Canadian Water Quality Guidelines for the Protection of Aquatic Life

CHLORIDE

The chloride ion (Cl^-) is the negatively charged chlorine atom (Cl) (CAS No. 7782-50-5, atomic mass 35.45 g/mol) formed when the chlorine atom picks up one electron. The chlorine atom is a halogen (boiling point of 33.9°C), and never exists in free form in the environment (Nagpal *et al*., 2003). The chloride ion commonly occurs as a salt. Some common chloride salts include NaCl, KCl, $MgCl_2$ (for de-icing of roads and walkways), $CaCl_2$ (used as a dust suppressant on roads), $AlCl_2$ (used in municipal drinking water and wastewater treatment facilities for removal of suspended particles and bacteria from the water), as well as $FeCl_3$ (used at municipal wastewater treatment plants to enhance the removal of phosphorus). Chloride-containing compounds are highly soluble in water (e.g. solubility of NaCl is 35.7g/100g water at 0^oC), hence they easily dissociate and tend to remain in their ionic forms (e.g. Na^+ and Cl^-) once dissolved in water. The chloride ion is highly mobile and concentrations in water are not affected by chemical reactions. Hence chloride does not biodegrade, readily precipitate, volatilize, or bioaccumulate. The chloride ion does not adsorb readily onto mineral surfaces and therefore concentrations remain high in surface water and sediment pore water, and low in sediment (Mayer *et al* 1999; Evans and Frick 2001; WHO 2003). Overall, inorganic chloride is generally considered to be a hydrologically and chemically inert substance. However, research by Oberg (2006) has revealed that a large portion of inorganic chloride that is deposited in terrestrial environments is transformed to organic chloride (chlorinated organic matter) in soil or vegetation (with the reverse occurring as well whereby chlorinated organic matter converts to inorganic chloride), although the underlying mechanisms are not fully understood.

It is advised to read the section "Guidance on the Use of Guidelines" found on page 11 of this factsheet before applying the above noted guidelines.

Sources to the environment: The chloride ion is naturally occurring, and therefore detection of increased levels of chloride in surface waters does not necessarily imply an anthropogenic source (although chloride is often used as an indicator of increasing urbanization in a watershed). Natural sources of chloride in aquatic systems include naturally-occurring saline lakes and groundwater discharges from saline aquifers. Canada has many known naturally occurring salt deposits. Major salt deposits (marine evaporite) are found in Nova Scotia, New Brunswick, Quebec, Ontario, Manitoba, Saskatchewan and Alberta (Dumont 2008; CANMET 1991). Other natural sources include volcanic emanations, sea spray, seawater intrusion

Table 1. Canadian Water Quality Guideline for the Chloride ion[a] for the protection of aquatic life.

	Long-Term Exposure[b] ($mg\ Cl^-/L$)	Short-Term Exposure[c] ($mg\ Cl^-/L$)
Freshwater	120[d]	640
Marine	NRG	NRG

NRG = no recommended guideline.

[a]Chloride toxicity to freshwater organisms was evaluated using tests with both $CaCl_2$ and NaCl salts.

[b]Derived with mostly no- and some low-effect data and are intended to protect against negative effects to aquatic ecosystem structure and function during indefinite exposures (e.g. abide by the guiding principle as per CCME 2007).

[c]Derived with severe-effects data (such as lethality) and are not intended to protect all components of aquatic ecosystem structure and function but rather to protect most species against lethality during severe but transient events (e.g. inappropriate application or disposal of the substance of concern).

[d]The long-term CWQG may not be protective of certain species of endangered and special concern freshwater mussels (as designated by the Committee on the Status of Endangered Wildlife in Canada, or COSEWIC). This specifically applies to two species; the wavy-rayed lampmussel (*Lampsilis fasciola*) (COSEWIC 2010a) and the northern riffleshell mussel (*Epioblasma torulosa rangiana*) (COSEWIC 2010b) (Table 2). The wavy-rayed lampmussel is indigenous to the lower Great Lakes and associated tributaries, specifically western Lake Erie, the Detroit River, Lake St. Clair and several southwestern Ontario streams. The northern riffleshell mussel is indigenous to the Ausable, Grand, Sydenham and Thames Rivers in Ontario, as well as the Lake St. Clair delta. Discussion with provincial regulators should occur if there is a need to develop more protective site specific values.

Table 2. 24h EC_{10} values (survival of glochidia) for 2 species of COSEWIC assessed freshwater mussels

COSEWIC Assessed Species	24h EC_{10} (mg Cl^-/L).	95% Confidence Intervals
Lampsilis fasciola Wavy-rayed lampmussel (COSEWIC special concern)	24 (Bringolf, 2010)	-79[1], 127
Epioblasma torulosa rangiana Northern riffleshell mussel (COSEWIC endangered)	42 (Gillis, 2009)	24, 57

[1] The negative lower fiducial limit is an artefact of the statistics. Biologically this can be interpreted as meaning that a 10% effect can be observed between a concentration of 0 and the upper 95% confidence limit. Therefore, the effect is not significantly different from the control (no-effect concentration) and could be due to natural variability.

in coastal areas (NRC 1977), as well as wildfires and logging (remobilization of major ions in lake watersheds impacted by these perturbations) (Pinel-Alloul *et al* 2002). Seawater salt concentrations are approximately 35,000 mg/L of which approximately 55% is chloride, which equates to 19,250 mg Cl^-/L (Evans and Frick 2001). Chloride compounds from anthropogenic sources enter the aquatic ecosystem through various pathways, such as wastewater effluents, stream inflow, road or overland runoff, groundwater inputs, and leaching from contaminated soils (Evans and Frick, 2001). A major non-industrial anthropogenic source of chloride to densely populated regions of Canada (e.g. southern Ontario and Quebec) is the application and storage of road salt for snow and ice control in the winter (97% of road salt used in Canada is in the form of NaCl, 2.9% in the form of $CaCl_2$, and 0.1% as $MgCl_2$ and KCl) (Chapra *et al*., 2009; L. Trudell, Environment Canada, pers. comm.). Road salt is the single largest source of chloride entering Lake Ontario from local sources (Evans and Frick 2001), and is also a significant source of chloride loading into Lake Simcoe in Ontario (Winter *et al.*, 2011). During the 1997 to 1998 winter, Morin and Perchanok (2000) estimated that 2,950,728 tonnes of chloride was released into the Canadian environment as a result of road salt (as NaCl) and dust suppressant (as $CaCl_2$) application. The provinces with the most chloride use on roadways were Ontario (1,148,570 tonnes) and Quebec (950,444 tonnes). However, Nova Scotia was found to have the highest loading per unit area of the province (230,182 tonnes) (Morin and Perchanok 2000). In comparison, the estimated discharge of chloride into Ontario waters in 2008 from municipal wastewater treatment plant effluent was 175,000 tonnes (M. Manoharan, Ontario Ministry of the Environment, pers. comm.). An often unquantified but likely significant use of road salt is private de-icing operations such as applications onto sidewalks, driveways, and parking lots (Perera *et al* 2009; Chapra *et al* 2009). Elevated concentrations of chloride associated with de-icing have been documented in groundwater, wetlands, streams, and ponds adjacent to snow dumps and salt-storage areas, and also those draining major roadways and urban areas in Canada (Evans and Frick 2001). Other anthropogenic sources include disposal of snow cleared from roadways, application of chloride brine solutions for dust suppression in the summer, water softeners, industrial effluent, domestic sewage, landfill leachate, irrigation drainage (Evans and Frick 2001), and industrial site drainage. Chloride (from inorganic salts) is not tracked by Environment Canada's National Pollutant Release Inventory. Ontario tracks chloride releases from a small number of sectors (e.g. electric power generation, industrial minerals, inorganic chemical, metal mining) covered under MISA (Municipal/Industrial Strategy for Abatement) regulations, but not from other industries (Chapra *et al* 2009).

