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Copper Water Quality Guideline for the Protection of Freshwater Aquatic Life

Technical Report

Ministry of Environment and Climate Change Strategy

Water Protection & Sustainability Branch

BRITISH
COLUMBIA

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 watering, 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:

http://www2.gov.B.C.ca/gov/content/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-water-quality-guidelines

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

EXECUTIVE SUMMARY

The 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 direct legal standing but are used to provide a basis for evaluating the quality of water, sediment, and aquatic biota and 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). For some substances, both a long-term chronic (30-day average) and a short-term acute (maximum) 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 document provides information on the derivation of a copper (Cu) WQG for the protection of aquatic life. Copper is an essential metal for all organisms; however, elevated concentrations can negatively affect aquatic life. Exposure to Cu can inhibit photosynthesis in algae and macrophytes resulting in a reduction in growth. Acute exposure to Cu can cause mortality and chronic exposure can affect growth, reproduction and survival of fish, amphibians and invertebrates. Furthermore, exposure to Cu can impair swimming performance and reduce olfactory acuity in several fish species.

Copper has long been a metal of concern in B.C. because of mining and other anthropogenic sources. B.C.'s first Cu WQG was published in 1987 and since that time, many scientific studies have been published on the different aspects of Cu toxicity. The economic importance and high production of Cu, combined with its relatively high toxicity to aquatic organisms has made it a metal of concern for jurisdictions around the world, with updated guidelines published by the United States Environmental Protection Agency (USEPA, 2007), European Union (European Commission, 2009), and Australia and New Zealand (ANZECC, 2000a).

Copper is a naturally occurring element and background concentrations need to be considered when deriving WQGs for B.C. Ambient Cu concentrations vary across the province depending upon the underlying geology. The median dissolved Cu concentration is 0.61 µg/L and the 90th percentile is 2.5 µg/L. The median total Cu concentration is slightly higher at 0.68 µg/L with a 90th percentile of 3.0 µg/L. Vancouver Island, the Peace and the Cariboo have higher total Cu values compared to other regions.

Dissolved Cu can be found in different chemical forms depending on water chemistry. The bioavailability of Cu to the biochemical receptors of aquatic organisms is determined by its concentration in water and the chemistry of that water. The major factors influencing Cu toxicity are dissolved organic carbon (DOC), water hardness and pH. DOC binds to the toxic inorganic forms of Cu in water forming organic compounds that are not bioavailable. Calcium (Ca), a major component of water hardness, can ameliorate Cu toxicity through the competition between Ca^{2+} and Cu^{2+} (the toxic form of Cu) for biological uptake. At elevated pH, the concentration of Cu^{2+} drops dramatically and other less toxic forms become more abundant. Alkalinity also influences Cu toxicity, but to a lesser degree.

Biotic Ligand Models (BLM) incorporate metal speciation and the protective effects of competing cations to predict toxic concentrations. A Cu BLM, named BC BLM, was developed for determining Cu WQGs in B.C. Calculating a WQG using the BC BLM requires 11 essential water chemistry parameters. However, not all these water chemistry parameters are routinely measured. To overcome this issue, a "simplified" version of the BLM was incorporated in the BC BLM, which requires only four water chemistry

parameters: temperature, DOC, pH, and hardness. From these parameters, the other seven can be estimated.

The long-term chronic and short-term acute Cu WQGs for the protection of aquatic life are based on dissolved Cu and are calculated using the BC BLM[1] software. Dissolved Cu provides a better estimate of bioavailable Cu since the Cu associated with suspended particulates is generally not available for biological uptake. Total metal concentrations still provide valuable information, especially in systems with high total Cu to dissolved Cu ratios, as changes in water chemistry (e.g., pH) can change the dynamics of particulate and dissolved Cu.

The Cu toxicity database developed for this WQG meets the minimum requirements for the derivation of "full" chronic and acute WQGs. Considering the novelty of the BLM approach and the differences from how past B.C. WQGs have been developed, these Cu WQGs may be reviewed after five years, considering new data and feedback received.

As the Cu WQGs are determined in relation to water chemistry conditions, Cu WQG values under several water chemistry scenarios are provided below in Table E.1. To calculate the Cu WQG for a particular scenario, visit the BC BLM software.

Table E.1. 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 (°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

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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_setup.exe

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LIST OF ABBREVIATIONS

AEP: Alberta Environment and Parks

Ag: Silver

Al: Aluminum

ANZECC: Australia and New Zealand Environment and Conservation Council

ASTM: American Society for Testing and Materials

ATSDR: Agency for Toxic Substances and Disease Registry

BAF: Bioaccumulation Factor

B.C.: British Columbia

BCF: Bioconcentration Factor

BLM: Biotic Ligand Model

Ca: Calcium

CABIN: Canadian Aquatic Biomonitoring Network

CCC: Criteria Continuous Concentration

CCME: Canadian Council of Ministers of the Environment

Cd: Cadmium

CMC: Criteria Maximum Concentration

Cu: Copper

DL: Detection Limit

DOC: Dissolved Organic Carbon

DPH: Days Post Hatch

EC: Effect Concentration

ECCC: Environment and Climate Change Canada

EMS: Environmental Management System

ENV: British Columbia Ministry of Environment and Climate Change Strategy

EOG: Electro-olfactography

EQS: Environmental Quality Standards

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

Fe: Iron

IC: Inhibitory Concentration

LC: Lethal Concentration

LOEC: Lowest Observed Effect Concentration

MATC: Maximum Allowable Toxicant Concentration

MDL: Method Detection Limit

Mg: Magnesium

Na: Sodium

Ni: Nickel

NOEC: No Observed Effect Concentration

NOM: Natural Organic Matter

Pb: Lead

PQL: Practical Quantitation Limit

TGV: Trigger Value

TOC: Total Organic Carbon

USEPA: United States Environmental Protection Agency

WQC: Water Quality Criteria

WQG: Water Quality Guideline

Zn: Zinc

DEFINITIONS

Lowest Observed Effect Concentration (LOEC): The lowest tested concentration of a substance that has been reported to have statistically significant harmful effects on organisms tested.

No Observed Effect Concentration (NOEC): The highest tested concentration of a substance that has been reported to have no statistically significant harmful effects on organisms tested.

EC_X: The concentration affecting X percent of the population within a certain amount of time.

IC_X: The concentration causing an X% inhibition in exposed individuals within a certain amount of time.

LC_X: The concentration which causes X% mortality in the exposed population within a certain amount of time.

Uncertainty Factor: Mathematical adjustments to guideline values to account for incomplete knowledge.

1. **INTRODUCTION**

The 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 direct legal standing but are used to provide a basis for the evaluation of data on water, sediment, and biota for water quality and environmental impact assessments.

The approach to develop WQGs for aquatic life is based on the guiding principle that guideline values are protective of all forms of aquatic life and all aquatic life stages over indefinite exposure (ENV, 2012). For some substances both a long-term chronic (30-day average) and a short-term acute (maximum) 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.

Water quality guidelines are based on toxicological studies conducted under laboratory conditions. There are several uncertainties associated with applying WQGs in field conditions including:

- Laboratory to field differences in conditions;
- Single contaminant tests in laboratories vs exposure to multiple contaminants in the field (additive, synergistic, antagonistic effects);
- Intra and inter-specific differences (laboratory studies are conducted on a limited number of individuals within a species and a limited number of species which may or may not include the most sensitive species);
- Indirect effects (e.g., behavioral responses, food web dynamics);
- Partial-life cycle studies (many toxicity studies are only conducted on partial life-cycles and may not include the most sensitive life stage);
- Delayed effects (effects may not occur within the life stage tested, or may occur across generations); and
- Cumulative effects (compared with laboratory studies, organisms in the field are faced with various stressors such as habitat loss and climate change).

Given the uncertainties, WQGs can be considered as predicted no effect concentrations. However, it is an estimated value based on laboratory studies. Therefor, ongoing ecological monitoring is generally recommended to ensure the WQG is protective under field conditions.

Copper is an essential metal for all organisms. However, elevated concentrations can negatively affect aquatic organisms. Exposure to Cu can inhibit photosynthesis in algae and macrophytes resulting in a reduction to 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 swimming performance and reduce olfactory acuity in several fish species (Grosell, 2012).

Copper has long been a metal of concern in B.C. because of mining and other anthropogenic sources. B.C.'s first Cu WQG was published in 1987 (ENV, 1987). Since that time, many scientific studies have been published on the different aspects of Cu toxicity. The economic importance and high production of Cu combined with its relatively high toxicity to aquatic organisms has made it a metal of concern for jurisdictions around the world with updated guidelines published by the United States Environmental

Protection Agency (USEPA, 2007), European Union (European Commission, 2009) and Australia and New Zealand (ANZECC, 2000a).

This report provides the scientific rationale for B.C.'s updated Cu WQG, including a review of the current scientific literature related to the toxicity of Cu to freshwater aquatic life. Key studies were evaluated for their applicability in deriving long-term chronic and short-term acute WQGs. The updated Cu WQG is calculated using a Biotic Ligand Model (BLM), which incorporates specific water chemistry data using specialized software. The BC BLM[1] software and BC BLM User's Manual[2] accompany this technical report (ENV, 2019).

2.   PHYSICAL AND CHEMICAL PROPERTIES OF COPPER

Copper is a soft, reddish metal with a molar mass of 63.54 g and a melting point of 1,083.4° C (Eisler, 1998). While Cu has four oxidation states (Cu^0, Cu^{+1}, Cu^{2+} and Cu^{3+}), Cu^{2+} (cupric) is the most common in water and forms various soluble compounds (ATSDR, 2004). In natural aquatic environments, Cu can be found in many forms, including free ions, copper hydroxides, carbonate complexes, and many organic complexes (Meador, 1991). Several factors control the abundance of the different Cu forms, including pH, the abundance of cations (e.g., Na^+ and Ca^{2+}) and anions (e.g., carbonates and phosphates), and the concentration of organic matter (Meador, 1991). The major chemical complexes of Cu in fresh water are copper carbonates ($CuHCO_3^+$, $CuCO_3$ and $Cu(CO_3)_2^{-2}$) and copper hydroxychloride ($Cu(OH)Cl$), while copper hydroxide ($Cu(OH)_2$) and copper hydroxychloride are the dominant complexes in seawater (Eisler, 1998).

3.   INDUSTRIAL AND ECONOMICAL IMPORTANCE OF COPPER

Copper was probably the first metal used by humans, with the earliest evidence of human usage dating back about 8,000 years (Radetzki, 2009) and smelting about 4,500 years ago (Eisler, 1998). Due to its unique chemical and physical properties, Cu still has vast applications including building construction, electrical equipment, transportation equipment, plumbing, telecommunications, power utilities, in-plant equipment, and air conditioning (Eisler, 1998; ATSDR 2004).

Cu is produced around the world, with more than 16.8 million tonnes of Cu mined globally in 2014 with an approximate value of $129.6 billion (US) (USGS, 2014). Canada has large Cu reserves and is one of the top producers in the world (The Mining Association of Canada, 2014). In 2013, mining activities produced 557,000 tonnes of Cu in Canada with a total value of $4.6 billion (US) (Mining Association of Canada, 2014; USGS, 2014). Canada has an estimated 10 million tonnes of Cu in reserve and about 64% of this reserve is in B.C. (Natural Resources Canada, 2014).

4.   ENVIRONMENTAL FATE AND TRANSPORT OF COPPER

Copper is the 29th most abundant element in the Earth's crust and occurs in both mineralized forms and as an uncombined metal (Turekian and Wedepohl, 1961; Eisler, 1998). While Cu is naturally present in soil, water, and the atmosphere, anthropogenic activities can increase its concentration. 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, including smelting and refining, manufacturing, and

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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_setup.exe

[2] 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

domestic wastewater treatment (Reiley, 2007). For example, while the natural concentration of Cu in freshwater aquatic ecosystems ranges from 0.2 to 30 µg/L, anthropogenic activities have been reported to raise Cu concentrations up to 200 mg/L in waterbodies close to mine sites (USEPA, 2007; Grosell, 2012).

The global average natural Cu concentration in soil is 50 mg/kg (ATSDR, 2004). However, anthropogenic activities such as application of pesticides and crop preservatives increase concentrations, with most of the deposited Cu being absorbed by the top layer of soil (Nriagu and Pacnya, 1988; ATSDR, 2004). Although the majority of added Cu will stay bound to soil, some will eventually be washed out to the hydrosphere (Georgopoulos et al., 2001). The physical, chemical and biological properties of soil determine the absorption and movement dynamics of Cu. For example, basic soils with high humic content retain Cu, whereas acidic sandy soils leach Cu (ATSDR, 2004)

Copper is emitted to the atmosphere from natural (e.g., windblown dust) and anthropogenic sources such as smelting, ore processing, and fossil fuel combustion of coal. Atmospheric Cu can travel great distances and will eventually be removed from the air by gravitational settling or washout through precipitation (ATSDR, 2004). Direct atmospheric fallout can be a major input of Cu to waterbodies (Eisler, 1998). For example, atmospheric inputs account for 60% – 80% of the Cu input to Lake Superior (Georgopoulos et al., 2001). While the transportation time and distance depend on several factors, including particle size and wind velocity, the average persistence time of Cu in the air is 13 days (Eisler, 1998).

Copper is released to aquatic ecosystems through the natural weathering and chemical decomposition of rocks and soils (Georgopoulos et al., 2001) and the leaching of Cu deposited from anthropogenic sources. The direct discharge of municipal wastes and urban runoff to surface waters also contributes to increased Cu concentration in aquatic ecosystems (Nriagu and Pacnya, 1988). Effluents and runoff from active metal mines and refineries (Cu and non-Cu) and runoff from non-active metal mines can increase Cu concentration in receiving waters (Nriagu and Pacnya, 1988).

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).

5.   ANALYSIS OF COPPER IN ENVIRONMENTAL SAMPLES

Both total Cu and dissolved Cu can be analysed in water samples. Dissolved Cu analysis measures only the fraction that passes through a 0.45 µm filter, while total Cu analysis includes the dissolved fraction and any Cu associated with particulates (e.g., suspended sediments). While neither method provides accurate information on the speciation or ratio of toxic forms (e.g., ionic Cu), the dissolved fraction provides a better estimate of bioavailable Cu (Brungs et al., 1976; Chakoumakos et al., 1979; Erickson et al., 1996; Paquin et al., 2002).

The B.C. Environmental Laboratory Manual (ENV, 2015) recommends four common laboratory techniques for the measurement of Cu in environmental samples:
- Atomic Absorption Spectroscopy (AAS);
- Graphite Furnace Atomic Absorption Spectrometry (GFAAS);

- Inductively Coupled Plasma Atomic Emission (ICP-AES); and
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The Method Detection Limit[1] (MDL) typically attained by AAS is about 20 µg/L, while the more sensitive methods of GFAAS, ICP-AES and ICP-MS can attain MDLs as low as 1 µg/L, 5.0 µg/L, and 0.02 - 0.5 µg/L respectively (USEPA, 1994; ENV, 2015; ENV, 2017). The Practical Quantitation Limit (PQL), defined as "the lowest achievable level of analytical quantitation during routine laboratory operating conditions within specified limits of precision and accuracy" (USEPA, 1985), is in practice about 5-10 times higher than the MDL (USEPA, 1985). Therefore, MDLs should be, at a minimum, five times below the ambient WQG to ensure a high level of precision and accuracy in the laboratory results. In cases where laboratories have defined PQLs for the substance of interest, it is recommended that the PQL be at or below the ambient WQG.

6.   BACKGROUND CONCENTRATIONS OF COPPER IN BRITISH COLUMBIA WATERS

Copper is a naturally occurring element and background concentrations need to be considered when deriving guidelines for B.C. (ENV, 2012). Background concentrations of Cu vary across the province depending upon the underlying geology.

6.1 Methods for Estimating Background Concentrations

Data to characterize background Cu concentrations in B.C. were taken from two sources: the B.C. Environmental Management System (EMS) database and the Canadian Aquatic Biomonitoring Network (CABIN) database. EMS does not identify reference stations, so the database was screened to create a sub-set of water quality stations known to be minimally impacted. To do this, water quality sampling stations that were sampled at least three times over the last 20 years for any water quality parameter (1996/01/01 to 2017/05/03) were extracted. Next, the list of stations with location information was given to ENV environmental impact assessment biologists to identify sites that they considered minimally impacted by human activities. No strict definition of 'minimally impacted' was given to the biologists and station selection was left to their professional judgement. The list of minimally impacted stations was then used to extract copper water quality data from the EMS database.

The dataset underwent several additional automated and manual data cleaning steps. First, only one surface sample site from each lake was included. Next the data set was visually inspected to remove samples where:

1) Results from more recent analyses with lower MDLs showed lower concentrations than earlier results with higher detection limits. This included consideration of concentrations assumed to be ½ the MDL;
2) Results were >MDL, but were not characteristic of the dataset for that site;
3) The results were <MDL, but were not characteristic of the dataset for that site;
4) Results were reported as NA or 0; and
5) The results appeared to be obvious errors, assumed to be attributed to either data entry or analytical errors.

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[1] The MDL is defined as "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte" (CFR 2011).

Arithmetic means were calculated for laboratory replicates (analytical replicates taken from one field sample) with the detection limit substituted for values below detection. However, all field replicates were included as independent samples.

The resultant data set was augmented with samples collected by ENV and Environment and Climate Change Canada (ECCC) at B.C. reference stations as part of the CABIN program. Reference stations are minimally impacted by anthropogenic activities. The CABIN stations only had data for total Cu and were generally sampled once during the late summer/early fall.

The combined EMS and CABIN dataset had 740 minimally impacted stations[1] with data for dissolved and/or total Cu (Figure 6.1). Mean total and dissolved Cu concentrations were calculated for each station, giving equal weight to each station within an ENV region (Figure 6.1), rather than over representing stations with large sample sizes. Station means were calculated using four different approaches depending on the number of samples above (detects) and below (non-detects) the MDL (Table 6.1). A value of ½ the minimum MDL was used to represent station means when all samples were below the MDL (Group 1). The minimum MDL was chosen to account for decreasing MDLs over time. For stations with less than three detects, ½ of the MDL was substituted for non-detect values and the arithmetic mean of all station results was calculated (Group 2). Regression on order statistics (ROS) were used to calculate an estimate of the mean for stations that had a mixture of non-detects and detects with at least three detected values (Huston and Juarez-Colunga, 2009) (Group 3). Although Huston and Juarez-Colunga (2009) state that ROS can be used on sample sizes >0, a minimum of three detects is required to calculate a valid regression using the NADA package (Lee 2017) in R (R Core Team, 2016). The arithmetic mean was calculated for stations where all samples were above the MDL (Group 4). Statistics to summarize the distribution of station means (median, the 10th and 90th percentile) were calculated for each ENV region.

