# **APPENDIX 7.VII**

Site-specific Water Quality Objectives

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## 7.VII.1 INTRODUCTION

The Terms of Reference (TOR) for the NICO Cobalt-Gold-Bismuth-Copper Project (NICO Project) developed by the Mackenzie Valley Review Board (MVRB) note that site-specific water quality objectives (SSWQOs) are to be proposed for all contaminants of potential concern (COPC) identified for the NICO Project to protect downstream water quality (MVRB 2009). This appendix details the approach used to develop the SSWQOs and provides preliminary objectives for consideration by the NICO Project team. Aluminum, ammonia, antimony, arsenic, cadmium, chloride, cobalt, copper, iron, lead, nitrate, selenium, sulphate, uranium, and zinc have been identified as COPCs because their predicted surface water concentrations during and/or post Site operations are greater than baseline conditions and/or the Canadian Council of Ministers of the Environment (CCME) Canadian water quality guidelines (CWQGs) for the protection of freshwater aquatic life.

## 7.VII.2 APPROACH TO DEVELOPMENT OF SITE-SPECIFIC WATER QUALITY OBJECTIVES

The approach to the development of SSWQOs described herein is adopted from the approaches developed by the CCME and provincial agencies in the development of the CWQGs. The approach is based on the overall objective of the CWQGs for the protection of aquatic life: *to be protective of the most sensitive species, in the most sensitive life stage, over an indefinite period of exposure,* and the policy objectives and guiding principles as described in the Mackenzie Valley Land and Water Board & Effluent Quality Management Policy, dated 29 April 2010, and the effluent discharge limits for mining projects in the Northwest Territories (NWT) (INAC 2009).

The CWQGs are developed in consideration of the end water use, and protection of aquatic life is generally considered to be the most sensitive end use. The CCME has also developed drinking water guidelines, though these are generally less stringent, since these are based on consumption patterns.

The numerical CWQGs for the protection of aquatic life are considered generic, since they are intended for application in all regions of Canada and do not, in most cases, make allowance for regional differences (although the CCME [2003a] has provided methods for calculating site-specific objectives). Guidelines based on bulk water concentrations of metals can be overly conservative in some situations, due to the influence of local physico-chemical factors and the presence of natural complexing ligands. These include the presence of calcium and magnesium ions, as well as sodium ions that can effectively reduce metal toxicity in aquatic biota through competitive interactions at uptake sites, and natural complexing ligands such as the ubiquitous humic and fulvic material from plant decomposition that can reduce the bioavailable portion of a metal. As well, sulphides can reduce the bioavailable portion of a metal. Traditionally, it has been assumed that sulphides are negligible in oxygenated waters; however, recent evidence suggests concentrations can be appreciable in both marine and freshwater environments. Sulphide has a strong affinity for many metals and is therefore an important consideration in determining metal speciation and bioavailability. In other cases the reverse may also be true. Where concentrations of the biologically active forms of a metal are high due to a paucity of competing ions or complexing ligands, or ingestion is a significant pathway, the guidelines may be under-protective.

The CWQGs for the protection of aquatic life are generally based on laboratory toxicity tests using laboratory or reconstituted water to which the metal is introduced in a highly soluble (and bioavailable) form. It is extremely difficult to simulate under laboratory conditions the variations in natural conditions that would reflect the influence of materials such as naturally occurring ligands on metal availability. As a result, in the laboratory tests used to





develop the generic guidelines, the concentrations of a metal will typically exert a more profound effect on the organisms being tested than is likely to be the case within a natural setting. Due to the diverse geologic conditions within Canada, the natural distribution of metals, ions and organic matter can be highly variable. Therefore, site-specific approaches to setting water quality guidelines have been developed to reflect this variability by incorporating into the guidelines locally occurring factors that can affect bioavailability and toxicity. For example, the CWQGs for the protection of aquatic life for copper and lead allow for the derivation of a site-specific guideline based on site water hardness.

Because direct toxicity tests cannot be undertaken for the NICO Project at this time, the development of sitespecific objectives relied upon the existing water quality data in adjacent waterbodies to characterize levels of naturally occurring ions and ligands, and a review of the toxicity data from a variety of literature sources. In particular, recent studies in the scientific literature that have characterized levels of calcium, magnesium, and dissolved organic carbon (DOC) with respect to their influence on the toxicity of specific metals were considered. Recent studies on copper, for example, have shown that the presence of these parameters can significantly increase the concentrations at which copper becomes toxic to test organisms. While the roles of competing ions (sodium, calcium, and magnesium) and complexing ligands (such as DOC) in reducing metal toxicity have been studied extensively for some metals, sulphide is only beginning to be investigated. Still, results suggest that sulphide can significantly reduce the toxicity of metals (such as copper) to aquatic life. The availability of this type of data, therefore, permitted an approach that incorporated naturally occurring parameters that reduce toxicity into the development of SSWQOs for the NICO Project.

Based on this understanding, the development of SSWQOs for the NICO Project was generally conducted through the following step-wise approach:

- available toxicity literature was reviewed to characterize biological effect levels that correspond to concentrations of toxicity modifying parameters specific to each metal of concern;
- existing water quality was characterized with respect to these substances in Nico Lake and Peanut Lake;
- baseline aquatic ecology data was reviewed to identify species of aquatic biota that are present within Nico Lake and Peanut Lake; and
- site-specific toxicity concentrations were developed for each metal of concern that are protective of the most sensitive receptor in Nico Lake and Peanut Lake.

The SSWQOs provided herein have been derived for the potential discharge receivers (i.e., Nico Lake and Peanut Lake). Potential impacts on Burke Lake and the Marian River will be assessed relative to appropriate toxicity reference values that will be derived on a similar basis to the SSWQOs in the aquatic risk assessment for the NICO Project.

## 7.VII.3 SITE-SPECIFIC WATER QUALITY OBJECTIVES

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The specific approaches used to derive the SSWQOs for the identified COPCs is detailed in the following sections. Table 7.VII.3-1 summarizes the proposed SSWQOs for the identified COPCs for Nico Lake and Peanut Lake.





COPC	CCME CWQG for the Protection of Aquatic Life <sup>a</sup> (µg/L)	Site-Specific Water Quality Objective (µg/L)	
		Nico Lake	Peanut Lake
Aluminum	100 <sup>b</sup>	420 (dissolved aluminum)	410 (dissolved aluminum)
Ammonia	ia 1100 (μg-N/L) <sup>c</sup> 4160 (μg-N/L)		ug-N/L)
Antimony	NV	30	
Arsenic	5	50	
Cadmium	0.017 <sup>d</sup>	0.15	
Chloride	NV	353 000	
Cobalt	NV	10	
Copper	2 <sup>e</sup>	25 (dissolved copper)	22 (dissolved copper)
Iron	300 1500		00
Lead	1 <sup>e</sup>	7.6	
Nitrate	13 000	133 000	
Selenium	1	5.0	
Sulphate	NV	500 000	
Uranium	NV	27	
Zinc	30	110	

Table 7.VII.3-1: Proposed Site-Specific Water Quality Objectives for the NICO Project

<sup>a</sup> Canadian Council of Ministers of the Environment (CCME) Canadian Water Quality Guideline (CWQGs) for the Protection of Aquatic Life.

<sup>b</sup> Based on the guideline for a pH of  $\geq$ 6.5.

<sup>c</sup> Based on a temperature of 7 <sup>o</sup>C and a pH of 8.

<sup>d</sup> Based on a water hardness of 47 mg/L as CaCO<sub>3</sub>.

<sup>e</sup> The minimum CCME CWQG, regardless of water hardness.

NV = No guideline value; COPC = contaimants of potential concern;  $\mu g/L$  = microgram per litre

## 7.VII.3.1 Aluminum

The CCME guideline for aluminum is based on pH, as provided below (CCME 2007):

Aluminum guideline = 5 micrograms per litre ( $\mu$ g/L) at pH <6.5

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= 100 µg/L at pH ≥6.5

The guideline was divided based on pH in consideration of the work by Neville (1985; as cited in CCREM 1987) who demonstrated that at a pH of 6.1 the physiological response of juvenile rainbow trout to 75  $\mu$ g/L aluminum is severe but minimal at a pH of 6.5. A guideline of 5  $\mu$ g/L, which is based on a no observed effect concentration (NOEC) for the toad (*Bufo americanus*), was recommended for waters with a pH below 6.5 (Clark and LaZerte 1985; as cited in CCREM 1987). *Bufo americanus* is not known to occur in the NWT. A guideline of 100  $\mu$ g/L was recommended for waters with a pH equal to or greater than 6.5 based on a value first proposed by the United States Environmental Protection Agency (U.S. EPA) (1973; as cited in CCREM 1987).

