TECHNICAL REPORT - WATER QUALITY GUIDELINES FOR COBALT

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1.0 SUMMARY

This document is one in a series that establishes water quality guidelines, formerly known as criteria, for British Columbia.

Cobalt is an essential element for the growth of many marine algal species, including diatoms, chrysophytes, and dinoflagellates (Bruland *et al.*, 1991). Cobalt has also been shown to enhance growth of some plants at low concentrations. In higher concentrations, cobalt is toxic to humans and to terrestrial and aquatic animals and plants.

At the time of issuing the report, British Columbia Ministry of Water, Land and Air Protection (BC MWLAP) uses the Ontario guideline for the protection of freshwater aquatic life (0.9 μg/L) as a working water quality guideline. There are currently no national Canadian water quality guidelines for the protection of freshwater or marine aquatic life from adverse effects of cobalt. The Canadian Water Quality Guidelines (CCREM, 1987) for irrigation (50 μg cobalt /L for continuous use on all soils and 5,000 μg cobalt/L for a 20-year period on neutral and alkaline fine textured soils) and livestock watering (1,000 μg cobalt/L) have been adopted as working water quality guidelines by BC MWLAP. The CCREM guidelines were taken from the 1972 U.S. EPA publication (NAS/NAE, 1972) and were based on very old studies (1953 study in the case of irrigation water and 1971 study for livestock). However, according to the recent protocols for the derivation of water quality guideline for agricultural water uses (CCME, 1993), there are insufficient data to develop water quality guidelines for cobalt in irrigation and livestock water uses. Hence, water quality guidelines to protect agricultural water uses from cobalt were not developed in this document. There are also insufficient data to develop a water quality guideline to protect wildlife from adverse effects of cobalt.

A review of the literature suggested that although acute toxicity of cobalt to freshwater aquatic life is dependent on water hardness in the range of 50 to 200 mg/L as $CaCO_3$, chronic toxicity is not (Diamond *et al*., 1992). This trend was not all apparent in the Golder/EVS study with the Ceriodaphnia dubia, the most sensitive species to cobalt effects, in British Columbia. Hence, the recommended cobalt water quality guidelines are not expressed in terms water hardness.

To protect aquatic life in freshwater environments, an interim acute (maximum) guideline of 110 μg cobalt/L and an interim chronic (30-day average) guideline of 4 μg cobalt/L are recommended cobalt based on a literature review and toxicity testing. There was insufficient data to develop a water quality guideline for cobalt to protect marine life.

2.0 INTRODUCTION

Cobalt is a hard silver-grey metal of the first transition series of Group 9 of the periodic table. It is a relatively rare element of the earth's crust with concentration approximately 25 µg/g (Hamilton, 1994). Cobalt is essential in trace amounts for humans and other mammals as it is an integral component of the vitamin B12 complex. Cobalt is reportedly an essential element for the growth of many marine algal species, including diatoms, chrysophytes, and dinoflagellates (Bruland *et al.*, 1991). It is also a micronutrient essential for some blue-green algae (Holm-Hansen *et al.*, 1954) and is required by microorganisms for nitrogen fixation in legumes. Although its essentiality in higher, non-leguminous plants is not clearly proven, there is some evidence of favourable effect of cobalt on plant growth (Kabata-Pendias and Pendias, 1984). In higher concentrations, cobalt is toxic to humans and to terrestrial and aquatic animals and plants.

At the time of issuing the report, BC MWLAP uses the Ontario guideline for the protection of freshwater aquatic life (0.9 µg cobalt/L) as a working water quality guideline. There is currently no national Canadian cobalt guideline for the protection of freshwater aquatic life. The Canadian Water Quality Guidelines (CCREM, 1987) for irrigation (50 µg cobalt/L for long term use and 5,000 µg cobalt/L for short term use) and livestock watering (1,000 µg cobalt/L) have been adopted as working water quality guidelines by BC MWLAP.

The purpose of this document is to establish concentrations of cobalt in surface water that are safe for a number of water uses:

i. Freshwater aquatic life
ii. Marine aquatic life
iii. Wildlife
iv. Irrigation
v. Livestock watering

3.0 PARAMETER SPECIFIC INFORMATION

3.1 Physical and Chemical Properties

Cobalt is a silver-grey, hard metal. It can exist in six oxidation states, but in aquatic environment the +2 and +3 valence states predominate and form organic and inorganic salts. It is an element of the first transition series of Group 9 of the periodic table with properties similar to those of its neighboring Group 9 elements, iron and nickel. Cobalt has a melting point of 1,495 ^{o}C and a boiling point of 2,870 ^{o}C and only one stable isotope, which has an atomic weight of 59. Although, metallic cobalt is insoluble in water, the solubility of cobalt salts is highly variable and depends on its form. For instance, whereas the basic cobaltous carbonate ($2CaCo_3.Co(OH)_2.H_2O$) is insoluble in water, the water solubility of cobalt

salts such as $CoCl_2$, $CoSO_4$, and CoS are given to be 450 000 mg/L, 362 000 mg/L, and 3.8 mg/L, respectively (Handbook of Chemistry and Physics, 1968). In freshwater systems, the dominant species are Co^{+2}, $CoCO_3$, $Co(OH)_3$, and CoS whereas chloride complexes of cobalt dominate in seawater (Moore, 1991).

Cyanocobalamin, or vitamin B_{12}, is organic cobalt complex found in surface water, sediments, and sewage sludge. Numerous plants and microorganisms use vitamin B_{12} as their primary source of cobalt. The concentration of cobalt in aquatic environments has been shown to correlate significantly with pH (inverse correlation) and suspended solids (positive correlation) in water (Moore, 1991).

3.2 Production and Uses

Most cobalt resources are present in nickel-bearing laterite deposits, with the remainder occurring primarily in nickel-copper sulfide deposits present in mafic and ultramafic rocks and in sedimentary copper deposits. The largest cobalt deposits are found in Australia, Canada, Russia, Congo and Zambia. Canada began commercially producing cobalt in 1905 and according to recent figures from the U.S. Geological Survey (USGS, 1998), Canada contributes approximately 20% of the total world production of cobalt.

Currently, the major use for cobalt is in some types of steel, and in several types of alloys, including high-temperature steel alloys, magnetic alloys and abrasion-resistant hard-facing alloys (Hamilton, 1994). Cobalt is used in magnets to increase the saturation of magnetization of iron. It is also used as a pigment in glass, ceramics, and paints, as paint drier, as a catalyst for the petroleum industry, and in batteries. Many fertilizers are enriched with cobalt, generally in the range of 1 mg/kg to 12 mg/kg in order to amend agricultural soils that are cobalt-deficient.

3.3 Sources and Pathways in the Environment

Small amounts of cobalt are present naturally in rock, soil, water, plants, animals and air. Approximately 0.0025% of the earth's crust is comprised of cobalt, which is often present in association with nickel, silver, lead, copper and iron ores. Cobalt occurs in mineral form as arsenides, sulfides and oxides, such as linnaeite (Co_3S_4), carrolite ($CuCo_2S_4$), safflorite ($CoAs_2$), skutterudite ($CoAs_3$), erythrite ($Co_3(AsO_4)_2*8H_2O$), and glaucodot (CoAsS) (Smith and Carson, 1981).

Natural sources of cobalt to the environment include volcanic eruptions, seawater spray and forest fires. Anthropogenic sources of cobalt to the atmosphere include coal-fired power plants and incinerators, and exhaust from vehicles. Cobalt mining and processing activities, the production of alloys and chemicals

containing cobalt, sewage effluents, urban run-off, and agricultural run-off are major anthropogenic contributors of cobalt to the aquatic environment.

3.4 Environmental Concentrations

3.4.1 Surface Water - Fresh

Concentrations of cobalt measured in fresh surface water in the province of British Columbia range from non-detectable (detection limit 0.1 μg/L) to 27,000 μg/L (BCMWLAP). The total and dissolved cobalt concentrations in ambient, uncontaminated environments are generally low (<5 μg/L); however, aquatic environment contaminated with effluents, originating from mine site or mineral rich areas, often record much higher levels. Durum (1960) reported cobalt concentrations ranging from less than the detection limit to 1.9 μg/L in the Fraser River at Mission City in British Columbia.

Maximum cobalt concentrations reported by Durum (1960) for Canadian freshwater were 4.0 μg/L in the St. Lawrence River, Quebec, 5.0 μg/L in the Mackenzie River, Northwest Territory, and 5.1 μg/L in the Nelson River, Manitoba.

Durum *et al*. (1971) reported the results of a sampling program for minor elements, including cobalt, in surface water in the United States and Puerto Rico. Greater than 720 samples were collected from rivers and lakes and analysed for dissolved cobalt during October and November 1970. Cobalt concentrations exceeded the detection limit of 1 μg/L in only 37 % of samples. The majority of detected concentrations were less than 5 μg/L, which the authors reported to be approximately the upper limit of solubility of cobalt in natural river water. (This observation is not consistent with the solubility of cobalt complexes indicated in Section 3.1). This is probably due to the fact that most Co in the aquatic environment is adsorbed or associated with suspended solids or sediments. Also, uptake of cobalt by plants appears to be extremely rapid (Moore, 1991).

Smith and Carson (1981) have compiled literature values for cobalt in selected surface water in the United States. They report that cobalt concentrations are below the detection limit of 1 μg/L in the majority of natural freshwaters in the United States. Concentrations of cobalt in the range of 1 μg/L to 10 μg/L were detected in streams close to populated areas, while concentrations in the range of 11 μg/L to 50 μg/L were detected primarily in streams passing through mining districts and regions with heavy agricultural land use. Cobalt concentrations in the range of 11 μg/L to 50 μg/L were occasionally observed in urban areas.

3.4.2 Surface Water - Marine

Smith and Carson (1981) have also reviewed the literature with respect to cobalt concentrations found in seawater. They report cobalt concentrations ranging from 0.002 µg/L to 0.045 µg/L in the north central Pacific Ocean. Hamilton (1994) reported that the average concentration of cobalt in oceans is 0.3 µg/L, with concentrations approximately 0.078 µg/L in the Caribbean, 0.1 µg/L to 0.15 µg/L in the West Atlantic Ocean, and 0.17 µg/L to 0.39 µg/L in the Indian Ocean.

3.4.3 Groundwater

BC MWLAP reports that the mean ambient cobalt concentration in groundwater in BC is 21.1 µg/L with lower and upper 95 % confidence limits of 14.7 µg/L and 27.6 µg/L, respectively.

3.4.4 Soil

All of the following soil concentrations are expressed in a dry-weight basis unless otherwise stated. Smith and Carson (1981) reported that, in general, the cobalt concentration in soils falls in the range of 1 mg/kg to 40 mg/kg. Total cobalt in soils was reported by Hamilton (1994) to generally fall within the range of 0.1 mg/kg to 50 mg/kg. Cobalt concentrations exceeding the high end of the ranges reported by Smith and Carson (1981) and Hamilton (1994) have been reported in areas near ore deposits and occasionally in areas impacted by local industry. Soil samples collected from near the Blackbird mine in Idaho, USA were found to have elevated concentrations of cobalt. Average concentrations of cobalt in soils near the Blackbird mine varied from 13.13 mg/kg to 84.85 mg/kg according to rock types, with a small fraction of soil samples having cobalt concentrations exceeding 100 mg/kg.

3.4.5 Sediments

All of the following sediment concentrations are expressed on a dry-weight basis unless otherwise stated. Cobalt concentrations in most freshwater sediments are less than 20 mg/kg (Smith and Carson, 1981). Manganese nodules containing elevated cobalt concentrations have been reported in freshwater sediments. Smith and Carson (1981) reported the following cobalt concentrations in manganese nodules: 160 mg/kg in Green Bay, 234 mg/kg in northern Lake Michigan, 650 mg/kg in Lake Ontario, and 70 mg/kg in Lake Oneida. Elevated cobalt concentrations in sediment have also been reported near ore deposits and in areas of industrial pollution. Cobalt concentrations as high as 150 mg/kg were detected in stream sediments near the Blackbird mine in Idaho, USA.

Duursma (1973) analysed cobalt concentrations in marine sediments from 60 locations world-wide and reported a mean value of 24.5 mg/kg. The highest cobalt concentrations measured in marine sediments were in the Pacific Ocean, where a range of 38 mg/kg to 195 mg/kg was detected (Duursma,1973).

Cobalt concentrations reported in estuarine sediments in Solway Estuary, United Kingdom were in the range of 3.8 to 7.5 mg/kg. The concentrations reportedly varied from 0.6 mg/kg to 8.9 mg/kg in San Francisco Bay, California and a value of 13 mg/kg was reported for Upper Newport Bay, California (Duursma, 1973). As in freshwater sediment, cobalt is enriched in manganese nodules and other iron-rich sediment in the marine environment (Smith and Carson, 1981).

3.4.6 Biota

All concentrations reported in this section are on dry-weight basis unless otherwise reported. Total cobalt in freshwater plants is generally low and varies from less than 2 mg/kg to 2.6 mg/kg; however, much higher levels have been reported in the literature, probably from contaminated or cobalt-enriched areas (Moore, 1991; Kabata-Pendias and Pendias, 1984).

