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Canadian Environmental Protection Act, 1999

Federal Environmental Quality Guidelines

Cobalt

Environment 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 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. A previous freshwater Federal Water Quality Guideline (FWQG) was published for cobalt (Environment Canada 2013) based on the assessment of four cobalt-containing substances (Canada 2011). This assessment concluded that the four substances assessed were not toxic and developed a predicted no effect concentration (PNEC) in water that was subsequently adopted as the freshwater FWQG for cobalt (i.e. 2.5 µg/L). Since that time, Canada (2017) published an assessment on cobalt and cobalt-containing substances. The assessment concludes that cobalt and soluble cobalt compounds meet the definition of “toxic to the environment” under CEPA. In addition to the change in toxic conclusion, new scientific information permitted the development of a PNEC in water that accounts for water hardness, thereby requiring revision to the FWQG for cobalt. This factsheet describes the revised FWQG for the protection of aquatic life for cobalt. No FEQGs have been developed for the soil, sediment or biological tissue compartments 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 cobalt.

| Aquatic Life | Guideline Value (µg/L)* |
|---|-------------------------|
| Freshwater | 1.0 |
| *FWQG is for waters that have hardness of 100 mg/L. For other hardness values between 52-396 mg/L, the FWQG can be calculated with the following equation: $\text{FWQG} = \exp\{(0.414[\ln(\text{hardness})] - 1.887)\}$ | |

Substance Identity

Cobalt is a naturally occurring element. Cobalt is an essential micronutrient required for the formation of vitamin B₁₂ and for its function in enzymatic processes (Gál et al. 2008). Anthropogenic sources to the environment include activities related to the production of cobalt (i.e., mining, smelting and refining); manufacture, import and use of cobalt-containing substances, products and manufactured items (e.g. use in metallurgical processes, alloys and carbides, batteries, catalysts, rubber, paints and coatings, plastic, automobile manufacturing, cosmetics, pigment and dyes, printing inks, pesticides, livestock feed, fertilizers); burning of fossil fuels and disposal and waste management of products and wastes containing cobalt (Hodge and Dominey 2001; IPCS 2006; Canada 2017). Canada completed a

screening assessment of cobalt and cobalt-containing substances (Canada 2017). The assessment included the four previously assessed cobalt compounds for which a FWQG was previously developed (Environment Canada 2013). A list of the cobalt-containing substances identified as priorities for action and included in the assessment is provided in the screening risk assessment report (Canada 2017). This factsheet was developed in consideration of the above assessment which was based on data and information identified up to September 2014. Some of the data on uses, fate, ambient concentrations, and toxicity presented below relate to that assessment and the various compounds evaluated in the assessment. The FWQG derived (see Figure 1) is for the cobalt ion and can be considered pertinent for cobalt ion from all sources or forms.

Uses

The elemental form of cobalt is used in pigment manufacturing, chemical production and alloy production (Environment Canada 2009; ATSDR 2004), as well as in the manufacture of rechargeable batteries (CDI 2006). Cobalt chloride is used as a catalyst and desiccant. Cobalt sulphate is commonly used as a nutritional supplement in cattle feed (Environment Canada 2009). Cobalt-containing substances are also used in non-ferrous metal smelting and refining, as intermediates in metallurgical processes and in the manufacture of paints and coatings, magnets, rubber, adhesives and sealants, automobiles, plastic and food packaging (Canada 2017).

Fate, behaviour and partitioning in the environment

Cobalt can be found in various forms in ambient air, surface water, sediments, soils and groundwater. Cobalt is non-volatile, exerting zero partial pressure in air (Diamond et al. 1992). As such, it is emitted to air principally in the form of fine particulate matter. When released anthropogenically with fossil fuel and waste combustion, cobalt is mainly in the form of oxides. During ore extraction and refining, arsenide and sulphide forms are also released (IPCS 2006).

The water solubility of cobalt and cobalt-containing substances varies widely, from sparingly soluble to greater than 10^6 mg/L. Thus, if released to water bodies, some substances will release more cobalt ions than others upon dissolution or dissociation (Canada 2017). Elemental cobalt powders may also release cobalt ions if discharged to surface waters. Some undissolved elemental cobalt may be found in sediments and moist soils in cases where elemental cobalt has been directly released. For cobalt ions, the oxidation state (II) is more stable than the oxidation (III) state (Cotton and Wilkinson 1988), favouring chemical complexes with the divalent cobalt cation in aqueous solutions.

