Canadian Water Quality Guidelines for the Protection of Aquatic Life

MANGANESE (Dissolved) 2019

Manganese (Mn; CAS 7439-96-5) is a naturally occurring and abundant Group 7 metal. In the aquatic environment, manganese predominantly exists as manganous (Mn^{2+}) and manganic (Mn^{4+}) forms and transitions between these two forms via oxidation or reduction reactions. Manganese can form complexes with many organic ligands and has a variety of salts, which are mostly readily soluble in water.

Table 1. Canadian Water Quality Guidelines (CWQGs) for the protection of aquatic life for dissolved manganese for specified water quality conditions.

	Short-term benchmark (µg/L)	Long-term guideline (µg/L)
Freshwater	3,600[a]	430[b]
Marine	Not assessed	Not assessed

[a] The short-term benchmark is calculated using the CWQG and benchmark calculator in Appendix B of CCME (2019) or the following equation: **Benchmark = exp**$^{(0.878[\ln(\text{hardness})] + 4.76)}$. The value in the table is for surface water of 50 mg/L hardness. The benchmark equation is valid between hardness 25 and 250 mg/L.

[b] The long-term CWQG is found using the look-up table (see Table 5) or the CWQG and benchmark calculator in Appendix B of CCME (2019). The value in the table is for surface water of 50 mg/L hardness and pH of 7.5. The CWQG table is valid between hardness 25 and 670 mg/L and pH 5.8 and 8.4.

Production and Uses

Manganese is the fourth most widely used metal in the world behind iron, aluminum and copper (Webb 2008). In Canada, manganese is primarily used as both an additive and alloy for steel production (Health Canada 1987). The second-largest market for manganese is the production of dry-cell alkaline batteries, where manganese dioxide is used as a depolarizer. Manganese is also present in thousands of everyday metallic items and non-metallic products such as matches, glass, perfume, brick, paint, varnish, oil, disinfectant, fertilizer and animal food (Nagpal 2001; Webb 2008).

Extracting and processing manganese ore is currently not economically viable in Canada, and therefore Canada now imports all of its required manganese (Webb 2008). The main manganese ore producers are China, South Africa, Australia, Brazil and Gabon, which combined supply 80% of the world market (Webb 2008). Canada also imports a significant portion of silico-manganese and manganese oxide from the United States (Corathers 2014).

Fate, Behaviour and Partitioning

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

Environmental Concentrations

Manganese occurs naturally in the environment and can also be released into the environment due to human activity; therefore, environmental manganese concentrations vary across the country. In Canada, manganese is enriched in the bituminous (or Athabasca) oil sand deposits. Monitoring data for manganese concentrations in surface water were available for various water bodies of varying anthropogenic influence across Canada (Table 2).

Table 2. Concentrations of dissolved manganese in Canadian surface waters.

Location	Sampling years	Dissolved manganese		
		Mean (µg/L)	Min (µg/L)	Max (µg/L)
New Brunswick	2007–2008	31	0.4	74
Athabasca region[1]	2004–2015	48.1	<0.004	10,800
St. Lawrence	2000–2014	5.27	0.39	28.21
Québec[2]	2008–2015	6.45	0.31	400
Manitoba	2003–2014	46.56	0.38	1,170
Manitoba[3]	2000–2016	1.06	0.4	6,220
Alberta	2003–2015	22.20	0.05	3,300
Alberta[4]	2004–2016	23.06	<0.003	2,380
Saskatchewan	2003–2014	145.52	0.05	3,090

[1]Regional Aquatics Monitoring Program (2015); [2]Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques (2017); [3]Manitoba Sustainable Development (2016); [4]Alberta Environment and Parks (2017); all other entries are from federal monitoring (Environment and Climate Change Canada 2015).

