



Environment and
Climate Change Canada

Environnement et
Changement climatique Canada

Canadian Environmental Protection Act, 1999
Federal Environmental Quality Guidelines

Iron

Environment and Climate Change Canada

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Introduction

Federal Environmental Quality Guidelines (FEQGs) provide benchmarks for the quality of the ambient environment. They are based solely on the toxicological effects or hazard of specific substances or groups of substances. FEQGs serve three functions: first, they can be an aid to prevent pollution by providing targets for acceptable environmental quality; second, they can assist in evaluating the significance of concentrations of chemical substances currently found in the environment (monitoring of water, sediment and biological tissue); and third, they can serve as performance measures of the success of risk management activities. The use of FEQGs is voluntary unless prescribed in permits or other regulatory tools. Thus FEQGs, which apply to the ambient environment, are not effluent limits or “never-to-be-exceeded” values, but may be used to derive effluent limits. The development of FEQGs is the responsibility of the Federal Minister of Environment and Climate Change Canada under the *Canadian Environmental Protection Act, 1999* (CEPA) (Government of Canada (GC) 1999). The intent is to develop FEQGs as an adjunct to risk assessment/risk management of priority chemicals identified in the Chemicals Management Plan (CMP) or other federal initiatives. This factsheet describes the Federal Water Quality Guideline (FWQG) for the protection of aquatic life from adverse effects of iron (Table 1). The guideline is based on toxicity data identified up to August 2017. No FEQGs have been developed for the biological tissue compartments and sediment at this time.

Table 1. Federal Water Quality Guideline for Total Iron.

Aquatic Life	Guideline Value (µg/L) ^a
Freshwater	604

^a FWQG is for waters that have DOC concentration of 0.5 mg/L and pH of 7.5. The FWQG for other DOC and pH value can be calculated using the following equation: FWQG = $\exp(0.671[\ln(\text{DOC})] + 0.171[\text{pH}] + 5.586)$

Substance identity

Iron (Fe) is a naturally occurring element (CAS Number 7439-89-6) and is the 4th most abundant element by mass in the earth's crust. Iron ores are rocks and minerals from which metallic iron (Fe) can be extracted when heated in the presence of a reducing agent such as coke (NRCan 2012). The ores are usually rich in iron oxides and carbonates. Iron is a transition metal with a density of 7.87 g/cm³ and a molecular weight of 55.9 g/mol. Iron occurs in many minerals with the most important being magnetite, hematite, goethite, pyrrhotite, siderite, ilmenite and pyrite. It is often a major constituent of soils (especially clays) and is found in waterways as a result of natural runoff, erosion of clay-based soils, and other geologic sources. Iron is essential for all forms of life and plays an important role in metabolic processes, but at higher concentrations it can be toxic (Vuori 1995; Crichton et al 2002). Iron has complex chemistry in surface waters and can exist as ferrous (Fe(II)) and ferric (Fe(III)). Fe(II) is the dominant form of iron under reducing conditions, whereas Fe(III) is the dominant form under oxidizing conditions. Because Fe(II) is rapidly oxidized to Fe(III) under most conditions, including those under which Fe(II) toxicity tests are conducted and that the oxidized form predominates in most water bodies (UKTAG 2012), this FWQG is developed for Fe(III) iron.

Uses

Iron ore production in Canada is primarily in Newfoundland and Labrador and Quebec with British Columbia contributing <1% of the Canadian production. Between 2009 and 2012, the production ranged from 32 to 39 million tonnes annually with an increase of ~11% over this period (NRCan 2011, 2012). Canada exported 34.5 million tonnes (Mt) and imported 6,500 Mt of iron ore in 2012, representing an increase of 1.6% and decrease of 8.8% from 2011 (NRCan 2012). Approximately 98% of extracted iron ore is used in the production of steel, which is a key component in the majority of manufacturing, transport and building industries (Bury et al. 2012). In its final form as steel, iron is used 20 times more than all other metals combined (NRCan 2012). The many different kinds of steel consist almost entirely of iron with the addition of small amounts of

carbon (<1%) and other metals to form different alloys (e.g., stainless steel). The uses of iron include bridges, buildings, railways, ships, cars and electrical power lines (NRCan 2012). Other industrial uses of iron are in dyeing of cloth, blueprints, insecticides, water purification, sewage treatment, an additive in animal feed, an etching material for engraving, photography, printed circuits, pigment in paints, ceramics, rubber, plastics and glass (BCMOE 2008).