Ambient Concentrations: Ambient chloride concentrations in the Atlantic region (Newfoundland and Labrador, Nova Scotia, New Brunswick and Prince Edward Island) of Canada are normally <10 mg/L in inland lakes, with concentrations as high as 20 to 40 mg/L in lakes located closer to coastal areas (Mayer *et al* 1999; Evans and Frick 2001; D. Parent, Environment Canada, pers. comm.). Unimpacted lakes on the Canadian shield of Canada's central region (Quebec and Ontario) have measured chloride concentrations of <1 to 7 mg/L, with higher concentrations (10 to 30 mg/L) measured in the lower Great Lakes and the St. Lawrence River (Evans and Frick 2001). Chloride concentrations above background are commonly detected in densely populated areas (e.g. small urban watersheds) where road densities are high, and in fact, chloride concentrations are a commonly used indicator of increasing urbanization. Monitoring of Sheridan Creek in Ontario (pre-1980 to 2007), located in a fully-developed urban area containing a dense road network, measured chloride ranging from 14.5 to 5,320 mg Cl^-/L (median of 292 mg Cl^-/L) (OMOE 2009). Real-time monitoring of a Lake Ontario tributary (Cooksville Creek) in a highly urbanized watershed (Mississauga, Ontario) showed chloride levels exceeding that of seawater, with measurements made in February 2011 reporting chloride as high as 20,000 mg/L (K. vander Linden, Credit Valley Conservation Authority, pers. comm.). In the case of Canada's prairie region (Manitoba, Saskatchewan, and Alberta), low chloride concentrations (<5 mg/L) are reported in lakes located in the northern portions of the provinces, outside of the Interior Plains region. The Interior Plains region, which covers the southern portion of the prairie provinces, is an area with naturally elevated salinity (high total dissolved solids) (CEPA 1999). This salinity is usually due to high concentrations of sodium (mean range of 92 to 31,311 mg/L), bicarbonate (mean range of 427 to 16,352 mg/L) and sulphate (mean range of 2,305 to 108,069 mg/L), although chloride concentrations (mean range of 71 to 3,793 mg/L) are still significantly higher than other areas (Last and Ginn, 2005). For the Pacific region (British Columbia), the chloride concentration in unimpacted water bodies is <5 mg/L. However, several lakes in the southern interior plateau had measured chloride concentrations >100 mg/L (Evans and Frick 2001). Water quality monitoring data in the Yukon showed that dissolved chloride concentrations are low, ranging from 0.1 to 4.6 mg/L (Environment Canada 2009).

Chloride and Salinity of Canadian Surface Waters: Salinity is a measure of the total salt composition of water, with freshwater lakes being dominated by the cations Ca^{2+}, Mg^{2+}, K^+ and Na^+ and the anions HCO_3^-, CO_3^{2-}, SO_4^{2-} and Cl^- (Wetzel 1983). Water is classified according to salinity. Freshwater lakes are those with less than 500 mg/L salinity. The salinity of sub-saline lakes ranges from 500 to 3,000 mg/L, and the salinity of saline lakes exceeds 3,000 mg/L (Evans and Frick 2001). When chloride salts are added to freshwater systems (e.g. through the application of road salt), the salts dissolve and dissociate into respective ions and directly increase the salinity of the receiving system (Evans and Frick 2001). Salinity is a key factor in controlling survival and distribution of both freshwater invertebrates and fish (Holland *et al* 2010). Naturally saline lakes within Canada (commonly dominated by SO_4/CO_3 and relatively rarely by Cl) are systems with naturally low biodiversity (Derry *et al* 2003). Most freshwater organisms found within these systems are stenohaline (have a narrow range of tolerance to changes in salinity), although some organisms are euryhaline (able to tolerate and adapt to a wide range of salinities) (Derry *et al* 2003; Holland *et al* 2010).

Assessment of Road Salt under the Canadian Environmental Protection Act: The Priority Substances List Assessment Report for Road Salts was published on December 1, 2001 (Environment Canada 2001). The report concluded that road salts that contain inorganic chloride salts with or without ferrocyanide salts (anti-caking agent) have adverse impacts on the environment and are therefore toxic under subsections 64(*a*) and (*b*) of the *Canadian Environmental Protection Act, 1999* (CEPA 1999). This decision has led to the publication in April 2004 of a Code of Practice for the Environmental Management of Road Salts. This Code of Practice is aimed at helping municipalities and other road authorities better manage their use of road salts in a way that reduces the harm they cause to the environment while still maintaining road safety.

Several studies have indicated that even when road salt application decreases, surface water monitoring of chloride concentrations does not show an associated decrease in chloride concentration (Meriano *et al* 2009; Kilgour *et al* 2009). This is attributed to subsurface storage of chloride and the lag effect of chloride entering surface water systems, resulting in increased baseflow[1] chloride concentrations. Sensitive species located in surface waters within rapidly-urbanizing watersheds or fully-developed watersheds are at risk of being adversely impacted by increased baseflow chloride levels. Increased chloride in surface water has also been linked to reducing the vertical mixing of surface waters by way of changing the density gradient in lakes. This phenomenon is referred to as meromixis (layers of water that do not experience complete overturn or complete vertical mixing). One of the outcomes of stable stratification of deep and surface water layers is that the deep layer (monimolimnion) can become quite depleted of oxygen. The concentration of dissolved oxygen in the monimolimnion of a meromictic lake can be less than 1 mg/L, while the surface layer (mixolimnion) may have concentrations of 10 mg/L or higher (Lampert *et al*. 1997). Low dissolved oxygen concentrations in the monimolimnion will limit the survival of aquatic life in this layer. In addition to chloride (saline) input, other variables are also involved in inducing chemical-based density stratification between lower and upper water layers leading to a resistance of vertical mixing (e.g. lake morphometry, water residence time, watershed topography and wind fetch) (Wetzel 2001).

