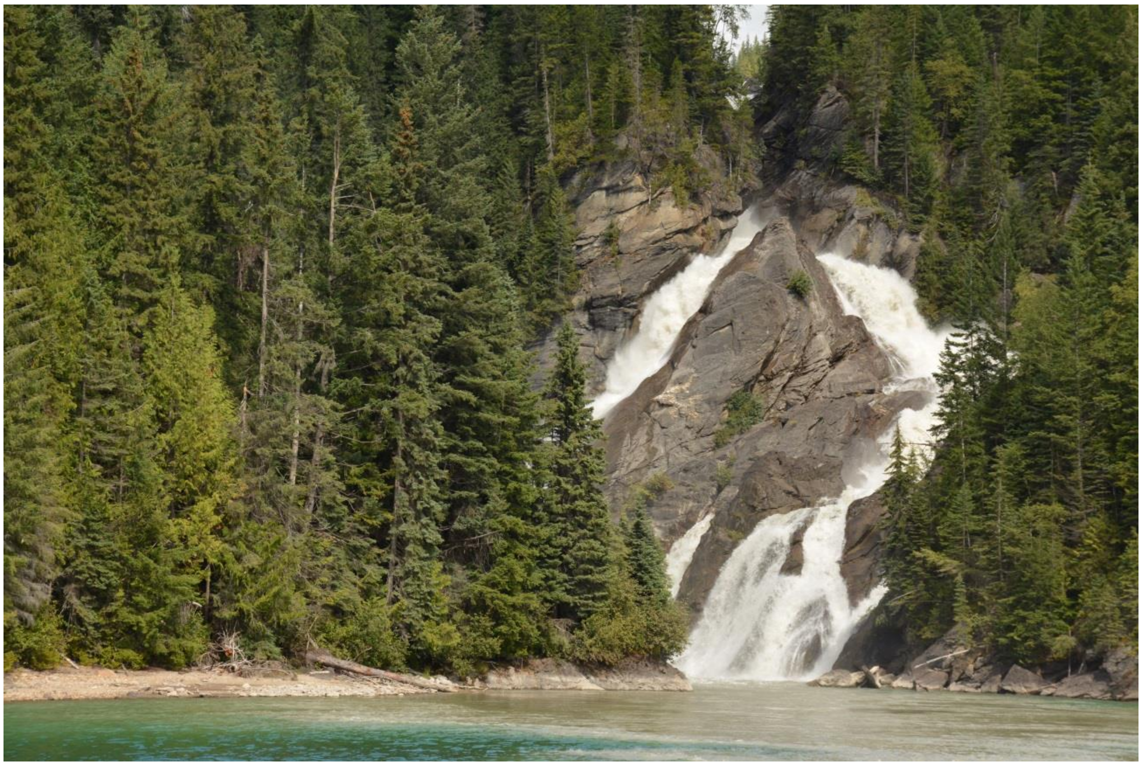
WATER QUALITY GUIDELINE SERIES

Copper Water Quality Guideline for the Protection of Freshwater Aquatic Life
User's Guide

Ministry of Environment and Climate Change Strategy

Water Protection & Sustainability Branch



No.WQG-03-3

The Water Quality Guideline Series is a collection of British Columbia (B.C.) Ministry of Environment and Climate Change Strategy water quality guidelines. Water quality guidelines are developed to protect a variety of water values and usages: aquatic life, drinking water sources, recreation, livestock, irrigation, and wildlife. The Water Quality Guideline Series focuses on publishing water quality guideline technical reports and guideline summaries using the best available science to aid in the management of B.C.'s water resources. For additional information on B.C.'s approved water quality parameter specific guidelines, visit: Approved Water Quality Guidelines.

ISBN: 978-1-988314-04-4

Document citation:

B.C. Ministry of Environment and Climate Change Strategy. 2019. Copper Water Quality Guideline for Protection of Freshwater Aquatic Life-User's Guide. Water Quality Guideline Series, WQG-03-2. Prov. B.C., Victoria B.C.

Cover Photograph:
Location: Quesnel Lake, B.C.

