Silver Water Quality Guidelines - Freshwater and Marine Aquatic Life

Ministry of Water, Land, and Resources Stewardship
Watershed Stewardship and Security Branch

BRITISH COLUMBIA

Cover Photograph:

Location: Nanaimo River, B.C.

EXECUTIVE SUMMARY

The British Columbia Ministry of Water, Land and Resource Stewardship (WLRS) develops province-wide ambient Water Quality Guidelines (WQGs) for substances or physical attributes that are important for managing both the fresh and marine surface waters of British Columbia (B.C.). WQGs provide a basis for water quality assessments and inform decision-making in the natural resource sector. WQGs may be created for the protection of designated values, including aquatic life, wildlife, agriculture, drinking water sources, and recreation. This document presents updated silver (Ag) WQGs for the protection of freshwater aquatic life.

Elevated concentrations of Ag can adversely affect aquatic and terrestrial life. While background Ag concentrations in B.C. are generally lower than the threshold for adverse effects to biota, anthropogonic activities such as mining can increase Ag concentrations in aquatic ecosystems. Silver has no biological function and uptake in fish and invertebrates can disrupt ion regulation leading to reduced growth rates, reduced reproductive success and lethality.

In 2015, Canadian Council of Ministers of Environment (CCME) published a long-term chronic Canadian WQGs for total Ag for the protection of freshwater aquatic life. CCME opted not to publish a short-term acute WQG as it was a similar concentration to the chronic WQG. B.C. has adopted the chronic guideline with the addition of an assessment factor (AF) to account for the sources of uncertainty. While the previous B.C. WQG included hardness as a toxicity modifying factor, the updated guideline is not dependant on any water quality factor. A comparison of the updated WQG for total Ag with province wide ambient background concentrations showed that 95% of the samples were below the updated WQG.

B.C. is also adopting the marine short-term acute Canadian WQG published by CCME in 2015 with the addition of an AF. CCME did not publish a long-term chronic WQG in 2015 citing a lack of data. Therefore, B.C. will use the chronic WQG developed by Australia and New Zealand Environment and Conservation Council (ANZECC) as a working WQG.

A summary of the WQGs is presented in Table E.1.

Table E.1. Summary of recommended water quality guidelines for silver.

Value	Acute Guideline (µg/L)	Chronic Guideline (µg/L)
Freshwater Aquatic life	NA	0.12
Marine Aquatic life	3.7	0.5*

* The chronic marine WQG was adopted from Australia and New Zealand as a working water quality guideline and an AF of 3 was applied.

ii

CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

The British Columbia Ministry of Water, Land, and Resource Stewardship (WLRS) develops province-wide ambient Water Quality Guidelines (WQGs) for substances or physical attributes that are important for managing both the fresh and marine surface waters of British Columbia (B.C.). WLRS defines a WQG as a scientifically derived numerical concentration or narrative statement considered to be protective of designated values in ambient conditions. WQGs provide a basis for water quality assessments, to inform decision-making in the natural resource sector and may be derived for the protection of designated uses including aquatic life, wildlife, agriculture (livestock watering and irrigation), source drinking water, and recreation.

In B.C., WQGs are developed to protect the most sensitive endpoint associated with a given value (e.g., aquatic life, wildlife, livestock). For substances with sufficient toxicological data, both short-term acute and long-term chronic guidelines are developed.

WQGs are typically based on toxicological studies conducted under laboratory conditions. There are several uncertainties associated with applying WQGs to field conditions, including:

- o Laboratory to field differences in exposure conditions;
- o Single contaminant tests in laboratories vs exposure to multiple contaminants in the field that may demonstrate additive, synergistic, or antagonistic effects;
- o Toxicity of metabolites;
- o Intra- and inter-specific differences between test species used to derive the WQG and those found in the field;
- o Indirect effects (e.g., behavioral responses, food web dynamics);
- o Laboratory studies conducted on partial life cycle studies which may not include the most sensitive life stage;
- o Delayed effects which may not occur within the life stage tested, or may occur across generations; and
- o Exposure of organisms to cumulative effects of the various stressors, such as habitat loss and climate change.

Given these uncertainties, WQGs are a predicted no-effect concentration (i.e., no effects are expected if exposure concentrations are below the WQG). An exceedance of the WQGs presented in this document does not imply that unacceptable risks are present, but that the potential for adverse effects is increased, and additional investigation and monitoring may be warranted. To that end, ongoing ecological monitoring is encouraged to ensure the WQG is indeed protective under field conditions.

In 2015, the Canadian Council of Ministers of the Environment (CCME) published an updated Canadian WQG for total silver (Ag) for both freshwater and marine aquatic life (CCME, 2015a; CCME, 2015b). B.C. has adopted these guidelines with the addition of assessment factors (AF) to address the sources of uncertainty. This document provides information on CCME's derivation of the aquatic life guidelines (replicated here verbatim from both the Scientific Criteria Document (CCME, 2015a) and the Canadian Water Quality Guidelines for Protection of Aquatic Life (CCME, 2015b) and highlighted grey) as well as a discussion of background concentrations in B.C. and the choice of AFs.

1

2. SUBSTANCE IDENTITY

Silver (symbol Ag, atomic number 47, atomic radius 144 pM) is a transition element with two naturally occurring stable isotopes, ^{107}Ag and ^{109}Ag. There are numerous radioisotopes, none of which occur naturally and most have a short half-life. Properties of silver and some common silver compounds are presented in Table 2.1.

Table 2.1. Physical properties of silver and some common silver compounds
(developed from WHO, 2002; FactSage, 2009)

	CAS no.	Formula	Molecular weight (g/mol)	Physical state	Melting point (ºC)	Specific density (g/cm3)	Water Solubility (20°C)
Silver	7440-22-4	Ag	107.87	Solid metal	961.9	10.49	Insoluble
Silver	7761-88-8	$AgNO_3$	169.89	Solid	212	4.352	2160 g/L
Silver	21548-73-	Ag_2S	247.80	Grey-black	825	7.33	Insoluble
Silver	7783-90-6	AgCl	143.34	White solid	455	5.56	1.9 mg/L
Silver(I)	20667-12-	Ag_2O	231.74	Solid	n/a	7.143	22 mg/L (@ 25°C)
Silver(II)	1301-96-8;	AgO	123.88	Solid	n/a	7.44	Reacts in water

3. SOURCES AND USES

Silver is a naturally occurring element that is ubiquitous in all environmental compartments. It is found in the environment in two oxidation states, 0 and 1+. Oxidation states of 2+ and 3+ also can exist but rarely occur in natural environments. The review of Purcell and Peters (1998) provides a summary of sources of silver in the environment; some highlights from this review are outlined below. Naturally occurring concentrations of silver in the environment tend to be low except in and near mineral deposits. Purcell and Peters (1998) estimated that approximately 62% of the total Ag in water comes from natural sources with the remainder coming from anthropogenic inputs. Anthropogenic sources of silver to the environment are diverse and occur along the extraction, manufacture, use, and disposal chain. Mining operations and metals production account for significant releases, particularly to air and soil. The photographic industry has been associated with inputs to the aquatic environment through the use of silver halides in film processing, previously being the major use and disposition. However, with the advent of digital photography in the last decade, this contribution has undoubtedly decreased, dropping to approximately 13% of the market (Wood, 2012). Other anthropogenic sources of Ag to the terrestrial environment are linked to wastewater treatment and biosolids disposal (Purcell and Peters, 1998). Atmospheric releases occur primarily from combustion; coal, petroleum, waste incineration, electrical production and cement kilning, which account for 47% of all releases into this compartment. Overall, air emissions only amount to less than 4% of all anthropogenic silver released to the environment. In terms of point sources of silver to the aquatic environment, effluents from municipal wastewater treatment plants as well as mine and smelter operations represent significant potential sources.

Silver is associated with copper, nickel, gold, lead and zinc. In Canada, operations actively producing silver can be found in British Columbia, Saskatchewan, Manitoba, Ontario, Québec and New Brunswick. The top four countries producing silver in 2012 were Mexico, China, Peru and Australia which collectively account for over half of worldwide production. Canada ranked eleventh, with about 3% of total world production (data from The Silver Institute, www.silverinstitute.org). Silver is a soft, white, lustrous element used in coins, jewellery, tableware, mirrors and photography. Demand for silver is generally restricted to three main uses; industrial and decorative uses, photography, and jewellery and silverware, together

2

accounting for 95% of annual silver consumption. Data from 2012 indicate the majority of silver was used in the industrial sector (466 Moz or 55%), followed by the jewellery market (186 Moz or 22%), the photographic sector (58 Moz or 7%), and finally the silverware market (45 Moz or 5%). Because silver is the best conductor of all metals, its use in electrical applications is widespread. It does not corrode and has low resistance, which makes silver the most safe and reliable material for electrical switches. Other unique characteristics of silver, such as its ductility, strength, its sensitivity to light and high reflectance of light, ability to withstand extreme temperature ranges, and malleability make silver indispensable in a variety of other applications and restrict substitutions (The Silver Institute, www.silverinstitute.org).

4. **FATE AND BEHAVIOUR**

Silver ions occur mainly as oxidation states 0 and 1+. Oxidation states of 2+ and 3+ rarely occur in natural environments. The majority (>94%) of silver released into the environment is expected to remain in soil or wastewater sludge at the site of silver emission, and in freshwater environments silver will also adsorb to sediments or suspended particles (Ratte, 1999). Silver in aquatic systems can be fractionated based on size, e.g., with the particulate phase being >0.45 µm, colloids being >10 kDa and <0.45 µm, and truly dissolved at <10 kDa. Truly dissolved silver includes the free ion plus hydroxides, chlorides, nitrates and sulphates. Concentration of dissolved silver is typically very low due to the stable complexes formed with dissolved organic carbon (DOC) or inorganic or organic sulphides. In estuarine and marine environments, chlorides play a key role in silver speciation. As salinity increases, from fresh water to estuaries and finally the ocean, colloid-bound silver dissociates and silver complexation with chloride predominates. In general, the majority of silver in estuarine systems is deposited to sediments (Ratte, 1999); however, there is also potential for chloride-bound silver to remain in solution.

Bioaccumulation and partitioning: The potential uptake of metals across respiratory, gastrointestinal or other epithelial surfaces is related to the structure and function of the surface, the geochemical forms (i.e., metal speciation) in the exposure medium and interactions that occur at the interface of the tissue with its environment. In fish, for example, uptake of silver occurs at cells that are specialized for physiological functions related to nutrient uptake and ionoregulation in the gastrointestinal tract and in the gills. Silver ion is most reactive and toxic but other forms can also be taken up, e.g., thiosulphate, undissociated AgCl, uncharged lipophilic organic complexes (e.g., some flotation agents used in mineral extraction) and sulphides, with variable contributions to toxicity (see below). In one study with rainbow trout (*Oncorhynchus mykiss*) (Galvez and Wood, 2002), most of the silver accumulated from water partitioned to the liver, intestine and gills. At the subcellular level about 60% was in the nuclear membrane fraction with the remainder in the cytosol. Of that, about 70% appeared to be bound to metallothionein-like proteins. Metallothionein binds silver very strongly and plays a significant role in the transport, metabolism and detoxification of metals in general. In fresh waters, algae may act as a very important source of metal introduction into the aquatic food chain due to its vital role in the biogeochemical cycling of silver (Ratte, 1999; Fortin and Campbell, 2001; Garnier and Baudin, 1989). Aquatic bryophytes (*Scapania undulate*) near lead mining streams in England showed higher silver, a co-product of lead mining, levels in their tissues than in the water, according to Jones *et al.* (1985). Other appropriate biomonitors of metal contamination in fresh waters include zebra mussels (*Dreissena polymorpha*) (Roditi and Fisher 1996). It is hypothesized that bioaccumulation of silver by filter-feeding invertebrates is related to grain size selection, as smaller grain sizes would accumulate faster (Ribeiro Guevara *et al.,* 2005). Uptake of silver by oligochaetes (*Lumbriculus variegatus*) exposed to silver sulphide showed little accumulation and no toxic effects, while uptake of silver by *Daphnia magna* was proportional to the aqueous silver concentration (Hirsch, 1998; Lam and Wang, 2006). In largemouth bass (*Micropterus salmoides*) and bluegill (*Lepomis macrochirus*), accumulation occurred over a 2 month period after which

3

equilibrium between the exposure water and tissue of the fish was reached (Coleman and Cearley, 1974). In marine waters as in fresh water, silver uptake by phytoplankton was rapid. Further, it was independent of taxonomic species, inversely proportional to salinity and directly proportional to macronutrient levels. In molluscs, there were numerous factors that influenced silver uptake such as taxonomic species (scallops and oysters accumulated more than mussels), sex, age, size, reproductive stage, season, and latitude. Molluscs generally are metal accumulators capable of storing metals in detoxified form. Results between taxonomic classes were sometimes paradoxical. Clams from a contaminated site accumulated twice the amount of silver as naïve clams but depurated more quickly. In contrast, naïve polychaete worms accumulated twice as much as worms from a polluted area. In crustaceans, silver uptake in shrimp correlated better with chloride than any other silver species, yet uptake declined as salinity increased (Warrington, 1996). In a study that was conducted on Dover sole the accumulation of silver was not found to be significant. Silver behaves differently from the other trace metals in that the speciation reactions that enhance silver solubility also enhance its bioavailability and dispersion in estuarine or marine environments (Luoma *et al.,* 1995). Dietary exposure to silver has been studied much less than waterborne exposure. In molluscs uptake from food was less than from water (Metayer *et al.,* 1990). Wang and Fisher (1998) found that 30 to 70% of the silver body burden in a marine copepod (*Temora longicornis*) is likely to come from aqueous uptake and not from the dietary route and that silver is retained by the organism less efficiently when accumulated from food.

