WATER QUALITY GUIDELINE SERIES

Manganese Water Quality Guidelines – Freshwater Aquatic Life

Ministry of Water, Land and Resources Stewardship
Water Protection and Sustainability Branch

No. WQG-27

BRITISH COLUMBIA

The Water Quality Guideline Series is a collection of British Columbia Ministry of Water, Land and Resource Stewardship water quality guidelines. Water quality guidelines are developed to protect a variety of water values and uses, including 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:

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EXECUTIVE SUMMARY

The British Columbia Ministry of Water, Land and Resource Stewardship (WLRS) 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 British Columbia. WQGs provide a basis for water quality assessments and inform decision-making in the natural resource sector. WQGs may be created for the protection of designated values, including aquatic life, wildlife, agriculture, drinking water sources and recreation. This document presents updated manganese (Mn) WQGs for the protection of aquatic life.

Elevated manganese concentrations can adversely affect aquatic life. While background levels vary across B.C., activities such as mining, smelting, manufacturing, fossil fuel combustion and waste disposal can raise manganese concentrations to harmful levels.

Manganese is an essential micronutrient; however, toxicity has been observed in aquatic organisms at elevated levels. Studies on manganese chloride, manganese sulfate and other soluble manganese compounds indicate that manganese can be harmful to aquatic life, with toxicity varying depending on environmental conditions. The toxicity of metals is generally influenced by factors such as water hardness, pH and dissolved organic carbon. For manganese, hardness and pH have been identified as the primary factors affecting its toxicity. When toxicity data are standardized for hardness, invertebrates such as amphipods tend to be the most sensitive in long-term exposure, whereas fish show higher sensitivity in short-term exposures.

In 2019, the Canadian Council of Ministers of the Environment (CCME) published national WQGs for manganese to protect freshwater aquatic life. B.C. has adopted these guidelines, applying an additional assessment factor to account for uncertainties. The 2025 B.C. WQG for manganese differs from the 1999 guideline in several ways. While the previous guideline was based on total manganese and incorporated hardness for both acute and chronic values, the updated guideline applies to dissolved manganese. In the 2025 WQG, the acute (short-term) guideline is calculated based on hardness, whereas the chronic (long-term) guideline considers both hardness and pH. Manganese exceedances at background sites were similar under both the 1999 and 2025 WQGs.

A summary of the manganese WQGs is presented in Table E.1. The freshwater aquatic life guidelines are calculated using site-specific hardness and, therefore, are variable. As an example, for a waterbody with hardness of 50 mg/L and pH of 7.5, aquatic life long-term WQG for dissolved Manganese is 215 µg/L.

Table E.1. Summary of recommended water quality guidelines for manganese.

Designated use	Guideline µg/L	Guideline Type
Freshwater aquatic life	Variable*	Short-term acute
Freshwater aquatic life	Variable*	Long-term chronic
Marine aquatic life	100**	Long-term chronic
Irrigation	200***	Long-term chronic

* The equation for the B.C. freshwater aquatic life manganese WQG, which accounts for hardness, is provided in Section 8.4.
** Working guideline to protect wildlife consumers of fish or shellfish.
***Working guidelines adopted from the Canadian Council of Ministers of the Environment (CCME).

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Appendix 1. British Columbia Manganese Water Quality Guidelines Calculator.

1. INTRODUCTION

The British Columbia Ministry of Water, Land, and Resource Stewardship (WLRS) 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 British Columbia. WLRS defines a WQG as a scientifically derived numerical concentration or narrative statement considered to be protective of designated values in ambient conditions. WQGs provide a basis for water quality assessments and informed decision-making in the natural resource sector and may be derived for the protection of designated uses, including aquatic life, wildlife, agriculture (livestock watering and irrigation), drinking water sources and recreation.

In B.C., WQGs are developed to protect the most sensitive receptor and life stage associated with a given value (for example, aquatic life, wildlife, livestock). For substances with sufficient toxicological data, both short-term acute and long-term chronic guidelines are developed. Interim WQGs are developed when the available toxicological data are insufficient (CCME, 1999; ENV, 2019).

WQGs are typically based on toxicological studies conducted under laboratory conditions. There are several uncertainties associated with applying WQGs to field conditions, including:

- Laboratory to field differences in exposure conditions;
- Single contaminant tests in laboratories vs. exposure to multiple contaminants in the field that may demonstrate additive, synergistic or antagonistic effects;
- Toxicity of metabolites;
- Intra- and inter-specific differences between test species used to derive the WQG and those found in the field;
- Indirect effects (for example, behavioral responses, food web dynamics);
- Laboratory studies conducted on partial life cycle studies, which may not include the most sensitive life stage;
- Delayed effects that may not occur within the life stage tested or that may occur across generations; and,
- Cumulative effects of the various stressors, such as habitat loss and climate change, that organisms in the field are exposed to.

Given these uncertainties, WQGs are an estimate of a no-effect concentration (i.e. no effects are expected if exposure concentrations are below the WQG). An exceedance of the WQGs does not imply that unacceptable risks are present but that the potential for adverse effects is increased, and additional investigation and monitoring may be warranted. To that end, ongoing ecological monitoring is encouraged to ensure the WQG is protective under field conditions.

In 2019, Canadian Council of Ministers of Environment (CCME) published Canadian WQGs for manganese (Mn) for the protection of freshwater aquatic life (CCME, 2019 a, b). B.C. has adopted these guidelines with the addition of an assessment factor to account for sources of uncertainty. This document provides information on CCME's derivation of the aquatic life guideline (replicated here verbatim and highlighted grey, based on content from two CCME-published documents for manganese [CCME, 2019a, b]), as well as a discussion of background concentrations in B.C. and the rationale and selection of an assessment factor.

2. PHYSICAL AND CHEMICAL PROPERTIES

Manganese is ubiquitous in the environment as a Group VII element (UKTAG 2012). It is the second most abundant heavy metal and the 12th most common element in the earth's crust (Webb 2008). The Chemical Abstract Service (CAS) number for manganese is 7439-96-5. There are 11 possible oxidation states, and the most commonly occurring include +2 (e.g., manganese chloride or sulphate), +4 (e.g., manganese dioxide) and +7 (e.g., potassium permanganate), although the +7 state is unstable in the environment (International Manganese Institute [IMnI] 2012). Most manganese salts are readily soluble in water, except for phosphates and carbonates, which have low solubilities. Even less soluble are the manganese oxides, which are practically insoluble in water. In the aquatic environment, manganese predominantly exists as manganous (Mn8.0 and 10.0, respectively), manganese chloride (MnClTable 2.$^{2+}$) and manganic (Mn^{4+}), and the transition between them occurs via oxidation and reduction reactions (Heal 2001). The thermodynamically stable form of manganese is manganic (Mn^{4+}), which exists as an insoluble manganese oxide (IMnI 2012), while the form of most interest in this document is the in-solution manganous (Mn^{2+}) due to the behaviour of the metal species and toxic mode of actions. Manganese chloride ($MnCl_2$) and manganese sulphate ($MnSO_4$) are the forms of manganese used in the derivation of the guideline and benchmark. Physical and chemical properties of these manganese compounds, as well as elemental manganese, are presented in Table 2.1.