The objective for aluminum has been derived using the equation that is currently used by the British Columbia Ministry of Environment, Lands and Parks to derive water quality guidelines for dissolved ammonia at a pH of less than 6.5 (BCMELP 1994), as follows:





Dissolved aluminum benchmark (mg/L) =  $e^{(1.6-3.327 \text{ pH} + 0.402 \text{ K})}$ 

Where:

 $K = pH^2$ 

In Peanut Lake, the average pH is 7.44. In Nico Lake, the average pH is 7.45. Using the equation provided above, values of 0.41 milligrams per litre (mg/L) and 0.42 mg/L dissolved aluminum are calculated for Nico Lake and Peanut Lake, respectively. These values are proposed as the SSWQOs for aluminum for Nico Lake and Peanut Lake. The objectives derived for dissolved aluminum can be conservatively applied to total aluminum.

## 7.VII.3.2 Ammonia

In surface waters, ammonia exists as 2 chemical species: unionized ammonia ( $NH_3$ ) and ionized ammonia (or ammonium ion,  $NH_4^+$ ). The sum of  $NH_3$  and  $NH_4^+$  is termed "total ammonia". In surface waters a chemical equilibrium exists between unionized and ionized ammonia, which is highly dependent on temperature and pH. For example, an increase in pH by one unit can increase the unionized ammonia concentration nearly tenfold. A temperature increase of 5 degrees Celsius (°C) can increase the unionized ammonia concentration by 40 to 50%.

Unionized ammonia is more toxic to aquatic organisms than the ammonium ion. This is because unionized ammonia is a neutral molecule so it is able to more easily diffuse across biological membranes and exert toxicity as compared to the ammonium ion.

The CWQG for ammonia for the protection of aquatic life was developed using the CCME protocol (CCME 1991; as cited in CCME 2010) and the community ecological risk criteria from Environment Canada (1999; as cited in CCME 2010). The rainbow trout (*Oncorhynchus mykiss*) was the most sensitive freshwater species identified by the CCME, with a lowest observed effect concentration (LOEC) of 0.04 mg/L for unionized ammonia in a 5 year (chronic) study. Exposure to this and higher concentrations resulted in lesions on the gills and kidney tissue degradation (Thurston et al. 1984; as cited in CCME 2010). Using 13 sublethal endpoints (EC<sub>20</sub> values) for various freshwater species (including invertebrates and fish but not mussels of the family Unionidae, discussed further below) and a regression-based approach, Environment Canada showed that 5% of the species in an aquatic community would exhibit a 20% reduction in growth or reproduction at an unionized ammonia concentration of 0.041 mg/L (Environment Canada 1999; as cited in CCME 2010). This value (0.041 mg/L) is consistent with the value reported by the CCME (0.04 mg/L) for the sensitive rainbow trout. Environment Canada went on to predict 95% confidence intervals for the toxicity data which were 0.019 to 0.063 mg/L. The CCME adopted the lower 95% confidence limit of 0.019 mg/L as the guideline for unionized ammonia.

The CCME also provides a guideline for total ammonia (as  $mg/L NH_3$ ). The guideline is a range of values over various pHs and temperatures (CCME 2010). The range of values is based upon the guideline for unionized ammonia of 0.019 mg/L and equations developed by others which calculate the concentration of unionized ammonia based on pH and temperature (Emerson et al. 1975; U.S. EPA 1998; as cited in CCME 2010). This was done in consideration of the influence of pH and temperature on the chemical speciation of ammonia (and hence toxicity to aquatic life) and the variability of pH and temperature in surface waters on a national level.

Recently, the U.S. EPA updated the freshwater national ambient water quality criteria (NAWQC) for ammonia (U.S. EPA 2009a). This is because recent toxicity tests indicated that ammonia is particularly toxic to freshwater



mussel species in the family Unionidae. There was concern that the acute and chronic AWQC for ammonia were not adequately protective of freshwater mussels which are found in many waters of the United States. At a pH of 8 and a temperature of 25 °C, a chronic criterion of 0.26 mg total ammonia-N/L or 1.8 mg total ammonia-N/L is proposed by the U.S. EPA, depending on whether freshwater mussels are present in the waterbody of concern.

Site-specific water quality objectives for ammonia for Nico Lake and Peanut Lake have been derived from the guideline for total ammonia (mg total ammonia-N/L) developed by the U.S. EPA based on pH and temperature (U.S. EPA 2009a). In brief, water quality objectives for ammonia were derived from the series of historical pH and temperature observations available for Nico Lake and Peanut Lake assuming that freshwater mussels are absent in the study area. Only 2 species of freshwater mussels are found in the NWT. The fatmucket (*Lampsilis siliquoidea*) is found in southern NWT and the giant floater (*Pyganodon grandis*) can be found at Shell Lake near Inuvik and may be found across the NWT (Working Group on General Status of NWT Species 2006). Both species belong to the family Unionidae, which as described above are the most sensitive freshwater species to ammonia. The Aquatic Baseline Report (Annex C) for the NICO Project did not identify these species (or any other species of freshwater mussel) in either Nico Lake or Peanut Lake.

Specifically, water quality objectives for ammonia were derived based on the average temperature and pH of the historical pH and temperature observations. For Nico Lake, the average temperature and pH were 11.5 °C and 7.45, respectively. For Peanut Lake, the average temperature and pH were 11.3 °C and 7.44, respectively. Based on these measurements, the SSWQOs are 4.16 mg total ammonia-N/L for both Nico Lake and Peanut Lake.

## 7.VII.3.3 Antimony

The CCME has not derived a CWQG for antimony for the protection of freshwater aquatic life. Antimony has been identified as a COPC and a site-specific objective has been derived for this metal because predicted concentrations are greater than baseline conditions.

Data on the chronic toxicity of antimony to freshwater aquatic life is limited. The U.S. EPA reported a 96-h EC50 (median effect concentration) (chlorophyll) for the green alga *Selenastrum capricornutum* of 730  $\mu$ g/L (1978; as cited in the U.S. EPA ECOTOX Database). In a life-cycle test with the cladoceran *Daphnia magna*, a 28-d LC50 (median lethal concentration) of 4510  $\mu$ g/L was calculated for exposure to antimony trichloride in water of hardness 220 mg/L as CaCO<sub>3</sub> (Kimball 1978; as cited in the U.S. EPA ECOTOX Database). There were no effects on reproduction at 4160  $\mu$ g/L but there was a significant decrease in the number of progeny at 7050  $\mu$ g/L. A maximum acceptable toxicant concentration (MATC) of 5420  $\mu$ g/L was calculated.

Chronic studies for vertebrates include 28-d LC50 values for rainbow trout (*Oncorhynchus mykiss*) eggs of 580 and 660  $\mu$ g/L (Birge 1978; Birge et al. 1980; as cited in the U.S. EPA ECOTOX Database). In aquatic toxicity tests with fathead minnow (*Pimephales promelas*) eggs, growth was the most sensitive endpoint (Kimball 1978; as cited in the U.S. EPA ECOTOX Database). The 28-d LOEC for effects on growth (length) was 2310  $\mu$ g/L. There were no significant effects on growth at 1130  $\mu$ g/L. The MATC was calculated to be 1620  $\mu$ g/L. Birge (1978; as cited in the ECOTOX Database) conducted studies on the mortality of antimony trichloride on embryo-larval stages of the toad *Gastrophryne carolinensis*. The calculated LC50 for the toad was 300  $\mu$ g/L.

The Ontario Ministry of Environment (MOE) has derived an aquatic protection value for antimony of 1600 µg/L based on a final chronic criterion provided by the U.S. EPA (1986; as cited in MOE 2009).

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The U.S. EPA provides a draft freshwater national ambient water quality criteria for antimony of 30  $\mu$ g/L (U.S. EPA 1988a). In brief, the final acute value of 175  $\mu$ g/L was divided by an acute-to-chronic ratio (ACR) of 5.871 to derive a final chronic value of 30  $\mu$ g/L.

A SSWQO for antimony of 30  $\mu$ g/L is proposed based on the draft freshwater ambient water quality criteria for antimony provided by the U.S. EPA (1988a). Predicted antimony concentrations in surface water do not exceed the guideline values described above.