Bioconcentration, bioaccumulation and biomagnification factors: These factors are of less utility with inorganic substances than they are with organics since many organisms are able to sequester metals in inactive forms. Bioaccumulation of silver increases with increasing exposure but disproportionately. BCFs and BAFs decreased with increasing exposure (reviewed by McGeer *et al.,* 2003). Silver can bioaccumulate to very high levels, yet depending on the form, may not be associated with physiological effects (Hogstrand *et al.* 1996). There is no evidence for silver biomagnification (Terhaar *et al.,* 1977; Ratte, 1999; McGeer *et al.,* 2003). In fact, bioconcentration and bioaccumulation factors actually decrease with increasing exposure concentration (McGeer *et al.,* 2003).

5. BACKGROUND CONCENTRATION OF SILVER IN BRITISH COLUMBIA

Silver is a naturally occurring element in aquatic and terrestrial ecosystems, therefore, background concentrations must be considered when deriving provincial Ag WQGs.

5.1. Methods for Estimating Background Concentrations of Silver in British Columbia Surface Waters

Background (i.e., from minimally sites) total Ag concentrations vary across B.C. as a function of local geology and hydrology; therefore, a regional approach was used to estimate background concentrations. Silver concentrations were estimated following methods used in recent WQG derivation documents (e.g., ENV, 2021). Data were obtained from two sources: the B.C. Environmental Management System (EMS) database and the Canadian Aquatic Biomonitoring Network (CABIN) database. EMS does not identify reference stations, so the database was screened to create a sub-set of water quality stations known to be minimally impacted. To do this, "background" water quality sampling stations that were sampled at least three times over 20 years for any water quality parameter (1996/01/01 to 2017/05/03) were extracted. Next, the list of stations with location information was given to ENV environmental impact assessment biologists to identify sites that they considered minimally impacted by human activities. No strict definition of 'minimally impacted' was given to the biologists and station selection was left to their professional judgement.

4

The list of minimally impacted stations was then used to extract Ag data from the EMS database within the following date range: 2000/01/01 to 2021/12/31.

The dataset underwent several additional automated and manual data cleaning steps summarized below:

- Where lake samples were available at multiple depths, only surface samples were included;
- non-detect results with a method detection limit (MDL) ≥5 µg/L were removed as these would influence the results of the analysis;
- samples were excluded where results were missing or reported as 0; and
- outliers were visually inspected and removed if deemed to be a reporting error.

Arithmetic means were calculated for laboratory replicates (analytical replicates taken from one field sample) with ½ the MDL substituted for values below detection. All field replicates were included as independent samples. The final data set consisted of 583 stations with 1514 samples.

The results from each station were given equal weight within an ENV administrative region by calculating the mean Ag concentrations for each station. Station means were calculated using four different approaches depending on the number of samples above (detects) and below (non-detects) the MDL (Table 5.1). A value of ½ the minimum MDL was used to represent station means when all samples were below the MDL (Group 1). The minimum MDL was chosen to account for decreasing MDLs over time. For stations with less than three detects, ½ of the MDL was substituted for non-detect values and the arithmetic mean of all station results was calculated (Group 2). Regression on order statistics (ROS) was used to calculate an estimate of the mean for stations that had a mixture of non-detects and detects with at least three detected values (Huston and Juarez-Colunga, 2009; Group 3). Although Huston and Juarez-Colunga (2009) state that ROS can be used on sample sizes >0, a minimum of three detects is required to calculate a valid regression using the NADA package (Lee, 2017) in R (R Core Team, 2022). The arithmetic mean was calculated for stations where all samples were above the MDL (Group 4). Statistics to summarize the distribution of station means (median, the 10th and 90th percentile) were calculated for each ENV region.

Table 5.1. Statistical approach used to calculate station means.

Group	Conditions	Approach	Total Stations	Total Samples
1	% non-detects = 100	½ of minimum station MDL	535	877
2	0 < % non-detects < 100 AND # detects < 3	Substitute ½ MDL for non-detects and calculate arithmetic mean for all samples	14	127
3	0 < % non-detects < 100 AND # detects ≥ 3	Regression on order statistics	15	434
4	% non-detects = 0	Arithmetic mean	6	33

5.2. Background Concentration Results - Freshwater

The distribution of total Ag concentrations by ENV administrative region is summarized in Table 5.2 and
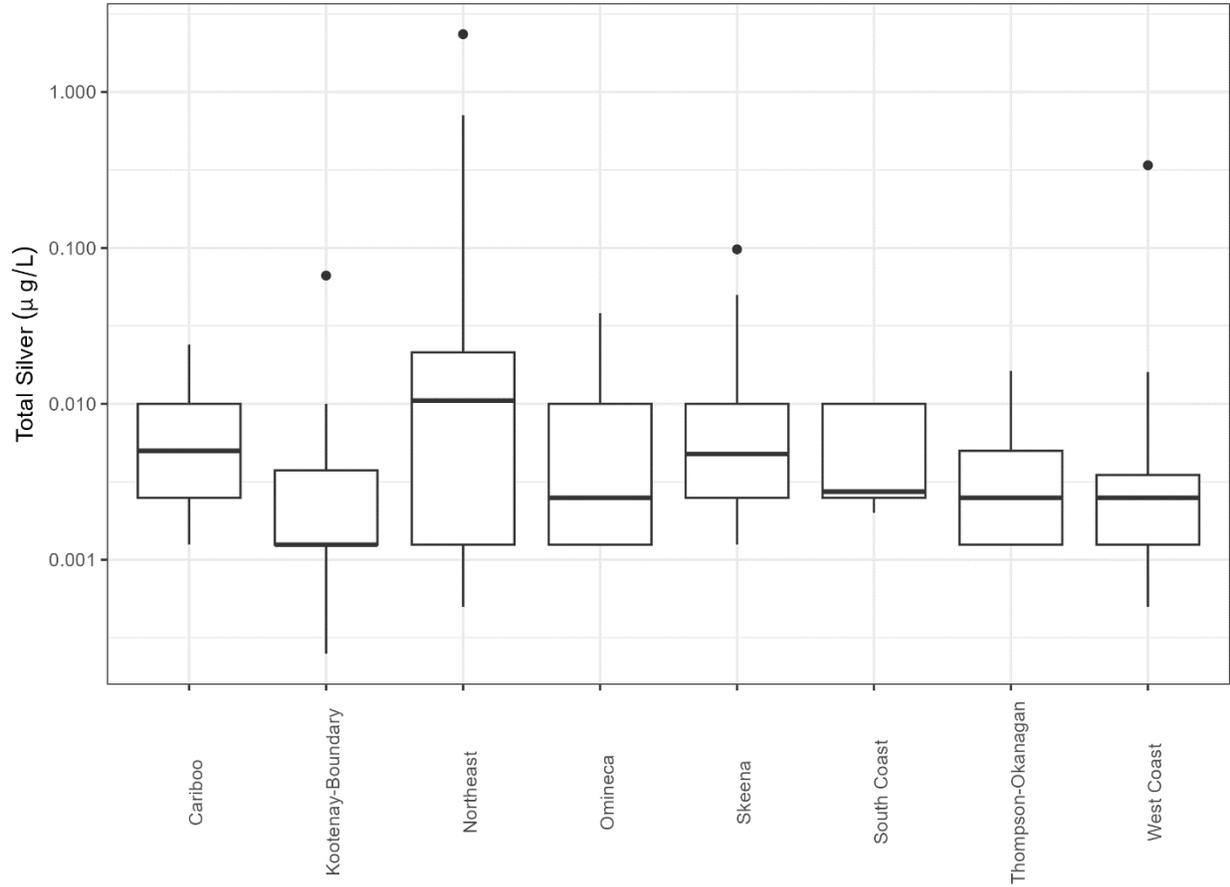
Figure 5.1. The median of station means ranged from 0.00125 µg/L (Kootenay-Boundary) to 0.011 µg/L (Northeast). Of the 570 stations, 54 stations were on lakes and 516 were on rivers. The median of the distribution of station means in lakes was the same as rivers (0.0025 µg/L).

Table 5.2. Summary statistics for mean dissolved Ag at minimally impacted freshwater stations in British Columbia.

Region	Number of Stations	Number of Samples	Date Range	Concentration Range Across all Samples (µg/L)	MDL Range Across all Samples	% Samples < MDL	Distribution of Station Means (µg/L)		
							Median	10th Percentile	90th Percentile
Cariboo	48	342	2000 - 2023	0.001 - 0.117	0.001 - 0.1	54	0.005	0.0025	0.01
Kootenay-Boundary	43	92	2001 - 2023	0.0005 - 0.133	0.005 - 0.02	45	0.00125	0.00125	0.005
Northeast	150	167	2009 - 2023	0.001 - 4.7	0.005 - 0.005	8	0.011	0.00125	0.03605
Omineca	39	132	2000 - 2023	0.001 - 0.2	0.001 - 0.1	33	0.0025	0.00125	0.01
Skeena	168	344	2000 - 2023	0.001 - 0.6	0.001 - 0.1	30	0.005	0.00125	0.01
South Coast	8	18	2003 - 2023	0.004 - 0.02	0.005 - 0.02	89	0.00275	0.00235	0.01
Thompson-Okanagan	53	237	2000 - 2023	0.0025 - 5.0	0.005 - 5.0	79	0.0025	0.00125	0.01
West Coast	61	139	2001 - 2023	0.001 - 0.339	0.001 - 0.05	72	0.0025	0.00125	0.01
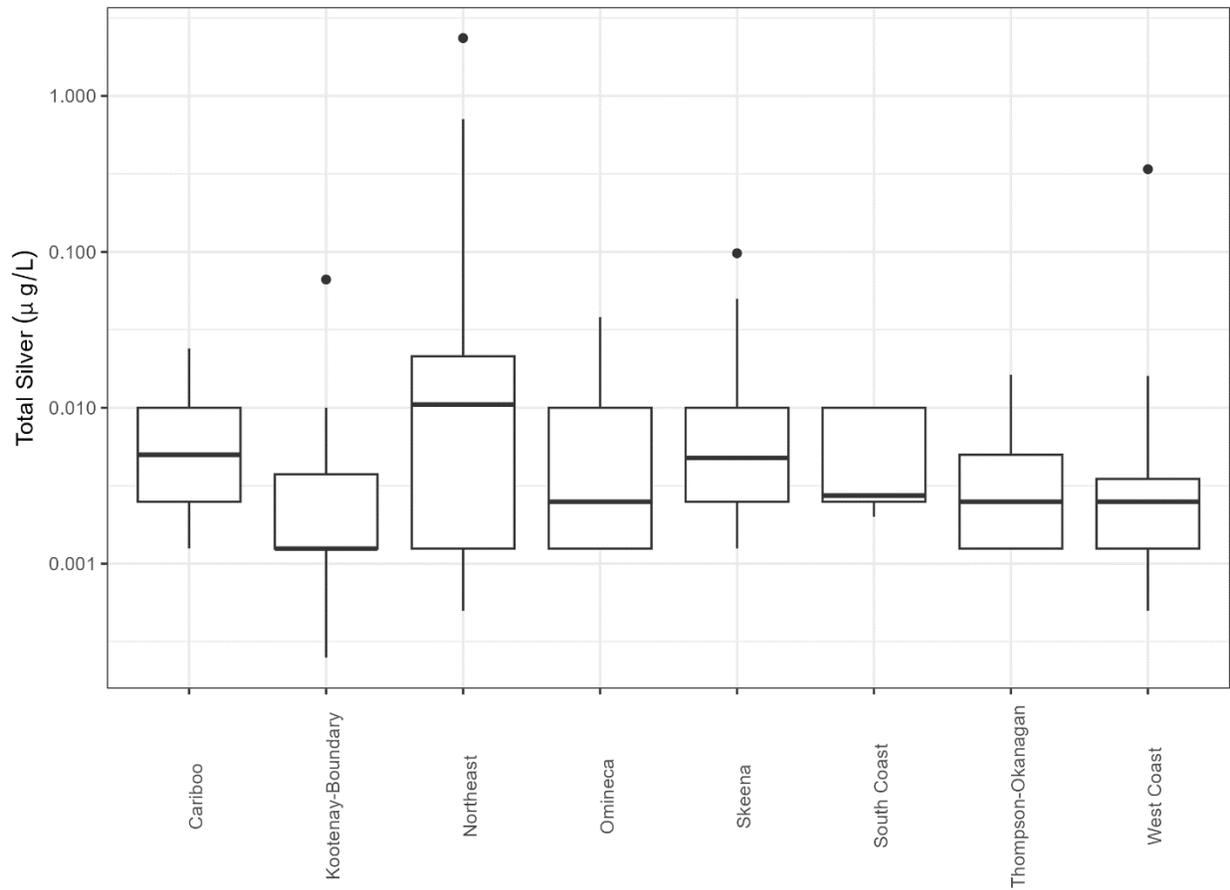
Figure 5.1. Ambient mean total Ag in British Columbia by region. Solid horizontal bar and the lower and higher whiskers represent median, 10th and 90th percentile of station means.

