II. EXECUTIVE SUMMARY

The Canadian Council of Ministers of the Environment (CCME, 2011) provided an updated Water Quality Guideline (WQG) for chloride (from 230 to 120 mg/L for the long-term exposure), applicable to freshwater aquatic life species. In the 2011 derivation, the CCME also identified water hardness as an important factor modifying the toxicity of chloride to aquatic life. As a result of limitations with the long-term dataset, a hardness-derived guideline was not established in 2011. Long-term hardness-toxicity data were either not available or did not meet the minimum data requirements for hardness-adjusted water quality guidelines at the time based on the methods of Stephen (1985).

Due to existing data limitations, the Petroleum Technology Alliance Canada (PTAC) commissioned a multi-year study, working with a third party consulting group Equilibrium Environmental Inc. (EEI) and associated research laboratories in Canada (Nautilus Environmental) and the United States (University of Georgia, Research Foundation Inc., Warnell School of Forestry and Natural Resources; Wisconsin State Laboratory of Hygiene, Environmental Health Division), in order to generate additional toxicity information for species sensitive to chloride toxicity, and data analysis on the topics described above, with a focus on water hardness.

The objectives of the present study were to:

1. identify relevant new data that has been published on chloride toxicity to aquatic life (since the CCME (2011) water quality guideline) and assess whether these data are of sufficient quality to be incorporated into a water quality guideline update;
2. summarize PTAC sponsored toxicity testing work that has been conducted from 2015 to 2019 on hardness influences towards chloride toxicity in algae, amphibians, fish, mussels, and aquatic insects (sensitive species from *Ephemenoptera*, *Plecoptera*, and *Tricoptera* (EPT) orders were selected);
3. provide a re-assessment of chloride water quality guidelines, post CCME (2011) analysis, given available new toxicology information;
4. provide an assessment of hardness influences on chloride toxicity and determine how, and to what extent, this may quantitatively affect a chloride water quality guideline; and,
5. summarize recent information on aspects of multi-ion toxicity.

An aquatic toxicological database for chloride was established using data from 167 long-term exposure studies, and 120 of them were considered acceptable. From these 88 studies, 21 represented the newest (2012-2019) additions to the CCME (2011) dataset. Besides effect concentrations, toxicity endpoints, and exposure durations, other experimental variables included: information on other ions in solution (water hardness, major ion concentrations), organism data (taxonomic, life history, geographic distribution), and environmental conditions (temperature, pH, dissolved oxygen, and light exposure).

The first task scope was to incorporate newly published information, and data from the PTAC sponsored toxicity testing work, excluding the influence of hardness, into the WQG derivation process

and determine whether the resulting WQG differed from the previously derived CCME (2011) WQG derived from a Species Sensitivity Distribution (SSD) approach and toxicity data for NaCl. The CCME (2011) dataset included the endpoints for 28 species. The current dataset includes the endpoints for 35 species, and it was evaluated for the best fit cumulative distribution function. In both derivations (CCME and herein), the Logistic model was found to best fit the data. The chloride long-term WQGs were based on CCME protocols for Type A (statistical - SSD derivation) data (CCME, 2007) and utilized endpoints for NaCl as chloride salt found to satisfy the requirements for Type A analysis.

The guideline derived from the unadjusted long-term SSD was 125 mg/L, which is 5 mg/L higher (4% relative percent difference) than the 120 mg/L value established previously by the CCME (2011). The differences may be due in part to the addition of new toxicological information to the dataset and/or minor differences in curve fitting to the data using the Logistic model.

To derive the long-term hardness-adjusted guidelines, chloride toxicity values from different studies were compared by converting them to a standardized hardness value. The standard hardness of 50 mg/L ($CaCO_3$ equivalents) was used, as has been done in previous guideline derivations for cadmium (CCME, 2014, US EPA, 2001). The hardness-toxicity relationships were assessed with statistical analysis. Individual hardness-toxicity slopes were estimated for organisms where effect concentrations were available over a wide range of water hardness concentrations and similar experimental conditions. The pooled slope was analyzed to determine an overall coefficient of the hardness-toxicity relationship within the long-term dataset.