Table 2.1. Physical and chemical properties of elemental manganese, manganese chloride and manganese sulphate

Name	Formula	CAS number	Molecular weight (g/mol)	Melting point (°C)	Boiling point (°C)	Solubility	Reference
Manganese	Mn	7439-96-5	54.93	1,246	2,061	Practically insoluble in water; readily dissolves in dilute mineral acids	PubChem 2015a
Manganese Chloride	$MnCl_2$	7773-01-5	125.84	650	1,190	72.3 g/100 mL water (25°C)	PubChem 2015b
Manganese Sulphate	$MnSO_4$	7785-87-7	151.00	700	Decomposes >850	52 g/100 mL of water (5°C)	PubChem 2015c

3. FATE, BEHAVIOUR AND PARTITIONING IN THE ENVIRONMENT

There are 11 possible oxidation states for manganese; the most commonly occurring include +2 (e.g., manganese chloride or sulphate) and +4 (e.g., manganese dioxide) (International Manganese Institute 2012). Most manganese salts are readily soluble in water, except for manganese phosphates and carbonates, which have low water solubilities. Manganese oxides are even less soluble than manganese phosphates and carbonates and are practically insoluble in water. Of all chemical species of manganese found in aquatic environments, the aqueous manganese ion (Mn^{2+}) is believed to be the most bioavailable and toxic form. Changes in environmental conditions that influence manganese speciation, such as redox potential, pH and hardness, can result in changes to manganese toxicity. In oxic conditions, Mn^{2+} oxidizes to insoluble MnO_2, and settling of MnO_2 moves manganese from water column to the bottom (Graham *et al*. 2012). In anoxic waters, Mn^{2+} is produced from the reduction of insoluble Mn^{4+} and is mobilized from sediments back to the water column (Hedgecott et al. 1998).

4. BACKGROUND CONCENTRATIONS OF MANGANESE IN BRITISH COLUMBIA

Manganese is a naturally occurring element in aquatic and terrestrial ecosystems, so background concentrations must be considered when deriving provincial manganese WQGs. Further details on the comparison between background concentrations and the proposed guideline are provided in Section 9.

4.1 Methods for Estimating Background Concentrations

Background (i.e. from non-impacted sites) dissolved manganese concentrations vary across B.C. as a function of local geology and hydrology. A regional approach was used to estimate background levels in aquatic environments following methods used in recent WQG derivation documents (e.g., ENV, 2021). Data were obtained 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, background water quality sampling stations that were sampled at least three times over the last 23 years for any water quality parameter (2000/01/01 to 2023/01/01) were extracted. Next, the list of stations with location information was given to environmental impact assessment biologists with the Ministry of Environment and Parks (ENV) 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 manganese data from the EMS database.

The dataset underwent several additional automated and manual data cleaning steps, summarized below:

- Where lake samples were available at multiple depths, only surface samples were included;
- Non-detect results with a method detection limit (MDL) ≥ the upper 95th percentile of the dataset were removed as these would influence the results of the analysis; and
- Samples were excluded where results were missing or reported as 0.

Arithmetic means were calculated for laboratory replicates (analytical replicates taken from one field sample) with the MDL substituted for values below detection. All field replicates were included as independent samples. The final dataset consisted of 102 stations with 655 samples.

The results from each station were given equal weight within an ENV administrative region by calculating the mean manganese concentrations for each station. Station means were calculated using four different approaches depending on the number of samples above (detects) and below (non-detects) the MDL (Table 4.1). A value of half 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, half 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) was 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, 2024). 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.

Table 4.1. Statistical approach used to calculate station means.

Group	Conditions	Approach	Total Stations	Total Samples
1	% non-detects = 100	½ of minimum station MDL	6	8
2	0 < % non-detects < 100 AND # detects < 3	Substitute ½ MDL for non-detects and calculate arithmetic mean for all samples	4	15
3	0 < % non-detects < 100 AND # detects ≥ 3	Regression on order statistics	13	171
4	% non-detects = 0	Arithmetic mean	79	461

4.2 Background Concentration Results

The distribution of dissolved manganese concentrations by ENV administrative region and the summary statistics for station mean values are summarized in Figure 4.1 and Table 4.2. The median of station means ranged from 0.42 µg/L (Kootenay-Boundary) to 12.9 µg/L (Omineca). There were no data for dissolved manganese concentrations at background sites in the Lower Mainland. Of the 102 stations, 33 were on lakes and 69 were on rivers. The median of the distribution of station means was 2.81 and 3.07 µg/L for lakes and rivers, respectively (Table 4.2).

Table 4.2. Summary statistics for station mean dissolved manganese at minimally impacted stations in British Columbia.

Region	Number of Stations	Number of Samples	Date Range	% Samples < MDL	MDL Range (µg/L)	Concentration Range (µg/L)	Distribution of Station Means (µg/L)		
							Median	10th Percentile	90th Percentile
Cariboo	37	248	2000 – 2023	6%	0.05 – 5	0.05 – 7200	2.59	0.505	23.5
Kootenay-Boundary	8	30	2002 – 2023	53%	0.1 – 1	0.084 – 1	0.419	0.182	0.5
Lower Mainland	0	0	NA	NA	NA	NA	NA	NA	NA
Northeast	1	4	2012 – 2014	NA	NA	0.45 – 3.14	0.894	0.894	0.894
Omineca	4	19	2010 – 2023	16%	0.02 – 1	0.02 – 88.2	12.9	1.4	68.2
Skeena	17	76	2001 – 2023	5%	0.1 - 1	0.01 – 4640	2.64	0.388	10.7
South Coast	2	6	2004 - 2023	NA	NA	0.15 – 1.09	0.322	0.184	0.461
Thompson-Okanagan	9	177	2001 – 2023	7%	1 – 5	0.11 – 1670	1.42	0.434	4.7
West Coast	24	95	2001 – 2023	5%	0.05- 1	0.05 – 16.8	0.815	0.323	2.96