Anthropogenic sources of iron into surface water are often related to mining activities (BCMOE 2008). In addition, iron pyrites (FeS_2), which are common in coal seams, are exposed to weathering and bacterial action during mining, the oxidation of which results in the production of sulphuric acid and release of soluble ferrous ($\text{Fe}[\text{II}]$) iron (Smith et al. 1973; BCMOE 2008).

Fate, behaviour and partitioning in the environment

Iron can occur in the environment as $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ oxidation states. The reduced form (i.e., $\text{Fe}(\text{II})$) occurs under low redox conditions (e.g., groundwater, sediment porewater, acidic streams) and exhibits a relatively high solubility. Under oxic aqueous conditions $\text{Fe}(\text{II})$ is rapidly oxidized to $\text{Fe}(\text{III})$, which forms oxides and hydroxides that have low solubility (Stumm and Morgan 1996; Bury et al. 2012). The relative presence of almost insoluble $\text{Fe}(\text{III})$ and the bioavailable and bioactive $\text{Fe}(\text{II})$ iron in surface waters are dependent on a wide range of factors including pH, dissolved oxygen, dissolved organic carbon (DOC), humic and other organic acids, exposure to sunlight and chloride concentrations (BCMOE 2008). It has been found that $\text{Fe}(\text{II})$ has a relatively minor impact on biota compared to iron precipitates of $\text{Fe}(\text{III})$ in laboratory studies and that it is difficult to separate the effects of these two forms of iron in field studies (Rousch et al. 1997).

The oxidation rate of $\text{Fe}(\text{II})$ in water is faster in well-oxygenated waters at neutral pH (Bury et al. 2012). Under saturated oxygen and alkaline conditions (e.g., $\text{pH} \geq 8$), the oxidation of iron is rapid and does not change with increasing pH. Under these conditions, the half-life of $\text{Fe}(\text{II})$ is on the order of seconds (Bury et al. 2012). In mildly acidic (e.g., pH 6) and oxygen-saturated water, the oxidation rate of $\text{Fe}(\text{II})$ 100 mg/L is approximately two hours at 25°C (Morgan and Lahav 2007). Thus, over the pH ranges associated with natural waters (i.e., pH 6 to 9), $\text{Fe}(\text{II})$ is expected to have a short half-life (seconds to a few hours) when present in oxic conditions.

When iron is released into natural bodies of water in the form of sulphate (FeSO_4) or pyrite (FeS_2), it oxidizes and forms $\text{Fe}(\text{OH})_3$. This iron hydroxide may precipitate out and form a yellow brown slime on bottom sediments (Smith and Sykora 1976), which decreases light penetration and thus inhibits algal growth, causing an overall decrease in the production of the ecosystem (Maltby et al. 1987). Smith and Sykora (1976) reported mortality of trout and salmon eggs coated with Fe particulates. The hydroxide precipitate can also plug the gills of fish and benthic invertebrates, causing death by the suffocation (Loeffelman 1985) and even interfere with the respiration in fish eggs (OME 1979).