## 7.VII.3.4 Arsenic

Arsenic and its compounds are widely distributed in the environment primarily in 2 oxidation states; arsenite (trivalent, III) and arsenate (pentavalent, V). Arsenic is a hazardous element and toxicity may occur even when biota are exposed to trace concentrations via ingestion or direct uptake across membranes (e.g., gill surfaces). The toxic effects are mediated through the trivalent (arsenite) form. Pentavalent arsenic (arsenate) forms are believed to be reduced to trivalent forms in vivo (Thomas et al. 2001). The main mode of arsenic toxicity is inhibition of enzyme activity by binding to the sulfhydryl groups (-SH) which inhibits succinic dehydrogenase activity, thereby uncoupling oxidative phosphorylation (Ellenhorn and Barceloux 1988). Arsenic is also substituted for phosphorus in the oxidative phosphorylation chain, further increasing the loss of production of high-energy phosphate bonds in ATP, which causes widespread multisystem effects (Thomas et al. 2001).

The speciation of arsenic in freshwater is strongly controlled by redox potential of the medium while the availability is influenced by the presence of iron oxyhydroxides (Senn and Hemond 2004), which have been shown to be effective scavengers of arsenic, rendering the latter unavailable for bioactive interactions with aquatic organisms. The presence of natural organic matter has also been shown to strongly influence arsenic mobility in freshwater (Redman and Macalady 2003). It has been generally found that arsenite is sorbed to, and co-precipitates with other metal sulphides while arsenate typically sorbs to iron and aluminum hydroxides (Senn and Hemond 2004). Arsenic can also be biologically transformed to methyl species, with bacteria acting as mediating agents (Faust et al. 1987). Arsenite reduction is reportedly mediated by bacteria, fungi, and algae (Faust et al. 1987).

Some studies (Senn and Hemond 2004) have indicated that arsenic released to overlying water from sediments occurs predominantly complexed to particulate matter. Arsenic in the water column also exhibits a strong affinity for particulate organic matter (operationally defined as organic matter larger than the 0.45  $\mu$ m filter pore size), and complexation with dissolved and particulate organic matter are responsible for removal of most arsenic in surface waters.

The CCREM (1987) notes that humans are more sensitive to arsenic than fish, and the recommended arsenic concentration for raw water supplies (50  $\mu$ g/L) was therefore lower than the recommended limit of 100  $\mu$ g/L for protection of aquatic life proposed by the MOE (MOE 1984). The freshwater aquatic life guideline was subsequently revised to 5  $\mu$ g/L, based on the results of a chronic algal bioassay, which was the most sensitive endpoint measured (CCME 2001). The CCME guideline is based on growth reduction (as an EC<sub>50</sub>, over a 14-day exposure) in the green algae *Scenedesmus obliquus* at 50  $\mu$ g/L (as discussed below, green algae, including *Scenedesmus* sp., have been identified in both Nico Lake and Peanut Lake in the Aquatic Baseline Report for the Project [Annex C]). The guideline of 5  $\mu$ g/L was derived by applying a 0.1 safety factor to this endpoint. The CCME (2001) notes that the lowest estimate for fish toxicity was 550  $\mu$ g/L (28-day LC<sub>50</sub> for rainbow trout embryos and larvae), while the lowest estimate for invertebrates was 320  $\mu$ g/L.





The lowest exposure concentrations of arsenic to induce mortality in fish were observed in rainbow trout, which is one of most sensitive fish to dissolved arsenic exposure (CCME 2001). Rankin and Dixon (1994) calculated an  $LC_{50}$  (96-hour, flow through bioassay design) for this species at 20,200 µg/L, which was adjusted using a 0.1 times safety factor to provide an estimated acute LOAEC (lowest-observed-adverse-effect concentration) value of 2020 µg/L.

A search of the US EPA ECOTOX Database revealed 2 arsenic NOECs of 2,650  $\mu$ g/L and 9,500  $\mu$ g/L for a 10 day and 3 day exposure, respectively (Holland *et al.* 1960; as cited in the U.S. EPA ECOTOX Database). These toxicity tests were performed on pink salmon.

The U.S. EPA provides a National Recommended Water Quality Criterion Continuous Concentration (CCC) of 150 µg/L for arsenic (U.S. EPA 2009b). This recommended water quality criterion was derived from data for arsenic (III), but was applied to total arsenic, which might imply that arsenic (III) and arsenic (V) are equally toxic to aquatic life and that their toxicities are additive. In the arsenic criteria document (U.S. EPA 1985a), Species Mean Acute Values are given for both arsenic (III) and arsenic (V) for 5 species and the ratios of the species mean acute values for each species range from 0.6 to 1.7. Chronic values are available for both arsenic (III) and arsenic (V) for one species; for the fathead minnow, the chronic value for arsenic (V) is 0.29 times the chronic value for arsenic (III). No data are known to be available concerning whether the toxicities of the forms of arsenic to aquatic organisms are additive (U.S. EPA 2009b).

All of the toxicity tests referenced above were performed in laboratory environments with laboratory fresh water that does not contain the ligands present in natural waters. Therefore, as shown in the discussions above, toxicity tests in laboratory settings do not account for possible interactions of metals with organic matter that can reduce arsenic availability and toxicity. Therefore, the  $EC_{50}$  of 50 µg/L over a 14-day exposure to the green algae *Scenedesmus obliquus* has been chosen as the site specific arsenic water quality objective. Green algae (Phylum Chlorophyta), including *Scenedesmus* sp., were identified in both Nico Lake and Peanut Lake in the Aquatic Baseline report for the NICO Project (Annex C). The safety factor of 0.1 that was used by CCME in the derivation of their water quality guideline is considered overly conservative for the water bodies surrounding the NICO Project, and therefore 50 µg/L is considered to be protective of the receptors that may be present in Nico Lake and Peanut Lake. Based on the review of the toxicity data above, the chosen site specific arsenic water quality guideline is well below the concentrations that would be expected to result in adverse effects on fish species.

## 7.VII.3.5 Cadmium

The route of exposure and the form of cadmium are the 2 main factors that determine the toxicity of cadmium. The mechanism of action, however, is the same through all routes: the cadmium cation binds to metallothionein in body tissues, where it may be retained or excreted (Suzuki and Cherian 1987), can interfere with other divalent cationic metabolic processes (Petering et al. 1979), and can deplete various antioxidant enzymes (Jamall and Smith 1985).

The CWQG for the protection of aquatic life for cadmium has been set at 0.017  $\mu$ g/L (CCME 1999). The CWQG is based on a chronic LOAEL (lowest observed adverse effect level) for *Daphnia magna* of 0.17  $\mu$ g/L (based on a 21-d EC<sub>16</sub> for effects on mobility) with application of a 0.1 safety factor. *Daphnia magna* was the most sensitive freshwater invertebrate to cadmium exposure identified by the CCME (1999). *Daphnia* sp. were identified in both Nico Lake and Peanut Lake in the Aquatic Baseline report for the NICO Project (Annex C).

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For fish, acute toxicity was noted in CCME (1999) at <0.5  $\mu$ g/L for rainbow trout fry (96-hr and 168-hr tests), with other studies reporting acute lethality (10-50%) in the range of 0.8 to 1.4  $\mu$ g/L for rainbow trout and other salmonids. Chronically exposed fish demonstrated toxic effects (i.e. mortality) at cadmium concentrations similar to those used in acute tests (CCME 1999). Rainbow trout exhibited a 200-hour LC<sub>50</sub> and LC<sub>10</sub> of 0.9 and 0.7  $\mu$ g/L, respectively (Chapman 1979; cited in CCME 1999). The CCME (1999) notes that the lowest chronic toxicity endpoint for fish was 0.47  $\mu$ g/L from a 48-d EC<sub>11</sub> (11% reduction in body weight and fork length over a 48 day exposure period) in Atlantic salmon (*Salmo salar*) alevins. The most sensitive freshwater plant species identified by the CCME (1999) was the diatom *Tabellaria flocculosa*. At 1 and 10  $\mu$ g/L, this species displayed changes in morphology and inhibition of growth, respectively, following a 14-d exposure.

Suter and Tsao (1996) calculated a chronic LOAEL of 0.15 µg/L for cadmium based on responses of both aquatic vertebrates and invertebrates (the LOAEL was driven by a low concentration for *Daphnia magna*).

The lowest acute LOAEL value found in the U.S. EPA ECOTOX Database for fish was  $1.5 \mu g/L$ , calculated from a 96-hour flow through bioassay using rainbow trout exposed to inorganic cadmium (Goettl *et al.* 1974; cited in the U.S. EPA ECOTOX Database). A review of the toxicity data in the ECOTOX Database indicated that the toxicity of cadmium in the studies conducted is highly dependent on the form in which the cadmium was introduced. Cadmium introduced in the form of sulphates or oxides was toxic at much higher concentrations than elemental cadmium or cadmium chloride. Thus, the presence of natural ligands in receiving waters can significantly influence the availability and toxicity of cadmium.