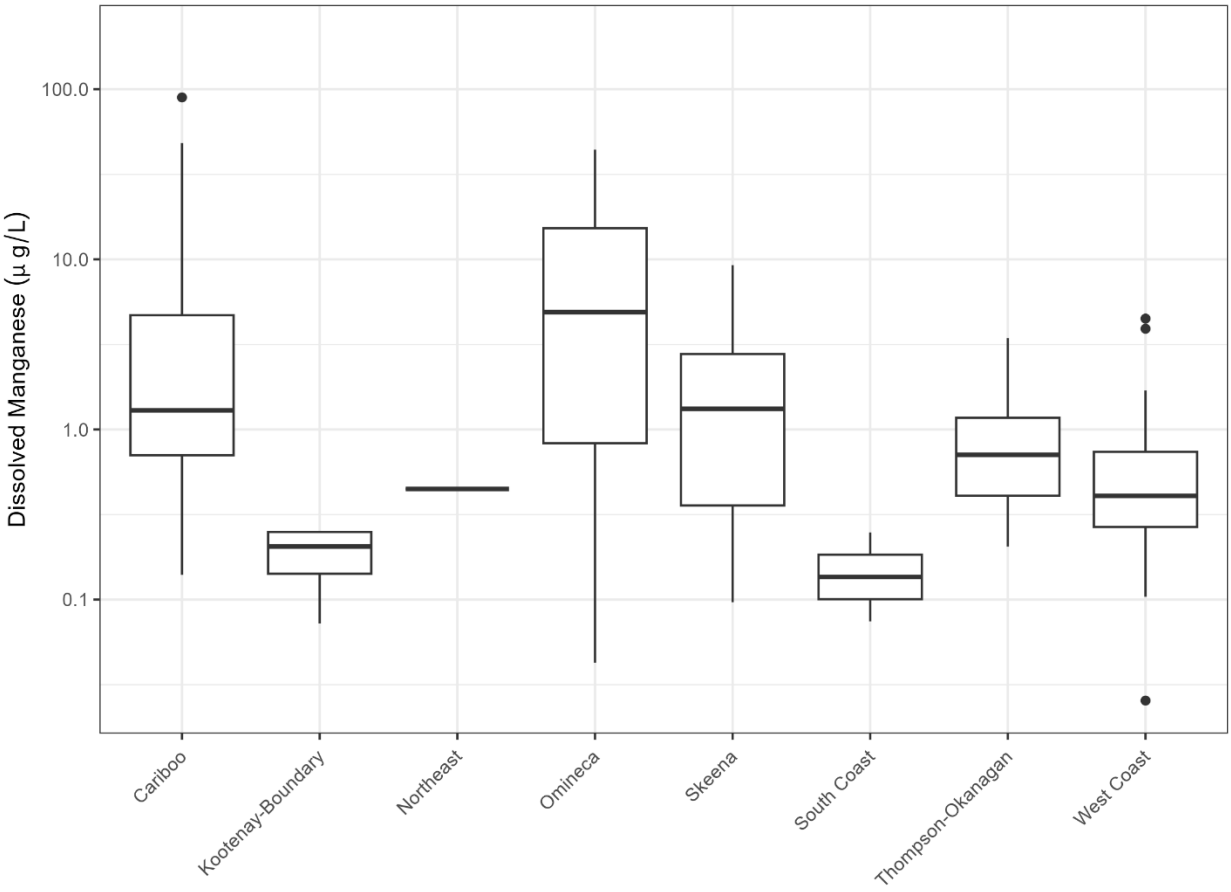

Figure 4.1. Distribution of station mean values for regions in British Columbia. Note: There were no data available in EMS for dissolved manganese concentrations at background sites in the Lower Mainland.

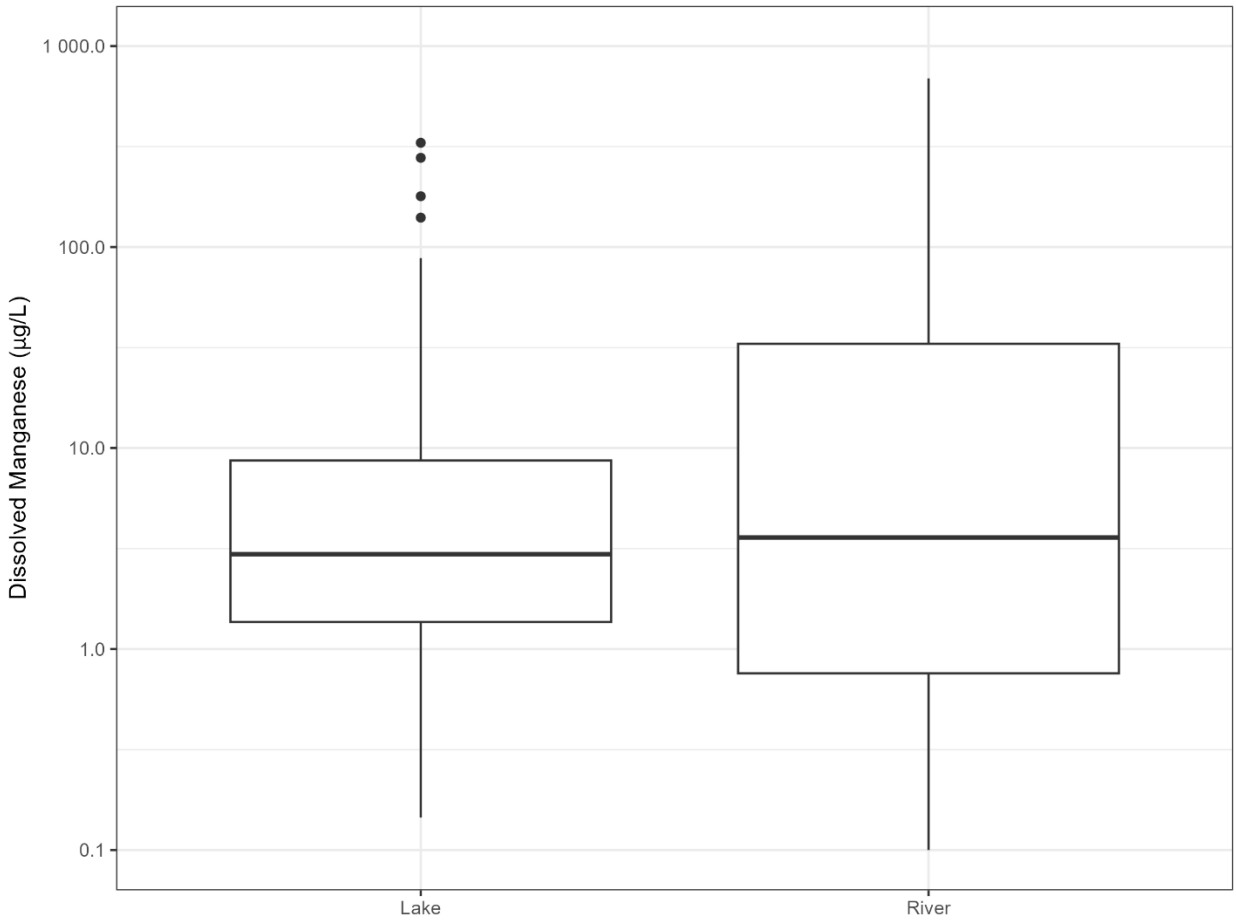

Figure 4.2. Distribution of station means for lakes and rivers for dissolved manganese. Solid horizontal bar and the lower and higher whiskers represent median, 10th and 90th percentile of station means.

5. EFFECTS ON AQUATIC LIFE

Manganese is a biologically essential element that plays an important role in a number of physiological processes as a constituent of multiple enzymes and an activator of other enzymes; tissue concentrations of manganese are typically homeostatically controlled (Martin 1974 as cited in Steenkamp et al. 1994). Environmental concentrations that are well below a species' optimal concentration range can disrupt homeostasis and may result in manganese deficiencies with observable effects (Knox et al. 1981; McHargue and Calfee 1932; Tan et al. 2012). Nutritional manganese requirements vary widely among species; however, concentrations higher than those requirements may result in toxic effects. In fish, the manganous free ion (Mn^{2+}) is mainly taken up via the gills; however, the olfactory nerve cells may be another uptake route of manganese (Rouleau et al. 1995). Once uptake of manganese occurs, the metal moves quickly through the blood to other parts of the body and can cross biological membranes into the kidney, brain and liver. Information on the toxic mode of action of manganese in aquatic organisms is limited and has been more widely investigated in mammalian species. There is evidence to suggest manganese promotes the formation of reactive oxygen species inducing oxidative stress, damage to tissues, inflammation and neurodegeneration in fish (Vieira et al. 2012; Valavanidis et al. 2006). In some algal species, manganese may induce iron deficiency, which can lead to inhibition of chlorophyll synthesis. Manganese is also suspected to ameliorate the toxicity of other metals to microalgae (World Health Organization 2004).

