A User's Guide for the Ambient Water Quality Guidelines for Cadmium

What is a Water Quality Guideline?

The British Columbia Ministry of Environment develops ambient water quality guidelines (WQGs) to assess and manage the health, safety and sustainability of BC's aquatic resources. Guidelines are developed to protect aquatic life, wildlife, agriculture (irrigation and livestock watering), drinking water sources, recreation and aesthetics. Water quality guidelines are science-based and intended for generic provincial application. Water quality guidelines do not have any direct legal standing. They are used to inform resource management decisions affecting water quality.

Water quality guidelines for the protection of aquatic life are developed to be protective of the most sensitive species at its most sensitive life-stage (MOE 2012). For most substances, two guidelines are developed: a short-term maximum guideline to prevent acute effects and a long-term average guideline to prevent chronic effects. This User's Guide provides an overview of BC's Ambient Water Quality Guidelines for Cadmium; for the full technical report please see MOE (2015).

What is cadmium and why is it a concern?

Cadmium is a soft, silver-white metal, often associated with zinc, lead, and copper ores, found in the earth's crust. Cadmium has been identified as a metal of major importance by multiple agencies, such as Environment Canada, Health Canada and U.S. Environmental Protection Agency, because of its toxicity to humans and wildlife.

In aquatic ecosystems, excess cadmium interferes with the uptake of calcium by organisms. In fish and aquatic invertebrates this results in cellular damage, decreases in metabolic activity, increased mortality, decreased growth, and decreased reproductive capacity and success. In aquatic plants and algae, cadmium uptake causes adverse effects by inhibiting photosynthesis, growth, and chlorophyll synthesis.

There is some evidence to suggest that, in addition to uptake (i.e. bioconcentration) of cadmium through direct contact (e.g. at the gill-water interface), bioaccumulation of cadmium through ingestion of contaminated food sources may contribute to the overall cadmium body burden in fish and invertebrates. However, there is no evidence to support the possibility that cadmium biomagnifies (i.e., tissue concentrations increase with trophic levels) in the aquatic environment.

Cadmium in the Environment

Cadmium enters aquatic ecosystems naturally through the weathering of minerals and forest fires, and through human activities such as non-ferrous metal mining, the application of phosphate fertilizers and waste disposal. Combustion processes associated with smelting operations, waste incineration and fossil fuel combustion emit cadmium into the atmosphere as part of oxide, chloride, and sulphate complexes. These particles can be transported over long distances (hundreds to thousands of kilometres) before being deposited onto the soil or surface water. In B.C., wastewater treatment plants, non-ferrous ore production and processing, and pulp and paper mills are the important anthropogenic sources of cadmium.

Compared to most other heavy metals, cadmium is relatively mobile in aquatic systems. Elemental cadmium is insoluble in water but the cadmium ion (Cd^{2+}) can form salts, such as cadmium chloride ($CdCl_2$), which are soluble. In organic-rich or polluted waters, cadmium readily adsorbs to organic substances and can be found suspended in the water column. Under high pH (i.e., alkaline) conditions, cadmium can form insoluble complexes with carbonate ($CdCO_3$) or hydroxide [$Cd(OH)_2$] and settle out in bottom sediments.

In general, background cadmium concentrations in natural (i.e., unimpacted) surface waters in BC were found to be lower in southern regions (Vancouver Island and Kootenay regions) compared to central and northern regions (Cariboo, Skeena, and Omineca-Peace regions) (see Figure 1 in MOE (2015) for a map of sampling locations). This may be attributed to variability in local rock composition and ambient conditions such as climate, soil type, pH, and water quantity and flow regime. In general, background concentrations across BC ranged from 0.00287 to 0.173 µg/L for total cadmium, and from 0.00275 to 0.145 µg/L for dissolved cadmium (see MOE 2015, Tables 2 to 4 for a summary of total and dissolved cadmium concentrations ranges in each of the seven regions in BC).

How do ambient conditions affect the toxicity of cadmium?

Dissolved cadmium in the water column is readily taken up by aquatic organisms through specialized calcium receptor cells. However, the uptake rate is dependent upon the bioavailability of cadmium which in turn is dependent upon ambient conditions. Both water hardness and alkalinity can reduce the bioavailability of cadmium to aquatic organisms.

