CCME

Canadian Council of Ministers of the Environment
Le Conseil canadien des ministres de l'environnement

SCIENTIFIC CRITERIA DOCUMENT FOR THE DEVELOPMENT OF THE CANADIAN WATER QUALITY GUIDELINES FOR THE PROTECTION OF AQUATIC LIFE

Manganese

PN 1601
ISBN 978-1-77202-058-8 PDF

NOTE TO READER

The Canadian Council of Ministers of the Environment (CCME) is the primary minister-led intergovernmental forum for collective action on environmental issues of national and international concern.

This document was prepared by the National Guidelines and Standards Office of Environment and Climate Change Canada (ECCC). It provides background information and rationale for the development of the Canadian Water Quality Guidelines for manganese.

CCME would like to thank the International Manganese Institute for sharing data to support the development of guidelines and for their review of draft documents as well as Doreen McGough, David DeForest and Bill Stubblefield for their reviews of draft documents. Thank you to Angeline Tillmanns, Ali Azizishirazi, Carl Schwarz and Joe Thorley for guidance on the statistical methodology.

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Reference listing:
Canadian Council of Ministers of the Environment. 2019. Scientific criteria document for the development of the Canadian water quality guidelines for the protection of aquatic life: manganese. Canadian Council of Ministers of the Environment, Winnipeg, MB.

Aussi disponible en français.

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LIST OF ABBREVIATIONS

AAS	atomic absorption spectroscopy
ACR	acute:chronic ratio
AES	atomic emission spectrometry
AIC	Akaike information criterion
ATSDR	Agency for Toxic Substances and Disease Registry
BAF	bioaccumulation factors
BCF	bioconcentration factors
BLM	biotic ligand model
CAS	Chemical Abstract Service
CCME	Canadian Council of the Ministers of the Environment
CF	conversion factor
CWQG	Canadian Water Quality Guideline
DOC	dissolved organic carbon
ECCC	Environment and Climate Change Canada (formerly Environment Canada)
EC_x	effect concentration – concentration affecting x% of the test organisms
EU	European Union
HC_5	hazardous concentration for 5% of the species
IC_x	inhibitory concentration – concentration causing x% inhibition
ICP	inductively coupled plasma
IMnI	International Manganese Institute
IPCS	International Programme on Chemical Safety
LCL	lower confidence limit
LC_x	lethal concentration for x% of the test organisms
LOEC	lowest observed effect concentration
MATC	maximum acceptable toxicant concentration
MDDELCC	Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques
MDL	method detection limit
MLR	multiple linear regression
Mn	manganese
MS	mass spectrometry
NOEC	no observed effect concentration
OES	optical emission spectrometry
RAMP	Regional Aquatics Monitoring Program
SSD	species sensitivity distribution
SM	Standard Method
UCL	upper confidence limit
UKTAG	United Kingdom Technical Advisory Group
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WHO	World Health Organization

EXECUTIVE SUMMARY

Manganese (Mn) (Chemical Abstract Service number: 7439-96-5) is a naturally occurring and abundant Group VII metal (International Programme on Chemical Safety 1981; United Kingdom Technical Advisory Group [UKTAG] 2012). Manganese occurs naturally in the environment and in a variety of concentrations depending on the location. In the aquatic environment, manganese predominantly exists as manganous (Mn^{2+}) and manganic (Mn^{4+}) forms, and the transition between them occurs via oxidation or reduction reactions that may be abiotic or microbially mediated (Heal 2001). Manganese is an 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 are typically homeostatically controlled (Martin 1974 as cited in Steenkamp *et al*. 1994).

Manganese enters the environment from geological weathering, as well as from point sources related to coal mining, bitumen extraction, steel manufacturing, pulp and paper mills, and wastewater and sewage discharge (Nagpal 2001; National Pollutant Release Inventory 2016; UKTAG 2012; World Health Organization 2004). It is widely distributed in the earth's crust, is the second most abundant heavy metal and is the fourth most widely used metal globally behind iron, aluminum and copper (Webb 2008). In Canada and worldwide, manganese is primarily used as both an additive and an alloy for steel production, with the world's second largest market being the production of dry-cell alkaline batteries (Health Canada 1987, Webb 2008). Manganese is also present in thousands of everyday metallic items and non-metallic products such as matches, glass, perfumes, bricks, as a dryer in paints, varnish, oil, disinfectant, fertilizers and animal foods (Nagpal 2001, Webb 2008).

The bioavailability and toxicity of manganese in aquatic environments is dependent to a great extent on the physico-chemical properties of a location's water. Therefore, relationships between toxicity and water chemistry variables were examined where sufficient data were available. 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 competing for binding sites on the biotic ligand (Lasier *et al*. 2000). A toxicity modifying effect of pH on algae using chronic data was found, whereby increased H^{+} ions reduce manganese toxicity due to competition (Peters *et al*. 2011). Empirical relationships were derived for short-term and long-term studies to normalize toxicity data to water hardness (fish and invertebrates) and pH (plants/algae).

The freshwater short-term benchmark and long-term Canadian Water Quality Guideline (CWQG) for manganese for the protection of aquatic life followed the Canadian Council of Ministers of the Environment (CCME) protocol using the statistical or Type A approach (CCME 2007). Species sensitivity distributions (SSDs) were created using the normalized toxicity data and fit to several regression models. The models were then weighted using Akaike information criterion (AIC), which is a measure of the relative quality of fit to the data set. The guideline is defined as the intercept of the fifth percentile of the y-axis with the fitted weighted average SSD curve.

The short-term benchmark is presented as an equation while the CWQG is presented as a look-up table that allows users to derive benchmark and guideline values based on the water chemistry of the site under consideration. The CWQG and benchmark calculator (Appendix B) is a tool that can be used to generate site-specific manganese guideline and benchmark values automatically using

Microsoft Excel. Both the benchmark and guideline values were derived for dissolved manganese in order to represent the bioavailable form. Marine environments are beyond the scope of this document, and therefore no marine short-term benchmark or long-term CWQG for manganese was developed.

CWQG and short-term benchmark for the protection of aquatic life for manganese

	Short-term benchmark (µg/L)	Long-term guideline (µg/L)
Fresh Water	3,600	430
Marine	Not assessed	Not assessed

Notes: These values are for a water hardness of 50 mg/L as $CaCO_3$ and pH 7.5. The freshwater benchmark equation and the CWQG table found below must be used in order to obtain a site-specific benchmark and CWQG, respectively, based on the hardness and pH of the water body of interest. Note that it is not appropriate to apply the manganese freshwater guidelines to marine or estuarine environments.

The short-term benchmark is for **dissolved** manganese and is calculated using the equation:

$$\textbf{Benchmark} = \exp^{(0.878[\ln(\text{hardness})] + 4.76)}$$

The value given in the table above is for surface water of 50 mg/L hardness. The benchmark equation is valid between hardness of 25 and 250 mg/L, which is the range of data used to derive the hardness slope. Extrapolations should not be made above the upper hardness limit of 250 mg/L. For hardness below 25 mg/L, where users want a more stringent benchmark, they could extrapolate with caution and contact their local authority for advice.

Example short-term benchmark concentrations (µg/L) for manganese in fresh water at various levels of water hardness

Water hardness (mg/L)	Short-term benchmark concentration (µg Mn/L)[a]
25	2,000
50	3,600
75	5,200
100	6,600
150	9,500
200	12,000
250	15,000

[a] Concentration of **dissolved** manganese.

The long-term CWQG is for **dissolved** manganese and is found manually using the look-up table below or using the CWQG and benchmark calculator (Appendix B). The CWQG table is valid between hardness of 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 for hardness above 670 mg/L. 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 guideline users only have water sample concentrations of total manganese, it is recommended to 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 and/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.

Water hardness (mg/L as $CaCO_3$)	**Long-term CWQG values for dissolved manganese (µg/L)**										
	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	290	290	310	330	350	380	380	350	320	270	200
50–74	390	400	430	460	490	500	490	430	390	320	220
75–99	470	480	530	560	590	590	560	490	440	350	240
100–124	530	550	610	640	670	650	610	530	470	370	250
125–149	590	620	670	710	730	710	660	570	500	390	260
150–174	640	670	740	770	790	750	700	600	520	400	260
175–199	690	720	790	830	840	790	730	620	540	420	270
200–299	730	770	840	880	890	830	760	640	560	430	270
300–399	880	940	1,000	1,000	1,000	940	860	710	610	460	290
400–669	1,000	1,100	1,200	1,200	1,200	1,000	930	770	650	480	300
≥670	1,300	1,400	1,500	1,400	1,400	1,200	1,100	860	720	520	320

*If pH is in between column values, round to the pH that would give you the most conservative (lower) CWQG value. Guideline values are rounded to two significant figures.

1.0 INTRODUCTION

Manganese (Mn) is an essential trace element that is naturally occurring and abundant in the environment. Manganese sources are both natural, from geologic weathering, and anthropogenic, from coal mining, bitumen extraction and steel manufacturing (Nagpal 2001; National Pollutant Release Inventory 2016; United Kingdom Technical Advisory Group [UKTAG] 2012). Manganese is an important component of enzyme systems that metabolize energy and proteins; however, it can also be toxic in high amounts (Tan *et al*. 2012). The toxicity in the aquatic environment is low to moderate and can be affected by water chemistry variables such as pH, hardness, salinity or other metals (Nagpal 2001).

Development of the Canadian Water Quality Guideline (CWQG) and short-term benchmark involves compiling and interpreting aquatic toxicity data, providing an important tool in the evaluation of ambient water quality. Long-term guidelines for the protection of aquatic life are derived to protect all forms of aquatic life indefinitely, including the most sensitive life stage of the most sensitive species (CCME 2007). By comparing environmental concentrations of manganese with the guideline value, it is possible to determine the level of manganese below which no adverse impact on the ecosystem is expected.

The *Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Lif*e: (i) accounts for the unique properties of contaminants, which influence their bioavailability and toxicity; and (ii) incorporates a species sensitivity distribution (SSD) method, which uses all available toxicity data (provided these data pass quality control criteria) in a more flexible approach (CCME 2007). All of the customary components of scientific supporting documents have been included (physical and chemical properties, production and uses, environmental fate and behaviour, environmental concentrations, toxicity data). In addition, cornerstones of the protocol, such as bioavailability and toxicity modifying factors, have been given special attention.

2.0 EXISTING MANGANESE WATER QUALITY GUIDELINES FOR OTHER JURISDICTIONS AND PREVIOUS CANADIAN CRITERIA

There is no pre-existing CWQG for manganese.

No federal ambient water quality criteria have been established for manganese in the United States; however, to derive enforceable standards, several states have relied on the recommendation of McKee and Wolf (1963) and adopted a manganese standard of 1,000 µg/L for the protection of aquatic life. This value was based on limited toxicity data and did not consider potential modifying factors such as water hardness as $CaCO_3$ (herein referred to as hardness), pH or dissolved organic carbon (DOC).

Existing manganese water quality guidelines for other jurisdictions are summarized in Table 1. All values are for total manganese unless otherwise denoted. It is important to note that there are many different derivation methods for guidelines, and each value is limited by the data available at the time of assessment. Chronic (=long-term) guidelines range from 120 to 1,900 µg/L, while acute (=short-term) guidelines range from 1,091 to 4,614 µg/L.

Table 1. Existing manganese water quality guidelines for other jurisdictions

Guideline (µg/L)	Guideline at 50 mg/L hardness (µg/L)	Acute/ chronic	Derivation method	Main jurisdiction	Reference
11.02 ($CaCO_3$) + 540	1,091	Acute	Based on LC_{50}, water hardness, and an application factor of 0.25 (4:1 safety factor)	British Columbia	Nagpal 2001
4.4 ($CaCO_3$) + 605	825	Chronic	Based on LOEC, water hardness, and an application factor of 0.25 (4:1 safety factor)	British Columbia	Nagpal 2001
$e^{0.8784\ [\ln \text{hardness}] + 4.2889}$	2,265	Acute	Based on the State of Michigan's Part 4, Rule 57–Water Quality Values	Québec	MDDELCC 2017b
$e^{0.8784\ [\ln \text{hardness}] + 3.5199}$	1,050	Chronic	Based on the State of Michigan's Part 4, Rule 57–Water Quality Values	Québec	MDDELCC 2017b
120	Not adjusted for hardness	Chronic	Geometric mean of EC_{50} values divided by an adjustment factor and an ACR – Tier 2 Value	United States – USEPA Region 3	USEPA 2006
1,680	Not adjusted for hardness	Acute	Lowest genus mean acute value divided by an adjustment factor – Tier 2 Value	USEPA Region 4 – Hazardous Waste Sites	USEPA 2015
93	Not adjusted for hardness	Chronic	Acute value divided by an ACR – Tier 2 Value	USEPA Region 4 – Hazardous Waste Sites	USEPA 2015
$e^{0.3331\ [\ln \text{hardness}] + 6.467}$	2,369	Acute	Final acute value (fifth percentile of LC_{50} values normalized for hardness) divided by 2	Colorado and New Mexico	Stubblefield and Hockett 2000; New Mexico Environment Department 2011
$e^{0.3331\ [\ln \text{hardness}] + 5.8743}$	1,309	Chronic	Acute value divided by the geomean ACR	Colorado and New Mexico	Stubblefield and Hockett 2000; New Mexico Environment Department 2011
$e^{0.8784\ [\ln \text{hardness}] + 5.0006}$	4,614	Acute	Tier 1 assessment – includes water hardness	Michigan	Michigan Department of Environmental Quality 2015
$e^{0.8784\ [\ln \text{hardness}] + 3.5385}$	1,069	Chronic	Tier 1 assessment – includes water hardness	Michigan	Michigan Department of Environmental Quality 2015

Guideline (µg/L)	**Guideline at 50 mg/L hardness (µg/L)**	**Acute/ chronic**	**Derivation method**	**Main jurisdiction**	**Reference**
123[a]	Not adjusted for hardness	Chronic	Predicted no-effect concentration estimator – HC_5 of SSD (NOEC or EC_{10}) divided by an assessment factor	United Kingdom	UKTAG 2012; Department of Environment and Rural Affairs, Welsh Government 2014
1,900	Not adjusted for hardness	Chronic	Derived from acute toxicity data by applying acute-to-chronic conversion factors to protect 95% of species	Australia & New Zealand	Australian and New Zealand Environment and Conservation Council 2000

[a] Bioavailable Mn is defined as “the fraction of the dissolved concentration of manganese likely to result in toxic effects as determined in accordance with the UKTAG Metal Bioavailability Assessment Tool” (Department of Environment and Rural Affairs, Welsh Government 2014).

3.0 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 rather low solubilities. Even less soluble are the manganese oxides, which are practically insoluble in water. In the aquatic environment, manganese predominantly exists as manganous (Mn^{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 action discussed in Sections 8.0 and10.0, respectively. 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.

Table 2. 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 (25ºC)	PubChem 2015b
Manganese Sulphate	$MnSO_4$	7785-87-7	151.00	700	Decomposes >850	52 g/100 mL of water (5ºC)	PubChem 2015c

4.0 ANTHROPOGENIC, NATURAL SOURCES AND EMISSIONS OF MANGANESE

Manganese is a component of more than 100 minerals and is also found in coal and crude oil (IPCS 1981). Manganese is estimated to comprise between 0.085 and 0.95% of the Earth's crust, and natural weathering of rocks and minerals releases manganese into the environment. The primary ores of manganese include manganite ($Mn_2O_3H_2O$), hausmannite (Mn_3O_4), pyrolusite (MnO_2) and rhodocrosite ($MnCO_3$). Ferromanganese minerals, including biotite mica ($K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$) and amphibole ($(Mg,Fe)Si_8O_{22}(OH)_2$), also contain large amounts of manganese (Nagpal 2001).

Atmospheric manganese originates from crustal rock particulates, ocean spray, vegetation, volcanic activity and forest fires (World Health Organization [WHO] 2004). Main sources of dissolved manganese include: aerobic and anaerobic environments whereby particulate manganese oxides are reduced, weathering of minerals containing manganese, and manganese liberated from soils and sediments in acidic environments. In soil, manganese originates mostly from crustal weathering, and to a lesser degree from atmospheric deposition, plant wash-off, animal excretion and dead plant material (WHO 2004).

Principal anthropogenic sources of manganese in the environment include wastewater and sewage discharge, mining and mineral processing, combustion of fossil fuels and emissions from alloy, steel and iron production, pulp and paper mills, and, to a small extent, combustion of fuel additives (WHO 2004). Data on releases, disposal and recycling of manganese in Canada can be seen in Table 3.

Table 3. Release, disposal and recycling data for manganese from facilities in Canadian provinces and territories in 2015

Province	On-site releases (tonnes)				Disposal (tonnes)		Off-site recycling (tonnes)
	Air	Water	Land	Total	On-site	Off-site	
Alberta	4.9	58	27	90	18,180	1,352	152
British Columbia	13	411	0	425	60,547	287	871
Manitoba	2.1	4.4	0	6.5	247	100	838
New Brunswick	0.981	148	0	149	169	322	154
Newfoundland and Labrador	18	39	0	58	167,708	48	0.611
Northwest Territories	0.004	0.985	0	0.989	2,726	0	0
Nova Scotia	0.145	3.0	5.9	9.2	160	18	13
Nunavut	0	0	0	0.033	2,250	0	0
Ontario	26	126	95	252	54,086	3,363	14,800
Prince Edward Island	0.285	0	0	0.285	0	16	0
Québec	20	364	159	543	48,514	1,653	911
Saskatchewan	1.0	0.575	0.031	4.3	772	351	43
Yukon*	-	-	-	-	-	-	-
Total	**86**	**1,156**	**286**	**1,537**	**355,359**	**7,509**	**17,783**

*Information for Yukon was not available.
Source: National Pollutant Release Inventory (2016).