Organic matter may control both the oxidation state and size of Fe species present in waters. Reduction in the ratio of Fe:organic carbon causes reduction in oxidation of $\text{Fe}(\text{II})$ and this has a potential for the iron load in natural waters to remain in a reduced form, even in well oxygenated waters (Gaffney et al. 2008). $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ differ in their binding affinities to humic and fulvic acids (UKTAG 2012). $\text{Fe}(\text{III})$ binds to fulvic and humic acids in fresh waters and these $\text{Fe}(\text{III})$ -dissolved organic matter (DOM) complexes are important for maintaining iron solubility (Tipping et al. 2002). The proportion of Fe found in this form is pH- and temperature-dependent, with the $\text{Fe}(\text{III})$ -DOM ratio decreasing as pH increases (Lofts et al. 2008). When complexed with organic compounds, $\text{Fe}(\text{III})$ can be photo-reduced by UV light to the soluble $\text{Fe}(\text{II})$ state, which can cause large diurnal fluctuations in the speciation and concentration of iron (BCMOE 2008).

Ambient concentrations

Iron concentrations in fresh water can be in the mg/L range, such as in rivers that pass through sulphide-rich soils, receive acid-mine drainage, or are otherwise exposed to various anthropogenic sources (Myllynen et al. 1997; Winterbourn et al. 2000; Linton et al. 2007). Environment and Climate Change Canada (ECCC) monitoring data, along with data from Alberta's Regional Aquatics Monitoring Program (RAMP) for total iron concentrations in surface waters are summarized in Table 2. The total Fe concentrations ranged from <0.5 to 89200 µg/L with the mean and median concentrations of 21 to 1888 and 5 to 6889 µg/L, respectively.

Table 2. Concentrations of total iron in Canadian surface waters.

Location	Sampling Years	Mean (µg/L)	Median (µg/L)	Minimum (µg/L)	Maximum (µg/L)
Lake Erie	2004-2014	185	32	0.5	2400
Lake Huron	2004-2014	35	565	<0.5	424
Lake Ontario	2005-2013	45	5	<0.5	2090
Lake Superior	2005-2013	21	6	<0.5	229
Great Lakes Connecting Channels	2003-2014	364	56	<1.4	8470
St. Lawrence	2007-2014	632	452	0.03	12200
Newfoundland	2003-2013	354	212	3	15200
New Brunswick	2011-2013	113	85	20	350
Nova Scotia	2011-2013	311	250	20	1860
Manitoba	2003-2014	1888	6889	3.8	24200
Saskatchewan	2003-2014	1005	506	<0.5	41700
Athabasca Region	1997-2015	1653	973	4	46500
Alberta	2003-2015	1063	145	4.8	57100
Northwest Territories	2003-2014	1870	224	<0.5	89200

Mode of action

Dissolved concentrations of metals are typically considered to be most relevant to any evidence of ecological effects. However, this may not be the only cause of toxicity for iron. If the mode of action of iron is not only exerted via chemical toxicity then other expressions of iron concentrations may be required. Total or particulate iron concentrations usually cause ecological effects via physical effects, such as smothering. Iron can adversely affect macroinvertebrates by reducing habitat quality and structure and by constraining food access (Linton et al. 2007). The precipitation of ferric hydroxide onto stream or lake bottoms can reduce light penetration and decrease plant productivity and thus decreasing food sources for the fish (Sykora et al. 1972).

Iron oxide precipitates in well-oxygenated and circum-neutral pH waters that receive acid mine drainage and naturally high iron input can result in smothering of fish gills (Bury et al. 2012). In non-acid mine exposure scenarios, toxicity in Atlantic salmon (*Salmo salar*) was associated with increased iron accumulation on the gills, respiratory disruption, interference with gas exchange, fusion of gill lamellae, separation of the outer epithelial layer and/or necrosis of the lamellar epithelium (Peuranen et al. 1994; Dalzell and MacFarlane 1999; Teien et al. 2008). Iron was detected only at the gill epithelium, not inside, which indicated that the toxicity was mediated through action on the gill surface (Peuranen et al. 1994). High iron concentrations during fertilization have been shown to cause hardening of fish eggs, which may be of particular importance

for salmonid spawning in headwaters that may receive high iron concentrations (Bury et al. 2012). Finally, iron can contribute to free radical production and oxidative damage (Bury et al. 2012).

