



Canadian Sediment Quality Guidelines for the Protection of Aquatic Life

CHROMIUM

Chromium (Cr) is an essential trace element that can be toxic to aquatic biota at elevated concentrations. Chromium exists in two oxidation states in aquatic systems: hexavalent Cr (i.e., Cr⁶⁺) and trivalent Cr (i.e., Cr³⁺). Independent assessments of the potential for toxicity of Cr⁶⁺ and Cr³⁺ in the Canadian environment were carried out according to the Canadian Environmental Protection Act (CEPA). The CEPA assessment reported that dissolved and soluble forms of Cr⁶⁺ are entering the Canadian environment in quantities or concentrations, or under conditions that are having, or may have, a harmful effect on the environment (Government of Canada 1994). However, for Cr³⁺, the CEPA assessment reported that it was not possible to determine whether dissolved and soluble forms were entering the Canadian environment according to the above conditions (Government of Canada 1994). Chromium enters aquatic systems through aerial deposition or surface runoff, and, subsequently, its association with particulate matter results in its deposition in bed sediments. Because a variety of organisms live in contact with bed sediments, sediments are an important route of exposure for aquatic organisms to Cr. Canadian interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for Cr can be used to evaluate the degree to which adverse biological effects are likely to occur as a result of exposure to Cr in sediments.

Canadian ISQGs and PELs for Cr were developed using a modification of the National Status and Trends Program approach described in CCME (1995) (Table 1). The ISQGs and PELs refer to total concentrations of Cr in surficial sediments (i.e., top 5 cm), as quantified by digestion with a strong acid (e.g., aqua regia, nitric acid, and hydrochloric acid) followed with determination by a standard analytical protocol.

The majority of the data used to derive ISQGs and PELs for Cr are from studies on field-collected sediments that measured concentrations of Cr, along with concentrations of other chemicals, and associated biological effects, as compiled in the Biological Effects Database for Sediments (BEDS) (Environment Canada 1998). In most studies that evaluated the distribution of Cr in the environment, only total Cr was measured; little information was provided on the species of Cr present in the sediment. However, results of recent studies in Canada and other countries, indicate that Cr⁶⁺ is the dominant form in the dissolved phase, whereas nearly all of the Cr in sediments (excluding that immediately below the sediment–water interface with

overlying aerobic waters) is likely present in the form of Cr³⁺ (Government of Canada 1994).

The Cr data sets for freshwater and marine sediments are large, with the freshwater data set containing 68 effect entries and 384 no-effect entries, and the marine data set containing 53 effect entries and 310 no-effect entries (Figures 1 and 2). The BEDS represents a wide range of concentrations of Cr, types of sediments, and mixtures of chemicals. Evaluation of the percentage of effect entries for Cr that are below the ISQGs, between the ISQGs and the PELs, and above the PELs (Figures 1 and 2) indicates that these values define three ranges of chemical concentrations: those that are rarely, occasionally, and frequently associated with adverse biological effects, respectively (Environment Canada 1998).

Toxicity

Adverse biological effects for Cr in the BEDS include decreased diversity and abundance, reduced mortality, and behavioural changes of benthic organisms, among others (Environment Canada 1998, Appendixes IIa and IIb). For example, the richness of benthic species and the abundance of Amphipoda and Chironomidae in Toronto Harbour, Ontario, were lower at sites where the mean concentration of Cr was 95 mg·kg⁻¹, which is above the freshwater PEL, compared to sites with concentrations from 10.2 to 11 mg·kg⁻¹, which are below the freshwater ISQG (Jaagumagi 1988).

In marine sediments, McGreer (1982) reported that the estuarine tellinid clam, *Macoma balthica*, was absent from sites in the Fraser River estuary, British Columbia, at concentrations of 87.3 mg·kg⁻¹; however, the clam was present at sites with 42 mg·kg⁻¹, which is below the marine ISQG.

A limited number of spiked-sediment toxicity tests have been conducted for Cr (Environment Canada 1998). In freshwater lake sediments, Dave (1992) reported 48-h

Table 1. Interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for chromium (mg·kg⁻¹ dw).