Water hardness is a measure of the dissolved mineral content in the water. High concentrations of dissolved minerals can lower the toxicity of cadmium by competing for access to receptor sites. Alkalinity is the capacity of water to buffer against acid and is measured as the concentration of carbonate ions (CO_3^{2-}) in the water column. Carbonate ions can bind with cadmium creating insoluble complexes and therefore prevent cadmium from competing with calcium for uptake by aquatic organisms. Most carbonate enters the water column as calcium bicarbonate [$Ca(HCO_3)_2$] as a result of the weathering of certain rocks such as limestone. Calcium bicarbonate dissociates in water creating free calcium and carbonate ions. Therefore, hardness and alkalinity are typically positively correlated in natural water bodies.

Other environmental factors such as temperature and pH can also alter the toxicity of cadmium though these are less well understood. Toxicity tests have shown that the uptake of cadmium by aquatic organisms increases as the temperature increases. This is likely due to the increases in organism metabolism with temperature. The pH of the aquatic system also has the potential to affect the bioavailability of cadmium. Dissolved cadmium is more common in acidic waters (i.e., pH < 7), than alkaline waters (i.e. pH > 7) where it forms insoluble complexes with carbonate (CO_3^{2-}) or hydroxide (OH^-). In acidic waters, however, the increased concentration of hydrogen ions (H^+) increases competition with cadmium at receptor cells and therefore reduces cadmium uptake. Several studies support the hypothesis that cadmium is most toxic between a pH of 6 and 7.

How was this guideline developed?

The WQGs for cadmium were developed from the results of published laboratory toxicity studies conducted on a variety of aquatic organisms. For each study, information on the test species, test conditions, experimental design, chemical and physical properties of the test water, and statistical analyses were reviewed and each study was classified as primary, secondary or unacceptable. Studies classified as primary must: employ currently acceptable laboratory practices; at a minimum measure and report the concentration of a substance at the beginning and end of the exposure period; use ecologically relevant endpoints; measure and report the response and survival of controls; and report measurements of abiotic variables such as temperature, pH, dissolved oxygen and water hardness. Studies classified as secondary can: employ a wider array of toxicity testing methods; calculate substance concentrations; include additional endpoints; use static tests; however, they still need to measure and report the survival of controls and all the relevant environmental variables. Studies are classified as unacceptable if the toxicity data do not meet the requirements of primary or secondary. More than 124 studies were reviewed for the preparation of this guideline; of these, more than half (60%) could not be used because the experimental design did not follow standardized protocols or key information was missing. Altogether, 20 short-term and 28 long-term studies were found to be acceptable and classified as primary (i.e., the study met all the data requirements). These studies were used to develop the guidelines.

The previous working cadmium water quality guidelines were based on total cadmium. The new guideline is based on dissolved cadmium, rather than total cadmium, for several reasons: dissolved cadmium is the more bioavailable, and therefore ecologically relevant form; published toxicity tests were based on experiments using dissolved salts, and are best represented as dissolved cadmium; and concentrations of dissolved cadmium are less variable than total cadmium in BC waters due to the association between total cadmium, water flow, and suspended sediment concentrations.

Since water hardness affects the bioavailability of dissolved cadmium, an initial step in developing the guideline was to normalize cadmium toxicity to a consistent water hardness concentration. To do this, studies that measured toxicity at a range of water hardness were selected to develop a standardizing equation for both short- and long-term studies. A total of 6 species, comprising 39 data points, were used to develop the relationship between short-term toxicity of cadmium and water hardness (MOE 2015, Figure 2), and a total of 7 species, comprising 44 data points, were used for the long-term guideline (MOE 2015, Figure 4).

The 20 primary short-term studies contained data on 9 resident fish species (including 6 cold-water species), 13 resident invertebrate species, and 1 resident amphibian species (MOE 2015, Table 9). The effect concentrations from these studies were normalized to a standard hardness of 50 mg/L and then plotted to show the distribution of effect concentration by species (MOE 2015, Figure 6). Following ministry policy, the lowest severe effect concentration from a primary study (0.576 µg/L; LC_{50} for rainbow trout fry; Hansen *et al.* 2002a) was selected to support the derivation of a short-term maximum water quality guideline. Salmonid fish were the most sensitive species group to short-term increases in cadmium concentrations (MOE 2015, Figure 7).