5.0 PRODUCTION AND USES

Manganese is the fourth most widely used metal in the world behind iron, aluminum and copper (Webb 2008). Manganese and its compounds can be produced from manganese metal or from naturally occurring ores. Chemical reactions with various compounds such as hydrochloric or sulphuric acids are used to create manganese chloride or manganese sulphate from manganese oxide. Ferromanganese is produced from the smelting of manganese ores and is used extensively in the production of steel (Agency for Toxic Substances and Disease Registry [ATSDR] 2012).

There are known Canadian deposits in the Maritime provinces and British Columbia with only a few small bog deposits in other parts of the country (Hanson 1932). Small mines have been functional in the past for low- to medium-grade manganese ore. However, the extraction and processing of ore is currently not economically viable, and therefore Canada now imports all of their manganese requirements (Webb 2008). The main suppliers of manganese are China, South Africa, Australia, Brazil and Gabon, which supply 80% of the market combined (Webb 2008). Canada also imports a significant portion of silicomanganese and manganese oxide from the United States (Corathers 2014).

In Canada, manganese is primarily used as both an additive and an alloy for steel production (Health Canada 1987). As an additive, manganese binds excess oxygen and sulphur and allows them to be easily removed. As an alloy, manganese increases the strength of steel and renders it less brittle and more resistant to shock, abrasion and corrosion (Webb 2008).

The majority of steel production is used to create low-carbon steels that have a variety of applications and contain manganese ranging from 0.15 to 0.8% or less (IMnI 2015). Only about 3–4% of steel produced are high strength sheets that contain over 1% manganese, often used for oil or gas pipelines, transport equipment or building ships (IMnI 2015).

Stainless steel is a high-manganese metal alloy that contains at least 13% manganese. This steel is used for applications that require immense strength and toughness such as gyratory crushers, jaw-crusher plates, earth-moving equipment and railway points (IMnI 2015).

Global production of manganese alloys in 2011 was a total of 17.7 million tonnes, which continues to rise from steel mill demand. In 2011, total global production of silico-manganese was 11.8 million tonnes; high-carbon ferromanganese and refined ferromanganese were 4.4 and 1.6 million tonnes, respectively (IMnI 2015).

Other metallurgical uses of manganese include alloys with aluminum, copper, zinc and a variety of specific applications. While still well below the production of steel, aluminum is the second most relevant metal for alloy use with manganese. Small amounts of manganese are used in production of aluminum to reduce corrosion (IMnI 2015). The aluminum and manganese alloys are commonly used for beverage cans, as well as roofing, transportation and kitchen devices (IMnI 2015). Manganese is a versatile addition for copper alloys and is used as a deoxidizing element in addition to improving toughness. Manganese can also be used as a cheaper alternative to nickel in nickel-silver alloys. The majority of copper alloy products contain about 10–20% manganese; however, some may contain 50% or more for specific applications. Zinc alloys typically contain minimal amounts of manganese, ranging from 0.1 to 1.5% (IMnI 2015).

The world's second largest market for manganese is the production of dry-cell alkaline batteries. Manganese dioxide, which is used as a depolarizer, is naturally occurring, so either natural or synthetic sources may be used in standard cells. About 300,000 tonnes of synthetic manganese dioxides are produced annually either chemically or by electrolysis, and this number is expected to dramatically increase over time (IMnI 2015).

Manganese is present in electrical coils, matches, as a dryer in paints, varnish, oil, disinfectant, and is also used in fertilizers and animal foods (Nagpal 2001). Inorganic manganese is used in dry-cell battery production, glass and fireworks, leather and textiles, and as a pigment in cosmetics and paints (ATSDR 2012). Uses of organic forms of manganese can include as fungicides (e.g., maneb), fuel-oil additives, smoke inhibitors and as an anti-knock additive in gasoline (e.g., methylcyclopentadienyl manganese tricarbonyl or MMT) (ATSDR 2012). Manganese is also used in artificial flavours such as vanilla extract and in cake mix (IMnI 2015). Manganese phosphatation can produce surface films that are sealed with wax or oil to protect steel and improve lubrication for efficient moving parts. Potassium permanganate is often used to treat drinking and wastewater. It has bactericidal and algicidal properties and is a strong oxidizer. Potassium permanganate can also be used to reduce odours for paint factories or fish plants (IMnI 2015).

Data on worldwide mine production of manganese can be seen in Table 4.

Table 4. World mine production of manganese for 2012 and 2013 and estimated reserves

Country	**Mine production (kilotonnes)**		**Reserves (thousand metric tons gross weight)**
	2012	**2013***	
Australia	3,080	3,100	97,000
Brazil	1,330	1,400	54,000
Burma	115	120	n/a**
China	2,900	3,100	44,000
Gabon	1,650	2,000	24,000
India	800	850	49,000
Kazakhstan	380	390	5,000
Malaysia	429	250	n/a**
Mexico	188	200	5,000
South Africa	3,600	3,800	150,000
Ukraine	416	350	140,000
Other	920	950	small
Total	**15,800**	**13,400**	**570,000**

*Estimated. **n/a = not available.
Source: United States Geological Survey (2014).

6.0 ANALYTICAL METHODS AND DETECTION LIMITS

Sampling and measurement of manganese in water generally involves either total or dissolved concentrations. Measurement of the total concentration does not comprise filtration, and therefore both particulate bound and dissolved fractions are included. In contrast, the dissolved concentration is defined as the concentration recovered after being passed through a filter (generally 0.45 µm membrane filters).

Manganese in fresh water is most often measured using an inductively coupled plasma (ICP) mass spectrometry method, as it provides the most sensitive method detection limit and can be run simultaneously with other metals. Sample water is first filtered through a 0.45 µm filter for dissolved measurements and then preserved using nitric acid. The sample in aerosol form is then passed through an inductively coupled argon plasma torch where ionized metal atoms are produced. Next, the sample runs through the mass spectrometer where the metal of interest is quantified.

Atomic absorption spectrometry (AAS) can be used to measure manganese in water by direct aspiration into an air-acetylene flame with a detection limit of 10 µg/L. Low concentrations can alternatively be measured by first chelating with ammonium pyrolidine dithiocarbamate, then extracting into methyl isobutyl ketone and then aspirating into an air-acetylene flame (Health Canada 1987).

Various analytical methods for manganese in environmental samples and their detection limits are provided in Table 5 (adapted from USEPA 2004 and ATSDR 2012).

Table 5. Analytical methods and detection limits for measuring manganese in environmental samples

Sample matrix	Preparation method	Analytical method	Sample detection limit
Water	Acidify with HNO_3 and HCl	Method USEPA 200.7 (ICP OES/AES)	1.0 µg/L
		Method USEPA 200.9 (Stabilized Temperature Graphite Furnace AAS)	0.3 µg/L
	Acidify with HNO_3	AAS (furnace technique)	0.2 µg/L
		AAS (flame)	2 µg/L
		AAS (furnace)	0.01 µg/L
		ICP-AES	1 µg/L
		Method 311 (AAS)	<10 µg/L
		Method SM 3111B (AAS direct aspiration)	10 µg/L
	Filter and acidify filtrate with HNO_3 and analyze	Method 3113A (AAS furnace technique)	0.2 µg/L
	Digest sample with HNO_3/HCl and analyze	Method SM 3120B (ICP-AES)	2 µg/L
	Acid digest and analyze	Method 3125A (ICP-MS)	0.002 µg/L
	Preconcentration manganese-containing solution and 3,3'5,5'-tetramethylbenzidine (TMB) onto filter paper; add oxidant KIO_4 to catalyze oxidation; measure absorbance	Catalytic kinetic method of analysis	0.005 µg/L
Water, wastewater, sludge, and soils	For dissolved constituents: filter, acidify filtrate and analyze; for samples containing solids: digestion with HNO_3/HCl prior to analysis	Method USEPA 200.8 (ICP-MS)	0.01–0.04 µg/L (liquids)
			0.05 mg/kg (solids)
Water and wastes	Acid digestion	AAS	10 µg/L
Water, solids, sediment	For dissolved constituents: filter, acidify filtrate and analyze; for samples containing solids: digestion with HNO_3/HCl prior to analysis	Method 6010C (ICP-AES)	0.93 µg/L

*Percent recovery at manganese concentration >80 µg/L; at lower concentrations (10–20 µg/L), percent recoveries were >120%.

AAS = atomic absorption spectrometry; AES = atomic emission spectroscopy; USEPA = United States Environmental Protection Agency; ICP = inductively coupled plasma; OES = optical emission spectrometry; MS = mass spectrometry; SM = Standard Methods.

Source: Adapted from USEPA (2004) and ATSDR (2012).

7.0 ENVIRONMENTAL CONCENTRATIONS

Manganese occurs naturally in the environment and in a variety of concentrations depending on the location. Some areas contain naturally elevated concentrations of manganese in underlying rock that can be released and transported to other environmental media. Areas of unpolluted atmosphere or pristine surface waters may contain very low concentrations of manganese that may be close to the detection limits of certain analytical methods (ATSDR 2012). In other areas, anthropogenic activity may cause elevated concentrations of manganese that will exceed the natural background levels. In such situations, statistical methods and comparisons with pristine environments can be used to distinguish anthropogenic contributions of manganese.

The following sections include a summary of manganese concentrations in Canadian surface waters, sediment and aquatic biota.

7.1 Concentrations in Surface Water

The total manganese concentration can vary between fresh and sea water, where fresh water typically has a higher concentration. Environment and Climate Change Canada (ECCC) unpublished monitoring data for manganese concentrations in surface water were available for various water bodies of varying anthropogenic influence across Canada. These data, along with data from Alberta’s Regional Aquatics Monitoring Program (RAMP) for the Athabasca region of Alberta and other provincial programs, have been summarized in Table 6 (total) and Table 7 (dissolved). Samples below detection limits were included in the calculation of mean and median concentrations as the method detection limit.

Table 6. Concentrations of total manganese in Canadian surface waters

Location	Sampling years	Total manganese						
		Number of samples	Mean (μg/L)	Median (μg/L)	Min (μg/L)	Max (μg/L)	MDL (μg/L)	Number of non-detects
Georgian Bay	2004–2014	37	1.34	0.68	<0.05	10.5	0.05	1
Lake Erie	2004–2014	145	4.61	2.08	<0.05	44.6	0.05	15
Lake Huron	2004–2014	68	1.85	0.765	<0.05	14.8	0.05	7
Lake Ontario	2005–2013	167	3.79	0.66	<0.05	45.5	0.05	18
Lake Superior	2005–2013	104	1.20	0.45	<0.05	16.4	0.05	15
Great Lakes connecting channels	2003–2014	1,462	17.3	6.03	0.13	1,190		
Northwest Territories	2003–2014	707	48.2	11.2	<0.05	2,850	0.05	5
Newfoundland and Labrador	2003–2013	2,771	68.5	16.4	<0.05	1,991	0.05	1
New Brunswick	2011–2013	23	29.2	20	2.5	105		
Nova Scotia	2011–2013	295	47.7	29.9	<2	382	2	17
Athabasca region[1]	2004–2015	1,459	106.3	53.2	1.19	12,200		
St. Lawrence	2007–2014	576	23.9	19.5	2.4	134		
Manitoba	2003–2014	572	237	117	2.59	3,650		
Manitoba[2]	2000–2016	11,770	27.73	25.5	<0.2	10,700	0.3, 0.2,	407
Alberta	2003–2015	1,306	59.4	8.22	0.12	3,580		
Alberta[3]	2004–2016	4,036	82.44	17.25	<0.003	12,600	0.003	3
Québec[4]	2008–2015	1,258	20.72	20	0.2	810	0.03	
Saskatchewan	2003–2014	842	230	117	0.13	3,470		

Source: [1]RAMP (2015); [2]Manitoba Sustainable Development (2016); [3]Alberta Environment and Parks (2017); [4]MDDELCC (2017a). All other entries are from ECCC's unpublished water quality monitoring data.

MDL= method detection limit

Table 7. Concentrations of dissolved manganese in Canadian surface waters

Location	Sampling years	Dissolved manganese						
		Number of samples	Mean (µg/L)	Median (µg/L)	Min (µg/L)	Max (µg/L)	MDL (µg/L)	Number of non-detects
New Brunswick	2007–2008	31	31	8.1	0.4	74	2	2
Athabasca region[1]	2004–2015	1,459	48.1	8.98	<0.004	10,800	0.004	1
St. Lawrence	2000–2014	577	5.27	3.92	0.39	28.21		
Québec[2]	2008–2015	1,113	6.45	6.9	0.31	400	0.004	
Manitoba	2003–2014	571	46.56	4.35	0.38	1,170		
Manitoba[3]	2000–2016	793	1.06	0.2	0.4	6,220	5, 0.2	470
Alberta	2003–2015	1,315	22.20	1.42	0.05	3,300	0.05	1
Alberta[4]	2004–2016	3,370	23.06	1.58	<0.003	2,380	0.003	16
Saskatchewan	2003–2014	841	145.52	35.4	0.05	3,090		

Source: [1]RAMP (2015); [2]MDDELCC (2017a); [3]Manitoba Sustainable Development (2016); [4]Alberta Environment and Parks (2017). All other entries are from ECCC's unpublished water quality monitoring data.

MDL= method detection limit

7.2 Concentrations in Sediment

ECCC monitoring data for manganese concentrations in sediment were available for various water bodies of varying anthropogenic influence across Canada. These data have been summarized in Table 8 by location or region, along with data from RAMP for the Athabasca region of Alberta. Samples below detection limits were included in the calculation of mean and median concentrations as the method detection limit.

Table 8. Concentrations of manganese in sediment from Canadian surface waters

Location	Sampling years	Number of samples	Mean (µg/g)	Median (µg/g)	Min (µg/g)	Max (µg/g)
Northwest Territories[1]	2004	4	438	315	112	1,010
Athabasca region	2004–2014	227	267.6	229	5	1,670
St. Lawrence[2]	2003–2013	429	742	370	37	64,500
Ottawa River	2008	22	1,061	878	379	2,740
Atlantic sector[3]	2011–2013	13	996	372	215	6,100
Lake Ontario and tributaries	2011	13	785	757	199	1,790
Lake Erie	2012	1	545	n/a	n/a	n/a
Lake Huron	2011	5	9,394	9,380	1,660	15,200
British Columbia	2011–2013	6	441	383	241	822

[1] Includes Hay River, Flat River, South Nahanni River and Prairie Creek

[2] Includes St. Lawrence Estuary, St. Lawrence River, Lake St. Pierre, Lake St. Francois, Lake St. Louis and St. Lawrence Seaway locks

[3] Includes samples from Nova Scotia, New Brunswick, and Newfoundland and Labrador

Source: RAMP (2015); ECCC’s unpublished water quality monitoring data.

7.3 Concentrations in Biota

Monitoring data for manganese concentrations in fish tissue were available from ECCC’s National Fish Contaminants Monitoring and Surveillance Program. A total of 37 fish species, including larger predator fish (e.g., lake trout) and smaller forage fishes (e.g., rainbow smelt), were collected from 35 water bodies in major Canadian watersheds from 2004 to 2013. For all sampled water bodies, concentrations of manganese in whole-body homogenized fish tissue ranged from 0.1 to 106 mg/kg, with an average of 2.1 mg/kg and a median of 0.44 mg/kg (Table 9). Note that, since manganese is an essential element and is homeostatically controlled, it will always be found within living organisms at reasonably constant concentrations.

Table 9. Concentrations of manganese in whole-body homogenized fish tissue from Canadian surface waters

Location	Sampling years	Number of samples	Mean (mg/kg)	Median (mg/kg)	Min (mg/kg)	Max (mg/kg)
Lake Erie	2006–2013	390	0.81	0.45	0.15	9.5
Lake Huron	2006–2013	290	0.57	0.31	0.14	3.8
Lake Ontario	2004–2013	737	1.3	0.30	0.10	41
Lake Superior	2006–2013	412	0.57	0.34	0.12	3.4
All other water bodies	2007–2013	1,408	3.5	0.87	0.11	106
All water bodies (including Great Lakes)	2004–2013	3,237	2.1	0.44	0.1	106

Source: ECCC (2015).

8.0 ENVIRONMENTAL FATE AND BEHAVIOUR

8.1 Speciation of Manganese in the Aquatic Environment

In the aquatic environment, manganese predominantly exists as manganous (Mn^{2+}) and manganic (Mn^{4+}) and the transition between them occurs via oxidation and reduction reactions that may be abiotic or microbially mediated (Heal 2001). Many aspects of manganese chemical behaviour are similar to those of iron (Brezonik and Arnold 2011). For example, both manganese and iron have multiple oxidation states, and the stability of the reduced states is greater at decreased pH. Additionally, reduced states of manganese and iron are generally soluble in water but only stable in anoxic conditions, while oxidized states are insoluble at neutral pH (Brezonik and Arnold 2011).