For cobalt, soil-water partitioning is highly variable, depending on soil properties (Canada 2011). Cobalt binds strongly with sediments and suspended particulate matter; high sediment-water partition coefficients suggest that cobalt will remain for the most part in bottom sediments after entering this compartment.

For aquatic organisms, bioaccumulation factors for cobalt range from 7.4 to 3110 L/kg, whereas values range from 0.091 to 0.645 for biota-sediment (Canada 2017). Field and laboratory investigations indicated a lack of biomagnification of cobalt in food webs. It is concluded that the bioaccumulation potential of cobalt in natural ecosystems is not high and therefore, despite meeting the criteria for persistence, elemental cobalt and cobalt-containing compounds do not meet the criteria for bioaccumulation as set out in the *Persistence and Bioaccumulation Regulations* of CEPA (Government of Canada (GC) 2000).

Based on the information presented in the Screening Assessment Report (SAR), the Government of Canada (Canada 2017) concluded, at this time, that cobalt and soluble cobalt compounds meet the criteria under paragraph 64(a) of CEPA, that is, they are entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity and are considered to be toxic under CEPA such that risk management action may be required.

Measured concentrations

Worldwide, cobalt concentrations in relatively pristine areas vary with bedrock-type and surface geological conditions and typically are: 20-25 mg/kg in soil, less than 1 µg/L in surface freshwater, 0.3-1.7 µg/L in rainwater and ~1 ng/m³ in the atmosphere in remote areas (IPCS 2006). Surface water measurements taken from three of the most highly contaminated sites in Canada ranged from 0.025 to 2028 µg/L (Percival et al. 1996; NRCan 2001; City of Greater Sudbury 2001, 2004). Recent Canada-wide water quality monitoring revealed that dissolved and total cobalt concentrations range from 0.002 to 64 µg/L and 0.002 to 3.9 µg/L, respectively, in Canadian water bodies (Canada 2017). While natural inputs likely exceed anthropogenic emissions of cobalt to the environment (Smith and Carson 1981), small-scale anthropogenic contamination may still be important and cause environmental harm, especially where industrial activity has resulted in elevated ambient concentrations.

Mode of action

As mentioned above, cobalt is an essential micronutrient. Nevertheless, the toxic mode of action of cobalt is not entirely understood. It is known to inhibit various enzymes, causing a reduction in tissue respiration and metabolism (Smith and Carson 1981). For example, cobalt impedes the citric acid cycle and can also inhibit or stimulate different enzymes in the liver, including drug-metabolizing enzymes. In its 2+ state, the cobalt ion can substitute for other divalent cations, reacting with the thiol group of amino acids, proteins, and other coenzymes and cofactors, resulting in altered enzyme activity (Smith and Carson 1981).

Aquatic toxicity

Cobalt toxicity has been demonstrated in aquatic organisms, sometimes occurring at concentrations observed in contaminated environments. Many empirical data are available in the literature for the short- and long-term aquatic toxicity of cobalt chloride, cobalt sulphate and other soluble cobalt compounds, which after entering water transform to a greater or lesser extent into bioavailable dissolved cobalt species, in particular, the free ion, Co²⁺. Because the toxicity of metals is often influenced by hardness, pH, ionic strength and dissolved organic carbon (CDI 2009; Canada 2017), toxicity data are standardized for the effects of these factors where possible depending on the assessment needs. In Canada (2017), hardness was identified as the key toxicity modifying factor for cobalt among the various water quality parameters that can influence metal uptake and toxicity. Within the acceptable dataset, one study (Parametrix 2010) evaluated the influence of water hardness on cobalt toxicity to *Ceriodaphnia dubia* and fathead minnow. From this study, an equation relating cobalt toxicity to water hardness (ranging from 52 to 396 mg/L) was developed. All acceptable cobalt toxicity data were subsequently corrected to a hardness value of 100 mg/L using this equation as part of the FWQG development process.