The CCME data reported above suggests that salmonids may be the most sensitive family of fish to cadmium exposure, when compared to other families identified in Nico and Peanut Lakes. For example, estimated acute LOAEL values for several potential receptors for the NICO Project were 42, 220, and 280 µg/L for white sucker (*Catostomus commersoni*), pumpkinseed (*Lepomis gibbosus*), and golden shiner (*Notemigonus crysoleucas*), respectively (Benson et al. 1987; Hartwell et al. 1989; Munkittrick and Dixon 1988; all cited in the U.S. EPA ECOTOX Database). In the Aquatic Baseline report for the NICO Project (Annex C), white sucker was identified in waterbodies in the NICO Project area. As a result, the selection of toxicity data from rainbow trout bioassays should be sufficiently conservative to protect those species of salmonids inhabiting Nico Lake and Peanut Lake.

Based on the above review, the chronic LOAEL value of 0.15  $\mu$ g/L was selected as the cadmium SSWQO.

## 7.VII.3.6 Chloride

The CCME has not derived a CWQG for chloride for the protection of freshwater aquatic life. Chloride has been identified as a COPC and a site-specific objective has been derived for this parameter because predicted concentrations are greater than baseline conditions.

The British Columbia Ministry of Environment (BCMOE) derived a chronic water quality guideline for chloride for the protection of freshwater aquatic life of 150 mg/L (as NaCl) (Nagpal et al. 2003). The value was derived by multiplying a LOEC of 735 mg/L for the cladoceran *Ceriodaphnia dubia* by a safety factor of 5. The LOEC for *Ceriodaphnia dubia* was the lowest LOEC from chronic toxicity tests representing 9 different taxa. In the study, exposure for 7 days to 735 mg/L resulted in a 50% reduction in reproduction (brood size).

The U.S. EPA has derived a NAWQC for chloride. The CCC (4 day average) for chloride is 230 mg/L (as NaCl) and it is not to be exceeded more than once every 3 years on the average (U.S. EPA 1988b). The value was derived by dividing the final acute value of 1720 mg/L by an ACR of 7.594. The ACR is based on the geometric





mean of ACR values from tests with the rainbow trout (7.308), the fathead minnow (15.17) and *Daphnia pulex* (3.951).

Recently, the Iowa Department of Natural Resources worked closely with the U.S. EPA to revise Iowa's water quality standard for chloride. In brief, the U.S. EPA developed an equation to calculate the chronic chloride criteria based on water hardness and water sulphate levels, as follows (http://www.iowadnr.gov/water/standards/files/ws\_fact.pdf):

CCC (mg/L) = 177.87 [hardness (mg/L as  $CaCO_3$ )]<sup>0.205797</sup>[sulphate (mg/L)]<sup>-0.07452</sup>

For example, at a water hardness of 50 mg/L as  $CaCO_3$  and a water sulphate concentration of 5 mg/L, which are comparable to values measured in Peanut Lake and Nico Lake, the CCC for chloride is 353 mg/L.

Given that the water quality standard for chloride used by the Iowa Department of Natural resources is based on site-specific considerations with respect to water hardness and sulphate concentration, a site-specific water quality objective for chloride of 353 mg/L is proposed for both Peanut Lake and Nico Lake. Predicted chloride concentrations in surface water do not exceed the guideline values described above.

## 7.VII.3.7 Cobalt

The concentration of total cobalt in freshwaters is generally low ( $\leq 1 \mu g/L$ ). Higher concentrations are generally associated with industrialized or mining areas. Concentrations of cobalt ranging from non-detectable (detection limit of 0.1  $\mu g/L$ ) to 27,000  $\mu g/L$  have been measured; the total and dissolved concentrations in ambient, uncontaminated environments are, however, generally below 5  $\mu g/L$  (BCMOE 2004).

There is currently no CCME CWQG for cobalt to protect freshwater aquatic life. The MOE has derived an aquatic protection value of 5.2 µg/L for cobalt based on a 28-d LOEL of 5.2 µg/L for effects on reproduction (number of progeny) in *Daphnia magna* (Kimball 1978; as cited in MOE 2009).

The New York State Department of Environmental Conservation (NYSDEC) water quality standard for surface and ground water for cobalt is 5  $\mu$ g/L (NYSDEC 1986). The province of Quebec has adopted a surface water quality guideline for the protection of freshwater aquatic life from the chronic effects of cobalt of 5  $\mu$ g/L. The Quebec guideline is based on the NYSDEC (1986) standard.

The British Columbia Ambient Water Quality Guidelines provide 2 values for cobalt (BCMOE 2004). It is recommended that to protect aquatic life in the freshwater environment from the acute effects of cobalt, the maximum concentration of total cobalt should not exceed 110  $\mu$ g/L. The recommended maximum guideline is based on a LOEC causing 50% mortality in *Daphnia magna* exposed to 1110  $\mu$ g/L cobalt for 48 hours and a safety factor of 0.1. The safety factor was selected to protect from possible delayed mortality of the organisms exposed to the metal and is consistent with the British Columbia protocols for guideline development.

The British Columbia Ambient Water Quality Guidelines also recommend that to protect aquatic life from the chronic effects of cobalt, the 30-day average concentration of total cobalt (based on 5 weekly samples) should not exceed 4  $\mu$ g/L (BCMOE 2004). This is based on the invertebrates *Daphnia magna* and *Ceriodaphnia dubia that* exhibited chronic effects when exposed to low concentrations of cobalt. A LOEC (geometric mean) of about 8  $\mu$ g/L total cobalt was determined to cause reproductive effects in these organisms. The 30-day average concentration to protect aquatic life from the chronic effects of cobalt was obtained by applying a safety factor of





2 to the LOEC. A lower (than 10) safety factor was justified because cobalt is essential in the synthesis of vitamin  $B_{12}$  which is necessary for animal and human nutrition (BCMOE 2004).

Fish and aquatic plants are less sensitive to the effects of cobalt than daphnids. Chronic LC50 values for 28-d embryo-larval tests using rainbow trout (*Oncorhynchus mykiss*), the most sensitive fish species to cobalt, were reported at 470  $\mu$ g/L and 490  $\mu$ g/L. A value of 520  $\mu$ g/L was reported for a 144-h test using rainbow trout fry. 14-d NOEC and LOECs for effects on growth and survival in rainbow trout were reported to be 132 and 255  $\mu$ g/L, respectively. 10- to 14-d LOECs for growth of 500  $\mu$ g/L were reported for the most sensitive plant species, *Chlamydomonas eugametos* (BCMOE 2004). Given the greater sensitivity of daphnids to cobalt, the development of the site-specific water quality objective for cobalt has focused on these organisms.

The toxicity data available from the literature for cobalt for daphnids is limited to 3 key studies. Kimball (1978; as cited in Nagpal 2004)) reported a NOEC of 2.8  $\mu$ g/L and a LOEC of 9.3  $\mu$ g/L for reproduction from 2 28-day tests using *D. magna*. Kimball (1978; as cited in Nagpal 2004) also conducted a screening test on *Daphnia magna* prior to the 28-day chronic toxicity tests and identified a NOEC of 10  $\mu$ g/L and a LOEC of 20  $\mu$ g/L for reproductive effects. Biesinger and Christensen (1972; as cited in Nagpal 2004) conducted 21-day chronic toxicity tests with *Daphnia magna* and reported a 21-day EC16 of 10  $\mu$ g/L for reproduction at a water hardness of 45.3 mg/L as CaCO<sub>3</sub>. Diamond et al. (1992; as cited in Nagpal 2004) investigated cobalt toxicity to *Ceriodaphnia dubia* using a range of water hardnesses. At water hardnesses of 57 and 256 mg/L CaCO<sub>3</sub>, the 7-day NOECs were <50  $\mu$ g/L. At water hardnesses of 470 and 882 mg/L as CaCO<sub>3</sub>, the 7-day NOECs were 50  $\mu$ g/L.

In support of the development of the BCMOE guideline for cobalt, Golder/EVS performed additional toxicity testing using *Daphnia magna* and *Ceriodaphnia dubia* (Nagpal 2004). In brief, a 21-day *Daphnia magna* toxicity test and a 7-day *Ceriodaphnia dubia* toxicity test examining reproductive and survival endpoints were performed. *Daphnia magna* and *Ceriodaphnia dubia* were exposed to 5 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 as CaCO<sub>3</sub>. *Ceriodaphnia dubia* were also exposed to a nominal concentration of 100 µg/L cobalt at each water hardness. The LOEC for reproduction for *Daphnia magna* was 50 µg/L at a water hardness of 50 mg/L as CaCO<sub>3</sub>. The NOEC at this water hardness was 25 µg/L. The results of the 7-day *Ceriodaphnia dubia* test indicated a NOEC for reproduction of 12.5 µg/L at a water hardness of 50 mg/L at the same water hardness. The results of the *Daphnia magna* test are consistent with the results of Biesinger and Christensen (1972) who reported an EC16 of 10 µg/L at a water hardness of 45.3 mg/L as CaCO<sub>3</sub>.