Note, the y-axis is presented using a logarithmic scale. Outliers 4.7 µg/L (Northeast Region), and 5.0 µg/L (Thompson-Okanagan Region) have been removed to better illustrate the data.
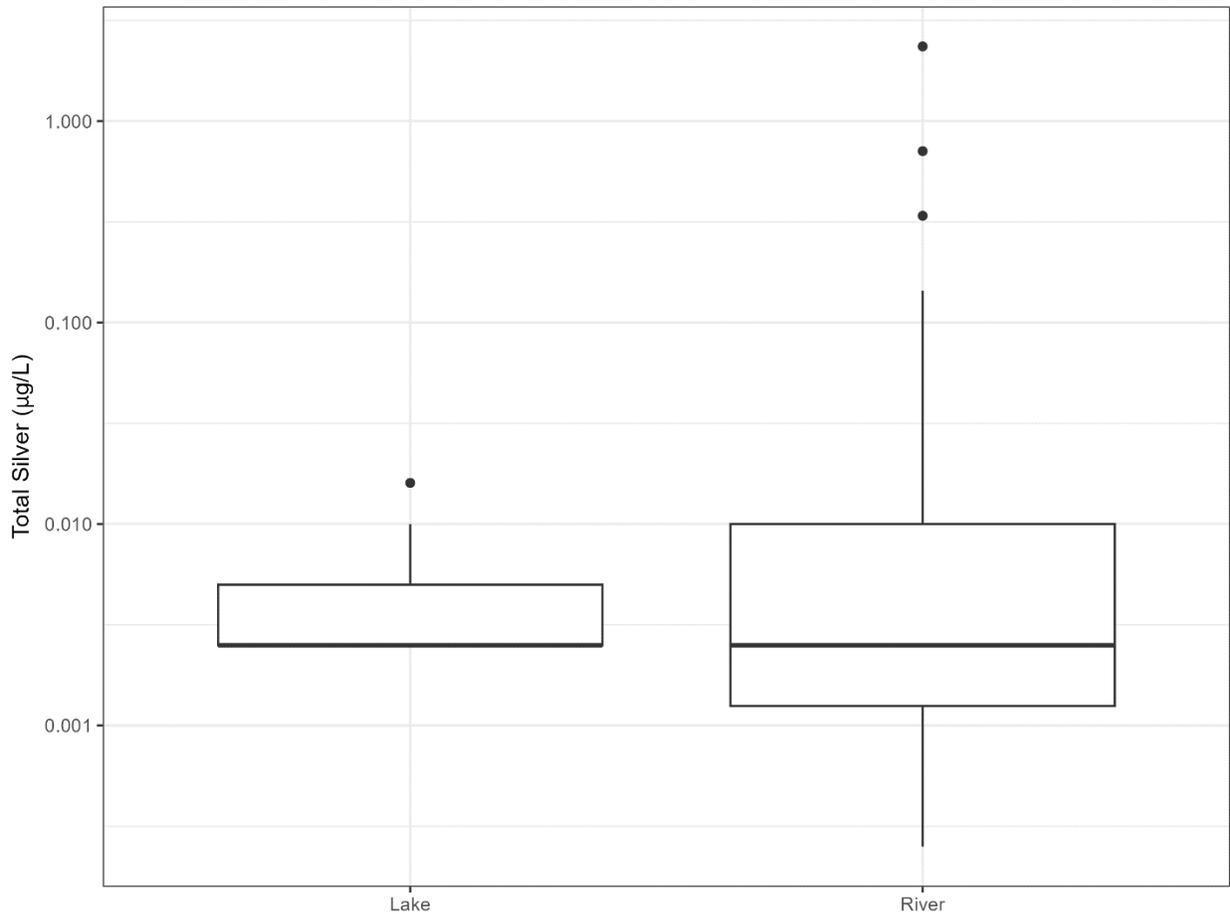
Figure 5.2 Ambient mean total Ag in British Columbia by waterbody type.

Solid horizontal bar and the lower and higher whiskers represent median, 10th and 90th percentile of station means. Note, the y-axis is presented using a logarithmic scale.

6. EFFECTS ON AQUATIC LIFE

6.1. Essentiality

There is no evidence to date that silver has any essential biological function in aquatic systems.

6.2. Mode of Action and Toxicokinetics

Much of the understanding of silver toxicity has arisen through studies on fish, particularly rainbow trout. The free ion form of silver (Ag^+) disrupts ion balance via competition at the Na^+ specific uptake channel. Ag^+ is an ionoregulatory toxicant to the gill that reduces Na^+ and Cl levels, disrupts fluid volume, and causes circulatory failure (Wood, 2012). Silver accumulation leads to a poisoning of the basolateral Na^+K^+ adenosinetriphosphatase (Na^+/K^+ ATPase or NKA) in the chloride cells of the gill epithelium. NKA is a multisubunit protein embedded in the basolateral (blood) side of the cell and is one of the key proteins driving the uptake of Na^+ (and indirectly other cations and Cl^-). Its function is essential for ionoregulation.

The cause of Ag^+ toxicity to aquatic organisms through this mechanism is the interference of the function of NKA by binding to a Mg site on one of the subunits (Morgan *et al.*, 1997). This binding irreversibly inhibits activity of the enzyme, resulting in ionoregulatory disturbance. If sufficient ion transport capacity is lost, the fish will die. Morgan *et al.* (1997) showed a dose dependent inhibition of Na^+ and Cl^- uptake by silver, and inhibition of NKA has been shown in a number of studies.

Another site of action for acute toxicity is inhibition of the enzyme carbonic anhydrase in the branchial ionocytes (Wood, 2012). Carbonic anhydrase catalyzes hydration of carbon dioxide to form acidic and basic counterions (H^+ and HCO_3), against which uptake of the ions Na^+ and Cl are exchanged at the apical surface (Evans *et al.*, 2005 as reported in Wood, 2012).

With respect to mechanisms of chronic toxicity, interference with Na^+ and Cl^- regulation is similar to that seen in acute toxicity where whole-body levels of the two ions gradually decrease (Wood, 2012). Physiological disturbances associated with the decrease are also similar to acute toxicity including decreases in whole-body Na^+ uptake and Na^+/K^+ -ATPase activity and increases in whole-body cortisol and ammonia levels (Brauner and Wood, 2002b; Brauner *et al.*, 2003 as reported in Wood, 2012). Furthermore, in fish, silver may induce the detoxifying protein metallothionein, potentially causing decreases in growth, hatching or survival due to increased metabolic costs. In some invertebrate species, silver may inhibit reproduction by disrupting the synthesis of vitellogenin (Wood, 2012).

In marine fish, the main toxicity mechanism appears to involve osmoregulatory failure, as seen in freshwater fish. However, while this failure can be attributed to only one organ (gills) and one function (branchial ionoregulation) in freshwater fish, marine teleosts have two possible target organs (gills and gut) and two possible target functions (branchial ionoregulation and gastrointestinal ionoregulation) (Wood, 2012). This is due to marine fish drinking the aquatic medium continually to remain hypotonic and therefore bringing Ag from the water column in direct contact with the gut surface (Wood, 2012).

6.3. Aquatic toxicity and toxicity modifying factors: an understanding through speciation

Much of the research discussed previously is based on the effects of Ag in laboratory water, often with low ionic strength and typically low in dissolved organic carbon (DOC) or other complexing ligands. In such laboratory testing, $AgNO_3$, which readily dissociates into the free Ag^+ ion, was found to be one of the most toxic of the Ag forms to freshwater species (Bury *et al.*, 1999; Karen *et al.*, 1999; Rodgers *et al.*, 1997). However, under field conditions the levels of free Ag^+ would be very low. Also, it has been well documented that Ag accumulation and toxicity is mitigated by organic and inorganic complexation, and by competing cations for binding sites on the biotic ligand (i.e., fish gills). It is therefore recognized that a generic guideline value with no modifying factors will be conservative and silver complexation as well as the presence of competing cations must be considered to appropriately assess the potential toxicity of silver in natural waters.

In the past, this influence of water chemistry was recognized in the form of a 'hardness correction' where limits were expressed as a function of total water hardness. This relationship was based on limited data, and its shortcomings have been recognized. Today's understanding is that hardness cations (Ca^{2+} and Mg^{2+}) are relatively ineffective in acute studies at reducing Ag accumulation and toxicity (Karen *et al.*, 1999). Hardness has been determined to have a weak protective effect (Davies *et al.*, 1978; Erickson *et al.*, 1998; Bury *et al.*, 1999, as reported in Wood, 2012) and it appears to be mainly attributed to Ca^{2+} rather than Mg^{2+} (Schwartz and Playle, 2001 as reported in Wood, 2012).

Sodium (Na^+) has a protective effect against Ag toxicity. Janes and Playle (1995) showed that Na (added as NaOH) decreased gill Ag^+ accumulation. This effect was seen at relatively high amounts of Na (~37 mg/L), but similar results were found by Morgan *et al.* (1997), and Paquin *et al.* (2002) at levels in the

range of 1-37 mg/L. Efforts to investigate the effect of alkalinity on Ag toxicity to *C. dubia* resulted in an increase in LC_{50} (0.15 to 0.2 µg/L) that was later attributed to the presence of additional Na in the medium (Naddy *et al.*, 2007b). In this study, alkalinity was adjusted using $NaHCO_3$ from 100 to 200 mg/L as $CaCO_3$, which increased the level of Na from 36 to 72 mg/L. Speciation calculations determined that the change in alkalinity did not affect Ag speciation since Ag does not form complexes with CO_3, however the increase in Na led to an increase in LC_{50}. Lam and Wang (2006) showed a clear negative relationship between Ag uptake and Na concentration (0.05 – 10 mM) in exposures with *D. magna*.

Protons (H^+) have also been considered as a possible competing cation for Ag uptake. Janes and Playle (1995) showed that H^+ ions do not compete with Ag^+ for gill binding sites in rainbow trout over a pH range of 4.5-6.8 in ion-poor, low dissolved organic carbon (DOC) water. Though seemingly inconsistent results have been seen with respect to H^+ competition, it is expected that any effect of pH would be due to interactions with DOC. That is, as pH is raised, less H^+ is available to bind to DOC leaving sites open for Ag^+ complexation. Because pH does not have an appreciable effect on inorganic Ag speciation, it is thought that pH changes would have very little effect of Ag bioavailability in low DOC conditions (for a more detailed discussion on DOC, see below).

In comparison to $AgNO_3$, silver inorganic complexes such as silver thiosulphate, silver chloride and silver sulphide were found to exert very low toxicity (LeBlanc *et al.*, 1984; Hogstrand *et al.*, 1996), indicating the effect of complexation on silver toxicity. As a Group-B metal, inorganic speciation of Ag is expected to be controlled by complexation by sulphides and chlorides. As discussed previously, reduced sulphur is a strong inorganic ligand binding Ag with a LogKAg-S of ~13. Studies by Bianchini and Bowles (2002) and Bianchini and Wood (2008) demonstrate protective effects of sulphide on silver toxicity and highlight the need to include reduced sulphur in the Biotic Ligand Model (BLM). Bianchini and Bowles (2002) demonstrate the importance of sulphide as a ligand, even in fully oxygenated aquatic systems in which reduced sulphur tends to be unstable.

The presence of natural organic matter (NOM; measured as DOC, in mg C/L) in natural waters is probably the most important complexing ligand, other than sulphide, for Ag and most other metals. In contrast to AgCl complexes, Ag-NOM complexes are large in size and as such, their ability to passively diffuse through a target membrane is limited. Studies with Aldrich humic acid (commonly used as a surrogate for NOM) have revealed a large protective effect against Ag toxicity. For example, work with fathead minnows exposed to Ag in the presence or absence of DOC has resulted in ~4-fold increase in LC_{50} (Karen *et al.*, 1999; Bury *et al.*, 1999; Erickson *et al.*, 1998). Similarly, Ag toxicity in invertebrates is also greatly reduced in the presence of DOC (Karen *et al.*, 1999; Glover *et al.*, 2005a; 2005b; Naddy *et al.*, 2007b). Since Aldrich humic acid is low in sulphide, there is some question as to whether some laboratory results underestimate the impact of DOC in natural waters. Therefore, efforts have been made recently to use NOM sourced from natural waters, concentrated from large volumes of water and reconstituted in lab water (Glover *et al.*, 2005a). An interesting characteristic of NOM is its variability depending on its source. This variability also translates into its effectiveness in reducing Ag toxicity. Currently, it appears that relatively simple optical measurements that reflect the aromaticity of NOM, such as fluorescence index, may correlate to reduction in metal toxicity, including Ag (Schwartz *et al.*, 2004; Glover *et al.*, 2005b). An interesting indirect effect of Ca^{2+} to Ag^+ toxicity is the possibility that Ca^{2+} can compete with Ag^+ for available binding sites on DOC, thus reducing the protective effect of DOC against Ag. This is supported by results with *D. magna* done by Karen *et al.*, 1999 where increasing Ca^{2+} concentrations led to an actual decrease in Ag LC_{50}. Recent work by Naddy *et al.*, 2007b with *Ceriodaphnia dubia* are consistent with this result as well. In natural waters, however, levels of Ag would rarely exceed the capacity for sulphide complexation (Adams and Kramer, 1999), and if this were to occur, NOM would be present to bind up any additional Ag, making any effects of Ca^{2+} described above unlikely.