For some species, such as the water flea *Daphnia magna,* inverse hardness-toxicity relationships were established but could not be included in pooled slope calculations since hardness-toxicity relationships were not investigated over a wide enough range of hardness (*sensu* Stephen *et al.,* 1985) or came from the different laboratories with different experimental conditions. The pooling of data from different laboratories for a particular species, where experiments were conducted at different hardness levels, may support an amelioration of chloride toxicity with increasing hardness (such is the case for *Daphnia magna*), however the potential influence of different experimental conditions between labs can not be quantified and the pooling of data from multiple studies/labs for one species was considered to be of insufficient rigor for including in the quantitative analysis of hardness and chloride toxicity.

The long-term hardness-adjusted (50 mg $CaCO_3$/L) chloride toxicity dataset was then assessed using the SSD, and the best fit cumulative distribution function was utilized for guideline derivation. The resulting SSD was built based on the data from 27 species modeled with a logistic function (8 out of 35 endpoints from an unadjusted SSD in a first step, had no reported hardness, and therefore, were not included in the hardness-adjusted model). The derived long-term WQG are presented as an exponential (natural log) function, which can be used to calculate a chloride WQG at a particular water hardness level. The guideline equation is shown below, along with the results chloride concentrations at various water hardness concentrations.

$$\textbf{Long-term WQG} = \exp^{[\,0.38\,(\ln(\text{hardness})) + 3.18]}$$

Notes:

Hardness measured as mg/L as $CaCO_3$;
The long-term hardness equation is applicable from 5 to 350 mg $CaCO_3$ /L. For the hardness from 0 to 5 mg $CaCO_3$/L, the lower limit of 44 mg/L is applied. For the hardness >350 mg $CaCO_3$/L, the upper limit of 222 mg/L is applied.

Guidelines for the Protection of Fresh Water Aquatic Life at Various Hardness Values

Water hardness (mg/L as $CaCO_3$)	Long-term exposure (mg Cl^-/L)
Lower limit (0-5) *	*44*
Soft (50)	*106*
Moderately hard (150)	*161*
Hard (300)	*209*
Upper limit (350 and greater) **	*222*

Notes: *the long-term hardness equation can be used for direct calculation from 5 to 350 mg $CaCO_3$ /L.*
** 44 mg Cl-/L is the lower limit long-term WQG value that applies to waters with 5 mg $CaCO_3$/L and less.*
*** 222 mg Cl-/L is the upper limit long-term WQG value that applies to waters of 350 mg $CaCO_3$/L and greater.*

To ensure the resulting chloride guideline provides an adequate protection for $MgCl_2$ and $CaCl_2$ toxicity, given the toxicological dataset was primarily NaCl based, an analysis of protectiveness was conducted. Acceptable toxicity values, non-adjusted for hardness, were plotted against the hardness-adjusted guideline. No $MgCl_2$ or $CaCl_2$ toxicity values fell below the guidelines, indicating the hardness adjusted WQG derived from the NaCl toxicological dataset was also protective of aquatic life exposures to other chloride salts such as $MgCl_2$ and $CaCl_2$.

Comparative toxicity from the major salt ions, present in all fresh waters, such as Na+, K+, Ca^2, Mg^2, Cl-, SO_4^2-, and HCO_3^-, was evaluated additionally to the current guideline development. PTAC-funded studies by UGARF (2016b) and WSLH (2017) compared the long-term toxicity of the major salts to the freshwater mussel *Lampsilis siliquoidea*, and to the microalgae *Raphidocelis subcapitata*. Generally, for the freshwater mussels the salt-based toxicity values and the anion-based toxicity values had the similar order as observed in the literature review and as mentioned in CCME (2011), decreasing from KCl (the most toxic salt) to NaCl (the least toxic salt). For the microalgae, $CaSO_4$ was observed as the most toxic salt, whereas the least toxic effect was observed in $CaCl_2$ or NaCl.