Cobalt concentration factors (i.e., the ratio of the concentration of cobalt in an organism to the concentration in the surrounding water) were reported by Smith and Carson (1981) for a variety of aquatic plants, invertebrates and fish. They reported concentration factors ranging from 1,000 to 10,000 for zooplankton whole animals and concentration factors on the order of 100 for the soft parts of zooplankton. Marine shellfish were found to have concentration factors in the thousands to tens of thousands, while other marine benthic invertebrates had concentration factors ranging from 100 to 40,000. Concentration factors for marine fish were generally in the range of 100 to 4,000. For marine plants, concentration factors were in the thousands to tens of thousands.

Smith and Carson (1981) report cobalt concentration factors for a wide variety of freshwater organisms. Freshwater fish generally had concentration factors of 10 to 1,000, while the range for invertebrates was 1 to 100,000. Freshwater algae had the highest concentration factors, with a range of 400 to approximately 2 million.

Hamilton (1994) reviewed the literature for cobalt content in marine biota and reported an average value of approximately 1 mg/kg. Cobalt concentrations reported in seaweeds in Japan, Atlantic Canada and the Irish Sea varied from 0.09 mg/kg to 6.25 mg/kg (Hamilton, 1994). Cobalt concentrations in marine plankton have been detected in the range of 3 mg/kg to 7 mg/kg, while marine mollusks contained approximately 4 mg/kg of cobalt. Based on a review of literature on the effects of pollution on saltwater organisms, Reish *et al*. (1997) reported cobalt concentrations in the ranges of 0.4 µg/g to 23 µg/g for algae, 3 µg/g to 18 µg/g for spermatophyte, 0.9 µg/g to 62 µg/g for polychaete and 0.7 µg/g to 24 µg/g for pelecypod.

Smith and Carson (1981) also reviewed literature concerning cobalt content in marine organisms. They reported concentrations in marine seaweeds generally below 1 mg/kg and in algae varying from 0.1 mg/kg to 100 mg/kg. Data compiled by Smith and Carson (1981) indicated that cobalt concentrations in marine invertebrate soft tissues generally varied from 0.05 mg/kg to 8.5 mg/kg while cobalt concentrations in the shells generally ranged from 0.15 mg/kg to 1.2 mg/kg. Mean cobalt concentrations in fish generally fell within the range of 0.002 mg/kg wet-weight to 0.05 mg/kg wet-weight.

3.5 Forms, Fate and Essentiality in the Environment

Cobalt occurs in two oxidation states (Co^{2+} and Co^{3+}). However, with the exception of certain complexes, Co^{3+} is thermodynamically unstable under the redox and pH conditions that commonly occur in natural waters.

Mineral precipitation and adsorption are two processes that may limit metal concentrations in waters. Typically, metal oxides, hydroxides and carbonates are considered when evaluating mineral solubility controls in natural waters. In mine waters, sulfate minerals may also be important solubility controls. Hem (1992) states that cobalt hydroxide [$Co(OH)_2$] is unlikely to influence cobalt concentrations in natural waters; however, under alkaline conditions, cobalt carbonate [$CoCO_3$] may limit cobalt concentrations. Cobalt can also substitute for other trace metals (e.g., Cu, Pb, Zn, Cd) in a wide variety of minerals due to its similar geochemical properties. In such cases, formation of mixed cobalt-metal solids (e.g., sulfates, carbonates, hydroxides), may limit dissolved cobalt concentrations as well. The formation of cobalt complexes should be considered in the determination of solubility limits.

Cobalt co-precipitation or adsorption with manganese and iron oxides may affect cobalt mobility (Hem, 1992). Smith (1999) referenced a number of studies in which cobalt showed a greater affinity for manganese oxide than other divalent metal ions (Cu, Ni, Zn and Zn). In aluminum and iron oxide adsorption studies, cobalt selectivity was generally low in comparison to other divalent ions. Sorption of cobalt generally increases with increasing pH. Cobalt sorption commences at a pH of approximately 5, and reaches maximum effectiveness at pH values around 6.5. As conditions become more alkaline, (i.e. pH > 8), adsorption becomes less efficient again (Smith, 1999; Theis *et al*., 1988)

In freshwater, cobalt is generally found in the Co^{2+}, carbonate, hydroxide, sulfate, and adsorbed forms, as well as in the form of oxide coatings and crystalline sediments (Smith and Carson, 1981). In marine water, cobalt is typically present as Co^{2+}, the chloride, the carbonate and the sulfate (Smith and Carson, 1981; Hamilton, 1994).

A review of the literature on the speciation of cobalt in freshwater revealed that the proportion of the dissolved and suspended fractions of the metal in ambient water is highly variable (Smith and Carson, 1981). In the Danube River, the authors reported that the dissolved form of cobalt varied from 14.1 % to 72.6 % of the total during the period from 1961 to 1970 at one of the sites. The proportion of cobalt in

the dissolved form for other rivers was: 14 % for the Rio Puerco, New Mexico; 96.8 to 98.6 % for Joe Mill Creek in Tennessee, USA; and 2 % to 5 % in the Columbia River in Washington, USA. Cobalt in Lake Washington in Washington, USA was present exclusively in the dissolved form.

Smith and Carson (1981) also reviewed the available literature for cobalt speciation in marine waters. In the North Sea dissolved cobalt accounted for 66 % of the total cobalt. Dissolved cobalt accounted for 85 % to 89 % of total cobalt in the Straight of Juan de Fuca, Washington, USA.

Smith and Carson (1981) reported that the adsorption of cobalt by oxide minerals increased with increasing pH. The presence of soluble organic matter in water increases desorption and solubilization of cobalt from inorganic fractions of sediments or suspended material.

A review by Smith and Carson (1981) of the literature describing the speciation of cobalt in suspended material in freshwater systems revealed a wide variation in speciation. They reported that in the Amazon and Yukon Rivers (both considered unpolluted) cobalt in the water was less than 2 % dissolved, 5 % to 8 % adsorbed, 27 % to 29 % precipitated and co-precipitated in metallic coatings, 13 % to 19 % in inorganic solids, and 44 % to 51 % in crystalline sediments. In the Haw and Hope rivers, cobalt in the water was on average 8 % dissolved, 31 % adsorbed, 21 % in oxide coatings, 11 % in solid organics and 29 % in crystalline forms. Smith and Carson (1981) also reported that at contaminated sites, cobalt in water was on average 12 % dissolved, 27 % adsorbed, 19 % in oxide coatings, 15 % in solid organics and 27 % in crystalline minerals.

Cobalt has not been demonstrated to be essential for the growth of higher plants; however, it is required by certain blue-green algae. Cobalt is essential for N_2 fixation by free-living bacteria, blue-green algae, and symbiotic systems; e.g., *rhizobium* in the root nodules of legumes. In higher plants, cobalt supplements have been reported to increase growth of rubber plants and tomatoes and length of pea stem sections (Adriano, 1986). Whereas cobalt is not essential to plants, its level in plant tissues is of concern because of its essentiality in animal nutrition (constituent of vitamin B_{12}). Low levels of cobalt in feedstuff can cause nutritional diseases in ruminants; e.g., ‘bush sickness’ in cattle or sheep or ‘pinning’ in sheep (Adriano, 1986).

4.0 AQUATIC LIFE

4.1 Freshwater Life

4.1.1 Recommended Guidelines

To protect freshwater aquatic life from acute toxic effects of cobalt, it is recommended that the interim maximum concentration of total cobalt should not exceed 110 μg/L.

To protect freshwater aquatic life from chronic toxic effects of cobalt, it is recommended that the interim average concentration of total cobalt should not exceed 4 μg/L. The average concentration is determined from at least 5 samples taken over a period thirty days.

4.1.2 Summary of Existing Guidelines

There is currently no national Canadian water quality guideline for cobalt to protect freshwater aquatic life. The province of Ontario has derived its freshwater quality objective of 0.9 μg/L cobalt, based on a statistically computed chronic LOEC of 9.3 μg/L for reproduction in *Daphnia magna* (Kimball, 1978). The New York State Department of Environmental Conservation (NYSDEC) water quality standard for surface and ground water is 5 μg /L cobalt. The province of Quebec has adopted a surface water quality guideline of 5 μg/L for the protection of freshwater aquatic life from chronic effects of cobalt, based on the NYSDEC (1986) standard. Australia (ANZGFMWQ, 2000a) has developed a low reliability trigger (LRT) value of 1.4 μg/L as a water quality guideline for the protection of freshwater aquatic life. The Australian LRT was derived by applying an uncertainty factor of 2 to a statistically computed NOEC (reproduction) of 2.8 μg/L for *Daphnia magna* from Kimball (1978). The LRT is defined as a guideline "derived in absence of a data set of sufficient quantity, using larger assessment factors to account for greater uncertainty". The LRT is considered an interim guideline, with a relatively high uncertainty.

4.1.3 Rationale

The data compiled and reviewed for the development of the guideline is summarized in Tables 1 through 5 inserted at the end of the report. The focus of the following section is on the key studies used in the development of the guideline for freshwater aquatic life.

Based on the literature reviewed, aquatic invertebrates appear to be the most sensitive group of organisms to cobalt exposure, followed by fish and plants. Table 6 and Figures 1 and 2 (at the end of the report) summarize the ranges of toxicity endpoints identified in the literature.

Table 6: Range of toxicity endpoints for freshwater organisms

Class	NOEC (µg/L)	LOEC (µg/L)	EC50 (sublethal) (µg/L))	LC50 (µg/L)
Plants	500-550*	550*	522-23,800	N/A
Fish	132-10,000	225-1,610	not available	470-225,000
Invertebrates	10-600	20 - >50	12*	21-450,000

* based on very limited data; 1 study for LOEC and NOEC for plants and 1 study for EC50 for invertebrates

4.1.3.1 Vertebrate Studies

Based on the literature review, the most sensitive fish species was rainbow trout (*Oncorhynchus mykiss*). Chronic LC50 values established for *O. mykiss* include 470 µg/L (Birge, 1978) and 490 µg/L (Birge *et al.*, 1980) for 28 day embryo-larval toxicity tests, and 520 µg/L (Marr *et al.*, 1998) for a 144-hour (6 day) test using fry. Marr *et al.* (1998) established 14-day NOEC and a 14-day LOEC for growth and survival of 132 µg/L and 255 µg/L, respectively, for fry. Effect concentrations for acute toxicity tests using rainbow trout include a 96-hour LC50 of 1,406 µg/L (Marr *et al.*, 1998).

Marr *et al.* (1998) reported a temporal pattern to cobalt toxicity in rainbow trout. Cobalt concentrations that would eventually cause 100% lethality caused no lethality until at least 72 hours of exposure. In calculation of the incipient lethal level (ILL; time-independent concentration resulting in 50% lethality), the authors noted that the majority of the lethality occurred between 72 and 192 hours, suggesting that the standard short term 96-hour LC50 could under-predict cobalt toxicity substantially. It should be noted that the 96-hour LC50 was 1,406 µg/L, but the ILL was 346 µg/L (Marr *et al.*, 1998).

Other fish species that have been studied for adverse effects of cobalt exposure include goldfish (*Carassius auratus*) and fathead minnow (*Pimephales promelas*). Birge (1978) reported a seven-day embryo-larval LC50 of 810 µg/L for *C. auratus*. Kimball (1978) reported a 96-hour LC50 of 3,610 µg/L for juvenile *P. promelas*. Kimball also conducted chronic toxicity testing using embryo-larval *P. promelas* and reported a NOEC and a LOEC for growth of 210 µg/L and 390 µg/L, respectively, as well as a NOEC and a LOEC for survival of 810 µg/L and 1,610 µg/L, respectively.

Only two studies were reviewed concerning the toxicity of cobalt to amphibians. A frog embryo teratogenic assay evaluated the effects of cobalt on the clawed frog (*Xenopus laevis*) reported an EC50 for malformations of 1,473 µg/L and a LOEC for growth of 2,475 µg/L. An embryo-larval study of the toxicity of cobalt to narrow-mouth toad (*Gastrophryne carolinensis*) found a 7-day LC50 of 50 µg/L (Birge 1978). Although, amphibian data are not required for the derivation of water quality guidelines, it is still considered in the derivation when applicable.

4.1.3.2 Invertebrate Studies

The most sensitive freshwater invertebrate species were found to be daphnids, based on the studies of Kimball (1978), Biesinger and Christensen (1972) and Diamond *et al.* (1992).

Kimball (1978) reported 48-hour LC50 values of 7,370 µg/L and 5,990 µg/L for fed and unfed *Daphnia magna*, respectively. Kimball also reported a LC50 of 27 µg/L and a LOEC for reproduction of 9.3 µg/L from two 28-day tests using *D. magna* (hardness 100 mg/L).

Although the Kimball study appears to be a quality study, the data from the author's two 28-day tests indicated that the results were not consistent and reproducible in the concentration range where they overlapped (i.e., between 0 and 5.2 µg/L). The data used by Kimball in the derivation of his 28-day LOEC for reproduction is summarized in Table 7.