6. TOXICITY MODIFYING FACTORS

Water chemistry conditions influence the toxicity of manganese to aquatic organisms by affecting its environmental fate, behaviour and bioavailability. Sufficient data were available to assess the influence of three variables on manganese toxicity: hardness as $CaCO_3$ (herein referred to as hardness), pH and dissolved organic carbon (DOC), where the variable of interest was varied and other variables were held constant. Toxicity to invertebrates and fish for both short- and long-term exposures was found to decrease with increasing water hardness, likely due to Ca^{2+} and Mg^{2+} cations in harder waters competing for binding sites on the biotic ligand (Lasier et al. 2000). A toxicity modifying effect of pH on algae was found through examination of chronic data, whereby increased H+ ions reduce manganese toxicity due to competition (Peters et al. 2011). There was no discernable trend in long-term toxicity with changes in DOC. This finding is consistent with the known chemistry of manganese in solution whereby manganese has shown little affinity for organic matter. Empirical relationships were derived for short-term and long-term exposures to normalize toxicity data to common water hardness (fish and invertebrates) and pH (plants and algae). Complete details of the assessment are available in the scientific criteria document (Canadian Council of Ministers of the Environment [CCME] 2019b).

7. CRITERIA FROM OTHER JURISDICTIONS

Manganese WQGs from provincial and national jurisdictions are either static values or hardness-based equations. Values are summarized in Table 7.1.

7.1 British Columbia

In B.C., the WQG for manganese was established in 1999 (ENV, 1999) to protect freshwater aquatic life (Table 7.1). The guideline applied to total manganese and used hardness-dependent equations to

determine acceptable concentrations (Table 7.1). The chronic (long-term) guideline was expressed as a 30-day average, while the acute (short-term) guideline represented the maximum allowable concentration for brief exposure events. For example, at a water hardness of 50 mg/L (as $CaCO_3$), the chronic guideline was approximately 0.83 mg/L, and the acute guideline was approximately 1,090 µg/L.

7.2 Canadian Council of Ministers of Environment

In 2019, CCME published a national WQG for dissolved manganese to protect freshwater aquatic life (CCME 2019a, b). The guideline applies to dissolved manganese and includes both acute and chronic values. The acute benchmark is calculated using a hardness-dependent equation, while the chronic guideline is derived from a lookup table based on both hardness and pH (Table 7.1). For example, at a water hardness of 50 mg/L (as $CaCO_3$) and pH 7, the acute benchmark is approximately 3,600 µg/L, and the chronic guideline is approximately 430 µg/L.

7.3 Australia and New Zealand

Australia and New Zealand have joint WQGs, described as trigger values, where the protection level signifies the percentage of species expected to be protected (ANZECC, 2000a, b). Although four trigger values 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 to protect highly disturbed ecosystems, moderately disturbed ecosystems and high conservation/ecological value ecosystems, respectively (ANZECC, 2000a). For example, to protect 95% of aquatic life, ANZECC (2000a) developed a trigger value for total manganese of 1900 µg/L (Table 7.1).

Table 7.1. Summary of manganese freshwater aquatic guidelines in different jurisdictions.

Jurisdiction (Year Published)	Chronic Guideline (µg/L)	Acute Guideline (µg/L)	Fraction
British Columbia (1999)	0.0044 * hardness + 0.605	0.01102 * hardness + 0.54	Total
CCME (2019)	Variable*	$\exp^{(0.878[\ln(\text{hardness})] + 4.76)}$	Dissolved
Australia/New Zealand (2000)	1,900	NA	Total

*The CCME chronic WQG is based on pH and hardness and is available in a published lookup table.

8. RECOMMENDED GUIDELINE

8.1 Aquatic Toxicity Data

Manganese is a biologically essential element that plays an important role in a number of physiological processes as a constituent of multiple enzymes and an activator of other enzymes; tissue concentrations of manganese are typically homeostatically controlled (Martin 1974 as cited in Steenkamp et al. 1994). Environmental concentrations that are well below a species' optimal concentration range can disrupt homeostasis and may result in manganese deficiencies with observable effects (Knox et al. 1981; McHargue and Calfee 1932; Tan et al. 2012). Nutritional manganese requirements vary widely among species; however, concentrations higher than those requirements may result in toxic effects. In fish, the manganous free ion (Mn^{2+}) is mainly taken up via the gills; however, the olfactory nerve cells may be another uptake route of manganese (Rouleau et al. 1995). Once uptake of manganese occurs, the metal moves quickly through the blood to other parts of the body and can cross biological membranes into the kidney, brain and liver. Information on the toxic mode of action of manganese in aquatic organisms is limited and has been more widely investigated in mammalian species. There is evidence to suggest manganese promotes the formation of reactive oxygen species inducing oxidative stress, damage to tissues, inflammation and neurodegeneration in fish (Vieira et al. 2012; Valavanidis et al. 2006). In some algal species, manganese may induce iron deficiency, which can lead to inhibition of chlorophyll synthesis. Manganese is also suspected to ameliorate the toxicity of other metals to microalgae (World Health Organization 2004).

8.2 Toxicity Modifying Factors

Water chemistry conditions influence the toxicity of manganese to aquatic organisms by affecting its environmental fate, behaviour and bioavailability. Sufficient data were available to assess the influence of three variables on manganese toxicity: hardness as $CaCO_3$ (herein referred to as hardness), pH and dissolved organic carbon (DOC), where the variable of interest was varied and other variables were held constant. Toxicity to invertebrates and fish for both short- and long-term exposures was found to decrease with increasing water hardness, likely due to Ca^{2+} and Mg^{2+} cations in harder waters competing for binding sites on the biotic ligand (Lasier et al. 2000). A toxicity modifying effect of pH on algae was found through examination of chronic data, whereby increased H^+ ions reduce manganese toxicity due to competition (Peters et al. 2011). There was no discernable trend in long-term toxicity with changes in DOC. This finding is consistent with the known chemistry of manganese in solution whereby manganese has shown little affinity for organic matter. Empirical relationships were derived for short-term and long-term exposures to normalize toxicity data to common water hardness (fish and invertebrates) and pH (plants and algae). Complete details of the assessment are available in the scientific criteria document (Canadian Council of Ministers of the Environment [CCME] 2019b).

8.3 National Water Quality Guideline Derivation

The derivation of the short-term benchmark and long-term guideline followed the general steps outlined below:

1. Effect concentrations were converted from total to dissolved where necessary using a conversion factor of 0.978.

2. Relationships between manganese toxicity and toxicity modifying factors (water hardness for fish and invertebrates, pH for plants and algae) were established for both short- and long-term exposures.

3. Using the developed toxicity modifying equations, the toxicity dataset was normalized to either 50 mg/L hardness for fish and invertebrates or pH 7.5 for plants and algae.