The 28 primary long-term studies contained data on 1 BC resident aquatic plant species, 1 resident algal species, 13 resident fish species (including 8 salmonids), 11 resident invertebrate species, and 1 resident amphibian species (MOE 2015, Table 10). The experiments from these studies included multiple endpoints and effect levels for the same species, life-stage, and test duration; therefore the data were sorted and only the lowest experimental endpoint (i.e., most sensitive) from each study was selected. These values were normalized to a standard hardness of 50 mg/L and plotted to show the distribution of effect concentrations by species (MOE 2015, Figure 8). The minimum effect concentration from a primary study (0.253 µg/L; IC_{20} for *H. azteca* biomass; Chadwick Ecological Consultants, Inc. 2004) was used to support the derivation of the long-term average water quality guideline. Invertebrate species were generally found to be the group most sensitive to chronic exposures of cadmium (MOE 2015, Figure 9).

A final step in developing a water quality guideline is to apply an uncertainty factor to the minimum effect concentration to account for the uncertainty associated with this value. Sources of uncertainty include:

- laboratory to field differences;
- single to multiple contaminants (additive, synergistic, antagonistic effects);
- toxicity of metabolites;
- intra and inter-species differences (limited species to conduct tests on, which may not include the most sensitive species);
- indirect effects (e.g. foodweb dynamics);
- whole life-cycle vs. partial life-cycle (many toxicity studies are only conducted on partial life-cycles and it can be difficult to determining the most sensitive life stage);
- delayed effects;
- other stressors (habitat loss) or contaminants in the environment that may have an unknown effect (cumulative effects); and,
- impacts of climate change (species may be more vulnerable with additional stressors).

The appropriate uncertainty factor to be applied is decided on a case-by-case basis and is based on data quality and quantity, toxicity of the contaminant, severity of toxic effects, and bioaccumulation potential. Scientific judgement is used to maintain some flexibility in the derivation process. The minimum uncertainty factor of 2 was applied to derive both the short-term and long-term water quality guidelines.

How should the guideline be applied?

The water quality guidelines for dissolved cadmium represent concentrations that should protect aquatic life. The short-term maximum guideline represents a level that protects against severe effects over short-term exposures (i.e. 96 hours or less), whereas the long-term average guideline (calculated as the average of 5 weekly samples within 30 days) represents a level that protects against lethal and non-lethal effects over long-term exposures. Note that exceeding a long-term water quality guideline does not imply that an unacceptable risk exists, but rather that the potential for adverse effects may be increased and additional investigation should be conducted and considered in resource management decisions.

The water quality guidelines for cadmium have been developed as equations that take into account the water hardness of the water body. The equations are only valid for the range in water hardness specified in the toxicity studies used to derive the guidelines. It is not known how organisms will respond to cadmium at hardness concentrations outside of the range tested.

The following equation is recommended to calculate short-term maximum water quality guidelines for water with different water hardness concentrations (MOE 2015, Table ES 1):

$$WQG_{\text{Short-term}} = e^{[1.03 * \ln(Hss) - 5.274]}$$

Where H_{SS} = site-specific water hardness (mg/L $CaCO_3$). This equation is valid for water hardness concentrations between 7 and 455 mg/L $CaCO_3$. When water hardness is greater than the upper bound (i.e. highest water hardness tested), a site-specific assessment may be required.

At a water hardness of 50 mg/L $CaCO_3$, the recommended short-term maximum water quality guideline for dissolved cadmium to protect aquatic life is 0.288 µg/L. Figure 1 can be used to estimate the short-term maximum water quality guideline for other hardness values.

