

Canadian Environmental Protection Act, 1999

Federal Environmental Quality Guidelines

Hexavalent Chromium

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 hazards 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 under the *Canadian Environmental Protection Act, 1999* (CEPA) (Government of Canada (GC) 1999). The intent is to develop FEQGs as an adjunct to the 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 hexavalent chromium (Table 1). The derivation of the FWQG here is largely based on the aquatic toxicity data evaluated and considered in deriving a predicted no-effect concentration (PNEC) by the European Union (EU 2005) and UK Environmental Agency (UKTAG 2007). Additional data searches were also carried out to incorporate recently published data up to February 2016. No FEQGs have been developed for biological tissue compartments and sediment at this time.

FEQGs are similar to Canadian Council of Ministers of the Environment (CCME) guidelines in that they are benchmarks for the quality of the ambient environment and are based solely on toxicological effects data. Where data permit, FEQGs are derived following CCME methods. FEQGs are developed where there is a federal need for a guideline (e.g. to support federal risk management or monitoring activities) but where the CCME guidelines for the substance have not yet been developed or are not reasonably expected to be updated in the near future.

Table 1. Federal Water Quality Guideline for hexavalent chromium.

Aquatic Life	Guideline Value (µg/L)
Freshwater	5

Substance Identity

Chromium (CAS 7440-47-3) is a naturally-occurring metal and its natural atmospheric sources include volcanic emissions, forest fires, vegetative debris and marine aerosols. In Canada, large chromium-containing ore deposits are located in Quebec, Ontario, British Columbia and Newfoundland. The recently discovered chromium deposits in the northern Ontario area referred to as the “Ring of Fire” are considered to be the largest deposits found in North America, and possibly in the world (MiningWatch Canada 2012).

In the natural environment, chromium typically occurs in divalent [Cr(II)], trivalent [Cr(III)] and hexavalent [Cr(VI)] oxidation states, with Cr(III) and Cr(VI) being the most stable forms (Velma et al. 2009; WRF 2012). Cr(III) mainly occurs as Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})^3$ and $\text{Cr}(\text{OH})^4$, whereas Cr(VI) forms a number of stable oxyacids and anions, including HCrO_4^- (hydrochromate), $\text{Cr}_2\text{O}_7^{2-}$ (dichromate) and CrO_4^{2-} (chromate). Cr(VI) is more toxic than Cr(III) because it has high oxidizing potential, high solubility and greater permeability through the biological membranes. Cr(VI) is the principal species found in surface waters and aerobic soils, whereas Cr(III) dominates in mildly-reducing environments such as sediments and wetlands (Bailar et al. 1973). Cr(VI) is a carcinogen with mutagenic and teratogenic properties (Velma et al. 2009; ASTDR 2012). Based on the Priority

Federal Environmental Quality Guidelines

Substances List Assessment Report (GC 1994), Cr(VI) is on the List of Toxic Substances (Schedule 1) under the *Canadian Environmental Protection Act, 1999* (GC 1999).

Uses

Chromium ores have not been mined in Canada since the early 1900s, although there are deposits across Canada (e.g., Manitoba, Ontario, Quebec and Newfoundland) (NRCan 1995; CAREX Canada 2011; MiningWatch 2012). Approximately 74,000 t of chromium-containing compounds were imported into Canada in 1991 (55% ferroalloys, 28% chromite ores and concentrates, and 9% other compounds) (Statistics Canada 1991). In 2010, imported amounts were 954 t of chromium trioxide (mainly from Turkey) and 3,814 t of sodium dichromate from the USA, and the exported amount was 116 t of chromium trioxide mainly to USA (CAREX Canada 2011). The metallurgical, refractory and chemical industries are the primary users of chromium. The metallurgical uses of chromium include production of stainless steels, alloy cast irons, nonferrous alloys, and other miscellaneous materials (ATSDR 2012). In the chemical sector, both Cr(III) and Cr(VI) are used in pigments. A major industrial use of Cr(VI) is in metal finishing and as an anti-corrosive agent in waters for cooling towers, oil drilling and power plants. Cr(III) is used in leather tanning. Other uses of chromium are as catalysts and in applications such as textiles, toners for printers, magnetic tapes and dietary supplements (ATSDR 2012). Both Cr(III) and Cr(VI) are released into the environment in Canada as a result of many of these industrial uses, as well as from the production and combustion of fossil fuels, and the smelting and refining of nonferrous base metals (GC 1994).