	Freshwater	Marine/estuarine
ISQG	37.3	52.3
PEL	90.0	160

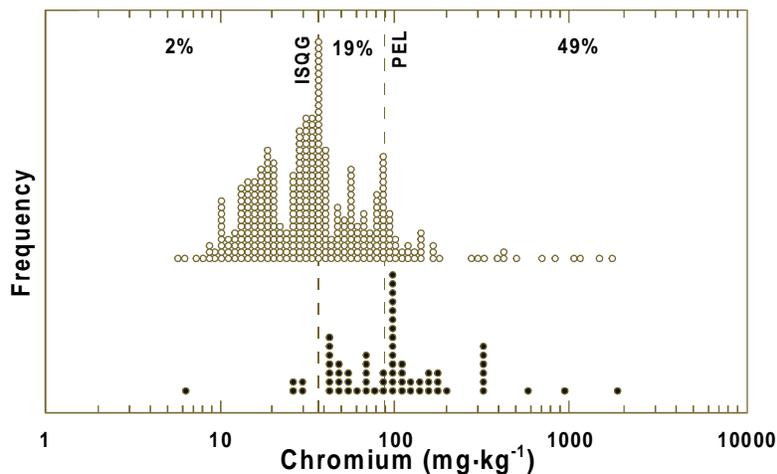


Figure 1. Distribution of Cr concentrations in freshwater sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.

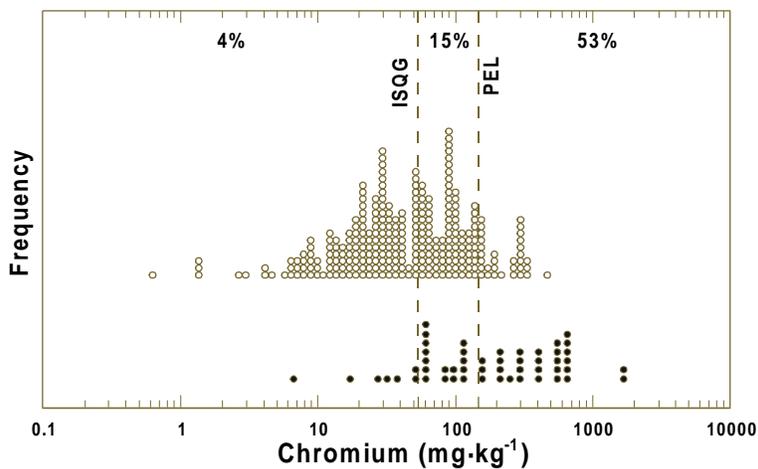


Figure 2. Distribution of Cr concentrations in marine and estuarine sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.

LC₅₀s for *Daphnia magna* of 195 mg·kg⁻¹ and 167 mg·kg⁻¹ for Cr³⁺ and Cr⁶⁺, respectively. In marine sediments, Capuzzo and Sasner (1977) observed that filtration rates of *Mytilus edulis*, the blue mussel, were significantly reduced after 24 weeks of exposure to 150 mg·kg⁻¹ Cr. Neither of these studies examined the relationship between observed toxicity and any factors that may modify toxicity.

Although limited in number, the results of these freshwater and marine spiked-sediment toxicity tests indicate that toxic levels of Cr are consistently above the ISQGs. This confirms that ISQGs adequately represent concentrations below which adverse biological effects will rarely occur. Further, these studies provide additional evidence that toxic levels of Cr in sediments are similar to or greater than the PELs, and confirms that adverse effects are more likely to be observed when concentrations exceed the PELs (Environment Canada 1998). The ISQGs and PELs are therefore expected to be valuable tools for assessing the ecotoxicological relevance of Cr in sediments.

Concentrations

Concentrations of Cr in marine and freshwater sediments vary substantially across Canada (Environment Canada 1998). In the National Geochemical Reconnaissance (NGR) program database by the Geological Survey of Canada (GSC) (Friske and Hornbrook 1991), the mean background concentrations in lake and stream sediments are 47 mg·kg⁻¹ and 81 mg·kg⁻¹, respectively (R.G. Garrett 1997, GSC, Ottawa, pers. com.). When compared with concentrations in the combined lake and stream NGR database (n = 51 311), the freshwater ISQG and PEL for Cr fall at percentiles 38.6 and 83, respectively, of background concentrations (R.G. Garrett 1997, GSC, Ottawa, pers. com.). Background concentrations of Cr across most of Canada are higher than the ISQG of 37.3 mg·kg⁻¹. This situation may be explained in part by the different digestion methods used in deriving ISQGs and PELs versus those used in determining concentrations of metals for the NGR database. The ISQGs and PELs are derived from ecotoxicological studies that use weak acid digestion methods that attempt to remove only the bioavailable fraction of metals. In contrast, the NGR protocol for determining concentrations of metals in sediment involves a strong acid digestion that removes both the bioavailable and residual fractions of metals. This difference and the fact that Cr is primarily associated with the residual fraction of the sediment (i.e., alumino-silicate minerals) may help explain why the ISQG falls at percentile 38.6 of background concentrations (R.G. Garrett 1997, GSC, Ottawa, pers. com.). In marine systems, mean background concentrations of Cr, estimated from deep layers of sediment cores (>10 cm) from a variety of published sources, ranged from 20 mg·kg⁻¹ to 85 mg·kg⁻¹,