Because there is some evidence to suggest that cobalt toxicity in freshwater organisms may be influenced by water hardness (Diamond et al. 1992; as cited in Nagpal 2004), the development of the SSWQO for cobalt has relied upon the results of the toxicity tests for which the water hardness is similar to that of the NICO Project area. As such, a SSWQO of 10 µg/L is proposed for cobalt. This value is based on the work of Biesinger and Christensen (1972; as cited in Nagpal 2004) using *Daphnia magna*. The data from the Kimball study (1978; as cited in Nagpal 2004) was not used because water hardness was not reported in this study and consistent results were obtained in the other 2 studies which were considered in the derivation of the objective (i.e., Biesinger and Christensen 1978; Golder/EVS as cited in Nagpal 2004).

## 7.VII.3.8 Copper

The CCME guideline for copper is based on water hardness, as provided below (CCME 2007):





Copper guideline = 2  $\mu$ g/L at water hardness of 0-120 mg/L as CaCO<sub>3</sub>

= 3  $\mu$ g/L at water hardness of 120-180 mg/L as CaCO<sub>3</sub>

= 4 µg/L at water hardness >180 mg/L as CaCO<sub>3</sub>

In brief, the guideline was derived using the regression equation of chronic toxic copper concentrations versus hardness developed by the U.S. EPA (1985b), as follows:

Cu conc. =  $e^{(0.8545[ln(hardness)] - 1.465)}$  ug/L

The lowest hardness within each hardness category was used to calculate the copper guideline for that hardness category. The guideline for the hardness category of 0 to 120 mg/L as  $CaCO_3$  is based on the guideline recommended by Demayo and Taylor (1981; as cited in CCREM 1987) for soft water (0 – 60 mg/L as  $CaCO_3$ ) of 2 µg/L and the calculated value based on a hardness of 60 mg/L as  $CaCO_3$  of 2 µg/L.

The equation for chronic toxicity derived by the U.S. EPA was derived from a final acute value and an acute to chronic ratio. In the development of the guideline for copper, the CCREM (1987) considered the effects of hardness on chronic copper toxicity to be inconclusive and the result from the equation was multiplied by an application factor of 0.2 to derive the guideline.

Recently, the U.S. EPA revised the aquatic life ambient freshwater quality criteria for copper (U.S. EPA 2007). In the revision, a Biotic Ligand Model (BLM)-based approach was used in place of the formerly applied hardness-based approach to calculate the water quality criteria for copper. The BLM approach offers a vast improvement over the hardness-based approach because in addition to water hardness, it incorporates the protective effects of other water chemistry parameters on copper toxicity, including the competitive influences of various cations (e.g., calcium, hydrogen, magnesium, and sodium) as well as the influence of important copper complexing anions (e.g., DOC and chloride).

In essence, the BLM predicts acute metal toxicity by estimating metal accumulation at the "biotic ligand", which is the site of metal accumulation and acute toxicity on an aquatic organism, taking into consideration the protective effects of water chemistry. The model assumes that accumulation of metal at the biotic ligand at or above a critical threshold concentration leads to acute toxicity. This critical accumulation at the biotic ligand is also termed the LA50 (lethal accumulation of metal at the biotic ligand that results in 50% mortality). For example, complexing anions (such as DOC and chloride) bind metal, thereby decreasing accumulation at the biotic ligand. Similarly, competing cations (such as calcium, hydrogen, magnesium, and sodium) compete with metal for binding sites at the biotic ligand, decreasing metal accumulation at the biotic ligand. Because water hardness is primarily a function of calcium and magnesium ions in the water, the protective effect of water hardness cations (i.e., calcium and magnesium) at the biotic ligand. Depending on water chemistry, the amount of metal in the water required to reach the LA50 will vary. In this way, the BLM can be used to predict the concentration of metal that would result in acute toxicity to aquatic life based on water chemistry.

Accordingly, the BLM is a useful tool for deriving site-specific water quality criteria for metals, and for this reason, the U.S. EPA revised the water quality criteria for copper based on the BLM. The U.S. EPA also plans to update the water quality criteria for other metals, including silver and zinc using the BLM approach.

7.VII.11



The BLM-based approach developed by the U.S. EPA was used to derive SSWQOs for copper for the Project, specifically for Nico Lake and Peanut Lake. The Biotic Ligand Model, Windows Interface, Version 2.2.1 (HydroQual 2007) was used.

The U.S. EPA does not provide any specific recommendation on data requirements for use of the BLM, except that enough data should be collected to characterize the spatial and temporal variability in water chemistry of a water body (Training Materials on Copper BLM: Data Requirements, accessed on-line at http://www.epa.gov/waterscience/criteria/copper/faq/data-requirements.pdf). Water quality samples were collected from Nico Lake from 4 sampling locations, including the Nico Lake inflow, a shallow location, a deep location, and the Nico Lake outflow. Water quality was monitored during open water from 2005 to 2008 (April, June, and August) and under ice in March 2008. In total, the water chemistry from 12 samples were used in the calculation of the SSWQO for copper for Nico Lake (2 samples from the Nico Lake inflow, 5 samples from the deep basin, 3 samples from the shallow basin, and 2 samples from the Nico Lake outflow).

Water quality samples were collected from Peanut Lake from 3 sampling locations, including a shallow location, a deep location, and the Peanut Lake outflow. As with Nico Lake, water quality was monitored during open water from 2005 to 2008 (April, June, and August) and under ice in March 2008. In total, the water chemistry from 8 samples was used in the calculation of the SSWQO for copper for Peanut Lake (4 samples from the deep basin, 2 samples from the shallow basin, and 2 samples from the Peanut Lake outflow).

The BLM generates acute (Criterion Maximum Concentration, CMC) and chronic (CCC) water quality criteria for copper (based on dissolved copper). The chronic water quality criterion is calculated using an ACR. For Nico Lake, the calculated chronic water quality criteria ranged from 25.8 to 57.2  $\mu$ g/L. For Peanut Lake, the calculated chronic water quality criteria ranged from 22.4 to 54.7  $\mu$ g/L. The lowest calculated criteria are proposed as the SSWQOs for copper, which are 25.8  $\mu$ g/L and 22.4  $\mu$ g/L for Nico Lake and Peanut Lake, respectively.

Based on a water hardness of 23 mg/L as  $CaCO_3$  for Nico Lake and 27 mg/L as  $CaCO_3$  for Peanut Lake, the CCME guideline for copper for these waterbodies is 2 µg/L. The calculated site-specific values are approximately 10 times higher than the CCME guideline.

#### 7.VII.3.9 Iron

The CCME has established a guideline for iron of 300  $\mu$ g/L, based on a guideline developed by the International Joint Commission (IJC) and the MOE (CCREM 1987). This value is based on the concentration of iron in water that could result in precipitation of iron hydroxides on stream substrates and potentially smother habitat and not toxicological responses. Suter and Tsao (1996) note that the U.S. EPA chronic guideline for iron of 1000  $\mu$ g/L is based on a field study at a site receiving acid mine drainage (the guideline is cited in the 1985 EPA "Gold Book" but due to the specific conditions under which the guideline was developed, is not included in more recent guidelines). Thus, both guidelines are based on specific conditions under which iron precipitates are a concern, but may not be applicable in natural waters.

Suter and Tsao (1996) indicate that a concentration of 4380  $\mu$ g/L that resulted in reproductive impairment of 16% in *Daphnia magna* exposed to FeCI was more applicable to natural waters, while a chronic value for fish of 1300  $\mu$ g/L was applicable. Guay et al. (2000) undertook a review of toxicity data for iron and noted that iron toxicity generally occurred at much higher concentrations than those associated with precipitation effects (chronic NOECs, ranged upwards from 1.5 mg/L for trout).





The CCREM (1987) cites acute values for iron for aquatic insects that ranged from 320 to 16 000  $\mu$ g/L. The CCREM goes on to note that chronic toxicity to fathead minnows was recorded in a study by Sykora et al. (1972; as cited in CCREM 1987) at an acid mine drainage site at 1500  $\mu$ g/L (50% reduction in egg hatchability) (similar responses were noted in brook trout eggs at 12 000  $\mu$ g/L, indicating that brook trout were much less sensitive than fathead minnows). The CCREM cites the safe concentration for brook trout juveniles as ranging between 7500 and 12 500  $\mu$ g/L.

The site-specific iron water quality objective is 1.5 mg/L, based on the toxicity review by Guay et al. (2000). This value is well below other chronic toxicity values reported above.