The precipitation of ferric hydroxide can also affect fish according to their life stage. At low iron concentrations (~1.5 mg/L) the hatchability of fathead minnows (*Pimephales promelas*) was lower than at higher concentrations (Smith et al. 1973). Smaller particles have a greater potential to clog the pores of egg chorion and thus cause reduced dissolved oxygen diffusion and increased mortality. However, high concentrations of iron (up to 52.9 mg/L) can reduce visibility in the water and cause impaired food perception to fry and juvenile stages, causing prolonged stress and reduced growth (Smith et al. 1973).

Aquatic toxicity

The chronic freshwater toxicity studies for iron were identified and evaluated following the CCME (2007) protocol. Because iron solubility is low and it readily sorbs to surfaces, iron toxicity studies were only considered if total iron concentrations were measured in the toxicity test. Unlike other divalent metals, the total iron fraction correlates best with toxicity (CIMM 2010a,b; CIMM 2011; OSU 2013). This suggests that there are non-dissolved iron species that are bioavailable to the test organisms. An underlying assumption for the selection of toxicity data was that the iron guideline developed here would be also protective of physical effects, such as smothering.

Acceptable long-term toxicity data (Table 3) were available for seven species (3 fish, 3 invertebrates and 1 plant) and the dataset met the CCME's (2007) minimum data requirements for developing the SSD based guideline (i.e., Type A guideline) for iron. Within the acceptable dataset, several long-term studies have focused on how varying dissolved organic carbon (DOC), pH and hardness concentrations influence the bioavailability, and hence toxicity. These species include an alga (*Pseudokirchneriella subcapitata*), an invertebrate (*Ceriodaphnia dubia*) and fish (*Pimephales promelas*) (CIMM 2010a,b; 2011; 2012a,b,c; OSU 2013). The chronic toxicity data for these species were used to evaluate toxicity modifying factors (TMFs) so that the FWQG for iron could be adjusted for site-specific water chemistry.

Step-wise multiple linear regression (MLR) was used to evaluating the role of DOC, pH and hardness on iron toxicity, as one or more of these parameters have been shown to have important influence on iron bioavailability (ECCC 2018). The results of MLR analysis are presented in Table 3. In summary, DOC was a significant parameter in MLR models for *P. subcapitata*, *C. dubia* and *P. promelas*, while pH was significant in *P. subcapitata* and *P. promelas* models, but not in *C. dubia* model. Hardness was only significant in *P. promelas* model. These MLR relationships for individual species are referred to as MLR models hereon in this factsheet.

Table 3. Summary results of multiple linear regression analysis.

Species	n	r ²	Significance (p)			Model Coefficients			
			DOC	pH	Hardness	DOC	pH	Hardness	Intercept
<i>P. subcapitata</i>	25	0.88	<0.001	0.057	0.096	0.671	0.171	-	6.585
<i>C. dubia</i>	18	0.44	0.002	0.861	0.121	0.465	-	-	7.476
<i>P. promelas</i>	13	0.78	0.001	0.003	0.066	1.303	0.936	0.405	-0.888

Table 4. *Pseudokirchneriella subcapitata* multiple linear regression model based normalized toxicity data used in deriving the FWQG for iron.

Species	Group	Endpoint	Concentration (µg/L)	Reference
Water flea <i>Daphnia pulex</i>	Invertebrate	21-d MATC (surv., growth, rep.)	946	Birge et al. (1985)
Water flea <i>Ceriodaphnia dubia</i>	Invertebrate	7-d EC10 (reproduction) ^a	1090	CIMM (2010a,b)
Fathead minnow <i>Pimephales promelas</i>	Fish	7-d EC10 (biomass) ^a	1067	OSU (2013)
Coho salmon <i>Oncorhynchus kisutch</i>	Fish	60-d EC10 (survival)	1290	Smith and Sykora (1976)
Algae <i>Pseudokirchneriella subcapitata</i>	Plant	3-d EC10 (growth) ^a	1640	CIMM (2011, 2012a,b,c)
Water flea <i>Daphnia magna</i>	Invertebrate	21-d EC16 (reproduction)	2477	Biesinger and Christensen (1972)
Brook trout <i>Salvelinus fontinalis</i>	Fish	90-d NOEC (survival, growth)	5100	Smith and Sykora (1976)