CONTENTS

LIST OF TABLES

WHAT IS A WATER QUALITY GUIDELINE?

The British Columbia (B.C.) Ministry of Environment and Climate Change Strategy (ENV) 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 B.C. WQGs do not have any direct legal standing but are used to provide a basis for evaluating the quality of water, sediment, and aquatic biota in environmental impact assessments, and to inform resource management decisions.

The development of WQGs for aquatic life is based on the principle that guideline values are protective of all forms of aquatic life and all aquatic life stages over indefinite exposure (ENV, 2012). Long-term chronic WQGs are intended to protect the most sensitive species and life stage against sub-lethal and lethal effects for indefinite exposures. Short-term acute WQGs are intended to protect the most sensitive species and life stage against severe effects such as lethality, over a defined short-term exposure period (e.g., 96 hours) and can be used to assess risks associated with infrequent exposure events such as spills. For some substances, both a long-term chronic (30-day average) and a short-term acute guideline are recommended as provincial WQGs, provided sufficient toxicological data are available. To meet a WQG, both of its components (i.e., chronic long-term and acute short-term) must be met. However, an exceedance of the WQGs does not imply that unacceptable risks are present, but that the potential for adverse effects may be increased and additional investigation and monitoring may be warranted.

This User's Guide provides an overview of B.C.'s ambient WQGs for copper (Cu) for the protection of aquatic life and provides instruction on how this WQG should be used. A full technical description of the toxicity data set and derivation procedure can be found in the accompanying document: Copper Water Quality Guideline for the Protection of Freshwater Aquatic Life-Technical Report.[1]

WHY IS COPPER A CONCERN FOR AQUATIC LIFE?

Copper is an essential metal for all organisms; however, elevated ambient concentrations can negatively affect aquatic life. Excess Cu can be absorbed by organisms via different uptake pathways (e.g., gill). Elevated Cu in tissues can overwhelm homeostatic systems which may result in adverse effects. Exposure to high Cu concentrations can inhibit photosynthesis in algae and macrophytes resulting in a reduction in growth (e.g., Küpper et al., 2003). Acute exposure to Cu can cause mortality and chronic exposure can affect growth, reproduction, and survival of fish, amphibians and invertebrates (e.g., Brix et al., 2011; Grosell, 2012; Leduc et al., 2016). Furthermore, exposure to Cu can impair the sense of smell in fish, which is vital for several species to mediate biological processes, such as finding food and detecting predators (Vilhunen, 2006; Døving and Lastein, 2009).

COPPER IN THE ENVIRONMENT

Copper is a naturally occurring element and is released to aquatic environment through the natural weathering and chemical decomposition of rocks and soils (Georgopoulos et al., 2001). However, anthropogenic activities such as smelting and refining, manufacturing, application of pesticides, and domestic wastewater treatment may increase Cu concentrations significantly (Reiley, 2007). In fact, Cu is one of the most ubiquitous environmental contaminants worldwide due to the range of anthropogenic activities that release it to the environment. In B.C., Cu has long been a metal of concern because of mining in combination with other anthropogenic sources.

[1] Available at: https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc_copper_wqg_aquatic_life_technical_report.pdf

Ambient Cu concentrations in freshwater aquatic ecosystems vary across the province depending upon the underlying geology. The median dissolved Cu concentration across the province is 0.61 µg/L and the 90th percentile is 2.5 µg/L. Total Cu concentrations are slightly higher, with a median of 0.68 µg/L and 90th percentile of 3.0 µg/L. Regionally, Vancouver Island and the Cariboo have higher total Cu values compared with other regions (ENV, 2019a).

In natural waters, the majority of Cu binds to suspended particles, eventually settling in the sediments. Most Cu is adsorbed to particulate matter within the first few hours; however, a fraction of Cu will always remain in the dissolved form (Georgopoulos et al., 2001). Copper is generally associated with mineral or organic materials in fine sediments (ATSDR, 2004). Sediment affinity is related to the composition of the sediment and water chemistry conditions. Changes in water chemistry (e.g., changes in pH or dissolved oxygen) or physical changes (e.g., lake turnovers) can increase or decrease the ratio of dissolved to particulate Cu. For example, the ability of sediments to retain Cu is lower in acidic conditions (Georgopoulos et al., 2001)

WHAT FORMS OF COPPER ARE TOXIC TO AQUATIC LIFE?