Fate, Behaviour and Partitioning in the Environment

The environmental chemistry of chromium is largely dependent on the form in which it enters the environment, redox potential, transformation, precipitation/dissolution and adsorption/desorption reactions (UKTAG 2007). Most metals of concern are cations and interact with negatively charged areas of biological membranes. Because of its anionic nature, Cr(VI) interacts differently from most metals and its toxicity likely to be less influenced by the water chemistry (UKTAG 2007). In general, Cr(VI) compounds cross biological membranes much more readily than Cr(III) compounds (GC 1994, ATSDR 2012). Having crossed biological membranes Cr(VI) is then rapidly reduced to Cr(III) (ATSDR 2012).

Cr(VI) compounds are reduced to the trivalent form in the presence of oxidizable organic matter; however, they are persistent in natural waters where there is a low concentration of reducing materials (Velma et al. 2009; ATSDR 2012). Cr(III) is less toxic than Cr(VI) and its low solubility in water limits its bioavailability. Cr(VI) is highly soluble in alkaline waters (WRF 2012). Chromium compounds do not volatilize from water (ATSDR 2012). Cr(VI) is thermodynamically stable under highly-oxidizing conditions, whereas Cr(III) predominates under reducing conditions (DSIS 2005). The oxidation of Cr(III) to Cr(VI) is slow and is not significant (ATSDR 2012). The soluble Cr(VI) may persist in water for some time, it is eventually reduced to Cr(III) by organic matter or other reducing agents in water (USEPA 1985).

Chromium rapidly partitions to sediments ($\log K_p=5.28$ L/kg) (Crommentuijn et al. 1997). The adsorption of Cr(III) onto suspended solids and sediment increases as pH increases, whereas for Cr(VI), the adsorption decreases with increasing pH (DSIS 2005). Factors affecting the microbial reduction of Cr(VI) to Cr(III) include biomass concentration, initial Cr(VI) concentration, temperature, pH, carbon source, redox potential and the presence of both oxyanions and metal cations (UKTAG 2007). High levels of Cr(VI) are toxic to most microbes, although several resistant bacterial species have been identified (ATSDR 2012).

Chromium compounds bind tightly to soil and are not likely to migrate to groundwater (Velma et al. 2009). In most soils, Cr(III) is the predominant form of chromium. The fate of chromium in soil is greatly dependent upon its speciation and is a function of redox potential and the pH (DSIS 2005; ATSDR 2012). The field and experimental soil–water partition coefficients ($\log K_p$) for chromium are

Federal Environmental Quality Guidelines

2.04 and 3.94 L/kg, respectively (Crommentuijn et al. 1997). The reduction of Cr(VI) most rapidly occurs in acidic soils with high iron, sulphide or organic contents. Under these conditions, reduction of Cr(VI) to Cr(III) can complete within a few hours. Under aerobic conditions and at higher pH (~7–8 and above), Cr(VI) appears to be more stable to reduction than at lower pH under anaerobic conditions.

Chromium compounds have potential for accumulation in aquatic biota (Velma et al. 2009). Cr(VI) bioconcentration factors (BCFs) of ~1 L/kg (22–30 days exposure) and 2.8 L/kg (180 day exposure) are reported for rainbow trout (Fromm and Stokes 1962; USEPA 1980; Calamari et al. 1982). BCFs of up to ~9,100 L/kg in mussels and ~500 L/kg in algae have been determined for Cr(VI) (UKTAG 2007). In the tissues Cr(VI) may reduce to Cr(III) and the resulting build-up of Cr(III) may overestimate the true BCF for Cr(VI) (UKTAG 2007).

Measured Concentrations

Atmospheric emissions of Cr(VI) in Canada have been successively declining since 2005 from a high of about ~3.3 t in 2005 to ~0.8 t in 2011 (EC 2013). The decrease is largely attributed to emission reductions from facilities in the electricity generation, transmission and distribution sector, from a forging and stamping plant, and from paint, coating and adhesive manufacturing facilities. The water quality monitoring data collected between 2003 and 2015 (Environment and Climate Change Canada (ECCC) unpublished data) recorded a range of chromium concentrations in surface waters of Canada: <0.005 to 3.67 µg/L (mean 0.08 to 0.33; median 0.08 to 0.14 µg/L) in the Great Lakes; 0.07 to 0.78 µg/L (mean 1.16; median 0.78 µg/L) in the St. Lawrence River; <0.01 to 14.7 µg/L (mean 0.16 to 0.32; median 0.15 to 0.18 µg/L) in New Brunswick, Nova Scotia and Newfoundland; 0.03 to 24.4 µg/L (mean 1.92; median 0.07 µg/L) in Manitoba; <0.005 to 29.2 µg/L (mean 0.61; median 0.02 µg/L) in Saskatchewan; and 0.01 to 70.4 µg/L (mean 0.85; median 0.16 µg/L) in Alberta. An analysis of the Regional Aquatics Monitoring Program RAMP) data (unpublished) collected between 1997 and 2015 indicated that in the rivers and tributaries of the lower Athabasca region minimum, maximum, mean and median chromium concentrations were <0.03, 76.2, 1.4 and 0.6 µg/L, respectively.