The environmental chemistry of manganese is largely influenced by pH and redox potential. Studies in dilute waters of the Canadian Precambrian shield found manganous forms dominate at lower pH and redox potential, with an increasing proportion of colloidal manganese oxyhydroxides above pH 5.5 in non-dystrophic waters (LaZerte and Burling 1990). In anoxic waters, Mn^{2+} is produced from the reduction of insoluble Mn^{4+}, is mobilized from sediments and diffuses to the water column. Its solubility is influenced by the precipitation of insoluble manganese species (Hedgecott *et al*. 1998). In the majority of oxygenated waters, the thermodynamically stable form of manganese is Mn^{4+}, present as insoluble manganese oxide. However, due to kinetics and complexation, manganese in oxic conditions may be present as Mn^{2+}, as soluble inorganic complexes, or as insoluble carbonates and oxides (Hedgecott *et al*. 1998; UKTAG 2012; WHO 2004). There is little evidence for manganese–organic associations in natural waters, with manganese only weakly bound to DOC (L'Her Roux *et al*. 1998). Hence, organic complexation does not play a major role in controlling manganese speciation in natural waters (WHO 2004).

The properties and bioavailability of manganese depend on speciation, which is controlled by pH and pE (electron activity) (UKTAG 2012). Manganese precipitated out of solution as insoluble oxides or carbonates may be less bioavailable. Furthermore, manganese may reversibly bind to inorganic anions or organic compounds. Manganese aqueous and solid species can be represented in a pE–pH diagram (Figure 1) (Freitas *et al*. 2013). The Eh (V) axis represents the equilibrium partial pressure of O_2 and H_2 in the system (or the oxidizing or reducing power of the environment) and the x-axis represents pH. The two doted lines enclose the region of stability of water to reduction or oxidation.

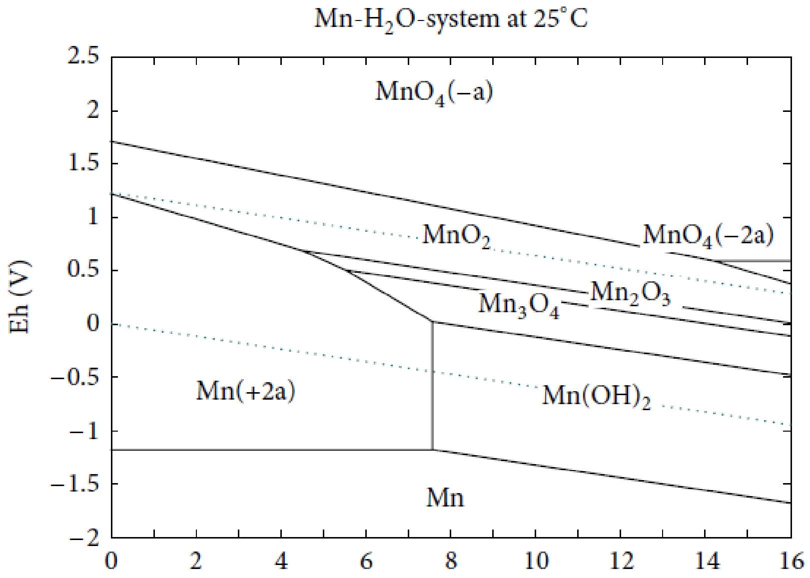

Figure 1. Eh-pH diagram of predominant manganese species

Source: Freitas *et al.* (2013).

8.2 Partitioning and Transport in the Environment

In soil, manganese can migrate to air or water as particulate matter. Alternatively, soluble manganese compounds can leach from the soil, with solubility determined by pH and redox potential (WHO 2004). Generally, adsorption is increased with increasing pH, and mobility is increased under reducing conditions. Due to the ionic character of manganese compounds, volatilization does not occur from soil surface (WHO 2004).

In air, elemental manganese and inorganic manganese compounds have negligible vapour pressures but can exist as suspended particulate matter derived from industrial emissions or soil erosion (USEPA 1984). Fate and transport of manganese particulate matter can be determined by particle size and density, as well as by wind speed and direction (WHO 2004). Particles containing manganese can be removed from the air by gravitational settling or rainfall, with the former being the most significant (USEPA 1984).

In water, the Mn^{2+} ion is more soluble than Mn^{4+}. Manganese solubility in water can be increased by the presence of chlorides, nitrates and sulphates, which thus increase aqueous mobility (WHO 2004). In rivers, manganese is often transported as adsorbed to suspended sediments (WHO 2004). In aerobic environments Mn^{2+} undergoes a complex series of oxidation/precipitation and adsorption reactions, which makes it biologically unavailable as insoluble manganese dioxide (WHO 2004). The kinetics of Mn^{2+} oxidation are slow in waters with pH below 8.5 (Zaw and Chiswell 1999), and the time required for the oxidation and precipitation of manganese ranges from days in natural waters to years in synthetic waters (Stokes *et al*. 1988). In waters of pH 4–7, Mn^{2+} predominates, but it may be oxidized in alkaline conditions at pH greater than 8 (ATSDR 2012).

In sediment, manganese cycling is affected by the oxygen content of the overlying water, the penetration of the oxygen into the sediments and the benthic organic carbon supply (WHO 2004). In oxic conditions, Mn^{2+} oxidizes to insoluble MnO_2 and settling of MnO_2 moves manganese from the water column to the bottom sediment (Graham *et al*. 2012). In shallow oxygenated waters, oxic conditions can penetrate the sediment layer and allow for a sink of MnO_2. As sediment depth increases to adequately reducing conditions, reductive dissolution of MnO_2 results in the release of Mn^{2+} into sediment porewater. Upwards diffusion causes re-oxidation and precipitation: a diagenetic process (Graham *et al*. 2012).

9.0 ESSENTIALITY AND BIOACCUMULATION

9.1 Essentiality of Manganese; Effects Due to Deficiency

Manganese is an essential element for biological functioning. It is a constituent of various enzymes and functions as an activator of enzyme systems in animals (Martin 1974 as cited in Steenkamp *et al*. 1994). Nutritional manganese requirements vary widely between species; however, toxic effects can be observed at concentrations higher than these requirements (WHO 2004).

Manganese deficiency can cause reduced growth, skeletal deformities, defective egg shell formation or impaired glucose tolerance (Knox *et al*. 1981). An aquatic plant, *Lemna major*, demonstrated lighter colouring and smaller fronds when grown in a manganese-deficient environment. It also developed chlorosis, failed to reproduce, and exhibited necrosis and mortality after utilization of the residual metal. Chlorotic plants were also grown in a manganese-deficient solution but were successfully restored to the healthy dark green state when traces of manganese sulphate were added (McHargue and Calfee 1932). Manganese deficiency in fish often results in deformed growth, increased mortality, skeletal abnormalities, lens cataracts and low Mn-superoxide dismutase. Depressed growth has been observed in a variety of fish species, including the rainbow trout, yellow catfish, common carp, grass carp and gibel carp (Tan *et al*. 2012). Rainbow trout (*Oncorhychus mykiss)* demonstrated bone deformities in the manganese-deficient setting but not in the control (Knox *et al*. 1981).

9.2 Bioaccumulation of Manganese in Aquatic Organisms

Since manganese is an essential element, it will always be found within living organisms at reasonably constant concentrations. Bioconcentration factors (BCFs) and bioaccumulation factors (BAFs) are often used in chemical assessments to indicate how bioaccumulative the substances are. However, these models may not be as useful when assessing metals, especially essential metals, due to underlying assumptions of the models, accumulation from background levels, homeostatic control of metal concentrations, and internal detoxification and storage (McGeer *et al*. 2003). Research has shown that BCFs and BAFs for metals tend to be inversely related to exposure concentration; in other words, when the concentration in the surrounding water is low, the BCF is high, and when the concentration in the water is high, the BCF is low (McGeer *et al*. 2003). This contradicts toxicological evidence for higher hazard at higher concentrations. Since the BCF and BAF models cannot distinguish between nutritional accumulation and accumulation that causes adverse effects, it should be used with caution when assessing bioaccumulative hazard (McGeer *et al.* 2003).

For reference, laboratory BCFs for manganese can range from 2,000 to 20,000 for marine and freshwater plants, 2,500 to 6,300 for phytoplankton, 800 to 5,500 for marine macroalgae, 800 to 830 for intertidal mussels and 35 to 930 for fish (UKTAG 2012). The bioaccumulation of manganese in a freshwater crab was determined to have the highest concentrations of manganese in the carapace, followed by the midgut gland, gills and gonads, with the lowest concentration in the muscle tissue (Steenkamp *et al.* 1994). Nussey *et al.* (2000) found manganese concentrations to be highest in the gills, followed by liver, muscle and skin, for a field-collected cyprinid fish, suggesting the gills are the main uptake pathway instead of through the gut by food.

The rate of uptake for manganese by aquatic biota is influenced by temperature, pH and salinity. The uptake was found to significantly increase with temperature but decrease with pH and salinity (WHO 2004). Dissolved oxygen was not found to have a significant effect on the rate of uptake.

10.0 TOXICITY OF MANGANESE TO AQUATIC ORGANISMS

10.1 Bioavailability and the Biotic Ligand Model

The Biotic Ligand Model (BLM) was not used for derivation of the CWQG for manganese, as it has not been developed or validated based on Canadian monitoring data, surface waters or framework of assessment, in addition to the relative complexity of the model.

The BLM develops a relationship between the accumulation of a metal at a specific site (the biotic ligand) of an aquatic organism and toxicity. For fish, the biotic ligand for acute toxicity is considered to be the sodium or calcium channel proteins on the surface of the gills, which regulate blood ionic balance (Di Toro *et al.* 2001). The BLM is built on the assumption that other constituents present in the surrounding water influence the degree of metal binding to the biotic ligand (Paquin *et al.* 2002). For example, DOC forms complexes with metals, thus reducing its free ion activity, and ions such as calcium and sodium compete with metals for binding sites on the biotic ligand. If sufficient metal accumulation does occur at the biotic ligand, toxicity will occur, and this toxicity can be predicted using the model (Paquin *et al.* 2002).

A central premise of the BLM is that the water chemistry of the system is at equilibrium, and therefore thermodynamic and conditional binding constants can be used to calculate the metal concentrations in the system, including metal bound to the biotic ligand (Paquin *et al.* 2002). There are three components to the conceptual model: (i) the chemistry of the solution in bulk water, allowing estimation of the free metal ion of interest; (ii) binding of the metal to the biotic ligand; and (iii) the relationship between the binding of the metal to the biotic ligand and the toxic response (Paquin *et al.* 2002).

Chronic manganese BLMs are available for the three main trophic levels within a freshwater environment, represented by the fathead minnow (*Pimephales promelas*), the water flea (*Ceriodaphnia dubia*) and an alga (*Pseudokirchneriella subcapitata*) (Peters *et al*. 2011). Toxicity tests were conducted over varying water chemistry conditions, including pH, DOC and ion concentrations, to assess the effect of water physico-chemistry on manganese ecotoxicity in the form of the Mn^{2+} ion (measured as dissolved manganese concentrations). For fish and invertebrates, toxicity of manganese is primarily affected by aqueous calcium concentrations, with high calcium having a protective effect on manganese toxicity. Fish and invertebrates are relatively sensitive to manganese in low calcium concentrations (Peters *et al*. 2011). For plants and algae, the toxicity of manganese is only influenced by protons (pH), with plants and algae being especially sensitive to manganese at high pH. DOC has a relatively limited effect on manganese toxicity (Peters *et al*. 2011). The BLM was validated using data from natural European waters with a wide range of water chemistries, and in most cases BLM predictions were found to be within a factor of two (Peters *et al*. 2011).

Using the manganese BLM to make site-specific predictions of toxicity is a relatively complex process and is best performed by someone with experience/expertise in chemical speciation modelling (IMnI 2014). Essentially, the process includes the following steps:

i) Calculate the solution speciation based on water chemistry
ii) Calculate free manganese activity at the toxicity threshold
iii) Calculate dissolved manganese concentration at the toxicity threshold from the free manganese activity (IMnI 2014).

Due to the relative complexity of the model and process described above, as well as intensive data input requirements and the need for specialized software packages, a simplified approach named the Manganese BLM Screening Tool was developed by consultants for the IMnI (IMnI 2014). The screening tool is a simplified version of the full BLM that requires only three input parameters (Ca^{2+}, pH and DOC) and has a user-friendly interface. Although less accurate than the full BLM, the screening tool errs on the side of conservatism (IMnI 2014). The screening tool can be used as an early tier of tiered risk assessments, as it is simple yet precautionary. The screening tool can be found on the Water Framework Directive–UKTAG website (UKTAG 2014).

The screening tool described above was not used for derivation of the CWQG for manganese, as it was developed and validated based on European Union (EU) monitoring data, including relationships between ions established for EU surface waters, and was developed for the EU framework of risk assessment. The applicability of the screening tool to Canadian waters and in the context of Canadian guideline development and implementation has not yet been determined. The full BLM described above was also not used for derivation of the CWQG for manganese due to the relative complexity of the model and the reasons described above. Instead, linear regression methods were used to explore and incorporate pertinent water chemistry variables affecting manganese toxicity (Section 10.0) into the CWQG for manganese where possible and appropriate.

10.2 Mode of Action

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). The metal then 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. However, there is evidence to suggest manganese promotes the formation of reactive oxygen species, inducing oxidative stress, damage to tissues, inflammation and neurodegeneration in fish (Valavanidis *et al*. 2006; Vieira *et al*. 2012). The enhancement of reactive oxygen species disrupts the antioxidant defence system composed of both enzymatic and non-enzymatic antioxidants. For example, decreased activities of the antioxidant enzyme catalase were observed in the brains of *Colossoma macropomum* (Gabriel *et al.* 2013) and *Rhamdia quelen* (Dolci *et al*. 2013) as well as for brain superoxide dismutase in *C. macropomum* (Gabriel *et al.* 2013) and *Carassius auratus* (Vieira *et al*. 2012). In addition, lipid peroxidation, a biomarker for oxidative cell damage, was enhanced in these fish species. Antioxidant activity and lipid peroxidation vary throughout the body of fish, therefore the Mn-induced oxidative effects are thought to be organ and tissue specific (Vieira *et al*. 2012).

In some algal species, manganese may induce iron deficiency, which can lead to inhibition of chlorophyll synthesis. Conversely, manganese is suspected to ameliorate the toxicity of other metals to microalgae (WHO 2004).

10.3 Toxicity Modifying Factors

Water chemistry survey data have an important role in the application of some CWQGs since the toxicity of many metals is modified by various factors (e.g., water hardness, alkalinity, pH, DOC etc.) (CCME 2007). Because these water quality variables are important in the application of CWQGs, development of the guidelines should incorporate water chemistry characteristics if they can be shown to affect toxicity. For the purposes of the manganese CWQG and benchmark derivation, all relevant literature was examined for trends in the effect of a given toxicity modifying factor over a range of species. Sufficient data were available to assess the independent influence of three variables on manganese toxicity: hardness, pH and DOC, where the variable of interest was varied and other variables were held constant.

10.3.1 Hardness

Hardness has been shown to be an important toxicity modifying factor for manganese for several species of fish and invertebrates (Davies *et al.* 1998; Parametrix 2010b, 2010d; Peters *et al.* 2011; Reimer 1999; Stubblefield *et al.* 1997). Peters *et al.* (2011) found that Ca^{2+} cations reduced manganese toxicity to fish and invertebrates, while Mg^{2+} cations also reduced manganese toxicity to invertebrates (although not to the same extent as Ca^{2+} cations). Generally, as water hardness increases, the toxicity of manganese to fish and invertebrates decreases (Davies *et al*. 1998; Lasier *et al*. 2000; Parametrix 2010b, 2010d; Reimer 1999; Stubblefield *et al.* 1997). The hardness of the water likely influences manganese toxicity by creating competition between the Ca^{2+} and Mg^{2+} cations and manganese for binding to the biotic ligand (Lasier *et al*. 2000).

The methods used to develop hardness–toxicity relationships were based on those described by Stephan *et al*. (1985) and those used in the cadmium CWQG (CCME 2014). Relationships between short-term total manganese toxicity and water hardness can be seen in Figure 2 where, within an individual study, hardness varied by 100 mg/L and the highest hardness was at least three times the lowest with other variables kept relatively constant. *Oncorhynchus kisutch* (Reimer 1999), *O. mykiss* (Davies *et al.* 1998; Reimer 1999), *Salvelinus fontinalis* (Davies *et al.* 1998), *C. dubia* (Lasier *et al.* 2000), *Chironomus tentans* (Reimer 1999) and *Hyalella azteca* (Lasier *et al.* 2000) all demonstrated decreased toxicity (or increasing effect concentrations) with increasing water hardness.