Table 7: Summary of data from Kimball (1978): 28 day *D. magna* toxicity tests

Test #1							
Concentration (µg/L)	0	4.4	9.3	17.3	31.2	51.9	88.0
Mean young/female	126.9	18.8*	8.2*	2.7*	40*	0*	0*
Test #2							
Concentration (µg/L)	0	1.2	1.4	1.5	1.9	2.8	5.2
Mean young/female	88.5	50.7	87.1	71.0	89.2	70.1	77.4

* indicated that reproductive effects were significantly different from the control (or zero µg/L)

Kimball (1978) also conducted a screening test on *D. magna* prior to the 28-day chronic toxicity test. The seven-day screening test identified a NOEC of 810 µg/L and a LOEC of 1,610 µg/L for survival and a NOEC of 10 µg/L and a LOEC of 20 µg/L for reproductive effects.

Biesinger and Christensen (1972) conducted 48-hour acute and 21-day chronic toxicity tests with *D. magna*. Acute LC50 values were 1,620 µg/L and 1,110 µg/L for fed and unfed organisms, respectively. Biesinger and Christensen (1972) established a 21-day LC50 of 21 µg/L for *D. magna*, which was consistent with the 28-day LC50 reported by Kimball (1978).

The 21-day EC16 of 10 µg/L for reproduction reported by Biesinger and Christensen (1972) was considered by the authors to be the "minimal reproducible value below which the variability in reproduction could not be detected from controls". The EC16, therefore, was interpreted as a LOEC. The authors also noted a stimulatory effect (hormesis) of low concentrations of the metals tested, and reported that potentially significant adverse effects from exposure to metals were determined based on a comparison to either control values or the concentrations associated with the hormesis effect. It was not disclosed in the publication, if cobalt was one of the metals displaying a hormesis effect. Therefore, it is unknown if the 21-day EC16 of 10 µg/L was based on a comparison to laboratory controls or one of the test concentrations.

Diamond *et al.* (1992) report 24-hour LC50 concentrations for cobalt toxicity to *Ceriodaphnia dubia* using a range of water hardnesses. The LC50 concentration ranged from 2,347 µg/L to greater than 5,300 µg/L for water hardnesses of 57, 256, 476 and 882 mg/L as $CaCO_3$. The seven-day NOEC for survival for *C. dubia* was 50 µg/L at a water hardness of 476 mg/L as $CaCO_3$. At water hardnesses of 57 mg/L and 256 mg/L as $CaCO_3$, the NOEC was less than the lowest cobalt concentration studied (50 µg/L). Therefore, the sensitivity of *C. dubia* to cobalt in surface water hardnesses more common in British Columbia (57 and 256 mg/L $CaCO_3$) could not be determined.

Other invertebrates studied in the literature include the crayfish *Austropotamobius pallipes pallipes* and *Orconectes limosus*. Boutet and Chaisemartin (1973) conducted acute and chronic toxicity test on each of these species. They report 96-hour LC50 concentrations of 8,800 µg/L for *A. pallipes pallipes* and 10,200 µg/L for *O. limosus*. The results of the chronic toxicity tests indicate 30-day LC50 concentrations of 770 µg/L and 790 µg/L for *A. pallipes pallipes* for fed and unfed organisms, respectively, and 790 µg/L and 880 µg/L for *O. limosus* for fed and unfed organisms, respectively. This study was considered secondary as the test conditions were not adequately described and cobalt concentrations were not measured.

Sodergren (1976) reported growth and emergence inhibition in the mayfly (*Ephemerella ignita*) exposed to cobalt at concentrations of 32 µg/L and 5.2 µg/L, respectively. However, there is a possibility of co-contaminants in the test water as the source of water was from a Swedish river that is influenced by a variety of local industries. Therefore, this test was considered secondary in nature.

4.1.3.3 Aquatic Plant Studies

Seven studies on the effects of cobalt on freshwater aquatic plants, particularly freshwater algae, were reviewed. All seven studies were considered secondary. Based on the results of these studies, the sensitivity of algae to cobalt exposure appeared to be similar to that of fish and lower than that of invertebrates.

The most sensitive species was *Chlamydomonas eugametos* with a 10- to 14-day LOEC for growth of 500 µg/L (Hutchinson, 1973). The exact duration of the test was not provided and the cobalt concentrations were not measured. Coleman *et al.* (1971) reported a 21-day NOEC (growth) for *Chlorella vulgaris* and a 21-day LOEC (growth) for *Pediastrum tetras* and *Euglena viridis* at a concentration of 550 µg/L. Coleman *et al.* (1971) also reported a LOEC of 1,550 µg/L for *C. vulgaris*, while Rachlin and Grosso (1993) reported a 96-hour EC50 for growth of 522 µg/L.

In the remaining studies reviewed, the effects of cobalt exposure on growth were generally observed in the concentration range of 5,000 µg/L to 25,000 µg/L. Acute exposure (≤96 hours) to cobalt concentrations in the range of 5,000 µg/L to 20,000 µg/L have been shown to result in a reduction in growth of *Anabaene variabilis* (Ahluwalia and Kaur, 1988). A reduction in growth of *Anacystis nidulans* has been reported following an approximate 14-day exposure to cobalt concentrations of 15,000 µg/L (Lee *et al.*, 1992). Sharma *et al.* (1987) reported a 50 % reduction in growth of *Spirulina platensis* at cobalt concentrations of 23,800 µg/L and 8,130 µg/L following exposure durations of 96 hours and 168 hours, respectively.

4.1.3.4 Potential Modifying Factors of Toxicity

There is some evidence to suggest that cobalt toxicity in freshwater aquatic organisms may be influenced by water hardness. If true, this would be consistent with the toxicity of other cationic metals and metalloids. For instance, Diamond *et al*. (1992) reported that the 24-hour LC50 for *C. dubia* varied from 2,347 µg/L to greater than 5,275 µg/L in water with hardness ranging from 57 to 882 mg/L as $CaCO_3$. Also, the 7-day NOEC for *C. dubia* was <50 µg/L cobalt at a water hardness of 57 and 256 mg/L as $CaCO_3$, 50 µg/L cobalt at 470 mg/L as $CaCO_3$, and 600 µg/L cobalt at a water hardness of 882 mg/L as $CaCO_3$.

Diamond *et al*. (1992) also reported that the 7-day NOEC for *P. promelas* varied from 1,232 µg/L to 3,833 µg/L in the water hardness range of 57 mg/L as $CaCO_3$ to 882 mg/L as $CaCO_3$. The 48-hour NOEC values for *P. promelas* varied from 1,245 µg/L cobalt at a water hardness of 57 mg/L as $CaCO_3$ to 6,200 µg/L cobalt at a water hardness of 882 mg/L as $CaCO_3$.

Using all available data from the literature including their own, Diamond *et al*. (1992) attempted to develop the cobalt toxicity relationship with water hardness. Although the authors concluded that there

was an inverse relationship between acute toxicity of cobalt and water hardness in the 50 to 200 mg/L as $CaCO_3$ hardness range, no relationship in chronic toxicity of cobalt with water hardness was found. Also, these investigators were not able to explain the acute toxicity-water hardness relationship based on the conventional trends that other metals have shown (i.e., there is an increase in the precipitation of metals as insoluble/unavailable carbonate complexes, such as cobaltous carbonate, as water hardness increased, thus reducing the metal toxicity to aquatic organisms). They attributed this departure from the conventional trend to a different mode of action for cobalt toxicity at elevated water hardness; however, the mode of cobalt toxicity was not identified. Obviously, this leads us to speculate whether: (a) the observed toxicity-water hardness relationship for cobalt was real, or (b) there were other factors related to, for instance, data quality, data sufficiency, experimental design etc., that may have influenced cobalt toxicity in their experiment, but were not considered. The salient features of the Diamond *et al*. study are as follow:

- In their toxicity tests, Diamond *et al*. exposed *P. Promelas* and *C. dubia* to variety of cobalt concentrations at four water hardnesses (57, 256, 470, and 882 mg/L as $CaCO_3$. Both vertebrates (*P. promelas*) and invertebrates (*C. dubia*) displayed non-linear but inverse relationships between the metal acute toxicity and water hardness. (*It is worth noting that although the acute toxicity-water hardness relationship seem to be well defined at the lower end from 57 to 256 mg/L $CaCO_3$, there were only two data points in that range: one at 57 mg/L CaCO3 and the other at 256 mg/L $CaCO_3$. Also, if the 57 mg/L as $CaCO_3$ hardness value is excluded from the data set, the toxicity-hardness relationship between 256 and 882 mg/L $CaCO_3$ hardness could not be ascertained from the data with any certainty.*)

- Acute toxicity data generated by Diamond *et al*. in their study with *P. promelas* exposed to cobalt supported a hardness-dependent relationship between water hardness of 57 and 256 mg/L as $CaCO_3$. However, the authors indicated that their data did not support the conventional understanding of reduced cobalt toxicity with increased water hardness (as suggested in the above bullet). They noted that, in their study, the concentrations of both the carbonate and calcium (or magnesium) ions in water increased with increasing hardness and they could not separate the potential chelating effects (due to the formation of cobaltous carbonate complexes) from competition effects for sites of potential toxic action (Ca^{2+} or Mg^{2+} preferentially binding to sites instead of cobalt). The former mechanism (viz. alkali effect) seemed unlikely as they did not observe precipitation of cobaltous carbonates or significant difference in dissolved versus total recoverable cobalt in testing. Hence, the idea that the non-toxic cations, calcium and magnesium, competed with cobalt for potential toxic sites seems more plausible since cobalt is known to have a higher density and higher ionization potential than either calcium or magnesium.

- A relationship between chronic toxicity of cobalt and water hardness for *C. dubia* could not be ascertained due to unexpected survival and reproduction problems in the synthetic dilution water which may have caused nutritional problems. *C. dubia* survived and reproduced better, albeit suboptimally, in water with hardness of 256 and 470 mg/L as $CaCO_3$ compared to water

hardness of 57 or 882 mg/L $CaCO_3$. Very hard water (882 mg/L as $CaCO_3$) may have been toxic in itself to *C. dubia*. (*One may assume that similar problems could have occurred in the acute tests, although the authors did not report as such*.)

- Diamond *et al*. analysed the available data from the literature and found that the acute response of *D. magna* exposed to cobalt was linear and more sensitive to changes in water hardness (between 50 and 200 mg/L as $CaCO_3$). In their acute tests with *C. dubia*, however, they found that the dose-response relationship was non-linear in waters ranging in hardness from 57 to 882 mg/L as $CaCO_3$. Diamond *et al*. noted that their organisms may have been stressed under the hard water conditions since cultures were normally maintained at 50 mg/L hardness. (*This sheds a doubt on validity of the acute toxicity-water hardness relationship obtained by the authors in their experiment*.)

- Based on literature data from carp, *Cyprius carpio*, (two data points), *D. magna* (three data points), and *P. promelas* (three data points), Diamond *et a*l. indicated that within the range of 50 to 200 mg/L as $CaCO_3$, cobalt acute toxicity was inversely related to water hardness. This trend was explained by the fact that high levels of calcium carbonate in soils, for instance, decreased the solubility and bioavailability of cobalt (due to precipitation of cobaltous carbonate) to plants and animals.

Obviously, further tests are required to ascertain the cobalt toxicity-water hardness relationship, both for acute and chronic effects.

4.1.3.5 Summary of Key Acute Studies and Guideline Derivation

The sensitivities of fish and invertebrates were similar in acute exposure toxicity tests. Therefore, the most sensitive fish and invertebrate studies were considered in the derivation of the acute guideline. The key acute studies of the effects of cobalt exposure on freshwater aquatic life are summarized in Table 8.

The most sensitive acute (96-h) LC50 was 1110 μg/L[1] in *D. magna*. The range of potential safety factors suggested by the BC Protocol for the acute guideline derivation is 0.1 to 0.5. Applying a safety factor of 0.1 to the most sensitive LC50 results in an interim acute guideline of 110 μg/L (rounded to nearest tenth) for the protection of aquatic life. The more conservative safety factor of 0.1 (instead of 0.5) was chosen to protect the aquatic life from mortality. The choice of 0.1 as safety factor is considered more prudent, given the fact that standard short-term 96-h acute toxicity test with certain aquatic organisms (e.g., rainbow trout) can under-predict cobalt toxicity substantially (Marr *et al*.,1998). The primary

[1] The final acute value (FAV) of 336 μg/L by Diamond *et al*. (1992) in Table 1 was not accepted as the threshold acute LOEC (Figure 1) for this purpose because it is a mathematically derived value based on acute values of several species rather than the most sensitive species.

reason for this was the fact that cobalt-induced toxicity lethality may be delayed for several hours past start of the exposure (e.g., 72 to 192 hours in rainbow trout exposed to cobalt; Marr *et al*., 1998). An interim status was assigned to the acute guideline because of the data set did not meet all the requirements of the full guideline as specified in the CCME (1991) or WLAP (1995) protocols.