Mode of Action

The reduction of Cr(VI) to Cr(III) inside cells may be an important mechanism for the toxicity of Cr compounds, whereas the reduction of Cr(VI) to Cr(III) outside of cells is a major mechanism of protection (ATSDR 2012). Thaker et al. (1996) found that Cr(VI) exposure duration was more important than dose in the inhibition of enzyme activity and suggested that this metal ion alters the membrane permeability of the intestinal epithelial cells and other layer of cells by altering the activity of ATPases, resulting in a breakdown of the active transport mechanism needed for the absorption of nutrients, ions and metabolites. Chronic exposure to chromium inhibits the activities of enzymes like pyruvate dehydrogenase (PDH), succinate dehydrogenase (SDH) and lactate dehydrogenase (LDH) in kidney, brain, liver, gills, intestine and/or muscles (Velma 2009). Inhibition of ATPase activity in these organs is important in understanding the toxic effects of the metal because such alterations have a significant impact on osmoregulation and ion transport systems along the cell membrane. Cr(VI) suppresses *in vivo* immune responses more effectively than Cr(III) (Velma 2009). Chromium-DNA interactions cause apoptosis and carcinogenesis where chromium associates with both DNA bases and the phosphodiester backbone and the binding occurs through both coordinate covalent binding or electrostatic/ionic interactions (Shanker 2009).

Aquatic Toxicity

The ecotoxicology of Cr(VI) is linked to its environmental persistence and the ability to induce a variety of adverse effects in biological systems (Velma et al. 2009). Although the toxicity of Cr(VI) can be influenced by a number of factors, including pH, water hardness, salinity and temperature (EU 2005), available long-term toxicological studies do not show any clear dependence of Cr(VI) toxicity on the properties of the water (UKTAG 2007). Detailed relationships between chromium toxicity and environmental factors could not be developed in EU's (2005) risk assessment and the additional sources consulted were also not sufficient to allow for the normalization of Cr(VI) toxicity for water

Federal Environmental Quality Guidelines

quality parameters such as hardness, pH, DOC (UKTAG 2007). Based on these findings no equation was derived to account for toxicity modifying factors in deriving FWQG for Cr(VI).

Chronic freshwater toxicity data were compiled from the EU (2005), UKTAG (2007) and recent publications (up to February 2016). Similar to UKTAG (2007) all toxicity results are expressed as the concentration of Cr(VI). Following the Canadian Water Quality Guideline protocol (CCME 2007) acceptable endpoints for 24 species were selected for developing the FWQG for Cr(VI) (Table 2). The toxicity values ranged from 5 to 3500 µg/L for various endpoints with no one group any more sensitive to Cr(VI) toxicity. Chronic toxicity to fish ranged from 10 µg/L for brook trout (*Salvelinus fontinalis*) to 3500 µg/L for medaka (*Oryzias latipes*) and guppy (*Poecilia reticulata*). Among invertebrates, the chronic toxicity effects ranged from 5 µg/L for water flea *Daphnia magna* to 1100 µg/L for brown hydra (*Hydra oligactis*). Among plant species, duckweed *Lemna minor* was most sensitive (EC₁₀ of 7 µg/L), whereas blue-green alga *Microcystis aeruginosa* was most tolerant (NOEC of 500 µg/L).

Table 2. Chronic freshwater aquatic toxicity data considered for developing FWQG for Cr(VI).