Effects on Aquatic Life

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

Toxicity Modifying Factors

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

Water Quality Guideline Derivation

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

1. Effect concentrations were converted from total to dissolved where necessary using a conversion factor of 0.978.
2. Relationships between manganese toxicity and toxicity modifying factors (water hardness for fish and invertebrates, pH for plants and algae) were established for both short- and long-term exposures.
3. Using the developed toxicity modifying equations, the toxicity data set was normalized to either 50 mg/L hardness for fish and invertebrates or pH 7.5 for plants and algae.
4. The species sensitivity distribution (SSD) data set was then selected using the criteria outlined in CCME (2007).

5. Model averaged SSDs and associated statistics including the HC_5 were generated using the ssdtools software package in R (Thorley and Schwarz 2018) (see Figures 1 and 2).
6. The short-term benchmark equation (equation 4) was then developed using the HC_5 from the SSD. It allows users to calculate the benchmark at other water hardness values.
7. For the long-term guideline, steps 3 and 6 were repeated to cover the range of water chemistry data, and all resulting HC_5 values were incorporated into a final long-term guideline look-up table (Table 5).

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

Short-term Freshwater Benchmark Concentration

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

The minimum data requirements for the Type A (SSD) approach were met, and 17 species were included in derivation of the benchmark concentration (Table 3). Effect concentrations were normalized to a hardness of 50 mg/L using the following equation:

Equation 1.

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

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

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

Equation 2.

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

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

Table 3. Endpoints used to determine the short-term freshwater benchmark concentration for dissolved manganese.

SSD rank	Species	Endpoint	Normalized effect concentration [a] (µg dissolved Mn/L)
1	*Oncorhynchus kisutch* (coho salmon)	96-h LC_{50} [b]	4,994
2	*Oncorhynchus mykiss* (rainbow trout)	96-h LC_{50} [b]	5,009
3	*Hyalella azteca* (amphipod)	96-h LC_{50} [b]	5,148
4	*Daphnia magna* (water flea)	48-h LC_{50} [b]	6,149
5	*Ceriodaphnia dubia* (water flea)	48-h LC_{50} [b]	7,498
6	*Salvelinus fontinalis* (brook trout)	96-h LC_{50} [b]	8,849
7	*Pimephales promelas* (fathead minnow)	96-h LC_{50} [b]	11,288
8	*Chironomus tentans* (chironomid)	96-h LC_{50}	17,386
9	*Megalonaias nervosa* (washboard mussel)	96-h LC_{50}	18,387
10	*Lampsilis siliquoidea* (fatmucket clam)	96-h LC_{50}	25,275
11	*Agosia chrysogaster* (gila longfin dace)	96-h LC_{50}	34,077
12	*Aeolosoma* sp.(annelid)	48-h LC_{50}	38,124
13	*Bufo boreas boreas* (boreal toad)	96-h LC_{50}	39,568
14	*Tubifex tubifex* (sludge worm)	96-h EC_{50} [b]	57,631
15	*Lymnaea stagnalis* (great pond snail)	96-h LC_{50} [b]	75,146
16	*Asellus aquaticus* (water louse)	96-h LC_{50}	325,674
17	*Crangonyx pseudogracilis* (amphipod)	96-h LC_{50}	678,732

[a] Normalized to 50 mg/L hardness; see text for details.

[b] Based on a geometric mean of multiple comparable values.

