invertebrate	Chironomus tent ans	AgNO₃	10-day NOEC (biomass)	1700	Call et al. 1999

#### Table E-1. Ag toxicity on sediment-dwelling organisms

Invertebrate	Chironomus tent ans	AgNO <sub>3</sub>	10-day LOEC (biomass)	2200	Call et al. 1999
Invertebrate	Chironomus tent ans	AgNO₃	10-day LC <sub>50</sub>	1170	Call et al. 1999
Invertebrate	Chironomus tent ans	AgNO <sub>3</sub>	10-day NOEC (biomass)	200	Call et al. 1999
Invertebrate	Chironomus tent ans	AgNO₃	10-day LOEC (biomass)	500	Call et al. 1999
Invertebrate	Lumbriculus variegatus	AgNO₃	28-day IC <sub>50</sub> (reproduction)	23.9 <sup>b</sup>	Rajala et al. 2016
Invertebrate	Lumbriculus variegatus	AgNO <sub>3</sub>	28-day IC <sub>50</sub> (reproduction)	129	Rajala et al. 2016
Invertebrate	Lumbriculus variegatus	AgNO <sub>3</sub>	28-day IC <sub>50</sub> (reproduction)	214	Rajala et al. 2016
Invertebrate	Lumbriculus variegatus	AgNO <sub>3</sub>	28-day IC <sub>50</sub> (number of worms)	38	Rajala et al. 2016
Invertebrate	Lumbriculus variegatus	AgNO₃	28-day IC <sub>50</sub> (number of worms)	525	Rajala et al. 2016
Invertebrate	Lumbriculus variegatus	AgNO <sub>3</sub>	28-day IC <sub>50</sub> (number of worms)	688	Rajala et al. 2016
Invertebrate	Ampelisca abdita <sup>d</sup>	AgNO <sub>3</sub>	10-day LC50	1037 <sup>c</sup>	Berry et al. 1999
Invertebrate	Potamopyrgus antipodarum	AgNO₃	14-day NOEC (mortality and growth)	78.5ª	Ramskov et al. 2015
Invertebrate	Potamopyrgus antipodarum	AgNO <sub>3</sub>	14-day NOEC (mortality and growth)	82.8 <sup>a</sup>	Ramskov et al. 2015
Invertebrate	Capitella teleta <sup>d</sup>	AgNO <sub>3</sub>	14-day NOEC (mortality and growth)	84.1 <sup>a</sup>	Ramskov et al. 2015
Invertebrate	Capitella sp. S <sup>d</sup>	AgNO <sub>3</sub>	14-day LOEC (mortality)	96.3 <sup>a</sup>	Ramskov et al. 2015

Abbreviations: dw = dry weight;  $LC_{50}$  = the concentration of a stressor that is estimated to be lethal to 50% of the test organisms over a specific time interval;  $EC_{50}$  = the concentration of a stressor that is estimated to be effective in producing a biological response, other than mortality, in 50% of the test organisms over a specific time interval;  $IC_{50}$  = the concentration of a stressor that is estimated to inhibit a biological response, other than mortality, in 50% of the test organisms over a specific time interval;  $IC_{50}$  = the concentration of a stressor that is estimated to inhibit a biological response, other than mortality, in 50% of the test organisms over a specific time interval; NOEC = No observed effect concentration; LOEC = Lowest observed effect concentration.

<sup>a</sup> Values represent maximum concentrations tested for sediments studies.

<sup>b</sup> Selected as critical toxicity value (CTV).

° The endpoint was estimated based on the data presented in the reference.

<sup>d</sup> Marine species.

## Appendix F. Silver soil toxicity dataset

Group	Test organism	Endpoint	Value <sup>a</sup> (mg/kg dw)	Reference
Plant	Barley, <i>Hordeum vulgare</i>	5-day EC <sub>10</sub> , root length	25	Langdon et al. 2015
Plant	Barley, <i>Hordeum vulgare</i>	5-day EC <sub>50</sub> , root length	88	Langdon et al. 2015
Plant	Northern wheatgrass, <i>Elymus</i> <i>lanceolatus</i>	21-day EC <sub>10</sub> , root/shoot dry mass	3 <sup>b</sup>	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus</i> <i>lanceolatus</i>	21-day EC <sub>50</sub> , shoot dry mass	16	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus</i> <i>lanceolatus</i>	21-day EC <sub>50</sub> , shoot dry mass	40, 184	Velicogna et al. 2016
Plant	Northern wheatgrass, <i>Elymus</i> <i>lanceolatus</i>	21-day EC <sub>50</sub> , root dry mass	33	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus</i> <i>lanceolatus</i>	21-day EC <sub>50</sub> , root dry mass	99, 98	Velicogna et al. 2016
Plant	Northern wheatgrass, <i>Elymus</i> <i>lanceolatus</i>	21-day EC <sub>10</sub> , shoot length	7	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus</i> <i>lanceolatus</i>	21-day EC <sub>10</sub> , root length	20	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus</i> <i>lanceolatus</i>	21-day EC <sub>50</sub> , shoot length	68	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus</i> <i>lanceolatus</i>	21-day EC₅₀, shoot length	77, 413	Velicogna et al. 2016
Plant	Northern wheatgrass, <i>Elymus</i> <i>lanceolatus</i>	21-day EC <sub>50</sub> , root length	59	ECSTL 2011
Plant	Northern wheatgrass, <i>Elymus</i> <i>lanceolatus</i>	21-day EC₅₀, root length	45, 106	Velicogna et al. 2016