Species	Group	Endpoint	Concentration (µg/L)	Reference
Water flea (<i>Daphnia magna</i>)	●	63-d MATC (survival)	5	Gorbi et al. (2002)
Duckweed (<i>Lemna minor</i>)	▲	7-d EC ₁₀ (growth)	7	Naumann et al. (2007)
Brook trout (<i>Salvelinus fontinalis</i>)	■	8-month NOEC (growth)	10	Benoit (1976)
Water flea (<i>Ceriodaphnia dubia</i>)	●	7-d IC ₂₅ (reproduction)	20	Baral et al. (2006)
Green Alga (<i>Scenedesmus subspicatus</i>)	▲	72-h EC ₁₀ (biomass)	32	Kuur and Pattard (1990)
Green Alga (<i>Selenastrum capricornutum</i>)	▲	72-h EC ₁₀ (growth)	33*	Christensen and Nyholm (1984); Nyholm (1991)
Hydra (<i>Hydra littoralis</i>)	●	11-d LOEC (reproduction)	35	Corradi et al. (1998)
Fathead minnow (<i>Pimephales promelas</i>)	■	30-d NOEC (growth)	50	Broderius and Smith (1979)
Rainbow trout (<i>Oncorhynchus mykiss</i>)	■	110-d MATC (growth)	51	Sauter et al. (1976)
Water flea (<i>Daphnia carinata</i>)	●	14-d MATC (reproduction)	71	Hickey (1989)
Green alga (<i>Chlorella pyrenoidosa</i>)	▲	4-d NOEC (biomass)	100	Meisch and Schmitt-Backman (1979)
Lake trout (<i>Salvelinus namaycush</i>)	■	60-d NOEC (growth)	105	Sauter et al. (1976)
Green alga (<i>Scenedesmus pannonicus</i>)	▲	96-h NOEC (growth)	110	Slooff and Canton (1983)
Snail (<i>Lymnaea stagnalis</i>)	●	40-d NOEC (reproduction)	110	Slooff and Canton (1983)
Channel catfish (<i>Ictalurus punctatus</i>)	■	30-d NOEC (growth)	150	Sastry and Sunita (1983)
Copepod (<i>Mesocyclops pehpeiensis</i>)	●	9-d EC ₅₀ (development)	268	Wong and Pak (2004)
White sucker (<i>Catostomus commersoni</i>)	■	60-d NOEC (growth)	290	Sastry and Sunita (1983)
Green alga (<i>Chlorella vulgaris</i>)	▲	4-d (EC ₅₀) (growth)	332	Rodriguez (2011)
Blue-green alga (<i>Microcystis aeruginosa</i>)	▲	4-d NOEC (biomass)	350	Slooff and Canton (1983)
Clawed toad (<i>Xenopus laevis</i>)	◆	100-d NOEC (mortality)	350	Slooff and Canton (1983)
Mosquito	●	25-d NOEC	1100	Slooff and Canton (1983)

Federal Environmental Quality Guidelines

(<i>Culex pipiens</i>)		(survival/growth)		
Brown hydra (<i>Hydra oligactis</i>)	●	21-d NOEC (growth)	1100	Slooff and Canton (1983)
Medaka (<i>Oryzias latipes</i>)	■	40-d NOEC (mortality)	3500	Slooff and Canton (1983)
Guppy (<i>Poecilia reticulata</i>)	■	28-d NOEC (mortality)	3500	Slooff and Canton (1983)

Legend: ◆ = Amphibian; ■ = Fish; ● = Invertebrate; ▲ = Plant

*Geomean

Federal Water Quality Guideline Derivation

Federal Water Quality Guidelines (FWQGs) are preferably developed using the current Canadian Council of Ministers of Environment (CCME 2007) protocol. While there is an existing CCME (1999) freshwater quality guideline for the protection of aquatic life for Cr(VI), it was developed using the older 1991 protocol (CCME 1991). In the case of Cr(VI), sufficient chronic toxicity data are now available to meet the minimum data requirements for a CCME Type A guideline¹. Therefore, since the CCME updated its protocol in 2007 to reflect the current scientific understanding in water quality guidelines development, the FWQG developed here is consistent with the current CCME guiding principle and 2007 protocol and is therefore intended to protect all forms of freshwater aquatic life for indefinite exposure periods.

Each species for which appropriate toxicity data were available (Table 2) was ranked according to sensitivity and its position on the species sensitivity distribution (SSD) was determined (Figure 1). Several cumulative distribution functions (normal, logistic, extreme value and Gumbell) were fit to the data using regression methods and the model fit was assessed using statistical and graphical techniques. Based on goodness of fit, the log logistic model provided the best fit; the 5th percentile of the SSD plot is 5 µg/L, with lower and upper confidence limits of 4 and 7 µg/L, respectively.