Inorganic complexation by Cl^- can effectively reduce the bioavailability of Ag and its toxicity, however, it depends on which Ag-chloro-complex is present and varies among aquatic life species. A number of different chloro-complexes will form, with AgCl being the dominant species when Cl ranges from 10 to 300 mg/L and the $AgCl^{2-}$ complex predominant at higher Cl concentrations. Though Cl^- levels do not often exceed 100 mg/L in fresh water, the exception would be near wastewater discharge points or in areas where fresh water meets an estuary. The complicating factor with Cl^- is that the small, neutral AgCl complex is readily taken up by aquatic organisms by passive diffusion, though its contribution to toxicity appears to be minimal. Many studies that have tried to clarify the mitigating effect of Cl^- on Ag toxicity have been confounded by the accompanying cation, i.e., many have used NaCl as the source of Cl^-. Therefore, any reduction in toxicity seen is likely partially due to the Na present in solution. Investigations on the protective effect of Cl^- (0.3 to 43 mg/L) with various species of freshwater fish (*P. promelas*, *F. heteroclitus* and *D. rerio*; Bielmyer *et al.* (2007) and the European Eel (*Anguilla anguilla*; Grosell *et al.*, 2000) found that Cl^- offers little protection, which is inconsistent with studies using rainbow trout (Galvez and Wood, 1997; McGeer and Wood, 1998). It appears that, with fish, only rainbow trout are protected from Ag toxicity by Cl^-. Invertebrates (*C. dubia* and *D. magna*), however, seem to benefit from Cl^- but any protective effects are only seen when Cl^- concentrations are higher than 50 mg/L (Karen *et al.*, 1999; Naddy *et al.*, 2007a).

Water quality criteria that are based on total metal concentrations regardless of water chemistry cannot account for the toxicity modifying factors discussed above. The acute toxicity of Ag is largely based on the concentrations of free Ag^+, and the key characteristics that determine this are DOC, reduced sulphide and Cl^-. A tool with the most promise of incorporating these determinants is the Biotic Ligand Model (BLM). The model is based on the early Free Ion Activity Model (FIAM; Morel, 1983) which focussed on cationic metal binding to critical sites, and recognized the importance of DOC complexation. However, in addition to complexation, the BLM recognizes competitive effects of other cations present in water.

Several BLMs have been developed for predicting the acute toxicity of silver in freshwater species. The first was developed by Hydroqual (Paquin *et al.*, 1999) and integrated acute toxicity data for rainbow trout and fathead minnow with 2-hour gill binding data and was adapted for daphnids by downwardly adjusting the lethal accumulation (LA_{50}) value (Wood, 2012). The model was able to predict within a factor of two the variations in 96-h LC_{50} values based on water levels of Cl^-, Ca^{2+}, and DOC. However, this version of the BLM uses an assumed LA_{50} value that is higher than what has since been measured, and a lower log K value (Wood, 2012). These factors may explain why the model has tended to under predict toxicity to fathead minnows in soft water, as shown by a validation study in natural waters by Bielmeyer *et al.* (2007). The second acute BLM version (McGeer *et al.*, 2000) is physiologically based and predicts toxicity in fish from inhibition of gill Na^+/K^+-ATPase rather than based on the total Ag burden at the gill. It was tested over a range of water chemistry parameters including Cl^-, Ca^{2+}, Na^+, pH and DOC, and the vast majority of predicted values were within a factor of two of measured values (Wood, 2012). Finally, there is an acute BLM developed by Bury *et al.* (2002) that is directly based on daphnid toxicity data. Currently there is no BLM for predicting the chronic toxicity of silver to freshwater organisms (Wood, 2012). The use of BLMs in the derivation of CWQGs is currently under examination and will be a consideration for future guidelines.

6.4. Toxicity interactions with other substances and metals

Until recently, much focus has been placed on the effects of single metals in laboratory exposures. However, aquatic biota undoubtedly face metal mixtures in the field, especially at impacted sites, and thus the toxicity of mixtures containing metals and other substances is a relatively new and valuable area of research. To date, there is limited information available on the effect of interactions of potential toxicants.

Bertram and Playle (2002) studied the effect of silver exposure to fed and unfed rainbow trout (*Oncorhynchus mykiss*). No significant physiological differences were found between the fed and unfed fish. This study concluded that once Ag enters the fish, the subsequent elimination is not affected by food-related process such as increased metabolic rate or food debris in water.

A study examining the interactions of five trace elements on bioaccumulation in zebrafish (*Brachydanio rerio*) in 12-d waterborne exposures revealed that Ag bioaccumulation is proportional to water Ag concentration and Ag has a negative effect (approx. 30% decrease) on Hg accumulation (as MeHg; Ribeyre *et al.*, 1995). Mercury concentrations in the fish decrease when the concentration of Ag increases, in a nonlinear fashion. This antagonistic effect of Ag on Hg accumulation is not likely due to competition between ions at metallothionein binding sites since the affinity of MT for methyl-Hg (MeHg) is very low. The study also concluded that Zn, Cu and Se had a significant positive effect on Ag bioaccumulation, increasing Ag concentrations by 10% when compared with Ag accumulation in isolated Ag exposures. They made no attempt at reconciling accumulation with toxicity.

In model simulations with multiple metals using MINEQL+, Playle (2004) showed that in conditions where metal concentrations are low (total concentration of all metals are less than 1 toxic unit (TU), or the expected level that would result in 1 TU) the expected result is less than strict additivity, or an "antagonistic" effect on accumulation. Generally, this is accounted for by the nonlinearity of the BLM, where at low concentrations, there is 'easy' binding to the biotic ligand (high affinity sites) and at higher metal concentrations the high affinity sites are filled first and subsequently the lower affinity sites are filled.

To date, there are not enough data to be able to incorporate synergistic or antagonistic effects of other substances into a revised CWQG for silver.

6.5. Short-term and long-term toxicity of silver

A number of studies have elucidated the long-term impacts of Ag on early life stages of rainbow trout. These studies investigated the accumulation and distribution in eggs or whole body, the mechanisms of toxicity, relative sensitivities of different life stages, and the effect of water chemistry on Ag toxicity.

Guadagnolo *et al.* (2001) showed that the stage of development in the rainbow trout embryo is an important factor in sensitivity to Ag. The chorion of the rainbow trout embryo is a protein-rich membrane (~14% total protein), containing amino acids such as proline, glutamic acid and cysteine. Sulphydryl-rich cysteine plays a particularly important role in defending the embryo against Ag toxicity by limiting the rate by which Ag enters the egg (Guadagnolo *et al.*, 2000). The majority of the silver accumulated in the egg was in the chorion (65-85%). The long-term physiological effect of Ag exposure to rainbow trout embryos and larvae appear to be similar to that of short-term effects, where there is an impairment in the organism's ability to regulate Na^+ and Cl^- balance, by a reduction in NKA activity (Brauner and Wood, 2002a).

Physiological effects in juvenile rainbow trout to long-term exposure of silver nitrate in moderately hard fresh water were studied by Galvez *et al.* (1998). Exposure length of the study was 28 days for two different concentrations of silver (0.5 and 2.0 µg/L) added to dechlorinated tap water. At the lower concentration of silver exposure (0.5 µg/L) fish showed a small increase in food consumption (15%) and no change in growth rates while the 2.0 µg/L Ag exposure resulted in a 29% decrease in food consumption and 43% reduction in growth rate. Sodium and chloride levels in the plasma decreased significantly at day 16 and day 7 of exposure for the low and high silver exposure, respectively, but recovered thereafter. For the high silver exposure, accumulation of silver increased gradually in the liver up to day 15 when the wet

weight of Ag reached 39.7 µg/g (285-fold higher than controls). Also, MT levels increased by 81% by day 7, and mortality reached 15% by the end of the exposure period (Galvez *et al.*, 1998).

Galvez and Wood (2002) investigated effect of silver exposure on juvenile rainbow trout, during a 23-day exposure to 0, 0.1, 1, 3 and 5 µg/L of silver nitrate. The 5 µg/L exposure showed significant toxic effects in terms of growth rate, food consumption, food-conversion efficiency and the critical swimming speed. Although plasma levels of Na$^+$ and Cl$^-$ decreased initially, the levels came back to normal by the end of the exposure period. Based on their results, they concluded that changes in Na$^+$ transport at gills cause physiological acclimation and may eventually lead to toxicological acclimation (Galvez and Wood, 2002).

Invertebrates tend to be more sensitive to metals when compared to fish. *Ceriodaphnia dubia* and *D. magna* are listed as the two most acutely sensitive species in the 1998 U.S. EPA draft silver Ambient Water Quality Criteria (AWQC) update, with genus mean acute values of ~1 and 2 µg/L, respectively. Because of their high sensitivities, these crustacea are important organisms to study, however their small size has been a limiting factor for detailed physiological studies. On the basis of long-term toxicity, it appears that relative sensitivity to Ag and the toxicokinetics of Ag toxicity is similar. In one study with *D. magna*, neonates (newly hatched offspring) were exposed to 2 µg/L dissolved Ag over 21-days and various reproductive and physiological endpoints were observed, such as survival, growth, time to first brood, mean young produced per adult, number of broods produced, mean number of young per brood, whole body Na$^+$ and NKA activity. There was a 20% mortality in the Ag-exposed group and a 14% decrease in neonates produced per adult per productive day. The remaining reproductive endpoints were not affected. Ionoregulation in *D. magna* was affected, however, with an 81% inhibition of Na$^+$ influx and a 65% decrease in whole body Na$^+$ content despite a 60% increase in whole body NKA activity. This overall increase in NKA activity is suspected to be due to acclimation, i.e., an increased synthesis of NKA in response to decreasing Na$^+$ levels. One main difference in the ionoregulatory response of invertebrates is the lack of Cl$^-$ disturbance (Bianchini and Wood, 2003). In this regard, the response of crustaceans to Ag appears to differ from rainbow trout.

It is worth noting that an eminent researcher in the aquatic toxicity of silver (Wood 2012) observed that the differences in testing procedures for acute versus chronic testing using invertebrates (organisms were not fed during acute exposures) resulted in the perception that acutely lethal responses occurred at silver concentrations the same as or lower than those causing chronic sublethal toxicity. This would be contrary to the usual acute-to-chronic ratios for most substances. In fact, he said, the results with fish confirmed that chronic sublethal effects occurred at about one tenth the concentrations than caused acute lethality. This has resulted in some undue regulatory concern. This fact was considered in detail in deciding not to publish the short-term benchmark for silver in fresh water (see below).

6.6. Marine life

There is a marked difference in the toxicity of silver in brackish and marine waters compared with fresh water. Until recently there has been little effort put forth to study Ag toxicity in marine environments, most likely because of the relatively high short- and long-term toxicity of Ag in fresh water compared to saltwater environments.

To discuss Ag toxicity in marine settings, it is important to understand two key differences from Ag toxicity in freshwater environments. First, is the physiological difference between freshwater fish, for example, and marine fish. The site of Ag toxicity in freshwater fish is the gill, since this is the principal site of ionoregulation. In fresh water, fish are constantly pumping ions into the blood to combat losses due to differences in osmolality between the blood and surrounding water. Thus, when Ag disrupts ionoregulation, ion-loss will occur resulting in eventual death. In contrast, marine teleosts experience osmotically driven water loss across the gill, due to the higher osmolality in the ambient water compared

to the blood. To combat water loss, marine fish need to take in water to replace lost fluid. This is achieved by actively transporting ions in the gut so water follows by osmosis. They then excrete excess ions at the gills and kidney. This fundamental difference leads to Ag exposure in the gut rather than the gills (Wood *et al.*, 1999).