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[1] CABIN data may be duplicated as ENV data is also part of the EMS database and it is often difficult to identify CABIN samples. However, this should have a minimal impact on the analysis as mean values are reported.
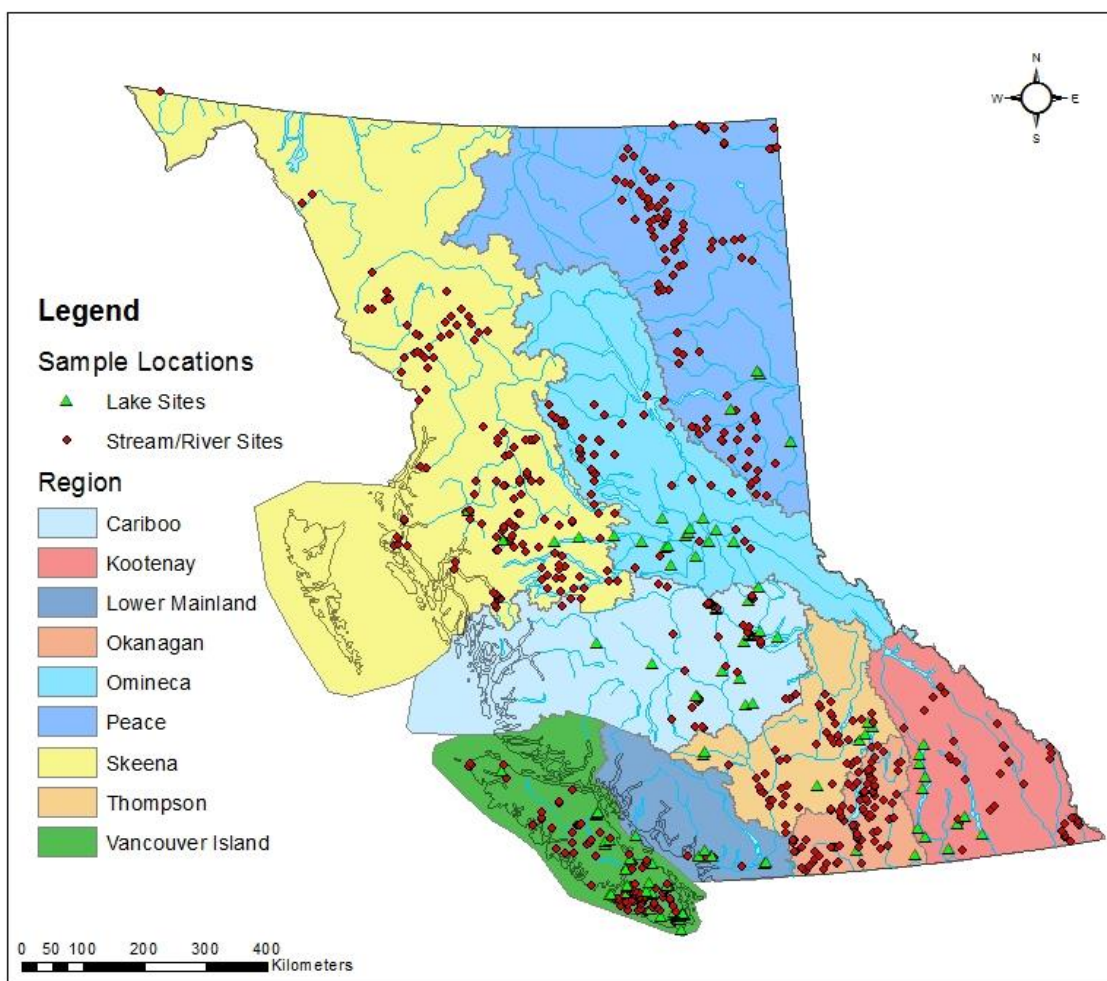
Figure 6.1. Sampling stations in each ENV region with dissolved or total Cu data.

Table 6.1. Statistical approach used to calculate station means.

Group	Conditions	Approach	Dissolved Copper		Total Copper	
			Total Stations	Total Samples	Total Stations	Total Samples
1	% non-detects = 100	½ of minimum station MDL	17	35	80	282
2	0 < % non-detects < 100 <u>AND</u> # detects < 3	Substitute ½ MDL for non-detects and calculate arithmetic mean for all samples	2	4	50	177
3	0 < % non-detects < 100 <u>AND</u> # detects ≥ 3	Regression on order statistics	20	1,992	38	2,333
4	% non-detects = 0	Arithmetic mean	125	1,257	567	3,087

6.2 Background Concentration Results

Concentrations of dissolved and total Cu were analyzed separately, and the results are given below. Dissolved Cu is the more bioavailable fraction (see Section 5). However, total Cu concentrations were also examined as more total Cu samples have been taken across the province and therefore provides a better geographical representation. A plot of total vs dissolved paired Cu samples revealed that 11% of the dissolved values were higher than total (Figure 6.2). This may be the result of lower analytical precision at very low concentrations. Given the variability in the total compared to dissolved Cu concentrations, no attempt was made to estimate the proportion of dissolved Cu under field conditions, nor were total and dissolved estimates directly compared. Regional summaries were used to minimize the effect of individual sampling errors.
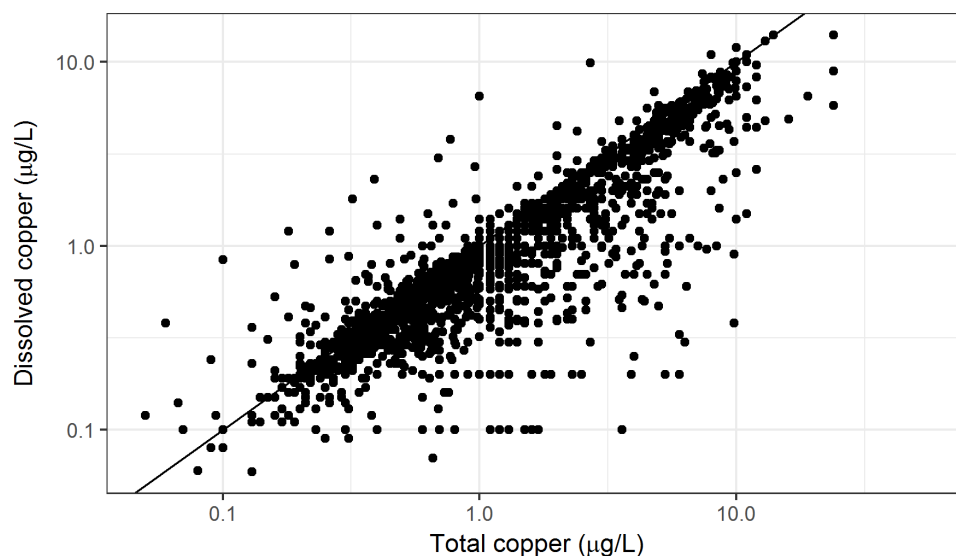
Figure 6.2. Total vs dissolved Cu from paired field samples where both total and dissolved Cu were above detection.

Solid line is 1:1 line. N = 2,418

6.2.1 *Dissolved Copper*

Dissolved Cu data were summarized by ENV region in Table 6.2 and Figure 6.2. There were 164 stations with dissolved Cu data, which included 3,288 samples. The number of stations within each region with dissolved Cu data ranged from 1 (Peace) to 56 (Cariboo). Four regions had less than 10 stations (Peace, Lower Mainland, Thompson and Okanagan), making the characterization of dissolved Cu difficult. The Cariboo, Vancouver Island, and Skeena regions had the most stations with dissolved Cu data (n = 56, 43, and 28, respectively) and the median of station means was <1 µg/L for each of these regions.

The median dissolved Cu across the province was calculated based on station means and was 0.61 µg/L, however the median value for the Okanagan (1.70 µg/L) and Omineca (2.50 µg/L) were three to four times higher. The 90th percentile of station means was 2.5 µg/L, which was equal to or less than the 90th percentile for the individual regions, except for the Okanagan (3.59 µg/L). Sampling at more stations is needed to better characterize dissolved Cu concentrations across the province, but especially in the Lower Mainland, Okanagan, Omineca, Peace and Thompson regions.

Of the 164 stations with data for dissolved Cu, 55 stations were on lakes and 109 were on rivers. The median of the distribution of station means was slightly higher for rivers (0.65 µg/L) than for lakes (0.54 µg/L) (see Figure 6.5).

6.2.2 *Total Copper*

Total Cu data were summarized by ENV region in Table 6.3 and Figure 6.3. There were 735 stations with total Cu data, which included 5,879 samples. All regions had more than 50 stations except the Lower Mainland, which had 9 stations. The median of station means in each region was <1 µg/L. The median of the distribution of station mean total Cu concentrations across the province was 0.68 µg/L and the 90th percentile was 3.0 µg/L. Regionally, Vancouver Island and the Cariboo had higher median and 90th percentile of stations means compared with other regions.

Of the 735 stations with total Cu data, 93 stations were on lakes and 641 were on rivers. For total Cu, the median of the distribution of station means in rivers (0.67 µg/L) was very close to that of lakes (0.68 µg/L) (see Figure 6.5).

Table 6.2. Summary statistics for background dissolved Cu concentrations in each ENV region.

Region	# Stations	# Samples	Date Range	Concentration Range Across All Samples (µg/L)	MDL Range Across All Samples (µg/L)	% Samples <MDL	Distribution of Station Means (µg/L)		
							Median	10th Percentile	90th Percentile
Cariboo	56	581	1997 - 2016	0.05 - 27	0.05 - 2.5	4%	0.80	0.23	2.38
Kootenay	13	125	1998 - 2016	0.2 - 5	0.2 - 5	13%	0.47	0.35	2.28
Lower Mainland	3	19	2002 - 2005	0.08 - 1	N/A	0%	0.39	0.26	0.43
Okanagan	7	1602	1996 - 2017	0.1 - 26	0.1 - 5	23%	1.70	0.64	3.59
Omineca	10	34	1997 - 2014	0.43 - 5	5 - 5	18%	2.50	0.67	2.50
Peace	1	41	2012 - 2014	0.059 - 0.93	N/A	0%	0.25	0.25	0.25
Skeena	28	270	1996 - 2017	0.1 - 5	0.2 - 5	8%	0.51	0.23	1.41
Thompson	4	126	1997 - 2017	0.13 - 3.5	1 - 1	2%	0.50	0.45	0.60
Vancouver Island	42	490	1998 - 2017	0.05 - 71	0.05 - 0.05	1%	0.54	0.25	1.25

Table 6.3. Summary statistics for background total Cu in each ENV region.

Region	# Stations	# Samples	Date Range	Concentration Range Across All Samples (µg/L)	MDL Range Across All Samples (µg/L)	% Samples <MDL	Distribution of Station Means (µg/L)		
							Median	10th Percentile	90th Percentile
Cariboo	63	1231	1996 - 2016	0.02 - 67	0.02 - 4	1%	0.97	0.33	3.65
Kootenay	50	244	1996 - 2016	0.04 - 6.3	0.04 - 6	32%	0.24	0.06	1.04
Lower Mainland	9	51	2000 - 2016	0.1 - 8.7	0.2 - 6	25%	0.67	0.36	3.28
Okanagan	96	1433	1996 - 2017	0.05 - 35	0.05 - 7	11%	0.60	0.26	3.00
Omineca	50	708	1996 - 2016	0.05 - 41	N/A	0%	0.65	0.18	2.15
Peace	108	173	2008 - 2016	0.071 - 9.29	0.071 - 0.15	3%	0.90	0.27	2.59
Skeena	154	801	1996 - 2017	0.02 - 74	0.02 - 6	3%	0.62	0.28	2.80
Thompson	51	271	1997 - 2017	0.087 - 7	0.5 - 6	6%	0.63	0.35	2.00
Vancouver Island	153	965	1997 - 2017	0.05 - 95	0.05 - 6	30%	0.91	0.27	4.50
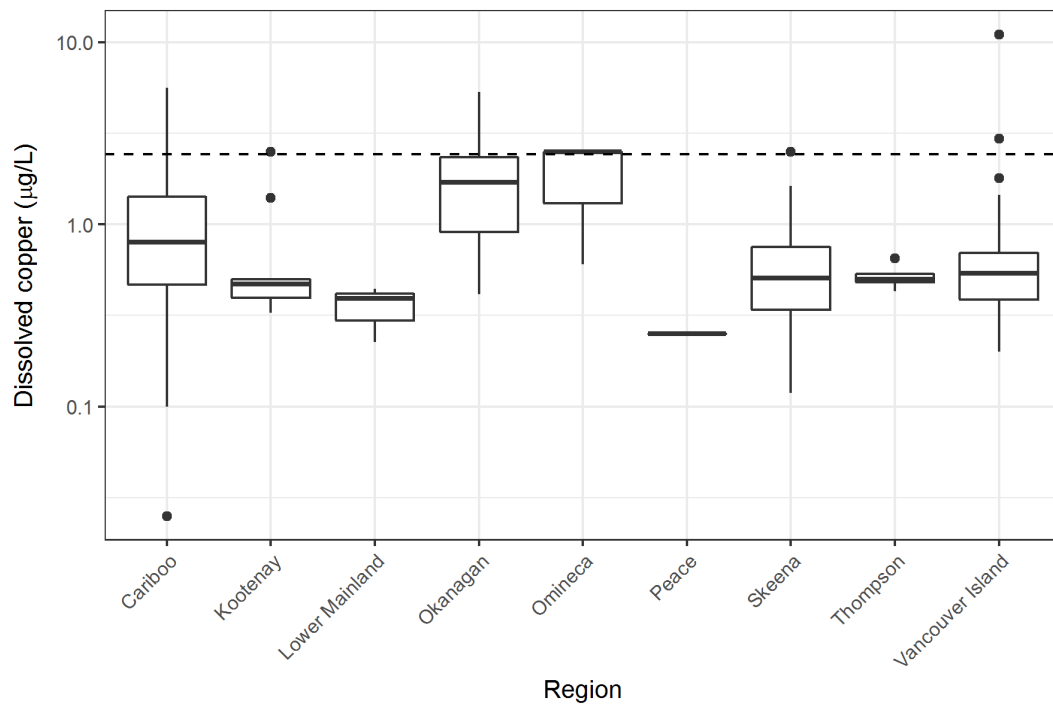
Figure 6.3. Distribution of station means for dissolved Cu in each region.

Note y-axis is on a log scale. Solid horizontal bar within each box represents median of station means. Dashed line indicates 90th percentile for all station means.
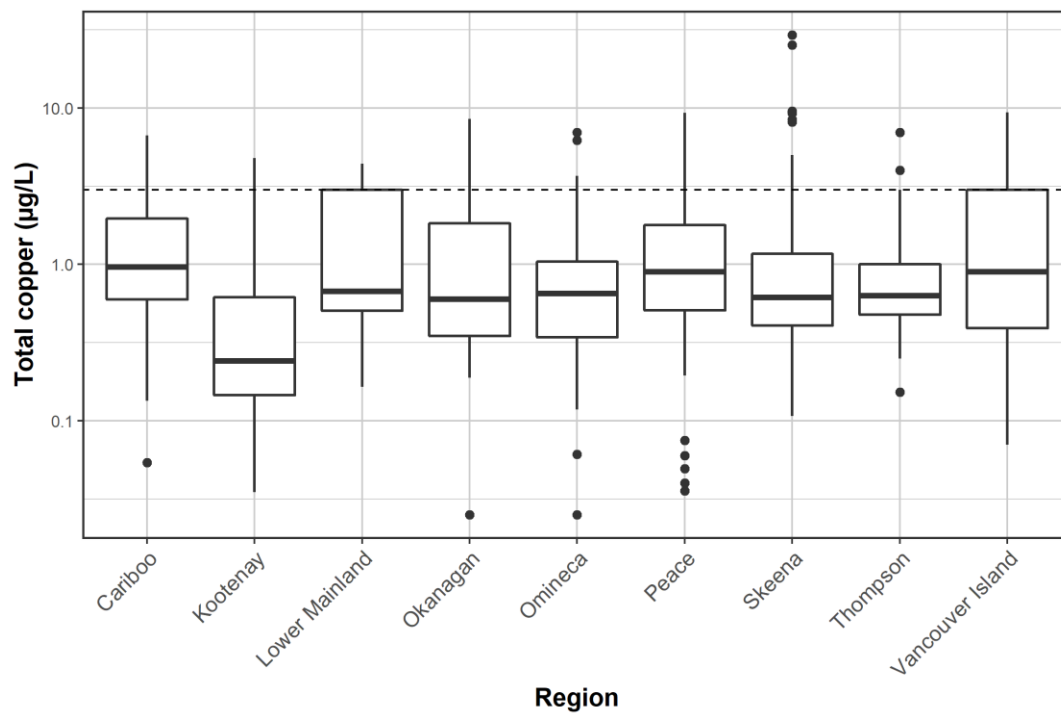
Figure 6.4. Distribution of station means for total Cu in each region.

Note y-axis is on a log scale. Solid horizontal bar within each box represents median of station means. Dashed line indicates 90th percentile for all station means.
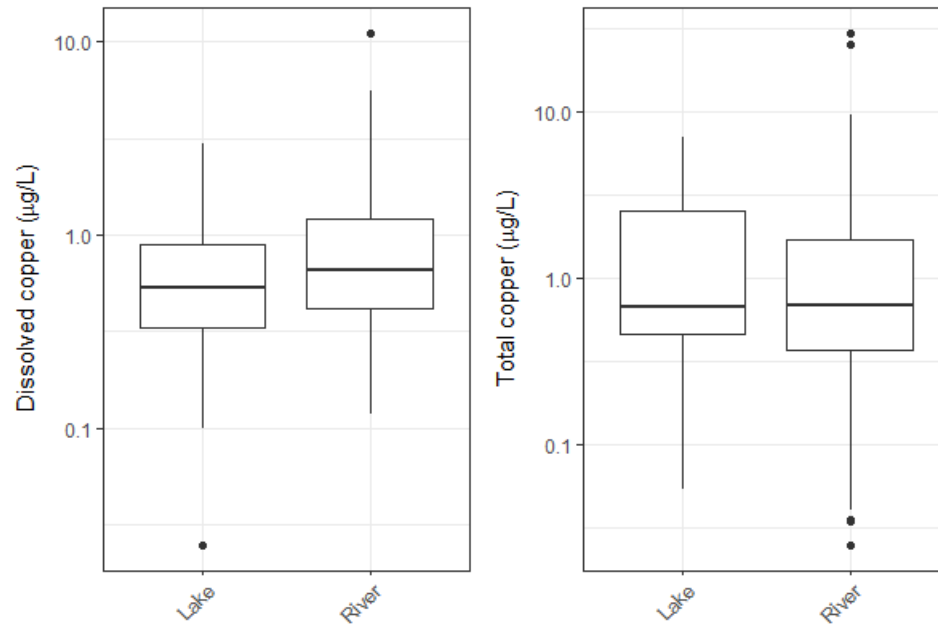
Figure 6.5. Distribution of station means for lakes and rivers by dissolved Cu (left) and total Cu (right).
Note y-axis is on a log scale.

