Canadian Water Quality Guidelines for the Protection of Aquatic Life

CHROMIUM

hexavalent chromium
trivalent chromium

Chromium (Cr) (CAS 7440-47-3) is a lustrous, grey metal with an atomic number of 24 and atomic weight of 51.996. Chromium can exist in nine different oxidation states from -II to +VI. Oxidation states of (II), (III), and (VI) are the most common with (III) being the most stable. Compounds with chromium oxidation states of (II) are strongly reducing while (VI) compounds are strongly oxidizing. Oxidation state (V) compounds are unstable, while (-II), (-I), (0), (I), and (IV) compounds are rare. Cr(VI) is the principal species found in surface waters and aerobic soils while Cr(III) dominates in mildly reducing environments such as sediments and wetlands (Bailar et al. 1973).

Trivalent chromium is an acid that forms strong complexes with various O-, N- and S-containing ligands and many organic compounds. The principal species of trivalent chromium are Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_3$, and $Cr(OH)_4^-$. The solubility of Cr(III) is limited by the formation of highly insoluble oxides, hydroxides, and phosphates and its strong tendency to adsorb to surfaces (Pawlisz et al. 1997).

Hexavalent chromium forms a number of stable oxyacids and anions including $HCrO_4^-$ (hydrochromate), $Cr_2O_7^{2-}$ (dichromate), and CrO_4^{2-} (chromate). Most Cr(VI) salts are soluble and very mobile, with a long residence time in surface and groundwater. The high oxidizing potential, high solubility, and ease of permeation of biological membranes make Cr(VI) generally more toxic than Cr(III). Hexavalent chromium can be reduced to the trivalent state by S^{2-}, Fe(II), fulvic acid, low molecular weight organic compounds, and proteins inside organic cells. Indirect photoreduction mediated by Fe(II) may also be important (Environment Canada 1997; Pawlisz et al. 1997).

In 1991, approximately 74 000 t of chromium-containing compounds were imported into Canada (55% ferroalloys, 28% chromite ores and concentrates, and 9% other compounds) (Statistics Canada 1991). The most commonly used compounds in Canadian industry are chromium oxide, chromium chloride, and chromium sulphate. These compounds are mainly used in metal plating and finishing, pigments and paints, leather tanning, wood preservation, corrosion inhibition, and as catalysts. Small quantities of chromium are used in producing cosmetics, toners for copying machines, magnetic tapes, fertilizers, rubber products, plastics, soaps, and cleaning products. Chromium is used in the metal plating industry for corrosion inhibition and decoration purposes. Chromic acid is used in metal finishing to create a protective film on soft and galvanized metals that also helps in the adhesion of paint. Sodium dichromate is used in descaling copper and brass. Many printing inks, paints, plastics, and wall coverings contain lead chromate and potassium zinc chromate as the main pigment. Chromic and sodium dichromate solutions are essential in leather tanning and wood protection. Chromium-based corrosion inhibitors in cooling towers function to protect heat exchange materials against rust (Government of Canada 1993).

Natural atmospheric sources of chromium 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. These ores, however, are of low and medium grade and Canada is not a chromite-producing country. Major anthropogenic atmospheric sources include cooling towers, chromium plating, fossil fuel combustion, municipal waste and sewage sludge incineration, chromite ore refining, manufacture of refractories, ferrochromium and chromium chemicals production, nonferrous metal smelting, specialty steel, and cement production. Minor sources include road dust containing chromium as a result of wear of tires and brake linings. Toners used in photocopiers can be a large source of chromium indoors (Environment Canada 1997; Pawlisz et al. 1997).

The primary sources of chromium entering the aquatic environment are from tanneries, cooling towers, steel and nonferrous foundries, metal finishing and plating operations, flat glass and asbestos producing plants, wood treatment facilities, paint and chemical works, oil drilling and recovery rigs. Large quantities of chromium may be released from pulp and paper mills, cement and fertilizer plants, textile mills, power plants, chlor-alkali plants, and petrochemical industries. Chromium is widely used by

Table 1. Water quality guidelines for chromium for the protection of aquatic life (Environment Canada 1997).