The second consideration when discussing Ag toxicity in marine organisms is the speciation of Ag. Silver is highly influenced by Cl$^-$ in brackish and marine waters, while complexation with organic matter, Br$^-$ and I$^-$ are negligible. In fresh water, Ag has a high affinity for particulates, however, in waters with higher salinity, the vast majority (>90%) of Ag is complexed by Cl$^-$ and very little is contained within the filterable organic colloids and particles (Pedroso *et al.*, 2007). Though the small, neutral AgCl complex is known to enter biological membranes via passive diffusion, the formation of higher order chloro-complexes will occur, to a point where in full strength seawater (35‰ salinity), 83% of Ag is present as AgCl$_3$ $^{2-}$ (0.0003% as Ag$^+$; Ward and Kramer, 2002). This Ag-chloro-complexation appears to reduce toxicity. The 96-h LC$_{50}$ values for *Americamysis bahia* calculated from 28-d and 7-d toxicity tests initiated with 7-d old mysids were 260 µg/L Ag at 20‰. Shaw *et al.* (1998) report a 96-h Ag LC$_{50}$ of 3.07 – 6.2 µM (331-669 µg/L) for tidepool sculpins (*Oligocottus maculosus*) over a salinity range of 25 to 32‰. Results from Nichols *et al.* (2006) demonstrate a constant decrease in Ag accumulation and the reduced importance of NOM to Ag toxicity in gulf toadfish (*Opsanus beta*) with increasing salinity. Work by Pedroso *et al.* (2007) reported a 20-fold increase in LC$_{50}$s (7.1-156.7 µg/L dissolved Ag) with the euryhaline copepod, *Acartia tonsa*, with increasing salinity (5-30‰).

7. CRITERIA FROM OTHER JURISDICTIONS

Silver WQGs/criteria from nine provincial and national jurisdictions are summarized in Table 7.1. Two types of guidelines are used: a static number, and a hardness-based equation. In general, most of the guidelines are a static number.

7.1. British Columbia

The B.C. Ministry of Environments, Land and Parks established a hardness-based Ag WQG in 1996 (ENV, 1996) for freshwater aquatic life. This guideline was for total Ag, is based on hardness, and provides both chronic and acute WQGs. In 1996 marine WQGs for total Ag were also established; a chronic (30-day mean) marine WQG of 1.5 µg/L, and an acute maximum WQG of 3.0 µg/L (ENV, 1996).

7.2. Canadian Council of Ministers of the Environment (CCME)

The CCME develops national WQGs for the protection of aquatic life and other values. The CCME aquatic life WQG is for total Ag and only has a long-term component for freshwater aquatic life (Table 7.1) which is 0.25 µg/L. For marine aquatic life, CCME only has a short-term component (Table 7.1) which is 7.5 µg/L.

7.3. Provincial Water Quality Guidelines

Canadian provinces typically develop their own WQGs or adopt WQGs from another jurisdiction (e.g., CCME). Ontario's Provincial Water Quality Objective (PWQO) for Ag is 0.1 µg/L and was derived in 1979 (OMOE, 1979). Ontario's PWQOs are for the protection of freshwater aquatic life and are based on the total concentration of an unfiltered sample (OMOE, 1979). The Government of Alberta adopted the 2015 CCME guidelines for Ag of 0.25 µg/L (Government of Alberta, 2018). Saskatchewan adopted the Surface Water Quality Objectives for the Protection of Aquatic Life from CCME in 1999 of 0.1 µg/L (Water Security Agency, 2015). Quebec adopted the 1980 United States Environmental Protection Agency (USEPA) hardness-based guideline for total Ag (Government of Quebec, 2024) Coastal provinces such as Nova Scotia and New Brunswick utilize CCME guidelines for marine and freshwaters.

7.4. USEPA Water Quality Criteria

The USEPA developed a national water quality criterion for the protection of aquatic life based on total Ag (USEPA, 1980). The USEPA acute Ag criteria is hardness-based and is calculated using the equation presented in Table 7.1. The chronic guideline is 0.12 µg/L. For saltwater aquatic life the acute guideline for total recoverable Ag is 2.3 µg/L (USEPA, 1980). The USEPA has no chronic saltwater guideline for Ag.

7.5. European Union

The European Commission Scientific Committee on Health, Environmental and Emerging Risks (SHEER) derived a maximum allowable concentration quality standard for freshwater (MAC-QS$_{fw\ eco}$) of 0.022 µg/L and an annual average quality standard (AA-QS$_{fw\ eco}$) of 0.01 µg/L (SCHEER, 2021). For saltwater, the AA-QS$_{sw\ eco}$ is 0.17 µg/L for a salinity of 30% (SCHEER, 2021). For both the freshwater and saltwater quality standards, it is not stated if it is for the total or dissolved fractions of Ag. Therefore, as per B.C. protocol, it is assumed that these standards apply to the total Ag sampled.

7.6. Australia and New Zealand

Australia and New Zealand have joint WQGs under the Australian and New Zealand Environment and Conservation Council (ANZECC). These WQGs are described as trigger values, that invoke a response if exceeded (ANZECC, 2000). Although four trigger values have been calculated to provide various levels of protection (i.e., 80-99% of species), ANZECC (2000) recommends application of the 80%, 95% and 99% protection levels to protect highly disturbed ecosystems, slightly-moderately disturbed ecosystems, and high conservation/ecological value ecosystems, respectively (ANZECC, 2000). It is suggested that when applying the ANZECC trigger values to a site, to first compare to total concentrations of the metal. If this exceeds the trigger value, then sampling for the filtered metal is required (ANZECC, 2000). A freshwater high reliability trigger value of 0.05 µg/L was calculated for silver using the statistical distribution method with 95% protection (ANZECC, 2000). A chronic marine high reliability trigger value of 1.4 µg/L was calculated using the statistical distribution method with 95% protection (ANZECC, 2000).

Table 7.1. Summary of freshwater aquatic life water quality guidelines for Ag by jurisdiction.

Jurisdiction	Freshwater		Marine		Total/ dissolved	Year published
	Chronic (µg/L)	Acute (µg/L)	Acute (µg/L)	Chronic (µg/L)		
British Columbia	Hardness ≤ 100 = 0.05 Hardness > 100 = 1.5	Hardness ≤ 100 = 0.1 Hardness > 100 = 3.0	1.5	3.0	Total	1996
CCME	0.25	NA	7.5	NA	Total	2015
Alberta	0.25	NA	NA	NA	Total	2018
Ontario	NA	0.1	NA	NA	Total	1979
Saskatchewan	0.1	NA	NA	NA	Total	1999
Quebec	$e^{(1.72[\ln(hardess)]-6.52)}$	NA	NA	NA	Total	1980
USEPA	0.12	$e^{(1.72[\ln(hardess)]-6.52)}$	2.3	NA	Total	1980
European Committee SCHEER	AA-QS$_{fw,eco}$ =0.01	MAC-QS$_{fw,eco}$ = 0.022	NA	0.17*	Total	2021
Australia/ New Zealand	NA	0.05	NA	1.4	Total	2000

* AA-QS$_{sw\ eco}$ applies to salt water with a salinity of 30% (ANZECC 2000).

8. RECOMMENDED GUIDELINE

8.1. Aquatic Toxicity Data

The long-term freshwater Canadian Water Quality Guideline (CWQG) for silver for the protection of aquatic life was developed based on CCME protocol (CCME, 2007) using the statistical (Type A) approach. No short-term freshwater benchmark was recommended as the concentration was essentially equal to the CWQG (see below for details).

Type A guidelines employ the use of a regression-based approach called a species sensitivity distribution (SSD). Toxicity data are collected and, the most preferred and/or sensitive endpoint per species is plotted as per the Protocol (CCME, 2007) to ensure only one data point per species is represented on the SSD. To account for intra-species variability, species mean values can be calculated (geometric mean of similar toxicity data points) where applicable and if experimental conditions are comparable. This was not the case with the silver datasets, as factors affecting metal toxicity were either variable or unreported between endpoints, and hence the most sensitive endpoint per species was plotted in the SSD. The data are plotted in an SSD and one of five regression models (Normal, Logistic, Extreme Value, Gumbel and Weibull) are chosen as the best fit to the distribution using statistical and graphical techniques. The model chosen as the best fit to the data is based on goodness-of-fit and model feasibility, including examination of probability-probability plots, quantile-quantile plots, residual plots, Anderson-Darling goodness of-fit test, mean sum of squared error terms in the lower tail, as well as overall visual assessment of model fit. The guideline for both short- and long-term exposure is defined as the intercept of the 5th percentile of the y-axis with the fitted SSD curve. The software package, "SSD Master version 3.0" (CCME, 2013) was used to generate the SSDs, and included five cumulative distribution functions (Normal, Extreme Value, Weibull, Logistic and Gumbel). Available toxicity data for Ag in fresh water are compiled in Appendix A, (CCME, 2015a). Minimum data requirements were also met to derive a Type A short-term marine water guideline, however there were insufficient data to generate a guideline for long-term effects in marine water. (Tables 5.2 and 5.3, CCME, 2015a). This is due to a lack of available fish data

Data were categorized as primary or secondary based on the guidance given in the CCME draft protocol for derivation of a water quality guideline (CCME, 2007). Primary data, at a minimum, included measured Ag concentrations, and included measurements of relevant water quality variables such as Ca, Mg, Na, pH, dissolved oxygen, dissolved organic matter (as DOC).

8.2. Toxicity Modifying Factors

There are various silver chemical species that can be toxic to aquatic life. In a laboratory setting salts such as $AgNO_3$ readily dissociate into the free Ag^+ ions with high bioavailability. In contrast, in natural waters, silver ions are complexed by abundant negatively-charged organic matter and sulphides, with a consequent decrease in toxicity.

Hardness. The hardness cations, (Ca^{2+} and Mg^{2+}) are relatively ineffective in acute studies at reducing silver accumulation and toxicity (Karen *et al.* 1999).

Sodium. At high concentrations (>37 mg Na/L) silver accumulation on fish gill was reduced (Janes and Playle 1995). At lower concentrations (1-37 mg/L) there was no reduction of silver accumulation but there was still a protective effect (Goss and Wood 1991) presumably related to a physiological protection being offered by excess sodium being available.

Alkalinity. Evidence that alkalinity reduced silver toxicity was later attributed to the sodium effect above (Naddy *et al.* 2007b). Since silver does not form complexes with carbonate it is unlikely that alkalinity has any protective effect.

pH. Janes and Playle (1995) showed that H^+ ions do not compete with Ag^+ for gill binding sites in rainbow trout (*Oncorhynchus mykiss*) over a pH range of 4.5-6.8 in ion-poor water at low dissolved organic carbon (DOC) concentrations. There may be indirect effects due to interactions between pH and DOC (see below).

Anions. In comparison to $AgNO_3$, silver inorganic complexes such as silver thiosulphate, silver chloride and silver sulphide were found to exert very low toxicity (LeBlanc *et al.* 1984; Hogstrand *et al.* 1996), indicating the effect of complexation on silver toxicity. As a type-B metal, inorganic speciation of silver is expected to be controlled by complexation by sulphides and chlorides. Many studies that have tried to clarify the mitigating effect of Cl^- on silver toxicity have been confounded by the accompanying cation, i.e., many have used NaCl as the source of Cl^-. Therefore, any reduction in toxicity seen is likely partially due to the Na present in solution. Investigations on the protective effect of Cl^- (0.3 to 43 mg/L) with various species of freshwater fish (*Pimephales promelas*, *Fundulus heteroclitus* and *Danio rerio*; Bielmyer *et al.* (2007) and the European eel (*Anguilla anguilla*; Grosell *et al.* 2000) found that Cl- offers little protection, which is inconsistent with studies using rainbow trout (Galvez and Wood 1997; McGeer and Wood 1998). It appears that, with fish, only rainbow trout are protected from silver toxicity by Cl^-. Daphnids (*Ceriodaphnia dubia* and *Daphnia magna*), however, seem to benefit from Cl^- but any protective effects are only seen when Cl^- concentrations are higher than 50 mg/L (Karen *et al.* 1999; Naddy *et al.* 2007a).

Dissolved organic carbon. The presence of natural organic matter (NOM; measured as DOC, in mg C/L) in natural waters is probably the most important complexing ligand, other than sulphide, for silver and most other metals. Studies with Aldrich humic acid (commonly used as a surrogate for NOM) have revealed a large protective effect against silver toxicity. For example, work with fathead minnows (*Pimephales promelas*) exposed to silver in the presence or absence of DOC has resulted in ~4-fold increase in LC_{50} (Karen *et al.* 1999; Bury *et al.* 1999; Erickson *et al.* 1998). Similarly, silver toxicity in invertebrates is also greatly reduced in the presence of DOC (Karen *et al.* 1999; Glover *et al.* 2005a; 2005b; Naddy *et al.* 2007b). Efforts have been made recently to use natural organic matter (NOM) sourced from natural waters, concentrated from large volumes of water and reconstituted in lab water (Glover *et al.* 2005a). An interesting characteristic of NOM is its variability depending on its source. This variability also translates into variable effectiveness in reducing silver toxicity. Currently, it appears that relatively simple optical measurements that reflect the aromaticity of NOM, such as fluorescence index, may correlate to reduction in metal toxicity, including silver (Schwartz *et al.* 2004; Glover *et al.* 2005b).

Despite what is known regarding the above toxicity modifying factors it is not currently possible to develop Canadian Water Quality Guidelines as a function of any single modifying factor. A chronic Biotic Ligand Model BLM for silver is not available at this time. The use of BLMs in future guideline development is currently being investigated.

8.3. CCME Water Quality Guideline Derivation

Two WQGs have been adapted from CCME (2015): the long-term chronic WQG for freshwater and the short-term acute WQG for marine. CCME found that the short-term acute WQG for freshwater was similar to the chronic value and therefore opted to only include the chronic value (CCME 2015). For marine waters, CCME found only adequate data to derive a short-term acute WQG. The description of the derivation for these WQGs were taken directly from CCME 2015a and CCME 2015b and pasted below.