Toxicity: Chloride toxicity tests have been conducted through the addition of chloride salts such as sodium

[1] Streamflow which is not a direct result of rainfall or melting snow. Baseflow is the streamflow which is sustained primarily through ground-water discharges.

chloride, calcium chloride, magnesium chloride and potassium chloride. Results of tests with potassium and magnesium chloride suggest toxic effects observed are due to the potassium and magnesium cation, rather than the chloride anion. Conversely, it has been observed that the toxic effects of calcium chloride and sodium chloride are likely due to the chloride anion. Generally speaking, the effect concentrations resulting from exposures to KCl and $MgCl_2$ salts are lower (e.g. more toxic) than the effect concentrations resulting from exposures to $CaCl_2$ and NaCl salts (when effect concentrations are assessed on a chloride anion basis). For example, the fathead minnow 96-h LC50 effect concentration resulting from exposure to a KCl salt, a $MgCl_2$ salt, a $CaCl_2$ salt and a NaCl salt was 419 mg Cl/L, 1579 mg Cl/L, 2958 mg Cl/L and 3876 mg Cl/L, respectively (Mount et al., 1997). Therefore, the approximate order of chloride salt toxicity to freshwater organisms is KCl > $MgCl_2$ > $CaCl_2$ > NaCl (Mount *et al* 1997). Based on these observations, chloride toxicity to freshwater organisms was only evaluated using tests with $CaCl_2$ and NaCl in order to ensure that the effect concentrations utilized for chloride guideline derivation were derived from tests where effects were based on the chloride anion, and not on associated cations.

Freshwater organisms are generally hyperosmotic (internal solute or salt concentration is higher when compared to the surrounding water) and thereby have to continuously excrete water (with some solute loss) to maintain equilibrium (Holland *et al* 2010). Freshwater organisms therefore have to take up ions to replace the ones lost, which can result in elevated energy expenditures until a threshold of intolerance is reached (Holland *et al* 2010). Increasing chloride in surface waters results in increased salinity, thereby affecting the ability of some organisms (stenohaline more so than euryhaline) to effectively osmoregulate, which could in turn affect endocrine balance, oxygen consumption following chronic exposures, and overall changes in physiological processes (Holland *et al* 2010). In both invertebrates and fish, the main site of osmoregulation is the gill, which is also the site of active uptake of lost salts. The sodium pump (Na^++K^+-ATPase) is the main mechanism for moving ions across gills in aquatic animals. The mechanism of osmoregulation used is dependent on the life stage of the organism. For example pre-larval fish osmoregulate largely through the skin, whereas larval stages regulate through the gills (Varsamos and Charmantier, 2005). Insects possess a network of Malpighian tubules lined with secretory cells extending throughout much of the body cavity which is involved in the reabsorption of ions (Dettner and Peters 1999). In the case of spotted salamander (*Ambystoma maculatum*) egg clutches, disruption in osmoregulation has not been determined but is likely related to chemical changes in the egg capsule (perivitelline) membrane, as has been documented in egg clutches exposed to highly acidic conditions (Karraker and Gibbs 2011). As with exposure to acid, high chloride concentrations may result in making the egg capsule membrane more rigid, reducing permeability, and therefore impacting the ability for water uptake (Karraker and Gibbs 2011).

Toxicity Modifying Factors: Some studies have indicated that increased hardness may have an ameliorating effect on the toxicity of chloride. One long-term study by Elphick *et al.* (2011) assessed the effect of hardness (10, 20, 40, 80, 160, 320 mg/L as $CaCO_3$) on sodium chloride toxicity to the water flea *Ceriodaphnia dubia* during a 7-day exposure. An approximate 4-fold difference was observed in the 7-day $IC_{25/50}$ (reproduction) effect concentrations, and a 9-fold difference in 7-day LC_{50} concentrations over the hardness range tested. Gillis (2011) exposed glochidia of the freshwater mussel *Lampsilis siliquoidea* to water of varying hardness (47, 99, 172, 322 mg/L as $CaCO_3$). An approximate 2.5-fold difference in 24-hour EC_{50} (glochidia survival) values was observed over the hardness range tested. GLEC and INHS (2008) also conducted some short-term exposures indicating the existence of a hardness-chloride toxicity relationship for the water flea *Ceriodaphnia dubia*, the fingernail clam *Sphaerium simile*, the oligochaete *Tubifex tubifex* and the aquatic snail *Gyraulus parvus*. Insufficient data were available to develop a hardness relationship for chronic toxicity and thus, a hardness-based CWQG was not developed. CCME will re-visit the chloride guidelines when sufficient studies are available. Jurisdictions may choose to derive site-specific hardness-adjusted water quality criteria (or objectives) where appropriate.

Water Quality Guideline Derivation: Both the freshwater short and long-term Canadian water quality guideline (CWQG) for the chloride ion for the protection of aquatic life were developed based on the CCME protocol (CCME 2007) with the statistical (Type A) approach.

Short-term Freshwater Quality Guidelines: Short-term exposure guidelines are derived with severe-effects data (such as lethality) of defined short-term exposure periods (24 to 96-hour). These guidelines identify estimators of severe effects to the aquatic ecosystem and are intended to give guidance on the impacts of severe but transient situations (e.g., spill events to aquatic receiving environments and infrequent releases of short-lived/non-persistent substances). Short-term benchmark concentrations *do not* provide guidance on protective levels of a substance in the aquatic environment, as short-term benchmark concentrations are levels that *do not* protect against adverse effects.

The minimum data requirements for the Type A short-term benchmark concentration approach were met and a total of 51 data points (14 of which are EC_{50} values) were used in the derivation of the value (Table 3). Each species for which appropriate short-term toxicity data were available was ranked according to sensitivity. Intra-species variability was accounted for by taking the geometric mean of the studies considered to represent the most sensitive lifestage and endpoint.