Of the studies considered in the SAR, seven studies provided acceptable long-term toxicity data for 13 different species, with hardness-corrected values ranging from 2.2 to 2055 µg/L for various endpoints (Table 1). Invertebrates are more sensitive to cobalt than fish, however, the sensitivities do overlap across taxa. *Hyalella azteca* was the most sensitive species, while rainbow trout (*Oncorhynchus mykiss*) was the least sensitive. The most sensitive fish and plant species were zebrafish (*Brachydanio=Danio rerio*) and duckweed (*Lemna minor*), respectively. The least sensitive invertebrate and plant species were the oligochaete *Aeolosoma* and green algae (*Chlamydomonas reinhardtii*), respectively.

Federal Water Quality Guideline Derivation

The Federal Water Quality Guideline (FWQG) developed here identifies hardness-dependent benchmarks for aquatic ecosystems that are intended to protect all forms of aquatic life for indefinite exposure periods. A species sensitivity distribution (SSD) curve was developed using the long-term toxicity data (normalized to a hardness of 100 mg/L) (Table 2), for a total of thirteen species: three fish, six invertebrates and four plant/algae species (Figure 1). Each species for which appropriate toxicity data were available was ranked according to sensitivity, and its position on the SSD was determined. Concentrations are expressed in micrograms of cobalt per litre ($\mu\text{g Co/L}$). Therefore, the FWQG derived from these data applies to total cobalt rather than the compounds tested (e.g., CoCl_2).

Table 2. Long-term toxicity data (normalized to a hardness of 100 mg/L) used for developing the Federal Water Quality Guideline for cobalt.

| Species | Group | Endpoint | Concentration ($\mu\text{g/L}$) | Reference |
|---|-------|---|-----------------------------------|---|
| Amphipod (<i>Hyalella azteca</i>) | ● | 28-d IC_{10} (growth) | 2.2* | Norwood et al. (2007); Heijerick et al. (2007) |
| Water flea (<i>Daphnia magna</i>) | ● | 21-d EC_{10} (reproduction) | 22.6 | Heijerick et al. (2007) |
| Duckweed (<i>Lemna minor</i>) | ▲ | 7-d EC_{10} (growth) | 6.3 | Heijerick et al. (2007) |
| Water flea (<i>Ceriodaphnia dubia</i>) | ● | 21d EC_{10} (reproduction) | 7.7 | Parametrix 2010 |
| Snail (<i>Lymnea stagnalis</i>) | ● | 28-d EC_{10} (growth) | 8.36 | Heijerick et al. (2007) |
| Green algae (<i>Pseudokirchneriella subcapitata</i>) | ▲ | 4-d EC_{10} (growth) | 31 | Heijerick et al. (2007) |
| Midge (<i>Chironomus tentans</i>) | ● | 20-d EC_{10} (survival) | 202 | Pacific Ecorisk (2005) |
| Giant duckweed (<i>Spirodela polyrhiza</i>) | ▲ | 4-d EC_{50} (growth) | 257 | Gaur et al. (1994) |
| Oligochaete (<i>Aeolosoma</i>) | ● | 14-d EC_{10} (growth) | 200 | Parametrix 2010 |
| Zebrafish (<i>Brachydanio rerio</i>) | ■ | 16-d EC_{10} (survival) | 348 | Dave and Xiu (1991) |
| Fathead minnow (<i>Pimephales promelas</i>) | ■ | 35-d EC_{10} (survival) | 339 | Parametrix 2010 |
| Green algae (<i>Chlamydomonas reinhardtii</i>) | ▲ | 5-d EC_{30} (growth) | 2055 | Macfie et al. (1994) |
| Rainbow trout (<i>Oncorhynchus mykiss</i>) | ■ | 81-d EC_{10} (biomass) | 2049 | Parametrix 2010 |

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

*Geomean

Notes: IC_x/EC_x = Concentration at which there is inhibition/ effect on X percent of the population;

Following the CCME protocol (CCME 2007), 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. The Normal model provided the best fit of the models tested upon visual inspection, lowest levels of statistical variability (residuals), even distribution of the residuals, lowest normalized confidence interval spread and best significance of the Anderson-Darling Statistic test ($A^2 = 0.384$ ($p < 0.05$)). The 5th percentile (HC_5), i.e., hazardous concentration to 5% of species, of the SSD plot is 1.0 $\mu\text{g/L}$ with lower and upper confidence limits of 0.5 and 2.0 $\mu\text{g/L}$, respectively.