4. The species sensitivity distribution (SSD) dataset was then selected using the criteria outlined in CCME (2007).

5. Model averaged SSDs and associated statistics including the HC_5 were generated using the ssdtools software package in R (Thorley and Schwarz 2018) (see Figure 8.1**Error! Reference source not found.** and Figure 8.2).

6. The short-term benchmark equation (equation 4) was then developed using the HC_5 from the SSD. It allows users to calculate the benchmark at other water hardness values.

7. For the long-term guideline, steps 3 and 6 were repeated to cover the range of water chemistry data, and all resulting HC_5 values were incorporated into a final long-term guideline look-up table (Table 5 of CCME manganese factsheet [CCME, 2019a]).

For more details and references regarding the approach and the data included in the SSDs, see the scientific criteria document for the CWQG for manganese and its spreadsheet Appendix A (CCME 2019b).

8.3.1 Short-term Freshwater Benchmark Concentration

CCME derives short-term benchmark concentrations using severe effects data (such as lethality) for defined short-term exposure periods. These benchmarks are estimators of severe effects to the aquatic ecosystem and are intended to give guidance on the impacts of severe but transient situations, such as spill events and inappropriate use or disposal. Short-term benchmark concentrations do not provide guidance for protective levels of a substance in the aquatic environment, as they are levels that do not protect against adverse effects.

The minimum data requirements for the Type A (SSD) approach were met, and 17 species were included in derivation of the benchmark concentration (Table 8.1). Effect concentrations were normalized to a hardness of 50 mg/L using the following equation:

Equation 1. $LC_{50\ (\text{at 50 mg/L hardness})} = e^{((\ln(\text{original LC50})) - 0.878*(\ln(\text{original hardness}) - \ln(50)))}$

Each species was ranked according to sensitivity. Overall, salmonids were found to be the most sensitive to short-term manganese exposure.

Because water hardness was a significant toxicity modifying factor in the short-term analysis, CCME expresses the short-term benchmark as an equation into which the local water hardness must be entered in order to produce an appropriate site-specific benchmark concentration. Full details of the derivation are provided in CCME (2019b).

Equation 2. Short-term benchmark = $e^{(0.878[\ln(\text{hardness})] + 4.76)}$

—where the benchmark is expressed in dissolved manganese concentration (µg/L), and hardness is measured as $CaCO_3$ equivalents in mg/L.

Table 8.1. Endpoints used to determine the short-term freshwater benchmark concentration for dissolved manganese.

SSD rank	Species	Endpoint	Normalized effect concentration [a] (µg dissolved Mn/L)
1	*Oncorhynchus kisutch* (coho salmon)	96-h LC50[b]	4,994
2	*Oncorhynchus mykiss* (rainbow trout)	96-h LC50[b]	5,009
3	*Hyalella azteca* (amphibod)	96-h LC50[b]	5,148
4	*Daphnia magna* (water flea)	48-h LC50[b]	6,149
5	*Ceriodaphnia dubia* (water flea)	48-h LC50[b]	7,498
6	*Salvenius fontinalis* (brook trout)	96-h LC50[b]	8,849
7	*Pimephales promelas* (fathead minnow)	96-h LC50[b]	11,288
8	*Chironumus tentans* (chironomid)	96-h LC50	17,386
9	*Megalonaias nervosa* (washboard mussel)	96-h LC50	18,387
10	*Lampsilis siliquoidea* (fatmucket clam)	96-h LC50	25,275
11	*Agosia chrysogaster* (gila longfin dace)	96-h LC50	34,077
12	*Aeolosoma sp.* (annelid)	48-h LC50	38,124
13	*Bufo boreas boreas* (boreal toad)	96-h LC50	39,568
14	*Tubifex tubifex* (sludge worm)	96-h EC50[b]	57,631
15	*Lymnaea stanglis* (great pond snail)	96-h LC50[b]	75,146
16	*Asellus aquaticus* (water louse)	96-h LC50	325,647
17	*Crangonyx pseudogracilis* (amphipod)	96-h LC50	678,732

[a] Normalized to 50 mg/L hardness; see text for details.
[b] Based on a geometric mean of multiple comparable values.

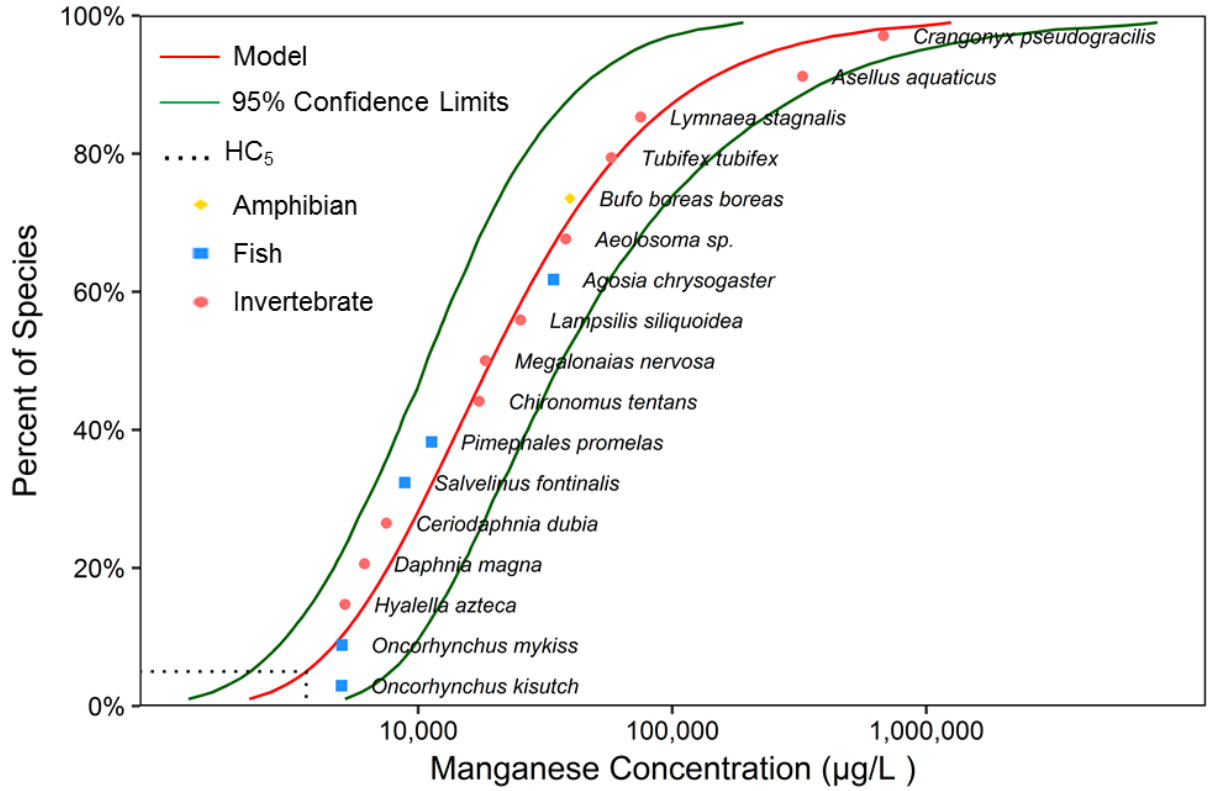

Figure 8.1. Short-term model averaged SSD for dissolved manganese in fresh water at 50 mg/L water hardness. The fifth percentile (HC5) on the short-term SSD is 3,600 µg/L manganese.