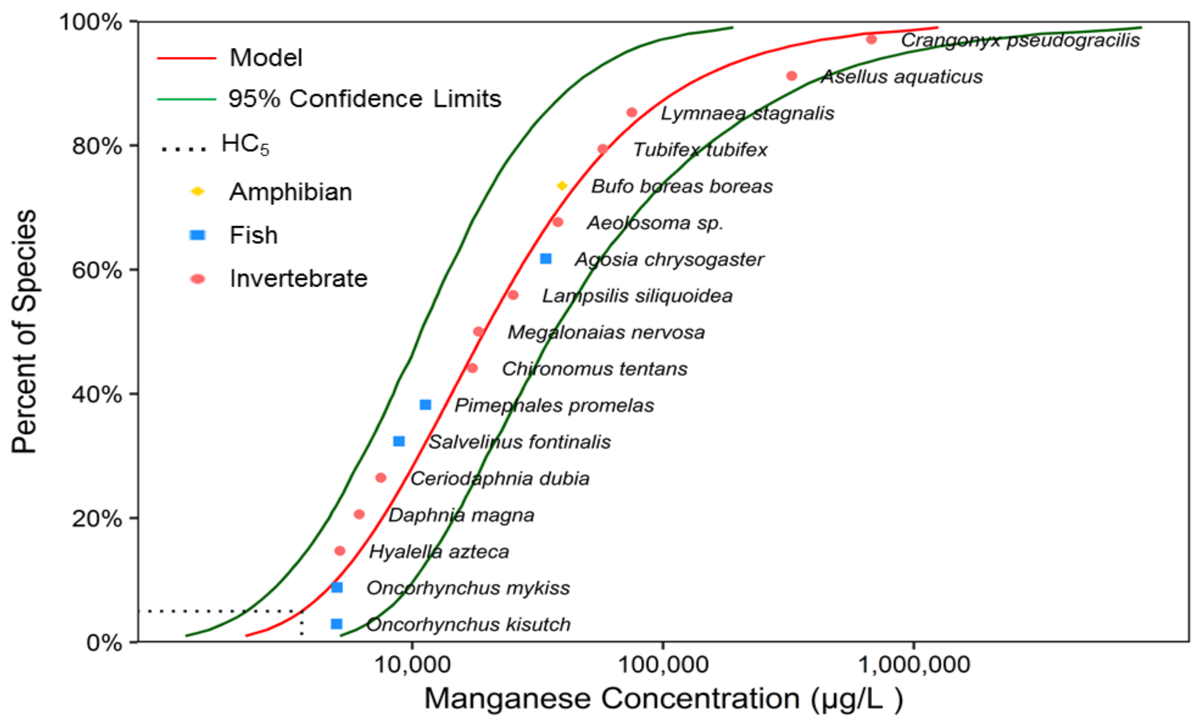

Figure 1. Short-term model averaged SSD for dissolved manganese in fresh water at 50 mg/L water hardness. The fifth percentile (HC_5) on the short-term SSD is 3,600 µg/L manganese.

The CWQG and benchmark calculator is a tool that can be used to calculate manganese site-specific guidelines and benchmarks automatically using Microsoft Excel (see Appendix B in

CCME [2019]). The benchmark equation is valid between 25 and 250 mg/L hardness, which is the range of data used to derive the hardness slope. Extrapolations should not be made above 250 mg/L hardness. For hardness below 25 mg/L where users want a more stringent benchmark, they should extrapolate with caution and contact their local authority for advice. Where users have only water sample concentrations of total manganese, it is recommended they first compare these samples to the dissolved guideline, and where there is an exceedance, re-sample for a dissolved concentration.

Long-term Freshwater Quality Guideline

Long-term exposure guidelines identify waterborne concentrations intended to protect all forms of aquatic life for indefinite exposure periods. The minimum data requirements for the Type A guideline approach were met, and 14 species were used to derive the guideline (Table 4). For the long-term SSD data set, measured effect concentrations were normalized (using equations 2 and 3) for multiple hardness and pH combinations ranging from 25 to 670 mg/L and 5.8 to 8.4, respectively.

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

Equation 3.

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

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

Equation 4.

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

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

Table 4. Endpoints used to determine the long-term freshwater CWQG for dissolved manganese.