Table 8: Summary of key acute freshwater studies from the literature

Species	LC50/ EC50 (µg/L)	Duration	NOEC (µg/L)	Hardness (mg/L $CaCO_3$)	Study
P. promelas	>5830	48 hr	1245	57	Diamond *et al.*, 1992
P. promelas	3610	96 hr	-	235*	Kimball, 1978
O. mykiss	1406	96 hr	-	24.9	Marr *et al.*, 1998
D. magna	1110	48 hr	-	45.3	Biesinger & Christensen, 1972
D. magna	1490	48 hr	-	245	Khangarot *et al*., 1987
D. magna	1490	48 hr	-	240	Khangarot & Ray, 1989
C. dubia	2347	24 hr	-	57	Diamond *et al.*, 1992
E. padamus	4000	48 hr	-	not given	Baudoin & Scoppa, 1974
D. hyalina	1320	48 hr	-	not given	Baudoin & Scoppa, 1974

[+] alkalinity in mg/L

4.1.3.6 Golder/EVS Chronic Study

Given (i) the secondary nature of the key chronic data (e.g., Kimball, 1978; Biesinger and Christensen, 1972), and ii) the potential influence of water hardness on cobalt toxicity, provision was made in this guideline development process to conduct additional toxicity studies in-house (Golder/EVS study) to confirm results found in the literature. Studies were undertaken to:

i.) Corroborate chronic toxicity of *C. dubia* and *D. magna*, the most sensitive species identified in the literature; and;

ii.) Determine if the toxicity of cobalt to these species is affected by water hardness, in a range that is relevant to surface waters in British Columbia (50 to 200 mg/L as $CaCO_3$).

A 21-day *D. magna* toxicity test examining reproductive and survival endpoints was carried out to compare the results with the Kimball (1978) study. Additionally, the 7-day *C. dubia* toxicity test with reproductive and survival endpoints was conducted to assess the toxicity-hardness relationship that is more relevant to British Columbia. In both cases, the *D. magna* and *C. dubia* were exposed to five nominal concentrations of 3.13, 6.25, 12.5, 25, and 50 µg/L cobalt at each water hardness of 50, 100, and 200 mg/L $CaCO_3$. The 7-d toxicity test with C. *dubia* was also performed at a nominal concentration 100 µg/L cobalt at each water hardness. The details of these bioassays are reported in a separate data report.

The results of the Golder/EVS toxicity study are summarized in Tables 9 and 10. The LOEC for reproduction for *D. magna* was 50 µg/L at water hardnesses of 50 and 200 mg/L as $CaCO_3$. No effects on reproduction were observed at the highest cobalt concentration tested (50 µg/L) at a water hardness of 100 mg/L as $CaCO_3$ (i.e., the LOEC was greater than 50 µg/L). The NOEC ranged from 25 µg/L to 50 µg/L. The results of the 7-day *C. dubia* test indicated a NOEC for reproduction in the range of 6.25 µg/L to 12.5 µg/L and a LOEC for reproduction in the range of 12.5 µg/L to 25 µg/L, indicating that *C. dubia* was more sensitive to water-borne cobalt than *D. magna*.

Table 9: Summary of the 21-day *D. magna* test results : Golder/EVS study

Hardness (mg/L as $CaCO_3$)	Reproduction Endpoints (µg/L)		Survival Endpoints (µg/L)		
	NOEC*	LOEC*	NOEC*	LOEC*	LC50*
50	25	50	50	>50	>50
100	50	>50	50	>50	>50
200	25	50	25	50	>50

* NOEC and LOEC are point estimates, whereas LC50 are computed values from a statistical analysis.

Table 10: Summary of the 7-day *C. dubia* test results : Golder/EVS study

Hardness (mg/L as $CaCO_3$)	Reproduction Endpoints (µg/L)		Survival Endpoints (µg/L)		
	NOEC*	LOEC*	NOEC*	LOEC*	LC50*
50	12.5	25	100	>100	>100
100	12.5	25	50	>50	>50
200	6.25	12.5	50	>50	>50

* NOEC and LOEC are point estimates, whereas LC50 are computed values from a statistical analysis.

The results of the 7-day *C. dubia* partial lifecycle toxicity test and a 21-day *D. magna* partial lifecycle toxicity test conducted as part of this guideline development process, did not clearly support the cobalt toxicity-water hardness relationship as suggested by Diamond *et al*. (1992). The 95 % confidence limits for test endpoints were overlapping for each of the three water hardnesses tested. The range of water hardness values tested in our (Golder/EVS) study was 50 to 200 mg/L as $CaCO_3$. This range is much narrower and closer to the lower end of the range tested by Diamond *et al.* (1992) (i.e., 57 to 882 mg/L as $CaCO_3$). The NOEC and LOEC reported from the tests conducted as part of the guideline development process (the Golder/EVS study), however, were generally consistent with the results of other studies (e.g., Biesinger and Christensen, 1972).

4.1.3.7 Golder/BC Research Chronic Study

Another study was conducted by BC Research Inc. (Golder/BC Research study) to confirm the results obtained by the Golder/EVS study. The 7-day *C. dubia* study was initiated on May 29, 2003 at a hardness of 100 mg/L as $CaCO_3$. In addition to the study conducted by BC Research., EVS repeated their experiment at a hardness of 100 mg/L as $CaCO_3$ as an internal QA/QC. A summary of the results from the *C. dubia* 7-day test at a hardness of mg/L as CaCO3 for all three studies is shown below for the reproduction endpoint (Table 11). Test organisms in the BC Research study exhibited a greater sensitivity to the reference toxicant (zinc) than the organisms tested by EVS (both studies). Although the protocol used by the two labs was replicated as closely as possible, there is always potential variability between labs. Possible reasons for the variability include the source of the testing water, source of the stock organisms and the relative success of the acclimation period to the specified hardness. The test water used by EVS was deionized water, while the test water used by BC Research was pond water collected from the University of British Columbia.

A summary control chart was obtained from both labs to determine the response of control organisms. Typically BC Research uses sodium chloride (NaCl) as a standard reference toxicant and EVS uses zinc as their standard reference toxicant. Therefore, it was not possible to compare the control charts for previous studies, although both labs were within their acceptable range of deviation. However, the reproducibility of the toxicity data by EVS indicates a high level of confidence in that study. In addition, the LOEC and the NOEC derived from the BC Research data appeared to be inconsistent with the most conservative literature value.

Table 11: Results of the 7-day *C. dubia chronic* tests : Golder/EVS and Golder/BC Research studies

Study	Species	LOEC (µg/L cobalt)	NOEC (µg/L cobalt)
Golder/EVS	*C. dubia*	25	12.5
Golder/EVS	*C. dubia*	25	12.5
Golder/EVS	*C. dubia*	12.5	6.25
Golder/EVS	*C. dubia*	12.5	6.25
Golder/ BC Research	*C. dubia*	3.13	<3.13

4.1.3.8 Summary of Key Chronic Studies and Guideline Derivation

Invertebrates were consistently more sensitive to chronic cobalt exposure than fish. Therefore, the most sensitive invertebrate studies were considered in the derivation of the chronic guideline. The key

chronic studies (i.e., LOEC's at the lower end of the range and considered acceptable) of the effects of cobalt exposure on freshwater aquatic organisms are summarized in Table 12.

Table 12: Summary of key chronic freshwater studies from the literature

Species	**EC50/ LC50**$^{+}$ (µg/L)	**LOEC**$^{+}$ (µg/L)	**NOEC**$^{+}$ (µg/L)	**Hardness** (mg/L as $CaCO_3$)	**Duration** (days)	**Study**
D. magna	21	10	-	45.3	21	Biesinger & Christensen, 1972
	12 (EC50)			45.3	21	Biesinger & Christensen, 1972
	27	9.3	2.8	not given	28	Kimball, 1978* (28-d chronic)
	-	20	10	not given	10	Kimball, 1978* (7-d screening test)
C. dubia	-	-	<50	400	7	Diamond *et al.*, 1992

$^{+}$ The EC50, LOEC and NOEC concentrations are for reproduction;

* NOEC and LOEC values are based on test concentrations. Kimball also reported a statistically derived maximum acceptable toxic concentrations (MATC) of 5.1 µg/L (28-d test) and 14 µg/L (7-d screening test) from these tests.

The accepted protocol for deriving guidelines for the protection of aquatic life in BC involves applying a safety factor to the most sensitive LOEC. Although Golder/EVS study produced consistent and reproducible results (LOEC of 12.5 µg/L for *C. dubia*), there was not a strong a basis to reject LOEC values obtained by other investigators in the literature (e.g., 3.13 µg/L for *C. dubia* by Golder/BC Research; 10 µg/L for *D. magna* by Kimball, 1978; and 12 µg/L for *D. magna* by Beisinger and Christensen, 1972). As a result, a geometric mean value of 8.2 µg/L, based on the above indicated four values, was selected as the threshold LOEC for purpose of guideline derivation. There are three values below this in Figure 2. Two of them are the no observed effect concentration and the third value for mayfly (5.2 µg/L in a 28-d test with emergence inhibition as end point) was considered unacceptable due to potential effects of co-contaminants.

The Canadian Council of Ministers of the Environment (CCME, 1991) protocol recommends that a safety factor of 0.1 be used with the LOEC to derive a guideline for the protection of aquatic life. A safety factor ranging from 0.1 to 0.5 is recommended by British Columbia based on factors that include abundance of data, professional judgment, etc. For the purpose, a safety factor of 0.5, in conjunction with the LOEC of 8.2 µg/L, was chosen for the derivation of the cobalt guideline. The choice of the safety factor was dependent on a number of considerations: (i) the ratio NOEC to the LOEC for the most sensitive species in chronic tests is around 0.5 (Kimball, 1978; Biesinger and Christensen, 1972, Golder/EVS, 2003 in Tables 11 and 12), and (ii) more importantly, cobalt is an essential micronutrient for animals and some plants since it is required in vitamin B_{12} synthesis (Lehninger, 1972 as quoted in Diamond *et al*., 1992). In general, a deficiency of cobalt is of far greater concern than the metal's potential toxicity in the environment (Adriano, 1986). Table 13 lists the data used for the derivation of

the water quality guideline to protect aquatic life from chronic effects of cobalt, mean (geometric) LOEC, and the recommended guideline.

Table 13: Critical chronic toxicity data and recommended guideline

Study	Species	LOEC (µg/L)	NOEC (µg/L)	Guideline (µg/L)
Biesinger & Christensen, 1972	*D. magna*	12 (EC50 reproduction)	-	
Kimball, 1978	*D. magna*	9.3 (reproduction)	5.1	
Golder/BC Research	*C. dubia*	3.3*+	<3.13	
Golder/EVS	*C. dubia*	12.5*	6.25	
Geometric mean		***8.2***		
Recommended Guideline				***4***

* These values were not plotted in Figure 2.

+ This value, although appeared to be an outlier, was considered for geometric mean calculations.

An interim water quality guideline of 4 µg/L (rounded from 4.1 µg/L) has been recommended for the protection of aquatic life from adverse chronic effects of cobalt. This value is based on applying a safety factor of 0.5 to mean LOEC of 8.2 µg/L.

4.2 Marine Life

4.2.1 Recommended Guideline

A water quality guideline for the protection of marine aquatic life from adverse effects of cobalt has not been proposed due to insufficient data.

4.2.2 Summary of Existing Guidelines

Australia has derived a cobalt water quality guideline of 1 µg/L for the protection of marine aquatic life. The Australian guideline was calculated using the statistical distribution method at 95 % protection (i.e., the guideline is designed to protect 95 % of the species). The key study in the derivation of the Australian guideline was an investigation by Amiard (1976) of the acute and chronic effects of cobalt on marine crustaceans and fish. The study by Amiard (1976) is described further in section 4.2.3.

Australia was the only jurisdiction for which cobalt water quality guidelines for the protection of marine aquatic life were identified.

4.2.3 Rationale

Limited studies were available with respect to acute and chronic toxicity of cobalt in the marine environment. Marine cobalt toxicity data were available for two species of diatoms, a copepod, an isopod, a nematode, a lobster, a crab, a shrimp and several fish. However, the lobster, crab, shrimp, squid and some fish data were obtained from a single study (Amiard, 1976). The data compiled and reviewed for the development of marine aquatic life guidelines for cobalt is summarized in Tables 14 and 15. Each of the studies reviewed regarding cobalt toxicity to marine organisms was considered secondary.

The relative sensitivity of marine species versus freshwater species to cobalt toxicity could not be conclusively determined based on the available data. Effect concentrations reported for marine organisms were often comparable to those reported for similar tests using similar freshwater organisms.

The majority of the marine toxicity data for cobalt is from a study by Amiard (1976) in which acute (96-hour) and chronic (216-hour) toxicity tests were conducted using larval and adult stages of several crustaceans and adult teleosts. The results of this study indicate that the sensitivity of adult crustaceans and adult fish to cobalt exposure is similar with LC50 concentrations ranging from 225,000 µg/L to 675,000 µg/L. The acute and chronic LC50 concentrations reported for adult marine crustaceans and fish are generally greater than those reported for freshwater organisms.