7.   COPPER TOXICITY-MODIFYING FACTORS

Dissolved Cu occurs in various chemical forms in fresh waters, and the relative amounts of those chemical forms vary as a function of water chemistry. However, not all chemical species of Cu can be taken up by the biochemical receptors (i.e., biotic ligands) of an organism (e.g., gill) (Meyer et al., 2007). Therefore, Cu toxicity is not only determined by its concentration in water, but also the chemistry of water. Free ionic Cu (Cu^{2+}) is the main toxic form (Howarth and Sprague, 1978; Meador et al., 1991; Grosell, 2012). Some hydroxyl species of Cu (e.g., $CuOH^-$) can be toxic, however, many other species, such as copper carbonates, are generally less bioavailable and consequently less toxic (Howarth and Sprague, 1978; Meador, 1991; Eisler, 1998). Some water quality factors influence the speciation of Cu thereby modifying Cu toxicity. In addition, some ions (i.e., calcium) compete with Cu at biological binding sites and decrease its uptake at biotic ligands. These toxicity modifying factors are discussed further below.

7.1 Dissolved Organic Carbon

Dissolved organic carbon (DOC) binds to the toxic inorganic forms of Cu in water (i.e. Cu^{2+} and $CuOH^-$) forming organic complexes that cannot bind to biotic ligands, such as gill (Erickson et al., 1996) and olfactory tissues (Kennedy et al., 2012). As a result, DOC can ameliorate Cu toxicity significantly (Meador, 1991; Erickson et al., 1996; Grosell, 2012), which has been demonstrated in algae (Heijerick et al., 2005), macrophytes (Antunes et al., 2012), invertebrates (Meador, 1991; Wang et al., 2011), and fish (Erickson et al., 1996; McGeer et al., 2002; Luider et al., 2004; Schwartz et al., 2004; Sciera et al., 2004). The ameliorative effect of DOC, however, is weaker at low pH values because H^+ ions can compete with Cu at the binding sites of DOC (Playle et al., 1993; Welsh et al., 1993).

7.2 Hardness

Water hardness, defined as the concentration of calcium (Ca) and magnesium (Mg), can ameliorate Cu toxicity (Howarth and Sprague, 1978; Chakoumakos et al., 1979; Miller and Mackay, 1980; Erickson et al., 1996; Naddy et al., 2002; Sciera et al., 2004; Ryan et al., 2009) through the competition between Ca^{2+} and Cu^{2+} for branchial uptake on gill surfaces (Grosell, 2012). While Ca^{2+} is shown to provide a stronger ameliorative effect in fish, Mg seems to provide more protection in aquatic invertebrates (Meyer et al., 2007). Recognizing the influence of hardness on Cu toxicity, many jurisdictions have developed hardness-based equations for their Cu WQGs, including the Canadian Council of Ministers of Environment (CCME) and several provincial jurisdictions (Alberta, B.C., Manitoba, and Ontario) (ENV, 1987; CCREM, 1987; OMOEE, 1994; AEP, 1996; MWS 2011).

The ameliorative influences of hardness on Cu toxicity, however, are not consistent. For example, Winner (1985) observed very little protection against Cu toxicity in *Daphina pulex*. Hardness did not influence Cu uptake and the lethal effects of short-term Cu exposure in rainbow trout (*Oncorhynchus mykiss*) (Laurén and McDonald, 1986; Grosell and Wood 2002). These inconsistencies may be caused by variations in other water quality factors, such as alkalinity (Erickson et al., 1996) or the Ca:Mg ratio in the laboratory test water (Naddy et al., 2002). However, it is demonstrated that Ca^{2+} has only minor ameliorative effects in protecting olfactory tissues against Cu toxicity (McIntyre et al., 2008; Green et al., 2010; Dew et al., 2012).

7.3 pH

In de-ionized, low pH water (<6), the majority of Cu is in the toxic ionic form, Cu^{2+}. As pH increases, the concentration of Cu^{2+} drops dramatically and other less toxic forms become abundant (e.g., $CuOH^-$) (Meador, 1991; Eisler, 1998; Grosell, 2012). In natural waters, however, the influence of pH is

complicated by interactions with other water chemistry factors, such as the presence of other ions and DOC (Howarth and Sprague, 1978; Miller and Mackay, 1980; Cusimano et al., 1986; Erickson et al., 1996; Sciera et al., 2004).

The effects of pH on Cu toxicity vary among taxonomic groups. Tests on fish and invertebrates have generally shown decreasing Cu toxicity with increasing pH. Erickson et al. (1996) tested the Cu toxicity to larval fathead minnows (*Pimephales promelas*) in test waters with pH values 6.5, 7.4, 8.1 and 8.8 and demonstrated lower toxicity at higher pH values. Cladocerans also demonstrated lower sensitivity to Cu exposure at higher pH values (Hyne et al., 2005; Ryan et al., 2009). In contrast, freshwater algae (*Chlorella* sp.) and duckweed (*Lemna minor*) demonstrated higher sensitivity to Cu at higher pH values (Wilde et al., 2006; Antunes et al., 2012, respectively). The inconsistency might be due to different mechanisms of toxicity in algae and plants compared to fish and aquatic invertebrates.

7.4 Alkalinity

Copper toxicity to fish is reduced in waters of high alkalinity (Chakoumakos et al., 1979; Laurén and McDonald, 1986) because the anions associated with alkalinity (i.e., CO_3^{2-} and HCO_3^-) bind with free ionic Cu to form compounds like $Cu(CO_3)_x$, which are less toxic (Meador, 1991; Eisler, 1998). The protective effect of alkalinity, however, is further influenced by other water quality conditions. For example, Miller and Mackay (1980) demonstrated that alkalinity moderated Cu toxicity at high hardness but did not have the same ameliorative effect at low hardness. For aquatic plants, it has been suggested that compounds like $Cu(CO_3)_x$ and $Cu(HCO_3)$ may also be bioavailable (Antunes et al., 2012). Therefore, alkalinity may play less of a role in ameliorating Cu toxicity in aquatic plants than it does in aquatic animals.

7.5 Temperature

Generally, the effect of temperature on Cu toxicity is considered to be minor (Carvalho and Fernandes, 2006) although some major influences have also been reported (Richards and Beitinger, 1995). This inconsistency may be due to different sensitivities among species. For example, Smith and Heath (1979) found the modifying effect of temperature differed across the five fish species tested. In a study of two aquatic invertebrate species, *Daphnia pulex* (cladoceran) and *Diaptomus clavipes* (copepod), Boeckman and Bidwell (2006) found that increased temperature significantly increased Cu toxicity to the copepod but had little effect on the daphnids.

Temperature causes only slight shifts in the equilibrium of Cu species and therefore the availability of toxic forms. It is believed that temperature indirectly affects the toxicity of metals by: 1) increasing metabolism and consequently the uptake of metals; and 2) increasing temperature-related stress (Cairns et al., 1975; Heugens et al., 2003; Boeckman and Bidwell, 2006). Therefore, the role of temperature on Cu toxicity varies depending upon the species and its temperature optimal range.

8.   TOXICITY OF COPPER TO FRESHWATER AQUATIC ORGANISMS

Copper is an essential micronutrient and necessary for metabolic processes in all aerobic organisms (Flemming and Trevos, 1989). Enzymes such as cytochrome c oxidase, ceruloplasmin, and tyrosinase utilize the redox potential of Cu (Eisler, 1998; Grosell, 2012). Copper is also required for proper nervous system function and the synthesis of hemoglobin (Nordberg et al., 2014). Aquatic organisms obtain Cu from their diet, as well as the ambient environment through regulated uptake in water. A lack of Cu can cause decreased growth, increased larval mortality and larval deformities in aquatic organisms (Kamunde et al., 2002; Mackenzie et al., 2004; Grosell, 2012).

Despite the essentiality of Cu, elevated concentrations can have several acute and chronic effects on aquatic organisms. For example, exposure to Cu can impair ammonia excretion, acid-base balance, Na^+/K^+-ATPase activity, and apical Na^+ entry in several species of fish (Flemming and Trevos, 1989; Grosell, 2012). These physiological impairments can translate to several adverse effects in fish including olfactory deficiency, mechanoreception impairment, reduced reproduction, growth limitation, and death. Many studies have also shown adverse effects of Cu exposure in other taxonomical groups of organisms such as algae, aquatic plants, invertebrates and amphibians (Flemming and Trevos, 1989; Fernandes and Henriques, 1991; Meador, 1991; Eisler, 1998); these are reviewed in the following sections.

8.1 Effects on Algae

The adverse effects of elevated Cu on freshwater algae include growth inhibition (Nyholm, 1990; Heijerick et al., 2005; De Schamphelaere and Janssen, 2006; Wilde et al., 2006; Perales-Vela et al., 2007; Stoiber et al., 2010; Bajguz, 2011; Kebeish et al., 2014), changes in cell size (Franklin et al., 2002), flagella loss (Winner and Owen, 1991), chlorophyll reduction (Fargašová et al., 1999; Perales-Vela, 2007) and decreased photosynthetic efficiency (Danilov and Ekelund, 2001; Perales-Vela et al., 2007). The mechanism of Cu toxicity varies in different algal species. For example, Küpper et al. (2003) reported that Cu is substituted for Mg^{2+} in the chlorophyll of *Scenedesmus quadricauda*, inhibiting photosynthesis. In another example, Stauber and Florence (1987) demonstrated that the main mechanism of Cu toxicity in *Chlorella pyrenoidosa* is oxidation of glutathione, which in turn leads to the suppression of mitosis.

While several studies have investigated the effects of Cu on various algal species (Appendix 1, tabs 3-5), few have provided supporting details on water chemistry. For example, Wilde et al. (2006) reported a 48-hour EC_{50} of 1 µg/L for growth in *Chlorella* sp. in water with the following conditions: hardness: 43 mg/L; pH: 8; DOC: 1 mg/L.

8.2 Effects on Macrophytes

The effects of Cu exposure on several species of macrophytes have been studied. While Cu accumulation has been used as the only endpoint in some studies (Gonçalves and Boaventura, 1998; Bourgeault et al., 2013), others demonstrated the adverse effects of Cu on biomass (Mal et al., 2002; Khellaf and Zerdaoui, 2010; Rofkar et al., 2014), chlorophyll concentration (Han et al., 2008), stem length (Markich et al., 2006), and CO_2 assimilation (Al-Hamdani and Blair, 2004). The main mechanisms of Cu toxicity in plants is the inhibition of photosynthetic electron transfer combined with production of hydroxyl radicals (-OH), which can oxidize some cell components, such as membrane lipids (Fernandes and Henriques, 1991).

Water quality data are generally not reported in studies investigating Cu toxicity to aquatic macrophytes (see Appendix 1, Tab 5), but there are exceptions. Antunes et al. (2012) investigated Cu toxicity to duckweed using the inhibition of root growth as the toxicity endpoint. They ran their toxicity tests in waters with different chemistry and calculated several 7-day IC_{10}s and 7-day IC_{50}s (e.g., 7-day IC_{10} of 0.72 µg/L in hard water with a pH of 8.3 and DOC of 1 mg/L). In another example, a 96-hour EC_{50} (growth) of 9.9 µg/L was reported for coontail (*Ceratophyllum demersum*) in neutral water with a hardness of 335 mg/L and alkalinity of 16 mg/L (Markich et al., 2006).

8.3 Effects on Invertebrates

Aquatic invertebrates are extremely susceptible to elevated Cu concentrations. Elevated Cu can inhibit growth, reduce reproduction, and increase mortality in aquatic invertebrates. The mechanism of Cu

toxicity in invertebrates is not completely understood, however, some physiological changes have been observed in various aquatic invertebrates in response to Cu exposure. Dave et al. (1984) demonstrated that increased Cu reduced the haemoglobin content in *D. magna*. Brix et al. (2011) demonstrated that excess Cu reduced hemolymph osmolality, reduced hemolymph pH, and inhibited Ca^{2+} uptake in the great pond snail (*Lymnaea stagnalis*). In a study conducted by Jorge et al. (2013), decreased Na^+ content and impaired Na^+/K^+ activity corresponded with excess Cu concentrations and exposure time in fatmucket clam (*Lampsilis siliquoidea*).

Copper toxicity has been studied extensively in pelagic aquatic invertebrates, especially cladocerans. *Ceriodaphnia dubia* and *D. magna* are the most studied cladoceran species. In general, invertebrates demonstrate a higher sensitivity to Cu at younger life stages (Nebeker et al., 1986; Brix et al., 2011). Acute and chronic effects of Cu to aquatic invertebrates are discussed further in the following sections.

8.3.1 *Short-term Acute Effects*

Aquatic invertebrates exposed to Cu demonstrate increased mortality as a result of short-term exposure periods (Rathore and Khangarot, 2002; Wang et al., 2007; De Schamphelaere et al., 2007). Belanger and Cherry (1990) reported 48-hour LC_{50} for *C. dubia* at 28 µg/L in river water with the following characteristics: hardness: 97.6 mg/L; alkalinity: 74.2 mg/L; pH: 8.0. Using great pond snails, Ng et al. (2011) calculated a 96-hour LC_{50} of 24.9 µg/L (hardness = 123 mg/L, pH = 8.1, DOC = 1.85 mg/L). Wang et al. (2009) tested the sensitivity of juvenile fatmucket clam to Cu in various natural and reconstituted water sources with different water chemistry and reported 96-hour LC_{50} values ranging from 10 µg/L to 475 µg/L.

8.3.2 *Long-term Chronic Effects*

The sub-lethal and lethal effects of long-term Cu exposure on aquatic invertebrates have been investigated in several studies. Long-term Cu exposure can decrease survival rates in aquatic invertebrates at concentrations lower than those that are lethal in short-term exposures. For example, Dave (1984) reported a 48-h LC_{50} for *D. magna* of 6.5 µg/L, (hardness = 250 mg/L, pH = 8), while the 21-day LC_{50} in the same water was 1.4 µg/L.

Growth impairment in aquatic invertebrates has been tested using both length (Dave, 1984; Wang et al., 2007) and weight measures (Brix et al., 2011; Besser et al., 2016) for fatmucket clam, great pond snail, and *D. magna*. Growth inhibition has been reported at concentrations as low as 32% and 50% of the concentrations that caused mortality in chronic exposures of the great pond snail (Brix et al., 2011) and fatmucket clam (Wang et al., 2007), respectively. However, sensitivity of growth impairment is not consistent across invertebrate species. In *D. magna*, growth impairment only occurred at concentrations close to those which decreased survival (Dave, 1984).

The reproductive impairment of Cu-exposed invertebrates has mainly been investigated using daphnids. A reduction in the number of neonates (i.e., offspring) in *C. dubia* and *D. magna* as a result of chronic long-term exposure to Cu has been demonstrated in several studies (Dave, 1984; Belanger and Cherry, 1990; Cerda and Olive, 1993; De Schamphelaere and Janssen, 2004; Villavicencio et al., 2011). Impairment of reproduction-related endpoints occurred at concentration below those which reduce survival. For example, Cerda and Olive (1993) exposed daphnids to Cu for 7 days in reconstituted water with a hardness of 85 mg/L and a pH of 7.6 and measured the 7-day EC_{50} (reproduction) as well as the 7-day LC_{50} for 8 groups of daphnids and reported an average of 0.59 for ratio of 7-day EC_{50}/7-day LC_{50}. Using identical experimental water, Cooper et al. (2009) demonstrated a 7-day LOEL for survival of 10.6 µg/L (60% survival compared to control), and a 7-day LOEL for reproduction of 2.6 µg/L (73% reduction in number of neonates) (hardness = 85 mg/L, pH = 7.5).

8.4 Effects on Fish

Acute exposures to elevated Cu concentrations can cause mortality in many fish species (Jones, 1938; Sprague and Ramsay, 1965; Erickson et al., 1996; Grosell, 2012; Vardy et al., 2013; Calfee et al., 2014), while chronic exposures can affect survival, growth, and reproduction (McKim et al., 1978; Pickering et al., 1977; Besser et al., 2007; Wang et al., 2014). Furthermore, impaired olfactory acuity and olfactory mediated behaviours, as well as altered swim performance in fish have been reported as a result of both short–term and long-term exposures to low concentrations of Cu (Waiwood and Beamish, 1978; McGeer et al., 2000; Tierney et al., 2010; Meyer and DeForest, 2018). Fish also tend to avoid extremely low concentrations of Cu when given a chance (e.g., Hansen et al., 1999). The adverse effects of Cu on fish are well studied and several mechanisms of action have been proposed for Cu-induced adverse effects.

The main mechanism of acute Cu toxicity is related to osmoregulation. Fish exposed to high Cu concentrations experience a reduction in Na^+ uptake and an increase in Na^+ loss in plasma, leading to a net loss of Na^+. This results in reduced plasma osmolality and increased blood viscosity, which in turn leads to cardiovascular failure and death (Grosell, 2012). Exposure to sub-lethal concentrations of Cu results in many adverse physiological effects, including elevated plasma ammonia/ammonium, acid-base balance disturbances, oxidative stress, and respiratory distress. If exposure to sub-lethal concentration continues, the adverse physiological effects, in addition to biological costs of Cu detoxification, results in chronic effects such as growth inhibition and reduced reproductive output. Although Cu is toxic to all life stages of fish, early life stages (e.g., larvae) are more susceptible.

To facilitate the assessment of Cu toxicity in fish, a summary of some key short-term and long-term studies are discussed in the following sections. Although sub-lethal effects generally occur after long-term exposures, olfactory impairment, avoidance behaviour, and affected swim performance are demonstrated to take place after both short- and long-term exposures. Since the above-mentioned endpoints are considered sub-lethal endpoints, both short and long-term examples are discussed in section 8.4.2 (long-term chronic toxicity to fish).

8.4.1 *Short-term Acute Effects*

Although elevated Cu concentrations are reported to cause mortality in fish after exposure periods as short as 24 hours (Taylor et al., 2000; Gravenmier et al., 2005), the majority of Cu toxicity studies used 96–hour exposure periods to investigate acute effects of Cu. The reported 96-hour LC_{50} values vary three orders of magnitude (µg/L to mg/L) depending on the species tested, water chemistry, and life stage (see Appendix 1, tabs 1 and 2).

Erickson et al. (1996) exposed fathead minnow larvae to Cu under various water chemistry conditions. The calculated 96-hour LC_{50} values ranged from 4.76 µg/L to 305 µg/L depending on hardness, pH, alkalinity and DOC. Several researchers have investigated the effects of short-term Cu exposure on rainbow trout at different life stages and under different water chemistry conditions (e.g., Chapman, 1978; Chakoumakos et al., 1979; Hansen et al., 2002a; Vardy et al., 2013; Calfee et al., 2014; Naddy et al., 2015) producing 96-hour LC_{50} values ranging from 3.4 µg/L to 514 µg/L (see Appendix 1, tabs 1 and 2).