## 7.VII.3.10 Lead

Lead speciation in surface water has been shown to be sensitive to pH. In the pH range 6 to 8 that characterizes most surface waters, solubility depends on  $CO_2$  and sulphur species present. At low pH (pH < 6), solubility appears to depend on sulphate concentration. Therefore, pH and hardness appear to be interrelated, with increased  $CO_3$  concentration resulting in a decrease in solubility throughout the pH range (Wershaw 1976). Lead also shows a very strong affinity to suspended matter, and readily complexes with organic matter, humic substances, and inorganic minerals (clays) to form insoluble compounds (Hem 1976).

Both the U.S. EPA and CCME note that lead toxicity is hardness-dependent (CCREM 1987). Toxicity of lead is reduced by the low solubility of many forms of lead in the natural environment, particularly in alkaline waters. As noted above, since lead is strongly complexed by a variety of ligands, lead in surface waters is typically present in bound forms.

Lead is believed to potentially interfere with calcium accumulation at the gills resulting in reduction of calcium in bones, with some studies indicating spinal scoliosis in fish exposed to high levels. Phillips and Russo (1978) note that lead accumulation in exposed fish is highest in the gill and kidney, followed by liver (site of most detoxification). The results suggest that most lead uptake is through the gill. Citing studies by Merlini and Pozzi (1977) they note that lead uptake was higher at lower pH (6.0) than higher pH (7.5) which was attributed to the higher concentration of divalent lead at the lower pH, and that there was a direct correlation between the ionic concentration of lead and accumulation by sunfish. The study concluded that the conditions that prevailed in most natural waters rendered lead generally unavailable for uptake.

Recent experiments by Borgmann et al. (2005) indicate that lead toxicity to *Hyalella azteca* (as  $LC_{50}$ ) decreased from 1 µg/L in soft water to 11 µg/L in hard water (Lake Ontario water). Similarly, Besser et al. (2005) found that hardness reduced toxicity of lead in their tests with *H. azteca*, but noted that the effects of hardness were reduced at very high hardness (275 mg/L CaCO<sub>3</sub>) (the effect of hardness was noted as being greatest at medium-hardness of 126 to 138 mg/L CaCO<sub>3</sub>). The authors noted that in their tests, dissolved lead constituted less than 50% of total lead. Schwartz et al. (2004) found that the addition of natural organic matter (as a mix of humic and fulvic acids) significantly reduced toxicity of lead to rainbow trout, while Richards et al. (2001) have noted that the type of organic matter affects the degree of toxicity modification.

Of the approximately 100 data points available for lead toxicity to fish available in the ECOTOX Database, the lowest acute (1190  $\mu$ g/L) and chronic (7.6  $\mu$ g/L) LOEC values for lead were from 96-hour and 19-month flow through bioassays, respectively, for rainbow trout exposed to dissolved inorganic lead (Goettl et al. 1976; as cited in U.S. EPA ECOTOX Database).





There is limited information on lead toxicity derived from bioassays using non-salmonid species. A chronic  $LC_{50}$  (24-day, flow through design) for northern pike (*Esox lucius*) was observed at 253 µg/L (Sauter et al. 1976; as cited in the U.S. EPA ECOTOX Database). The northern pike is a fish species relevant to the NICO Project; it was identified in Nico Lake and Peanut Lake in the Aquatic Baseline report for the NICO Project (Annex C). An acute  $LC_{50}$  for smallmouth bass under static test conditions was calculated at 2200 µg/L (Coughlan et al. 1986; as cited in the U.S. EPA ECOTOX Database).

Suter and Tsao (1996) provide lowest chronic values of 12.26 and 25.46  $\mu$ g/L for daphnids and non-daphnid invertebrates, respectively. They also provide lowest chronic values of 500 and 18.88  $\mu$ g/L for aquatic plants and fish, respectively.

In addition to the available toxicity data, the available aquatic freshwater life criteria for lead were reviewed. The Canadian lead water quality guideline was developed in 1987 by the CCREM and has not been updated since. The lead guideline is adjusted for hardness based on the U.S. EPA algorithm developed in 1985 for chronic toxicity (CCREM 1987). The adjustment factors are based on specific guideline values for defined ranges of hardness:

- 1  $\mu$ g Pb/L at [CaCO<sub>3</sub>] in the range of 0 to 60 mg/L;
- 2 μg Pb/L at [CaCO<sub>3</sub>] in the range of 60 to 120 mg/L;
- 4 μg Pb/L at [CaCO<sub>3</sub>] in the range of 120 to 180 mg/L; and

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**7** μg Pb/L at [CaCO<sub>3</sub>] greater than 180 mg/L.

The CCREM notes that the guideline for soft water was calculated using a hardness of 50 mg  $CaCO_3/L$  since toxicity data for very soft water was not available and that therefore, the guideline may be under-protective in these waters. The CCREM (1987) does not specifically mention how the values in each range were derived, but it is assumed that the same method as used for deriving the copper guidelines (by selecting the calculated value corresponding to the lowest hardness in each category) was followed in deriving the lead hardness-adjusted guidelines.

Water hardness measured at Nico Lake ranged from 23 to 57 mg/L as  $CaCO_3$ , while water hardness at Peanut Lake ranged from 27 to 37 mg/L as  $CaCO_3$  (Annex C). Therefore, based on the CCME guideline, the site-specific lead water quality objective is 1 µg/L. Based on the lowest of chronic values reported above, a SSWQO of 7.6 µg/L is proposed for the site, based on chronic effects in rainbow trout. This value is well below the chronic value for northern pike of 253 µg/L ( $LC_{50}$ , 24-day, flow-through design), a resident fish in the lakes surrounding the mines but the value is likely protective of salmonids in general and lake whitefish (a salmonid) has been identified in Peanut Lake (Annex C).

## 7.VII.3.11 Nitrate

The CCME CWQG for nitrate  $(NO_3)$  is 13 mg/L. This guideline is for the protection of aquatic life due to direct toxic effects. The guideline does not consider the indirect effects due to eutrophication.

The CCME guideline was derived by multiplying a 10-d LOEC of 133 mg/L for the pacific tree frog (*Pseudacris regilla*) (Schuytema and Nebeker 1999) by a safety factor of 0.1. In general, amphibians were the most sensitive receptors to chronic nitrate exposure (CCME 2003b). A 16-d LOEC of 129 mg/L is reported for the red-legged





frog (*Rana aurora*) for embryo growth reduction and a 56-d LOEC of 133 mg/L is reported for the northern leopard frog (*Rana pipiens*) for larval growth reduction. In the African clawed frog (*Xenopus laevis*), a 10-d LOEC of 2190 mg/L for growth reduction in tadpoles and a 5-d LOEC of 251 mg/L for growth reduction in embryos are reported. The CCME did not consider the endpoints for the red-legged frog and northern leopard frog to be ecologically significant because the reductions in growth represented only 3 to 6%. As such, the data available for the pacific tree frog was used by the CCME to derive the guideline.

Fathead minnow larvae exposed to  $NO_3^-$  for 7-d resulted in a range of LOECs from 3176 mg/L to 6363 mg/L for growth and mortality endpoints, respectively (Scott and Crunkilton 2000). The lowest effect concentration reported for salmonids for chronic exposure (7-d  $LC_{50}$ ) were 4700 and 4800 mg/L for rainbow trout and Chinook salmon early life stages (fingerlings), respectively (Westin 1974).

The most, and least sensitive invertebrates were *Ceriodaphnia dubia* and *Daphnia magna*, which exhibited 7-d LOECs for reduced reproductive effort of 189 and 3176 mg/L, respectively (Scott and Crunkilton 2000).

Nitrate is used by aquatic primary producers, such as plants and algae, and does not limit their growth (Pinar et al. 1997). Aquatic plants and algae do not appear to be adversely effected by elevated concentrations of nitrate. Growth was not inhibited for the green alga *Scenedesmus subspicatus* exposed to 283 mg/L of  $NO_3^-$  (Hund 1997). Nitrate is not considered to be toxic to aquatic primary producers and the plant toxicity protocols were waived in the development of the CWQG (CCME 2003b).

The reviewed toxicity data shows that amphibians may be the most sensitive receptor to nitrate. In Canada, the pacific tree frog and red-legged frog are found in British Columbia only. The northern leopard frog is found in the NWT; however, its range is limited to between the Alberta border and Great Slave Lake, which is well south of the NICO Project. As such, it is not likely that these species of frogs will be found in the waters near the site. In fact, of the 4 species of frogs found in the NWT, only one is known to occur in the vicinity of the NICO Project, the wood frog (*Rana sylvatica*).