In the study by Amiard (1976), juvenile life stages were generally more sensitive than more developed life stages. The most sensitive marine species studied were the larvae of two crustaceans (*H. vulgaris* and *P. serratus*), for which chronic (216-hour) effect concentrations of 225 µg/L and 45 µg/L, respectively were reported (Amiard, 1976). These concentrations were in the same range as those reported for freshwater invertebrates and similar endpoints. However, the results of the study by Amiard are questionable due to high mortality rates in the controls, particularly for toxicity tests using crustacean larvae. Mortality rates in the controls increased over time and varied between species, with up to 50 % mortality in the control for lobsters for 96-hour LC50 tests.

Outside of the data reported by Amiard (1976), the next most sensitive endpoint for marine species was an EC50 for growth of 300 µg/L for the diatom *Ditylum brightwellii* reported by Canterford and Canterford (1980). However, Canterford and Canterford (1980) did not clearly describe the test methods used or state the duration of the tests. Rosko & Rachlin (1975) reported 96-hour EC50 (growth) values for the diatom *Nitzschia closterium* of 10,200 µg/L and 23,600 µg/L in non-chelating and chelating media, respectively.

Bengtsson (1978) reported a 96-hour LC50 for adults of the harpacticoid copepod *Nitocra spinipes* of 4,500 µg/L. This concentration is approximately two orders of magnitude lower than LC50 values reported by Amiard (1976) for adult crustaceans and an order of magnitude greater than values reported by Amiard (1976) for juvenile crustaceans. El-Nady and Atta (1996) reported that for the isopod *Idotea*

baltica an exposure duration of 1248 hours (52 days) is required to elicit an LC50 at a cobalt concentration of 10,000 µg/L.

Krishnakumari *et al.* (1983) studied the acute toxicity of cobalt to the marine fish *Therapon jarbua*. They reported a 96-hour NOEC of 20,000 µg/L and a 96-hour LC50 of 52,500 µg/L. Vranken *et al.* (1991) report a 96-hour LC50 of 94,000 µg/L for the nematode *Monhystera disjuncta*. These acute lethality concentrations reported by Krishnakumari *et al.* (1983) and Vranken *et al.* (1991) fall within the range of those reported for freshwater fish and freshwater worms, respectively.

With the exception of the chronic data reported by Amiard, the marine effects data indicate that marine species exhibit similar or somewhat less sensitivity to water-borne cobalt compared to freshwater species. Further research is warranted to refine estimates of the toxicity of cobalt to sensitive marine species.

5.0 WILDLIFE

5.1 Recommended Guidelines

A water quality guideline for the protection of wildlife from adverse effects of cobalt is not recommended due to insufficient data.

5.2 Summary of Existing Guidelines

Water quality guidelines to protect wildlife from adverse effects of cobalt were not found in the literature.

5.3 Rationale

There are few data available in the literature on the toxicity of cobalt in drinking water to terrestrial animals. Pedigo *et al.* (1988) demonstrated that the reproductive potential of mice exposed to cobalt in drinking water was significantly affected. The body weights and testicular weights of mice exposed to 400,000 µg/L of cobalt were significantly reduced. Further, epididymal sperm concentration and the percent motile sperm were reduced in mice consuming drinking water with a cobalt concentration of 400,000 µg/L. By week 13 of the study, the fertility of the male mice was reduced and fertility remained depressed during a 20-week recovery period in which mice were placed on the same drinking water as the controls.

Krasovskii and Fridlyand (1971) report that rats administered cobalt in water solution six days per week over a period of seven months exhibited increased erythrocyte and hemoglobin formation, increased erythrocyte size and a decrease in phagocytic activity of white cells. The authors report that the lowest dose (0.5 mg/kg) producing negative effects corresponded to approximately 2,300 µg/L of cobalt in drinking water. Krasovskii and Fridlyand (1971) also reported behavioural effects in rats given cobalt in drinking water at dose levels of 0.5 mg/kg and 2.5 mg/kg.

A water quality guideline to protect wildlife from adverse effects of cobalt was not recommended in this document for a number of reasons: (a) sufficient data were not available in the literature to develop a such a water quality guideline to protect wildlife water use and (b) ambient water supplies are generally uses for multiple purposes, including a drinking water supply for wildlife. The ambient water quality guidelines to protect the most sensitive water use from adverse effects of cobalt (e.g., aquatic life in this case) for these water supplies will also protect wildlife.

6.0 IRRIGATION

6.1 Recommended Guidelines

A water quality guideline for the protection of crops from adverse effects of cobalt in irrigation water is not recommended due to insufficient data.

6.2 Summary of Existing Guidelines

For a long-term (up to 100 years) or continuous use on all soils, Canada (Canadian Council of Ministers of the Environment; CCREM, 1987), United States (NAS/NAE, 1973), South Africa (SAWQG, 1996) and Australia (ANZGFMWQ, 2000b) have adopted an irrigation water quality guideline of 50 µg/L for cobalt. Additionally, for a short-term use (i.e., up to 20 years), the U.S. recommended a guideline of 5,000 µg/L cobalt for neutral and alkaline fine textured soils whereas Australia recommended a guideline of 100 µg/L cobalt for all soils in irrigation water.

The Canadian Council of Ministers of the Environment (CCME, 1999) recommended an interim soil remediation criteria of 40 mg/kg cobalt to protect agricultural soils. The CCME guideline is based on 1991 remediation criteria for contaminated soils and not the recommended protocol, and there is no written rationale for it.

6.3 Rationale

Cobalt has been shown to be an essential element for legumes, which have nodules containing nitrogen-fixing bacteria. Smith and Carson (1981) report inconclusive evidence of low concentrations of cobalt being beneficial to non-leguminous plants. In a review on the effects of cobalt on plants, Palit and Sharma (1994) report that low concentration of Co^{2+} enhances growth in a wide variety of plants, while higher concentrations result in toxicity.

There is little evidence of cobalt toxicity to plants due to elevated concentrations in soil. Vanselow (1966) reported that concentrations of cobalt in soil of up to 100 mg/kg have little effect on citrus crops.

Data from a number of nutrient solution studies were used to evaluate the potential for toxicity to plants from irrigation water containing cobalt. Wallace *et al.* (1977) report reduction of leaf dry weight in bush beans grown in nutrient solution containing 60 µg/L of cobalt for 21 days. A reduction of seedling root weight after 21 days of growth in 60 µg/L of cobalt was reported by Patel *et al*. (1976).

Misra *et al*. (1994) studied the effects of heavy metals, including cobalt, alone and in combination, on germination and root elongation of broad bean (*Vicia faba*). They found that seed germination was not affected by exposure to cobalt; however, root elongation was reduced, but not significantly, at concentrations of 8,000 µg/L and 10,000 µg/L. Further, an increase in root elongation was observed at lower cobalt concentrations with a significant increase at the lowest concentration studied (2,000 µg/L).

Patterson and Olson (1983) assessed the toxicity of cobalt in solution to seedlings of white spruce (*Picea glauca*), black spruce (*Picea mariana*), paper birch (*Betula papyrifera*), jack pine (*Pinus banksiana*), white pine (*Pinus strobus*), red pine (*Pinus resinosa*), and honeysuckle (*Lonicera tatarica*). Toxic concentrations ranged from 5,000 μg/L for honeysuckle and paper birch to 100,000 μg/L for white pine.

NAS/NAE (1973) reports that toxicity to a variety of food crops has been observed due to the application of nutrient solution containing cobalt at concentrations of approximately 100 to 5,000 μg/L.

Data regarding the toxicity of cobalt to soil microorganisms is limited. Lighthart *et al.* (1977) studied the effects of several metals, including cobalt, at single concentrations on respiration of native soil micro flora in soil/litter microcosms. A 1,362,000 μg/L solution of cobalt mixed into the soil and litter in the microcosm resulted in a reduction in respiration of 23%.

Soil pH affects the uptake of cobalt by plants with cobalt becoming more available for uptake as pH decreases (Palit and Sharma, 1994; Hamilton, 1994). Cobalt uptake by plants has also been shown to be limited by the presence of humus and the presence of high concentrations of manganese in soil.

The U.S. EPA (NAS/NAE, 1973) recommended irrigation water quality guidelines of 50 μg/L for continuous use on all soils and 5,000 μg/L for short-term (≤20-year period) use on neutral and alkaline fine textured soils to protect agricultural crops from cobalt toxicity. These guidelines were essentially the basis of the Canadian, Australian, and South African guidelines as stated in Section 6.2. The U.S. guidelines were derived from two 1953 studies indicating that a concentration of 100 μg/L cobalt in nutrient solution showed toxicity to tomato plants, whereas 5,000 μg/L cobalt in nutrient solution was highly toxic to oats. These guidelines were not accepted in this document because no data were available in the literature on the interactions between cobalt in irrigation water and in soil solution.

A water quality guideline for cobalt in irrigation water was not recommended in this document for a number of reasons: (a) there is little evidence from the literature on cobalt toxicity in soils to agricultural crops; (b) there were not sufficient data available from the literature to develop an irrigation water quality guideline using the CCME (1993) protocol; and (c) in general, ambient water serving as a source for irrigation will be used for multiple purposes, including aquatic life. The ambient water quality guidelines to protect the most sensitive water use from adverse effects of cobalt (e.g., aquatic life in this case) for water supplies will also protect crops when irrigated.

7.0 LIVESTOCK WATERING

7.1 Recommended Guidelines

A water quality guideline for the protection of livestock from adverse effects of cobalt in drinking water is not recommended due to insufficient data.

7.2 Summary of Existing Guidelines

Canada (CCREM, 1987), the U.S. (NAS/NAE, 1973), Australia (ANZGFMWQ, 2000b) and South Africa (SAWQG, 1996) have adopted a livestock watering water quality guideline of 1,000 μg/L for cobalt.

7.3 Rationale

Although cobalt is essential for animal nutrition, it is not required by the animal in ionic form of the metal. It is, however, dietary essential element for ruminants and horses, in which it is incorporated into vitamin B12 molecules by gastrointestinal microbes.

There is very little information available regarding the toxicity of cobalt in drinking water to livestock. CCREM (1987) has estimated that drinking water would have to contain a minimum of 10,000 μg/L cobalt before symptoms would be evident in calves.

Underwood (1977) reported reduced appetite and loss in weight for calves given cobalt at 1.1 mg/kg body weight/day. According to NAS (1980), 10 mg/kg of cobalt in the diet should be safe for cattle, swine and poultry. Under practical conditions, NAS(1980) noted that cobalt deficiency in ruminants is more likely than cobalt toxicosis.

The U.S. (NAS/NAE, 1973) recommended livestock drinking water quality guideline of 1,000 μg/L to protect livestock from cobalt toxicity. This guideline formed the basis of the Canadian, Australian, and South African guidelines as stated in Section 7.2. In developing the U.S. guideline, it was recognized that vitamin B12 is essential for animal nutrition. While ruminants synthesized their own vitamin B12, non-ruminants required performed vitamin B12. When vitamin B12 is administered to non-ruminants in amounts well beyond what is normally present in foods and feeds, then cobalt in the vitamin can induce toxic reaction. This is also true in calves prior to rumen development. However, there is no evidence of such toxic reaction in the literature. Hence, this guideline was not accepted for this document.

Sufficient data were not available in the literature to derive a cobalt water quality guideline using the CCME (1993) protocol to protect livestock drinking water supplies. Also, it was deemed unnecessary since livestock watering is not the most sensitive use with respect to cobalt. Multiple use water supplies, protected by employing guidelines for the most sensitive water use (e.g., aquatic life in this case), will also protect livestock exposed to cobalt in water.

