

Canadian Water Quality Guidelines for the Protection of Aquatic Life

Silver 2015

S ilver is a naturally occurring element, and roughly 60% of silver in water comes from natural sources with the rest coming from anthropogenic inputs such as mining operations and metal production. Concentrations of silver in water are higher near mineral deposits, but very low elsewhere in the environment (Purcell and Peters 1998).

This revision of the 1987 Canadian Council of Resource and Environment Ministers' (CCREM) water quality guideline for silver (symbol Ag) is based on 33 years of research (1980-2013) concerning aquatic toxicity of silver and follows the revised protocol for the derivation of Canadian Water Quality Guidelines (CCME 2007). The Canadian Water Quality Guidelines for silver are presented in Table 1. Nanosilver in the aquatic environment, a relatively recent concern, is discussed briefly in the Scientific Criteria Document for the revised silver guideline but a water quality guideline for nanosilver is not recommended at this time due to the uncertainties of measuring the hazard of nanosilver.

Ambient concentrations: Silver is generally low in abundance in the environment when compared to other metals. In Canada, between 2008 and 2013, total silver concentrations were measured in thousands of surface water samples with varying water chemistry and varying levels of anthropogenic influence (Environment Canada 2013). In British Columbia and Yukon, concentrations ranged from below detection  $(0.001 \ \mu g/L)$  to  $10 \ \mu g/L$  with a mean of  $0.005 \ \mu g/L$ . In the Prairie and Northern region, including Alberta, Manitoba, Saskatchewan and Northwest Territories, concentrations ranged from below detection  $(0.001 \ \mu g/L)$  to  $0.69 \ \mu g/L$  with a mean of  $0.005 \ \mu g/L$ . In the Atlantic region, including Prince Edward Island, Nova Scotia,

Table 1. Revised Canadian Water Quality Guidelines (CWQGs) for the protection of aquatic life for silver<sup>1,2</sup> developed using CCME 2007. Guidelines were developed using the species sensitivity distribution (SSD) method (Type A).

	Long-term Exposure (µg Ag/L)	Short-term Exposure (µg Ag/L)
Freshwater	0.25	NRG <sup>3</sup>
Marine	$NRG^4$	7.5

NRG= no recommended guideline

<sup>1</sup> This guideline is not applicable to silver nanoparticles.

<sup>2</sup> CWQGs were derived based on the total concentration of Ag.

<sup>3</sup> Because the short-term SSD 5<sup>th</sup> percentile and the long-term SSD 5<sup>th</sup> percentile (CWQG) are essentially equal, no designated short-term freshwater benchmark is recommended.

<sup>4</sup> There were insufficient data to derive a long-term marine guideline.

Newfoundland and Labrador, and New Brunswick, concentrations ranged from below detection  $(0.001 \ \mu g/L)$  to 1.13  $\mu g/L$ , with the majority at or below detection limit (Environment Canada, 2013). Dissolved (<0.45  $\mu$ m filtered samples) silver concentrations measured in Québec rivers between 2008 and 2011 ranged from <0.001 to 0.032  $\mu$ g/L and total recoverable silver concentrations ranged from <0.001 to 0.085  $\mu$ g/L (Hébert 2012). The lower maximum values reported in Québec vis-à-vis the rest of the country are the result of clean sampling methods and high resolution analysis used for trace metals.

*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  $\mu$ m, colloids being >10 kDa and <0.45  $\mu$ m, 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 leadmining 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 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).

*Mode of Action:* There is no evidence that silver has any essential biological function in aquatic life. The acute toxicity of silver ion appears to be accidental active uptake across the apical surface of the gill via a Na<sup>+</sup> uptake channel that is linked to a proton extrusion pump, with subsequent poisoning of the basolateral Na<sup>+</sup>K<sup>+</sup>-adenosine triphosphatase (Na<sup>+</sup>/K<sup>+</sup> ATPase or NKA) in the chloride cells of the gill epithelium leading to ionoregulatory imbalance and

ultimately death. Another site of action for acute toxicity is inhibition of the enzyme carbonic anhydrase in the branchial ionocytes (Wood 2012). In terms of chronic toxicity mechanisms, interference with Na<sup>+</sup> and Cl<sup>-</sup> regulation is similar to that seen in acute toxicity where wholebody concentrations of the ions decrease (Wood 2012). In marine fish, target organisms include the gut as well as the gills, and the target functions include gastrointestinal ionoregulation as well as branchial ionoregulation (Wood 2012).