The log-Normal model provided the best fit of the five models (Normal, Logistic, Weibull, Gompertz, Fisher-Tippett) tested (Figure 1). 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, for the fitted model: x = log (concentration) of chloride (mg/L), y is the proportion of species affected, μ = 3.4390, σ = 0.3841 and *erf* is the error function (a.k.a. the Gauss error function). The short-term SSD is shown in Figure 1 and summary statistics are presented in Table 4. The 5^{th} percentile on the short-term SSD is 640 mg Cl^-/L which is essentially within the range of the data (to which the model was fit). Therefore the 5^{th} percentile and its fiducial limits (FL) (boundaries within which a parameter is considered to be located) are interpolations.

Two data points fall below the short-term SSD 5^{th} percentile value of 640 mg Cl^-/L. This includes the 24-hour EC_{50} of 244 mg Cl^-/L for the mantle lure spawning freshwater mussel (glochidia lifestage) *Epioblasma torulosa rangiana* (COSEWIC endangered) (Gillis, 2011), and the 48-hour EC50 (immobilization) of 621 mg Cl^-/L for the water flea *Daphnia magna* (Khangarot and Ray, 1989). Two other COSEWIC assessed species of freshwater mussels are also represented on the short-term SSD, with all data points above the 5^{th} percentile value. This includes the glochidia 24-hour EC_{50} of 746 mg Cl^-/L for the COSEWIC special concern wavy-rayed lampmussel (*Lampsilis fasciola*) (Valenti *et al* 2007; Gillis 2011; Bringolf *et al* 2007), and the juvenile 96-hour EC_{50} of 1,815 mg Cl^-/L for the COSEWIC endangered rainbow mussel (*Villosa iris*) (Wang and Ingersoll 2010). Both *L. fasciola* and *V. iris* are mantle lure spawners. Based on the short-term SSD, short-term exposures to levels of chloride exceeding the benchmark concentration of 640 mg Cl^-/L *may* pose the greatest hazard to the glochidia life stage of certain freshwater mussel species and to *Daphnia magna*. Note that meeting the proposed long-term guideline will protect from severe effects.

It is worth noting that glochidia of the COSEWIC special concern mussel *Lampsilis fasciola* are significantly more sensitive when tested in reconstituted laboratory water compared to natural river waters. Two separate tests derived 24-hour EC_{50} values of 113 mg Cl^-/L and 285 mg Cl^-/L for *L. fasciola* when conducted in moderately hard reconstituted water (99 mg/L as $CaCO_3$) (Gillis 2011). In comparison, the 24-hour EC_{50} values for *L. fasciola* tested in water collected from 4 different rivers in Ontario, Canada were 1,559 mg Cl^-/L (Grand River, hardness 278 mg/L as $CaCO_3$), 1,313 mg Cl^-/L (Sydenham River, hardness 292 mg/L as $CaCO_3$), 1,391 mg Cl^-/L (Maitland River, hardness 322 mg/L as $CaCO_3$) and 1,265 mg Cl^-/L (Thames River, hardness 306 mg/L as $CaCO_3$) (Gillis 2011). The ameliorating effect of natural water chemistry was attributed to more than just a difference in water hardness. A separate test looking at the impact of water hardness on chloride toxicity was conducted with *Lampsilis siliquoidea* (Gillis 2011). Resulting 24-hour EC_{50} values were 763, 1430, 1962 and 1870 mg Cl^-/L in soft (47 mg/L as $CaCO_3$), moderately hard (99 mg/L as $CaCO_3$), hard (172 mg/L as $CaCO_3$) and very hard (322 mg/L as $CaCO_3$) reconstituted water, respectively. The 4-fold difference in 24-hour EC_{50} values obtained for *L. fasciola* in natural river water, when compared to reconstituted water, is much larger than would be expected from hardness alone (as determined with *L. siliquoidea*), implying that other water chemistry variables are contributing to the reduction of chloride toxicity in natural waters. Short-term benchmark concentrations (as well as long-term CWQGs) are derived using laboratory-based studies which use reconstituted water to ensure consistency and the ability to compare results between studies. One disadvantage of using reconstituted waters is that results may not necessarily reflect organism responses in natural waters. Natural waters, on the other hand, contain variable water chemistry in addition to other potential contaminants resulting in variable toxic impacts to

Table 3. Endpoints used to determine the freshwater short-term CWQG for the chloride ion.

Species	Endpoint	Concentration (mg Cl^-/L)	Reference
Fish			
Pimephales promelas Fathead minnow	96-hour LC_{50} (geomean)	4,223	Mount *et al* 1997; Birge *et al* 1985
Lepomis macrochirus Bluegill sunfish	96-hour LC_{50} (geomean)	5,272	Birge *et al*. 1985; Trama 1954
Cyprinella leedsi Bannerfin shiner	96-hour LC_{50}	6,070	Environ 2009
Oncorhynchus mykiss Rainbow trout	96-hour LC_{50} (geomean)	8,634	Elphick *et al* 2011; Vosyliene *et al*. 2006
Gambusia affinis Mosquito fish	96-hour LC_{50}	9,099	Al-Daham & Bhatti 1977
Gasterosteus aculeatus Threespine stickleback	96-hour LC_{50}	10,200	Garibay & Hall 2004
Anguilla rostrata American eel	96-hour LC_{50}	13,012	Hinton and Eversol 1979
Amphibians			
Ambystoma maculatum Spotted salamander	96-hour LC_{50}	1,178	Collins & Russell 2009
Pseudacris triseriata feriarum Chorus frog	96-hour LC_{50}	2,320	Garibay & Hall 2004
Lithibates sylvatica (previously *Rana sylvatica*) Wood frog	96-hour LC_{50} (geomean)	2,716	Sanzo & Hecnar, 2006; Collins & Russell 2009; Jackman 2010
Pseudacris crucifer Spring peeper	96-hour LC_{50}	2,830	Collins & Russell 2009
Rana clamitans Green frog	96-hour LC_{50}	3,109	Collins & Russell 2009
Rana temporaria Common frog	96-hour LC_{50}	3,140	Viertel 1999
Lithibates pipiens (previously *Rana pipiens*) Leopard frog	96-hour LC_{50}	3,385	Jackman 2010
Bufo americanus American toad	96-hour LC_{50}	3,926	Collins & Russell 2009
Rana catesbeiana Bullfrog	96-hour LC_{50}	5,846	Environ 2009
Invertebrates			
Epioblasma torulosa rangiana Northern riffleshell mussel (COSEWIC[a] endangered)	24-hour EC_{50} (survival of glochidia)	244	Gillis 2011
Daphnia magna Water flea	48-hour EC_{50} (immobilization)	621	Khangarot and Ray 1989
Lampsilis siliquoidea Freshwater mussel	24-hour EC_{50} (survival of glochidia) (geomean)	709	Bringolf *et al* 2007; Gillis 2011
Lampsilis fasciola Wavy-rayed lampmussel (COSEWIC[a] special concern)	24-hour EC_{50} (survival of glochidia) (geomean)	746	Valenti *et al*. 2007; Bringolf *et al* 2007; Gillis 2011
Lampsilis cardium Plain pocketbook	24-hour EC_{50} (survival of glochidia)	817	Gillis 2011
Sphaerium simile Fingernail clam	96-hour LC_{50} (geomean)	902	GLEC & INHS 2008
Ceriodaphnia dubia	48-hour LC_{50}	1,080	Valenti *et al* 2007;