SSD rank	Species	Endpoint	Effect concentration [a] (µg dissolved Mn/L)
1	*Hyalella azteca* (amphipod)	35-d EC_{10} (mortality)	283
2	*Pseudokirchneriella subcapitata* (green algae)	72-h EC_{10} (cell yield)[b]	965
3	*Salvelinus fontinalis* (brook trout)	65-d EC_{10} (weight)[b]	1,096
4	*Oncorhynchus mykiss* (rainbow trout)	65-d EC_{10} (weight)[b]	1,232
5	*Scenedesmus quadricauda* (green algae)	12-d EC_{50} (chlorophyll content)	1,868
6	*Salmo trutta* (brown trout)	62-d EC_{10} (weight)	2,052
7	*Pimephales promelas* (fathead minnow)	7-d EC_{10} (dry biomass)[b]	2,223
8	*Aeolosoma* sp. (annelid)	14-d EC_{10} (population growth)	2,563
9	*Ceriodaphnia dubia* (Water flea)	7-d EC_{10} (reproductive impairment)[b]	3,194
10	*Danio rerio* (zebrafish)	30-d EC_{10} (mortality)	3,555
11	*Daphnia magna* (water flea)	21-d IC_{25} (reproduction)[b]	4,341
12	*Lymnaea stagnalis* (great pond snail)	30-d EC_{10} (growth)	4,612
13	*Chironomus tentans* (midge)	62-d EC_{10} (mortality)	12,892
14	*Lemna minor* (common duckweed)	7-d EC_{10} (frond count)	13,725

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

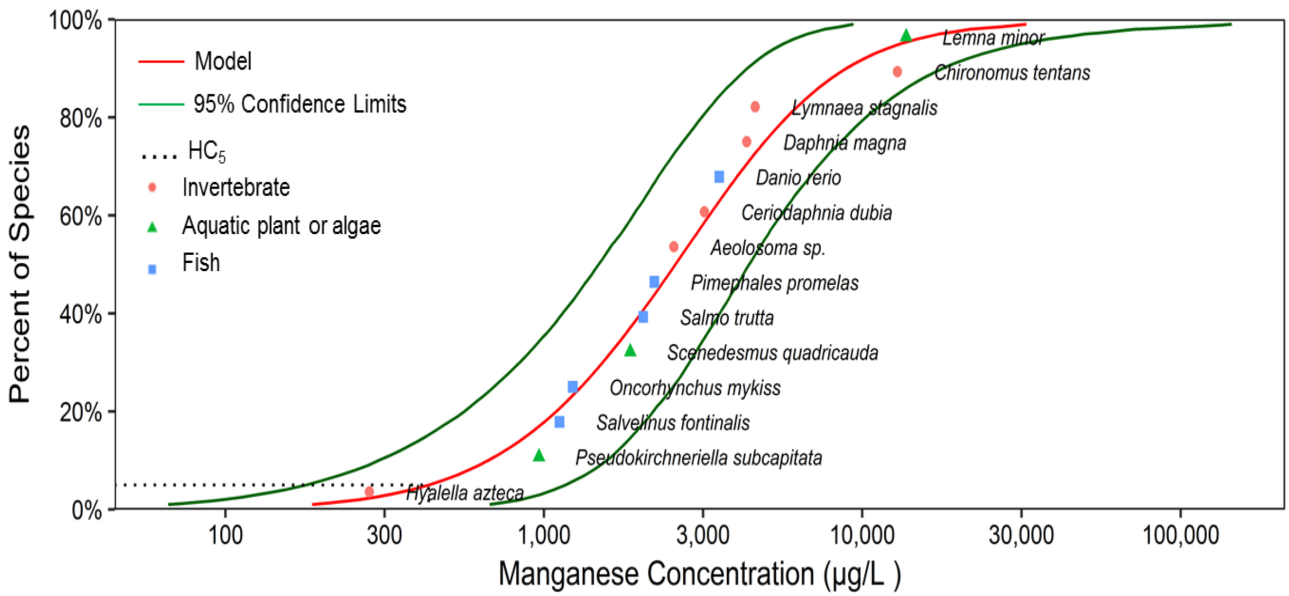

Figure 2. Long-term model-averaged SSD for dissolved manganese in fresh water at water hardness 50 mg/L (for invertebrates and fish) and pH 7.5 (for plants/algae). The fifth percentile (HC_5) on the long-term SSD is 430 µg/L manganese.