*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,  $(Ca^{2+} \text{ and } Mg^{2+})$  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<sub>3</sub>, 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<sup>-</sup> on silver toxicity have been confounded by the accompanying cation, i.e., many have used NaCl as the source of Cl<sup>-</sup>. Therefore, any reduction in toxicity seen is likely partially due to the Na present in solution. Investigations on the protective effect of Cl<sup>-</sup> (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<sup>-</sup> 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<sup>-</sup>. Daphnids (*Ceriodaphnia dubia* and *Daphnia magna*), however, seem to benefit from Cl<sup>-</sup> but any protective effects are only seen when Cl<sup>-</sup> 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 LC50 (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.

Short-term and long-term toxicity of silver: The freshwater long-term maximum acceptable toxicant concentration (MATC) for silver ranged from 0.24 to 1.33  $\mu$ g/L for fish (growth) and 0.78  $\mu$ g/L for invertebrates (reproduction). The no-observed-effect concentration (NOEC) ranged from 4 to 13  $\mu$ g/L for invertebrates, while the IC20 of invertebrate *Daphnia magna* was 2.95  $\mu$ g/L. Long-term mortality effect toxicity concentrations (LC10s) for silver range from 1.9 to 23  $\mu$ g/L for fish. One acceptable long-term endpoint was available for plants, a 7-d MATC of 0.63  $\mu$ g/L. Short-term 96-h and 48-h LC50s are reported in silver toxicity literature for a wide variety of fish and invertebrate species, respectively.

Guadagnolo *et al.* (2001) showed that the stage of development in the rainbow trout (*Oncorhynchus mykiss*) embryo is an important factor in sensitivity to silver. The chorion of the embryo plays an important role in defending the embryo against silver toxicity by limiting the rate by which silver enters the egg (Guadagnolo *et al.* 2001). Galvez *et al.* (1998) studied physiological effects of silver nitrate exposure on juvenile rainbow trout. Food consumption and growth rates were negatively affected when exposed to concentrations of 0.5 and 2.0 µg/L for 28 days (Galvez *et al.* 1998). Galvez and Wood (2002) later exposed juvenile trout to different concentrations of silver nitrate (0, 0.1, 1, 3 and 5 µg Ag<sup>+</sup>/L) for 23-days and found that food-conversion efficiency and the critical swimming speed were also significant toxic effects. Toxicity data reported for *Ceriodaphnia dubia* and *Daphnia magna* genus mean acute values of ~ 1 and 2 µg/L, indicating that they are the most sensitive species studied to date. Invertebrates tend to be more sensitive to metals when compared to fish. Various reproductive and physiological endpoints were observed when *D. magna* neonates (newly hatched offspring) were exposed to 2 µg/L of dissolved silver over 21-days, i.e., survival, growth, time to first brood, mean number of young produced per adult, number of broods produced, mean number of young

per brood, whole body Na<sup>+</sup> and Sodium-potassium activated adenosine triphosphatase (Na<sup>+</sup>/K<sup>+</sup> ATPase or NKA) activity. The response of crustaceans to silver appears to differ from rainbow trout because there is a lack of Cl<sup>-</sup> disturbance in the ionoregulatory response of invertebrates (Bianchini *et al.* 2002)

In marine waters, short-term severe effect toxicity concentrations (48-h to 12-d LC50s) for silver reported from acceptable studies ranged from 100 to 1876  $\mu$ g/L for fish, 5.8 to 647  $\mu$ g/L for invertebrates and 21 to 86  $\mu$ g/L for algae. The reported EC50s (20-min to 120-h) for fish ranged between 356 and 800  $\mu$ g/L.