Still, a study on the effects of ammonium nitrate on the survivorship and behaviour of wood frog tadpoles suggests that this species has a similar sensitivity to nitrate as other species of frogs (Burgett *et al.* 2007). Therefore, the SSWQO is based on the 10-d LOEC of 133 mg/L for the pacific tree frog. The safety factor of 0.1 that was used by the CCME in the derivation of the CWQG is considered overly conservative for the water bodies surrounding the Project, and therefore, 133 mg/L is considered to be protective of the receptors that may be present in Nico Lake and Peanut Lake. Based on the review of the toxicity data above, the chosen SSWQO for nitrate is well below the concentrations that would be expected to result in adverse effects on fish species. It is lower than the chronic value for the most sensitive salmonid reported, rainbow trout, even when the 7-d  $LC_{50}$  (4700 mg/L) is adjusted to 470 mg/L using an uncertainty factor of 0.1.

#### 7.VII.3.12 Selenium

The CCME guideline for selenium is 1.0  $\mu$ g/L (CCME 2007). This value was adopted from the IJC which introduced the value to protect aquatic life in the Great Lakes based on field studies which indicated that waterborne selenium concentrations of 5 to 10  $\mu$ g/L were associated with food web contamination that caused acute lethality to predatory fish (IJC 1981; as cited in CCREM 1987).

The U.S. EPA has developed a chronic water quality criterion for selenium of 5  $\mu$ g/L (total recoverable selenium in the water column) (U.S. EPA 2009b). It should be noted that the U.S. EPA recently developed a draft chronic





water quality criterion for selenium that is based on the concentration of selenium in fish tissue rather than the concentration of selenium in the water (U.S. EPA 2004). The U.S. EPA believes, as do other experts in the field, that a tissue-based criterion better addresses the highly bioaccumulative nature of selenium than a water-based criterion. The U.S. EPA's proposed tissue-based criterion of 7.91  $\mu$ g/g is founded on the whole-body concentration of selenium in juvenile bluegill associated with winter mortality. Fish are the most sensitive aquatic organisms to chronic selenium exposure, and for this reason, the chronic criterion is based on fish and not other aquatic organisms such as plants and aquatic invertebrates. However, there is much controversy with respect to the draft criterion and for this reason, the currently accepted chronic water quality criterion of 5  $\mu$ g/L is proposed as the SSWQO for selenium for both Nico Lake and Peanut Lake.

## 7.VII.3.13 Sulphate

The CCME has not derived a CWQG for sulphate for the protection of freshwater aquatic life. Sulphate has been identified as a COPC and a site-specific objective has been derived for this parameter because predicted concentrations are greater than baseline conditions.

The BCMOE derived a chronic water quality guideline for sulphate for the protection of freshwater aquatic life of 100 mg/L for dissolved sulphate (as  $SO_4$ ), which represents a maximum concentration that should not be exceeded at any time (Singleton 2000). A guideline value of 50 mg/L for dissolved sulphate (as  $SO_4$ ) is also provided as an "alert" level because some aquatic mosses appear to be particularly sensitive to the toxic effects of dissolved sulphate. The BCMOE recommends that when dissolved sulphate concentrations exceed 50 mg/L, the health of aquatic mosses should be monitored.

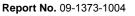
Three studies were used as the basis for the guideline values.

- In the first, 1-, 2-, 3- and 4-d LC50s of 2000, 1000, 500, and 250 mg/L, respectively, were reported for striped bass (*Morone saxitilus*) larvae. LC0's of 500, 100, 100, and 100 mg/L, respectively, were also reported.
- In the second, 96-h LC50s of 205, 3711, and 6787 mg/L in soft, medium (100 mg/L as CaCO<sub>3</sub>) and hard (250 mg/L as CaCO<sub>3</sub>) water, respectively, were reported for the amphipod, *Hyallela azteca*.
- In the final study, a concentration of 100 mg/L was toxic to the aquatic moss, *Fontinalis antipyretica*. Toxicity ranged from 100 to >250 mg/L for 4 other species of aquatic moss.

Working with the U.S. EPA, the Iowa Department of Natural Resources recently revised Iowa's water quality standard for sulphate (http://www.iowadnr.gov/water/standards/files/ws\_fact.pdf). For waters with hardness of less than 100 mg/L, or chloride concentrations of less than 5 mg/L (as for Peanut Lake and Nico Lake), the water criteria for sulphate is 500 mg/L.

Given that the water quality standard for sulphate used by the Iowa Department of Natural resources is based on site-specific considerations with respect to water hardness and chloride concentration, a SSWQO for sulphate of 500 mg/L is proposed for Peanut Lake and Nico Lake. Predicted sulphate concentrations in surface water do not exceed the guideline values described above.







## 7.VII.3.14 Uranium

There is currently no CCME CWQG for uranium to protect freshwater aquatic life. Uranium has been identified as a COPC and a site-specific objective has been derived for this metal because predicted concentrations are greater than baseline conditions.

In 1983, a water quality objective for uranium for aquatic life and wildlife of 300  $\mu$ g/L was established by the Inland Waters Directorate, Water Quality Branch (Environment Canada 1983). Provincial guidelines for uranium range from 5 to 15  $\mu$ g/L (MOEE 1994; Boudreau and Guay 2002; Saskatchewan Environment 2006). The MOE has developed an aquatic protection value for uranium of 33  $\mu$ g/L (MOE 2009), which is based on an IC25 for reproduction in *Ceriodaphnia dubia* as determined from the Vizon SciTec Inc. (2004) uranium aquatic toxicity investigation.

In 2003, Environment Canada and Health Canada assessed the toxicity of uranium to human health and the environment as part of the *Canadian Environmental Protection Act, 1999, Priority Substances List Assessment Report for Releases of Radionuclides from Nuclear Facilities* (Environment Canada and Health Canada 2003). The assessment included an assessment of the toxicity of uranium to freshwater aquatic life, including the identification of chronic toxicity values. For fish, a chronic toxicity value of 280 µg/L was derived based on a 96-h LC50 for *Pimephales promelas* (fathead minnow) in water with hardness 20 mg/L as CaCO<sub>3</sub> and an ACR of 10. For phytoplankton and zooplankton, a chronic toxicity value of 3 µg/L was derived for *Ceriodaphnia dubia*, a value of 13 µg/L was derived for *Chorella* sp. and a value of 22 µg/L was derived for *Daphnia pulex*. These values were derived for water with hardness less than 100 mg/L as CaCO<sub>3</sub>.

Vizon SciTec Inc. (2004) investigated the toxicity of uranium to freshwater plants. In 72-h growth inhibition tests with *Selenastrum capricornutum* (green algae), IC25 estimates ranged from 27 to 150  $\mu$ g/L depending on hardness (the water hardnesses tested were 5, 15, 64, 122, and 228 mg/L as CaCO<sub>3</sub>). NOECs ranged from 14 to 220  $\mu$ g/L and LOECs ranged from 29 to 430  $\mu$ g/L, depending on water hardness. In 7-d growth inhibition tests using *Lemna minor* (duck weed) in water with hardness 35 and 137 mg/L as CaCO<sub>3</sub>, IC25 values ranged from 4700 to 12 300  $\mu$ g/L based on frond number and from 6400 to 13 300  $\mu$ g/L based on dry weight. Water hardness was observed to have an effect on toxicity to duck weed.

For invertebrates, 14-d LC25 values ranging from 100 to 130 µg/L were calculated in water with hardnesses ranging from 61 to 238 mg/L as CaCO<sub>3</sub> for *Hyallela azteca*, demonstrating an effect of increasing water hardness on uranium toxicity (Vizon SciTec Inc. 2004). Borgmann *et al.* (2005) calculated an LC50 of 21 µg/L for the same species in soft water (18 mg/L as CaCO<sub>3</sub>) after 7 days of exposure. Based on reproduction, a LOAEL of 520 µg/L was derived for *Daphnia magna* in water with hardness of 66 to 73 mg/L as CaCO<sub>3</sub> after 21 days of exposure to uranium (Poston *et al.* 1984). The midge, *Chirnomus tentans*, is the least sensitive of the invertebrates. A 10-d LC50 of 6400 µg/L and a NOEC and LOEC based on mortality of 421 and 1519 µg/L, respectively, were reported for this species (Burnett and Liber 2006). An IC50 value for effects on growth of 10 200 µg/L was also reported in the study. In 7-d tests with *Ceriodaphnia dubia*, LC25 values were 54 to 150 µg/L depending on hardness (hardness varied from 17 to 252 mg/L as CaCO<sub>3</sub>) (Vison SciTec Inc. 2004). Based on effects on reproduction, a 7-d NOEC and LOEC of 1970 µg/L and 3910 µg/L, respectively, were determined (Vizon SciTec Inc. 2004). IC25s for reproduction ranged from 33 to 79 µg/L depending on water hardness. Pickett et al. (1993) reported lower NOEC and LOEC values for *Ceriodaphnia dubia*. Based on reproduction over 7 days, NOEC and LOEC values were 1.5 and 2.7 µg/L, respectively in water with hardness 6.1 mg/L as CaCO<sub>3</sub>.