Aquatic life		Guideline value ($\mu g \cdot L^{-1}$)
Freshwater	Cr(VI)	1.0
	Cr(III)	8.9*
Marine	Cr(VI)	1.5
	Cr(III)	56*

*Interim guideline.

many small industries, and as a result, municipal sewage can contain high concentrations. Industries can be responsible for as much as 75% of the chromium found in sewage (between 10 and 560 mg·L^{-1} chromium with an average 170 mg·L^{-1} in raw sewage, and often <30 mg·L^{-1} in treated sewage). The discharge from treated effluents is estimated to be up to 110 t per year. In addition, urban runoff and industrial storm waters contain between 5 and 500 mg·L^{-1} of chromium and can be important contributors to the aquatic environment. Chromium in the runoff comes from corrosion of painted surfaces, stainless steel, treated lumber, decorative trims, tar and asphalt, and automotive tire and brake wear (Government of Canada 1993; Pawlisz et al. 1997).

Groundwater contamination by chromium is a major problem where chromium-containing wastes are buried (with concentrations of 9–120 mg·L^{-1} at some Ontario sites) or discharged into lagoons. It is most severe in shallow sand and gravel aquifers, because hexavalent chromium is very mobile due to its high water solubility and low adsorption rate onto soil particles (Environment Canda 1997; Pawlisz et al. 1997).

Standard methods for analysis of chromium are subject to contamination and many estimates of environmental concentrations remain to be validated using ultra-clean techniques. Results obtained using an ultra-clean technique indicate that concentrations of chromium in pristine lakes and rivers in Canada are <0.001–0.005 mg·L^{-1} (Shiller and Boyle 1991). Groundwater in Canada usually contains approximately 0.002 mg·L^{-1} chromium (Environment Canada 1997; Pawlisz et al. 1997).

The measurement of total chromium will also include particulate chromium when surface water samples are not filtered. This may affect the validity of measurements in spring when erosion and turbidity is high. Under these conditions, high chromium readings may be found that are higher than the guidelines with no adverse effects on biota (Environment Canada 1997; Pawlisz et al. 1997).

While chromium can bioconcentrate to some extent in aquatic plants, it does not seem to bioaccumulate in fish or invertebrates, and chromium body burdens remain low even in contaminated water (Environment Canada 1997; Pawlisz et al. 1997).

Water Quality Guideline Derivation

The Canadian water quality guidelines for chromium for the protection of aquatic life were developed based on the CCME protocol (CCME 1991). For more information, see the supporting document (Environment Canada 1997).

Concentrations of chromium in this report represent total chromium (dissolved plus particulate). If chromium species are indicated [Cr(III) or Cr(VI)] then total chromium indicates the total concentration (dissolved plus particulate) of each valency. In unfiltered samples, 10 to 60% of total chromium is Cr(VI) in dissolved form, in filtered samples the range is between 70 and 90%.

Freshwater Life

Hexavalent Chromium

Estimates of chronic toxicity of hexavalent chromium to freshwater fish range from 0.01 mg·L^{-1} for *Salmo salar* (360-h increase in hatching time) to 74.9 mg·L^{-1} for *Anaba scandens* (30-d LC_{50}). The acute toxicity estimates range from 0.1 mg·L^{-1} for *Oncorhynchus mykiss* (72-h LC_{50}) to 930 mg·L^{-1} for *Lepomis macrochirus* (24-h LC_{50}). Among the more than 30 fish species studied, salmonids seem to be the most sensitive group (Figure 1). Invertebrates are the most sensitive organisms to hexavalent chromium. Among the more than 40 invertebrate species studied, the chronic toxicity effects range from 0.01 mg·L^{-1} for *Ceriodaphnia dubia* (14-d LOEC) to 1000 mg·L^{-1} for *Chironomus tentans* (decrease in rest time), while acute toxicity effects range from 0.015 for daphnids *Simocephalus vetulus* and

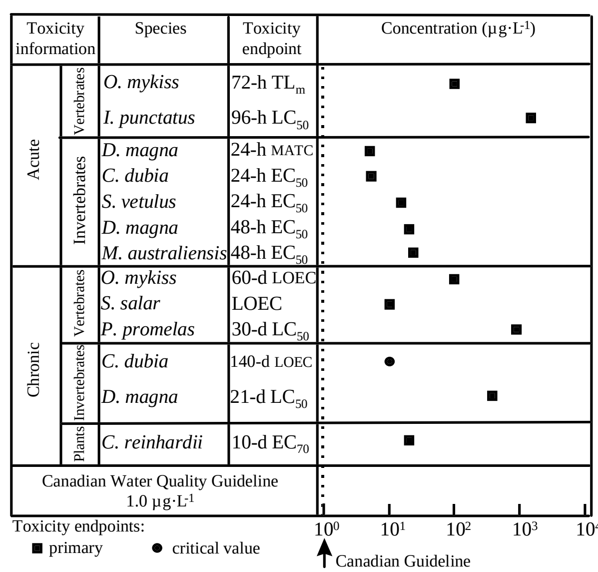

Figure 1. Select freshwater toxicity data for hexavalent chromium.