Species	Endpoint	Concentration ($mg\ Cl^-/L$)	Reference
Water flea	(geomean)		Hoke *et al* 1992; Mount *et al* 1997; GLEC & INHS 2008; Elphick *et al* 2011; Cowgill & Milazzo 1990
Daphnia ambigua Water flea	48-hour EC_{50} (immobilization)	1,213	Harmon *et al* 2003
Daphnia pulex Water flea	48-hour LC_{50} (geomean)	1,248	Palmer *et al* 2004 ; Birge *et al* 1985
Elliptio lanceolata Yellow lance mussel	96-hour LC_{50}	1,274	Wang & Ingersoll 2010
Brachionus patulus Rotifer	24-hour LC_{50}	1,298	Peredo-Alvarez *et al* 2003
Hyalella azteca Amphipod	96-hour LC_{50}	1,382	Elphick *et al* 2011
Elliptio complanata Freshwater mussel	24-hour EC_{50} (survival of glochidia)	1,620	Bringolf *et al* 2007
Epioblasma brevidens Cumberlandian combshell (endangered in USA)	24-hour EC_{50} (survival of glochidia)	1,626	Valenti *et al* 2007
Epioblasma capsaeformis Oyster mussel (endangered in USA)	24-hour EC_{50} (survival of glochidia)	1,644	Valenti *et al* 2007
Villosa constricta Freshwater mussel	24-hour EC_{50} (survival of glochidia)	1,674	Bringolf *et al* 2007
Villosa iris Rainbow mussel (COSEWIC[a] endangered)	96-hour EC_{50} (geomean)	1,815	Wang & Ingersoll 2010
Musculium transversum Fingernail clam	96-hour LC_{50}	1,930	US EPA 2010
Villosa delumbis Freshwater mussel	24-hour EC_{50} (survival of glochidia)	2,008	Bringolf *et al* 2007
Brachionus calyciflorus Rotifer	24-hour LC_{50} (geomean)	2,026	Elphick et al 2011; Peredo-Alvarez *et al* 2003; Calleja *et al* 1994
Physa gyrina Snail	96-hour LC_{50}	2,540	Birge *et al*. 1985
Lirceus fontinalis Isopod	96-hour LC_{50}	2,950	Birge *et al*. 1985
Gyraulus parvus Snail	96-hour LC_{50} (geomean)	3,043	GLEC & INHS 2008
Baetis tricaudatus Mayfly	48-hour EC_{50} (immobilization) (geomean)	3,266	Lowell *et al* 1995
Chironomus dilutus / tentans Midge	96-hour LC_{50}	3,761	Wang & Ingersoll 2010
Lumbriculus variegates Oligochaete	96-hour LC_{50} (geomean)	4,094	Elphick *et al* 2011; Environ 2009
Nephelopsis obscura Leech	96-hour LC_{50}	4,310	Environ 2009
Hexagenia sp. Mayfly	48-hour LC_{50}	4,671	Wang & Ingersoll 2010
Chironomus attenatus Midge	48-hour LC_{50}	4,850	Thornton & Sauer 1972
Daphnia hyalina Water flea[b]	48-hour LC_{50}	5,308	Baudouin & Scoppa 1974
Lepidostoma sp.	96-hour LC_{50}	6,000	Williams *et al* 1999

Species	Endpoint	Concentration ($mg\ Cl^-/L$)	Reference
Caddisfly			
Tubifex tubifex Oligochaete	96-hour LC_{50} (geomean)	6,119	Elphick *et al* 2011; Wang & Ingersoll 2010; GLEC & INHS 2008
Chironomus riparius Midge	48-hour LC_{50}	6,912	Wang & Ingersoll 2010
Eudiaptomus padanus padanus Copepod[b]	48-hour LC_{50}	7,077	Baudouin & Scoppa 1974
Cyclops abyssorum prealpinus Copepod[b]	48-hour LC_{50}	12,385	Baudouin & Scoppa 1974

[a]Committee on the Status of Endangered Wildlife in Canada; Canadian occurrence in Ontario.
[b]Based on testing with $CaCl_2$ salt (all others based on testing with NaCl salt).

biotic receptors. Therefore, short-term benchmark concentrations (as well as long-term CWQGs) may be relatively conservative values.

Therefore, the s hort-term exposure benchmark concentration indicating the potential for severe effects (e.g. lethality or immobilization) to senstive freshwater life during transient events is 640 mg Cl⁻/L for the chloride ion.

Table 4. Short-term freshwater CWQG for the chloride ion using the SSD method.

	Concentration
SSD 5th percentile	**640 mg Cl^-/L**
SSD 5th percentile, 90% LFL (5%)	605 mg Cl^-/L
SSD 5th percentile, 90% UFL (95%)	680 mg Cl^-/L

Long-term Freshwater Quality Guideline: Long-term exposure guidelines identify benchmarks in the aquatic ecosystem that are intended to protect all forms of aquatic life for indefinite exposure periods. Long-term exposure guidelines are derived using long-term data (≥7-day exposures for fish and invertebrates, ≥24-hour for aquatic plants and algae).

The minimum data requirements for the Type A guideline approach were met and a total of 28 data points were used in the derivation of the guideline (Table 5). Each species for which appropriate long-term toxicity data was available was ranked according to sensitivity. All datapoints were taken from single studies, therefore none of the concentrations listed in Table 5 are geometric means.