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Table 1: Acute toxicity of cobalt to freshwater invertebrates

Species	Conc. (µg/L)	Life stage	Duration	Endpoint	Hardness (mg/L $CaCO_3$)	pH	Temp °C	Alkalinity	DO	Author	Comments*
Mayfly (*E. subvaria*)	16,000	-	4 day	LC50	44.0	7.25	18	40.0	9.2	Warwich and Bell, 1969	Static test over a course of 2 weeks? no test replicates; no control replicates; secondary data
	16,000		96 hr	TLm	44.0	7.25	18	40.0	9.2	Warwich & Bell, 1969	Median tolerance limit; static; secondary data
Daphnia. magna	7,370	Neo-nate	48 hr	EC50	-	8.35	20.4	234	7.93	Kimball, 1978	Static tests; organisms fed; secondary data
	5,990	Neo-nate	48 hr	EC50	-	8.35	20.4	234	7.93	Kimball, 1978	Static tests; organisms unfed; secondary data
	1,860	Neo-nate	96 hr	EC50	-	8.35	20.4	234	7.93	Kimball, 1978	Static; organisms fed; secondary data
	1,620	<24 hr	48 hr	LC50	45.3	7.74	18	42.3	9	Biesinger & Christensen, 1972	Organisms fed; secondary data
	1,110	<24 hr	48 hr	LC50	45.3	7.74	18	42.3	9	Biesinger & Christensen, 1972	Organisms unfed; secondary data
	2,110	Various	24 hr	EC50	245	7.6	13	400	5.6	Khangarot *et al*. 1987	24-h renewal tests; Co conc. appear to be measured; secondary data
	1,490	Various	48 hr	EC50	245	7.6	13	400	5.6	Khangarot *et al*. 1987	24-h renewal tests; Co conc. appear to be measured; secondary data
	3,200	Juvenile	96 hr	LC50	130	7.4	20	93	-	Ewell *et al.*, 1986	Static multispecies bioassay; conc. Not measured; secondary data

Species	Conc. (µg/L)	Life stage	Duration	Endpoint	Hardness (mg/L $CaCO_3$)	pH	Temp °C	Alkalinity	DO	Author	Comments*
D. magna	2,610 (95%, 1,450-5,890)		24 hr	EC50	240	7.6	13			Khangarot & Ray, 1989	No renewal, conc. not measured; immobilization; secondary data
	1,490 (95%, 1,270-2,480)		48 hr	EC50	240	7.6	13	400	5.6	Khangarot & Ray, 1989	No renewal, conc. not measured; immobilization; secondary data
Daphnia Hyalina	1,320 (95%, 1,630-1,070)	Adult	48 hr	EC50	33	7.2	10	29	-	Baudouin & Scoppa, 1974	$CoCl_2$; concentrations not measured; no renewal; secondary data
Cyclops abyssorun	15,500 (95%, 18,800-12,800)	Adult	48 hr	LC50	33	7.2	10	29	-	Baudouin & Scoppa, 1974	$CoCl_2$; concentrations not measured; no renewal; secondary data
Insect (*Eudiaptomus padamus*)	4,000 (95%, 8,000-2,000)	Adult	48 hr	LC50	33	7.2	10	29	-	Baudouin & Scoppa, 1974	$CoCl_2$; concentrations not measured; no renewal; secondary data
Water flea (*Ceriodaphnia dubia*)	2347 4596 4196 >5300	<24 hr old	24 hr	LC50	57 256 476 882	-	20		-	Diamond *et al*., 1992	Static renewal tests; primary data
C. dubia	336			FAV	57	-	-	-	-	Diamond *et al*., 1992	Final Acute Value based on 'all available data'; static renewal tests; primary data

Species	Conc. (μg/L)	Life stage	Duration	Endpoint	Hardness (mg/L $CaCO_3$)	pH	Temp °C	Alkalinity	DO	Author	Comments*
Crayfish (*Austropotamobuis pallipes pallipes*)	8,800	19-32 mm	96 hr	LC50	-	7	-	-	Sat.	Boutet & Chaisemartin, 1973	$CoCl_2$; organisms not moving were considered dead; concentrations measured; secondary data
Crayfish (*Orconectes limosus*)	10,200	19-32 mm	96 hr	EC50	-	7	-	-	Sat.	Boutet & Chaisemartin, 1973	$CoCl_2$; organisms not moving were considered dead; concentrations measured; secondary data
Rotifer (*Philodina acuticornis*)	27,800		24 hr	EC50	25	7.4-7.9	20	24	-	Buikema *et al*., 1984	$CoCl_2$; effect = no visible internal or external movement; secondary data
	183,000		48 hr	EC50	25	7.4-7.9	20	24	-	Buikema *et al*., 1984	$CoCl_2$; effect = no visible internal or external movement; secondary data
	59,000		96 hr	EC50	25	7.4-7.9	20	24	-	Buikema *et al*., 1984	$CoCl_2$; effect = no visible internal or external movement; secondary data
Planarian (*Dugesia tigrina*)	3490 (C.I. 3010-4050)		240 hr	LC50						Solski and Piontek, 1987	$Co(NO_3)_2$; renewal 2X/week; successive generations produced by cutting organisms in two; secondary (unconventional methodologies)
Tubificid worm (*Tubifex tubifex*)	447,710 (95%, 358,990-561,200)		24 hr	EC50	245	7.6	30	400	5.8	Khangarot, 1991	$CoCl_2$; concentrations appear to be measured; immobilization; secondary data
	447,710 (95%, 358,990-561,200)		48 hr	EC50	245	7.6	30	400	5.8	Khangarot, 1991	$CoCl_2$; concentrations appear to be measured; immobilization; secondary data

Species	Conc. (μg/L)	Life stage	Duration	Endpoint	Hardness (mg/L $CaCO_3$)	pH	Temp °C	Alkalinity	DO	Author	Comments*
Tubificid worm	139,320 (95% CL, 113,140-148,790)		96 hr	EC50	245	7.6	30	400	5.8	Khangarot, 1991	$CoCl_2$; concentrations appear to be measured; immobilization; secondary data
	10,000		5 d	Nuclear expansion						Fischer *et al*., 1980	
Flatworm (*Dugesia tigrina*)	25,000	Juvenile	96 hr	LC50	130	7.4	20	93	-	Ewell *et al*., 1986	Static multispecies bioassay; no renewal; conc. not measured; secondary data
Stonefly (*Acroneuria lycorias*)	32,000		8 d	50% survival	44.0	7.25	18	40.0	9.2	Warwich & Bell, 1969	No renewal, concentration measured; secondary data
Caddisfly (*Hydropsyche betteni*)	32,000		7 d	50% survival	44.0	7.25	18	40.0	9.2	Warwich & Bell, 1969	No renewal, concentration measured; secondary data
Amphipod (*Crangonyx pseudogracilis*)	167,000 (95%, 148,000-199,000)		48 hr	LC50	50	6.75	13	50	9.6	Martin & Holdich, 1986	$CoCl_2*6H_2O$; concentrations not measured; secondary data
	39,200 (95%, 35,300-43,300)		96 hr	LC50	50	6.75	13	50	9.6	Martin & Holdich, 1986	$CoCl_2*6H_2O$; concentrations not measured; secondary data

* Primary and secondary data refer to quality of the data. This classification of data is consistent with the CCME (1991) and the Provincial protocols (Singleton *et al*., 1995), and depends upon such factors as: nature of the tests (static versus flow through), measured or unmeasured concentrations, measure of all parameters that may influence toxicity of the substance in question, etc. In general, primary data are preferred for the guideline development.

Table 2: Acute toxicity of cobalt to freshwater vertebrates

Species	Conc. (µg/L)	Life stage	Duration	Endpoint	Hardness (mg/L as $CaCO_3$)	pH	Temp (^oC)	Alkalinity (mg/L)	DO (mg/L)	Author	Comments*
Rainbow trout (*Oncorhynchus mykiss*)	1406 (95%CL 569, 3474)		96 hr	LC50	24.9	7.51	9.9	24.9	8.5	Marr *et al*., 1998	Primary
	533 (95% CL 237, 1201)		96 hr	LC20	24.9	7.51	9.9	24.9	8.5	Marr *et al*., 1998	Primary
Fathead minnow (*Pimephales promelas*)	3,610	Juvenile (8 wk old)	96 hr	LC50	-	8.16	25.4	235	7.02	Kimball, 1978	Static renewal, unmeasured; secondary
P. promelas	>5830	5-15 day	48 hr	LC50	57	-	20		-	Diamond *et al*., 1992	Static renewal; primary
	1245 7280 13733 6200		48 hr	NOEC	57 256 476 882	-	20		-	Diamond *et al*., 1992	Static renewal; primary
P. promelas	48,000	Juvenile	96 hr	LC50	130	7.4	20	93	-	Ewell *et al*., 1986	Static multispecies bioassay; conc. not measured; secondary
	91,900 (95%, 56,300-132,900)		96 hr	LC50	44	7.2-7.9	20	33	-	Curtis & Ward, 1981	$CoBr_2$; conc. measured, no renewal; secondary
Giant gouramis (*Colisa fasciatus*)	225,000	Adult female	96 hr	LC50	120	7.3	25	-	6.4	Srivastava & Agrawal, 1979	Static; secondary

Species	Conc. (µg/L)	Life stage	Duration	Endpoint	Hardness (mg/L as $CaCO_3$)	pH	Temp (^oC)	Alkalinity (mg/L)	DO (mg/L)	Author	Comments*
Clawed frog (*Xenopus laevis*)	1,473 612,905	Embryo	101 hr	EC50 LC50	-	6.8	23	-	-	Sunderman , 1992	teratogenic assay (malformations); static renewal; secondary
	2,475	Embryo	101 hr	LOEC (growth)	-	6.8	23	-	-	Sunderman, 1992	teratogenic assay; secondary

* Primary and secondary data refer to quality of the data. This classification of data is consistent with the CCME (1991) and the Provincial protocols (Singleton *et al*., 1995), and depends upon such factors as: nature of the tests (static versus flow through), measured or unmeasured concentrations, measure of all parameters that may influence toxicity of the substance in question, etc. In general, primary data are preferred for the guideline development.

Table 3: Toxicity of cobalt to freshwater plants

Species	Conc. (µg/L)	Duration	Endpoint	Author	Comments*
Blue-green algae (*Anabaene variabilis*)	5,000–20,000	96 hr	Reduced growth	Ahluwalia & Kaur, 1988	$CoCl_2$, concentration not measured; secondary
	50,000	96 hr	No growth	Ahluwalia & Kaur, 1988	$CoCl_2$, concentration not measured; secondary
Green algae (*Chlorella vulgaris*)	50,000-100,000	96 hr	Reduced growth	Ahluwalia & Kaur, 1988	$CoCl_2$, concentration not measured; secondary
	550	21 d	NOEC	Coleman *et al*., 1971	Three species combined to assess significant differences in % growth; secondary
	1,550	21 d	LOEC	Coleman *et al*., 1971	Three species combined to assess significant differences in % growth; secondary
	1,000	10-14 d	100% growth reduction	Hutchinson, 1973	Concentrations unmeasured, no stats, accurate endpoint not provided; secondary
	522	96 hr	EC50 (growth)	Rachlin & Grosso, 1993	Test conditions, except pH, not provided, combined exposure with Cd and Cu also studied; secondary
	4.2 µg at/L	3–4 mo.	NOEC	den Dooren, 1965	Unknown units; secondary
	8.2 µg at/L	3– 4 mo.	LOEC	den Dooren, 1965	Unknown units; secondary
Algae (*Pediastrum tetras*)	1,550		LOEC	Coleman *et al*., 1971	Three species combined to assess significant differences in % growth; secondary
Algae (*Euglena viridis*)	1,550	21 d	LOEC	Coleman *et al*., 1971	Three species combined to assess significant differences in % growth; secondary
Cyanobacterium (*Anacystis nidulans*)	15,000	10-14 d	Reduced growth	Lee *et al*., 1992	Exact duration not indicated, concentrations not measured; secondary
	30,000	10-14 d	No growth	Lee *et al*., 1992	Exact duration not indicated, concentrations not measured; secondary
Blue-green algae (*Spirulina platensis*)	23,800 (+/-6,400)	96 hr	EC50 (growth)	Sharma *et al*., 1987	$CoCl_2$, static, conc. not measured; secondary
	14,400 (+/-2,100)	120 hr	EC50 (growth)	Sharma *et al*., 1987	$CoCl_2$, static, conc. not measured; secondary

Species	Conc. (µg/L)	Duration	Endpoint	Author	Comments*
Blue-green algae	10,900 (+/-1,500)	144 hr	EC50 (growth)	Sharma *et al*., 1987	$CoCl_2$, static, conc. not measured; secondary
	8,130 (+/-930)	168 hr	EC50 (growth)	Sharma *et al*., 1987	$CoCl_2$, static, conc. not measured; secondary
	12,000	131 hr	TLm	Sharma *et al*., 1987	TLm: Time for biomass to be reduced to 50% of the control at a give concentration; secondary
	4,000	261 hr	TLm	Sharma *et al*., 1987	TLm: Time for biomass to be reduced to 50% of the control at a give concentration; secondary
Haematococcus capensis	5,000	10-14 d	Growth reduction 75%	Hutchinson, 1973	Concentrations not measured, no stats, accurate endpoint not provided; secondary
Chlamydomonas eugametos	500	10-14 d	LOEC (growth)	Hutchinson, 1973	Concentrations not measured, no stats, accurate endpoint not provided; secondary

* Primary and secondary data refer to quality of the data. This classification of data is consistent with the CCME (1991) and the Provincial protocols (Singleton *et al*., 1995), and depends upon such factors as: nature of the tests (static versus flow through), measured or unmeasured concentrations, measure of all parameters that may influence toxicity of the substance in question, etc. In general, primary data are preferred for the guideline development.