White Sturgeon (*Acipenser transmontanus*) are extremely sensitive to Cu exposure. Little et al. (2012) calculated LC_{50} for different early life stages of white sturgeon from Columbia and Kootenai rivers in well water (hardness: 80-120 mg/L, DOC: 0.2-0.5 mg/L and pH: 8.1-8.4) and reported the following 96-hour LC_{50}s: 4.5 µg/L (26 days post hatch (DPH)), 6.8 µg/L (27 DPH), 4.1 µg/L (38 DPH), 4.7 µg/L (40 DPH), 268.9 µg/L (123 DPH), 103.7 µg/L (167 DPH), 269 µg/L (450 DPH). Vardy et al (2013) also tested sensitivity of white sturgeon to Cu at the following early life stages: yolksac larvae (8 DPH), swim-up larvae (15 DPH),

early juvenile (40-45 DPH) and later juvenile (100 DPH) in lab water (hardness: 57 mg/L, DOC: 2.2 mg/L, pH:7.5). The most sensitive life stage was the swim-up larvae (96-hour LC_{50}: 10 µg/L), followed by the early juveniles (96-hour LC_{50}: 9–17 µg/L), the yolksac larvae (96-hour LC_{50}: 22 µg/L) and the later juvenile life stage (96-hour LC_{50}: 54 µg/L; Vardy et al., 2013).

8.4.2 *Long-term Chronic Effects*

Long-term exposure to Cu can induce sub-lethal adverse effects such as growth reduction, reduced reproduction, and impaired olfaction. Chronic long-term exposure to Cu is also known to decrease survival in fish (Chapman, 1978; Hansen et al., 2002b; Wang et al., 2014). In general, mortality from chronic Cu exposure occurs at concentrations below those that cause mortality in short-term exposures (i.e., 96-hour LC_{50}).

Reduced growth because of Cu exposure has been reported in several fish studies (e.g., McKim et al., 1978, Besser et al., 2007; Grosell, 2012; Wang et al., 2014). Length and weight are used to measure growth but do not respond equally to Cu exposure (Marr et al., 1996; Wang et al., 2014). For example, Marr et al. (1996) reported a LOEL of 4.6 µg/L in weight reduction after a 20-day exposure (17% reduction compared to control), while the LOEL for length reduction was 9.0 µg/L (5% reduction compared to control; hardness = 25 mg/L, pH = 7.5). Although growth reduction occurs at concentrations below lethal concentrations, results vary between studies (Grosell, 2012) depending on exposure duration (McKim et al., 1978). The life stage of the test animals is also a factor as larvae and early juvenile life stages appear to be more susceptible to Cu-induced growth reduction than embryos (McKim et al., 1978).

Fecundity and hatchability of eggs are two endpoints used to measure the adverse effects of Cu on the reproduction of fish (Mount, 1968; McKim and Benoit, 1971; Pickering et al., 1977). Studies of the effects of Cu on reproduction are limited; however, it is generally believed that reproduction is a more sensitive endpoint compared to survival or growth (Grosell, 2012). For example, using fathead minnows, Mount (1968) reported a LOEC of 32 µg/L for number of eggs produced after an 11-month exposure. The lowest concentration that had an effect on survival or growth was 95 µg/L (hardness = 198 mg/L, pH = 7.9).

The ability of fish to feed, avoid predators, maintain position, and move is dependent on swim performance (Waiwood and Beamish, 1978; Beamount et al., 1995). Swim performance is particularly vital for migratory fish (e.g., salmonids) (Beamount et al., 1995) and is usually investigated by measuring critical swimming speed (i.e., maximum sustained swimming speed). However, new behavioural monitoring software has allowed scientists to measure other endpoints, such as spontaneous swimming speed (Poulsen et al., 2014). Swim performance in fish can be affected by short-term (5 days) (Waiwood and Beamish, 1978) Cu exposures with effects persisting through longer exposure (100 days) (McGeer et al., 2000). Poulsen et al. (2014) demonstrated that the effect of Cu on swim performance is ameliorated at higher Ca concentrations.

Copper induces avoidance behaviour in fish, even at very low concentrations. Avoidance behaviour reduces the overall extent and diversity of available habitat which, in turn, can result in population decline (Hansen et al., 1999; Van Genderen et al., 2016; Meyer and Deforest, 2018). Copper avoidance behaviour has been demonstrated in several fish species including:

- Atlantic salmon (*Salmo salar*): 2.3 µg/L (Sprague, 1964a);

- Chinook salmon (*Oncorhynchus tshawytscha*): 0.7 µg/L (Hansen et al., 1999);

- cutthroat trout (*Oncorhynchus clarkia*): 7.4 µg/L (Woodward et al., 1997);

- rainbow trout: 1.6 µg/L (Hansen et al., 1999).

The mechanism of Cu detection in fish is still unknown. However, it is thought to involve the olfactory system (Hansen et al., 1999; Grosell, 2012).

High Ca concentrations can decrease the sensitivity of avoidance response in fish. Poulsen et al. (2014) demonstrated that at low Ca concentrations (3 mg/L), one-year-old rainbow trout avoided Cu at concentrations as low as 10 µg/L. However, when the Ca concentration was raised to 158 mg/L, the lowest concentration of Cu the fish avoided was 37 µg/L. The effects of other toxicity modifying factors on avoidance behaviour in fish have yet to be tested.

Chemosensation is vital for fish (Laberg and Hara, 2001). In fact, several essential biological processes, such as feeding, predator avoidance, mate selection, reproduction, and homing are mediated through chemosensation (mainly olfaction) (Li et al., 2002; Fine et al., 2004; Ari and Correia, 2008; Døving and Lastein, 2009). Olfactory sensory neurons are directly exposed to water and therefore unprotected against contaminants. In fact, olfaction in fish is impaired at Cu concentrations lower than those causing other adverse effects (Lürling and Scheffer, 2007). Olfactory impairments have been observed after both short-term (e.g., 30 minutes) (McIntyre et al., 2008) and long-term (e.g., 14 days) (Kennedy et al., 2012) exposure to low Cu concentrations.

Measuring changes in olfactory-mediated behaviours has been used to determine the effects of Cu on olfaction (Tierney et al., 2010; Meyer and Deforest, 2018). For example, some researchers have examined intactness, the natural avoidance behaviour of fish induced by alarm cues (i.e., conspecific skin extract), after exposure to Cu (e.g., Sandahl et al., 2007; Dew at el., 2014). Electro-olfactography (EOG) is another established technique which allows researchers to measure neurophysiological changes in the olfactory system as a result of exposure to Cu.

Kennedy at el. (2012) investigated the Cu-induced impairment of olfactory-mediated behaviours using juvenile Chinook salmon in 4-day and 14-day exposures to Cu in water with different DOC concentrations. At DOC concentrations of 0, 1, 5, 10 and 20 mg/L, the 4-day IC_{50} values were 4.3, 5.8, 30.0, 43.2 and 87.5 µg/L respectively, while 14-day IC_{50} values were 5.4, 6.2, 21.5, 25.8 and 69.4 µg/L respectively (hardness =6.12 mg/L, pH = 7). They concluded that DOC can effectively ameliorate olfactory toxicity of Cu (Kennedy et al., 2012).

Carreau and Pyle (2005) examined the long-term chemosensory effects of temporary exposures to low concentrations of Cu at early life stages in fish (hardness = 18 mg/L, pH = 7.37, DOC = 2.7 mg/L). Fathead minnow embryos were exposed to 10 µg/L of Cu from fertilization to hatch (5 to 10 days). After hatch, the fish were reared in clean water for 84-96 days and then tested for natural avoidance behaviour. While control fish avoided alarm cues, the test fish did not show the same behaviour. This example demonstrates that although chemosensory impairment is not generally considered an acute effect, even short–term exposure to Cu can result in long-term olfactory deficits.

McIntyre et al. (2012) demonstrated olfactory deficits because of short-term exposure to low Cu concentrations. They investigated the impairment of olfactory-mediated behaviours in juvenile coho salmon (*Oncorhynchus kisutch)* and the effects on predator-prey dynamics using chemical cues to signal the presence of a predator (cutthroat trout). In soft water (hardness: 56 mg/L, pH = 7.5, DOC = 0.07 mg/L), fish were exposed to 5, 10 and 20 µg/L of Cu for three hours. While control coho salmon reduced their swim speed after the addition of alarm cues, as a fright response, all Cu-exposed fish did not reduce their swim speed. Lack of fright response may significantly increase vulnerability of fish species in attack sequences. In a second test, they co-exposed both prey and predator (juvenile coho salmon and adult cutthroat trout) to 10 µg/L of Cu simultaneously and demonstrated that coho salmon were more vulnerable to predation based on an observed reduction in survival time and an increase in predator

capture success rates. Thus, they concluded that a shift in predator-prey dynamics can happen even when both species were co-exposed (McIntyre et al., 2012).

McIntyre et al. (2008) studied the influence of various water chemistry factors on Cu olfaction toxicity in juvenile coho salmon. They exposed the experimental fish to 20 µg/L Cu in water (hardness: 30 mg/L, temperature: 13 °C, pH: 7.5 alkalinity: 13 mg/L, and DOC: 0.25 mg/L) for 30 minutes and demonstrated an 82% reduction in EOG response. Increasing hardness (to 53, 99, or 190 mg/L) or alkalinity (to 41, 79, or 160 mg/L) only slightly ameliorated the Cu induced olfactory impairment. However, increased DOC (to 6.03 mg/L) significantly protected the EOG response against increased Cu.

8.5 Effects on Amphibians

The investigation of Cu toxicity in amphibians dates to 1926 (Dilling and Healey, 1926). However, in comparison to other taxonomic groups, few studies are available and very little is known about Cu toxicity in amphibians. Most studies were conducted on earlier life stages (Appendix 1, tabs 2 and 4) and although some water chemistry factors were reported (e.g., pH, hardness and alkalinity), most studies do not report DOC concentrations in exposure water (Appendix 1, tabs 2, 4 and 5).

8.5.1   *Short-term Acute Effects*
Short-term acute effects of Cu on amphibians occur at a wide range of Cu concentrations. While the 96-hour LC_{50} values for American bullfrog (*Lithobates catesbeianus*) are reported at the range of 2-4 mg/L, the 96-hour LC_{50} for other amphibian species range from 120 to 150 µg/L. American bullfrog tadpoles were used in two separate studies to investigate the effects of short-term Cu exposures. In different water chemistry conditions, Ferreira et al. (2004) and Ossana et al. (2010) reported 96-hour LC_{50} values of 2,400 and 3,960 µg/L respectively. Brown et al. (2012) reported a 96-hour LC_{50} of 162.6 µg/L for the green frog (*Lithobates catesbeianus*) in exposure water having a pH of 8.3 and a hardness of 160-180 mg/L. Dwyer et al. (2005) reported 96-hour LC_{50} of 120 µg/L for the boreal toad (*Bufo boreas boreas*) in relatively hard water.

8.5.2   *Long-term Chronic Effects*
Long-term exposures to Cu concentrations in the range of 65-200 µg/L can cause mortality to amphibians, depending on species and water chemistry, while sub-lethal effects can occur at lower concentrations (Chen et al., 2007; Peles, 2013; Leduc, 2016). For example, growth is impaired at Cu concentrations in the range of 25-50 µg/L (Chen et al., 2007; Peles et al., 2013), and metamorphosis is delayed at 10 µg/L (hardness = 114 mg/L, pH = 4.7) (Peles et al., 2013). Delayed completion of metamorphosis can have large biological costs for amphibians particularly in temporary ponds in which tadpoles have limited time to complete this phase. Cu-exposed amphibians have also demonstrated altered swim performance (at 100 µg/L), abnormal behaviour (at 36 µg/L) and body deformity (at 100 µg/L) (Redick and Lapoint, 2004; Chen et al., 2007).

8.6 Bioaccumulation and Bioconcentration of Copper in the Aquatic Environment

Field measurements of contaminants in water, sediment, and tissue provide information on their concentrations in the aquatic environment but provide little information on their bioaccumulation and bioconcentration in the tissues of aquatic organisms and the potential transfer of those contaminants to higher trophic levels. Bioconcentration factors (BCFs) and bioaccumulation factors (BAFs) express the ratio of contaminant concentration in the ambient environment to the contaminant concentration within an organism (Arnot and Gobas, 2006). The BCF estimates the relationship between the uptake and retention of a chemical by an aquatic organism from the ambient water and the excretion of that chemical (Barron, 1990; Meylan et al., 1999; Arnot and Gobas, 2006), whereas BAFs incorporate the

concentrations of a chemical from all surrounding media (i.e., water, sediment, and food) (Arnot and Gobas, 2006). Therefore, BCFs and BAFs express the competing rates of chemical uptake and loss by aquatic organisms. Biomagnification occurs when the tissue concentration of a substance is higher in the organism than in its food (DeForest et al., 2007).

Copper BCFs and BAFs have been calculated for aquatic species such as algae, mollusks, arthropods, and fish (McGeer et al., 2003, DeForest et al., 2007). While Cu accumulates in the tissues of several organisms as a result of exposure, the tissue concentrations are inversely proportional to the exposure concentrations (i.e., lower BCFs and BAFs at higher exposure concentrations; McGeer et al., 2003). This phenomenon is mainly due to essentiality of Cu which, in turn, leads to the strong regulation and control of Cu in aquatic organisms (Deforest et al., 2007). Homeostatic control enables aquatic organisms to establish a negative relationship between exposure and accumulation. Therefore, biomagnification of Cu does not generally occur in aquatic organisms (McGeer et al., 2003).

9.   THE BIOTIC LIGAND MODEL

The toxicity of Cu varies depending on water chemistry. However, when metal toxicity is reported as free metal ion concentrations, water chemistry plays less of a role in predicting toxicity (Meyer et al., 2007). Based on this idea, Pagenkopf (1983) developed a model, the Gill Surface Interaction Model (GSIM) that links metal speciation and toxicity to predict metal toxicity based on water chemistry. The Biotic Ligand Model (BLM) expands GSIM and predicts metal speciation, the binding capacity of available organic and inorganic compounds with various metal species, and the protective effects of competing cations to model the accumulation of the metal at a biologically sensitive receptor (i.e., biotic ligand) (Di Toro et al., 2001; Santore et al., 2001; Paquin et al., 2002; Santore et al., 2002). Therefore, the BLM can be used to predict the amount of metal accumulation at the biotic ligand (e.g., gill), which represents the site of action for metal toxicity, for a variety of water chemistry conditions and metal concentrations (Figure 9.1) (Di Toro et al., 2001; Paquin et al., 2002).
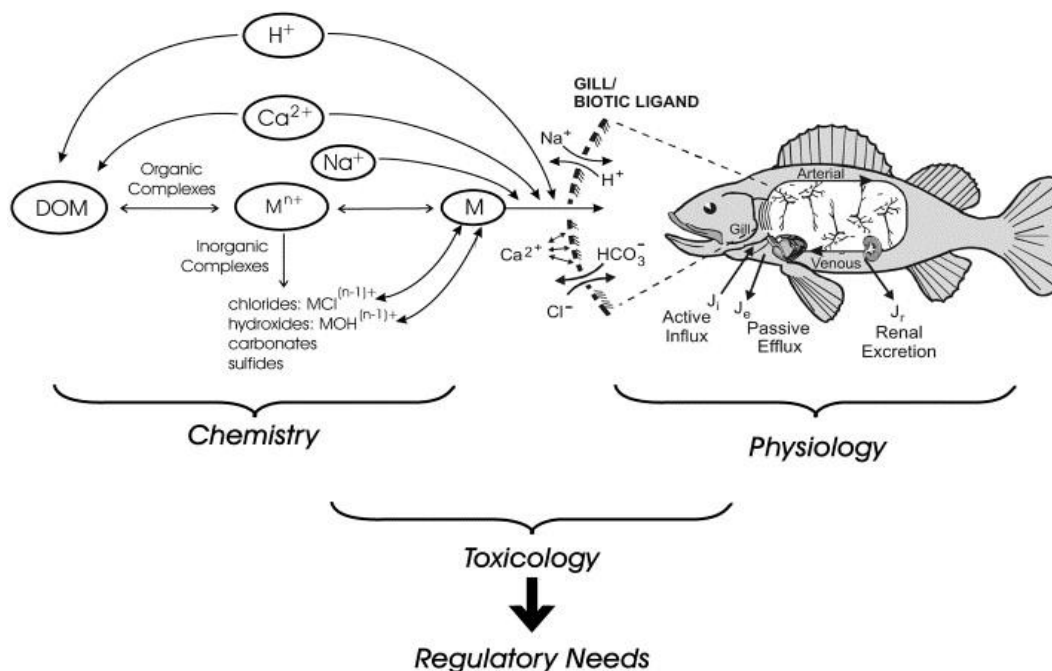
Figure 9.1. Schematic representation of the biotic ligand model. Letter "M" represents metals (reprinted with permission from Paquin et al., 2002).

According to the conceptual framework of the BLM, the accumulation of a metal at the biotic ligand at or above a critical threshold concentration leads to toxicity. Since the BLM includes inorganic and organic metal speciation and competitive complexation with the biotic ligand, it can estimate the amount of dissolved metal required to reach this threshold, depending on water chemistry. Using published information on the accumulation of Cu on a biotic ligand (i.e., gill) as a function of water chemistry, the Cu BLM was developed to establish the Cu accumulation-toxicity relationship in different water chemistry scenarios.

The relationship between Cu accumulation and toxicity was not determined for all aquatic biota, therefore, the original BLM was based largely on the lethal accumulation in fathead minnows (Playle et al., 1993) and rainbow trout (MacRae et al., 1999). However, the BLM has been shown to be a powerful tool in predicting toxicity for several fish species and invertebrates (e.g., Santore et al., 2001; Villavicencio et al., 2005; 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 plant model is capable of predicting toxicity for both algae and macrophyte in different water chemistry (Santore et al., 2019b). For both models, the predicted toxicity thresholds were compared to experimentally collected toxicity data in several studies and the results were congruent (Santore et al., 2019a-b; in prep).

The ability of BLM to predict toxicity in various water chemistry conditions can be used to normalize the toxicity data to any water chemistry which in turn can be used to calculate site-specific WQGs. The BLM is currently used to calculate the USEPA Cu Water Quality Criteria (USEPA, 2007). It should be noted, however, that since a BLM for fish is calibrated to the gill tissue, it is not necessarily predictive of Cu accumulation at other biotic ligands with different accumulation mechanisms (e.g., olfactory tissues). Therefore, it is possible that a BLM over or under estimates toxicity thresholds for olfactory ligands and therefore, its application to predict olfactory toxicity is not recommended.

10. Water Quality Guidelines from B.C. and Other Jurisdictions

Copper WQGs/criteria from seven provincial and national jurisdictions are summarized in Table 10.1. Three types of guidelines are used: a static number, an equation taking into account hardness, and BLM. In general, most of the older WQGs are hardness-based, while more recent WQGs are calculated using BLM software that considers a wider range of toxicity modifying factors. In addition, while older guidelines are for total Cu, recent guidelines use the dissolved fraction of Cu.

10.1 Previous B.C. Water Quality Guidelines for Copper

The first BC Cu WQG (ENV, 1987) used hardness-based equations to calculate both short-term and long-term WQGs. At hardness values ≤ 50 mg/L the chronic WQG was set at 2 µg/L; for hardness values above 250 mg/L the chronic WQG was 10 µg/L. For water hardnesses between 50 mg/L and 250 mg/L, the chronic WQG was calculated using an equation (Table 10.1). The acute BC WQG was also calculated using an equation for hardness values between 13 – 400 mg/L as $CaCO_3$ producing a minimum value of 3 µg/L and a maximum value of 40 µg/L.