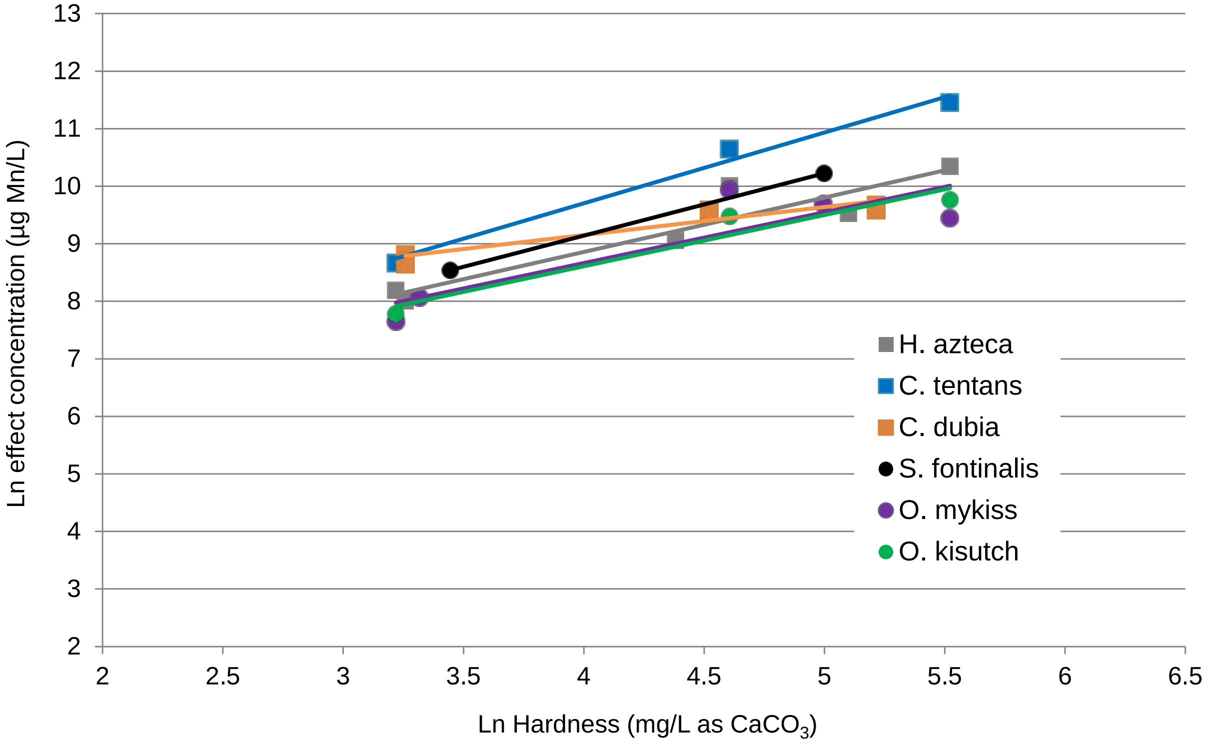

Figure 2. Hardness (mg/L) versus short-term manganese toxicity (μg Mn/L) for several species of fish (circles) and invertebrates (squares)

All are LC_{50} endpoints for total Mn concentrations.
Source: Data from Davies *et al.* (1998); Lasier *et al.* (2000); Reimer (1999).

Relationships between long-term manganese toxicity and water hardness can be seen in Figure 3 where, within an individual study, hardness varied by 100 mg/L and the highest hardness was at least three times the lowest, with other variables kept relatively constant. *C. dubia* (Parametrix 2010a, 2010b), *P. promelas* (Parametrix 2010c, 2010d), *O. mykiss* (Davies *et al.* 1998), *Salmo trutta* (Stubblefield *et al.* 1997) and *S. fontinalis* (Davies *et al.* 1998) all demonstrated decreased toxicity (or increasing effect concentrations) with increasing water hardness for both total and dissolved manganese concentrations.

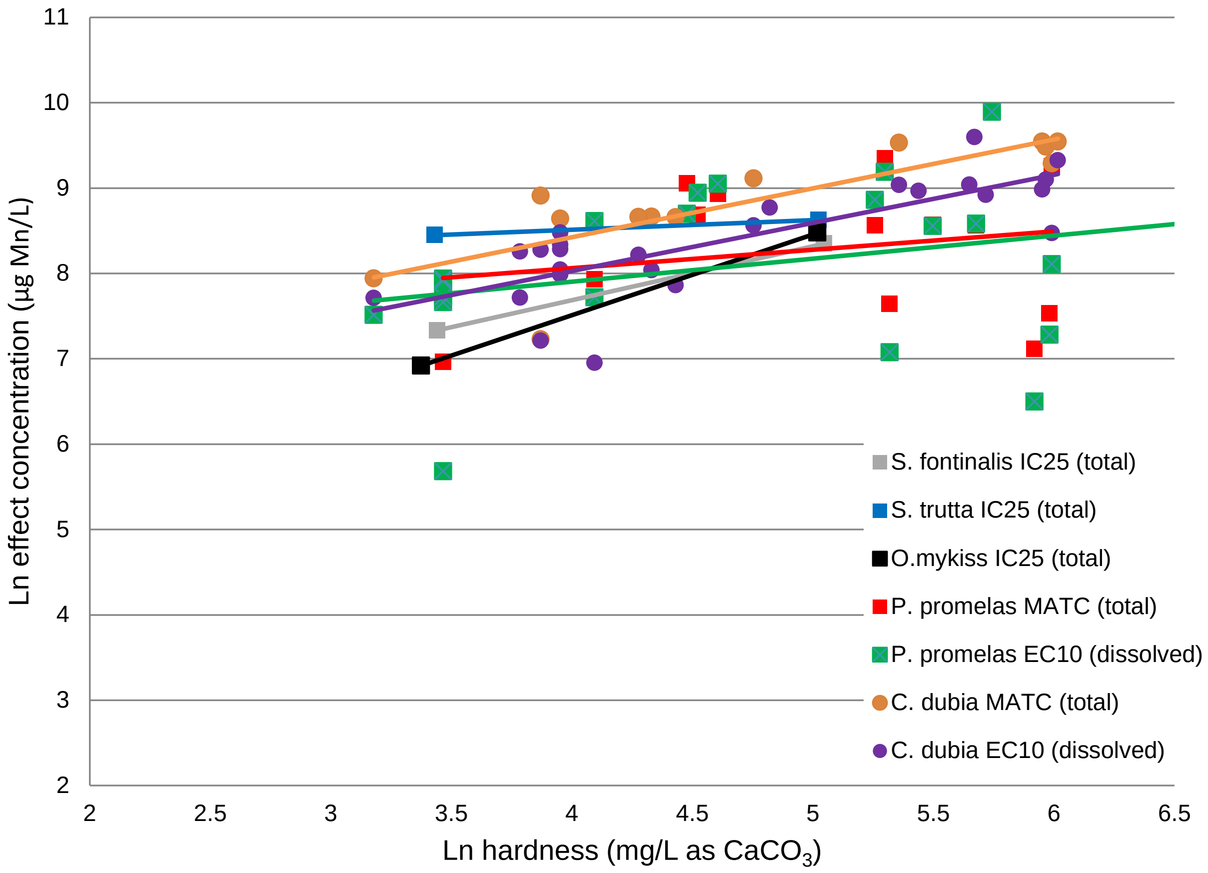

Figure 3. Hardness (mg/L) versus long-term manganese toxicity (µg Mn/L) for several species of fish (squares) and invertebrates (circles)

MATC= maximum acceptable toxicant concentration
Source: Data from Davies *et al*. (1998); Parametrix (2010a–d); Stubblefield *et al*. (1997).

Hardness has not been expected or shown to cause a toxicity modifying effect to aquatic plants or algae (Peters *et al*. 2011). No short-term toxicity data were available to demonstrate this lack of relationship; however, chronic data were available for the algae *P. subcapitata* (Parametrix 2009g, 2010e, 2010f) (Figure 4). The chronic algae data for water hardness versus manganese toxicity demonstrated no trend.

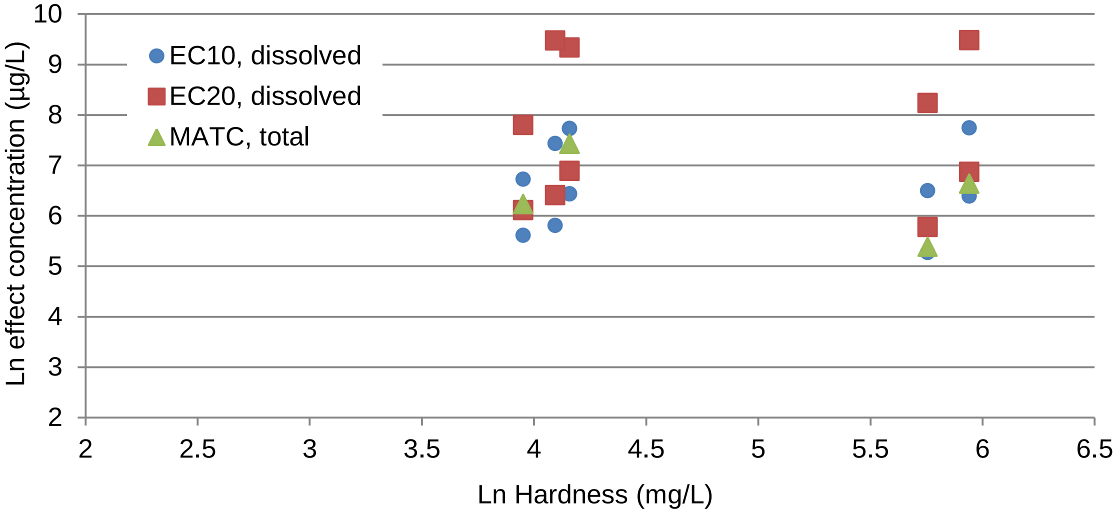

Figure 4. Hardness (mg/L) versus long-term manganese toxicity (µg Mn/L) to *P. subcapitata* (algae)

Source: Data from Parametrix (2009g, 2010e, 2010f).

10.3.2 pH

For manganese, pH has been found to be an important toxicity modifying factor for algae, whereby decreased pH decreases manganese toxicity due to competition of H^+ ions (Peters *et al*. 2011). The relationship between chronic manganese toxicity and pH for the green algae (*P. subcapitata*) can be seen in Figure 5. As pH increases, manganese toxicity increases to *P. subcapitata* (as evidenced by decreasing effect concentrations), affecting cell yield and growth in both total and dissolved manganese concentrations (Parametrix 2009g, 2010e, 2010f). Acceptable data were also available to assess the relationship between pH and dissolved manganese toxicity to fish (*P. promelas*) and invertebrates (*C. dubia*). As seen in Figure 6, there is no discernible trend, indicating that the toxicity of manganese to fish and invertebrates is not affected by pH. This finding is supported by conclusions in previous literature (Peters *et al*. 2011). For each endpoint and effect, pH spanned at least 1.5 units.

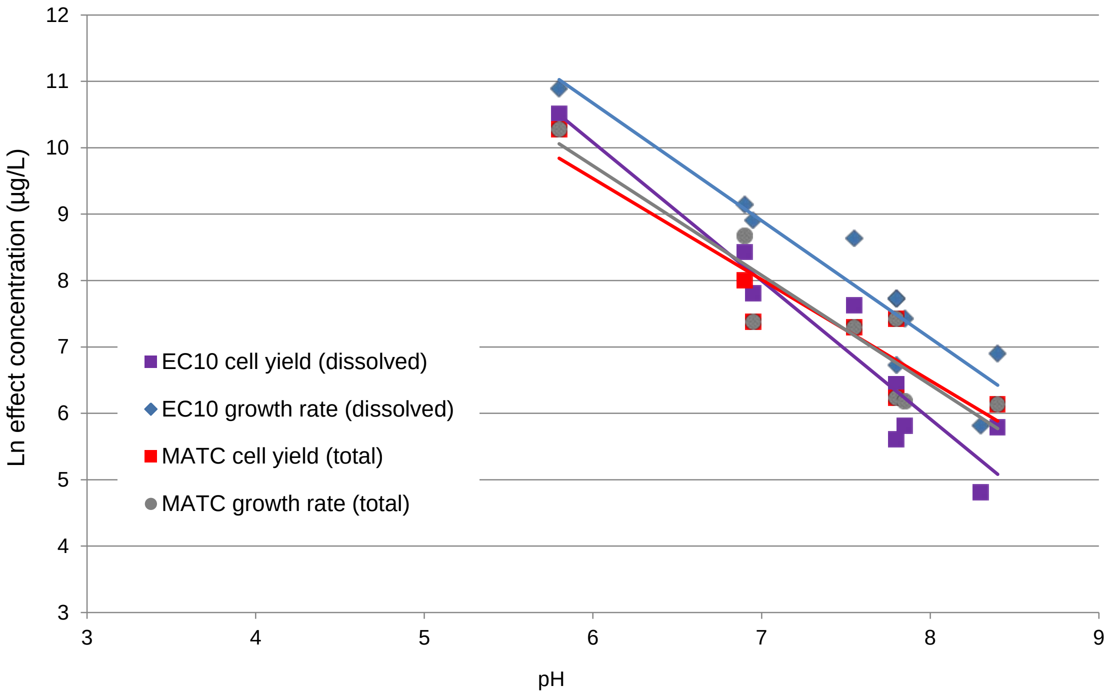

Figure 5. pH versus manganese toxicity (µg Mn/L) for *P. subcapitata*

Source: Data from Parametrix (2009g, 2010e, 2010f).

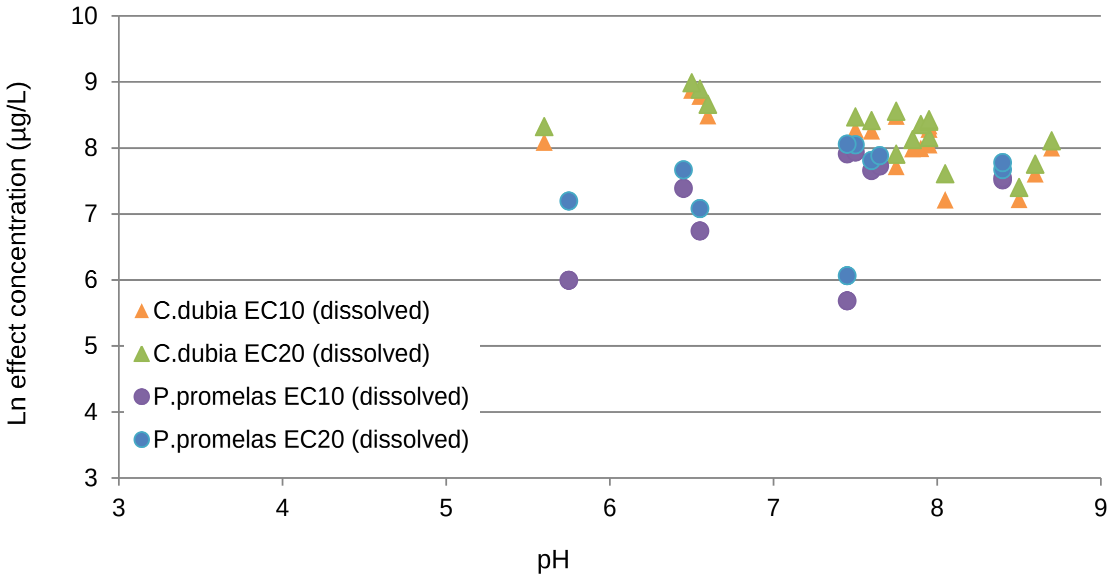

Figure 6. pH versus dissolved manganese toxicity (µg Mn/L) for *C. dubia* (EC_{10}/EC_{20} reproductive impairment) and the fish *P. promelas* (EC_{10}/EC_{20} dry biomass)

Source: Data from Parametrix (2010a–d).

10.3.3 Dissolved Organic Carbon

DOC has been found to have little effect on manganese toxicity to aquatic organisms (Peters *et al.* 2011). Data were available to plot DOC versus dissolved manganese effect concentrations for invertebrate (*C. dubia*) and fish (*P. promelas*) species (Figure 7) (Parametrix 2010a–d). There is 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.

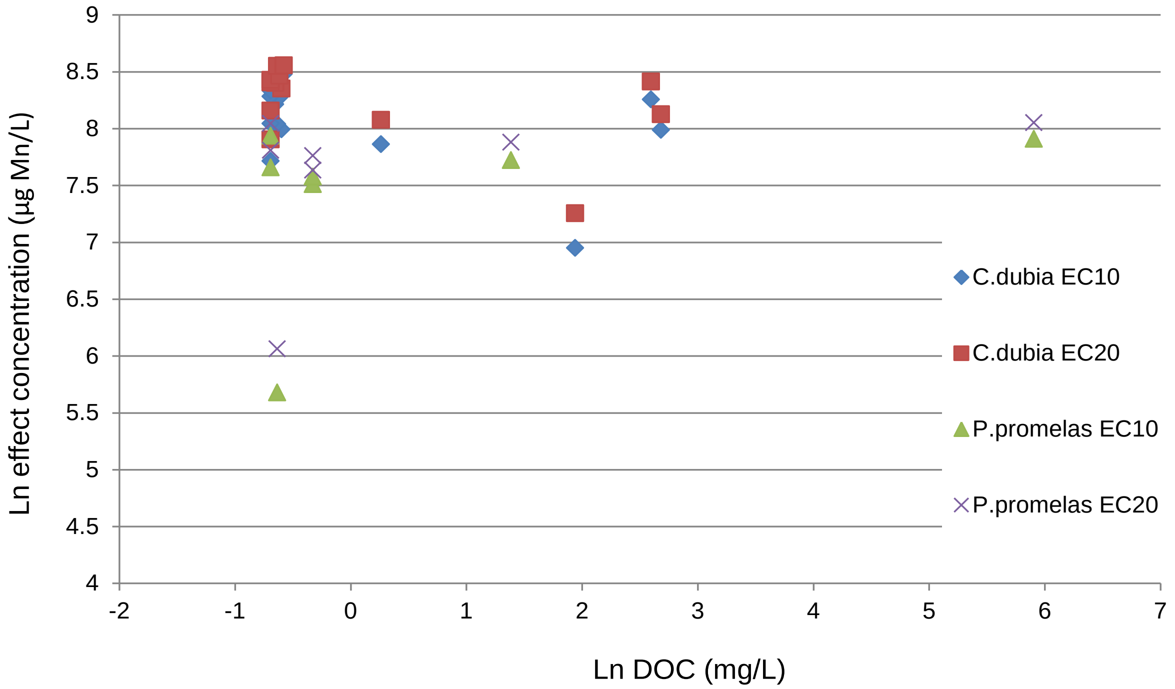

Figure 7. DOC (in mg/L) versus dissolved manganese long-term toxicity (µg Mn/L) for the aquatic invertebrate *C. dubia* and the fish *P. promelas*

Source: Data from Parametrix (2010a–d).