Ambient Cu concentrations in freshwater systems can be measured as either total or dissolved Cu. Dissolved Cu is defined as the fraction that passes through a 0.45 µm filter, while total Cu is both the dissolved fraction and any Cu associated with particulates found in an unfiltered water sample (e.g., suspended sediments). Copper associated with particulates is not bioavailable and therefore the dissolved fraction of Cu provides a more accurate estimate of Cu toxicity (e.g., Erickson, et al., 1996).

Not all dissolved forms of Cu can be taken up by the biochemical receptors of an organism and cause toxic effects. Free ionic Cu (Cu^{2+}) is the main form that is toxic to aquatic biota (Howarth and Sprague, 1978; Grosell, 2012). Some hydroxyl species of Cu (e.g., $CuOH^-$) can be toxic, however, many other species, such as copper carbonates (e.g. Cu_2CO_3), are generally less bioavailable to aquatic organisms and consequently less toxic (Howarth and Sprague, 1978; Eisler, 1998).

HOW DO WATER CHEMISTRY VARIABLES AFFECT THE TOXICITY OF COPPER?

The specific water chemistry conditions of a water body determine the proportions of the different forms of dissolved Cu and therefore the toxicity of dissolved Cu. The major factors influencing Cu toxicity are dissolved organic carbon (DOC), hardness, and pH: DOC binds to the inorganic forms of Cu in water, forming organic compounds that are not bioavailable to aquatic organisms (Erickson et al., 1996); water hardness can ameliorate Cu toxicity through the competition between Ca^{2+} and Cu^{2+}, reducing the biological uptake of Cu^{2+} in aquatic animals (Grosell, 2012); and at elevated pH, the concentration of Cu^{2+} drops dramatically and other less toxic forms become abundant. Other water chemistry factors such as temperature also have an effect but to a lesser degree.

WHAT IS THE BIOTIC LIGAND MODEL (BLM)?

The Biotic Ligand Model (BLM) is a series of linked equations that predicts the toxicity of dissolved Cu under specific water chemistry conditions. The model has four components: 1) it estimates the different chemical forms of dissolved Cu; 2) it estimates the capacity of organic and inorganic compounds to bind with dissolved copper; 3) it estimates the ameliorating action of competing cations (e.g. Ca^+) for active sites on a biological ligand (e.g. gills); and 4) it combines these three estimates to predict the accumulation of Cu at the biological ligand and compares this to a critical toxicity threshold (Paquin et al., 2002).

The relationship between Cu accumulation and toxicity has not been determined for all aquatic biota, therefore, the original BLM was based largely on the lethal accumulation in fathead minnows (*Pimephales promelas*) (Playle et al., 1993) and rainbow trout (*Oncorhynchus mykiss*) (MacRae et al., 1999). However, the BLM has been shown to be a powerful tool for predicting toxicity for several fish species and invertebrates (e.g., Santore et al., 2001; Ryan et al., 2009; Villavicencio et al., 2011). Recently the BLM was recalibrated using chronic toxicity data collected for fish and invertebrates, which predicted both chronic and acute toxicity for several fish and invertebrate species (Santore et al., 2019a). In addition, another model was created for plants to account for the different mechanisms of uptake and toxicity. This new plant model is capable of predicting toxicity for both algae and macrophytes in different water chemistry (Santore et al., 2019b). For each model, the predicted toxicity thresholds were compared to experimentally collected toxicity data in several studies and the results were congruent (Santore et al., 2019a-b).

The ability of BLM to predict toxicity in various water chemistry conditions can be used to calculate site-specific WQGs. However, given the complexity of the model, specialized software is needed to conduct the calculations. The BLM is currently used to calculate the USEPA Cu Water Quality Criteria (USEPA, 2007).

HOW WAS THIS WATER QUALITY GUIDELINE DEVELOPED?