The equation is based on the toxicity-hardness slope value of 0.414 and the 5th percentile value of 1.0 µg/L is derived from the SSD when hardness is 100 mg/L.

Based on the toxicity-hardness slope value and the SSD, the equation to derive FWQG for Manganeseis:

$$\text{y-intercept} = \ln(5^{th}\text{ percentile}) - [\text{hardness slope} \times \ln(\text{hardness})]$$

$$= \ln(1.02) - [0.414 \times \ln(100)]$$

$$= -1.887$$

$$\text{FWQG (µg/L)} = e^{\{0.414[\ln(\text{hardness})] - 1.887\}}$$

Since the slope relating hardness to toxicity was based on a study conducted over hardness levels from 52-396 mg/L, the FWQG should not be extrapolated beyond this hardness range. Accordingly, the minimum and maximum FWQG for manganese at water hardness levels of 52 and 396 mg/L are 0.78 and 1.80 µg/L, respectively.

8.3.2 Long-term Freshwater Quality Guideline

Long-term exposure guidelines identify waterborne concentrations intended to protect all forms of aquatic life for indefinite exposure periods. The minimum data requirements for the Type A guideline approach were met, and 14 species were used to derive the guideline (Table 8.2). For the long-term SSD

dataset, measured effect concentrations were normalized (using equations 2 and 3) for multiple hardness and pH combinations ranging from 25 to 670 mg/L and 5.8 to 8.4, respectively.

The slope value of 0.411 relating long-term manganese toxicity with hardness was used to normalize fish and invertebrate long-term toxicity values to a variety of different hardness levels (X) using the following equation:

Equation 3. $ECx_{(at\ X\ mg/L\ hardness)} = e^{[(\ln(original\ ECx)) - 0.411*(\ln(original\ hardness) - \ln(X))]}$

The slope value of −1.774 relating long-term manganese toxicity with pH was used to normalize algal long-term toxicity values to a range of pH values (X) using the following equation:

Equation 4. $EC_{X\ (at\ pH\ X)} = e^{[(\ln(original\ ECx)) + 1.774*(original\ pH-x)}$

Normalizing to multiple combinations is appropriate, since the relative sensitivities of invertebrates/fish and plants/algae vary depending on the combination of site-specific hardness and pH conditions. The normalized effect concentrations and the corresponding SSD for hardness of 50 mg/L for invertebrates and fish and pH 7.5 for plants and algae are presented below. *Hyalella azteca* was the most sensitive species at most hardness and pH combinations except at high pH, when toxicity to plants and algae becomes more significant. The green algae *Pseudokirchneriella subcapitata* has the lowest effect concentrations when normalized to pH 7.7 and hardness 670 mg/L, pH 8 and hardness 125–670 mg/L, and pH ≥8.3 and hardness 50–670 mg/L.

Table 8.2. Endpoints used to determine the long-term freshwater CWQG for dissolved manganese.

SSD rank	Species	Endpoint	Effect concentration [a] (µg dissolved Mn/L)
1	*Hyalella azteca* (amphibod)	35-d EC_{10} (mortality)	283
2	*Pseudokirchneriella subcapitata* (green algae)	72-h EC_{10} (cell yield)[b]	965
3	*Salvelinus fontinalis* (brook trout)	65-d EC_{10} (weight)[b]	1,096
4	*Oncorhynchus mykiss* (rainbow trout)	65-d EC_{10} (weight)[b]	1,232
5	*Scenedesmus quadricauda* (green algae)	12-d EC_{50} (chlorophyll content)	1,868
6	*Salmo trutta* (brown trout)	62-d EC_{10} (weight)	2,052
7	*Pimephales promelas* (fathead minnow)	7-d EC_{10} (dry biomass)[b]	2,223
8	*Aeolosoma sp.* (annelid)	14-d EC_{10} (population growth)	2,563
9	*Ceriodaphnia dubia* (Water flea)	7-d EC_{10} (reproductive impairment)[b]	3194
10	*Danio rerio* (zebrafish)	30-d EC_{10} (mortality)	3,555
11	*Daphnia magna* (water flea)	21-d IC_{25} (reproduction)[b]	4,341
12	*Lymnaea stagnalis* (great pond snail)	48-h LC50	4,612
13	*Chironomus tentans* (midge)	96-h LC50	12,892
14	*Lemna minor* (common duckweed)	96-h EC50[b]	13,725

[a]Normalized to hardness of 50 mg/L for invertebrates and fish and pH 7.5 for plant and algae.
[b]Based on a geometric mean of multiple comparable values.

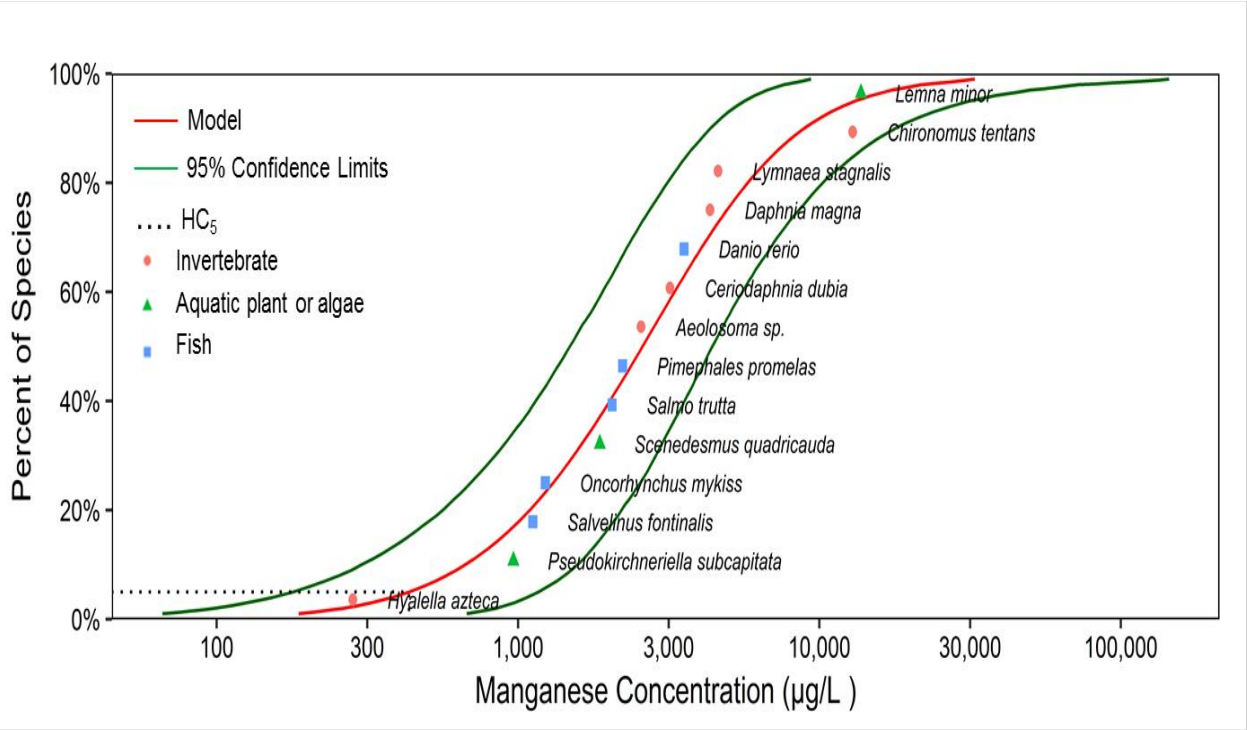

Figure 8.2. Long-term model-averaged SSD for dissolved manganese in fresh water at water hardness 50 mg/L (for invertebrates and fish) and pH 7.5 (for plants/algae). The fifth percentile (HC5) on the long-term SSD is 430 µg/L manganese.

