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. Where the FEQG is met there is low likelihood of adverse effects on the protected use (e.g., aquatic life or the wildlife that may consume them). They are based on the toxicological effects or hazards of specific substances or groups of substances and do not take into account analytical capability or socio-economic factors. 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 FEOGs 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 The development of FEQGs is the responsibility of the Federal Minister of Environment under the Canadian Environmental Protection Act, 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. This factsheet describes the Federal Water Quality Guideline (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.

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 burning of fossil fuels. sewage sludge, phosphate fertilizers, mining and smelting of cobalt-containing ores and industrial processes that use cobalt compounds (Hodge and Dominey 2001; IPCS 2006). Canada (2011a) focused its assessment of cobalt-containing substances on four specific compounds: elemental cobalt (Co, CAS Registry Number 7440-48-4), cobalt chloride (CoCl₂, CAS Registry Number 7646-79-9), cobalt II sulphate with a 1:1 cobalt-to-sulphate ratio (Co.H₂O₄S, CAS Registry Number 10124-43-3), and sulphuric acid-cobalt salt in which no specific cobalt ion is identified or the ratio between the acid and cobalt is unknown (Co., H₂O₄S, CAS Registry Number 10393-49-4). This factsheet was developed in consideration of the above assessment which was based on data and information identified up to February 2010. Some of the data on uses, fate, ambient concentrations, and toxicity presented below relate to that assessment and those compounds. However, the FWQG derived here (see Figure 1) is for the cobalt ion/moiety and can be considered pertinent for cobalt from all sources A more wide-ranging regulatory assessment of all cobalt-containing substances is currently under way (Canada 2011b).

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). The vast majority (99%) of the manufactured cobalt in Canada is exported and upwards of 22 million kilograms of cobalt were imported into Canada in 2006 in the form of products containing cobalt, cobalt chloride, cobalt sulphate, and sulphuric acid cobalt salts (Environment Canada 2009).

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).

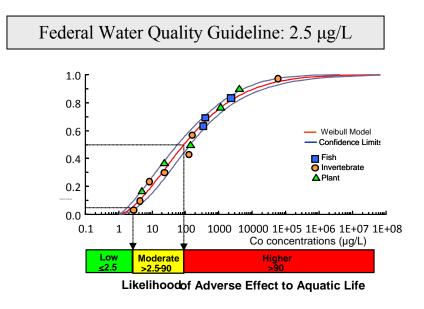


Figure 1. Species sensitivity distribution (SSD) for aquatic cobalt toxicity data and associated effect levels for aquatic life.

Cobalt chloride and cobalt sulphate are highly soluble, and are almost always in the dissolved form in the environment. Elemental cobalt powders may also release cobalt ions in solution 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 2011a). 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 2011a). 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, cobalt sulphate and cobalt chloride do not meet the criteria for bioaccumulation as set out in the *Persistence and Bioaccumulation Regulations* (Canada 2000).

Based on the information presented in the Screening Assessment Report (SAR), the Government of Canada (Canada 2011a) concluded, at this time, that elemental cobalt, cobalt sulphate and cobalt chloride are not 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 or that constitute or may constitute a danger to the environment on which life depends. It is therefore concluded that they do not individually meet any of the criteria set out in section 64 of *CEPA 1999*. Further assessment of the cobalt-moiety is currently under way as part of a more wide-ranging assessment of cobalt-containing substances.

Ambient 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). Levels measured in waters from selected regions of Canada where some of the industries that manufacture or use the cobalt compounds ranged from below the detection limit to 6.9 μg/L (Canada 2011a), whereas the 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). 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

While 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 cobalt compounds, which after entering water all 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 2011a), toxicity data are standardized for the effects of these factors where possible depending on the assessment needs. However, this could not be not done for cobalt because the required data are not available to apply appropriate standardizing equations.

Of the studies considered in the SAR, nine studies provided acceptable long-term toxicity data for 15 different species, with values ranging from 2.9 to 59 000 µg/L for various endpoints (Table 1). Invertebrates are more sensitive to cobalt than fish, however, the sensitivities do overlap among taxa. Among invertebrates, *Hyalella azteca* was the most sensitive species, while the rotifer *Philodina acuticornis* was the least sensitive. The most sensitive fish and plant species were zebrafish (*Brachydanio rerio*) and duckweed (*Lemna minor*), respectively. The least sensitive fish and plant

species were the rainbow trout (*Oncorhynchus mykiss*) and green algae (*Chlamydomonas acidophila*), respectively.