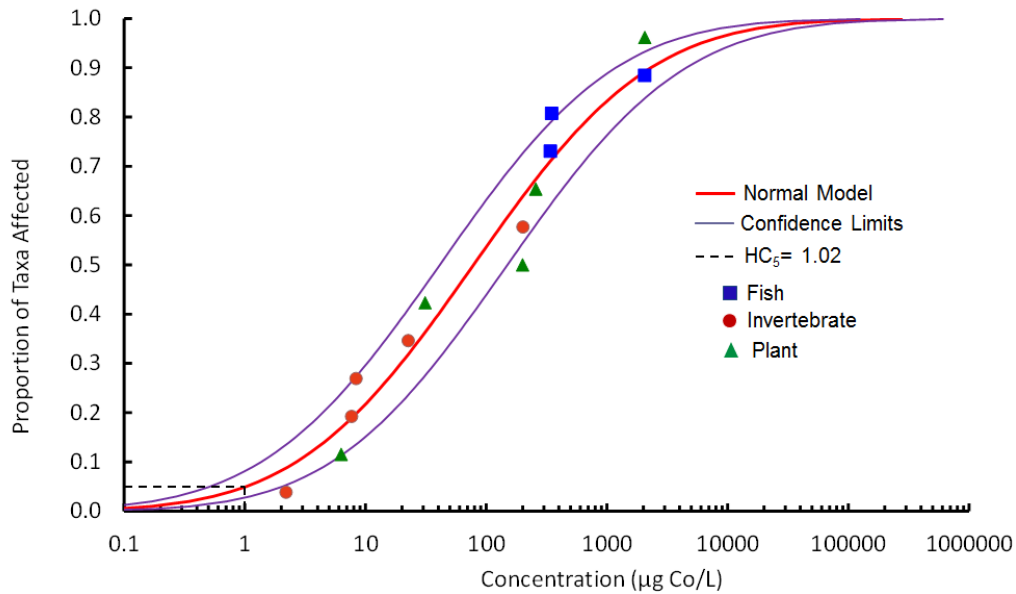


Figure 1. Species sensitivity distribution (SSD) for chronic toxicity of cobalt.

Because hardness was a significant toxicity modifying factor, the FWQG is expressed as an equation where the site-specific hardness must be entered in order to calculate a site-specific FWQG. The equation is based on the toxicity-hardness slope value of 0.414 and the 5th percentile value of 1.0 µg/L is derived from the SSD when hardness is 100 mg/L.

Based on the toxicity-hardness slope value and the SSD, the equation to derive FWQG for Co is:

$$\begin{aligned}
 \text{y-intercept} &= \ln(5^{\text{th}} \text{ percentile}) - [\text{hardness slope} \times \ln(\text{hardness})] \\
 &= \ln(1.02) - [0.414 \times \ln(100)] \\
 &= -1.887
 \end{aligned}$$

$$\text{FWQG } (\mu\text{g/L}) = e^{\{(0.414[\ln(\text{hardness})] - 1.887)\}}$$

Site-specific FWQGs for cobalt at discrete water hardness concentrations are provided in Table 3. Since the slope relating hardness to toxicity was based on a study conducted over hardness levels from 52-396 mg/L, the FWQG should not be extrapolated beyond this hardness range. Accordingly, the minimum and maximum FWQG for cobalt at water hardness levels of 52 and 396 mg/L are 0.78 and 1.80 µg/L, respectively.

Table 3. FWQGs ($\mu\text{g/L}$) for the protection of aquatic life for selected water hardness values.

| hardness (mg/L) | FWQG ($\mu\text{g/L}$) |
|-----------------|--------------------------|
| 52 | 0.78 |
| 100 | 1.0 |
| 150 | 1.2 |
| 200 | 1.4 |
| 250 | 1.5 |
| 300 | 1.6 |
| 350 | 1.7 |
| 396 | 1.8 |

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List of Acronyms and Abbreviations

ATSDR – Agency for Toxic Substances and Disease Registry

CCME – Canadian Council of Ministers of Environment
CDI – Cobalt Development Institute
CEPA – Canadian Environmental Protection Act
CMP – Chemical Management Plan
EC – Effect Concentration
FEQG – Federal Environmental Quality Guideline
FWQG – Federal Water Quality Guidelines
IC – Inhibition concentration
IPCS – International Programme on Chemical Safety
NRCan – Natural Resources Canada
PNEC – Predicted No-effect Concentration
SAR – Screening Assessment Report
SSD – Species Sensitivity Distribution