10.4 Incorporating Toxicity Modifying Factors into Normalization Equations

CCME (2007) protocol states that, where possible, it is important to account for exposure and toxicity modifying factors in guideline derivation. This may be done through single- or multi-factor equations, matrices or models (CCME 2007).

10.4.1 Multiple Linear Regression

Multiple linear regression (MLR) analysis was explored here first as an approach to account for the simultaneous effect of multiple water chemistry variables on manganese toxicity. Long-term toxicity data were available over a broad range of hardness, pH and DOC for three species, including *C. dubia*, *P. promelas* and *P. subcapitata*. Insufficient short-term data were available to conduct MLR.

Forward stepwise MLR analyses for long-term manganese toxicity data were conducted using SigmaPlot (Version 13) statistical software. The analysis determined whether a significant portion of variability in toxicity could be explained by hardness, pH and/or DOC. MLR analyses were conducted on a species-by-species basis, whereby toxicity values for a given species were the dependent variables and the water chemistry values were the independent variables. MLR analysis was conducted for a given species if toxicity data were available from tests in which the range of hardness exceeded 100 mg/L (with the highest hardness being three times the lowest), the range of DOC exceeded 5 mg/L (with the highest DOC being three times the lowest) and the range of pH spanned at least 1.5 units. The acceptable toxicity data could include data combined from multiple studies for the same species.

Based on the MLR results (not shown), this approach was not found to be favourable for development of the long-term manganese water quality guideline. The MLR models developed for the various species had one or more of the following short-comings: i) failed statistical assumptions of normality; ii) failed statistical assumptions of constant variance; iii) did not explain a large proportion of the variance in toxicity; iv) had low predictive capability (did not predict toxicity well); v) only one variable was found to be significant (in which case another approach, such as a pooled model, is preferable); vi) resulted in extremely over-protective guideline values; or vii) resulted in under-protective guideline values. For these reasons, MLR was determined not to be a suitable approach for the adjustment of manganese toxicity modifying factors based on the available data.

10.4.2 Single-variable Normalization Equation for Short-term Manganese Toxicity

Sufficient data were available to derive a relationship between short-term manganese toxicity and water hardness. Data were available for total concentrations of manganese only. Data were available over the required range of hardness for six species including *O. kisutch*, *O. mykiss*, *S. fontinalis*, *C. dubia*, *C. tentans* and *H. azteca* with a total of 25 endpoints (see Figure 2). For each species, hardness data spanned at least 100 mg/L, and the highest hardness for each species was at least three times the lowest. All data were of acceptable quality (primary or secondary according to CCME 2007) and concentrations of manganese were analytically measured. An empirical relationship between short-term manganese toxicity and water hardness was developed using this data in order to normalize short-term toxicity data to common water hardness.

The methods used to develop a hardness–toxicity relationship were based on those described by Stephan *et al.* (1985) and those used in the cadmium CWQG (CCME 2014). Statistical analyses were conducted in Systat (v. 13). An F-test showed that the slopes between species were not significantly different (p-Value=0.284, F-ratio=1.411, df=5). An analysis of covariance was performed to calculate a pooled hardness slope of 0.878, which is significantly different from zero (p-Value=<0.001, F-ratio=92.9, df=1).

The slope value of 0.878 relating short-term manganese toxicity with hardness was used to normalize short-term toxicity values to hardness of 50 mg/L using the following equation:

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

where LC_{50} is the short-term toxicity value in µg/L and hardness is measured as $CaCO_3$ equivalents in mg/L.

10.4.3 Single-variable Normalization Equations for Long-term Manganese Toxicity

As hardness and pH have been shown to be important toxicity modifying factors for fish/invertebrates and plant/algae, respectively, single-variable normalization equations were explored for long-term data in which fish and invertebrate data are normalized using a hardness equation, and plant and algae data are normalized using a pH equation.

10.4.3.1 Hardness Normalization Equation

Long-term toxicity data were available over a broad range of hardness for five species including *C. dubia*, *P. promelas*, *O. mykiss*, *S. trutta*, and *S. fontinalis* (see Figure 3). Data were available for both total and dissolved concentrations of manganese. For each species, hardness data spanned at least 100 mg/L, and the highest hardness for each species was at least three times the lowest. All data were of acceptable quality (primary or secondary according to CCME 2007) and concentrations of manganese were analytically measured. An empirical relationship between long-term manganese toxicity and water hardness was developed using this data (81 endpoints).

The methods used to develop a hardness–toxicity relationship were based on those described by Stephan *et al.* (1985) and those used in the cadmium CWQG (CCME 2014). Statistical analyses were conducted in Systat (v. 13). An F-test showed that the slopes between individual species and between total and dissolved data were not significantly different (p-Value=0.564, F-ratio=0.813, df=6). An analysis of covariance was performed to calculate a pooled hardness slope of 0.411, which applies to total and dissolved data and is significantly different from zero (p-Value=0.000, F-ratio=26.177, df=1).

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 using the equation:

$$EC_{x\ \text{(at X mg/L hardness)}} = e^{[(\ln(\text{original ECx})) - 0.411*(\ln(\text{original hardness}) - \ln(X))]}$$

where effect concentration (EC_x) is the long-term toxicity value in µg/L and hardness is measured as $CaCO_3$ equivalents in mg/L. Below is an example equation used to normalize long-term toxicity values to hardness of 50 mg/L:

$$EC_{x\ \text{(at 50 mg/L hardness)}} = e^{[(\ln(\text{original ECx}))-0.411*(\ln(\text{original hardness})-\ln(50))]}$$

10.4.3.2 pH Normalization Equation

Long-term toxicity data were available over a broad range of pH for the green algae *P. subcapitata* (see Figure 5). Data were available for both total and dissolved concentrations of manganese. For each endpoint and effect, pH spanned at least 1.5 units for a total of 35 data points. All data were of acceptable quality (primary according to CCME 2007), and concentrations of manganese were analytically measured. An empirical relationship was developed using this data in order to normalize algal data to a common pH.

Statistical analyses were conducted in Systat (v. 13). An F-test showed that slopes between different effects and endpoints and between total and dissolved *P. subcapitata* data were not significantly different (p-Value=0.408, F-ratio=1, df=3). An analysis of covariance was performed to calculate a pooled pH slope of -1.774, which applies to total and dissolved data and is significantly different from zero (p-Value=0.000, F-ratio= 216.113, df=1).

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 using the following equation:

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

where EC_x is the long-term toxicity value in µg/L and pH is measured in standard units. Below is an example equation used to normalize long-term toxicity values to a pH of 7.5:

$$EC_{x\ (at\ pH\ 7.5)} = e^{[(\ln(\text{original } ECx))+1.774*(\text{original pH}-7.5)]}$$

10.5 Toxicity to Freshwater Organisms

The following section presents an overview of the acceptable toxicity values reported for short-term and long-term toxicity of manganese to aquatic organisms. Note that this section relates only to those data selected for inclusion in the SSD (see Section 12.0 for further details on SSDs, guideline derivation and data selection criteria).

10.5.1 Short-term Toxicity

Short-term endpoint values have been normalized to hardness of 50 mg/L using the hardness normalized equation described in Section 10.4.2. One endpoint in the short-term SSD data set did not report hardness in the original study; therefore, for this, endpoint hardness was estimated based on the type of dilution water used in the test and its hardness classification as reported by the study authors. Short-term data points for total manganese concentrations were plotted in the SSD after being converted to a dissolved concentration using a total:dissolved conversion multiplier of 0.978 (see Section 11.0 for details on the dissolved:total conversion factor). Two endpoints in the short-term SSD are for dissolved concentrations measured experimentally. All data included in the short-term SSD are from tests using $MnSO_4$ or $MnCl_2$ forms of manganese. A list of the endpoints included in the short-term SSD can be seen in Table 10.

10.5.1.1 Fish

Short-term LC_{50} values for five species of fish were included in the SSD. The most sensitive fish species as well as the most sensitive species overall in the SSD was the coho salmon (*O. kisutch*) with a normalized 96-h LC_{50} value of 4,994 µg/L based on the geometric mean of three comparable 96-h LC_{50}s for the same life stage (Reimer 1999). Rainbow trout (*O. mykiss*) followed closely in sensitivity, with a normalized 96-h LC_{50} of 5,009 µg/L, also based on a geometric mean of three comparable values (Reimer 1999). The least sensitive fish species was the gila longfin dace (*Agosia chrysogaster*) with a normalized 96-h LC_{50} value of 34,077µg/L (Lewis 1978). Overall, salmonids were found to be the most sensitive fish.

10.5.1.2 Invertebrates

Short-term LC_{50} values were included in the SSD for 11 species of invertebrates. The most sensitive invertebrate species in the SSD was the amphipod *H. azteca,* with a normalized 96-h LC_{50} of 5,148 µg/L (Lasier *et al.* 2000). The least sensitive invertebrate species was the amphipod *Crangonyx pseudogracilis,* with a normalized 96-h LC_{50} of 678,732 µg/L (Martin and Holdich 1986).

10.5.1.3 Amphibians

Acceptable data for one amphibian species was available for inclusion in the short-term SSD. The boreal toad *Bufo boreas* had a normalized 96-h LC_{50} of 39,568 µg/L (Davies *et al.* 1998).

Table 10. Toxicity data points used in the short-term SSD to determine the benchmark concentration for manganese

SSD rank order	Species	Endpoint	Life stage	Data quality	Effect concentration (µg/L)	Dissolved/ total	Reference	Normalized effect concentration[1] (µg/L)
1	*Oncorhynchus kisutch* (Coho salmon)	96-h LC_{50}	Underyearling	Secondary	Geometric mean	Total	Reimer 1999	4,994
2	*Oncorhynchus mykiss* (Rainbow trout)	96-h LC_{50}	Underyearling	Secondary	Geometric mean	Total	Reimer 1999	5,009
3	*Hyalella. azteca* (Amphipod)	96-h LC_{50}	6–7 days	Secondary	Geometric mean	Total	Lasier *et al.* 2000	5,148
4	*Daphnia magna* (Water flea)	48-h LC_{50}	<24 h	Primary	Geometric mean	Total	Biesinger and Christensen 1972; Kimball 1978; Teodorovic *et al*. 2009	6,149
5	*Ceriodaphnia dubia* (Water flea)	48-h LC_{50}	<48 h	Secondary	Geometric mean	Total	Lasier *et al.* 2000	7,498
6	*Salvelinus fontinalis* (Brook trout)	96-h LC_{50}	Fry	Primary	Geometric mean	Total	Davies *et al*. 1998	8,849
7	*Pimephales promelas* (Fathead minnow)	96-h LC_{50}	Juvenile – 8 weeks	Primary	Geometric mean	Total	Kimball 1978	11,288
8	*Chironomus tentans* (Chironomid)	96-h LC_{50}	Larvae	Secondary	31,500	Total	Reimer 1999	17,386
9	*Megalonaias nervosa* (Washboard mussel)	96-h LC_{50}	<5 days	Primary	43,300	Total	USEPA 2010	18,387
10	*Lampsilis siliquoidea* (Fatmucket clam)	96-h LC_{50}	<5 days	Primary	33,800	Total	USEPA 2010	25,275
11	*Agosia chrysogaster* (Gila longfin dace)	96-h LC_{50}	Not reported	Secondary	130,000	Total	Lewis 1978	34,077
12	*Aeolosoma sp.* (Annelid)	48-h LC_{50}	<24 h	Primary	39,460	Dissolved	Parametrix 2009h	38,124

SSD rank order	Species	Endpoint	Life stage	Data quality	Effect concentration (µg/L)	Dissolved/ total	Reference	Normalized effect concentration[1] (µg/L)
13	*Bufo boreas* (Boreal toad)	96-h LC_{50}	Tadpole	Secondary	42,300	Total	Davies *et al*. 1998	39,568
14	*Tubifex tubifex* (Sludge worm)	96-h EC_{50}	Not reported	Secondary	Geometric mean	Total	Rathore and Khangarot 2003	57,631
15	*Lymnaea stagnalis* (Great pond snail)	96-h LC_{50}	3–4 weeks	Primary	Geometric mean	Dissolved	Parametrix 2009e	75,146
16	*Asellus aquaticus* (Water louse)	96-h LC_{50}	Not reported	Secondary	333,000	Total	Martin and Holdich 1986	325,674
17	*Crangonyx pseudogracilis* (Amphipod)	96-h LC_{50}	Not reported	Secondary	694,000	Total	Martin and Holdich 1986	678,732

[1] Normalized effect concentrations represent endpoints normalized to 50 mg/L hardness using the equation $LC_{50\ (\text{at 50 mg/L hardness})}$ = e((ln(original LC_{50}))-0.878*(ln(original hardness)-ln(50))) (see Section 10.4.2) and endpoints based on total concentrations converted to dissolved concentrations using a multiplier of 0.978 (see Section 11.0).

10.5.2. Long-term Toxicity

For the long-term SSD data set, measured effect concentrations were not normalized to only a single point value (hardness of 50 mg/L (for invertebrates and fish) and pH 7.5 (for plants and algae) but instead were normalized (using the equations described in Section 10.4.3) for multiple (n=132) hardness and pH combinations ranging from 25 to 670 mg/L and 5.8 to 8.4, respectively. Normalizing to multiple combinations is appropriate since the relative sensitivities of invertebrates/fish and plant/algae vary depending on the combination of site-specific hardness and pH conditions. The SSD data set is presented in Table 11. The "Effect Concentration" column contains the values reported by the authors, or a geometric mean. The "Normalized Effect Concentration" column contains values normalized for hardness of 50 mg/L (for invertebrates and fish) and pH 7.5 (for plant/algae). The data points were normalized to 132 unique combinations of hardness and pH (data not shown).

One algal (*Scenedesmus quadricauda*) endpoint in the long-term SSD dataset did not report pH in the original study, and a reliable pH estimate was not possible based on the limited information available. Therefore, for this endpoint, a default value of pH 7.5 was used for the calculation to represent common laboratory conditions. Most endpoints in the long-term SSD are for dissolved manganese measured experimentally. Four endpoints for total manganese were included in the long-term SSD after being converted to a dissolved concentration using a total:dissolved conversion multiplier of 0.978 (see Section 11.0 for details on the dissolved:total conversion factor). All data included in the long-term SSD are from tests using the $MnSO_4$ or $MnCl_2$ forms of manganese. *H. azteca* was the most sensitive species at most hardness and pH combinations, except at high pH, when toxicity to plants/algae becomes more significant. The green algae *P. subcapitata* had the lowest effect concentrations when normalized to pH 7.7 and hardness of 670 mg/L, pH 8 and hardness of 125–670 mg/L, and above pH 8.3 at hardness of 50–670 mg/L.

10.5.2.1 Fish

Acceptable long-term manganese toxicity values for fish included endpoints obtained in tests with a duration of 21 days or longer for adult fish, and seven days or longer for early life stages (CCME 2007). Long-term toxicity data in the SSD included five species of fish. The most sensitive fish species in the SSD was the brook trout (*S. fontinalis*), with a 65-day EC_{10} for a weight of 1,096 µg/L once normalized to 50 mg/L hardness and converted to dissolved (Davies *et al.* 1998). This value is the geometric mean of two comparable EC_{10} endpoints for the effect of weight, both calculated from data in the original report using the USEPA Toxicity Relationship Analysis Program (TRAP v. 1.22). The least sensitive fish species included in the SSD was the zebrafish (*Danio rerio*), with a 30-day EC_{10} for mortality of 3,551 µg/L dissolved manganese once normalized to hardness of 50 mg/L (Parametrix 2009a).

10.5.2.2 Invertebrates

One study reports some uncertainty in the sensitivity of manganese to *H. azteca* while using glass compared to high-density polyethylene containers (Norwood *et al*. 2007). The tests performed in glass containers appeared to result in greater sensitivity of *H. azteca* to manganese with a 61-fold difference in inhibitory concentration of IC_{25} (growth) effect concentrations. This result was unexpected and no reasoning was offered by the authors in the paper or through personal communication for the differences seen in the tests. While no other direct comparison has been made, both glass and plastic containers were used in manganese toxicity tests for the other species used in the CWQG, and no apparent trend can be seen that would suggest a difference in sensitivity to manganese. The two other reliable chronic studies for *H. azteca* in the CWQG database are Parametrix (2009b) (glass) and Borgmann *et al.* (2005) (plastic), which are both more numerically similar despite some differences in exposure (i.e., duration) to each other and the glass results from Norwood *et al.* (2007), even though the former was conducted in glass and the latter in polyethylene (see Appendix A for all toxicity endpoints). In the absence of any other reliable data to support the Norwood *et al.* (2007) results and in order to be protective, we determined that the results from the Parametrix (2009b) study conducted in glass containers as well as the many other acceptable studies that used glass containers for other species in the database are valid for guideline derivation.

Acceptable long-term endpoints for invertebrates include non-lethal endpoints of at least 96 hours for shorter-lived invertebrates, non-lethal endpoints of at least seven days for longer-lived invertebrates, and lethal endpoints of 21 days or longer for longer-lived invertebrates (CCME 2007). Acceptable long-term manganese toxicity values for inclusion in the SSD were available for six species of invertebrates. The most sensitive invertebrate species was *H. azteca*, with a 35-day EC_{10} for mortality of 283µg/L dissolved manganese once normalized to hardness of 50 mg/L (Parametrix 2009b). The least sensitive invertebrate included in the SSD was the midge *C. tentans*, with a 62-day EC_{10} for mortality of 12,877µg/L dissolved manganese once normalized to hardness of 50 mg/L (Parametrix 2009c).