8.3.1. CCME Derivation of Freshwater Chronic WQG

Long-term exposure guidelines identify concentrations in the aquatic ecosystem that are intended to protect all forms of aquatic life for indefinite exposure periods. The minimum data requirements for the Type A guideline approach were met, and a total of 9 data points were used in the derivation of the species sensitivity distribution (SSD) (Table 8.1). Each species for which appropriate long-term toxicity data were available was ranked according to sensitivity and plotted using the Hazen plotting position.

Table 8.1. Endpoints Used to Determine the Long-term Freshwater SSD for silver (from CCME 2015).

Species	Endpoint	Concentration (µg/L)
Fish		
O. mykiss	MATC (growth)	0.24
P. promelas	MATC (growth)	0.83
I. punctatus	LC_{10}	1.9
M. salmoides	LC_{10}	23
Invertebrates		
C. dubia	MATC (reproduction)	0.78
D. magna	IC_{20} (reproduction)	2.12
H. azteca	NOEC (reproduction)	4
C. tentans	NOEC (dry weight)	13
Plant		
L. gibba	7-d MATC (frond number)	0.63

Of the four models tested, the Gumbel model provided the best fit. One of the criteria for best fit was the Anderson-Darling goodness-of-fit statistic, where A2 = 0.181. The equation of the Gumbel model is of the form:

$$f(x) = e^{-e^{\frac{(L-x)}{s}}}$$

Where, in the case of the fitted model, L = 0.007 and s = 0.548.

The long-term freshwater SSD is presented in Figure 8.1 and the summary statistics for the long-term freshwater SSD are presented in Table 8.2. The 5th percentile on the long-term SSD is 0.25 µg/L.

Table 8.2. Long-term freshwater guideline concentration for silver derived using the SSD method. (LFL = lower fiducia limit; UFL = upper fiducial limit; from CCME 2015b).

Concentration (µg Ag/L)	
SSD 5th percentile	0.25
SSD 5th percentile, 95% LFL	0.17
SSD 5th percentile, 95% UFL	0.39

Therefore, the long-term freshwater guideline to protect all forms of aquatic life for indefinite exposure periods is 0.25 µg/L. The CCME protocol for guideline derivation (CCME 2007) states that the protection clause may be invoked "if an acceptable single (or, if applicable, geometric mean) lethal-effects endpoint (i.e., LCx, where x ≥15%) for any species is lower than the proposed guideline…". There are some lethality endpoints for *Ceriodaphnia dubia* in the short-term acceptable dataset that are below the CWQG of 0.25 µg/L. However, the majority of LC_{50}s for this data-rich species are above the CWQG, with a geometric mean of 0.68 µg/L. For the *C. dubia* LC_{50}s below the CWQG, all are from a single study where most or all silver is in the dissolved phase using very pure water (whereas the guideline is based on total silver). Other LC_{50}s for *C. dubia* from a different study, which were conducted in natural water or tap water, ranged from 0.34 to 9.52 µg/L, which is above the CWQG. The *C. dubia* data point plotted in the long-term SSD is a 30-d MATC of 0.78 µg/L for effects on reproduction. Therefore, there is a sensitive, non-lethal endpoint for *C. dubia* above 0.25 µg/L. Based on these findings, the protection clause was not invoked as there was no strong reason to question the long-term CWQG in achieving the intended level of protection.
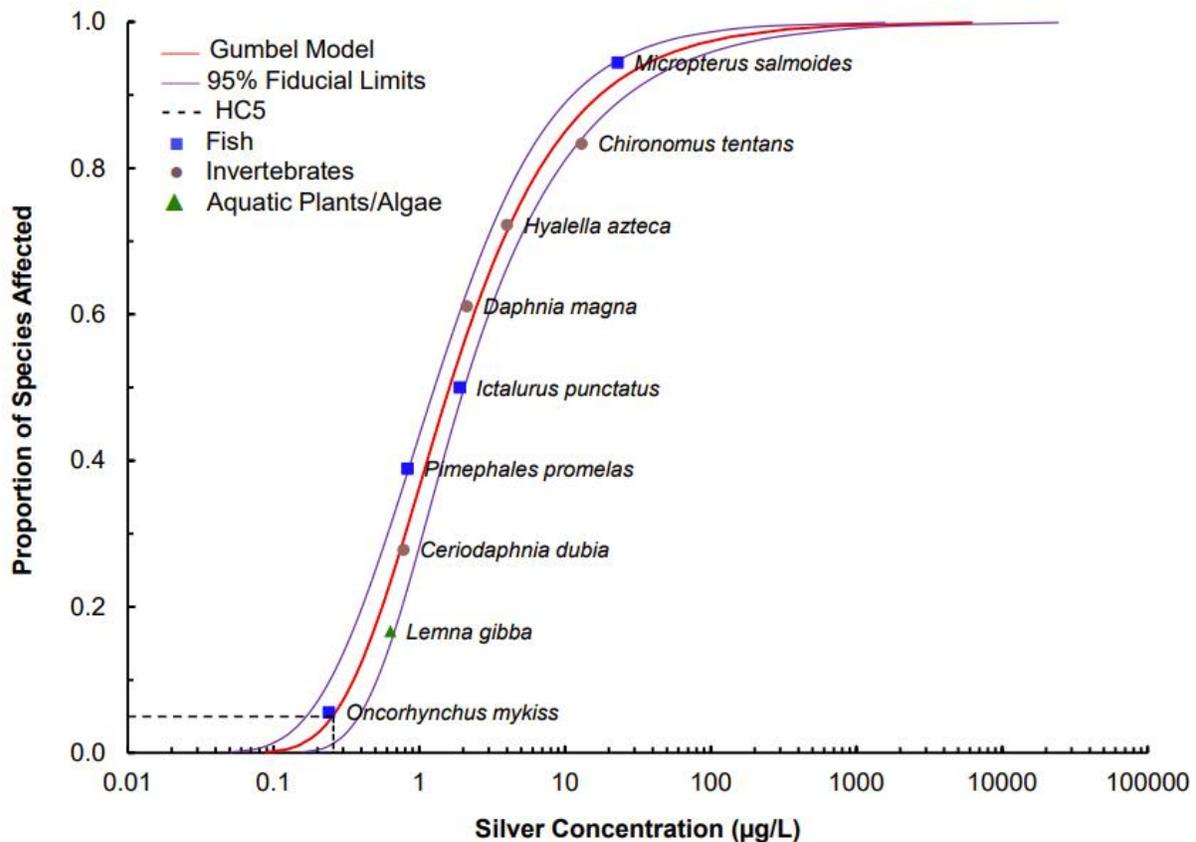
Figure 8.1. Long-term species sensitivity distribution (SSD) for silver in fresh water derived by fitting the Gumbel model to the long-term endpoints of 9 aquatic species (from CCME, 2015b)

The CCME did not recommend a short-term freshwater benchmark for Ag because the short-term SSD 5th percentile was 0.22 µg/L; quite similar to the long-term CWQG (CCME, 2015b). A full report on the derivation of and the rational for not recommending the short-term freshwater benchmark, can be found in the Canadian Water Quality Guidelines for the Protection of Aquatic Life – Silver (CCME, 2015b).

8.3.2. CCME Derivation of Marine Acute WQG

Short-term exposure benchmarks are derived using severe effects data (such as lethality) from short-term exposure periods (24 to 96-h). These guidelines are estimators of the lower limit of lethal effects to aquatic organisms and give guidance on the impacts of severe, but transient, situations (e.g., spills events to aquatic receiving environments and infrequent releases of short-lived/ non-persistent substances). It follows that short-term benchmarks do not protect aquatic life against adverse effects. The minimum data requirements for the Type A guideline approach were met, and a total of 19 data points were used in the derivation of the guideline (Table 6). Each species for which appropriate short-term toxicity data was available was ranked according to sensitivity, and a species sensitivity distribution (SSD) was plotted using the Hazen plotting position.

Table 8.3 Endpoints used to determine the short-term marine SSD for silver

(from CCME, 2015b)

Species	Endpoint	Concentration (µg/L)
Fish		
S. acanthus	96-h LC_{50}	100
O. maculosus	96-h LC_{50}	331
C. aggregata	96-h EC_{50} (mobility)	356
O. mykiss	96-h LC_{50}	401.5
C. variegatus	96-h LC_{50}	441
O. kisutch	96-h EC_{50} (mobility)	488
P. vetulus	96-h EC_{50} (mobility)	800
Invertebrates		
C. virginica	48-h LC_{50}	5.8
C. gigas	48-h LC_{50}	19
M. mercenaria	42-48h LC_{50}	21
A.punctulata	96-h EC_{50}	40
A.tonsa	48-h LC_{50}	43.2
A.hudsonica	48-h LC_{50}	43.2
A.bahia	96-h LC_{50}	65
T. brevicornis	96-h LC_{50}	95
N. areanaceodentata	96-h LC_{50}	145
H. diversicolor	4-d LC_{50}	647
Algae		
G. splendens	48-h LC_{50}	21
I.galbana	48-h LC_{50}	81

The Normal model provided the best fit of the models tested. The Anderson-Darling goodness-of-fit statistic was A2 = 0.349.

The equation of the Normal model is:

$$f(x) = \frac{1}{2}\left(1 + erf\left(\frac{x - \mu}{\sigma\sqrt{2}}\right)\right)$$

Where in the case of the fitted model, μ = 2.014, σ = 0.692, and *erf* is the error function.

The short-term marine SSD is presented in Figure 3 and summary statistics for the short-term marine SSD are presented in Table 7. The 5th percentile on the short-term SSD is 7.5 μg/L.

Table 8.4 Short-term marine benchmark concentration for silver derived using the SSD method.
(LFL = lower fiducial limit; UFL = upper fiducial limit; from CCME 2015b)

Concentration (μg/L)	
SSD 5th percentile	7.5
SSD 5th percentile, 95% LFL	5.8
SSD 5th percentile, 95% UFL	9.7

Therefore, the short-term benchmark concentration for the protection of marine life is 7.5 μg/L for silver.
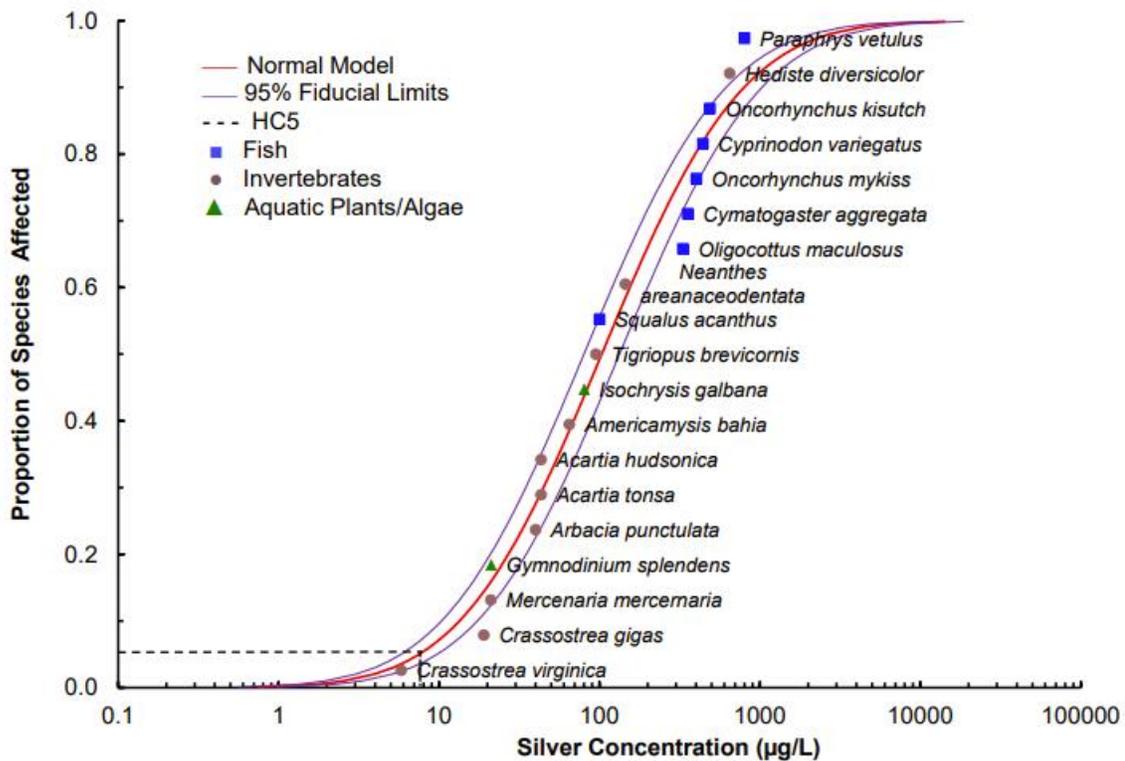
Figure 8.2 Short-term species sensitivity distribution (SSD) for silver in marine water
derived by fitting the log-normal model to short-term LC/EC50s of 19 aquatic species (from CCME, 2015b).