The log-Logistic model provided the best fit of the five models (Normal, Logistic, Weibull, Gompertz, Fisher-Tippett) tested (Figure 3). The equation of the Logistic model is:

$$y = 1/[1+e^{-((x-\mu)/\sigma)}]$$

where for the fitted model: x = log (concentration) of chloride (mg/L), y is the proportion of species affected, $\mu = 2.93$ and $\sigma = 0.29$. The long-term SSD is shown in Figure 2 and summary statistics are presented in Table 6. The 5th percentile on the long-term SSD is 120 mg Cl^-/L which is within the range of the data (to which the model was fit). Therefore the 5th percentile and its fiducial limits (FL) (boundaries within which a parameter is considered to be located) are interpolations.

Two data points fall below the long-term SSD 5th percentile value of 120 mg Cl^-/L. These include the 24-hour EC_{10}s of 24 mg Cl^-/L (Bringolf 2010) and 42 mg Cl^-/L (Gillis 2009) for two species of mantle lure spawning freshwater mussels (glochidia lifestage), including *Lampsilis fasciola* (COSEWIC special concern) and *Epioblasma torulosa rangiana* (COSEWIC endangered), respectively. The CCME guideline derivation protocol (CCME 2007) provides the option of implementing the Protection Clause in situations where a data point for a species at risk, a species of commercial or recreational importance, or an ecologically important species falls below the 5th percentile (CWQG) value on the long-term SSD. In areas where the COSEWIC special concern mussel (*L. fasciola*) or the COSEWIC endangered mussel (*E. torulosa rangiana*) are present, the protection clause can

Table 5. Endpoints used in the SSD to determine the long-term CWQG for the chloride ion where freshwater mussels are present.

Species	Endpoint	Concentration (mg Cl^-/L)	Reference
Fish			
Pimephales promelas Fathead minnow	33-day LC_{10} (survival)	598	Birge *et al* 1985 In: Elphick *et al* 2010
Salmo trutta fario Brown trout	8-day NOEC (survival)	607	Camargo & Tarazona 1991
Oncorhynchus mykiss Rainbow trout	7-day EC_{25} (embryo viability)	989	Beak 1999
Amphibians			
Xenopus laevis African clawed frog	7-day LC_{10} (survival)	1,307	Beak 1999
Rana pipiens Northern leopard frog	108-day MATC (survival)	3,431	Doe 2010
Invertebrates			
Lampsilis fasciola Wavy-rayed lampmussel (COSEWIC special concern)[a]	24-hour EC_{10} (glochidia survival)	24	Bringolf *et al* 2007
Epioblasma torulosa rangiana Northern riffleshell mussel (COSEWIC[a] endangered)	24-hour EC_{10} (glochidia survival)	42	Gillis 2009
Musculium securis Fingernail clam	60-80 day LOEC (reduced natality[b])	121	Mackie 1978
Daphnia ambigua Water flea	10-day EC_{10} (mortality and reproduction)	259	Harmon *et al* 2003
Daphnia pulex Water flea	21-day IC_{10} (reproduction)	368	Birge *et al* 1985 In: Elphick *et al* 2011
Elliptio complanata Freshwater mussel	24-hour EC_{10} (glochidia survival)	406	Bringolf *et al* 2007
Daphnia magna Water flea	21-day EC_{25} (reproduction)	421	Elphick *et al* 2011
Hyalella azteca Amphipod	28-day EC_{25} (growth, dry weight)	421	Bartlett 2009
Ceriodaphnia dubia Water flea	7-day IC_{25} (reproduction)	454	Elphick *et al* 2011
Tubifex tubifex Oligochaete	28-day IC_{10} (reproduction)	519	Elphick *et al* 2011
Villosa delumbis Freshwater mussel	24-hour EC_{10} (glochidia survival)	716	Bringolf *et al* 2007
Villosa constricta Freshwater mussel	24-hour EC_{10} (glochidia survival)	789	Bringolf *et al* 2007
Lumbriculus variegates Oligochaete	28-day EC_{25} (reproduction)	825	Elphick *et al* 2011
Brachionus calyciflorus Rotifer	48-hour IC_{10} (reproduction)	1,241	Elphick *et al* 2011
Lampsilis siliquoidea Freshwater mussel	96-hour EC_{10} (survival of juveniles)	1,474	Bringolf *et al* 2007
Gammarus pseudopinmaeus Amphipod	60-day NOEC (survival)	2,000	Williams *et al* 1999
Physa sp. Snail	60-day NOEC (survival)	2,000	Williams *et al* 1999

Species	Endpoint	Concentration ($mg\ Cl^-/L$)	Reference
Stenonema modestum Mayfly	14-day MATC (development)	2,047	Diamond *et al* 1992
Chironomus tentans Midge	20-day IC_{10} (growth, biomass)	2,316	Elphick *et al* 2011
Aquatic Plants and Algae			
Lemna minor Duckweed	96-hour MATC (frond production)	1,171	Taraldson & Norberg-King 1990
Chlorella minutissimo Algae	28-day MATC (growth)	6,066	Kessler 1974
Chlorella zofingiensis Algae	28-day MATC (growth)	6,066	Kessler 1974
Chlorella emersonii Algae	8-14day MATC (growth inhibition)	6,824	Setter *et al* 1982

[a]Committee on the Status of Endangered Wildlife in Canada; Canadian occurrence in Ontario.
[b]Natality is "a measure of population increase under an actual specific environmental condition varying with the size and composition of the population and the physical environmental conditions" (Mackie 1978).

be implemented, resulting in a guideline value ranging from 24 to 42 mg Cl^-/L. In all other areas where non-endangered freshwater mussels are present, the long-term SSD 5[th] percentile value of 120 mg Cl^-/L should be used as the guideline value. As was discussed earlier, mussel toxicity data that were used for long-term CWQG derivation (as well as short-term benchmark concentration) commonly relied on exposures in reconstituted water. Therefore by design, CWQGs will likely be conservative values.

One long-term study that was not added to the long-term SSD dataset used road salt in place of NaCl salt, and is worth discussing here. The study involved exposing egg clutches of the spotted salamander (*Ambystoma maculatum*) to three chloride concentration treatments: 1 mg/L (chloride measured in vernal pools >200m from a highway), 145 mg/L (mean chloride measured in vernal pools within 200m of a highway), and 945 mg/L (maximum chloride measured in vernal pools within 200m of a highway) (Karraker and Gibbs 2011). Egg clutches were exposed to these chloride concentrations for a 9 day period, after which they were transferred to control water for another 9 day period and were weighed at day 3, 6, and 9 following transfer into clean water. The transfer into clean water was intended to mimic the dilution that occurs in vernal breeding pools following spring rainfall. Over the entire 18 day test period, clutches in the 1 mg/L treatment increased in mass by an average 25%, those in the 145 mg/L treatment lost an average mass of 2%, while clutches in the 945 mg/L treatment lost an average mass of 45%. Diluting rains may therefore aid in ameliorating the effects of moderate chloride concentrations in vernal breeding pools. However high chloride in breeding habitats may permanently disrupt the ability of egg clutches to osmoregulate or take up water. This could result in increasing risk of predation, freezing, malformations and other adverse effects to embryos of the spotted salamander (Karraker and Gibbs 2011). The CWQG of 120 mg Cl^-/L is expected to be protective of the early life stage of the spotted salamander.