For fish, in 7-d survival and growth tests with *Pimephales promelas* (fathead minnow) early life stages there were no effects of water hardness on toxicity (Vizon SciTec Inc. 2004). Based on survival, NOECs ranged from 810 to 1200  $\mu$ g/L and LOECs ranged from 1300 to 2000  $\mu$ g/L, depending on water hardness. 7-d LC50 values ranged from 1500 (in water with hardness 244 mg/L as CaCO<sub>3</sub>) to 2100 (in water with hardness 72 mg/L as CaCO<sub>3</sub>). IC25 values based on growth ranged from 1300 to >2000  $\mu$ g/L, depending on water hardness. Two early life stage tests were also conducted with rainbow trout. Rainbow trout embryos were exposed for 31 and 30 days, from day of fertilization, to uranium at 2 water hardnesses (6 and 61 mg/L as CaCO<sub>3</sub>). LOECs for survival of 280 and 610  $\mu$ g/L were derived for water with hardness of 6 and 61 mg/L as CaCO<sub>3</sub>. Toxicity was higher in the softer water. In 30-d toxicity tests with white sucker (*Catostomus commersoni*) at a water hardness of 72 mg/L as CaCO<sub>3</sub>, a NOEC of 7330  $\mu$ g/L and a LOEC of 27860  $\mu$ g/L for effects on growth were determined (Liber et al. 2004b). In 141-d tests with lake trout (*Salvelinus namaycush*) at a water hardness of 74 to 80 mg/L as CaCO<sub>3</sub>, a NOEC of 6050  $\mu$ g/L and a LOEC of 29780  $\mu$ g/L were determined based on a number of endpoints (survival, reproduction and growth) (Liber *et al.* 2004a).

Based on the review of the aquatic toxicity of uranium provided above, a SSWQO for uranium of 27  $\mu$ g/L is proposed, which is based on an IC25 value for effects on growth in the green algae. It should be noted that a LOEC of 2.7  $\mu$ g/L was determined for *Ceriodaphnia dubia* in water of hardness 6.1 mg/L as CaCO<sub>3</sub> by Pickett *et* al. (1993); however, IC25s for effects on reproduction in this species are also available and for waters with hardness that approximate the water hardness of Nico Lake and Peanut Lake (Vizon SciTec Inc. 2004). The water used in the Pickett *et* al. (1993) study was much softer than the waters of Nico Lake and Peanut Lake. Toxicity to *Ceriodaphnia dubia* was lower at water hardnesses that approximate those in Nico Lake and Peanut Lake (Vizon SciTec Inc 2004).

## 7.VII.3.15 Zinc

Zinc is an essential element for humans and animals and is required for the proper function of a variety of metalloenzymes (alcohol dehydrogenase, alkaline phosphatase, carbonic anhydrase, leucine aminopeptidase, super-oxide dismutase, and DNA and RNA polymerases). Zinc is required for normal nucleic acid, protein and membrane function and metabolism, as well as proper gene structure (zinc finger phenomenon), and zinc deficiency is associated with a variety of pathologies (ATSDR 1994).

Zinc is a naturally-occurring metal in the earth's crust, and it can be released by both natural and anthropogenic sources. It does not readily volatilise, but rather adsorbs to soil and sediment, as well as particulates in groundwater. Leaching is not common, though it has been at some sites of contamination. Zinc may bioconcentrate in organisms, particularly aquatic organisms such as higher crustaceans and bivalve species, but not particularly in fish and other vertebrates as body content is modulated by homeostatic mechanisms that act principally on absorption and liver levels (ATSDR 1994).

Taylor et al. (1982), note that model calculations indicate that at pH < 7,  $Zn^{2+}$  was the dominant species (though this may be present as ionic complexes), while at pH > 7 the complexation with OH, CO<sub>3</sub> and humic substances increased. Zinc also formed complexes with suspended inorganic (clay) and organic (humic) matter and levels of dissolved and suspended organic matter in most freshwaters are generally sufficient to remove zinc toxicity. As noted above, the concentrations may not be similarly affected in very soft waters of low hardness or pH, since this can affect the complexation with organic ligands.





Bodar et al. (2005), note that in Dutch waters, approximately 25% of the Zn present is in "dissolved" form, while approximately 75% is present adsorbed to particulate matter. De Schamphelaere et al. (2005), found that the percentage of zinc calculated to be bound to DOC varied between 5% and 89%, with a tendency for more zinc to be complexed to DOC at lower zinc concentrations. In their study, they calculated that the other zinc species,  $ZnOH^+$ ,  $Zn(OH)_2$ ,  $ZnSO_4$ ,  $ZnCI^+$ , and  $ZnHCO_3$  generally accounted for only up to 12% of the zinc present in the dissolved phase. At higher pH (~8) and alkalinity,  $ZnCO_3$  accounted for approximately 10% of the dissolved zinc.

The CWQG for zinc of 30  $\mu$ g/L is based on the IJC limit (CCREM 1987). While most studies have indicated that acute toxicity is based on water hardness, the CCREM (1987) notes that chronic toxicity is not, and hence there is no CCME site-specific adjustment provided for zinc based on water hardness. The CCREM (1987) notes that acute toxicity to rainbow trout swim-up fry was observed at 93  $\mu$ g/L (96-hr LC<sub>50</sub>). However, a wide range of toxicities was noted in studies with rainbow trout (96-h LC50s ranged from 90 to 7210  $\mu$ g/L) (CCREM 1987). Maximum acceptable toxicant concentrations (MATCs) cited by CCREM (1987) based on spawning and hatching success and fry survival of fathead minnows ranged from 30 to 180  $\mu$ g/L.

A review of toxicity studies in the U.S. EPA ECOTOX Database indicated that algae are generally less sensitive to zinc than are fish or invertebrates. No response concentrations in algae ranged from 100 to 250  $\mu$ g/L, while LC50 concentrations were typically over 1000  $\mu$ g/L.

*Daphnia* species (including *Ceriodaphnia*) were more sensitive, with LOEC values of 120 up to 1000  $\mu$ g/L in waters of moderate hardness (225 mg CaCO<sub>3</sub>/L) in 21-day tests. NOEC values were reported in the range of 101 to 140  $\mu$ g/L (Carlson and Rouch 1985; as cited in the U.S. EPA ECOTOX Database).

Rainbow trout were generally more sensitive than fathead minnows to the effects of zinc. Reported LOECs for rainbow trout ranged from 110 to 3600  $\mu$ g/L, in waters of hardness ranging from 22 mg CaCO<sub>3</sub>/L to 314 mg CaCO<sub>3</sub>/L. LOECs for fathead minnows ranged from 270 to 2730  $\mu$ g/L. Reported NOECs were few for rainbow trout and ranged from 36 (at hardness of 30 mg CaCO<sub>3</sub>/L) to 320  $\mu$ g/L (at hardness of 350 mg CaCO<sub>3</sub>/L). NOECs for fathead minnows ranged between 117 and 291  $\mu$ g/L for growth as an endpoint and between 100 and 940  $\mu$ g/L for mortality as an endpoint.

The zinc site-specific water quality guideline has been set at 110  $\mu$ g/L, based on the rainbow trout LOEC and is likely to be sufficiently protective of the aquatic receptors that are expected to occur in Nico Lake and Peanut Lake. No safety factor was applied to the LOEC value for rainbow trout as the application of safety factors is considered overly conservative, since the laboratory tests upon which these thresholds are based do not incorporate the effects of naturally present ligands that would reduce the bioavailability and toxicity of zinc. The U.S. EPA is in the process of developing a BLM for zinc to specifically account for the modifying effects of other ligands in freshwaters. Also, rainbow trout are considered to be more sensitive than resident fish expected to be present in the waterbodies surrounding the mines.

## 7.VII.4 SUMMARY AND CONCLUSIONS

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Site-specific water quality objectives were developed for the following COPCs for the NICO Project: aluminum, ammonia, antimony, arsenic, cadmium, chloride, copper, iron, lead, nitrate, selenium, sulphate, uranium, and zinc. These parameters were identified as COPCs because their predicted surface water concentrations during and/or post site operations are greater than baseline conditions and/or CCME guidelines. Site-specific water quality objectives were developed for Nico Lake and Peanut Lake, if relevant, and are presented in Table 7.VIII.3-1.





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