Table 4: Chronic toxicity of cobalt to freshwater invertebrates

Species	Conc. µg/L	Life stage	Duration	Endpoint	Hardness mg/L as $CaCO_3$	pH	Temp °C	Alka-linity mg/L	DO mg/L	Author	Comments
Mayfly (*Ephemerella ignita*)	32.6	Nymph	28 days	Growth inhibition, 20% mortality	-	5.6-6.5	17.5	-	-	Sodergren, 1976	Potential for co-contaminants effects; other metals not measured; secondary
	5.2	Nymph	28 days	Emergence inhibition	-	5.6-6.5	17.5	-	-	Sodergren, 1976	Potential for co-contaminants effects; other metals not measured; secondary
	470	Nymph	28 days	100% mortality	-	5.6-6.5	17.5	-	-	Sodergren, 1976	Potential for co-contaminants effects; other metals not measured; secondary
Mayfly (*E. subvaria*)	16,000		96 hr	TLm	44	6.9	18.5	46	8.0	Warwich & Bell, 1969	Median tolerance limit; static; secondary
Water flea (*D. magna)*	27	Life-cycle	28 d	LC50	-	8.36	20.5	204	7.42	Kimball, 1978	$CoSO_4$,; static, renewal, concentration measured; fed; secondary
	10		7 d	NOEC reproduction	-	8.36	20.5	204	7.42	Kimball, 1978	$CoSO_4$,; static, renewal, concentration measured; fed; secondary
	20		7 d	LOEC reproduction	-	8.36	20.5	204	7.42	Kimball, 1978	$CoSO_4$,; static, renewal, concentration measured; fed; secondary
	<4.4	Life-cycle	28 d	NOEC reproduction	-	8.36	20.5	204	7.42	Kimball, 1978	$CoSO_4$,; static, renewal, concentration measured; fed; secondary
	>5.4	Life-cycle	28 d	LOEC reproduction	-	8.36	20.5	204	7.42	Kimball, 1978	$CoSO_4$,; static, renewal, concentration measured; fed; secondary
	2.8 (computed value)	Life-cycle	28 d	NOEC reproduction	-	8.36	20.5	204	7.42	Kimball, 1978	$CoSO_4$,; static, renewal, concentration measured; fed; secondary
	9.3 (computed value)	Life-cycle	28 d	LOEC reproduction	-	8.36	20.5	204	7.42	Kimball, 1978	$CoSO_4$,; static, renewal, concentration measured; fed; secondary

Species	Conc. µg/L	Life stage	Duration	Endpoint	Hardness mg/L as $CaCO_3$	pH	Temp °C	Alka-linity mg/L	DO mg/L	Author	Comments
D. magna	1,860	Neo-nate	96 hr	EC50	-	8.36	20.5	204	7.42	Kimball, 1978	$CoSO_4$,; static, renewal, concentration measured; fed; secondary
	21 (95%, CI 14-31)	<24 hr	21 d	LC50	45.3	7.74	18	42.3	9	Biesinger & Christensen, 1972	secondary
	24	<24 hr	21 d	EC50	45.3	7.74	18	42.3	9	Biesinger & Christensen, 1972	15 % decrease in weight, 12 % increase in protein, 45 % increase in glutamic oxalacetic transaminase; secondary
	10	<24 hr	21 d	EC16 reproduction	45.3	7.74	18	42.3	9	Biesinger & Christensen, 1972	secondary
	12	<24 hr	21 d	EC50 reproduction	45.3	7.74	18	42.3	9	Biesinger & Christensen, 1972	secondary
Water flea (*Ceriodaphnia dubia*)	<50 <50 50 600	neonate	7 d	NOEC	57 256 470 882	-	25	-	-	Diamond *et al*., 1992	Static renewal.; primary
Crayfish (*Austropotamobuis pallipes pallipes*)	770	19-32 mm	30 d	LC50 movement	-	7	16	-	Sat.	Boutet & Chaisemartin, 1973	$CoCl_2$; fed; organisms not moving were considered dead; secondary
	790	19-32 mm	30 d	LC50 movement	-	7	16	-	Sat.	Boutet & Chaisemartin, 1973	$CoCl_2$, Unfed, organisms not moving were considered dead; secondary
Crayfish (*Orconectes limosus*)	790	19-32 mm	30 d	EC50 movement	-	7	16	-	Sat.	Boutet & Chaisemartin, 1973	$CoCl_2$, fed, organisms not moving were considered dead; secondary
	880	19-32 mm	30 d	EC50 movement	-	7	16	-	Sat.	Boutet & Chaisemartin, 1973	$CoCl_2$; Unfed; organisms not moving were considered dead; secondary

Species	Conc. µg/L	Life stage	Duration	Endpoint	Hardness mg/L as $CaCO_3$	pH	Temp °C	Alka-linity mg/L	DO mg/L	Author	Comments
Planarian (*Dugesia tigrina*)	349,000		240 hr	LC50	-	-	20	-	-	Solski & Piontek, 1987	$Co(NO_3)_2$; renewal 2X/week; successive generations produced by cutting organisms in two (unconventional methodologies); secondary
Tubificid worm (*Tubifex tubifex*)	10,000		5 d	Nuclear expansion	-	-	-	-	-	Fischer *et al*., 1980	secondary
Stonefly (*Acroneuria lycorias*)	32,000		8 d	50% survival	50	7.2	18.5	66	8.0	Warwich & Bell, 1969	Static, no renewal, concentration measured
Caddisfly (*Hydropsyche betteni*)	32,000		7 d	50% survival	46	7.0	18.5	46	8.0	Warwich & Bell, 1969	Static, no renewal, concentration measured

* Primary and secondary data refer to quality of the data. This classification of data is consistent with the CCME (1991) and the Provincial protocols (Singleton *et al*., 1995), and depends upon such factors as: nature of the tests (static versus flow through), measured or unmeasured concentrations, measure of all parameters that may influence toxicity of the substance in question, etc. In general, primary data are preferred for the guideline development.

Table 5: Chronic toxicity of cobalt to freshwater vertebrates

Species	Conc. µg/L	Life stage	Dura-tion	End-point	Hardness mg/L as $CaCO_3$	pH	Temp °C	Alka-linity mg/L	DO mg/L	Author	Comments
Rainbow trout (*Oncorhynchus mykiss*)	470 (95% CL 380, 580)	embryo -larval	28 day	LC50	104	7.4	13	-	S	Birge, 1978	Exposure through fertilization and 4 day post hatch; static renewal; probably primary
	490 (95% CL 380, 590)		28 day	LC50	92-110	6.9-7.8	12-13		9.3-10.1	Birge *et al*., 1980	Probably Primary
	120 (95% CL 64, 176)		28 day	LC10	92-110	6.9-7.8	12-13		9.3-10.1	Birge *et al*., 1980	Probably Primary
	34 (95% CL 14, 61)		28 day	LC01	104	7.4	13	-	S	Birge, 1978	Probably Primary
	38 (95% CL 14, 70)		28 day	LC01	92-110	6.9-7.8	12-13		9.3-10.1	Birge *et al*., 1980	Probably Primary
	132 (SD5.6, n=6)		14 day	NOEC (growth & survival)	24.9	7.51	9.9	24.9	8.5	Marr *et al*., 1998	unfed; Co appeared to antagonize Cu toxicity in first 96h; then appeared to be additive; primary
	255 (SD 15.4, n=6)		14 day	LOEC	24.9	7.51	9.9	24.9	8.5	Marr *et al*., 1998	Primary
	520 (95% CL 286, 945)		144 hour	LC50	24.9	7.51	9.9	24.9	8.5	Marr *et al*., 1998	Primary
	346 (95% CL 180, 670)			ILL (50% mortality)	24.9	7.51	9.9	24.9	8.5	Marr *et al*., 1998	Incipient lethal level; primary
	228 (95% CL 99, 522)		144 hr	LC20	24.9	7.51	9.9	24.9	8.5	Marr *et al*., 1998	Primary
	145 (95% CL 49, 395)			ILL (20% mortality)	24.9	7.51	9.9	24.9	8.5	Marr *et al*., 1998	Incipient lethal level; primary

Species	Conc. µg/L	Life stage	Dura-tion	End-point	Hardness mg/L as $CaCO_3$	pH	Temp °C	Alka-linity mg/L	DO mg/L	Author	Comments
Goldfish (*Carassius auratus*)	810 (95% CL 270, 2270)	embryo -larval	7 day	LC50	195	7.4	22	-	S	Birge, 1978	Exposure through fertilization and 4 day post hatch; static renewal; primary
	6.8 (95% CL 0.0, 42.6)		7 day	LC01	195	7.4	22	-	S	Birge, 1978	Primary
Narrow-mouthed toad (*Gastrophryne carolinensis*)	50 (95% CL 20,80)	embryo -larval	7 day	LC50	195	7.4	22	-	S	Birge, 1978	Exposure through fertilization and 4 day post hatch; static renewal; primary
	0.9 (95% CL 0.3-2.0)		7 day	LC01	195	7.4	22	-	S	Birge, 1978	Primary
Fathead minnow (*Pimephales promelas*)	210	embryo -larval	28 day	NOEC (growth)	220	8.14	24.4	236	6.88	Kimball, 1978	Secondary
	390	embryo -larval	28 day	LOEC (growth)	220	8.14	24.4	236	6.88	Kimball, 1978	Secondary
	810	embryo -larval	28 day	NOEC (survival)	220	8.14	24.4	236	6.88	Kimball, 1978	Secondary
	1,610	embryo -larval	28 day	LOEC (survival)	220	8.14	24.4	236	6.88	Kimball, 1978	Secondary
	2,740	8 wk old	192 hr	LC50						Kimball, 1978	Secondary
	1232 1794 1932 〈3833		7 day	NOEC	57 256 476 882		25			Diamond *et al*., 1992	Static renewal; primary

Species	**Conc. µg/L**	**Life stage**	**Dura-tion**	**End-point**	**Hardness mg/L as $CaCO_3$**	**pH**	**Temp °C**	**Alka-linity mg/L**	**DO mg/L**	**Author**	**Comments**
Clawed frog (*Xenopus laevis*)	1,473	embryo	101 hr	EC50 (mal-formations)	-	6.8	23	-	-	Sunderman, 1992	Frog embryo teratogenic assay, media changed at 29, 53, 75 hours; secondary
	612,905	embryo	101 hr	LC50	-	6.8	23	-	-	Sunderman, 1992	Frog embryo teratogenic assay; secondary
	2,475	embryo	101 hr	LOEC (growth)	-	6.8	23	-	-	Sunderman, 1992	Frog embryo teratogenic assay; secondary
Stickleback (*Gasterosteus aculeatus*)	10,000	3.5 cm	10 d	NOEC (survival)	-	-	-	-	-	Jones, 1939	Secondary
Zebrafish (*Brachydanio rerio*)	60	embryo & larval	13 d	NOEC	100	7.5	26	-	S	Dave & Xiu, 1991	Embryo-larval toxicity test; secondary

* Primary and secondary data refer to quality of the data. This classification of data is consistent with the CCME (1991) and the Provincial protocols (Singleton *et al*., 1995), and depends upon such factors as: nature of the tests (static versus flow through), measured or unmeasured concentrations, measure of all parameters that may influence toxicity of the substance in question, etc. In general, primary data are preferred for the guideline development.

Table 14: Acute toxicity of cobalt to marine organisms

Species	Conc. (µg/L)	Life stage	Dura-tion	End-point	pH	Temp (^{o}C)	Sali-nity (%)	DO (mg/L)	Author	Comments
Harpacticoid Copepod (*Nitocra spinipes*)	4,500 (95% CI, 3,000-6,800)	Adult	96 hr	LC50	8.0	20	7	-	Bengtsson, 1978	Static, brackish water (alkalinity 1.5 meq/L), no renewal, unknown if Co measured; secondary
Diatom (*Nitzschia closterium*)	10,200 (+/- 164)		96 hr	EC50 (growth)	8.0-8.1	15.5	~37%	-	Rosko & Rachlin, 1975	Non-chelating media, Co not measured; secondary
	23,600 (+/- 277)		96 hr	EC50 (growth)	6.7-6.9	15.5	~37%	-	Rosko & Rachlin, 1975	Chelating media, Co not measured; secondary
Diatom (*Ditylum brightwellii*)	300 ppb		unclear	EC50 (growth)	-	-	Sea water	-	Canterford & Canterford, 1980	Methods not described well. Not known if concentrations analysed, 6.7 x10^{-7} M EDTA; secondary
Nematode (*Monhystera disjuncta*)	94,000 (95% CI, 40,000-220,000)	Juvenile stage 2 larvae	96 hr	LC50	7.5-8.0	17	30	-	Vranken *et al.*, 1991	Other test conditions not specified, concentrations not measured; secondary
	10,000	Juvenile stage 2 larvae	96 hr	MEC	7.5-8.0	17	30	-	Vranken *et al.*, 1991	Minimum Effective Concentration, other test conditions not specified, concentrations not measured; secondary
Fish (*Therapon jarbua*)	52,500 25,000 20,000	Juvenile (length 2.4-3.6 cm, weight 0.2-0.7 g)	96 hr	LC50 LC10 NOEC	-	-	Sea water	4 ml/L	Krishnakumari *et al.*, 1983	Static, continuous slow aeration, $CoSO_4*6H_2O$, unknown if concentrations measured, test conditions not indicated; secondary

Species	Conc. (µg/L)	Life stage	Dura-tion	End-point	pH	Temp (^{o}C)	Sali-nity (%)	DO (mg/L)	Author	Comments
Lobster (*Homarus vulgaris*)	225-450 4,500-9,000 4,500-22,500	Larvae (stage 1) (stage 2) (stage 3)	96 hr	LC50	7.4-7.8	22	Sea water	-	Amiard, 1976	$CoCl_2$, unfed, no aeration, exact LC50 not calculated, high mortality for controls; secondary
Crab (*Carcinus maenas*)	225,000-450,000 22,500	Adult Larvae	96 hr	LC50	7.4-7.8	15	Sea water	-	Amiard, 1976	$CoCl_2$, unfed, no aeration, exact LC50 not calculated, high mortality for controls; secondary
Shrimp (*Palaemon serratus*)	225,000-450,000 22,500-45,000	Adult Larvae	96 hr	LC50	7.4-7.8	15	Sea water	-	Amiard, 1976	$CoCl_2$, unfed, no aeration, exact LC50 not calculated, high mortality for controls; secondary
Maia squinado	<4,500	Larvae	96 hr	LC50	7.4-7.8	15	Sea water	-	Amiard, 1976	$CoCl_2$, unfed, no aeration, exact LC50 not calculated, high mortality for controls; secondary
Teleost (*Blennius pholis*)	450,000-675,000	Adult	96 hr	LC50	7.4-7.8	15	Sea water	-	Amiard, 1976	$CoCl_2$, exact LC50 not calculated, high mortality for controls; secondary
Teleost (*Pleuronectes platessa*)	450,000-675,000	Adult	96 hr	LC50	7.4-7.8	15	Sea water	-	Amiard, 1976	$CoCl_2$, exact LC50 not calculated, high mortality for controls; secondary

* Primary and secondary data refer to quality of the data. This classification of data is consistent with the CCME (1991) and the Provincial protocols (Singleton *et al*., 1995), and depends upon such factors as: nature of the tests (static versus flow through), measured or unmeasured concentrations, measure of all parameters that may influence toxicity of the substance in question, etc. In general, primary data are preferred for the guideline development.