10.2 Canadian Council of Ministers of the Environment (CCME)

The CCME develops national WQGs for the protection of aquatic life. The CCME WQG for long-term exposure to total Cu is presented as a hardness-based equation (Table 10.1). When water hardness is below 50 mg/L $CaCO_3$, the WQG is 2 µg/L (CCREM 1987). The CCME long-term hardness equation is valid for water hardness values between 50 and 180 mg/L CaCO3. At hardness concentrations greater than 180 mg/L $CaCO_3$, the long-term WQG is 4 µg/L. The CCME does not have an acute WQG for Cu.

10.3 Provincial Water Quality Guidelines

The provinces of Canada typically develop province-specific WQGs or adopt the WQG from another jurisdiction (e.g., CCME). Alberta Environment and Parks (AEP) developed a WQG for Cu and recommended a static value of 7 µg/L of Cu as the chronic value. For the acute WQG, AEP applies a hardness-based equation (AEP, 1996) (Table 10.1). AEP recommends measurement of dissolved Cu, however, in absence of clean techniques to determine dissolved Cu, measurement of acid-extractable Cu is recommended as an alternative approach.

The Ontario Ministry of Environment sets policies to manage Ontario's water resources, including providing Provincial Water Quality Objectives (PWQOs) for surface water to protect aquatic life (OMOEE, 1994). The chronic PWQO for total Cu is a static value of 5 µg/L. However, an interim PWQO was also developed: 1 µg/L for water with hardness between 0 and 20 mg/L $CaCO_3$ and 5 µg/L for water with hardness > 20 mg/L $CaCO_3$ (OMOEE, 1994).

Saskatchewan adopted the chronic CCME WQG as an interim surface water quality objective with some minor modifications (Water Security Agency, 2015). The Saskatchewan Water Security Agency used the CCME equation as the basis for developing static guideline values of 2, 3 and 4 µg/L for hardness ranges of 0-120, 120-180 and >180 mg/L $CaCO_3$, respectively.

Both Manitoba and Quebec have adopted the USEPA's previous Cu Water Quality Criteria (WQC) published in 1985 for protection of aquatic life (MDDEFP 2013; MWS, 2011).

Table 10.1. Summary of water quality guidelines from other jurisdictions.

Jurisdiction	Chronic guideline (µg/L)	Acute guideline (µg/L)	Type of guideline	Total/ Dissolved	Publication Year
CCME	when hardness<82 mg/L; 2 when 82<hardness<180 mg/L; use the equation: WQG = 0.2 x $e^{(0.8545[ln(hardness)]-1.465}$ when hardness>180 mg/L; 4	NA	Hardness based	Total	1987
USEPA	Calculated using BLM	Calculated using BLM	Bioavailability based	Dissolved	2007
Australia/ New Zealand	NA	a* x TV*(hardness/30)$^{0.85}$	Based on hardness and intended level of protection	Dissolved	2000
European Union	Recommended application of BLM	NA	Bioavailability based	Dissolved	2009
Alberta	7	$e^{0.979123*ln(hardness)-8.64497}$ x 1000	Hardness based	Dissolved	1996
British Columbia (1987)	When hardness≤50 mg/L; 2 When hardness > 50 mg/L; use the equation: WQG= 0.04 x (mean hardness in mg/L)	0.094 x (hardness) + 2	Hardness based	Total	1987
Ontario	5	NA	Hardness based	Total	1994

TV*: trigger value varies depending on intended level of protection.
a*: constant varies based on hardness.

10.4 USEPA Water Quality Criteria

The USEPA develops acute (i.e., short-term) and chronic (i.e., long-term) national WQC for the protection of aquatic life based on dissolved metal concentrations (USEPA 2007). The USEPA currently recommends a bioavailability modeling approach to calculate WQCs. The BLM software used by USEPA criterion requires several water chemistry parameters, such as DOC, pH, temperature, and ion concentrations, to calculate final acute values, which are used to calculate Criterion Maximum Concentrations (CMC) and Criterion Continuous Concentrations (CCC) (USEPA, 2007).

10.5 Australia and New Zealand

Australia and New Zealand have joint WQGs described as trigger values (TGVs) that trigger a response if exceeded (ANZECC 2000a; 2000b). Although four TGVs have been calculated to provide various levels of protection (i.e., 80-99% of species), ANZECC (2000a) recommends application of the 80%, 95% and 99% protection levels for protection of highly disturbed ecosystems, slightly-moderately disturbed ecosystems, and high conservation/ecological value ecosystems, respectively (ANZECC, 2000a). As an example, to protect 95% of aquatic life, ANZECC (2000a; 2000b) has developed a trigger value for Cu of 1.4 µg/L for waters with a hardness of 30 mg/L $CaCO_3$. The Cu trigger value can be adjusted using site-specific water hardness and then be used in the equation presented in Table 10.1.

10.6 European Union

The European Union does not consider Cu a substance of priority and therefore does not have a European Environmental Quality Standard (EQS) for Cu (European Commission, 2000; 2008; 2013). Substances that are considered a concern at the national level are termed "River-Basin-Specific Pollutants" and Member States are responsible for developing specific national EQSs (European Commission 2008). The European Copper Institute, however, submitted a voluntary report on risk assessment that was reviewed and supported by the European Scientific Committee on Health and Environmental Risks (European Commission, 2009). This report supports the application of BLMs in developing EQS for Cu.

11. DERIVATION OF COPPER WATER QUALITY GUIDELINES

11.1 Acquisition, Evaluation and Classification of Toxicological Data

The current scientific literature on Cu toxicity to freshwater aquatic organisms was searched using Google Scholar and USEPA ECOTOX producing a total of 850 studies. Only studies on B.C. species (both indigenous and exotic species) were selected for classification to ensure the resultant WQG is highly representative of BC ecosystems. 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 (ENV, 2012).

Selected studies were further evaluated to ensure that only those studies that were scientifically sound and of high-quality 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 classified as primary, secondary or unacceptable based on the criteria listed below.

To be considered as primary data, studies must have included the following:

- Cu concentrations measured and reported at the beginning and end of the exposure period, at a minimum;

- Flow-through or renewal test, unless a static test included evidence that Cu concentrations did not change, and environmental conditions were acceptable throughout the test;

- Two or more replicate test chambers per concentration;

- Ecologically relevant endpoints (i.e., related to growth, reproduction, hatching success, or survival);

- Acceptable negative control performance reported (less than 10% mortality for short-term [96-hour] tests and less than the American Society for Testing and Materials (ASTM) test acceptability criteria for long-term exposures);

- Measurements of water temperature, pH, dissolved oxygen, DOC and water hardness reported and acceptable (e.g., dissolved oxygen meets the requirements in ASTM E729 for short-term tests [ASTM, 2012]); and,

- Appropriate statistical analyses were applied.

Guidance for secondary data includes:

- Calculated (vs. measured) concentrations of Cu in exposure chambers are acceptable;

- Static (non-renewal) tests are acceptable;

- Broader array of endpoints is acceptable, though endpoints need to be ecologically relevant (e.g., time for metamorphosis); and,

- Must meet the same requirements for negative control performance, water quality measurements, and statistical analyses as primary data sets. However, if the source of water used in the study is specified, the data is considered secondary despite the lack of data on DOC which is estimated (see Section 11.4.1);

If any of the conditions for primary or secondary data were not met, the data were given a ranking of unacceptable (ENV, 2012). A summary of all short-term and long-term primary and secondary data is provided in Appendix 1, as well as a list of the studies that were classified as unacceptable.

11.2 Grouping of Data Points to Acute and Chronic

The classification of data points as chronic long-term or acute short-term was conducted in accordance with published protocols (ENV, 2012; CCME, 2007). Toxicity tests of 96 hours or less using acute endpoints (e.g., mortality) were considered to be acute short-term studies. The exception to this was studies using organisms with short life cycles, such as algae, where exposure periods as short as 24 hours may be considered to be long-term chronic (CCME, 2007).

To be considered for the chronic data set, experiments had to meet the criteria specified for fish and invertebrates in the CCME protocol (CCME, 2007). Although, sub-lethal endpoints (e.g., growth and inhibition) were preferred in the chronic data set, survival data were used when chronic endpoints were not available for a given species.

11.3 Distribution of Toxicity Studies Between Taxonomic Groups

In total, 59 studies were classified as primary, 64 as secondary, and 196 as unacceptable (Table 11.1). 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. Some studies investigated both acute and chronic effects and therefore included both acute and chronic data points. In addition, some studies investigated the toxic effects of Cu on species belonging to more than one taxonomic group (Table 11.1). Table 11.2 provides a list of all aquatic species represented in the toxicity database compiled for guideline preparation.

As mentioned in Section 11.1, only studies on B.C. species were used to populate the database. However, considering the limited number of studies on algae, macrophytes and amphibians, a second literature review was conducted to include species resident to Canada or Western USA to increase the number of data points in theses taxonomic groups. However, no additional acceptable data points were found.

While toxicological data from both primary and secondary studies were considered in the development of this technical report, only primary studies were used to derive the short-term acute and long-term chronic WQGs, given the abundance of primary data. Descriptions of the distribution of primary and secondary data within each taxonomic group are provided in the following sections.

Table 11.1. Distribution of primary and secondary data points between different taxonomic groups.

Primary						
Taxonomic group	Total number of studies	Acute data points	Chronic data points			
			Total	Growth	Reproduction	Survival
Algae	4	NA*	110	110	0	0
Macrophytes	1	NA*	8	8	0	0
Aquatic invertebrates	33	255	111	4	95	12
Fish	27	245	25	11	0	14
Amphibians	0	0	0	0	0	0
Total	59**	498	254	133	95	26
Secondary						
Taxonomic group	Total number of studies	Acute data points	Chronic data points			
			Total	Growth	Reproduction	Survival
Algae	1	NA*	24	24	0	0
Macrophytes	0	NA*	0	0	0	0
Aquatic invertebrates	31	145	21	2	10	9
Fish	27	85	14	7	2	5
Amphibians	7	4	4	3	0	1
Total	64**	232	63	36	12	15

*: no data point was considered as acute for algae and macrophytes.
**: the total numbers of studies do not match with summation of studies for each taxonomic group as some papers investigated species belonging to more than one taxonomic group.

Table 11.2. List of aquatic species included in the toxicity data set.

Taxonomic Group	Common Name	Species	Primary/Secondary
Algae	Green Alga	*Chlamydomonas reinhardtii*	P
	Green Alga	*Chlorella* sp.	P & S
	Green Alga	*Chlorella vulgaris*	P
	Microalga	*Pseudokirchneriella subcapita*	P & S
Macrophytes	Duckweed	*Lemna minor*	P
Aquatic invertebrates	Amphipod	*Hyalella azteca*	P & S
	Caddisfly	*Clistoronia magnifica*	S
	Cladoceran	*Acantholeberis curvirostris*	P
	Cladoceran	*Acroperus harpae*	P
	Cladoceran	*Alona quadrangularis*	P
	Cladoceran	*Bosmina longirostris*	P
	Cladoceran	*Ceriodaphnia dubia*	P & S
	Cladoceran	*Ceriodaphnia pulchella*	P & S
	Cladoceran	*Ceriodaphnia reticulate*	P & S
	Cladoceran	*Chydorus sphaericus*	P & S
	Cladoceran	*Daphnia ambigua*	P & S
	Cladoceran	*Daphnia magna*	P & S
	Cladoceran	*Daphnia pulex*	S
	Cladoceran	*Daphnia similis*	S
	Cladoceran	*Diaphanosoma brachyurum*	S
	Fatmucket Clam	*Lampsilis siliquoidea*	P & S
	Great Pond Snail	*Lymnaea stagnalis*	P & S
	Mayfly	*Rhithrogena hageni*	S
	Rotifer	*Brachionus calyciflorus*	P
	Oligochaete	*Lumbriculus variegatus*	S
	Oligochaete	*Tubifex tubifex*	S
	Pebblesnail	*Fluminicola sp*	P
Fish	Arctic Grayling	*Thymallus arcticus*	S
	Bluegill	*Lepomis macrochirus*	P & S
	Brook Trout	*Salvelinus fontinalis*	S
	Bull Trout	*Salvelinus confluentus*	P
	Chinook Salmon	*Oncorhynchus tshawytscha*	P & S
	Chiselmouth	*Acrocheilus alutaceus*	P
	Coho Salmon	*Oncorhynchus kisutch*	P & S
	Common Carp	*Cyprinus carpio*	S
	Cutthroat Trout	*Oncorhynchus clarkii*, formerly *Salmo clarkii*	P
	Fathead Minnow	*Pimephales promelas*	P & S
	Mottled Sculpin	*Cottus bairdii*	P
	Northern Pikeminnow	*Ptychocheilus oregonensis*	S
	Pacific Lamprey	*Entosphenus tridentatus* formerly *Lampetra tridentata*	P
	Pink Salmon	*Oncorhynchus gorbuscha*	S

Table 11.2. Continued.

Taxonomic Group	Common Name	Species	Primary/Secondary
Fish	Rainbow Trout	*Oncorhynchus mykiss* formerly *Salmo gairdneri*	P & S
	Sockeye Salmon	*Oncorhynchus nerka*	P
	Threespine Stickleback	*Gasterosteus aculeatus*	S
	White Sturgeon	*Acipenser transmontanus*	P
	Yellow Perch	*Perca flavescens*	P
Amphibians	American Bullfrog	*Rana catesbeiana*	S
	Green Frog	*Rana clamitans*	S
	Northern Leopard Frog	*Rana pipiens*	S
	Western Toad	*Anaxyrus boreas*	S
	Wood Frog	*Rana sylvatica*	S

11.3.1   *Algae*

The majority of algae studies were classified as unacceptable because of missing water chemistry data (see Appendix 1, Tab 5). In total, 110 primary and 24 secondary chronic data points were collected from four primary studies and one secondary study, all on growth inhibition. The final database is populated by three algae species (Table 11.2).

11.3.2   *Macrophytes*

Despite the availability of numerous Cu toxicity studies on B.C. freshwater macrophytes, most were not acceptable due to a lack of reported water chemistry data. Only one study was classified as primary, which contained eight chronic data points on growth (root length) (Table 11.2; Appendix 1, Tab 3).

11.3.3   *Aquatic Invertebrates*

In total, 33 studies on aquatic invertebrates were classified as primary and 33 as secondary. These studies included data on 22 aquatic invertebrate species. *D. magna* and *C. dubia* are the most studied aquatic invertebrate species for Cu toxicity. A total of 534 data points on aquatic invertebrates are included in the database (Table 11.1).

11.3.4   *Fish*

Copper toxicity has been studied on 19 freshwater and anadromous fish species found in B.C. While primary data was found on 13 fish species of B.C., 6 species had only secondary data. Rainbow trout is the most commonly used species in Cu toxicity studies (Chakoumakos et al., 1979; Cusimano et al., 1986; Welsh et al. 1993; Naddy et al., 2002; Grosell, 2012; Price, 2013; Calfee et al., 2014).

11.3.5   *Amphibians*

Copper toxicity has been studied in five of the 22 species of amphibians found in B.C. (Table 11.2). All amphibian data points were classified as secondary studies with four acute (96-hour LC_{50}) data points and four chronic data points on growth and survival (Table 11.1; Appendix 1, tabs 2 and 4).

11.4 BC BLM

Software is necessary to run the BLM model and calculate a WQG for a specific set of water chemistry conditions. The BC BLM software is available at: BC BLM. A User's Manual accompanies the software (ENV, 2019). The BLM software allows users to enter water chemistry conditions and provides a guideline value specific to the input water chemistry. The software that accompanies this guideline was developed by Windward Environmental Ltd. from published information on Cu toxicity and accumulation of Cu on biotic ligands as a function of water chemistry and follows the ENV derivation protocol (ENV, 2012) to calculate WQGs specific to BC waterbodies.

Although the BC BLM software is based on the BLM Windows® Interface created by Windward Environmental Ltd.[1], it has several unique features. The BC BLM software allows the user to calculate either a chronic or acute guideline based on the underlying toxicity databases. Using the acute or chronic database, the BC BLM software first calculates a critical accumulation value and then normalizes this value to the water chemistry conditions specified in the input data. The normalized acute or chronic dataset of critical accumulations values is then used to identify the most sensitive endpoint of the most sensitive organism at the most sensitive life stage (see Figure 11.1). Other features of BC BLM is discussed in the following sections.
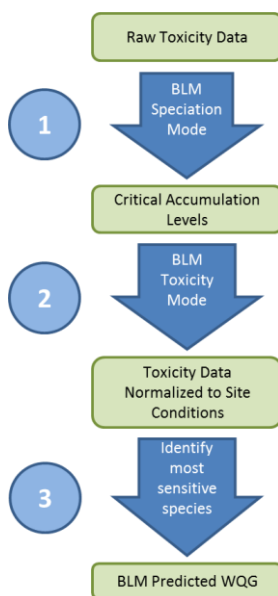
Figure 11.1 Steps and calculations involved in the BLM calculation of a WQG from the toxicity database.

11.4.1   *Estimating Water Quality Conditions from Laboratory Studies*

A minimum set of water chemistry data is needed to normalize toxicity values using the BC BLM. In some cases, toxicity studies lacked information on one or more water chemistry factors. For example, there were cases in which a primary or secondary study reported hardness but not the concentrations of individual ions. To include as much toxicity data as possible in the database, missing water chemistry data were estimated. The following rules were used to estimate concentrations of missing parameters:

- DOC
  - If the test took place in reconstituted water without natural organic matter (NOM) added, the DOC was assumed to be 0.3 mg C/L (USEPA, 2007).

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[1] Available at: http://www.windwardenv.com/biotic-ligand-model/

- o If TOC was reported instead of DOC, it was assumed all TOC was dissolved and was used directly as the measure of DOC.
- Humic Acid
  - o If percent humic acid (%HA) was not reported or able to be inferred from the type of NOM added (e.g., Aldrich humic acid), HA was assumed to be 10% for natural waters and reconstituted water with added NOM, and 1% for reconstituted water without NOM added.
- Alkalinity
  - o Alkalinity is estimated from pH, assuming an open system in equilibrium with atmospheric CO_2. The pCO_2 (negative logarithm of the ambient atmospheric CO_2 concentration) is also required. In most natural settings, it is reasonable to assume a CO_2 concentration of $10^{-3.1}$ atmospheres (pCO_2 of 3.1), therefore the default pCO_2 is set at 3.1.
- Major ions
  - o If only one ion was missing, an attempt was made to calculate a non-negative concentration so that the charge balance of H, OH, Ca, Mg, Na, K, SO_4, Cl, CO_3, and HCO_3 equaled 0 (after the estimation of alkalinity, if needed).
  - o If it was not possible to obtain a non-negative concentration by charge balance, the test water description was used to estimate ion ratios.
  - o Several studies used water from Great Lakes for their exposure water without reporting the exact ion ratios. For those studies, ion ratios for the Great Lakes were obtained from Chapra et al. (2012) for 1970 and 2009. The ratios for the closest date to the study in question were used.
  - o Ion ratios for reconstituted water were calculated based on the reconstitution recipe where a standard medium, such as EPA or ASTM water, was used.
  - o Where the ion ratios were not available, the North American median ion ratios were used (Ca:Mg = 1.99, Ca:Na = 1.08, Ca:K = 11.96, SO4:Cl = 0.57) (Windward Environmental, 2017) for both reconstituted and natural test waters.
- Cu
  - o If the effect concentration was reported as total Cu, a conversion factor of 0.96 was used to estimate dissolved Cu (Stephan, 1995).