In marine waters, silver is far less acutely toxic than in fresh waters. One of the fundamental differences between waters is that the site of silver toxicity in marine fish is the gut, since this is where these fish actively transport ions to combat water loss. The ions in excess are excreted at the gills, reducing accumulation within the organism. In freshwater fish, the gills are the principal site of ionoregulation because the fish are constantly pumping ions into their blood to make up for the difference in osmolality between blood and surrounding water (Wood *et al.* 1999). Secondly, there is a difference in speciation of silver and its influence on silver toxicity when in different aquatic environments. Silver speciation is highly influenced by CI<sup>-</sup> as it is largely present in the form of chloride complexes and this reduces toxicity in marine waters (Luoma *et al.* 1995). Complexation with organic matter is negligible. Although the mechanisms for toxicity in marine species are not entirely clear, the gut and gill are likely targets for silver uptake and toxicity due to the differences in ion regulation between fresh water and marine aquatic life.

*Water quality guideline derivation:* 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). The short-term marine benchmark was derived using the Type A approach. There were insufficient data to derive any type of long-term marine guideline.

Short-term freshwater benchmark concentration: Short-term exposure benchmarks are derived using severe effects data (such as lethality) of defined short-term exposure periods (24 – 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 18 points (all but two were LC50s values) were used in the derivation of the Species Sensitivity Distribution (SSD) (Table 2). Each species for which appropriate short-term toxicity data were available was ranked according to effect concentration, and its position on the SSD (proportion of species affected) was determined using the Hazen plotting position (estimate of the cumulative probability of a data point).

		Concentration
Species	Endpoint (µg/L)	
Fish		
O. mykiss	96-h LC50	1.48
P. promelas	96-h LC50	1.99
J. floridae	96-h LC50	10.7
L. macrochirus	96-h LC50	13
I. punctatus	96-h LC50	17.3
A. anguilla	96-h LC50	34.4
Invertebrate		
C. dubia	48-h LC50	0.16
D. magna	48-h LC50	0.26
G. pseudolimnaeus	48-h LC50	4.7
Simocephalus sp.	48-h LC50	27
C. diogenes	96-h LC50	65.9
diogenes		
N. obscura	96-h LC50	29
A. hypnorum	96-h LC50	83
T. dissimilis	48-h LC50	420
O. immunis	96-h LC50	560
Algae		
C. reinhardtii	6-h EC50	1.29
	(growth)	
P. subcapitata	6-h EC50	2.8
	(growth)	
Protozoan		
S. ambiguum	48-h LC50	8.8

#### Table 2. Endpoints used to determine the short-term freshwater SSD for silver.

The log logistic model provided the best fit of the models tested and the Anderson Darling goodness-of-fit statistic was  $A^2 = 0.141$ . The equation of the logistic model is of the form:

$$f(x) = \frac{1}{1 + e(-\frac{x - \mu}{\sigma})}$$

Where, in the case of the fitted model,  $\mu = 1.026$ , and  $\sigma = 0.574$ .

The short-term freshwater SSD is presented in Figure 1 and summary statistics for the short-term freshwater SSD are presented in Table 3. The 5<sup>th</sup> percentile on the short-term SSD is  $0.22 \mu g/L$ .

	Concentration
	$(\mu g Ag/L)$
SSD 5th percentile	0.22
SSD 5th percentile, 95% LFL	0.15
SSD 5th percentile, 95% UFL	0.31



Figure 1. Short-term species sensitivity distribution (SSD) for silver in fresh water derived by fitting the log-logistic model to the short-term LC/EC<sub>50</sub>s of 18 aquatic species.