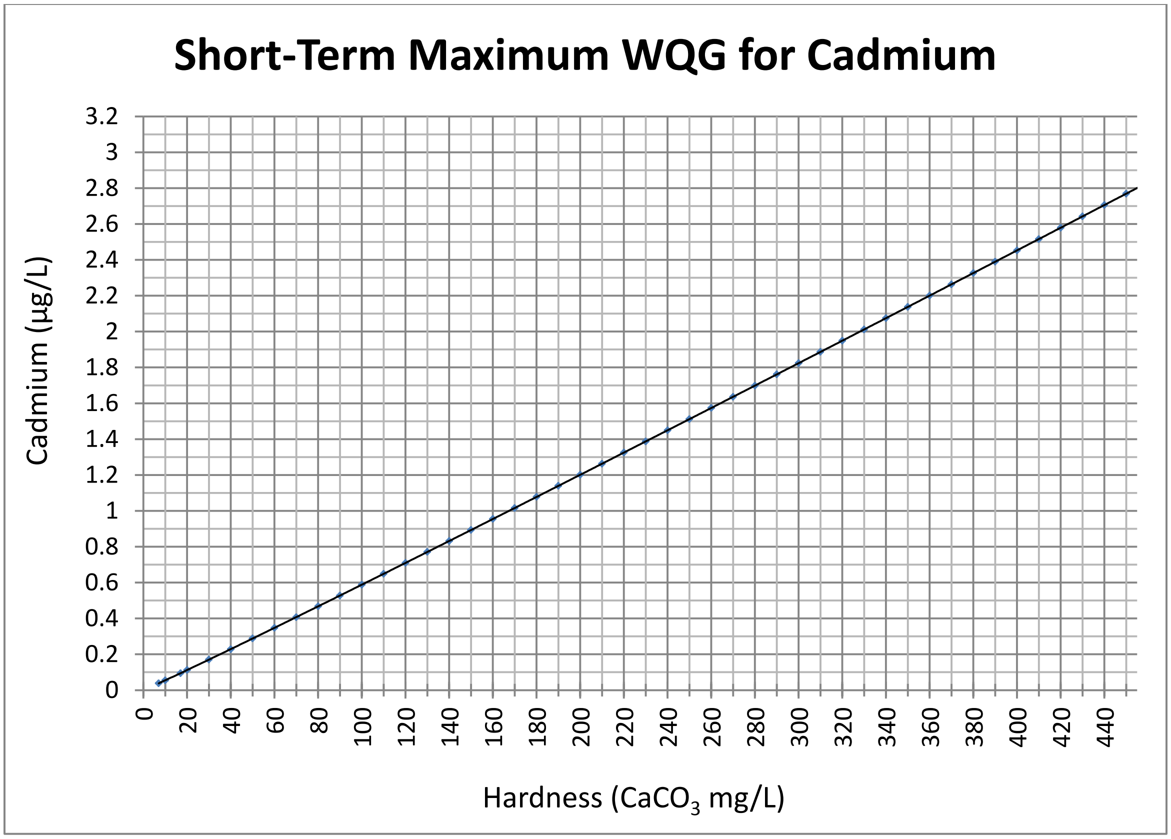

Figure 1: Graphic representation of the short-term maximum water quality guideline equation for dissolved cadmium.

The following equation is recommended to calculate long-term average water quality guidelines for water with different water hardness concentrations (MOE 2015, Table ES 2):

$$WQG_{\text{Long-term}} = e^{[0.736 * \ln(Hss) - 4.943]}$$

Where H_{SS} = site-specific water hardness (mg/L $CaCO_3$). This equation is valid for water hardness concentrations within the range of 3.4 to 285 mg/L $CaCO_3$. When water hardness is greater than the upper bound (i.e. highest water hardness tested), a site-specific assessment may be required.

At a water hardness of 50 mg/L $CaCO_3$, the recommended long-term (30-d) average water quality guideline for dissolved cadmium to protect aquatic life is 0.127 µg/L. Figure 2 can be used to estimate the long-term (30-d) average water quality guideline for other hardness values.