#### Table F-1. Ag toxicity on soil-dwelling organisms

Group	Test organism	Endpoint	Value <sup>a</sup> (mg/kg dw)	Reference
Plant	Northern wheatgrass, <i>Elymus</i> <i>lanceolatus</i>	21-day EC <sub>50</sub> , emergence	298, 1491	Velicogna et al. 2016
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC <sub>10</sub> , root/shoot dry mass	1 <sup>b</sup>	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC <sub>50</sub> , shoot dry mass	4	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC <sub>50</sub> , shoot dry mass	85, 498	Velicogna et al. 2016
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC <sub>50</sub> , root dry mass	7	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC <sub>50</sub> , root dry mass	106, 227	Velicogna et al. 2016
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC <sub>10</sub> , shoot length	33	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC <sub>10</sub> , root length	18	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC₅₀, shoot length	1845	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC <sub>50</sub> , shoot length	54, 304	Velicogna et al. 2016
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC <sub>50</sub> , root length	336	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC <sub>50</sub> , root length	75, 172	Velicogna et al. 2016
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC <sub>10</sub> /EC <sub>50</sub> , emergence	>3014	ECSTL 2011
Plant	Red clover, <i>Trifolium pratense L.</i>	14-day EC <sub>50</sub> , emergence	188, 1047	Velicogna et al. 2016
Plant	Tomato, Lycopersicum esculentum	21-day EC <sub>10</sub> , emergence	6.6	Langdon et al. 2015
Plant	Tomato, Lycopersicum esculentum	21-day EC <sub>50</sub> , emergence	73	Langdon et al. 2015

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

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

Group	Test organism	Endpoint	Value <sup>a</sup> (mg/kg dw)	Reference
Invertebrates	Springtail, Folsomia candida	28-day EC <sub>10</sub> , reproduction	47.6 <sup>b</sup>	Waalewijn- Kool et al. 2014
Invertebrates	Springtail, <i>Folsomia candida</i>	28-day EC <sub>20</sub> , reproduction	76	Mendes et al. 2015
Invertebrates	Springtail, <i>Folsomia candida</i>	28-day EC <sub>50</sub> , reproduction	94	ECSTL 2011
Invertebrates	Springtail, <i>Folsomia candida</i>	28-day EC <sub>50</sub> , reproduction	114, 177	Velicogna et al. 2016
Invertebrates	Springtail, Folsomia candida	28-day EC <sub>50</sub> , reproduction	152	Mendes et al. 2015
Invertebrates	Springtail, <i>Folsomia candida</i>	28-day EC <sub>50</sub> , reproduction	99.5	Waalewijn- Kool et al. 2014
Invertebrates	Springtail, <i>Folsomia candida</i>	28-day LC <sub>10</sub>	297	ECSTL 2011
Invertebrates	Springtail, <i>Folsomia candida</i>	28-day LC <sub>10</sub>	82	Mendes et al. 2015
Invertebrates	Springtail, <i>Folsomia candida</i>	28-day LC <sub>20</sub>	118	Mendes et al. 2015
Invertebrates	Springtail, <i>Folsomia candida</i>	28-day LC <sub>50</sub>	785	ECSTL 2011
Invertebrates	Springtail, Folsomia candida	28-day LC50	216, 356	Velicogna et al. 2016
Invertebrates	Springtail, Folsomia candida	28-day LC <sub>50</sub>	284	Waalewijn- Kool et al. 2014
Invertebrates	Springtail, <i>Folsomia candida</i>	28-day LC <sub>50</sub>	179	Mendes et al. 2015

Abbreviations: dw = dry weight; EC10/20/50 = 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; LC10/20/50 = 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.

<sup>b</sup> Geometric means applied for the species SSD data points.

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 (2006a). pH > 7, and/or soils with high silt/clay contents are considered case-by-case.