Therefore, the long-term exposure CWQG for the protection of freshwater life is 120 mg Cl^-/L for the chloride ion.

Marine Water Quality Guideline: approximately 35,000 mg/L of which approximately 55% is chloride, which equates to 19,250 mg chloride/L. For this reason, brine discharges to marine environments were not evaluated.

Table 6. Long-term freshwater CWQG for the chloride ion resulting from the SSD Method.

	Concentration
SSD 5th percentile	**120 mg Cl^-/L**
SSD 5th percentile, 90% LFL (5%)	90 mg Cl-/L
SSD 5th percentile, 90% UFL (95%)	150 mg Cl^-/L

Guidance on the Use of Guidelines: These guidelines for the chloride ion are only intended to protect against direct toxic effects of chloride, based on studies using NaCl and $CaCl_2$ salts. The guideline should be used as a screening and management tool to ensure that chloride does not lead to the degradation of the aquatic environment. Further guidance on the application of these guidelines is provided in the scientific criteria document (CCME 2011).

The short-term benchmark concentration and long-term CWQG for chloride are set to provide protection for short- and long-term exposure periods, respectively. They are based on generic environmental fate and behaviour and toxicity data. The long-term water quality guideline is a conservative value below which all forms of aquatic life, during all life stages and in all Canadian aquatic systems, should be protected – with one exception. As noted earlier, the CWQG may not be protective of the early (glochidia) life-stage certain species of COSEWIC endangered and special concern freshwater mussels (discussion with provincial regulators should occur if there is a need to develop more protective site specific values). Because the guideline is not corrected for any toxicity modifying factors (e.g. hardness), it is a generic value that does not take into account any site-specific factors. Moreover, since the guideline is mostly based on toxicity tests using naïve (i.e., non-tolerant) laboratory organisms, the guideline may be over-protective for areas with a naturally-elevated concentration of chloride and associated adapted ecological community (CCME 2007). Thus, if an exceedence of the guideline is observed (due to anthropogenically-enriched water or because of elevated natural background concentrations), it does not necessarily suggest that toxic effects will be observed, but rather indicates the need to determine whether or not there is a potential for adverse environmental effects. In some situations, such as where an exceedence is observed, it may be necessary or advantageous to derive a site-specific guideline that takes into account local conditions (water chemistry, natural background concentration, genetically-adapted organisms, community structure) (CCME 2007). CCME has outlined several procedures to modify the national water quality guidelines to site-specific water quality guidelines or objectives to account for unique conditions and/or requirements at the site under investigation (CCME 1991; CCME 2003; Intrinsik 2010).

Fiducial limits (FLs) are reported here (Table 6) along with the 5th percentile or guideline value, and are similar to confidence intervals. FLs help assess the fit of the selected curve or model to the dataset. As the number of data points plotted on an SSD increases, the fit of FLs should be tighter. FLs can also be used to help interpret monitoring data, particularly if the guideline and method detection limit are close. Only the 5th percentile is used as the guideline.

In general, Canadian Water Quality Guidelines (CWQG) are numerical concentrations or narrative statements that are recommended as levels that should result in negligible risk of adverse effects to aquatic biota. As recommendations, the CWQGs are not legally enforceable limits, though they may form the scientific basis for legislation, regulation and/or management at the provincial, territorial, or municipal level. CWQGs may also be used as benchmarks or targets in the assessment and remediation of contaminated sites, as tools to evaluate the effectiveness of point-source controls, or as “alert levels” to identify potential risks.

CWQG values are calculated such that they protect the most sensitive life stage of the most sensitive aquatic life species over the long term. Hence, concentrations of a parameter that are less than the applicable CWQG are not expected to cause any adverse effect on aquatic life. Concentrations that exceed the CWQGs, however, do not necessarily imply that aquatic biota will be adversely affected, or that the water body is impaired; the concentration at which such effects occur may differ depending on site-specific conditions. Where the CWQGs are exceeded, professional advice should be sought in interpreting such results. As with other CWQGs, the guidelines for chloride are intended to be applied towards concentrations in ambient surface waters, rather than immediately adjacent to point sources such as municipal or industrial effluent outfalls. Various jurisdictions provide guidance on determining the limits of mixing zones when sampling downstream from a point source (see, for example, BC MELP 1986 and MEQ 1991), though Environment Canada and CCME do not necessarily endorse these methods.