8.4. B.C. Silver Water Quality Guidelines

The CCME Ag WQGs are based on SSDs Type A guideline approach (CCME, 2015a). In the sections below the freshwater chronic and marine acute CCME WQGs are reviewed and the selected assessment factors (AF)s are discussed.

8.4.1. Freshwater chronic long-term water quality guideline

The toxicity dataset used to derive the Ag long-term WQG consists of data for four fish species, four invertebrate species, and one plant species. The chronic dataset used for the Ag FEQG fulfills the minimum number of species required for a type A2 guideline (ENV, 2019). It should be noted that of the 9 species with chronic data for Ag, all are native to Canada.

The CCME Ag WQG meets the conditions specified by the B.C. derivation protocol for Type A2 WQG. However, to account for the sources of uncertainty associated with WQG derivation, an AF must be applied to the calculated HC_5 (ENV, 2019). The minimum AF to be applied to Type A WQGs is 2 which accounts for the general sources of uncertainty in derivation of WQGs such as extrapolation of lab results to field conditions and the cumulative effects of other environmental stressors. While there are four data points for fish species, four for invertebrate species, and the data set includes low-effect and NOEC endpoints, sources of uncertainty specific to the dataset are that there are only 9 datapoints (10 are required for A1 guideline), and there is a lack of data for amphibians and EPT.

One additional source of uncertainty in the dataset is that one short-term lethality endpoint for *Ceriodaphnia dubia* falls below the 5th percentile of the long-term SSD. The LC_{50} value of 0.16 µg/L comes from a single study (Naddy et al., 2007) using very pure water, where silver was primarily in the dissolved phase. However, 35 EC_{50} values for *C. dubia* from the acceptable CCME short-term dataset range from 0.16 to 2.88 µg/L, with a geometric mean of 0.68 µg/L (Ratte, 1999; Bielmyer et al., 2007; Koltz et al., 2007; Naddy et al., 2007). Therefore, this single data source should not be considered in isolation, as multiple data points from the same and other studies with similar conditions have shown significantly higher EC_{50} values.

Considering all sources of uncertainty, a minimum AF of 2 was applied to the calculated HC_5. As a result, the B.C. chronic WQG for total Ag is 0.12 µg Ag/L, derived from the CWQG of 0.25 µg Ag/L with the AF of 2 applied.

8.4.2. Marine acute short-term water quality guideline

The toxicity dataset used to derive the Ag long-term freshwater WQG consists of data for seven fish species, ten invertebrate species, and two algal species. The acute dataset used for the Ag marine WQG fulfills the minimum number of species required for a Type A1 guideline (ENV, 2019). It should be noted that of the seven species of fish with acute data for Ag, six are native to Canada, of the ten species of invertebrates with acute Ag data, seven are native to Canada, and of the two algal species one is native to Canada.

The CCME Ag WQG meets the conditions specified by the B.C. derivation protocol for Type A1 WQG. However, to account for the sources of uncertainty associated with WQG derivation, an AF must be applied to the calculated HC_5 (ENV, 2019). A source of uncertainty specific to the dataset is that not all species included in the data set are native to Canada. However, considering that there are 19 data points, all of which are primary data, most species are native to Canada, and the data set meets the requirements for a Type A1 WQG, an AF of 2 was applied to the calculated HC_5. Therefore the B.C. acute WQG for total Ag when the AF of 2 is applied to the CWQG of 7.5 µg Ag/L, is 3.7 µg Ag/L.

8.4.3. Marine chronic long-term water quality guideline

CCME did not publish a long-term chronic WQG in 2015 due to insufficient data. Since the 1996 30-day marine WQG for Ag, is outdated, and based on a paucity of scientific data, B.C. will adopt a working WQG from another jurisdiction until a national update is made to the Canadian WQG for marine chronic Ag. As described in Section 7, two government agencies have developed long-term marine criteria for Ag. Australia and New Zealand published a chronic marine high reliability trigger value of 1.4 µg/L with 95% protection (ANZECC, 2000). This guideline was derived using the SSD statistical distribution method where 42 points of chronic data, from 5 taxonomic groups (ANZECC, 2000). This guideline does not have an assessment factor applied. The European Commission Scientific Committee on Health, Environmental and Emerging Risks (SCHEER) derived a AA-QS$_{sw\,eco}$ of 0.17 µg/L for a salinity of 30% (SCHEER, 2021). The annual average quality standard was derived using a deterministic method with an AF of 50 applied (SCHEER, 2021). In B.C., there are two types of WQGs: a Type A guideline which is determined using the SSD approach, and a Type B guideline which is derived using the deterministic approach. The Type A WQGs are the preferred approach. ANZECC published a chronic marine WQG for Australian and New Zealand which was developed following the SSD approach (ANZECC, 2000). The ANZECC chronic marine WQG for silver is 1.4 µg Ag/L (ANZECC, 2000). Since CCME did not publish a chronic marine WQG for silver, and the WQG published by ANZECC was derived using the preferred SSD approach, B.C. has adopted this guideline as a working water quality guideline (WWQG) with the addition of an AF. The marine chronic WQG from ANZECC was derived using 42 data points for 8 species of 5 taxonomic groups (ANZECC, 2000). However, of the five taxonomic groups there are no fish studies; four of these taxonomic groups are invertebrates,

and one, algae. For this reason, an AF of 3 was applied, making the B.C. WWQG 0.5 µg Ag/L.   This working WQG can also be found in the British Columbia Working Water Quality Guidelines: Aquatic Life, Wildlife & Agriculture (October 2024) document (WLRS, 2024).[1]

9.   COMPARISON OF AMBIENT SILVER CONCENTRATIONS TO WATER QUALITY GUIDELINES

Water quality guidelines are commonly used to determine the potential risk of toxicity to aquatic life from a given substance in ambient conditions. In general, if ambient concentrations are below the WQG the risk is assumed to be low. It is important to understand how the assessment of risk to aquatic life will change with the updated Ag WQG. To answer this question, water quality data for total Ag, from freshwater sites were extracted from the EMS and CABIN databases and ambient levels compared to the 1996 WQG and the 2025 WQG.

Data from minimally disturbed sites included a total of 856 records with hardness and total silver data to calculate the 1996 WQG and a total of 1459 records with total silver to compare to the 2025 WQG.

Total silver exceeded the 1996 WQGs concentrations 4.7% of the time (40/856). None of these exceedances were where hardness was > 100 mgCaCO$_3$/L (WQG = 1.5 µ Ag/L). Total silver exceeded the 2025 WQG 1.6% of the time (23/1459). The higher rate of exceedance of the old 1996 WQG compared to the new WQG is mainly because the 1996 WQGs are much lower (0.05 µg Ag/L) when hardness is below 100 mg CaCO$_3$/L.   However, the updated WQG was shown to be protective, with 98.4% of ambient silver concentrations at minimally disturbed sites being below the 2025 WQG.

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[1] The B.C. Working Water Quality Guidelines document can be found at https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/bc_working_water_quality_guidelines.pdf.

REFERENCES

Adams, N.W.H., and Kramer, J.R. 1999. Determination of silver speciation in wastewater and receiving waters by competitive ligand equilibration/solvent extraction. Environmental Toxicology and Chemistry 18: 2674- 2680.

ANZECC (Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand). 2000. National water quality management strategy: Australian and New Zealand guidelines for fresh and marine water quality, Volume 2, Aquatic Ecosystems – Rationale and Background Information. Available from: https://www.waterquality.gov.au/sites/default/files/documents/anzecc-armcanz-2000-guidelines-vol2.pdf

Bertram, B.O.B. and Playle, R.C. 2002. Effects of feeding on waterborne silver uptake and depuration in rainbow trout (Oncorhynchus mykiss). Canadian Journal of Fisheries and Aquatic Sciences 59(2): 350-360.

Bianchini, A. and Bowles, K.C. 2002. Metal sulfides in oxygenated aquatic systems: implications for the biotic ligand model. Comparative Biochemistry and Physiology Part C 133C: 51-64.

Bianchini, A., and Wood, C.M. 2003. Mechanisms of acute silver toxicity in Daphnia magna. Environmental Toxicology and Chemistry 22: 1361-1367.

Bianchini, A., and Wood, C.M. 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. Ecotoxicology and Environmental Safety 71: 32-40.

Bielmyer, G.K., Grosell, M., Paquin, P.R., Mathews, R., Wu, K.B., Santore, R.C., and Brix, K.V. 2007. Validation study of the acute biotic ligand model for silver. Environmental Toxicology and Chemistry. 26(10): 2241- 2246.

Brauner, C.J. and Wood, C.M. 2002a. Effect of Long-Term Silver Exposure on Survival and Ionoregulatory Development in Rainbow Trout (Oncorhynchus mykiss) Embryos and Larvae, in the Presence and Absence of Added Dissolved Organic Matter. Comparative Biochemistry and Physiology C-Toxicology & Pharmacology 133(1-2): 161-173.

Brauner, C.J. and Wood, C.M. 2002b. Ionregulatory development and the effect of chronic silver exposure on growth, survival, and sublethal indicators of toxicity in early life stages of rainbow trout (Oncorhynchus mykiss). J. Comp. Phiiol. B. 172:153-162.

Brauner, C., Wilson, J., Kamunde, C., and Wood, C.M. 2003. Water chloride provides partial protection during chronic exposure to waterborne silver in rainbow trout (Oncorhynchus mykiss) embryos and larvae. Physiol. Biochem. Zool. 76:803-815.

Bury, N.R. and Wood, C.M. 1999. Mechanism of branchial apical silver uptake by rainbow trout is via the protoncoupled Na+ channel. American Journal of Physiology 277 (5 PART 2), R1385-R1391.

CCME (Canadian Council of Ministers of the Environment). 2007. A protocol for the derivation of water quality guidelines for the protection of aquatic life. In Canadian environmental quality guidelines, Canadian Council of Ministers of the Environment, 1999. Canadian Council of Ministers of the Environment, Winnipeg, MB. Available from www.ccme.ca.

CCME (Canadian Council of Ministers of the Environment). 2013. Determination of Hazardous Concentrations with Species Sensitivity Distributions: SSD Master, Version 3.0 (unpublished). Available

from National Guidelines and Standards Office, Environment Canada, Gatineau (email: ceqg-rcqe@ec.gc.ca).

CCME (Canadian Council of Ministers of the Environment). 2015a. Scientific criteria document for the development of the Canadian water quality guidelines for the protection of aquatic life- Silver. Canadian Council of Ministers of the Environment, Winnipeg, MB.

CCME (Canadian Council of Ministers of the Environment). 2015b. Canadian Water Quality Guidelines for the Protection of Aquatic Life: Silver. Canadian Council of Ministers of the Environment, Winnipeg, MB.

Coleman, R.L. and Cearley, J.E. 1974. Silver toxicity and accumulation in largemouth bass and bluegill. Bulletin of Environment Contamination and Toxicology 12(1): 53-61.

Davies, P.H., Goettl J.P Jr., and Sinley J.R. 1978. Toxicity of Silver to Rainbow Trout (Salmo gairdneri). Water Research 12: 113-117

ENV (formally: British Columbia Ministry of Environment, Land and Parks), 1996. Ambient Water quality criteria for Silver. Water Quality Branch.

ENV (British Columbia Ministry of Environment and Climate Change Strategy), 2019. Derivation of Water Quality Guidelines for the Protection of Aquatic Life in British Columbia. Water Quality Guideline Series, WQG-06. Prov. B.C., Victoria B.C.

ENV (British Columbia Ministry of Environment and Climate Change Strategy), 2021. Molybdenum Water Quality Guideline for the Protection of Freshwater Aquatic Life, Livestock, Wildlife and Irrigation - Technical Report. Water Quality Guideline Series, WQG-07. Prov. B.C., Victoria B.C.

Erickson, R.J., Brooke, L.T., Kahl, M.D., Venter, F.V., Harting, S.L., Markee, T.P., and Spehar, R.L. 1998. Effects of laboratory test conditions on the toxicity of silver to aquatic organisms. Environmental Toxicology and Chemistry 17(4): 572-578.

Evans, D.H., Piermarini, P.M., and Choe, K.P. 2005. The multifunctional fish gill: dominant site of gas exchange, osmoregulation, acid-base regulation, and excretion of nitrogenous waste. Physiol. Rev. 85: 97-177.

FactSage. 2009. Facility for the Calculation of Chemical Thermodynamics. Version 6.2. www.crct.polymtl.ca.

Fortin, C. and Campbell, P.G.C. 2001. Thiosulfate enhances silver uptake by a green alga: Role of anion transporters in metal uptake. Environmental Science and Technology 35(11), 2214-2218.

Galvez, F., Hogstrand, C., and Wood, C.M. 1998. Physiological responses of juvenile Rainbow trout to chronic low level exposures of waterborne silver. Comparative Biochemistry and Physiology C-Toxicology & Pharmacology 119(2): 131-137.

Galvez, F. and Wood, C.M. 1997. The relative importance of water hardness and chloride levels in modifying the acute toxicity of silver to rainbow trout (Oncorhynchus mykiss). Environmental Toxicology and Chemistry 16, 2363-2368.