Daphnia magna (24-h EC_{50}) to 500 mg·L^{-1} for the crayfish *Procambarus clarkii* (96-h LC_{40}). Aquatic plants such as *Selenastrum capricornutum* can be inhibited in growth by levels of chromium as low as 0.6 mg·L^{-1} (Environment Canada 1997; Pawlisz et al. 1997).

The water quality guideline for hexavalent chromium [Cr(VI)] for the protection of freshwater life is 1.0 µg·L^{-1} (i.e., 0.001 mg·L^{-1}). It was derived by multiplying the 14-d LOEC of 0.01 mg·L^{-1} for *C. dubia* (Hickey 1989) by a safety factor of 0.1 (CCME 1991).

Trivalent Chromium

Chronic toxicity estimates for freshwater fish range from 0.006 mg·L^{-1} for *O. mykiss* (reduced growth) to 110 mg·L^{-1} for *Anabas scandens* (30-d LC_{50}). Acute toxicity estimates for more than 10 fish species range from 3.3 mg·L^{-1} for *Lebistes reticulatus* (96-h LC_{50}) to 77.5 mg·L^{-1} for *Pimephales promelas* (24-h LC_{50}). Chronic toxicity of trivalent chromium to invertebrates ranges from 0.6 mg·L^{-1} for *D. magna* (50% reproductive impairment) to 32 mg·L^{-1} for stonefly *Acroneria lycorias* (168-h LC_{50}). Acute toxicities in more than 12 invertebrate species range from 1.2 mg·L^{-1} for *D. magna* (64-h EC_{50}) to 937 mg·L^{-1} for *Asellus aquaticus* (48-h LC_{50}). Among aquatic plants, toxicity ranges from 0.32 mg·L^{-1} for *Cladophora glomerata* (96-h EC_{50}) to 580 mg·L^{-1} for *Chlorella pyrenoidosa* (growth inhibition) (Environment Canada 1997; Pawlisz et al. 1997). The interim water quality guideline for trivalent chromium [Cr(III)] for the protection of freshwater life is 8.9 µg·L^{-1}. It was derived by multiplying the 102-d LOEC (mortality) of 0.089 mg·L^{-1} for *O. mykiss* (Stevens and Chapman 1984) by a safety factor of 0.1 (CCME 1991).

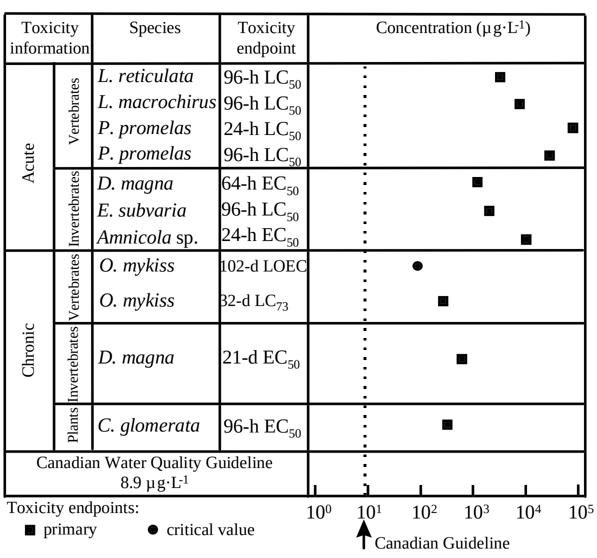

Figure 2. Select freshwater toxicity data for trivalent chromium.

Marine Life

Hexavalent Chromium

Estimates of chronic toxicity of hexavalent chromium to marine fish range from 0.5 mg·L^{-1} for *Pleuronectes platessa* (organ damage) to 44.0 mg·L^{-1} for *Fundulus heteroclitus* (7-d LC_{50},) Acute toxicity estimates range from 16.3 mg·L^{-1} for *Cyprinodon variegatus* (48-h LC_{50}) to 200 mg·L^{-1} for *Fundulus heteroclitus* (24-h LC_{50}) (Environment Canada 1997; Pawlisz et al. 1997).