11.4.2 *Water Chemistry Input Necessary for BC BLM*

There are 11 essential water chemistry parameters needed to calculate WQGs using the BC BLM software: temperature, pH, DOC, the humic acid ratio of DOC, alkalinity, Ca, Mg, Na, K, SO_4, and Cl. Some of the water chemistry parameters (i.e., pH, DOC, Ca, Mg, Na and alkalinity) have an important effect on BC BLM predictions, while others have only minor effects.

To overcome the fact that not all of these parameters are routinely measured, a simplified version of the BC BLM was included in the software and requires only four water chemistry parameters: temperature, DOC, pH, and hardness. The remaining seven parameters are estimated, however, due to the variability of natural waters, an accurate estimate of all parameters is not always possible. Therefore, a conservative approach to estimating water chemistry parameters has been taken.

The BC BLM simplified version estimates the humic acid content based on the methods described in Section 11.4.1. As described in Section 7, the toxicity modifying effect of alkalinity is different for plants and animals. Therefore, different pCO_2 values for plants and animals (3.0 and 3.2 respectively) are used to estimate alkalinity values protective of both groups which, in turn, ensures that the WQGs produced by the simplified BLM are protective of all species.

Estimates of the remaining water chemistry parameters are based on the following median molar ion ratios calculated from the minimally impacted water bodies described in Section 6:

- Ca:Mg - 3.33
- Ca:Na - 3.30
- Ca:K - 23.51
- SO_4:Cl - 3.86

11.4.3 *Steps to calculating the chronic and acute guideline*

The ENV WQG derivation protocol (ENV, 2012) specifies the process for WQG derivation. If two or more data points on the same species (e.g., rainbow trout), same life stage (e.g., larvae), same effect level (e.g., EC_{10}), and the same endpoint (e.g., growth) are available, BC BLM software replaces the effect concentrations with their geometric mean. Effect concentrations, or geometric means, are then sorted by sensitivity and the most sensitive primary data point is used as the basis for the guideline. Since the modifying effects of different water chemistry factors vary between animals and plants (Section 7), the order of sensitivity may be different under various water chemistry scenarios. Therefore, the most sensitive species may be different when water chemistry conditions differ.

The ENV protocol (2012) recommends the application of an uncertainty factor between two and 10, dependent upon data quality and quantity. The uncertainty factor is used to account for uncertainties including laboratory to field differences, single to multiple contaminants, intra- and inter-species differences, and indirect, delayed and cumulative effects. Considering the large number of data points, sensitivity of endpoints and low potential of Cu for bioaccumulation, an uncertainty factor of two is used in the calculation of both chronic and acute guidelines. The BC BLM rounds the WQG values to the nearest tenth for simplicity of application.

In most cases, the toxicological data included in the database were regression-based estimates (e.g., EC_{25}) with an associated source of error around the parameter estimate (confidence intervals). Caution should be exercised when the confidence intervals around the endpoint estimate are relatively large, since its application may result in under-protection. To address this risk, the BC BLM software compares the lower confidence interval of the lowest effect concentration with the effect concentration after application of the uncertainty factor and returns the lower value as the guideline. Figures 11.1 and 11.2 show the flowcharts used for calculation of chronic and acute guidelines, respectively.
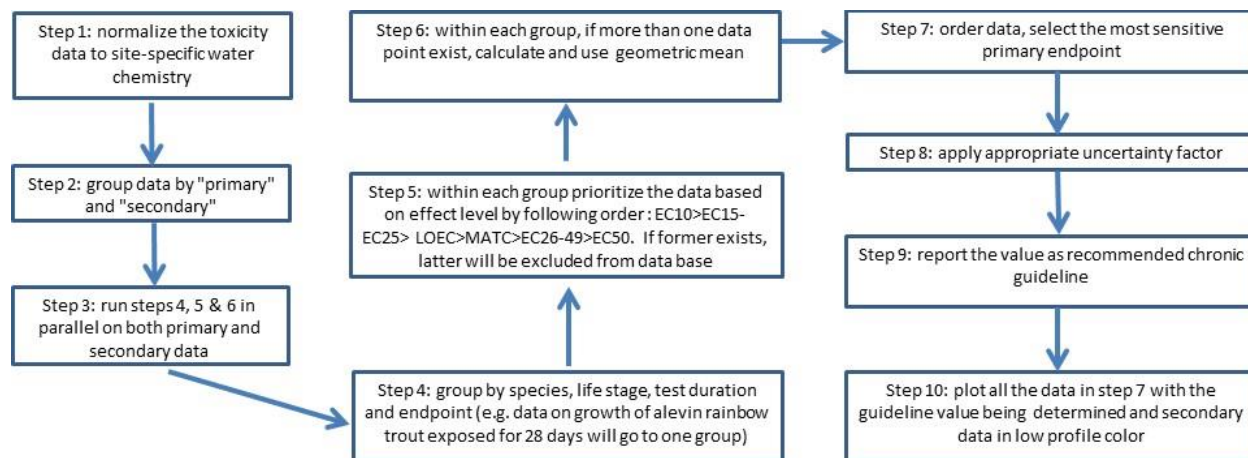
Figure 11.2. The methodology used for calculation of chronic guideline values.
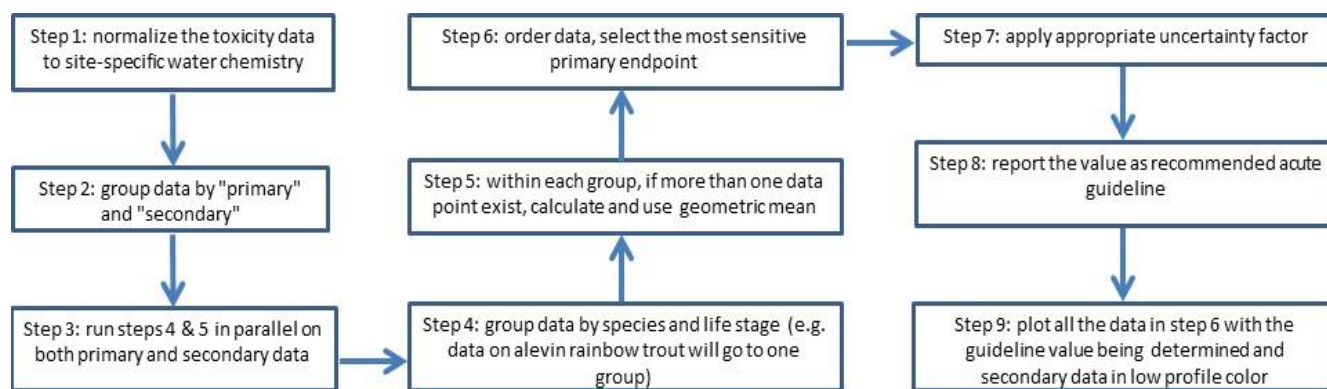
Figure 11.3. The methodology used for calculation of acute guideline values.

12. COMPARISON OF NORMALIZED EFFECT CONCENTRATIONS

In this section, the sensitivity of aquatic organisms is compared within each taxonomic group. Since Cu toxicity is dependent on water chemistry factors (see Section 7), toxicity data were normalized to a standard water chemistry using the BC BLM (see Section 11.4) to allow comparisons across studies. Although the relative sensitivity of aquatic organisms may change in different water chemistry conditions (Section 11.4.3), this direct comparison gives some indication of relative sensitivity. Toxicity data were normalized to the following water chemistry conditions:

- Temperature: 15 °C
- pH: 7
- DOC: 5 mg/L
- Hardness: 100 mg/L $CaCO_3$

The acute and chronic databases were normalized separately. The normalized data for each taxonomic group are presented in following subsections, with the exception of algae and macrophytes, which are presented together. Each point represents a single effect concentration or the geometric mean of the data when multiple data points occurred for the same species, life stage, effect level, and endpoint (section 11.4.3).

12.1 Aquatic plants

Figure 12.1 includes effect concentrations for both macrophyte and algae after chronic exposure to Cu. All data are for growth related experiments. The most sensitive aquatic plant was *L. minor*, with a normalized EC_{20} of 23.8 µg/L (Figure 12.1).[1]

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[1] EC_{20}s were calculated from raw data and the geometric mean of the four data points were calculated after normalization to standard water chemistry.
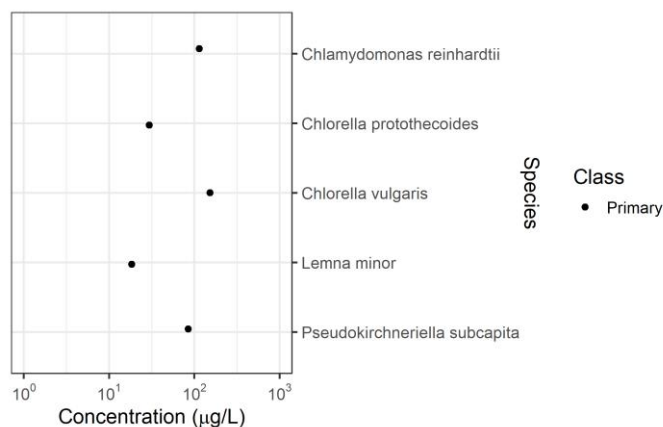
Figure 12.1. Relative sensitivity of freshwater algae and macrophytes to chronic exposure to Cu.

12.2 Aquatic invertebrates

After normalization, the most sensitive invertebrate to acute Cu exposure was great pond snail (*L. stanglis*) (96-hour LC_{50} of 15.4 µg/L). The least sensitive aquatic invertebrates to acute Cu exposure were *T. tubifex* (worm) and *R. hageni* (mayfly), with normalized effect concentrations of 476.4 µg/L and 434.9 µg/L, respectively.

The most sensitive chronic endpoint was for growth of newly hatched *L. stagnalis* (EC_{20} of 1.8 µg/L) (Figure 12.2B), which was also the most sensitive primary chronic effect concentration between all groups of organisms after normalization to the standard water chemistry.
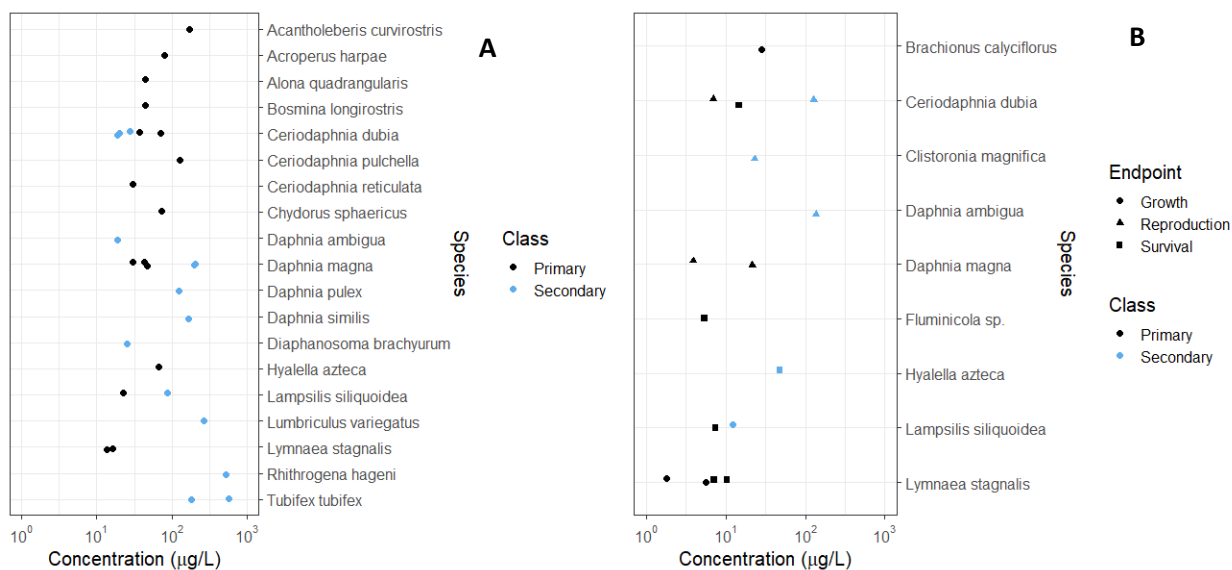
Figure 12.2. Relative sensitivity of aquatic invertebrates to acute (A) and chronic (B) exposure to Cu.

12.3 Fish

White sturgeon (*A. transmontanus*) was the most sensitive B.C. fish species to acute Cu exposure. The lowest normalized 96-hour LC_{50} was 11.0 µg/L and is classified as primary data point (Figure 12.3.A). This data point is also the lowest acute effect concentration across all taxonomical groups after

normalization to the standard water chemistry. The least Cu-sensitive B.C. fish species in the database was the Bluegill (*L. macrochirus*) (normalized LC_{50} of 984.1 µg/L).

The lowest effect concentration reported for chronic Cu exposures was for white sturgeon (growth EC_{20} of 5.6 µg/L) (Figure 12.3.B). This data point was classified as primary.

12.4 Amphibians

The number of studies on amphibians living in B.C. waters is limited and all are classified as secondary. The most sensitive amphibian to acute Cu exposure is green frog (*R. clamitans*) with the normalized 96-hour LC_{50} of 192.8 µg/L. American bullfrog (*R. catesbeiana*) is the least sensitive amphibian included in the BC BLM acute database with LC_{50} geometric mean of 1790.0 µg/L (Figure 12.4.A).

The lowest chronic effect concentration included in the database is for growth of northern leopard frog (*R. pipiens*) (normalized LOEC of 31.9 µg/L) (Figure 12.4.B).
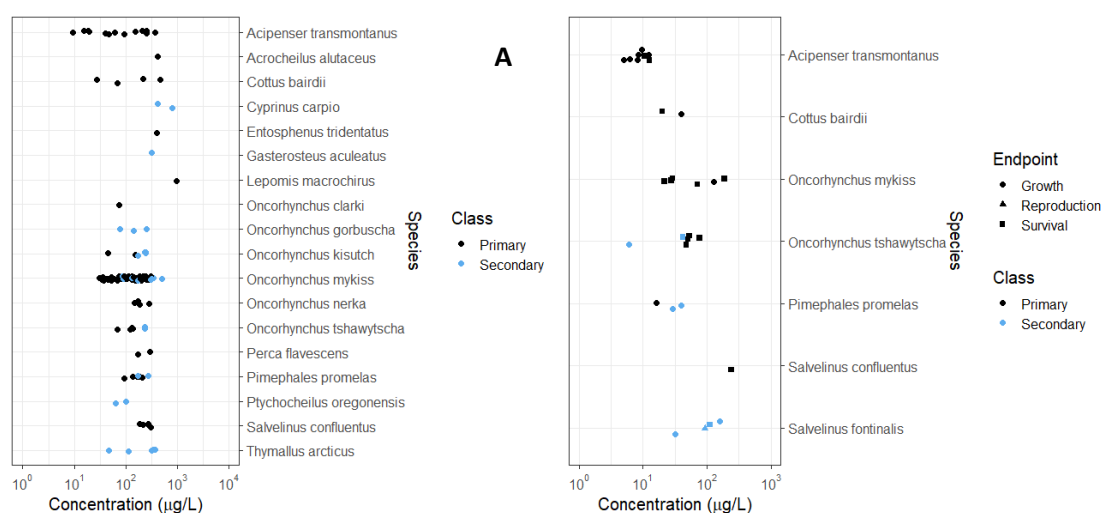
Figure 12.3. Relative sensitivity of fish to acute (A) and chronic (B) exposure to Cu.
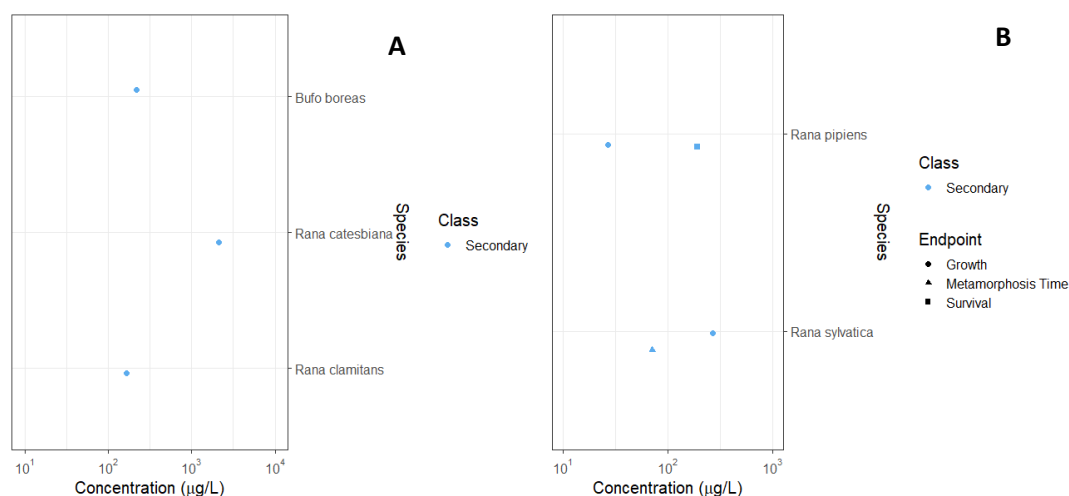
Figure 12.4. Relative sensitivity of amphibians to acute (A) and chronic (B) exposure to Cu.

13. PROTECTIVENESS OF BC BLM AGAINST SHORT-TERM AND LONG-TERM EFFECTS

13.1 Copper-Induced Olfactory Impairment

The BLM is designed to consider the water chemistry factors that protect gill tissue against Cu toxicity; however, those water chemistry parameters do not necessarily have the same protective effects on other biotic ligands, such as olfactory tissues (see sections 7 and 8). Considering the essentiality of olfaction for fish, it was necessary to determine if the WQGs produced by the BC BLM would also be protective against olfactory impairment. To test this, an olfactory toxicity database consisting of 64 data points was collated using a subset of the toxicity data presented in Meyer and Deforest (2018) (i.e. only data on chemosensation and olfactory mediated behaviours), and Lari et al., (2019). Depending on the exposure time of the experiment, chronic (exposures > 7 d) or acute (for exposures < 7 d) WQGs were calculated using the BC BLM with the water chemistry used in the corresponding laboratory test. The low-effect concentrations (with the following priority: $IC_{20} > LOEC$) and the calculated guidelines (chronic and acute) were then compared to check for protectiveness of BC BLM against olfactory toxicity (Appendix 1, Tab 6). The BC BLM WQGs were lower compared to the reported effect concentration in all cases, which demonstrated the protectiveness of BC BLM. However, the currently available olfactory toxicity data are from experiments conducted in normal ambient water chemistry. The protectiveness of BC BLM against olfactory impairment in extreme water chemistry (e.g., extremely high pH, Ca and DOC) has yet to be tested. Thus, application of the BC BLM is only recommended within the bounds that have been tested (see Section 13.3 below).