No short-term freshwater benchmark is recommended for silver. Because the short-term SSD 5<sup>th</sup> percentile (0.22  $\mu$ g/L) and the long-term SSD 5<sup>th</sup> percentile and CWQG (0.25  $\mu$ g/L) (see below) are essentially equal, no designated short-term benchmark concentration is recommended. Generally, one expects the short-term benchmark to be higher than the long-term guideline, as shorter exposure durations for most chemicals require higher concentrations to cause an effect. The closeness of the short-term and long-term  $5^{th}$  percentile values can be explained by low

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endpoints included in the short-term SSD that are from experiments conducted in reconstituted waters and in the absence of food. Reconstituted waters reflect highly bioavailable conditions (with limited complexing of silver) not seen in natural waters, and which result in low endpoint values. The absence of food during short-term exposures also represents highly bioavailable conditions with limited complexing. In contrast, long-term exposures necessitate feeding of test organisms, which results in complexation of silver by food particles, and consequently, reduced toxicity. While this concept is true for all metals, it is especially relevant for silver due to the strong relationship between binding affinity and toxicity.

*Long-term freshwater quality guideline:* 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 4). Each species for which appropriate long-term toxicity data were available was ranked according to sensitivity and plotted using the Hazen plotting position.

		Concentration
Species	Endpoint	(µg/L)
Fish		
O. mykiss	MATC	0.24
	(growth)	
P. promelas	MATC	0.83
	(growth)	
I. punctatus	LC10	1.9
M. salmoides	LC10	23
Invertebrates		
C. dubia	MATC	0.78
	(reproduction)	
D. magna	IC20	2.12
	(reproduction)	
H. azteca	NOEC	4
	(reproduction)	
C. tentans	NOEC	13
	(dry weight)	
Plant		
L. gibba	7-d MATC	0.63
	(frond number)	

## Table 4. Endpoints used to determine the long-term freshwater SSD for silver .

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  $A^2 = 0.181$ . 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 2 and the summary statistics for the long-term freshwater SSD are presented in Table 5. The 5<sup>th</sup> percentile on the long-term SSD is 0.25  $\mu$ g/L.

# Table 5. Long-term freshwater guideline concentration for silver derived using the SSDmethod. (LFL= lower fiducial limit; UFL= upper fiducial limit).

	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  $0.25 \ \mu g/L$ .

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  $\geq$ 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 LC50s for this data-rich species are above the CWQG, with a geometric mean of 0.68 µg/L. For the *C. dubia* LC50s 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 LC50s 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 2. 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.

*Marine Water Quality Guideline:* 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.

Species	Reported Endpoint	Concentration (µg/L)	
Fish			
S. acanthus	96-h LC50	100	
O. maculosus	96-h LC50	331	
C. aggregata	96-h EC50 (mobility)	356	
O. mykiss	96-h LC50	401.5	
C. variegatus	96-h LC50	441	
O. kisutch	96-h EC50	488	
P. vetulus	(mobility) 96-h EC50 800 (mobility)		
Invertebrates			
C. virginica	48-h LC50	5.8	
C. gigas	48-h LC50	19	
M. mercenaria	42-48h LC50	21	
A. punctulata	96-h EC50	40	
A. tonsa	48-h LC50	43.2	
A. hudsonica	48-h LC50	43.2	
A. bahia	96-h LC50	65	
T. brevicornis	96-h LC50	95	
N. areanaceodentata	96-h LC50	145	
H. diversicolor	4-d LC50	647	
Algae			
G. splendens	48-h LC50	21	
I. galbana	48-h LC50	81	

Table 6. Endi	points used to	determine f	the short-term	marine SSE	) for silver.
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The Normal model provided the best fit of the models tested. The Anderson-Darling goodness-of-fit statistic was  $A^2 = 0.349$ .

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,  $\mu = 2.014$ ,  $\sigma = 0.692$ , 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 5<sup>th</sup> percentile on the short-term SSD is 7.5  $\mu$ g/L.

Table 7. Short-term marine benchmark concentration for silver derived using the SSD
method. (LFL= lower fiducial limit; UFL= upper fiducial limit).

	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  $\mu$ g/L for silver.



Figure 3. Short-term species sensitivity distribution (SSD) for silver in marine water derived by fitting the log-normal model to short-term LC/EC<sub>50</sub>s of 19 aquatic species.

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