The WQGs for Cu were developed following the ENV WQG derivation protocol (ENV, 2012) and based on a search of the current scientific literature on Cu toxicity to freshwater aquatic organisms. Given the large number of species with Cu toxicity data, it was possible to tailor the database to include only B.C. species and still meet the minimum data requirements. Selected studies were further evaluated to ensure that only scientifically sound and high-quality studies were used in the WQG derivation (ENV, 2012). Information on the test species, test conditions, experimental design, chemical and physical properties of the test water, statistical analyses, and negative control performance were reviewed. Studies were then classified as primary, secondary or unacceptable based on the criteria specified in ENV WQG derivation protocol.

More than 319 studies were reviewed for the preparation of this guideline. Of these, 59 studies were classified as primary data sources, 64 as secondary, and 196 were classified as unacceptable and, therefore, were not used in derivation of the Cu WQG (Appendix 1[1]). From the 59 primary studies, 498 acute and 254 chronic data points were selected, and from the 64 secondary studies, 232 acute and 63 chronic data points were selected. Primary and secondary data were found on a total of 51 B.C. species, including 4 algae, 1 macrophyte, 22 invertebrate, 19 fish and 5 amphibian species.

The BC BLM[2] software was developed to calculate long-term chronic and short-term acute Cu WQGs for the protection of aquatic life in B.C. The software uses BLM to normalize the toxicity databases to the specified water chemistry and then determines the lowest effect concentration (i.e., most sensitive species) following ENV WQG derivation protocol (ENV, 2012). Depending on the water chemistry, either great pond snail (*Lymnaea stagnalis*) or duckweed (*lemna minor*) are the most sensitive organisms to chronic Cu exposure. White sturgeon (*Acipenser transmontanus*) is the most sensitive species to acute Cu exposure.

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[1] Available at: https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc_copper_wqg_appendix1.xls

[2] Available at: https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc_blm_setup.exe

WQGs are derived from the data reported in laboratory-based toxicity tests of single contaminants on a limited number of aquatic species. The extrapolation of these data to the biota living in a natural aquatic ecosystem in which they are exposed to mixtures of substances indefinitely comes with several sources of uncertainty, including: inter and intra-species variation; laboratory to field extrapolation; and modelling error. Therefore, in developing WQGs, it is essential to apply an assessment factor to the lowest effect concentration to account for these uncertainties.

The appropriate uncertainty factor to be applied is decided on a case-by-case basis and is based on data quality and quantity, toxicity of the contaminant, severity of toxic effects, and bioaccumulation potential. Scientific judgement is used to maintain some flexibility in the derivation process. Considering the large number of data points, sensitivity of endpoints and low potential of Cu for bioaccumulation, the minimum assessment factor of 2 was applied to derive both the short-term and long-term WQGs.

WHAT ARE THE GUIDELINES FOR COPPER AND HOW SHOULD THEY BE APPLIED?

The Cu WQGs are for dissolved Cu in ambient waters. This is in contrast to the previous 1987 B.C. WQG that was for total copper. The change to dissolved Cu was done for several reasons:

- dissolved Cu is the more bioavailable, and therefore ecologically relevant form;
- published toxicity tests are mostly based on the dissolved concentrations of Cu; and
- concentrations of dissolved Cu are less variable than total Cu in B.C. waters due to the association between total Cu, water flow, and suspended sediment concentrations.

Copper WQGs are dependent on the specific chemistry of the water body and can only be calculated using the BC BLM software. The BC BLM User's Manual [1] provides clear instruction of how the software should be used to calculate chronic and acute WQGs (ENV, 2019b). Calculating a WQG using the full BC BLM requires 11 water chemistry parameters. To overcome the fact these parameters are not always routinely measured, a simplified version of the BC BLM was included in the software and requires only four water chemistry parameters which cannot be estimated: temperature, DOC, pH, and hardness. The remaining seven parameters are estimated based on the criteria described in Cu WQGs Technical Report[2] (ENV, 2019a).