Galvez, F. and Wood, C.M. 2002. The mechanisms and costs of physiological and toxicological acclimation to waterborne silver in juvenile rainbow trout (Oncorhynchus mykiss). Journal of Comparative Physiology B Biochemical Systemic and Environmental Physiology 172(7): 587-597.

Garnier, J. and Baudin, J.P. 1989. Accumulation and depuration of 110mAg by a planktonic alga, Scenedesmus obliquus. Water, Air and Soil Pollution 45(3-4): 287-299

Goss, G. G. and Wood, C. M. 1991. Two-substrate kinetic analysis: a novel approach linking ion and acid–base transport at the gills of freshwater trout, Oncorhynchus mykiss. J. Comp. Physiol. B 161, 635–646.

Government of Alberta. 2018. Environmental Quality Guidelines for Alberta Surface Waters. Water Policy Branch, Alberta Environment and Parks. Edmonton, Alberta.

Government of Quebec. 2024. Critères de qualité de l'eau de surface. Ministère de l'Environnement, de la Lutte contre les changements climatiques, de la Faune et des Parc. Retrieved August 2024, from https://www.environnement.gouv.qc.ca/eau/criteres_eau/details.asp?code=S0036.

Glover, C., Playle, R.C., and Wood, C.M. 2005a. Heterogeneity of natural organic matter amelioration of silver toxicity to Daphnia magna: effect of source and equilibration time. Environmental Toxicology and Chemistry 24: 2934-2940.

Glover, C., Sharma, S., and Wood, C.M. 2005b. Heterogeneity of physiochemical properties explains difference in silver toxicity amelioration by natural organic matter to Daphnia magna. Environmental Toxicology and Chemistry 24: 2941-2947.

Grosell, M., Hogstrand, C., Wood, C.M., and Hansen, H. 2000. A nose-to-nose comparison of the physiological effects of exposure to ionic silver versus silver chloride in the European eel (Anguilla anguilla) and the rainbow trout (Oncorhynchus mykiss). Aquatic Toxicology Amsterdam 48(2-3): 327-342.

Guadagnolo, C.M., Brauner, C.J., and Wood, C.M. 2000. Effects of an acute silver challenge on survival, silver distribution and ionoregulation within developing rainbow trout eggs (Oncorhynchus mykiss). Aquatic Toxicology 51(2): 195-211.

Guadagnolo, C.M., Brauner, C.J., and Wood, C.M. 2001. Chronic effects of silver exposure on ion levels, survival, and silver distribution within developing rainbow trout (Oncorhynchus mykiss) embryos. Environmental Toxicology and Chemistry 20(3): 553-560.

Hirsch, M.P. 1998. Bioaccumulation of silver from laboratory-spiked sediments in the oligochaete (Lumbriculus variegatus). Environmental Toxicology and Chemistry 17: 605-609.

Hogstrand, C., Galvez, F., and Wood, C.M. 1996. Toxicity, silver accumulation and metallothionein induction in freshwater rainbow trout during exposure to different silver salts. Environmental Toxicology and Chemistry 15: 1102-1108.

Huston, C., and Juarez-Colunga, E. 2009. Guidelines for computing summary statistics for data sets containing non-detects. Written for the Bulkley Valley Research Center with assistance from the BC Ministry of Environment.

Janes, N. and Playle, R.C. 1995. Modeling silver binding to gills of rainbow trout. Environmental Toxicology and Chemistry 14: 1847-1858.

Jones, K.C., P.J. Peterson and Davies, B.E. 1985. Silver and other metals in some aquatic bryophytes from streams in the lead mining district of mid-Wales, Great Britain. Water Air and Soil Pollution 24: 329-338.

Karen, D.J., Ownby, D.R., Forsythe, B.L., Bills, T.P., La Point, T.W., Cobb, G.B., and Klaine, S.J. 1999. Influence of water quality on silver toxicity to rainbow trout (Oncorhynchus mykiss), fathead minnows (Pimephales promelas) and water fleas (Daphnia magna). Environmental Toxicology and Chemistry 18: 63-70.

Lam, I.K.S. and Wang, W-X. 2006. Accumulation and elimination of aqueous and dietary silver in Daphnia magna. Chemosphere 64: 26-35.Lide, D.R. 2006. CRC handbook of chemistry and physics. CRC Press, Boca Raton, FL.

Leblanc, G.A., Mastone, J.D., Paradice, A.P., Wilson, B.F., Lockhart Jr., H.B., and Robillard, K.A. 1984. The influence of speciation on the toxicity of silver to fathead minnow (Pimephales promelas). Environmental Toxicology and Chemistry 3:37-46.

Lee, L. 2017. NADA: Nondetects and data analysis for environmental data. Available online at: https://cran.r-project.org/web/packages/NADA/index.html

Luoma, S.N., Ho, Y.B., and Bryan, G.W. 1995. Fate, bioavailability and toxicity of silver in estuarine environments. Marine Pollution Bulletin 31(1-3): 44-54.

McGeer, J.C., and Wood, C.M. 1998. Protective effects of water Cl- on physiological responses to waterborne silver in rainbow trout. Canadian Journal of Fisheries and Aquatic Sciences 55(11), 2447-2454.

McGeer, J.C., Playle, R.C., Wood, C.M., and Galvez, F. 2000. A physiologically based biotic ligand model for predicting the acute toxicity of waterborne silver to rainbow trout in fresh waters. Environmental Science and Technology. 34:4199-4207.

McGeer, J.C., Brix, K.V., Skeaff, J.M., Deforest, D.K., Brigham, S.I., Adams, W.J., and Green, A. 2003. Inverse relationship between bioconcentration factor and exposure concentration for metals: Implications for hazard assessment of metals in the aquatic environment. Environmental Toxicology and Chemistry 22(5): 1017-1037.

Metayer, C., Amiard-Triquet, C., and J.P. Baud. 1990. Species related variations of silver related bioaccumulation and toxicity to three marine bivalves. Water Research 24(8): 995-1001.

Morgan, I.J., Henry, R.P., and Wood, C.M. 1997. The mechanism of acute silver nitrate toxicity in freshwater rainbow trout (Oncorhynchus mykiss) is inhibition of gill Na+ and Cl- transport. Aquatic Toxicology 38(1- 3): 145-163.

Morel, F. 1983. Principles of aquatic chemistry. John Wiley and Sons, New York, NY.

Naddy, R.B., Rehner, A.B., McNerney, G.R., Gorsuch, J.W., Kramer, J.R., Wood, C.M., Paquin, P.R., and Stubblefield, W.A. 2007a. Comparison of short-term chronic and chronic silver toxicity to fathead minnows in unamended and sodium chloride-amended waters. Environmental Toxicology and Chemistry 26(9): 1922- 1930.

Naddy, R., Gorsuch, J.W., Rehner, A., McNerney, G., Bell, R., and Kramer, J. 2007b. Chronic toxicity of silver nitrate to Ceriodaphnia dubia and Daphnia magna, and potential mitigating factors. Aquatic Toxicology 84: 1- 10.

Nichols, J.W., Brown, S., Wood, C.M., Walsh, P.J., and Playle, R.C. 2006. Influence of salinity and organic matter on silver accumulation in Gulf toadfish (Opsanus beta). Aquatic Toxicology 78: 253-261.

OMOE (Ontario Ministry of Environment and Energy). 1979. Rationale for the Establishment of Ontario's Water Quality Objectives. 236 pp. https://www.ontario.ca/page/water-management-policies-guidelines-provincial-water-quality-objectives#fn121. Accessed on August 2024.

Paquin, P., Di Toro, D., Santore, R., Trivedi, D., and Wu, B. 1999. A Biotic Ligand Model of the acute toxicity of metals III. Application to fish and Daphnia exposure to silver. EPA 822-E-00-001. US Government Printing Office, Washington, DC.

Paquin, P.R., Gorsuch, J.W., Apte, S., Batley, G.E., Bowles, K.C., Campbell, P.G.C., Delos, C.G., Di Toro, D.M., Dwyer, R.L., Galvez, F., Gensemer, R.W., Goss, G.G., Hogstrand, C., Janssen, C.R., McGeer, J.C., Naddy, R.B., Playle, R.C., Santore, R.C., Schneider, U., Stubblefield, W.A., Wood, C.M., and Wu, K.B. 2002. The Biotic Ligand Model: a historical overview. Special Issue: The Biotic Ligand Model for Metals – Current Research,

Future Directions, Regulatory Implications. Comparative Biochemistry and Physiology, Part C. 133(1-2): 3-35.

Pedroso, M.S., Bersano, J.G.F., and Bianchini, A. 2007. Acute silver toxicity in the euryhaline copepod Acartia tonsa: influence of salinity and food. Environmental Toxicology and Chemistry 26: 2158-2165.

Playle, R.C. 2004. Using mulitiple metal-gill binding models and the toxic unit concept to help reconcile multiplemetal toxicity results. Aquatic Toxicology 67: 359-370.

Purcell, T.W., and Peters, J.J. 1998. Sources of silver in the environment. Environmental Toxicology and Chemistry 17(4): 539-546.

R Core Team, 2022. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/.

Ratte, H. 1999. Bioaccumulation and toxicity of silver compounds: a review. Environmental Science and Technology 18(1): 89-108.

Ribeiro Guevara, S., 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. Science of the Total Environment 336: 119-134.

Ribeyre, F., Amiard-Triquet, C., Boudou, A., and Amiard, J.-C. 1995. Experimental study of interactions between five trace elements-Cu, Ag, Se, Zn, and Hg-toward their bioaccumulation by fish (Brachydanio rerio) from the direct route. Ecotoxicology and Environmental Safety 32(1): 1-11.

Rodgers, J.H. Jr., Deaver, E., Suedel, B.C., and Rogers, P.L. 1997. Comparative aqueous toxicity of silver compounds: laboratory studies with freshwater species. Bulletin of Environmental Contamination and Toxicology 58: 851-858.

Roditi, H.A., and Fisher, N.S. 1996. Metal assimilation in the zebra mussel, Dreissena polymorpha. Proceedings, 4th Argentum International conference on the Transport, Fate, and Effects of Silver in the Environment, Madison, WI, USA, August 25-28, pp. 241-244.

SCHEER (Scientific Committee on Health, Environmental and Emerging Risks), Final Opinion on "Draft Environmental Quality Standards for Priority Substances under the Water Framework Directive", silver and its compounds, 7-8 October 2021.

Schwartz, M.L., and Playle, R.C. 2001. Adding magnesium to the silver-gill binding model for rainbow trout (Oncorhynchus mykiss). Environmental Toxicology and Chemistry 20:467-472.

Schwartz, M.L., Curtis, P.J., and Playle, R.C. 2004. Influence of natural organic matter source on acute copper, lead, and cadmium toxicity to rainbow trout (Oncorhynchus mykiss). Environmental Toxicology and Chemistry 23(17): 2889-2899.

Shaw, J.R., Wood, C.M., Birge, W.J., and Hogstrand, C. 1998. Toxicity of silver to the marine teleost (Oligocottus maculosus): effects of salinity and ammonia. Environmental Toxicology and Chemistry 17(4): 594-600.

Terhaar, C.J., Ewell, W.S., Dziuba S.P., White W.W., and Murphy P.J. 1977. A laboratory model for evaluating the behavior of heavy metals in an aquatic environment. Water Research 11: 101-110.

USEPA (United States Environmental Protection Agency), 1980. Ambient Water Quality Criteria for Silver [EPA 440/5-80-071]. Office of Water Regulations and Standards, Washington, DC.

Wang, W., and Fisher, N. 1998. Accumulation of trace elements in a marine copepod. Limnology and Oceanography 43(2): 272-283.

Ward, T., and Kramer, J. 2002. Silver speciation during chronic toxicity tests with the mysid, Americamysis bahia. Comparative Biochemistry and Physiology C Pharmacology Toxicology and Endocrinology 133C: 75-86.

Warrington, P.D. 1996. Ambient Water Quality Criteria for Silver. Ministry of Environment, Lands and Park. Water Quality Branch, Environmental Protection Department. Victoria, British Columbia.

Water Security Agency, 2015. Surface Water Quality Objectives. Water Security Agency EPB356.

WHO (World Health Organization), 2002. Concise International Chemical Assessment Document 44. Silver and Silver Compounds: Environmental Aspects. http://www.inchem.org/documents/cicads/cicads/cicad44.htm#fwd.

WLRS (B.C. Ministry of Water, Land and Resource Stewardship) 2024. Working Water Quality Guidelines: Aquatic Life, Wildlife & Agriculture. Water Quality Guideline Series, WQG-08-01. Prov. B.C., Victoria B.C

Wood, C.M. 2012. Silver In: Metals: Homeostasis and Toxicology: Non-essential Metals. Fish Physiology, Vol. 31B. Ed: C.M. Wood, A.P. Farrell, and C.A. Brauner. pp: 1-65.

Wood, C.M., Playle, R.C., and Hogstrand, C. 1999. Physiology and modeling of mechanisms of silver uptake and toxicity in fish. Environmental Toxicology and Chemistry 18(1): 71-83.