Federal Water Quality Guideline Derivation

The Federal Water Quality Guideline (FWQG) developed here identifies 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 shown in Table 1, for a total of fifteen species: three fish, seven invertebrates and five 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 (µg Co/L). Therefore, the FWQG derived from these data applies to total cobalt rather than the compounds tested (e.g., CoCl₂).

Table 1. Long-term toxicity data used for developing the Federal Water Quality Guideline for cobalt.

Species	Group	Endpoint	Concentration (μg/L)	Reference
Amphipod	•	28d IC ₂₅	2.9	Norwood et al. (2007)
(Hyalella azteca) Water flea (Daphnia magna)	•	(growth) 28d LOEC (reproduction)	4.4	Kimball (unpublished)
Duckweed (Lemna minor)	Δ	7d EC ₁₀ (growth)	4.9	CDI (2009)
Water flea (Ceriodaphnia dubia)	•	21d EC ₁₀ (reproduction)	7.9	CDI (2009)
Snail (Lymnea stagnalis)	•	28d EC ₁₀ (growth)	22	De Schamphelaere et al. (2008)
Green algae (Pseudokirchneriella subcapitata)		4d EC ₁₀ (growth)	23	CDI (2009)
Midge (Chironomus tentans)	•	20d EC ₁₀ (growth)	123	CDI (2009)
Giant duckweed (Spirodela polyrhiza)	Δ	4d EC ₅₀ (growth)	140	Gaur et al. (1994)
Oligochaete (Aeolosoma)	•	14d EC ₁₀ (reproduction)	155	CDI (2009)
Zebrafish (Brachydanio rerio)		16d MATC (survival)	340	Dave and Xiu (1991)
Fathead minnow (Pimephales promelas)		35d EC ₁₀ (survival)	351	CDI (2009)
Green algae (Chlamydomonas reinhardtii)	Δ	5d EC ₃₀ (growth)	1120	Macfie et al. (1994)
Rainbow trout (Oncorhynchus mykiss)		81d EC ₁₀ (biomass)	2171	CDI (2009)
Green algae (Chlamydomonas acidophila)	Δ	4d EC ₅₀ (growth)	4100	Nishikawa and Tominaga (2001)
Rotifer (Philodina acuticornis)	•	4d EC ₅₀ (reproduction)	59000	Buikema et al. (1974)

Legend: \square = Fish; \bigcirc = Invertebrate; \triangle = Plant

Notes: ICx/ ECx = Concentration at which there is inhibition/ effect on X percent of the population; LOEC = Lowest observable effect concentration; MATC = maximum acceptable toxicant concentration.

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 Weibull model provided the best fit for these data and the 5^{th} percentile of the SSD plot is 2.5 μ g/L, with lower and upper confidence limits of 1.9 and 3.4 μ g/L, respectively (Figure 1).

The 5th percentile of 2.5 μg/L calculated from the SSD is selected as the predicted noeffect concentration (PNEC) and the Federal Water Quality Guideline for toxicity to freshwater organisms. 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 additional concentration ranges are provided for use in risk management. At concentrations between the 5th and 50th percentile of the SSD (2.5-90 μg/L) there is a moderate likelihood of adverse effects to aquatic life. Concentrations greater than the 50th percentile (>90 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 objectives for a phased risk management plan. The moderate to higher concentration range 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 federal water quality guideline (i.e., the 5th percentile).

As it was decided to focus on the potential for harm to aquatic organisms in the SAR (Canada 2011a), the presence and effects of cobalt in air, soil and sediment have not been assessed at this time. Furthermore, the release of cobalt to the atmosphere and subsequent deposition to soils occurs mainly in the form of oxides; this form of the metal was not considered in the assessment (Canada, 2011).

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List of Acronyms

CCME - Canadian Council of Ministers of Environment

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

LC₅₀ - Median Lethal Concentration

LOEC - Lowest-Observed-Effect Concentration

MATC - Maximum Acceptable Toxicant Concentration

SAR - Screening Assessment Report

SSD - Species Sensitivity Distribution