Among the more than 40 invertebrate species studied, the chronic toxicity effects from hexavalent chromium range from 0.01 mg·L^{-1} for yellow crab *(Cancer anthonyi)* (LC_{33}) to 195.1 mg·L^{-1} for the crustacean *Callinectes simulis* (reduced respiration), and the acute toxicity estimates range from 0.75 µg·L^{-1} for the mollusc *Villorita cyprinoides* (48-h EC_{50} filtering rate) to 54 mg·L^{-1} for the starfish *Asterias forbesi* (24 h LC_{50}). Several marine plants (*Prorocentrum mariae L.*, *Thalassiosira aestevalis, T. pseudonana, Pheaodactylum tricornutum*) showed reduced growth at 0.01–0.015 mg·L^{-1}, while the highest reported effect threshold was at 620 mg·L^{-1} (EC_{50} photosynthesis, *Dunaliella bioculata*) (Environment Canada 1997; Pawlisz et al. 1997).

Several toxicity studies with very low endpoints were deemed inappropriate for guideline derivation. The water quality guideline for hexavalent chromium [Cr(VI)] for the protection of marine life is 1.5 µg·L^{-1}. It was derived by multiplying the 15-d IC_{50} reduced growth of 0.015 mg·L^{-1}, (Reidel, 1989) for *Prorocentrum mariae L.* by a safety factor of 0.1 (CCME 1991).

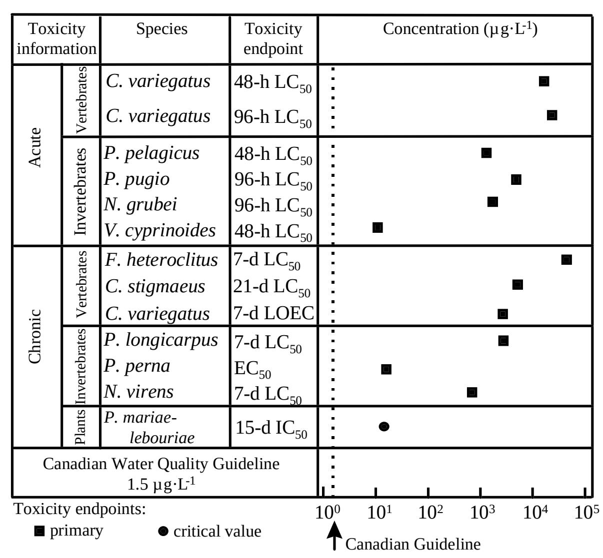

Figure 3. Select marine toxicity data for hexavalent chromium.

Trivalent Chromium

A 96-h LC_{50} of 53 $mg\cdot L^{-1}$ for juvenile *Aldrichetta forsteri* is the only marine fish study available. Estimates of chronic toxicity for marine invertebrates range from 0.15 $mg\cdot L^{-1}$ in molluscs *Mytilus edulis* and *Mya arenaria* (reduced filtration rate) to 80 $mg\cdot L^{-1}$ for brine shrimp *Artemia salina* (EC_{45}, reduced hatching), and estimates of acute toxicity range from 0.002 $mg\cdot L^{-1}$ for *Perna perna* (EC_{50}, reduced filtering rate) to 19.3 $mg\cdot L^{-1}$ for the copepod *Acartia clausi* (48-h LC_{50}) (Environment Canada 1997; Pawlisz et al. 1997). The interim water quality guideline for trivalent chromium [Cr(III)] for the protection of marine life is 56 $\mu g\cdot L^{-1}$ (i.e., 0.056 $mg\cdot L^{-1}$). It was derived by multiplying the 8-d LOEC (survival and reproduction) of 0.56 $mg\cdot L^{-1}$ for the invertebrate *Tisbe battagliai* (Hutchinson et al. 1994) by a safety factor of 0.1 (CCME 1991).

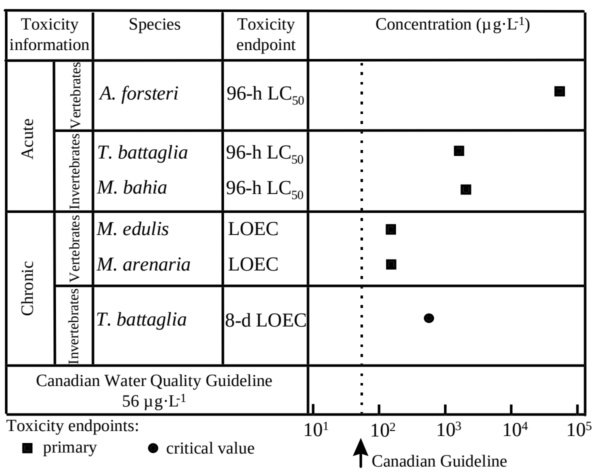

Figure 4. Select marine toxicity data for trivalent chromium.

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