Table 15: Chronic toxicity of cobalt to marine organisms

Species	Conc. (µg/L)	Life stage	Dura-tion	End-point	pH	Temp (^{o}C)	Salinity (%)	DO (mg/L)	Author	Comments
Isopod (*Idotea baltica*)	10,000	6-8 mm	1248 hr	LC50	8.0	22.3	37.62	5.19 ml/l	El-Nady & Atta, 1996	LT50 type tox test, static renewal at 48 hrs, Co measured, methods not described well; secondary
Diatom (*Ditylum brightwellii*)	300		Unclear; ~5 d	EC50 (growth)	-	-	Sea water	-	Canterford & Canterford, 1980	Methods not described well. Not known if concentrations analysed, 6.7 x10^{-7} M EDTA; secondary
Lobster (*Homarus vulgaris*)	225 450 450-4,500	Larvae (stage 1) (stage 2) (stage3)	216 hr	LC50	7.4-7.8	15	Sea water	-	Amiard, 1976	$CoCl_2$, unfed, no aeration, exact LC50 not calculated, high mortality for controls; secondary
Crab (*Carcinus maenas*)	225,000-450,000 45,000	Adult Larvae	216 hr	LC50	7.4-7.8	15	Sea water	-	Amiard, 1976	$CoCl_2$, unfed, no aeration, exact LC50 not calculated, high mortality for controls; secondary
Shrimp (*Palaemon serratus*)	45	Larvae	216 hr	LC50	7.4-7.8	15	Sea water	-	Amiard, 1976	$CoCl_2$, unfed, no aeration, exact LC50 not calculated, high mortality for controls; secondary
Teleost (*Blennius pholis*)	225,000	Adult	216 hr	LC50	7.4-7.8	15	Sea water	-	Amiard, 1976	$CoCl_2$, unfed, no aeration, exact LC50 not calculated, high mortality for controls; secondary

* Primary and secondary data refer to quality of the data. This classification of data is consistent with the CCME (1991) and the Provincial protocols (Singleton *et al.*, 1995), and depends upon such factors as: nature of the tests (static versus flow through), measured or unmeasured concentrations, measure of all parameters that may influence toxicity of the substance in question, etc. In general, primary data are preferred for the guideline development.

Table 16: Toxicity of cobalt to terrestrial plants and animals

Species	Conc. (µg/L)	Life stage	Dura-tion	Endpoint	Author	Comments
PLANTS						
Broad bean (*Vicia faba*)	2,000	Seed/ seedling	72 hours	58% increase in radicle length; no effect on germination	Misra *et al.*, 1994	$CoCl_2$; Temp.= 25+/-2 °C during 16 hour photoperiod and 20+/-2 °C during 8 hour dark period; relative humidity 60%; 5 replicates per treatment; 31% increase in radicle length in combination with Cd, Ni and Zn at same concentration
	4,000	Seed/ seedling	72 hours	34 % increase in radicle length; no effect on germination	Misra *et al.*, 1994	$CoCl_2$; Temp.= 25+/-2 °C during 16 hour photoperiod and 20+/-2 °C during 8 hour dark period; relative humidity 60%; 5 replicates per treatment; 47% increase in radicle length in combination with Cd, Ni and Zn at same concentration
	6,000	Seed/ seedling	72 hours	18% increase in radicle length; no effect on germination	Misra *et al.*, 1994	$CoCl_2$; Tem.= 25+/-2 C during 16 hour photoperiod and 20+/-2 °C during 8 hour dark period; relative humidity 60%; 5 replicates per treatment; 4% decrease in radicle length in combination with Cd, Ni and Zn at same concentration
	8,000	Seed/ seedling	72 hours	No effect on radicle length or germination	Misra *et al.*, 1994	$CoCl_2$; Temp.= 25+/-2 °C during 16 hour photoperiod and 20+/-2 °C during 8 hour dark period; relative humidity 60%; 5 replicates per treatment; 44% decrease in radicle length in combination with Cd, Ni and Zn at same concentration
	10,000	Seed/ seedling	72 hours	No effect on radicle length or germination	Misra *et al.*, 1994	$CoCl_2$; Temp.= 25+/-2 °C during 16 hour photoperiod and 20+/-2 °C during 8 hour dark period; relative humidity 60%; 5 replicates per treatment; 70% decrease in radicle length in combination with Cd, Ni and Zn at same concentration

Species	Conc. (µg/L)	Life stage	Dura-tion	Endpoint	Author	Comments
Bush bean (*Phaseolus vulgaris* L. cv. Improved Tendergreen)			21 days	16% decrease in yield of trifoliate leaves	Wallace & Abo-Zamzam, 1989	Actual yield for combination with Cu, Zn, Cd, Ni relative to control greater for combination with Cu, Zn, Cd, Ni than predicted relative yield based on multiplication of components.
Native soil microflora	1,362,000	-	24 days	32 % reduction in respiration	Lighthart *et al*., 1977	Native soil microflora in coniferous forest soil/ litter microcosm
Bush bean	60		21 days	22% reduction in leaf dry weight	Wallace *et al*., 1977	
Chrysan-themum	60	Seedling	21 days	55% reduction in seedling root weight	Patel *et al*., 1976	
Honey-suckle	5,000	seedling	5 to 21 days	35 % reduction in radicle elongation	Patterson and Olsen, 1983	pH 5 to 6
Paper birch	5,000	seedling	5 to 21 days	47 % reduction in radicle elongation	Patterson and Olsen, 1983	pH 5 to 6
White pine	100,000	seedling	5 to 21 days	53 % reduction in radicle elongation	Patterson and Olsen, 1983	pH 5 to 6
ANIMALS						
CD-1 mice	400,000	Adult	13 weeks	Reduction in body, testicular weight (70 %), epididymal sperm concentration (92 %), percent motile sperm (72 %) and fertility	Pedigo *et al*., 1988	$CoCl_2$ administered in drinking water *ad libitum*.

Species	Conc. (µg/L)	Life stage	Dura-tion	Endpoint	Author	Comments
CD-1 mice	200,000	Adult	13 weeks	Reduction in testicular weight (58 %), epididymal sperm concentration (71 %)	*Pedigo et al.*, 1988	$CoCl_2$ administered in drinking water ad libitum.
	100,000	Adult	13 weeks	Reduction in testicular weight (25 %), epididymal sperm concentration (34 %)	*Pedigo et al.*, 1988	$CoCl_2$ administered in drinking water ad libitum.
Rats	2,300		7 months		Krasovskii & Fridlyand, 1971	$CoCl_2$ administered in water solution 6 day/week at a dose of 0.5 mg/kg. Stimulation of erythrocyte and hemoglobin formation and production of larger diameter erythrocytes; suppression of phagocytic activity of white cells; negative effects on reflex learning
Albino rats	100,000	young	35 days		Smith & Carson 1981	Young male albino rats were given (a) water only, (b) water + 10% ethanol, (c) 1 mg Co as $CoCl_2$ per 10 mL water, and (d) the cobalt + the ethanol. Cobalt + ethanol depressed the growth rate and reduced wet and dry heart weights more than either Co or ethanol alone.

Figure 1: Distribution of Endpoint Concentrations for Acute Freshwater Aquatic Life Cobalt Toxicity Tests

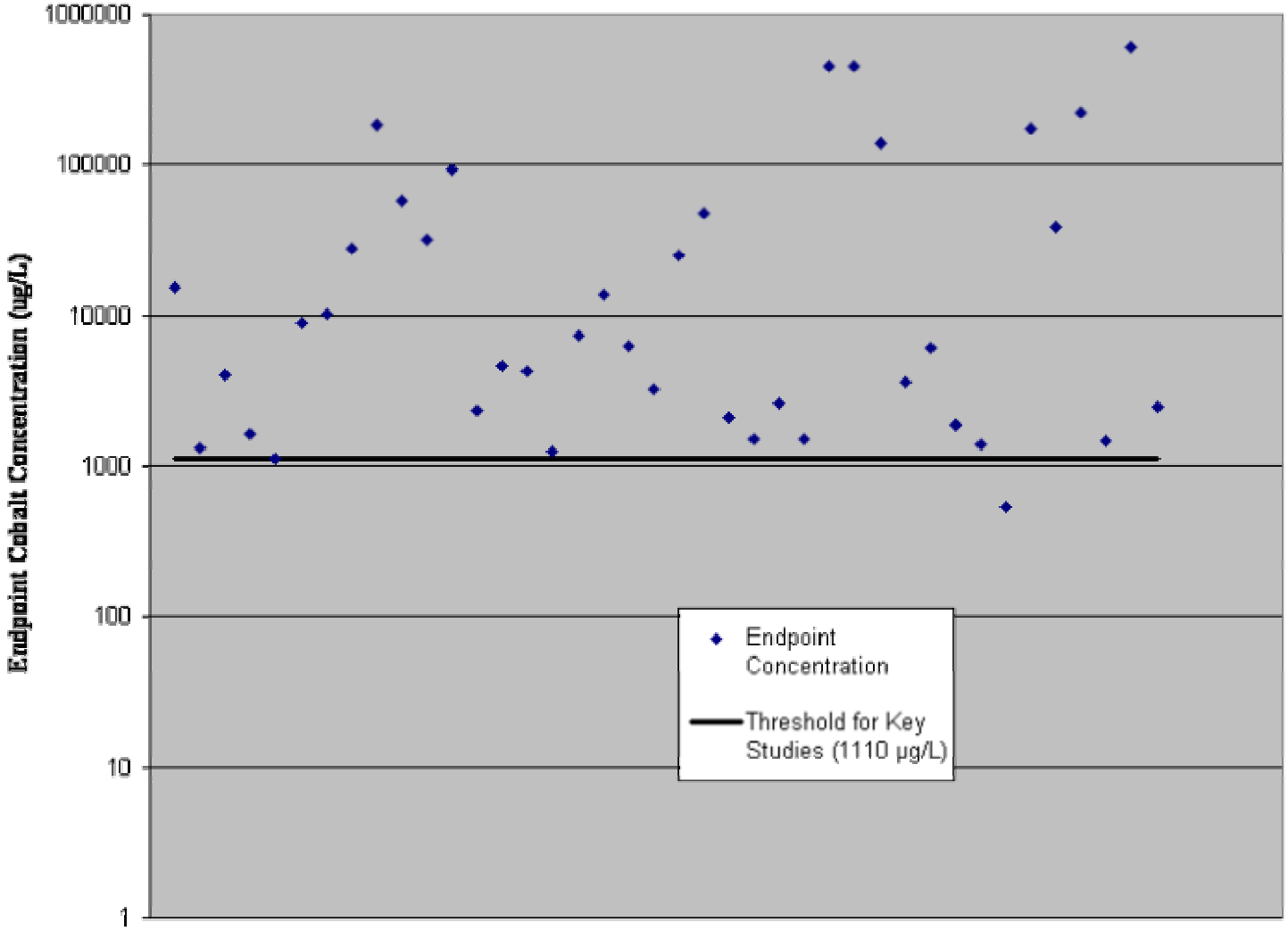

Figure 2: Distribution of Endpoint Concentrations from Chronic Freshwater Aquatic Cobalt Toxicity Tests