13.2 Protectiveness of BC BLM Acute Guidelines Against Short-term Effects on Survival

The WQG derivation protocol characterizes the protection of aquatic life by the protection of individual organisms, which results in the overall protection of populations (ENV, 2012). However, the most abundant effect level in short-term toxicity studies is the LC_{50} (i.e., the concentration that caused lethality to half of the test population). Although the addition of an uncertainty factor will offer further protection, acute WQGs that are derived based on LC_{50}s may not protect the whole population of the sensitive species. To test this, the acute WQG was compared against no effect concentrations for the sensitive species.

To determine if the acute WQG calculated by BC BLM is protective of the most sensitive organism at the most sensitive life stage, normalized LC_{10} values for the five lowest effect concentrations (belonging to white sturgeon and great pond snail) were compared against the acute WQG (Table 13.1). The LC_{10} values are generally considered as no-effect thresholds (CCME, 2007). White sturgeon was the most sensitive species to short-term Cu exposure (Little et al., 2012), with a normalized (see Section 12) primary LC_{50} of 11 µg/L. This value was used to derive a short-term acute WQG of 5.5 µg/L after the application of an uncertainty factor of two. Note that for the great pond snail study (Ng et al. 2011), LC_{10} values were not included and could not be calculated due to insufficient data; however, it was possible to calculate an LC_{20} using the data presented in the study, which is presented in Table 13.1.

The ratio of the acute WQG to the LC_{10} (or LC_{20}) was calculated for each study. Values <1.00 demonstrate that the acute WQG is lower and protective of that species at the specified life stage. The degree of protection increases with decreasing ratios. The ratios ranged from 0.45 to 0.9, demonstrating that the acute WQG would be protective of sensitive species against short-term effects on survival.

Table 13.1. Normalized effect concentrations of the most sensitive endpoints and their ratio to acute WQG.

Species	LC_{50} (µg/L)	Normalized LC_{50} (µg/L)	LC_{10} or LC_{20} (µg/L)	Normalized LC_{10} / LC_{20} (µg/L)	Acute WQG/ LC_{10} or LC_{20}	Reference
White Sturgeon (26 DPH)	4.5	11	2.5*	6.1	0.90	Little et al., 2012
White Sturgeon (15 DPH)	10	13.9	8.7*	12.1	0.45	Vardy et al., 2013
Great Pond Snail (Juvenile)	24.9	15.4	18.0**	11.1	0.49	Ng et al., 2011
Great Pond Snail (7 DPH)	30.7	15.7	22.5	11.4	0.48	Brix et al., 2011
White Sturgeon (40 DPH) †	4.7 9 18	23.68 12.44 21.49 18.5**	2.9 1.9 5.1	14.6 2.6 6.1 6.2**	0.89†	(Little et al., 2012) (Vardy et al., 2013) (Vardy et al., 2014)

* LC_{10} calculated from the data presented in the study.

** LC_{20} calculated from the data presented in the study.

† Geometric mean of three effect concentrations from three studies.

13.3 Model bounds

The BC BLM software was developed and calibrated for a range of values for each essential water chemistry parameter (e.g. pH, DOC, or hardness cations). For each parameter, the minimum and maximum reported values in the chronic and acute toxicity studies used to validate the BLM models were compiled (Santore et al., 2019 *in press*). The upper bounds of the model for the main toxicity modifying factors (i.e., pH, DOC, Alkalinity, Ca, Mg, Na and Cl; Section 11.4.2) have been set to the bounds of current available olfactory toxicity data compiled from Meyer and Deforest (2018) and Lari et al., (2019) (see Section 13.1). This method ensures that the vital and sensitive sense of smell in fish is also protected whenever BC BLM is used.

Table 13.2 lists the lower and upper bounds of each water chemistry factor for the BC BLM software. If a water chemistry value is outside of this range, the software substitutes the minimum or maximum value before normalizing the data since it is only within those bounds that the protectiveness of the WQGs calculated by BC BLM has been shown.

Table 13.2. Model bounds for the BC BLM.

Bounds	Temp (°C)	pH	DOC (mg/L)	Humic acid content (%)	Alkalinity (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO_4 (mg/L)	Cl (mg/L)	Hardness (mg/L)
Min	5.5	4.7	0.05	0.1	3.0	2.2	0.58	0.86	0.59	0.5	0.2	7.9**
Max	27	9.0	20.0*	99	160*	72.94*	18.4*	70.97*	156	1320	119.83	236.8**

*: the maximum bounds taken from water chemistry conditions associated with olfactory toxicity tests.

**: hardness minimum and maximum bounds considering the default B.C. Ca:Mg ratio.

The BC BLM calculates the WQGs based on the normalization of toxicity data to the specific water chemistry used in the test. There are situations where Cu bioavailability is very high (e.g., low DOC) and the calculated WQGs are extremely low. However, in practice, such low Cu concentrations may not be detectable using routine analytical methods. The lowest PQL for Cu using the current analytical methods (i.e., ICP-MS; see Section 5) is 0.2 µg/L. Therefore, in situations where either the chronic or acute WQGs are calculated below 0.2 µg/L, the software provides a WQG value of 0.2 µg/L.

14. LONG-TERM CHRONIC AND SHORT-TERM ACUTE WATER QUALITY GUIDELINES

The Cu toxicity database developed for this WQG meets the minimum requirements for the derivation of "full" chronic and acute WQGs (ENV, 2012). However, considering the novelty of the BLM approach and the anticipated challenges associated with its application, after five years, the updated Cu WQGs may be reviewed in consideration of new data and feedback received.

14.1 Examples of Copper Water Quality Guidelines in Various Water Chemistry

As the Cu WQGs are determined in relation to water chemistry conditions, values under various water chemistry scenarios are presented to provide a sense of the range in Cu WQGs. Commonly used ranges and the selected median values for hardness, DOC, and pH are presented in Table 14.1. The maximum hardness value accepted by the BC BLM is 236.8 mg/L, therefore this value was selected as the median of the very hard class. Since the effect of temperature on determining Cu WQGs is minor, a constant temperature (15° C) was considered for all scenarios. Using the BC BLM, both chronic and acute WQGs were calculated for the resultant 48 water chemistry scenarios (Table 14.2).

Table 14.1. Water quality parameters, their range and selected value for assumptive water chemistry scenarios.

Parameter	Classification	Range	Median
Hardness	Soft	0 to <60 mg/L	30
	Medium	60 to <120 mg/L	90
	Hard	120 to < 180 mg/L	150
	Very hard	≥180 mg/L	236.8
DOC	Extremely Low	0 to <1 mg/L	0.5
	Low	1 to <5 mg /L	3
	Moderate	5 to <10 mg/L	7.5
	High	DOC ≥10	15
pH	Acidic	6.5	6
	Neutral	6.5 to <7.5	7
	Basic	≥7.5	8

Table 14.2. Examples of chronic and acute WQGs calculated for B.C. waters.

Water Chemistry			Hardness (mg/L)	DOC (mg/L)	pH	Chronic WQG (µg/L)	Acute WQG (µg/L)
Hardness	DOC	pH					
Soft	Extremely Low	Acidic	30	0.5	6	0.2	0.2
Soft	Extremely Low	Neutral	30	0.5	7	0.2	0.4
Soft	Extremely Low	Basic	30	0.5	8	0.2	1.2
Soft	Low	Acidic	30	3.0	6	0.2	0.3
Soft	Low	Neutral	30	3.0	7	0.4	2.3
Soft	Low	Basic	30	3.0	8	1.2	7.3
Soft	Moderate	Acidic	30	7.5	6	0.2	0.7
Soft	Moderate	Neutral	30	7.5	7	0.9	5.9
Soft	Moderate	Basic	30	7.5	8	3.0	18.2
Soft	High	Acidic	30	15	6	0.2	1.4
Soft	High	Neutral	30	15	7	1.9	11.7
Soft	High	Basic	30	15	8	6.1	36.1
Medium	Extremely Low	Acidic	90	0.5	6	0.2	0.2
Medium	Extremely Low	Neutral	90	0.5	7	0.2	0.5
Medium	Extremely Low	Basic	90	0.5	8	0.3	1.7
Medium	Low	Acidic	90	3.0	6	0.2	0.4
Medium	Low	Neutral	90	3.0	7	0.5	3.2
Medium	Low	Basic	90	3.0	8	1.7	9.9
Medium	Moderate	Acidic	90	7.5	6	0.2	1.1
Medium	Moderate	Neutral	90	7.5	7	1.3	8.0
Medium	Moderate	Basic	90	7.5	8	4.1	24.5
Medium	High	Acidic	90	15	6	0.3	2.1
Medium	High	Neutral	90	15	7	2.6	16
Medium	High	Basic	90	15	8	8.2	48.6
Hard	Extremely Low	Acidic	150	0.5	6	0.2	0.2
Hard	Extremely Low	Neutral	150	0.5	7	0.2	0.6
Hard	Extremely Low	Basic	150	0.5	8	0.3	2.0
Hard	Low	Acidic	150	3.0	6	0.2	0.5
Hard	Low	Neutral	150	3.0	7	0.6	3.7
Hard	Low	Basic	150	3.0	8	2.0	11.4

Table. 14.2. Continued.

Water Chemistry			Hardness (mg/L)	DOC (mg/L)	pH	Chronic WQG (µg/L)	Acute WQG (µg/L)
Hardness	DOC	pH					
Hard	Moderate	Acidic	150	7.5	6	0.2	1.3
Hard	Moderate	Neutral	150	7.5	7	1.5	9.3
Hard	Moderate	Basic	150	7.5	8	4.9	28.3
Hard	High	Acidic	150	15	6	0.4	2.7
Hard	High	Neutral	150	15	7	3.1	18.7
Hard	High	Basic	150	15	8	9.6	56.3
Very hard	Extremely Low	Acidic	236.8	0.5	6	0.2	0.2
Very hard	Extremely Low	Neutral	236.8	0.5	7	0.2	0.7
Very hard	Extremely Low	Basic	236.8	0.5	8	0.4	2.3
Very hard	Low	Acidic	236.8	3.0	6	0.2	0.6
Very hard	Low	Neutral	236.8	3.0	7	0.7	4.3
Very hard	Low	Basic	236.8	3.0	8	2.3	13
Very hard	Moderate	Acidic	236.8	7.5	6	0.2	1.6
Very hard	Moderate	Neutral	236.8	7.5	7	1.8	10.7
Very hard	Moderate	Basic	236.8	7.5	8	5.6	32.2
Very hard	High	Acidic	236.8	15	6	0.5	3.2
Very hard	High	Neutral	236.8	15	7	3.5	21.5
Very hard	High	Basic	236.8	15	8	11.2	64.1

14.1 Simplified vs Full BLM

The simplified BLM estimates missing water chemistry information needed to run the BC BLM. This approach is a relatively new concept and due to the natural variation of water chemistry, an accurate estimation is impossible. Therefore, a conservative estimation of the water chemistry was made to ensure that the WQGs produced by the simplified BC BLM do not exceed the values produced by the full BC BLM. A description of the methods used to estimate water chemistry for the simplified BLM are given in Section 11.4.2.

To ensure the WQGs produced are comparable between the two models, a comparison of WQGs calculated using the simplified BC BLM and full BC BLM was conducted. The CABIN dataset (see Section 6) was used for this comparison as these were the only stations with the full set of BLM parameters.

A comparison of the calculated chronic WQGs showed that the simplified BC BLM WQGs were comparable but almost always below the full BC BLM WQGs (Figure 14.1), reflecting the additional conservatism applied in the calculation of WQGs using the simplified BLM. WQGs calculated for the 61 datapoints were within the range of -13.6% and 15% of the WQGs calculated using the full BC BLM.

A comparison of acute WQGs using the simplified and full BC BLMs showed that paired WQGs were comparable (Figure 14.2). For all calculations, the simplified BC BLM WQGs were within ±18% of the full BC BLM WQGs.

Given the limited availability of data to fully test the simplified BC BLM, the simplified model should be applied with caution, especially in systems with sensitive species or where ambient concentrations are approaching WQG concentrations. Whenever possible, WQGs should be calculated using the full BC BLM.
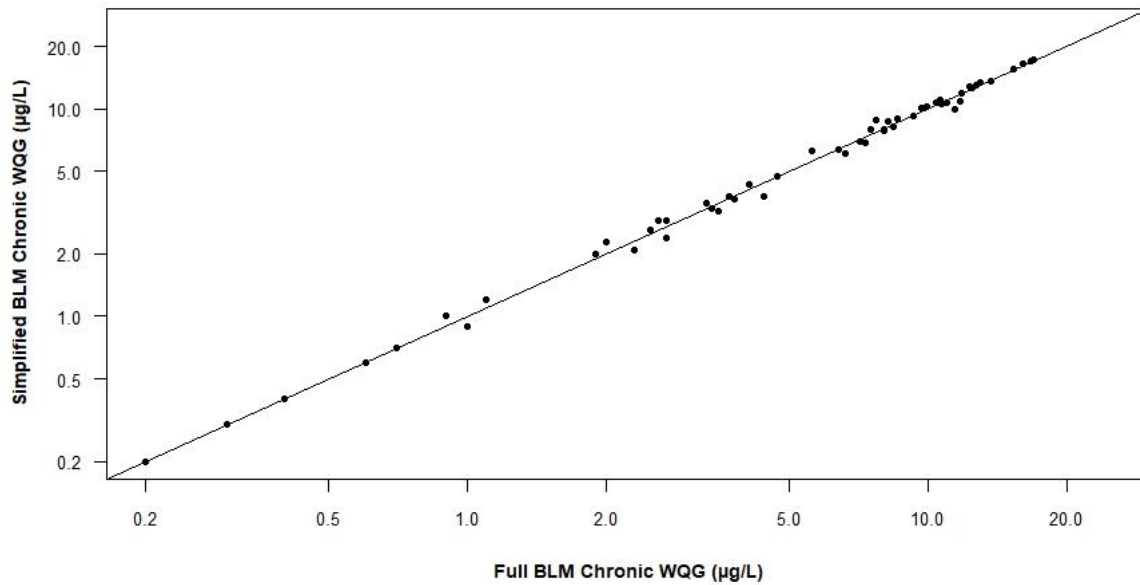
Figure 14.1. A comparison of chronic WQGs calculated using the simplified and full BC BLM software. The solid line represents the 1:1 line.
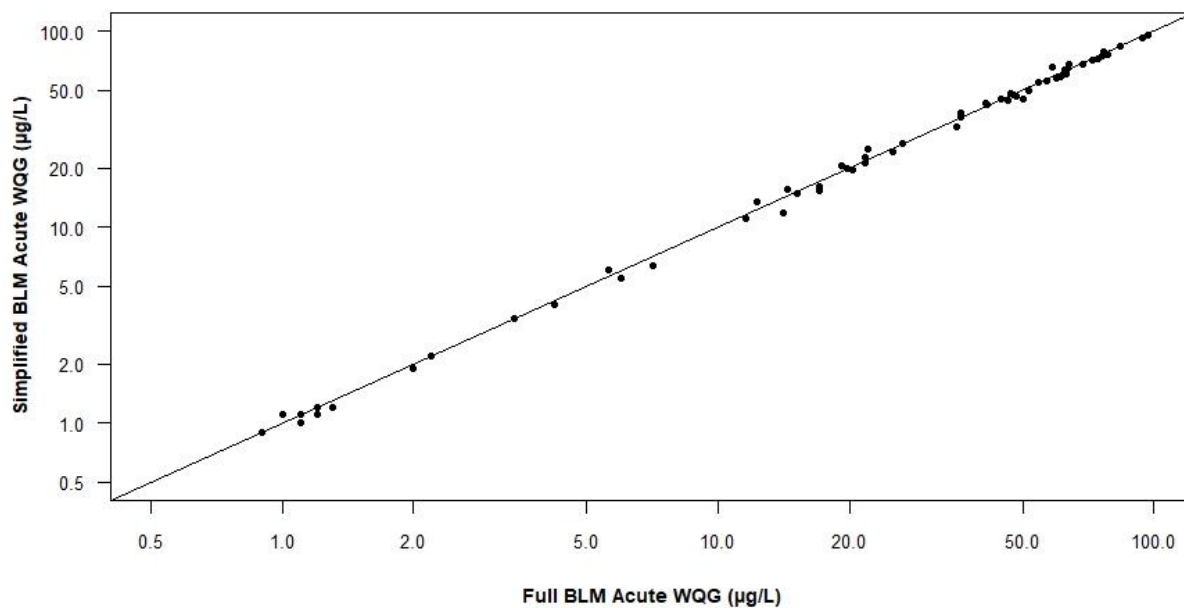

Figure 14.2. A comparison of acute WQGs calculated using the simplified and full BC BLM software. The solid line represents the 1:1 line.

15. APPLYING THE COPPER WATER QUALITY GUIDELINES

An accompanying document, the BC BLM User's Manual, provides instructions for installation and use of the BC BLM software (ENV, 2019). In general, water chemistry data is entered into the software, which then calculates a specific acute or chronic WQG that is specific to that input water chemistry. The output files include: a text file with the water chemistry inputs and the calculated guideline; an Excel spreadsheet with the normalized toxicity endpoints for each species; and a graph showing the normalized toxicity data and the final guideline value.

The long-term chronic and short-term acute Cu WQGs for the protection of aquatic life are calculated using the BC BLM software and are based on the dissolved fraction of Cu in water. The dissolved fraction provides a better estimate of bioavailable Cu (Brungs et al., 1976; Chakoumakos et al., 1979; Erickson, et al., 1996; Paquin et al., 2002) since Cu associated with suspended particulates is generally not available for biological uptake. Total metal concentrations still provide valuable information, especially in systems with high total Cu to dissolved Cu ratios, as changes in water chemistry (e.g., pH) can change the dynamics of particulate and dissolved Cu.

15.1 Application of Long-term Chronic and Short-Term Acute Water Quality Guidelines

Like any other water quality factor, Cu concentrations are 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 (i.e., 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 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.

Copper short-term acute WQGs is a concentration that should not be exceeded at any time to meet the intended protection of the most sensitive species and life stage against severe effects. Short-term maximum WQGs are intended to assess risks associated with infrequent and transient exposure events such as spills.

15.2 Comparison of Ambient Copper Concentrations to Previous (1987) and New (2019) Water Quality Guidelines

Water quality guidelines are commonly used to determine the potential risk of toxicity to aquatic life caused by a given substance in ambient conditions. In general, if ambient concentrations are below WQG concentrations, the risk is assumed to be low. Water quality guidelines are periodically updated to reflect the most current information available. These updates may result in different numerical WQG values for several reasons, including:

- toxicity studies using more sensitive species (e.g., great pond snail);
- lower MDLs;
- the inclusion of additional toxicity-modifying factors;
- WQGs based on the dissolved form, rather than the total form of a substance; and
- changes to the applied uncertainty factor(s).