The long-term CWQG is found using the look-up table (see Table 5) or the CWQG and benchmark calculator in Appendix B of CCME (2019). The CWQG table is valid between hardness 25 and 670 mg/L and pH 5.8 and 8.4, which are the ranges of data used to derive the hardness and pH slopes. Extrapolations should not be made above 670 mg/L hardness. Where users want a more stringent water quality guideline, the calculator provides extrapolated values for water hardness below 25 mg/L down to 10 mg/L, as well as below pH 5.8 to 5.5 and above pH 8.4 to 9. However, users should use these extrapolations with caution and contact their local authority for advice. Where users have only water sample concentrations of total manganese, it is recommended they first compare these samples to the dissolved guideline, and where there is an exceedance, re-sample for a dissolved concentration. If site-specific water hardness or pH are not known, use default values of 50 mg/L and 7.5, respectively, in order to represent conservative and common laboratory conditions.

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

Table 5. Long-term CWQGs for dissolved manganese (µg/L).

Water hardness (mg/L as $CaCO_3$)	pH 5.8	pH 6.0	pH 6.3	pH 6.5	pH 6.7	pH 7.0	pH 7.2	pH 7.5	pH 7.7	pH 8.0	pH 8.4
25–49	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	1000	1000	1000	940	860	710	610	460	290
400–669	1000	1100	1200	1200	1200	1000	930	770	650	480	300
≥670	1300	1400	1500	1400	1400	1200	1100	860	720	520	320

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

Marine Water Quality Guideline

Marine environments are beyond the scope of this document, and therefore no marine short-term benchmark or CWQG for manganese was developed. It is not appropriate to apply the manganese freshwater guideline to marine or estuarine environments.

References

Alberta Environment and Parks. 2017. Surface Water Quality Data - Manganese. Available upon request. Alberta Environment and Parks, Edmonton.

Canadian Council of Ministers of the Environment (CCME). 2007. A protocol for the derivation of water quality guidelines for the protection of aquatic life. CCME, Winnipeg, MB.

CCME. 2019. Scientific criteria document for the development of the Canadian water quality guidelines for the protection of aquatic life: manganese. CCME, Winnipeg, MB.

Corathers, L. 2014. Manganese (Advanced Release). 2012 Minerals Yearbook, USGS, 47.1-47.19. USGS, Reston.

Environment and Climate Change Canada. 2015. Water Quality Monitoring Data (unpublished).

Graham, M.C., Gavin, K.G., Kirika, A., and Farmer, J.G. 2012. Processes controlling manganese distributions and associations in organic-rich freshwater aquatic systems: The example of Loch Bradan, Scotland. Sci. Total Environ. 424: 239–250.

Health Canada. 1987. Manganese. Environmental and Workplace Health. Health Canada, Ottawa.

Hedgecott, S., Dixon, E., Bailey, K.L., and Jillians, S. 1998. Proposed Environmental Quality Standards for Manganese in Water. DETR 4497/1. Department of the Environment, Transport and Regions, London, UK.

International Manganese Institute. 2012. The Derivation of Limit Values for Manganese and Its Compounds in Freshwaters: Data Availability. Fact Sheet 1, 1-2. International Manganese Institute, Paris.

Knox, D., Cowey, C., and Adron, J. 1981. The effect of low dietary manganese intake on rainbow trout (*Salmo gairdneri*). Br. J. Nutr. 46: 495–501.