^aGeomean for species based on several studies

Federal water quality guideline derivation

Federal Water Quality Guidelines (FWQGs) are preferably developed using the CCME (2007) protocol. In the case of Fe, there were enough acceptable chronic toxicity data to meet the minimum data requirements for a CCME Type A guideline¹.

The first step in developing the FWQG for Fe was to normalize the toxicity values to a common water chemistry using the *P. subcapitata*, *C. dubia* and *P. promelas* MLR models (ECCC 2018). As discussed earlier these models included different TMFs. The model for *P. subcapitata* was based on DOC and pH whereas the model for *C. dubia* was based only on DOC. The *P. promelas* model was based on DOC, pH and hardness. The chronic toxicity data for all 7 species were normalized to water with a DOC concentration of 0.5 mg/L pH of 7.5 and hardness of 50 mg/L (as CaCO₃), as appropriate for each MLR model. The species-mean toxicity values were then calculated as the geometric mean of MLR-normalized toxicity values. Based on the model statistics and the relationship between observed and predicted EC_{10s}, the *P. subcapitata* was strongest among the three MLR models developed (ECCC 2018). The *P. subcapitata* MLR model normalized toxicity data are presented in Table 4. In this dataset *Daphnia pulex* was the most sensitive species with a species mean toxicity value of 946 µg/L and Brook trout (*Salvelinus fontinalis*) was the least sensitive species with a 90-d NOC value of 5,100 µg/L.

The species sensitivity distributions (SSDs) were fit to normalized datasets (ECCC 2018). In SSD normalized toxicity endpoints (Table 4) were ranked according to sensitivity, and their positions on the SSD were determined (Figure 1). Several cumulative distribution functions were fit to the data using regression methods and the best model was selected based on consideration of goodness-of-fit and protectiveness (ECCC 2018). The logistic model provided the best results and the 5th percentile of the SSD plot was 604 µg/L.

¹CCME (2007) provides two approaches for developing water quality guidelines, depending on the availability and quality of the available data. The preferred approach is to use the statistical distribution of all acceptable data to develop Type A guidelines. The second approach is based on extrapolation from the lowest acceptable toxicity endpoint to develop Type B guidelines. For further detail on the minimum data requirements for CCME guidelines see CCME (2007).