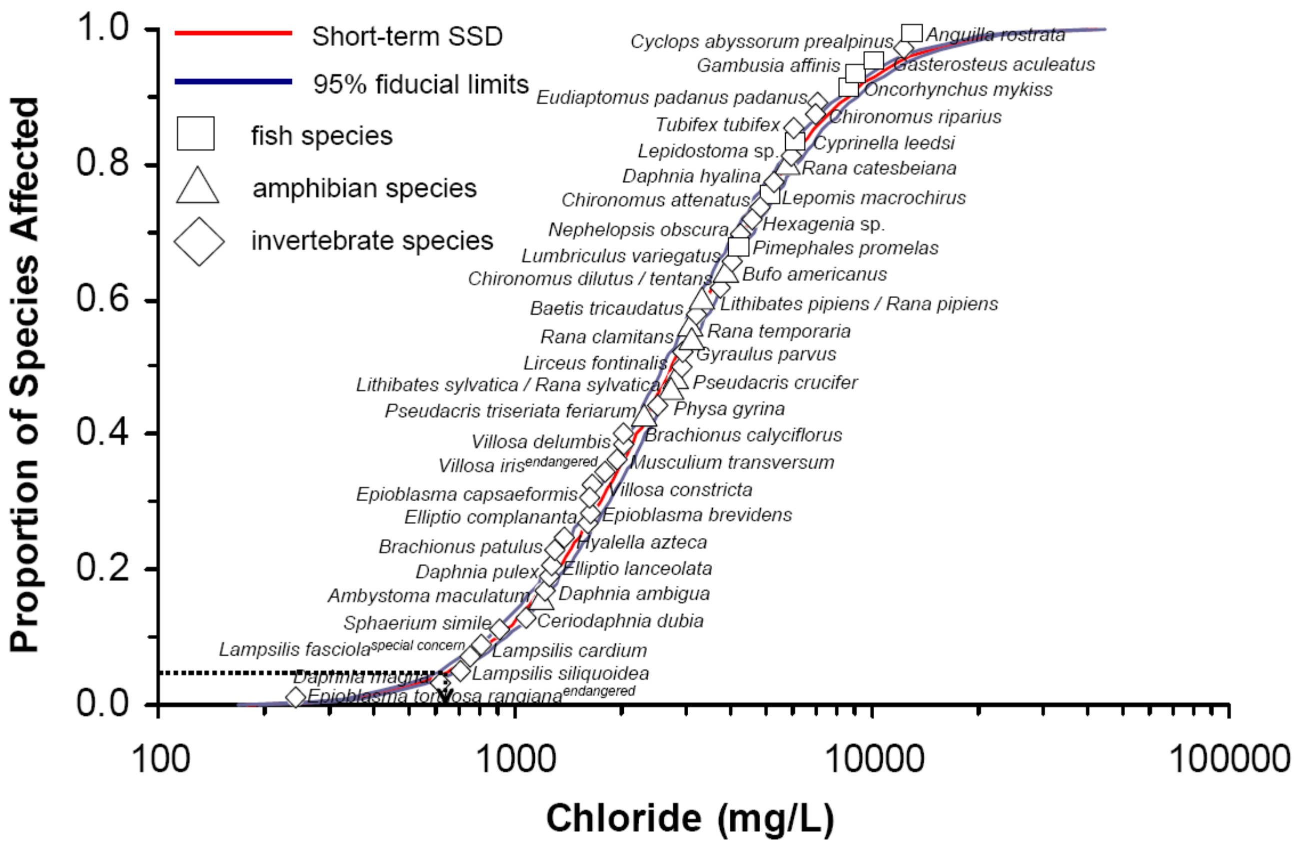

Figure 1. SSD of short-term L/EC_{50} toxicity data for the chloride ion in freshwater derived by fitting the Normal model to the logarithm of acceptable toxicity data for 51 aquatic species versus Hazen plotting position (proportion of species affected). The arrow at the bottom of the graph denotes the 5th percentile and the corresponding short-term benchmark concentration value.

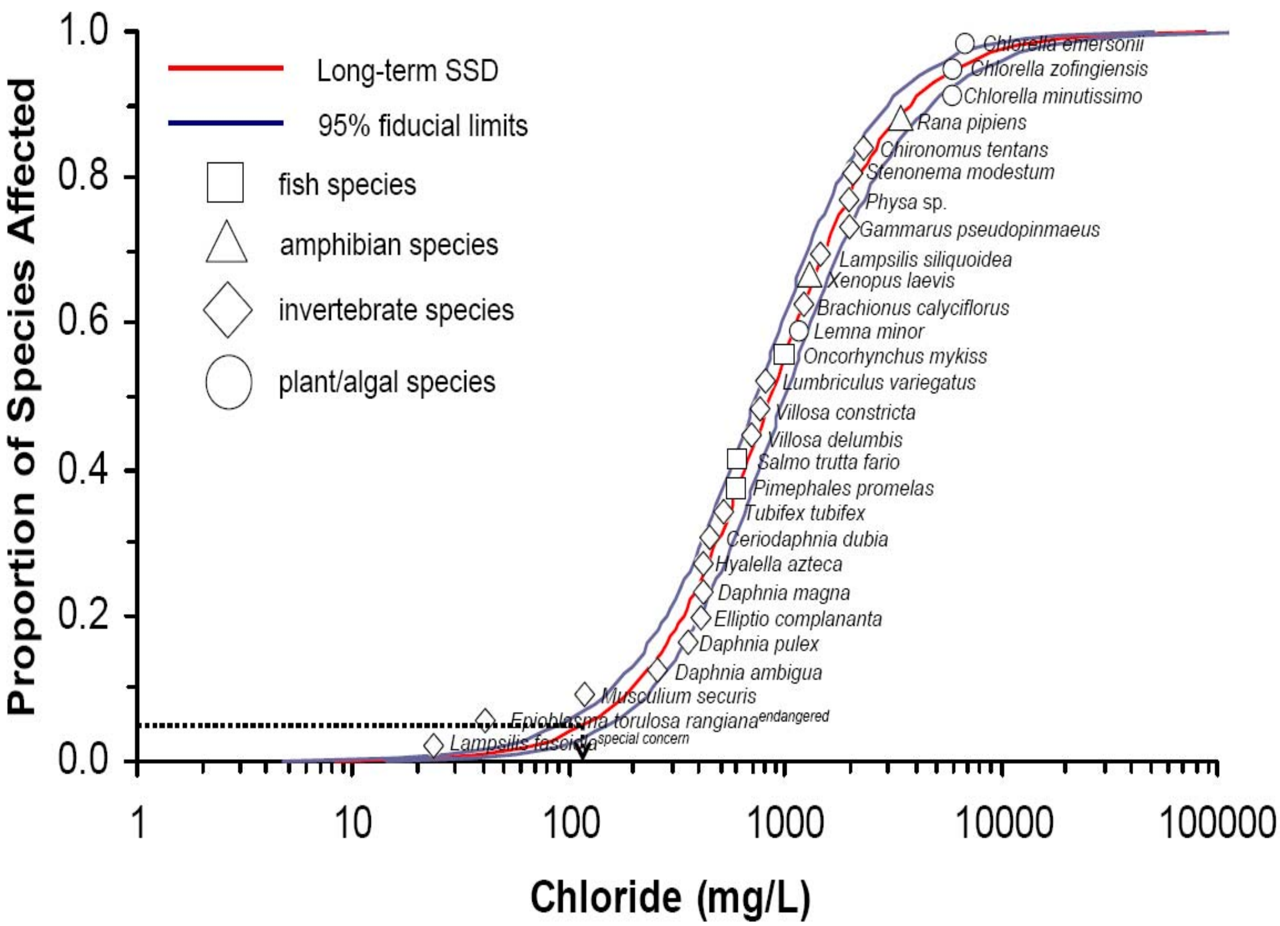

Figure 2. SSD of long-term no- and low-effect endpoint toxicity data for the chloride ion in freshwater (where mussels are present) derived by fitting the Logistic model to the logarithm of acceptable data for 28 aquatic species versus Hazen plotting position (proportion of species affected). The arrow at the bottom of the graph denotes the 5th percentile and the corresponding long-term Canadian Water Quality Guideline value.

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