10.5.2.3 Plants/Algae

Due to the rapid growth and turnover of algal/aquatic plant standard test species, most toxicity tests are considered “long term” relative to the lifespan of the alga/plant. All toxicity tests for *Lemna sp.* following standard test protocols are generally considered long-term exposures. All algal toxicity tests with durations longer than 24 hours are considered long-term exposures (CCME 2007). Acceptable data for inclusion in the long-term SSD included two algal species and one aquatic plant species. The green algae *P. subcapitata* had a 72-hour EC_{10} of 965 µg/L dissolved manganese (normalized to a pH of 7.5) for effects to cell yield (Parametrix 2009g, 2010e, 2010f). This endpoint represents the geometric mean of 18 comparable EC_{10} endpoints for cell yield for this species. The green algae *Scenedesmus quadricauda* had a pH 7.5 normalized EC_{50} of 1,868 µg/L (Fargasova *et al*. 1999). The common duckweed *Lemna minor* had a pH 7.5 normalized 7-day EC_{10} for frond count of 13,804 µg/L dissolved manganese (Parametrix 2009f).

Table 11. Toxicity data points used in the long-term SSD to determine the CWQG for manganese

SSD Rank Order	Species	Endpoint	Life stage	Data quality	Effect concentration (µg/L)	Dissolved/ total	Reference	Normalized effect concentration[1] (µg/L)
1	*Hyalella azteca* (Amphipod)	35-d EC_{10} mortality	7–9 days	Primary	382.8	Dissolved	Parametrix 2009b	283
2	*Pseudokirchneriella subcapitata* (Green algae)	72-h EC_{10} cell yield	3–4 days	Primary	Geometric mean	Dissolved	Parametrix 2009g, 2010e, 2010f	965
3	*Salvelinus fontinalis* (Brook trout)	65-d EC_{10} weight	Early life stage	Primary	Geometric mean	Total	Davies *et al.* 1998	1,096
4	*Oncorhynchus mykiss* (Rainbow trout)	65-d EC_{10} weight	Early life stage	Primary	Geometric mean	Total	Davies *et al.*1998	1,232
5	*Scenedesmus quadricauda* (Green algae)	12-d EC_{50} chlorophyll content	Exponential growth phase	Secondary	1,910	Total	Fargasova *et al.*1999	1,868
6	*Salmo trutta* (Brown trout)	62-d EC_{10} weight	Early life stage	Primary	3,239	Dissolved	Stubblefield *et al*. 1997	2,052
7	*Pimephales promelas* (Fathead minnow)	7-d EC_{10} dry biomass	<24 hours	Primary	Geometric mean	Dissolved	Parametrix 2010c, 2010d	2,223
8	*Aeolosoma sp.* (Annelid)	14-d EC_{10} population growth	<24 hours	Primary	2,520	Dissolved	Parametrix 2009d	2,563
9	*Ceriodaphnia dubia* (Water flea)	7-d EC_{10} reproductive impairment	<24 hours	Primary	Geometric mean	Dissolved	Parametrix 2010a, 2010b	3,194
10	*Danio rerio* (Zebrafish)	30-d EC_{10} mortality	Embryo	Primary	4,629	Dissolved	Parametrix 2009a	3,555
11	*Daphnia magna* (Water flea)	21-d IC_{25} reproduction	<24 hours	Secondary	Geometric mean	Total	Reimer 1999	4,341
12	*Lymnaea stagnalis* (Great pond snail)	30-d EC_{10} growth	Newly hatched	Primary	7,700	Dissolved	Parametrix 2009i	4,612
13	*Chironomus tentans* (Midge)	62-d EC_{10} mortality	<24 hours	Primary	16,340	Dissolved	Parametrix 2009c	12,892
14	*Lemna minor* (Common duckweed)	7-d EC_{10} frond count	9-day-old culture	Primary	23,370	Dissolved	Parametrix 2009f	13,725

[1] Normalized effect concentrations represent fish/invertebrate endpoints normalized to 50 mg/L hardness using the equation $EC_{x\ (at\ 50\ mg/L\ hardness)}$ = e((ln(original EC_x))-0.413*(ln(original hardness)-ln(50))), plant/algal endpoints normalized to pH 7.5 using the equation $EC_{x\ (at\ pH\ 7.5)}$ =e((ln(original EC_x))+1.774*(original pH-7.5)) (see Section 10.4.3), and endpoints based on total concentrations converted to dissolved concentrations using a multiplier of 0.978 (see Section 11.0)

11.0 CONVERSION FACTORS FOR DISSOLVED/TOTAL CONCENTRATIONS

Generally, free metal ions are the bioavailable fraction of manganese, being able to cross biological membranes and cause toxic effects. Dissolved concentrations are estimated using a filtered sample, thereby excluding non-bioavailable particulates that are included in measurements of total concentration. Therefore, dissolved concentrations better represent the free metal ions and, hence, bioavailable form compared to total concentrations. For this reason, as well as the availability and quality of data for dissolved manganese, the CWQG and benchmark were derived using dissolved concentrations of manganese.

However, toxicity studies, especially older ones, often report total concentrations as opposed to dissolved concentrations. In order to use the endpoints from these reports in deriving a guideline based on dissolved concentrations, conversion factors (CFs) were developed to convert total concentrations of manganese to dissolved concentrations of manganese, such that it more accurately represents the bioavailable form. CFs were derived based on laboratory analytical data and therefore can only be applied to laboratory toxicity data. Applying a laboratory-based conversion factor to field-collected water quality data can represent a large source of uncertainty, as various site-specific and seasonal factors can influence the dissolved:total ratio in the field. Indeed, high variability in ratios between total and dissolved manganese in monitoring data have been observed, including the example below from the Athabasca region of Alberta, Canada (Figure 8). Data points that fall along or close to the 1:1 ratio line indicate that most of the metal is in the dissolved phase. Seasonal influences can be clearly seen, as there was high variability between dissolved and total concentrations of manganese in spring, summer and fall, whereas during the winter season there was a stronger correlation (data from RAMP 2017). Therefore, the CFs developed here only apply to laboratory toxicity data. Where guideline users only have field water sample concentrations of total manganese, it is recommended to not use the CFs to convert to dissolved concentrations; instead, compare these samples to the dissolved guideline and where there is an exceedance, re-sample for a dissolved concentration.

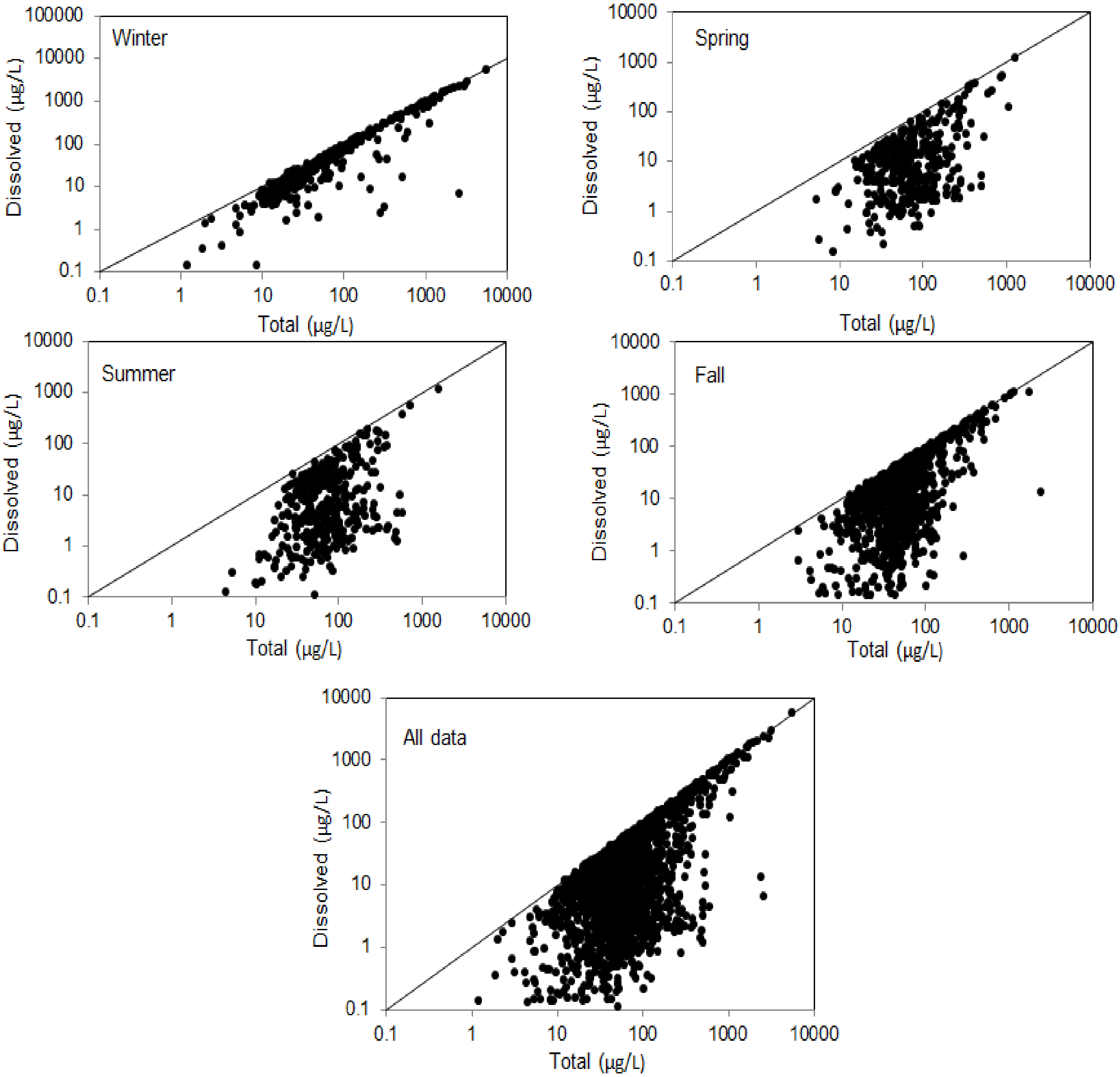

Figure 8. Dissolved versus total concentrations of manganese from sites in the Athabasca region of Alberta, Canada.

The black line represents a 1:1 ratio.
Source: Data from RAMP (2017).

Derivation of CFs for manganese were based on analytical data of paired dissolved and total concentration measurements from laboratory tests for nine species including *Aeolosoma sp., C. dubia, C. tentans, D. rerio, H. azteca, L. minor, L. stagnalis, P. promela* and *Pseduokirchneriella subcapitata* (Parametrix 2009a–i; 2010a–f). All total and dissolved manganese concentrations were measured using flame or graphite furnace atomic absorption spectroscopy following USEPA methods 243.1 or 243.2 (USEPA 1979, 1983). Various factors that could potentially influence the ratio of dissolved:total metal concentrations in an aquatic test were considered and examined, including water hardness, DOC, pH, temperature, test species, test concentration and exposure duration (acute versus chronic) (Stephan 1995).

In total, 567 measured values for dissolved and total manganese concentrations were available across the nine species listed above. Ratios were calculated between initial dissolved and initial total concentrations, and between average dissolved and initial total concentrations. The CFs were calculated as the average of these ratios. In most cases, dissolved concentrations were measured repeatedly throughout the test while total concentrations were only measured at test initiation, preventing calculation of a final dissolved:final total ratio or a ratio of dissolved:total over time. Ratios of average dissolved:initial total concentrations were only included in the calculation of the CFs where the measurement of the dissolved concentration over time had a coefficient of variation of less than 20%. This excluded tests where the dissolved concentration varied considerably with time from the calculation of an average. As all long-term tests considered for this analysis were either renewal or flow-through test systems, and likely due to the high water solubility of the $MnCl_2$ form used in the tests considered for this analysis, few test results ended up being excluded on the grounds of a coefficient of variation of more than 20%.

Short-term and long-term CFs were derived independently using acute and chronic exposure data, respectively. No discernable trend was observed between water hardness, DOC, pH, temperature, test species, or increasing test concentration and ratios of dissolved to total manganese concentrations.

The average short-term dissolved:total ratio was determined to be 0.978.

The average long-term dissolved:total ratio was determined to be 0.978.

Dissolved Concentration ≈ Total Concentration x CF

12.0 DERIVATION OF THE SHORT-TERM BENCHMARK CONCENTRATION AND THE CANADIAN WATER QUALITY GUIDELINE

12.1 Evaluation of Toxicity Data

All manganese toxicity data were evaluated for scientific acceptability before being considered for or used in the derivation of the short-term benchmark concentration and CWQG. Data from toxicity studies were ranked as primary, secondary or unacceptable in terms of acceptability for guideline derivation. The ranking criteria are described fully in the protocol (CCME 2007); however, they are briefly outlined here.

In order for a toxicity value to be considered primary, the concentration of the toxic substance must be measured at the beginning and end of the exposure period, and the measurement of water chemistry variables (hardness, pH, temperature, etc.) must be reported. Adequate replication must be performed, suitable statistical procedures should be used and control mortality should be low (typically less than 10%). Secondary data are those that originate from studies where primary data cannot be generated but are still of acceptable quality and documentation. For example, a study may use calculated (rather than measured) substance concentrations; however, the most relevant water chemistry variables must be reported. Appropriate test replication is still necessary, but pseudo-replication may be acceptable for secondary studies (e.g., all test organisms in only one aquarium per concentration). Unacceptable data are those that do not meet the criteria of primary or secondary data.

12.2 Toxicity Data Normalization for Water Chemistry Variables

Short-term manganese effect concentrations were normalized to hardness of 50 mg/L using the pooled hardness slope and equation described in Section 10.4.2. Long-term manganese effect concentrations for fish and invertebrates were normalized to multiple (n=11) hardness values ranging from 25 to 670 mg/L using the pooled hardness slope and equation described in Section 10.4.3. Long-term manganese effect concentrations for plants/algae were normalized to multiple (n=11) pH values ranging from 5.8 to 8.4 using the equation also described in Section 10.4.3.

12.3 Methods Used for Derivation of Guidelines (Type A, B1 or B2)

The *Protocol for the Derivation of Canadian Water Quality Guidelines* (CCME 2007) includes guideline values for both long-term and short-term exposure that risk assessors and risk managers in Canada can use to help protect aquatic species. The long-term exposure guideline is derived such that it is consistent with the guiding principle of the CWQG, namely to protect all species and all life stages over an indefinite exposure to the substance in water. Aquatic life may experience long-term exposure to a substance as a result of continuous release from point or non-point sources, gradual release from soils/sediments and gradual entry through groundwater/runoff, and long-range transport. The short-term exposure value is derived for use as an additional management tool. It is intended to protect most species against lethality during severe but transient events such as spills or inappropriate use/disposal of the substance in question.

While separate data sets are used to calculate short-term and long-term guidelines, both are derived using one of three approaches. The three approaches are detailed in CCME (2007) and only briefly outlined here. In order of preference, the approaches are:

1. Statistical Approach (Type A or SSD approach)
2. Lowest Endpoint Approach using only primary data (Type B1)
3. Lowest Endpoint Approach using primary and/or secondary data (Type B2).

A guideline derived using the statistical approach is called a Type A guideline. An SSD captures the variation in toxicological sensitivity among a set of species to a contaminant. An SSD is a cumulative distribution function, with effect concentrations plotted on the x-axis and cumulative probability, expressed as a percentage, plotted on the y-axis (Posthuma *et al.* 2002). Short-term, lethal endpoints (e.g., 24-h LC_{50}) comprise the data set for short-term benchmarks, while long-term exposure, no- or low-effect endpoints (e.g., 21-d EC_{10} for growth) comprise the data set for long-term guidelines. From each data set, the benchmark or guideline value is equal to the concentration on the x-axis that corresponds to 5% cumulative probability on the y-axis. In contrast, the lowest endpoint approach (Types B1 and B2) uses, as the name implies, the lowest acceptable endpoint with a safety factor to estimate the guideline.

The minimum data requirements for application of each of the three methods are presented in Table 12 (for short-term freshwater guideline values) and Table 13 (for long-term freshwater guideline values). If available data are insufficient for deriving a guideline using the statistical approach, the guideline is developed using the lowest endpoint approach. Depending on the quantity and quality of data, a Type B1 or Type B2 approach is used. The Type B1 approach uses only acceptable primary toxicity data to derive the guideline, while the Type B2 approach can use acceptable primary and/or secondary data. In every case, a guideline must be developed using the highest ranked method that the data allow.

The following sections describe the derivation of the short-term benchmark and long-term CWQG for the protection of freshwater life in surface water for manganese. Data requirements for the most preferred Type A (SSD) approach were met for both short-term and long-term exposures for manganese. The long-term SSD and final CWQG presented here are only for reference as they only apply to a water chemistry of hardness of 50 mg/L and pH 7.5. A long-term CWQG look-up table (Table 17) was developed so that long-term guideline values can be found for waters of other hardness or pH levels. For short-term data, the SSD-derived benchmark concentration (the fifth percentile of the SSD) applies to waters of hardness of 50 mg/L, since all short-term toxicity data were normalized to these conditions before being entered into the SSD. A short-term benchmark equation was developed so that benchmarks can be derived for waters of other hardness.