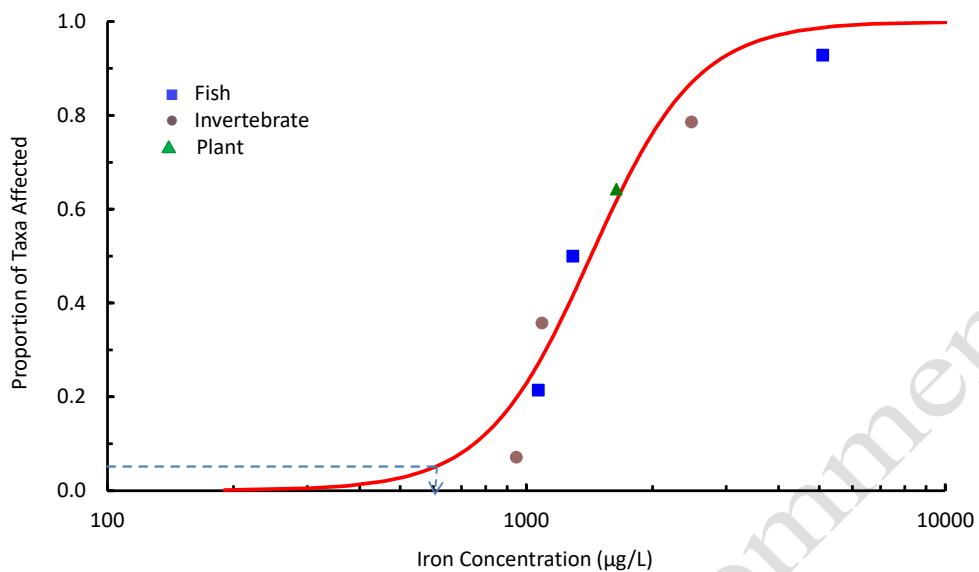


Figure 1. Species sensitivity distribution (SSD) for the chronic toxicity of iron at DOC of 0.5 mg/L and pH of 7.5.

Because the DOC and pH were significant toxicity modifying factors, the FWQG is expressed as an equation where the local water DOC and pH must be entered in order to calculate a site-specific FWQG. The equation is based on the DOC and pH MLR model slopes of 0.671 and 0.171, respectively, and the 5th percentile value 604 µg/L derived from the SSD at DOC of 0.5 mg/L and pH of 7.5.

Based on the *P. subcapitata* MLR model and the SSD, the equation to derive FWQG for iron is:

$$\begin{aligned}
 \text{y-intercept} &= \ln(5^{\text{th}} \text{ percentile}) - [\text{DOC slope} \times \ln(\text{DOC})] - [\text{pH slope} \times \text{pH}] \\
 &= \ln(604) - [0.671 \times \ln(0.5)] - [0.171 \times 7.5] \\
 &= 5.586
 \end{aligned}$$

$$\text{FWQG } (\mu\text{g/L}) = \exp(0.671[\ln(\text{DOC})] + 0.171[\text{pH}] + 5.586)$$

Specific example of FWQGs for Fe for selected DOC and pH values are given in Table 5.

Users can input site-specific DOC and pH measurements to calculate FWQG for the specific water chemistry. Because the influence of DOC and pH as toxicity modifying factors for iron in the *P. subcapitata* model was determined over DOC and pH ranges of 0.3 to 9.9 mg/L and 6.1 to 8.1, respectively, only these DOC and pH ranges can be entered into the guideline equation to ensure the equation is accurate and the FWQG is protective. The users should be extremely cautious while extrapolating beyond the recommended ranges of DOC and pH and should contact their local authority for advice. A sample of specific examples of FWQGs for iron for selected DOC and pH values are given in Table 5.

Table 5. FWQGs ($\mu\text{g/L}$) for iron for the protection of aquatic life for selected DOC and pH values.

DOC (mg/L)	pH 6.5	pH 7.0	pH 7.5	pH 8
0.5	509	555	604	658
1.0	811	883	962	1048
3.0	1694	1845	2010	2189
5.0	2387	2600	2832	3084

The calculation of FWQG for iron requires measurements of pH and DOC for the site. Although the pH is regularly measured during monitoring, DOC may not always be routinely measured. In the absence of site-specific DOC data, a DOC concentration of 0.5 mg/L may be assumed, which is conservative for most natural waters. For water bodies where iron concentrations are potentially of concern, it is recommended that DOC and pH be measured. It is to be also noted that the FWQG for iron is for total concentration of Fe.

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List of Acronyms and Abbreviations

CAS – Chemical Abstracts Service

CCME – Canadian Council of Ministers of Environment

CEPA – Canadian Environmental Protection Act

CMP – Chemicals Management Plan

DOC – dissolved organic carbon

DOM – dissolved organic matter

EC – effect concentration

FEQG – Federal Environmental Quality Guideline

FWQG – Federal Water Quality Guideline

MATC – maximum acceptable toxicant concentration

MLR – multiple linear regression

NOEC – no observed effect concentration

NRCan – Natural Resources Canada

SSD – species sensitivity distribution

TMF – toxicity modifying factor