The application of the BC BLM is only recommended within the bounds of the water chemistry variables in which the toxicity predictions of the BLM models were validated (ENV, 2019a). The BC BLM automatically substitutes the minimum or maximum value for water chemistry parameters that are outside the bounds. This approach is taken since it is only within these bounds that the protectiveness of the WQGs calculated by BC BLM is proven.

As the Cu WQGs can only be determined in relation to water chemistry conditions, Cu WQG values under several water chemistry scenarios are provided below in Table 1.

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[1] Available at: https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc_blm_users_manual.pdf

[2] Available at: https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc_copper_wqg_aquatic_life_technical_report.pdf

Table 1. Examples of long-term chronic and short-term acute WQGs calculated for eight different water chemistry scenarios.

Scenario	Water Chemistry Conditions				Chronic WQG (µg/L)	Acute WQG (µg/L)
	Temperature (^{0}C)	Hardness (mg/L)	DOC (mg/L)	pH		
1	15	30	3	6.5	0.2	0.9
2	15	30	3	8	1.2	7.3
3	15	30	12.5	6.5	0.6	3.8
4	15	30	12.5	8	5.1	30.2
5	15	150	3	6.5	0.2	1.6
6	15	150	3	8	2.0	11.4
7	15	150	12.5	6.5	1.0	6.8
8	15	150	12.5	8	8.1	46.9

Like any other water quality factor, Cu concentration is variable in natural waters. Therefore, an averaging period approach is recommended, which allows Cu concentrations to fluctuate above and below the chronic WQG over the specified averaging period (e.g., 5 samples in 30 days). For each sample, the water chemistry parameters needed for the full or simplified BC BLM are required to calculate the WQG. To meet the chronic WQGs, two criteria must be met:

1. Only 20 percent of the samples (e.g., 1 in 5 samples) can exceed the chronic WQG calculated for each sample using the associated water chemistry, provided that the short-term acute WQG is never exceeded.
2. The average Cu concentration should not exceed the average chronic WQG.

In cases where less than five samples are available, each Cu concentration should be compared against the chronic long-term WQG.

Although Copper WQGs only apply to the dissolved fraction as this is the more bioavailable form, there is still the potential for toxicity due to particulate-associated Cu, especially in systems with high total to dissolved Cu ratios. Since changes in water chemistry (e.g., pH) can change the dynamics of particulate and dissolved Cu, repeated measurements of Cu are recommended for comparison with the WQG, especially in waterbodies with variable water chemistry (e.g. downstream). Additionally, sedimentation of particulate Cu can increase concentrations in sediments. Therefore, caution should be exercised in the application of Cu WQGs in waters with high particulate Cu. The B.C. Working WQGS[1] for sediments provide a basis for evaluating the toxicity of particulate-associated metals (see Table 1; ENV 2017a).

To meet Cu WQGs, both of its components (i.e., chronic long-term and acute short-term WQGs) must be met. Nonetheless, an exceedance of the WQGs presented in this document does not imply that unacceptable risks are present, but that the potential for adverse effects may be increased and additional investigation and monitoring may be warranted.

[1] Available at: https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/bc_env_working_water_quality_guidelines.pdf

Copper WQGs for the protection of marine and estuarine aquatic life[1] (3 µg/L), wildlife[2] (300 µg/L), livestock water supply[3] (300 µg/L), and irrigation water supply[4] (200 µg/L) have not been updated and the 1987 WQGs still apply. The latest source drinking WQG for Cu can be found here (ENV, 2017b[5]). No WQGs for the aesthetic or recreational use are recommended for Cu (ENV, 2017c[6]). B.C. Working WQGs for Cu provides values for sediment quality (both marine and freshwater).

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[2] Available at: https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc_copper_wqg_agriculture.pdf

[3] Available at: https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc_copper_wqg_agriculture.pdf

[4] Available at: https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc_copper_wqg_agriculture.pdf

[5] Available at: https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/drinking-water-and-recreation/source_drinking_water_quality_guidelines_bcenv.pdf

[6] Available at: https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/drinking-water-and-recreation/recreational_water_quality_guidelines_bcenv.pdf

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