It is important to understand how the level of estimated risk to aquatic life will change with the new Cu WQG. To answer this question, water quality data were extracted from the ENV's EMS database for lakes, ponds, creeks, rivers and streams throughout B.C. Only records with results for total Cu, dissolved Cu, DOC, hardness, and pH were used to calculate both the previous (1987) and new (2019) WQGs for each sample. Non-detect data were not included if the MDL for dissolved Cu, total Cu, and DOC was greater than 0.2 μg/L, 2 μg/L and 0.5 mg/l, respectively. Results reported as "<MDL", were given the value of the MDL if the value was below these thresholds. An additional data cleaning step was conducted to focus on data from minimally disturbed sites (e.g., sites downstream of obvious effluent discharges were excluded). Using these selection criteria, a total of 1,962 records, from 1980 to 2019, were retrieved.

For each record, the 1987 total Cu chronic WQG (Section 10) was calculated and compared against the measured total Cu concentration and the 2019 dissolved Cu chronic WQG was calculated using the simplified BC BLM (Section 11.4) and compared against the measured dissolved Cu concentration. In total, 252 total Cu concentrations (13%) exceeded the 1987 WQGs (Table 15.1 and Figure 15.1), while 482 dissolved Cu concentrations (24.5%) exceeded the 2019 WQGs (Table 15.1 and Figure 15.2). Both WQGs were exceeded in 149 records (7.5%) while 1,376 records (70%) met both WQGs. One hundred and three records (5%) that exceeded the 1987 WQGs were at or below the 2019 WQGs, while 333 records (17%) at or below the 1987 WQGs exceeded the 2019 WQGs (Table 15.2). These results are due to differences between the two WQGs (e.g., inclusion of more toxicity modifying factors in the 2019 WQGs and the fact that the 2019 WQGs are based on the dissolved fraction instead of total Cu).

Table 15.1. Comparison of total exceedances between the 1987 total Cu chronic WQG and the 2019 dissolved Cu chronic WQGs for 1,982 B.C. water samples collected between 1980 and 2019.

	1987 Total Cu WQG (μg/L)	2019 BC BLM Dissolved Cu WQG (μg/L)
Average of WQGs	3.6	2.2
Range of WQGs	2-10	0.2- 14.7
Number of records with ambient Cu concentrations exceeding WQGs	252 (13%)	482 (24.5%)

Figure 15.1. Ambient Cu concentrations compared to the 1987 chronic total Cu WQGs.

Points above the solid 1:1 line represent exceedances. The minimum value for the 1987 chronic WQG is 2 µg/L total Cu. The maximum value for the 1987 chronic WQG is 10 µg/L total Cu, based on a water hardness of 250 mg/L. Both axes are on log scale.
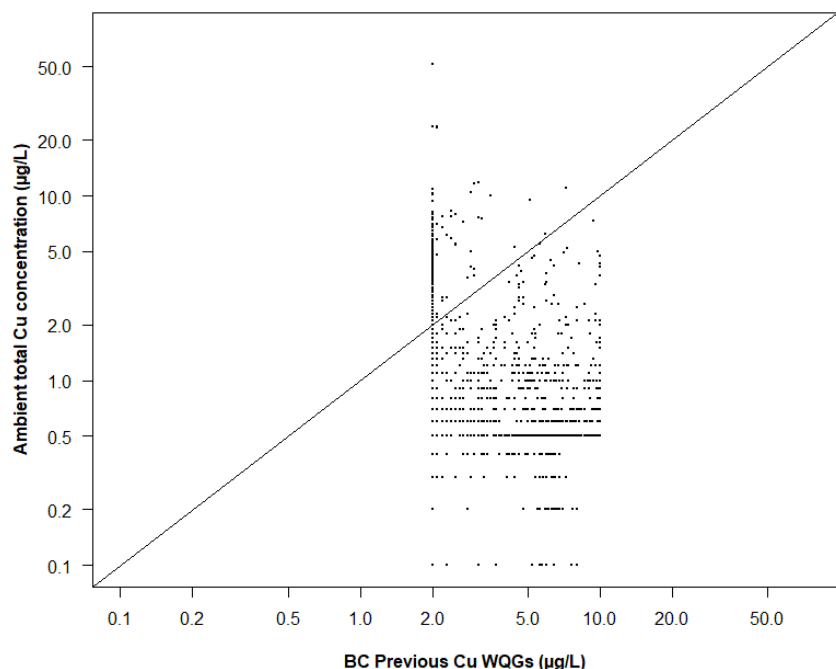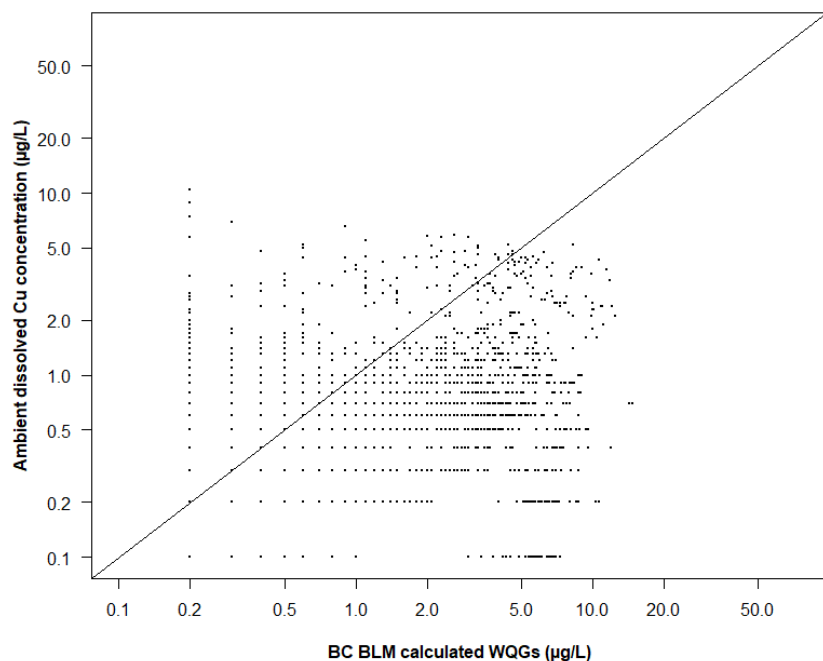

Figure 15.2. Ambient Cu concentrations compared to the 2019 chronic dissolved Cu WQGs.

Points above the solid 1:1 line represent exceedances. The minimum value for the 2019 chronic WQG is 0.2 µg/L dissolved Cu and the maximum value is 14.7 µg/L dissolved Cu based on the water chemistry data contained in the test Cu dataset. Both axes are on log scale.

The higher frequency of exceedances in the 2019 Cu WQGs is due, in part, to the fact that the minimum value in the 1987 WQGs is 2 µg/L (Figure 15.3), whereas the 2019 WQGs, based on several toxicity-modifying factors and the inclusion of recent toxicity data from more Cu-sensitive species, can be as low as 0.2 µg/L (Figure 15.4). Furthermore, since the simplified BC BLM is used in this comparison, additional conservatism is applied in calculating WQGs, resulting in lower WQGs overall and more frequent exceedances in ambient conditions. Users should bear in mind that WQGs represent low-risk conditions and ambient concentrations exceeding WQG concentrations do not necessarily imply increased risk. Further work would be required to assess site-specific conditions and the actual level of risk to aquatic life.

Table 15.2 provides a regional comparison of exceedances between the 1987 Cu WQGs and the 2019 Cu WQGs. Note that there were no data from the Thompson Region that met the criteria for inclusion in this analysis. While exceedances of the 2019 WQGs were more frequent in Vancouver Island, Cariboo, and Skeena regions, more samples exceeded the 1987 WQGs in Cariboo Region. As mentioned above, the minimum value of the 1987 WQGs is 2 µg/L, whereas the 2019 WQGs can be as low as 0.2 µg/L. Several samples from these regions had Cu concentrations between 0.2 and 2 µg/L, resulting in exceedances of the 2019 WQGs but not the 1987 WQGs (Figures 15.3 to 15.6). In the coastal regions (Vancouver Island, Lower Mainland and the Skeena), the low DOC concentration results in more sensitive waters and therefore low WQGs causing a higher frequency of exceedances compared to the 1987 WQG (Figure 15.3 to 15.5). In Cariboo Region, however, higher overall DOC concentration resulted in higher 2019 WQGs and fewer exceedances (Figure 15.6).

Table 15.2. Regional comparison of ambient Cu concentrations with the 1987 total Cu WQG and the 2019 dissolved Cu WQG.

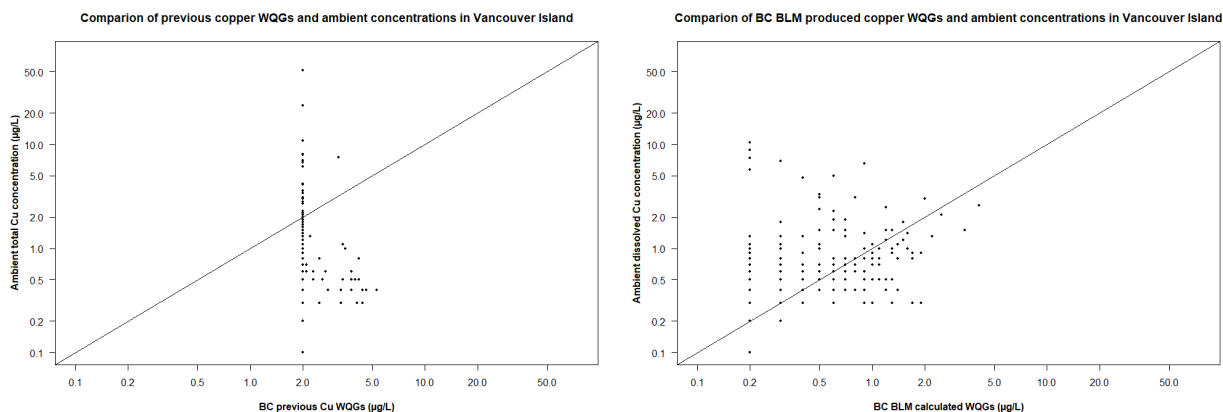| Region	Total samples	Number of Exceedances	
		Previous (1987) WQGs	2019 BC BLM dissolved WQGs
Vancouver Island	255	26 (10%)	126 (49.5%)
Lower Mainland	113	1 (1%)	41 (36.5%)
Thompson	0	0	0
Kootenays	357	2 (0.5%)	7 (2%)
Cariboo	468	152 (32.5%)	104 (22%)
Skeena	745	70 (9.5%)	203 (27%)
Omineca-Peace	8	0	1 (1%)
Okanagan	15	1 (7%)	0
Total	1962	255 (13%)	482 (24.5%)

Figure 15.3. Comparison of previous (A) and new (B) WQGs vs ambient Cu concentrations in Vancouver Island.
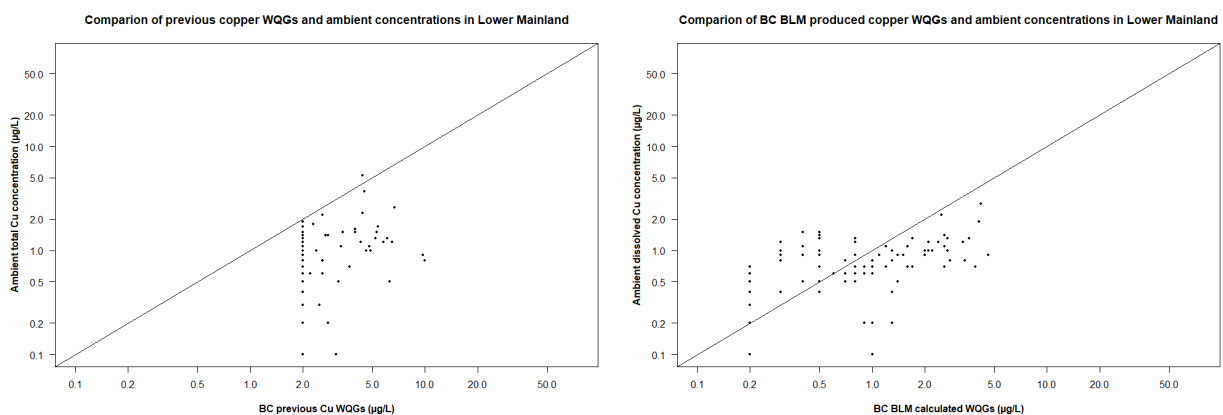

Figure 15.4. Comparison of previous (A) and new (B) WQGs vs ambient Cu concentrations in Lower Mainland.
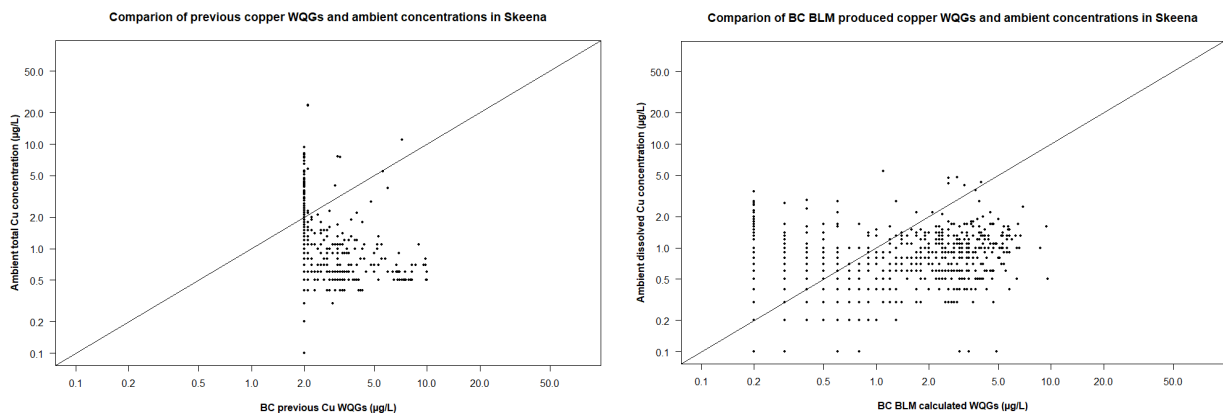

Figure 15.5. Comparison of previous (A) and new (B) WQGs vs ambient Cu concentrations in Skeena.
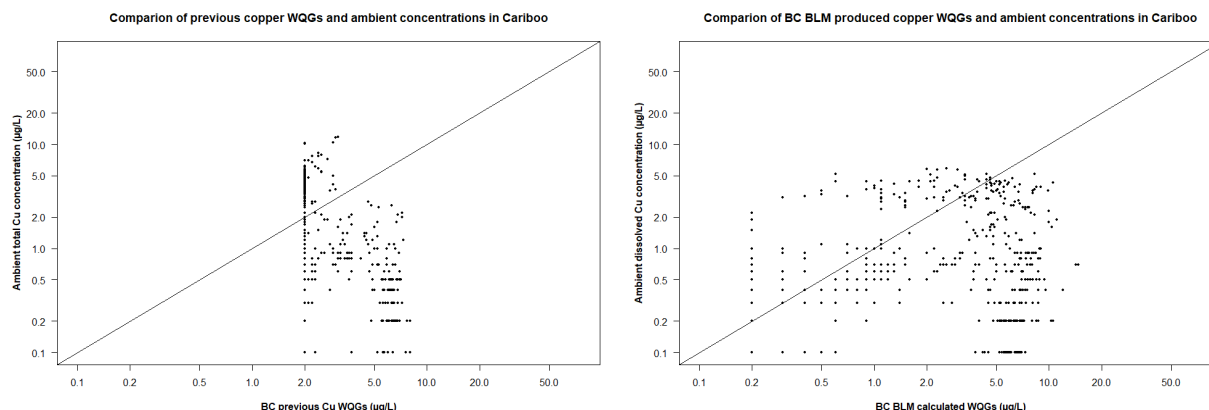
Figure 15.6. Comparison of previous (A) and new (B) WQGs vs ambient Cu concentrations in Cariboo.

15.3 Metal Mixtures

In field conditions, Cu is usually accompanied by other contaminants (e.g., other metals, organic compounds), which can alter its toxicity. In general, the toxicity of contaminants in the presence of other substances can be synergic (more than additive), additive, or antagonistic (less than additive). An additive effect occurs when each contaminant affects the organisms separately with no interaction (Lynch et al., 2016). The BC BLM does not account for the effects of other contaminants on Cu toxicity; therefore, in cases where the concentrations of other metals are high, caution should be exercised to make sure that the additive effects or synergism of other contaminants do not increase the toxicity of Cu.

There are few studies on the interaction of Cu with other metals and the majority of these are binary mixtures of Cu with Zinc (Zn), nickel (Ni), and Cadmium (Cd) (Norwood et al., 2003; Vijver et al., 2011). Studies of Cu-Zn toxicity have produced inconsistent results. For example, in 21 studies of Cu-Zn toxicity reviewed by Norwood et al. (2003), nine showed synergic effects, one was additive, and 11 were antagonistic. While Sprague (1964 b), Lynch et al. (2016), and Meyer et al. (2015) reported additive or synergic toxicity of Cu-Zn, Finlayson and Verrue (1982) reported antagonistic toxicity for the same mixture. The inconsistent results are likely due to different test species, variation in concentrations of substances, and/or variable concentrations of DOC in the exposure water. For instance, an indirect synergic effect of metals on Cu toxicity can happen when other metals bind to DOC and make it less available to bind with Cu. As an example, Smith et al. (2009) demonstrated that fulvic acid sampled from a metal enriched stream (Fe and Al) were three times less protective of *C. dubia* against acute toxicity than fulvic acid sampled from a pristine stream.

When effects of mixtures of Cu-Cd or Cu-Ni were studied, synergic effects were more frequent compared to additive or antagonistic effects (Norwood et al., 2003; Traudt et al., 2016). A review of nine studies on the effects of Ni on Cu toxicity, found six studies that reported synergic effects and one that reported additive effects (Norwood et al., 2003). In a recent study, Traudt et al. (2016) also demonstrated that Cu and Ni had synergic effects on *D. magna*. Norwood et al. (2003) found seven out of eight studies reported an additive or synergistic effect of Cd on Cu toxicity. Although some studies are available on the effects of other metals on Cu toxicity, such as lead (Pb) (Tao et al., 1999), aluminum (Al) (Fargašová, 2001) and iron (Fe) (Smith et al., 2009), information was insufficient to draw conclusions. Inconsistencies were also observed when ternary mixtures of Cu with Cd and Ni were tested (Traudt et al., 2017).

16. DATA GAPS AND RESEARCH NEEDS

Although Cu is considered a relatively well studied contaminant, there are still many unanswered questions. Major research and data needs include:

- Additional toxicity data with water chemistry information for:
    - freshwater algae, macrophytes and amphibians species;
    - sensitive yet ecologically relevant endpoints (e.g., olfactory toxicity and swim performance) for sensitive fish species;
- Further information on:
    - the ameliorating properties of the common toxicity modifying factors on Cu toxicity to olfactory tissues;
    - the effect of metal mixtures;
- Additional water quality data needed for running BC BLM in "full" mode, especially from lentic systems, to compares WQGs calculated using full and simplified BC BLM; and
- Environmental effects monitoring to determine if the guideline values calculated using BC BLM are protective of aquatic life in various water quality conditions.

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