Table 12. Minimum data set requirements for the derivation of a short-term exposure guideline for freshwater environments

Group	Guideline		
	Type A	**Type B1**	**Type B2**
Fish	Three species, including at least one salmonid and one non-salmonid.		Two species, including at least one salmonid and one non-salmonid.
Aquatic Invertebrates	Three aquatic or semi-aquatic invertebrates, at least one of which must be a planktonic crustacean. For semi-aquatic invertebrates, the life stages tested must be aquatic. It is desirable, but not necessary, that one of the aquatic invertebrate species be either a mayfly, caddisfly or stonefly.		Two aquatic or semi-aquatic invertebrates, at least one of which must be a planktonic crustacean. For semi-aquatic invertebrates, the life stages tested must be aquatic. It is desirable, but not necessary, that one of the aquatic invertebrate species be either a mayfly, caddisfly or stonefly.
Plants	Toxicity data for aquatic plants or algae are highly desirable, but not necessary. However, if a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and two studies on nontarget freshwater plant or algal species are required.		
Amphibians	Toxicity data for amphibians are highly desirable, but not necessary. Data must represent fully aquatic stages.		
Preferred Endpoints	Acceptable LC_{50} or equivalent (e.g., EC_{50} for immobility in small invertebrates).		
Data Quality Requirement	Primary and secondary LC_{50} (or equivalent) data are acceptable to meet the minimum data set requirement. Both primary and secondary data will be plotted. A chosen model should sufficiently and adequately describe data and pass the appropriate goodness-of-fit test.	The minimum data requirement must be met with primary LC_{50} (or equivalents) data. The value used to set the guideline must be primary.	The minimum data requirement must be met with primary LC_{50} (or equivalent) data. Secondary data are acceptable. The value used to set the guideline may be secondary.

Table 13. Minimum data set requirements for the derivation of a long-term exposure guideline for freshwater environments

<table>
<tr><th rowspan="2">Group</th><th colspan="3">Guideline</th></tr>
<tr><th>Type A</th><th>Type B1</th><th>Type B2</th></tr>
<tr><td>Fish</td><td colspan="2">Three species, including at least one salmonid and one non-salmonid.</td><td>Two species, including at least one salmonid and one non-salmonid.</td></tr>
<tr><td>Aquatic Invertebrates</td><td colspan="2">Three aquatic or semi-aquatic invertebrates, at least one of which must be a planktonic crustacean. For semi-aquatic invertebrates, the life stages tested must be aquatic.
It is desirable, but not necessary, that one of the aquatic invertebrate species be either a mayfly, caddisfly or stonefly.</td><td>Two aquatic or semi-aquatic invertebrates, at least one of which must be a planktonic crustacean. For semi-aquatic invertebrates, the life stages tested must be aquatic.
It is desirable, but not necessary, that one of the aquatic invertebrate species be either a mayfly, caddisfly or stonefly.</td></tr>
<tr><td>Aquatic Plants</td><td colspan="2">At least one study on a freshwater vascular plant or freshwater algal species.
If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and three studies on nontarget freshwater plant or algal species are required.</td><td>Toxicity data for plants are highly desirable, but not necessary.
If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and two studies on nontarget freshwater plant or algal species are required.</td></tr>
<tr><td>Amphibians</td><td colspan="2">Toxicity data for amphibians are highly desirable, but not necessary. Data must represent fully aquatic stages.</td><td>Toxicity data for amphibians are highly desirable, but not necessary. Data must represent fully aquatic stages.</td></tr>
<tr><td>Preferred Endpoints</td><td>The acceptable endpoints representing the no-effects threshold and EC$_{10}$/IC$_{10}$ for a species are plotted. The other, less preferred, endpoints may be added sequentially to the data set to fulfill the minimum data requirement condition and improve the result of the modelling for the guideline derivation if the more preferred endpoint for a given species is not available.
The preference ranking is done in the following order: Most appropriate EC$_x$/IC$_x$ representing a no-effects</td><td colspan="2">The most preferred acceptable endpoint representing a low-effects threshold for a species is used as the critical study; the next less preferred endpoint will be used sequentially only if the more preferred endpoint for a given species is not available.
The preference ranking is done in the following order: Most appropriate EC$_x$/IC$_x$ representing a low-effects threshold > EC$_{15-25}$/IC$_{15-25}$ > LOEC > MATC > EC$_{26-49}$/IC$_{26-49}$ > nonlethal EC$_{50}$/IC$_{50}$ > LC$_{50}$.</td></tr>
</table>

	threshold > EC_{10}/IC_{10} > $EC_{11\text{-}25}$/$IC_{11\text{-}25}$ > MATC > NOEC > LOEC > $EC_{26\text{-}49}$/$IC_{26\text{-}49}$ > nonlethal EC_{50}/IC_{50}. Multiple comparable records for the same endpoint are to be combined by the geometric mean of these records to represent the averaged species effects endpoint.		
Data Quality Requirement	Primary and secondary no-effects and low-effects level data are acceptable to meet the minimum data set requirement. Both primary and secondary data will be plotted. A chosen model should sufficiently and adequately describe data and pass the appropriate goodness-of-fit test.	The minimum data requirement must be met with primary data. The value used to set the guideline must be primary. Only low-effect data can be used to fulfill the minimum data requirement.	Secondary data are acceptable. The value used to set the guideline may be secondary. Only low-effect data can be used to fulfill the minimum data requirement.

12.4 Derivation of Short-term Benchmark Concentration

In total, 177 short-term freshwater toxicity data points from 27 different studies were obtained for manganese. Of these, 98 endpoints from 13 different studies were deemed acceptable for guideline derivation. (See Appendix A for a full list of toxicity endpoints, experimental conditions, water chemistry, etc.). Endpoints for 17 species were included in the short-term SSD (Table 10). Where multiple comparable endpoints were available for the same species, effect, life stage and exposure duration, a geometric mean was calculated. Because the most important water chemistry variables affecting toxicity to fish and invertebrates were accounted for using a hardness normalization equation, normalized endpoints at different hardness values could be included in the calculation of the geometric mean.

Endpoints included in derivation of the short-term benchmark concentration included LC_{50} values or equivalent (e.g., EC_{50} value for immobility). Low- or no-effect endpoints are not included in derivation of guidelines for short-term exposure (CCME 2007).

In some cases, there was more than one toxicity value available for a given species, but the duration and/or life stages differed, meaning that the geometric mean of the values could not be taken. In these cases, the most sensitive data point (or geometric mean value) was selected for inclusion in the short-term SSD. Full details regarding short-term data point selection are in CCME (2007).

The normalized values reported in Table 10 for the short-term SSD represent dissolved effect concentrations at hardness of 50 mg/L. Endpoints based on total concentrations were converted to dissolved concentrations using a total:dissolved conversion factor of 0.978 (see Section 11.0).

The software R (R version 3.4.2) and R package *ssdtools* (Thorley and Schwarz 2018) were used to create SSDs from the dataset. The package fit several cumulative distribution functions (log-normal, log-logistic, log-Gumbel, gamma, and Weibull) to the data using maximum likelihood estimation (MLE) as the regression method. MLE is defined as:

$$L(\theta) = \prod_{i=1}^{n} f(\,x_i|\theta)$$

where x_i is the n observations of variable X and $f(\cdot\,|\theta)$ is the density function of the parametric distribution (Delignette-Muller and Dutang 2015). MLE does not rely on plotting positions (e.g., the Hazen method) but uses the raw data directly.

Akaike information criterion (AIC), which is a measure of the relative quality of fit to the data set, was calculated for each distribution (Burnham and Anderson 2002). The AIC value takes into consideration the distribution fit and the number of parameters (i.e., complexity) of the distribution.

$$AIC = 2k - 2\log(\hat{L})$$

where k is the number of parameters of the distribution, and L is the maximum likelihood value. Using AICc, AIC corrected for small sample size, a model averaged HC_5 can be established. The smaller the AICc the better the distribution fits the data set. Each model was then weighted, representing how well each fit the data relative to the others. Models with high value weight fit the data well compared to the others. Model weight is calculated as:

$$W_i = \frac{e^{-\Delta AICc_i/2}}{\Sigma(all\ models)e^{-\Delta AICc_i/2}}$$

The log-Gumbel distribution demonstrated the best fit to the data with the lowest AICc criteria (402.2) and the highest attributed weight (0.755) (Table 14). Each Hazard Concentration for the fifth percentile (HC_5) is multiplied with weight and then summed to result in the final model averaged benchmark value. The 95% confidence intervals are calculated in the same way.

This is the first CCME guideline and benchmark that has been derived using the MLE and model averaging approach. The *ssdtools* package (Thorley and Schwarz 2018) and user-friendly web application (Dalgarno 2018) are new tools developed in 2018 and used to conduct these statistical analyses. The approach was adopted for derivation of both the short-term benchmark and long-term guideline for manganese. It is a statistically robust method, provides reliable confidence intervals, has the benefit of a model averaging multiple distributions, and is easily conducted using publicly available R software and a web application (Burnham and Anderson 2002; Dalgarno 2018; Kon Kam King *et al.* 2014; Thorley and Schwarz 2018).

Table 14. Short-term benchmark summary statistics at hardness of 50 mg/L

Distribution	AICc	Predicted HC$_5$ (µg/L)	95% LCL and UCL (µg/L)	Weight	Weighted HC$_5$ (µg/L)	Weighted 95% LCL and UCL (µg/L)
Log-Gumbel	402.2	4,088.9	(2,479.5–8,080.3)	0.755	3,087.1	(1,872–6,100)
Log-Logistic	405.9	2,079	(689.0–6,531.6)	0.121	251.6	(83.3–790.3)
Log-Normal	405.9	2,407.8	(979.6–7,423.8)	0.117	281.7	(114.6–868.6)
Weibull	412.2	480	(55.2–3,885.3)	0.005	2.4	(0.276–19.4)
Gamma	415.4	384.5	(21.9 –5,365.7)	0.001	0.38	(0.0219–5.4)
				Benchmark=	3,600	(2,070–7,784)

The short-term SSD is shown in Figure 9. The benchmark concentration at 50 mg/L hardness is **3,600 µg/L** dissolved manganese.

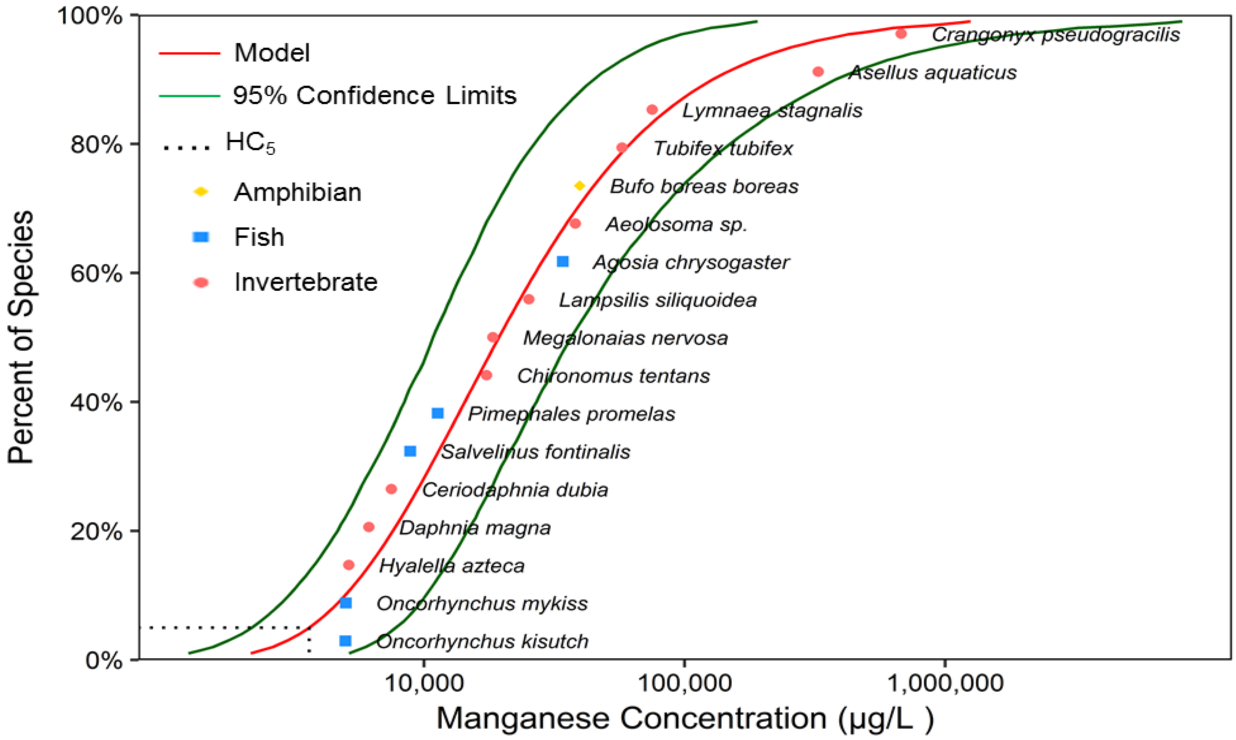

Figure 9. Short-term model averaged SSD for dissolved manganese in fresh water at 50 mg/L hardness

The fifth percentile is 3,600 µg/L manganese

12.4.1 Short-term Benchmark Equation

Based on the fifth percentile of the short-term SSD at hardness of 50 mg/L (i.e., 3,600 µg dissolved Mn/L; Figure 9), and given the slope of the relationship between the natural logarithms of hardness and short-term toxicity values (0.878; Section 10.4.2), the y-intercept can be calculated in order to derive a hardness-based short-term benchmark equation:

y-intercept= ln (5th percentile) – [hardness slope x ln(hardness)]
= ln (3600) - [0.878 x ln (50)]
= 4.76

Therefore, the resulting equation for deriving a short-term benchmark for manganese is:

$$\textbf{Benchmark} = e^{(0.878[\ln(\text{hardness})] + 4.76)}$$

where the benchmark is in µg/L **dissolved manganese** and hardness is measured as $CaCO_3$ equivalents in mg/L.

Users can enter site-specific water hardness to calculate what short-term benchmark concentration would apply to that particular water chemistry. The CWQG and benchmark calculator (Appendix B) is a tool that can be used to generate manganese site-specific guidelines and benchmarks automatically using Microsoft Excel. The benchmark equation is valid between hardness 25 and 250 mg/L, which is the range of data used to derive the hardness slope. Extrapolations should not be made for hardness exceeding 250 mg/L. Instead, round down to the upper hardness limit for use in the equation (i.e., hardness values >250 mg_3/L should be rounded to 250 mg/L). For hardness below 25 mg/L, where users want a more stringent benchmark, they could extrapolate with caution and contact their local authority for advice. Where guideline users only have water sample concentrations of total manganese, it is recommended to first compare these samples to the dissolved guideline, and where there is an exceedance, re-sample for a dissolved concentration.

Figure 10 shows short-term manganese benchmark concentrations as a continuous function of hardness (mg/L). Point values for short-term benchmark concentrations in fresh water for selected levels of hardness are provided in Table 15.

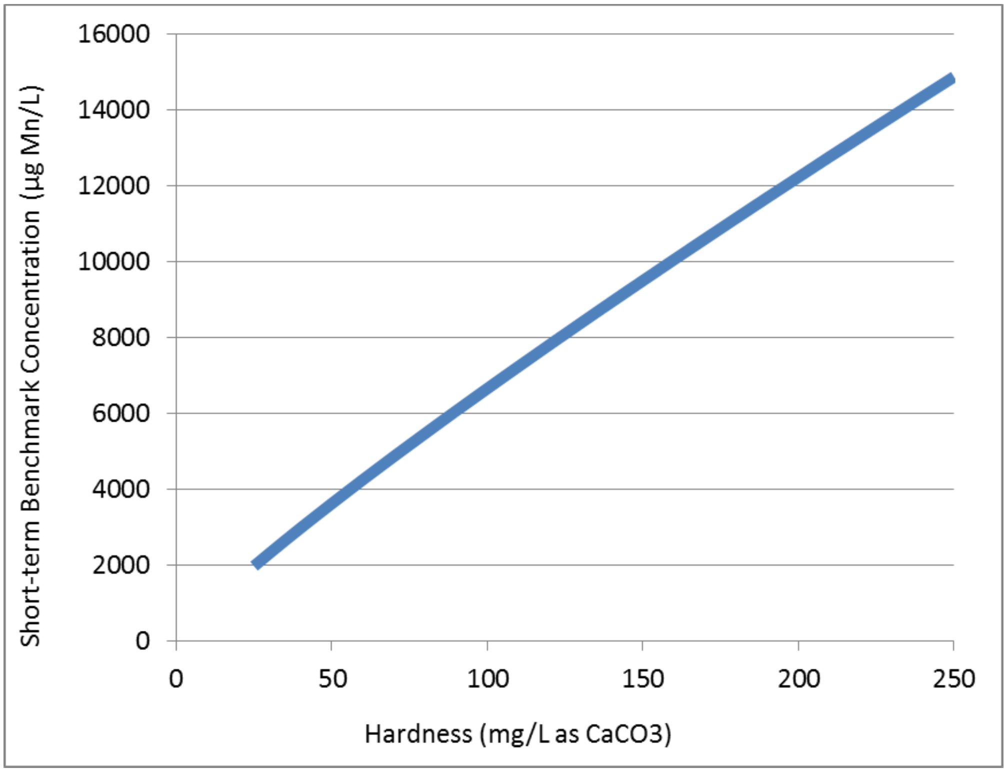

Figure 10. Short-term benchmark concentrations for manganese (in µg Mn/L) as a function of water hardness (mg/L)

Table 15. Example short-term benchmark concentrations for manganese (µg Mn/L) at various levels of water hardness

Water hardness (mg/L)	Short-term benchmark concentration (µg Mn/L)*
25	2,000
50	3,600
75	5,200
100	6,600
150	9,500
200	12,000
250	15,000

*Note the short-term benchmark concentration applies to the dissolved concentration of manganese.