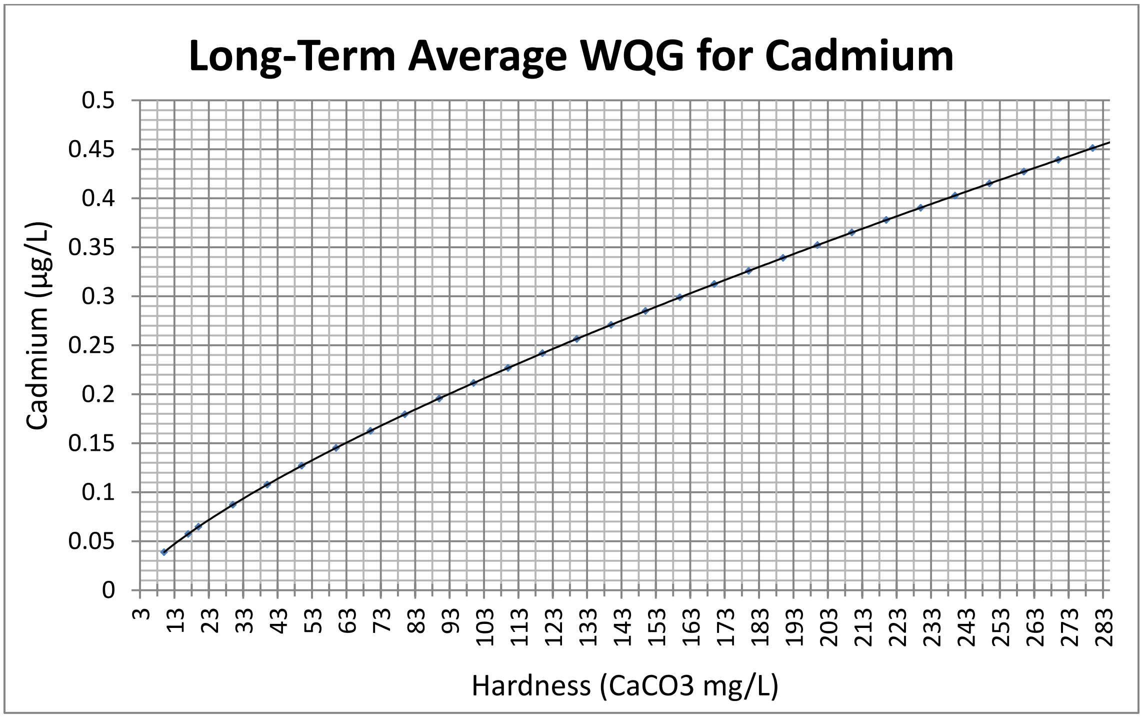

Figure 2: Graphic representation of the long-term average water quality guideline equation for dissolved cadmium.

Generally, the water quality guidelines for cadmium can be directly applied to water bodies in the province. However, the relationship between cadmium toxicity and water hardness assumes the natural correlation of hardness, alkalinity and pH that occurs in surface waters. Due care should be applied in systems in which water hardness is significantly altered by anthropogenic discharge and not primarily determined by natural geologic processes. In these systems, the recommended water quality guideline may not be protective of all freshwater aquatic species. Furthermore, the recommended water quality guidelines for cadmium may not be suitable in waters that exhibit elevated levels of dissolved organic matter, elevated levels of total dissolved solids (TDS), atypical pH, or saltwater intrusion. In these cases, further investigation to determine toxicity at the site may be required.

This guideline applies to the dissolved cadmium fraction only as this is the more bioavailable form however there is still the potential for toxicity due to particulate-associated cadmium.

The BC Working Guidelines for sediments provide a basis for evaluating the toxicity of particulate-associated metals (see Table 1; MOE 2006). The BC Working Guidelines for cadmium provides values for marine waters, sediment quality (both marine and freshwater), livestock watering, and irrigation.

Table 1. Summary of Working Water Quality Guidelines for Total Cadmium (MOE 2006).

Guideline Type	**Working WQG for Total Cadmium[1]**
Water (µg/L) - Marine	0.12
Sediment (µg/g) - Freshwater Interim Sediment Quality Guideline (ISQG) Probable Effect Level (PEL)	 0.6 3.5
Sediment (µg/g) Marine Interim Sediment Quality Guideline (ISQG) Probable Effect Level (PEL)	 0.7 4.2
Livestock watering (µg/L)	80
Irrigation (µg/L)	5.1

[1] A Compendium of Working WQGs for BC (MOE 2006).

References:

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