Lasier, P., Winger, P., and Bogenrieder, K. 2000. Toxicity of manganese to *Ceriodaphnia dubia* and *Hyalella azteca*. Arch. Environ. Contam. Toxicol. 38: 298–304

McHargue, R., and Calfee, R. 1932. Manganese essential for the growth of *Lemna major*. Plant Physiol. 7(4) : 697–703.

Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques. 2017. Banque de données sur la qualité du milieu aquatique (BQMA), Direction générale du suivi de l'état de l'environnement, Québec.

Manitoba Sustainable Development. 2016. Manitoba Water Quality Data: Total & Dissolved Manganese (Mn). Water Quality Management Section, Winnipeg.

Nagpal, N. 2001. BC Ambient Water Quality Guidelines for Manganese. BC Ministry of Environment,Water Protection and Sustainability Branch Environmental Sustainability and Strategic Policy Division, Victoria.

Peters, A., Lofts, S., Merrington, G., Brown, B., Stubblefield, W., and Harlow, K. 2011. Development of biotic ligand models for chronic manganese toxicity to fish, invertebrates and algae. Environ. Toxicol. Chem. 30(11): 2407–2415.

Regional Aquatics Monitoring Program. 2015. RAMP Alberta Monitoring Database. Available online: http://www.ramp-alberta.org/ramp/data.aspx (viewed 2015-12).

R Core Team. 2017. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna.

Rouleau, C., Tjalve, H., Gottofrey, J., and Pelletier, E. 1995. Uptake, distribution, and elimination of 54Mn(II) in the brown trout (*Salmo trutta*). Environ. Toxicol. Chem. 14(3): 483–490.

Steenkamp, V., du Preez, H., Schoonbee, H., and van Eeden, P. 1994. Bioaccumulation of manganese in selected tissues of the freshwater crab, *Potamonautes warreni* (Calman), from industrial and mine-polluted freshwater ecosystems. Hydrobiologia 288: 137–150.

Tan, X-Y., Xie, P., Luo, Z., Lin. H-Z., Zhao. Y-H., and Xi, W-Q. 2012. Dietary manganese requirement of juvenile yellow catfish Pelteobagrus fulvidraco, and effects on whole body mineral composition and hepatic intermediary metabolism. Aquaculture 326–329: 68–73.

Thorley, J., and Schwarz. C. 2018. ssdtools: Species Sensitivity Distributions. R package version 0.0.1. Available online: https://github.com/bcgov/ssdtools (viewed 2017-05).

Valavanidis, A., Vlahogianni, T., Dassenakis, M., and Scoullos, M. 2006. Molecular biomarkers of oxidative stress in aquatic organisms in relation to toxic environmental pollutants. Ecotoxicol. Environ. Saf. 64: 178–189.

Vieira, M.C., Torronteras, R., Cordoba, F., and Canalejo, A. 2012. Acute toxicity of manganese in goldfish Carassius auratus is associated with oxidative stress and organ specific antioxidant responses. Ecotoxicol. Environ. Saf. 78: 212–217.

Webb, T. 2008. Manganese. Mineral Commodity Profile No. 1. New Brunswick Department of Natural Resources; Minerals, Policy and Planning Division, Fredericton.

World Health Organization. 2004. Concise International Chemical Assessment Document 63. Manganese and Its Compounds: Environmental Aspects. World Health Organization, Geneva.

Reference listing:

Canadian Council of Ministers of the Environment. 2019. Canadian water quality guidelines for the protection of aquatic life: manganese. *In*: Canadian environmental quality guidelines, 1999. Canadian Council of Ministers of the Environment, Winnipeg, MB.

For further scientific information, contact:

Environment and Climate Change Canada
Place Vincent Massey
351 St-Joseph Blvd.
Gatineau, QC K1A 0H3
Phone: 800-668-6767 (in Canada only) or 819-997-2800 (National Capital Region)
E-mail : ec.rqe-eqg.ec@canada.ca

Aussi disponible en français.

Excerpt from Publication No. 1299; ISBN 1-896997-34-1