12.5 Derivation of a Long-term CWQG

In total, 1,219 long-term freshwater toxicity data points from 18 different studies were obtained for manganese. Of these, 1,160 endpoints from 13 studies were deemed acceptable for use in guideline derivation. (See Appendix A for full list of toxicity endpoints and experimental conditions, water chemistry, etc.) Endpoints for 14 species were included in creating the long-term SSDs (Table 11). Where multiple comparable endpoints were available for the same species, effect, life stage and exposure duration, a geometric mean was calculated. Because the most important water chemistry variables affecting toxicity were accounted for using normalization equations, endpoints could be included in a geometric mean if there were differences in test water chemistry, as long as all other parameters were consistent.

According to protocol, if there is more than one long-term endpoint type (e.g., an EC_{10} and a NOEC) for a given species and effect, the most preferred endpoint will be selected for inclusion in the SSD. The preferred rank order of endpoints for a long-term SSD is as follows (CCME 2007):

1. most appropriate EC_x/IC_x representing a no-effects threshold
2. EC_{10}/IC_{10}
3. EC_{11-25}/IC_{11-25}
4. MATC
5. NOEC
6. LOEC
7. EC_{26-49}/IC_{26-49}
8. Non-lethal EC_{50}/IC_{50}

If more than one toxicity value (or geometric mean) is available for a given species, effect and endpoint, but the duration and/or life stage differs (e.g., a 21-d EC_{10} and a 28-d EC_{10} value for adults, or a 21-d EC_{10} for juveniles and a 21-d EC_{10} for adults), the most sensitive data point (or geometric mean value) (i.e., the lowest endpoint value) will be selected for inclusion in the long-term SSD. The long-term SSD is preferentially derived from no-effects data for long-term effects. Full details of long-term endpoint selection are given in CCME (2007).

The same SSD derivation methodology that was followed for the short-term benchmark in Section 12.4 was applied for the long-term guideline. However, instead of only creating one SSD, multiple individual SSDs were created in order to incorporate the relative sensitivities of species to different combinations of pH and hardness (pH ranging from 5.8 to 8.4, and hardness ranging from 25 to 670 mg/L) as discussed in Section 10.5.2. The SSD and accompanying summary statistics normalized to a water hardness of 50 mg/L for invertebrates and fish and pH 7.5 for algae and plants are presented in Figure 12 and Table 16, respectively.

Table 16. Long-term CWQG summary statistics for water with hardness of 50 mg/L and pH of 7.5

Distribution	AICc	Predicted HC_5 (μg/L)	95% LCL and UCL (μg/L)	Weight	Weighted HC_5 (μg/L)	Weighted 95% LCL and UCL (μg/L)
Log-Logistic	263	500	(229–1,241)	0.32	160	(73–397)
Log-Normal	263	495	(243–1,164)	0.30	149	(73–349)
Gamma	264	323	(75.9–1,207)	0.16	52	(12–193)
Weibull	264	252	(60.9–960)	0.14	35	(9–134)
Log-Gumbel	266	497	(304–997)	0.07	35	(21–70)
				Guideline=	430	(188–1,143)

The fifth percentile (HC_5 value) of each SSD represents the long-term CWQG concentration at those specific water hardness and pH conditions and are presented in Table 17.

12.5.1 Long-term CWQG

The long-term CWQG is for dissolved manganese and is found using the look-up table (Table 17)or the CWQG and benchmark calculator (Appendix B), where the CWQG is in µg/L dissolved manganese, hardness is measured as $CaCO_3$ equivalents in mg/L and pH is in standard units. The CWQG table is valid between hardness of 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 for hardness above 670 mg/L. Where users want a more stringent water quality guideline, the calculator provides extrapolated values for water hardness of 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 guideline users only have water sample concentrations of total manganese, it is recommended to 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 and/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.

Marine environments are beyond the scope of this document, and therefore marine guidelines for manganese were not assessed. Note that it is not appropriate to apply the manganese freshwater guideline or benchmark to marine or estuarine environments.

Final long-term CWQG values are plotted as a function of hardness (mg/L) and pH in Figure 11.

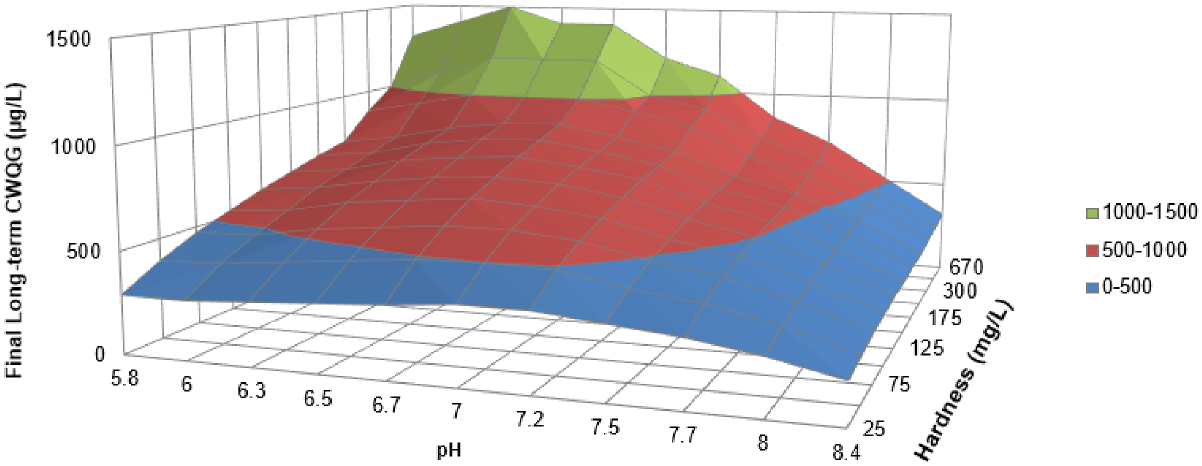

Figure 11. Long-term CWQG values for dissolved manganese as a function of hardness and pH

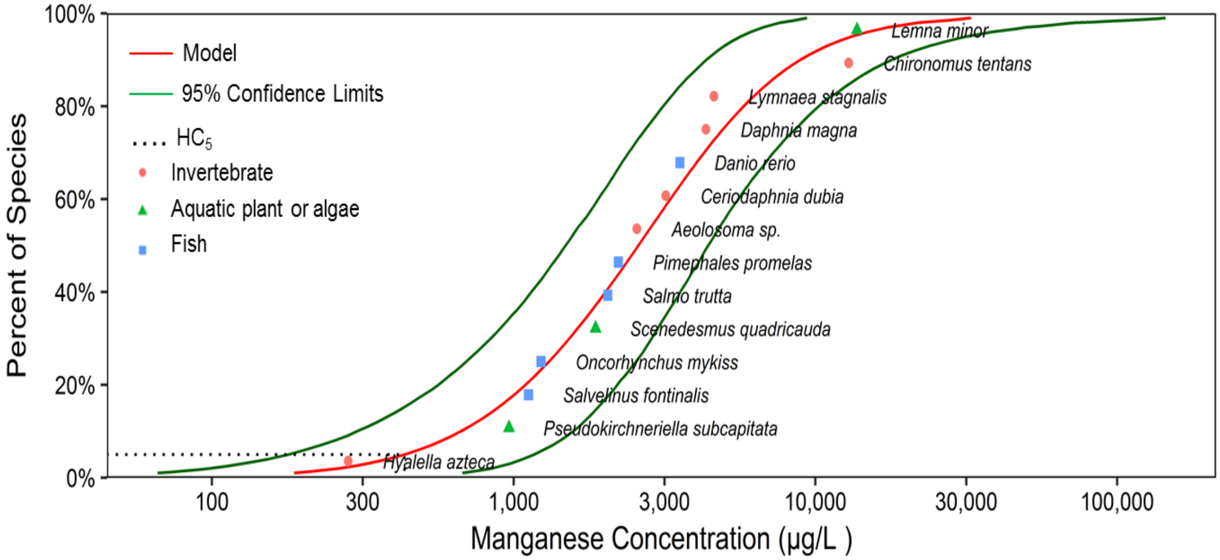

Figure 12. Long-term CWQG model averaged SSD for dissolved manganese in fresh water at 50 mg/L hardness

The 5th percentile is 430 µg Mn/L.

Table 17. Long-term CWQG site-specific look-up table

Water hardness (mg/L as $CaCO_3$)	Long-term CWQG values for dissolved manganese (µg/L)										
	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	290	290	310	330	350	380	380	350	320	270	200
50–74	390	400	430	460	490	500	490	430	390	320	220
75–99	470	480	530	560	590	590	560	490	440	350	240
100–124	530	550	610	640	670	650	610	530	470	370	250
125–149	590	620	670	710	730	710	660	570	500	390	260
150–174	640	670	740	770	790	750	700	600	520	400	260
175–199	690	720	790	830	840	790	730	620	540	420	270
200–299	730	770	840	880	890	830	760	640	560	430	270
300–399	880	940	1,000	1,000	1,000	940	860	710	610	460	290
400–669	1,000	1,100	1,200	1,200	1,200	1,000	930	770	650	480	300
≥670	1,300	1,400	1,500	1,400	1,400	1,200	1,100	860	720	520	320

*If pH is in between column values, round to the pH that would result in the more conservative (lower) CWQG value. Guideline values are rounded to two significant figures.

13.0 ASSESSING THE PROTECTION OF THE LONG-TERM CANADIAN WATER QUALITY GUIDELINE

To determine whether the long-term manganese guideline is sufficiently protective (meets the guiding principle), results of acceptable aquatic toxicity studies in which toxic effects were observed at concentrations below the long-term manganese guideline value were examined. The CCME (2007) protocol includes a section called the protection clause, which applies only to the long-term guideline:

> The protection clause may be invoked if an acceptable single (or, if applicable, geometric mean) no-effect or low-effect level endpoint (e.g., EC_x for growth, reproduction, survival, or behaviour) for a species at risk (as defined by the Committee on the Status of Endangered Wildlife in Canada [COSEWIC]) is lower than the proposed guideline (i.e., is below the 5th percentile intercept to the fitted curve), then that endpoint becomes the recommended guideline value. If this endpoint is a moderate- or severe-effect level endpoint for a species at risk (i.e., EC_x $x \geq 50\%$, or a lethality endpoint [LC_x]), then the guideline value shall be determined on a case-by-case basis (e.g., by using an appropriate safety factor) (Chapman *et al*. 1998).
>
> Similarly, if an acceptable single (or, if applicable, geometric mean) lethal-effects endpoint (i.e., LC_x, where x is ≥ 15%) for any species is lower than the proposed guideline (i.e., is below the 5th percentile intercept to the fitted curve), then that endpoint becomes the recommended guideline value.
>
> Furthermore, special consideration will be required if multiple endpoints for a single taxon (e.g., fish, invertebrates, or plant/algae) and/or an elevated number of secondary studies are clustered around the 5th percentile. Best scientific judgment should be used in deciding whether this situation is present (e.g., due consideration should be given to the percentage of data points in question to the whole data set) and in determining the best path forward to address this situation. (CCME 2007, p. 5–6)

To determine whether the long-term manganese guideline is sufficiently protective, a protectiveness assessment was completed using results of all long-term acceptable aquatic toxicity studies. All measured effect concentrations that were above the highest CWQG in the table (1,450 µg Mn/L) were automatically screened out, as they would be above the CWQG at all other water conditions as well. The remaining 213 data points that were below 1,450 µg Mn/L were further assessed to determine if they would be below the site-specific CWQG for their particular water chemistry. The final CWQG for each data point was determined by looking up the particular hardness and pH values of the study in the look-up table (Table 17). This protectiveness assessment resulted in 25 out of 1,160 (2.2%) acceptable toxicity data points being below the site-specific guideline. This is in alignment with the protection level of deriving guideline values using the fifth percentile of the SSD and therefore suggests that the method is adequately protective. To ensure protectiveness, each of the 26 endpoints was further examined to ensure none of them triggered the protection clause (CCME 2007).

The endpoints that were below the site-specific CWQGs included endpoints for *H. azteca* (n=9), *P. promelas* (n=3), and *P. subcapita* (n=13). Of these 25 endpoints, there were nine NOECs, five LOECs, one IC_{25} value, four EC_{20} values and six EC_{10} values.

For *H. azteca*, there were nine endpoints that were less than the site-specific CWQGs, including one EC_{10} value (dry weight), one EC_{20} value (dry weight), one IC_{25} value (growth), five NOECs (dry weight, biomass and mortality) and one LOEC (dry weight). There were 23 other endpoints for *H. azteca* that were above the CWQGs. Each site-specific CWQG for each particular study's water chemistry was then compared with the reported measured toxicity value to calculate a ratio. The geomean of all ratios for this species was 1.8, meaning on average the reported measured toxicity values were approximately 1.8 times higher than the site-specific CWQG. Therefore, the weight of evidence suggests this species is adequately protected by the CWQG.

For *P. promelas*, there were three endpoints above the guidelines; two NOECs (biomass and weight) and one EC_{10} value (biomass). There were 355 other long-term endpoints for *P. promelas* that were above the guidelines.

Thirteen individual endpoints for *P. subcapitata* were below the site-specific guidelines and included two NOECs, four LOECs, four EC_{10} values and three EC_{20} values for effects to growth and cell yield. There were 188 other endpoints that were above the guidelines for the species. The geomean of all ratios for this species was 4.1, meaning on average the reported measured toxicity values were approximately four-fold higher than the site-specific CWQGs.

None of the long-term endpoints that fell below the guidelines were for a species at risk or for lethal effects equal to or above a level of 15%. Furthermore, there were no acceptable data from the short-term dataset (acute lethality) that were below the long-term CWQG. Overall examination of the available data suggests the long-term CWQG is protective and that the protection clause is not applicable.

14.0 CONSIDERATION FOR USES OF THE SHORT-TERM BENCHMARK CONCENTRATION AND THE LONG-TERM CANADIAN WATER QUALITY GUIDELINE

A short-term benchmark concentration and the CWQG provide guidance for both short-term and long-term exposures, respectively. The short-term exposure value is intended to protect most species against lethality during severe but transient events such as spills or inappropriate use/disposal of the substance in question. Long-term guidelines are intended to protect the most sensitive species and life stage indefinitely. Aquatic life may be chronically exposed to a substance as a result of gradual release from soils/sediments and gradual entry through groundwater/runoff, emissions from industrial processes and long-range transport.

Before using the manganese short-term benchmark concentration or the long-term CWQG, it should be taken into consideration that they are both based on existing scientific information. The short-term benchmark concentration and CWQG for manganese are two of many tools for the assessment and interpretation of manganese monitoring data in water. The effect of manganese on aquatic organisms can vary greatly among sites because the species composition, physicochemical characteristics and presence of other toxicants that could interact additively or synergistically with manganese may differ through ecosystems (CCME 2007). Therefore, this document may be used as a basis for the derivation of site-specific guidelines and objectives when needed. For more information on site-specific water quality guideline derivation procedure, please refer to the CCME guidance document (2003).

15.0 GUIDELINE SUMMARY

The following are the short-term benchmark and long-term CWQG for dissolved manganese.

CWQG and short-term benchmark for the protection of aquatic life for manganese

	Short-term benchmark (µg/L)	**Long-term guideline (µg/L)**
Freshwater	3,600	430
Marine	Not assessed	Not assessed

Notes: The short-term benchmark given in this table is for surface water of 50 mg/L hardness and the long-term guideline given in this table is for surface water of 50 mg/L hardness and pH 7.5. The freshwater benchmark equation and the CWQG table (Or the CWQG and benchmark calculator (Appendix B)) found below must be used in order to obtain a site-specific benchmark and CWQG, respectively, based on the hardness and pH of the water body of interest. Note that it is not appropriate to apply the manganese freshwater guidelines to marine or estuarine environments.

The short-term benchmark is for **dissolved** manganese and is calculated using the equation:

$$\textbf{Benchmark} = e^{(0.878[\ln(\text{hardness})] + 4.76)}$$

The value given in the table above is for surface water of 50 mg/L hardness. The benchmark equation is valid between hardness 25 and 250 mg/L, which is the range of data used to derive the hardness slope. Extrapolations should not be made for hardness exceeding 250 mg/L. Instead, round down to the upper hardness limit for use in the equation (i.e., hardness values >250 mg/L should be rounded to 250 mg/L). For hardness below 25 mg/L, where users want a more stringent benchmark, they could extrapolate with caution and contact their local authority for advice.

The long-term CWQG is for **dissolved** manganese and is found using the look-up table (Table 17). The CWQG table is valid between hardness 25 and 670 mg/ 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 for hardness above 670 mg/L. 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 only have water sample concentrations of total manganese, it is recommended to 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 and/or pH is not known, use default values of 50 mg/L and 7.5, respectively, in order to represent conservative and common laboratory conditions. The CWQG and benchmark calculator (Appendix B) is a tool that can be used to generate site-specific manganese guidelines and benchmarks automatically instead of manually.

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