The long-term CWQG is found using the look-up table (see Table 5 of CCME manganese factsheet [CCME, 2019a]) or the CWQG and benchmark calculator in Appendix B of CCME (2019). The CWQG table is valid between hardness 25 and 670 mg/L and pH 5.8 and 8.4, which are the ranges of data used to derive the hardness and pH slopes. Extrapolations should not be made above 670 mg/L hardness. Where users want a more stringent water quality guideline, the calculator provides extrapolated values for water hardness below 25 mg/L down to 10 mg/L, as well as below pH 5.8 to 5.5 and above pH 8.4 to 9. However, users should use these extrapolations with caution and contact their local authority for advice.

Where users have only water sample concentrations of total manganese, it is recommended they first compare these samples to the dissolved guideline, and where there is an exceedance, re-sample for a dissolved concentration. If site-specific water hardness or pH are not known, use default values of 50 mg/L and 7.5, respectively, in order to represent conservative and common laboratory conditions.

A protectiveness assessment was completed for the long-term CWQG (CCME 2019b), which found it achieved the intended level of protection as per the protocol (CCME 2007).

8.4 B.C. Manganese Water Quality Guideline

8.4.1 Short-term Freshwater Quality Guideline

The acute CCME WQG for manganese is derived using an SSD approach and incorporates hardness as a toxicity-modifying factor, in accordance with the CCME framework (CCME, 2019a). The acute dataset comprises toxicity data from 17 species, including six fish, 11 invertebrates, and one amphibian, meeting the minimum taxonomic diversity requirements for a Type A2 guideline under provincial guidance (ENV, 2019). Three of the fish species are native to Canada, including coho salmon (*Oncorhynchus kisutch*),

rainbow trout (*Oncorhynchus mykiss*), brook trout (*Salvenius fontinalis*) and fathead minnow (*Pimephales promelas*), while one, gila longfin dace (*Agosia chrysogaster*) is non-native. All invertebrate and plant species included in the dataset are Canadian. All invertebrate species and the one amphipod species are Canadian species.

As per B.C. guideline development protocol, an assessment factor (AF) is applied to the computed HC_5 to address uncertainties in the dataset and to ensure protection under variable field conditions (ENV, 2019). For Type A WQGs, a default AF of 2 is recommended, accounting for uncertainty related to lab-to-field extrapolation, potential interactions with other stressors, and limited data for sensitive life stages and taxa. In this case, gaps in acute toxicity data for sensitive aquatic insects (for example, Ephemeroptera, Trichoptera, and Plecoptera) support the application of the default AF of 2.

The resulting acute WQG for dissolved manganese is determined using either the following equation or the guideline calculator tool provided in Appendix A.

$$\text{B.C. short-term WQG (µg/L)} = x = \frac{\exp(0.878[\ln(\text{hardness})] + 4.76)}{2}$$

The guideline is valid within the bounds of the supporting dataset, which is the hardness between 25 and 250 mg/L. Use of the calculator to estimate values beyond these ranges results in extrapolated values that should be interpreted with caution.

8.4.2 Long-term Freshwater Quality Guideline

The CCME long-term WQG is based on an SSD and uses hardness and pH as toxicity modifying factors (CCME, 2019a, b). The chronic toxicity dataset consists of data for 14 species: five fish, six invertebrates, and three plants/algae (CCME, 2019a) and fulfills the minimum number of species required for a Type A2 guideline (ENV, 2019). Of the five fish species, four are Canadian species (i.e. fathead minnow, rainbow trout, brook trout and brown trout (*Salmo trutta*), and one is not Canadian (zebrafish). All plant and invertebrate species are Canadian. The most sensitive species to manganese is *Hyalella azteca*, followed by an algae species, *Pseudokirchneriella subcapitata* (CCME, 2019a, b).

To account for the sources of uncertainty associated with WQG derivation, an AF must be applied to the calculated HC_5 (ENV, 2019). The minimum AF to be applied to Type A WQGs is 2, which accounts for the extrapolation of lab results to field conditions and the cumulative effects of other environmental stressors. Sources of uncertainty specific to the dataset include the lack of data for Canadian amphibians, lack of data for sensitive insects (i.e. Ephemeroptera (mayflies), Plecoptera (stoneflies), and Trichoptera (caddisflies)) and the lack of data for reproduction in fish. Given these sources of uncertainty, an AF of 2 was applied to the calculated HC_5.

Illustrative examples of the B.C. chronic manganese WQG are presented in the lookup table (Table 8.3). Because the toxicity data were normalized using two different equations, one for fish and another for invertebrates and algae, the relative positions of species on the SSD are dynamic. As a result, the HC5 varies with each unique water chemistry combination, and a single fixed equation cannot be provided for the chronic WQG. Instead, the lookup table and calculator are required to generate values under specific conditions. For additional parameter combinations not included in the table, users should consult the B.C. chronic long-term WQG calculator in Appendix A.

The B.C. manganese WQG is valid for hardness concentrations ranging from 25 mg/L to 670 mg/L and pH values of 5.8 and 8.4, which represent the range of data used by CCME (2019a). The calculator is not validated for hardness concentrations exceeding 670 mg/L, and extrapolation beyond this threshold is not advised. Extrapolations should not be made above 670 mg/L hardness. For users seeking a more stringent

water quality guideline, the calculator provides extrapolated values for hardness below 25 mg/L (down to 10 mg/L), as well as for pH values below 5.8 (down to 5.5) or above 8.4 (up to 9.0) (CCME, 2019a). These extrapolated values should be used with caution. Consultation with the appropriate regulatory authority is recommended prior to application.

Table 8.3. B.C. chronic dissolved manganese WQGs at various hardness and pH levels (adapted from CCME, 2019a).