The 5th percentile from the SSD (5 µg/L) is selected as the FWQG. The guideline represents the concentration below which one would expect either no or only a low likelihood of adverse effects on aquatic life. In addition to this guideline, two other concentration ranges are provided for use in risk management (Figure 1). At concentrations between >5th and 50th percentile of the SSD (>5-110 µg/L), there is a moderate likelihood of adverse effects to aquatic life. Concentrations > the 50th percentile (>110 µg/L) have a higher likelihood of causing adverse effects. Risk managers may find these additional concentration ranges useful in defining short-term or interim risk management plans. The moderate to higher concentration ranges may also be used in setting less protective interim targets for waters that are already highly degraded or where there are socio-economic considerations that preclude the ability to meet the FWQG.

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).

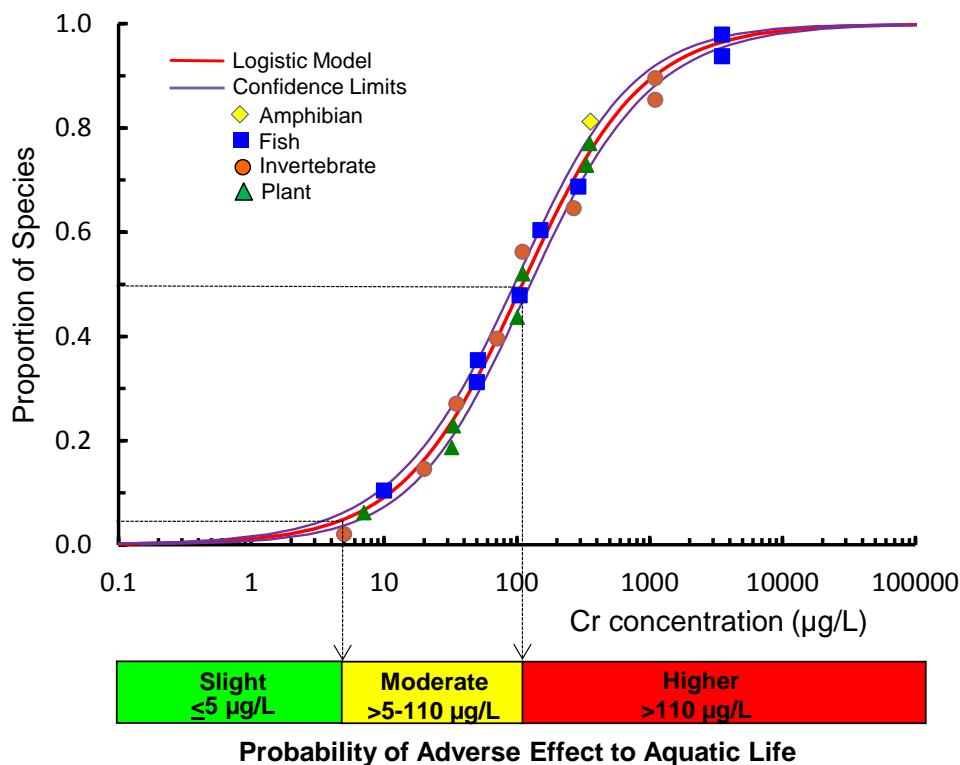


Figure 1. Species sensitivity distribution (SSD) for the chronic toxicity of Cr(VI) and relative likelihood of adverse effects for freshwater aquatic life.

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List of Acronyms and Abbreviations

- ATSDR – Agency for Toxic Substances and Disease Registry.
- BCF – Bioconcentration Factor: the ratio of the concentration of a chemical compound in an organism relative to the concentration of the compound in the exposure medium (e.g. soil or water)
- CAREX – CARcinogen EXposure Canada
- CCME – Canadian Council of Ministers of Environment
- CEPA – Canadian Environmental Protection Act
- CMP – Chemicals Management Plan
- DSIS – Division of Specialized Information Services
- EC – Effect Concentration
- EU – European Union
- FEQG – Federal Environmental Quality Guideline
- FWQG – Federal Water Quality Guidelines
- IC – Inhibition concentration
- LOEC – Lowest-Observed-Effect Concentration
- MATC – Maximum Acceptable Toxicant Concentration
- NOEC – No-Observed-Effect Concentration
- NRCan – Natural Resources Canada
- PNEC – Predicted No-effect Concentration
- RAMP – Regional Aquatics Monitoring Program
- SSD – Species Sensitivity Distribution
- UKTAG – UK Technical Advisory Group
- USEPA – United States Environmental Protection Agency
- WRF – Water Research Foundation