that is, from below the marine ISQG to approximately half of the marine PEL (Environment Canada 1998).

Concentrations of Cr in surficial sediments close to point sources of contamination frequently exceed background concentrations (Environment Canada 1998). For example, concentrations of Cr as high as 3 712 mg·kg⁻¹ have been measured in freshwater sediments of lakes and rivers near manufacturing plants, and concentrations of 85.2 mg·kg⁻¹ have been measured in marine harbours receiving various industrial and sewage inputs (Environment Canada 1998).

Additional Considerations

Regardless of the origin of Cr in sediments, aquatic organisms may be adversely affected by exposure to elevated levels. As is evident in Figures 1 and 2, the occurrence of adverse biological effects cannot be precisely predicted from concentration data alone, particularly in the concentration ranges between the ISQGs and PELs. The likelihood of adverse biological effects occurring in response to exposure to Cr at a particular site depends on the sensitivity of individual species and endpoints examined, as well as a variety of physicochemical (e.g., pH, redox potential, and chemical speciation of Cr), geochemical (e.g., particle size, metal oxide content, and organic content), and biological (e.g., feeding behaviour, and uptake rates) factors that affect the bioavailability of Cr (Environment Canada 1998).

Benthic organisms are exposed to dissolved and particulate Cr in the interstitial and overlying waters, as well as to sediment-bound Cr through surface contact and ingestion of sediments. In the dissolved phase, Cr⁶⁺ is the predominant form as it is relatively unreactive, with its removal controlled by adsorption and reduction to Cr³⁺. In contrast, Cr³⁺ strongly adsorbs to aquatic particles and can accumulate and persist in sediments. Thus, the fate of Cr in the aquatic environment will vary depending on its chemical form, with Cr⁶⁺ being the dominant form in oxic waters, and Cr³⁺ being the dominant form in sediment, anoxic waters, and waters of low pH (Environment Canada 1998).

In aquatic systems, dissolved metals are believed to be the most readily bioavailable (Campbell and Tessier 1996); however, relatively higher concentrations of Cr are measured in sediments and, therefore, represent a potential source of exposure for some aquatic organisms. The bioavailability of Cr will depend on its partitioning between the dissolved and particulate phases. It is generally believed that metals associated with sediment fractions that exhibit cation-exchange capacity or that are easily reduced are generally more bioavailable than those associated with other fractions (Environment Canada 1998).

However, for Cr, most studies have shown that bioavailability is independent of the easily reducible fractions in the sediment (Rule 1985; Bryan and Langston 1992). Changes in ambient environmental conditions (e.g., sediment turbation, decrease in pH, and increase in redox potential) can increase the bioavailability of Cr associated with sediment fractions, such as inorganic solid phases, organic matter, and oxides of iron and manganese. In contrast, Cr that is bound within the crystalline lattices of clay and some other minerals that are associated with acid-extractable or residual sediment fractions is generally considered to be the least bioavailable. Once Cr is ingested, its availability depends on various factors, including enzyme activity and gut pH (Environment Canada 1998).

Information regarding factors influencing the bioavailability and toxicity of Cr is limited. Thus, additional research into relationships that have been verified with other metals (e.g., AVS and organic matter) should be investigated with Cr. Further research should also be directed at determining the relationships between Cr speciation and the physical, chemical, and geochemical characteristics of aquatic systems and sediments that may influence the bioavailability of Cr.

Currently, the degree to which Cr will be bioavailable at particular sites cannot be predicted conclusively from the physicochemical characteristics of the sediments or the attributes of endemic organisms (Environment Canada 1998). Nonetheless, the incidence of adverse biological effects associated with exposure to Cr increases as concentrations of Cr increase in a range of sediment types (Figures 1 and 2). Therefore, the recommended Canadian ISQGs and PELs for Cr will be useful in assessing the ecotoxicological significance of Cr in sediments.

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