Water hardness (mg/L as $CaCO_3$)	pH 5.8	pH 6.0	pH 6.3	pH 6.5	pH 6.7	pH 7.0	pH 7.2	pH 7.5	pH 7.7	pH 8.0	pH 8.4
25–49	145	145	155	165	175	185	185	175	160	135	100
50–74	195	200	215	230	245	250	245	215	195	160	110
75–99	235	240	265	280	295	295	280	245	220	175	120
100–124	265	275	305	320	335	325	305	265	235	185	125
125–149	295	310	335	355	365	355	330	285	250	195	130
150–174	320	335	370	385	395	375	350	300	260	200	130
175–199	345	360	395	415	420	395	365	310	270	210	135
200–299	365	385	420	440	445	415	380	320	280	215	135
300–399	440	470	500	500	500	470	430	355	305	230	145
400–669	500	550	600	600	600	500	465	365	325	240	150
≥670	650	700	750	700	700	600	550	430	360	260	160

9. COMPARISON OF AMBIENT MANGANESE CONCENTRATIONS TO WATER QUALITY GUIDELINES

WQGs are commonly used to determine the potential risk of toxicity to aquatic life from a given substance in ambient conditions. In general, if ambient concentrations are below the WQG, the risk is assumed to be low. It is important to understand how the assessment of risk to aquatic life will change with the updated manganese WQG. To answer this question, water quality data (total manganese, dissolved manganese, pH and hardness) from freshwater sites were extracted from the EMS database and ambient levels compared to the 1999 WQG and the 2025 WQG.

Data from minimally disturbed sites included a total of 930 records with total manganese and hardness data to compare against the 1999 WQG and a total of 167 records with dissolved manganese, hardness and pH to compare with the updated 2025 WQG.

Total manganese exceeded the 2004 WQGs concentrations 3.9% of the time (37 out of 930 samples) (Figure 9.1), while dissolved manganese exceeded the 2025 WQG 3.6% of the time (6 out of 167 samples) (Figure 9.2). These exceedance rates are remarkably similar, indicating consistent patterns of manganese concentration relative to both guidelines, despite the methodological updates in the 2025 WQG.

These findings suggest that, while the basis of the guideline has changed from total to dissolved manganese and now incorporates hardness and pH in the chronic calculation, the overall assessment of risk at background sites remains similar. This consistency provides confidence that the updated 2025 WQG maintains continuity with the previous guideline while improving scientific accuracy and environmental relevance.

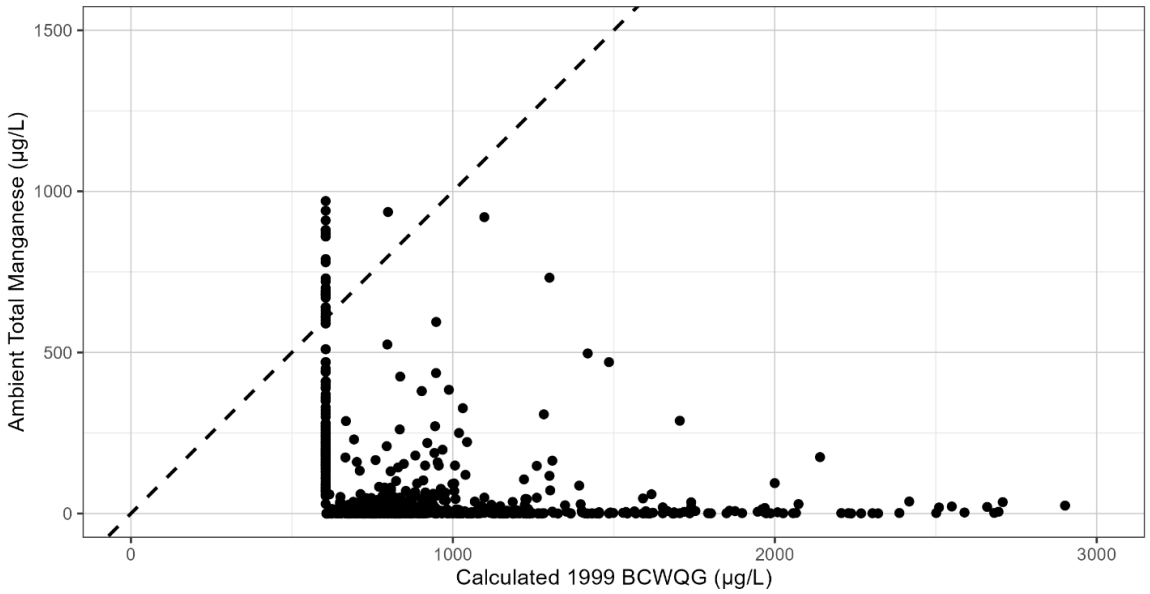

Figure 9.1. Ambient manganese concentrations compared to the 1999 chronic total manganese WQGs. Points above the dashed 1:1 line represent exceedances.

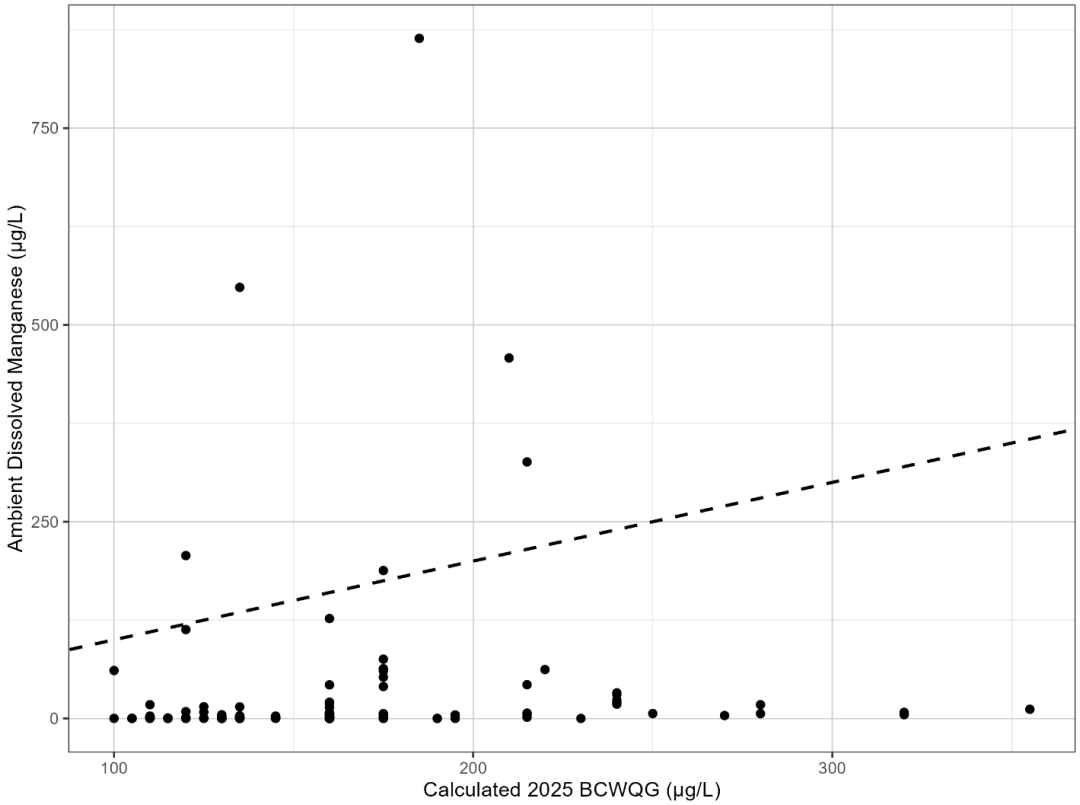

Figure 9.2: Ambient manganese concentrations compared to the 2025 chronic dissolved manganese WQGs. Points above the dashed 1:1 line represent exceedances.

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