

### **APPENDIX 6-N**

Site-specific Water Quality Objective – Arsenic





#### 6.N-1 INTRODUCTION

Golder Associates Ltd. (Golder) was retained by Agnico Eagle Mines Limited (Agnico Eagle) to develop a long-term site-specific water quality objective (SSWQO) for arsenic for the protection of freshwater aquatic life in Mammoth Lake and downstream lakes for the Environmental Impact Statement for the Whale Tail Pit and Haul Road. This technical memorandum describes the methods and results of the development of the long-term SSWQO for arsenic.

#### 6.N-2 GENERAL APPROACH

The SSWQO for arsenic was developed in general accordance with standard methods provided for the development of a long-term guideline for freshwater environments by the Canadian Council of Ministers of the Environment (CCME) in the guidance document "A Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life 2007" (CCME 2007). The CCME has developed a refined, stepwise method for site-specific derivations that is preferred by regulators and provides a consistent framework for evaluations. In an earlier guidance document, the CCME (2003) outlines several procedures that can be used to modify the generic water quality guidelines for the protection of freshwater aquatic life, including the background concentration procedure, recalculation procedure, water effect procedure, and resident species procedure. However, these approaches were not selected as options to develop the SSWQO for arsenic at this time. Where warranted, species resident in Mammoth Lake and downstream lakes as well as in the Project area and Nunavut were taken into consideration in the development of the SSWQO using the CCME (2007) protocol based on guidance provided by the CCME in their 2003 document.

The CCME (2007) guidance document provides two approaches for deriving water quality guidelines that depend on the adequacy of the toxicity data (availability and quality) for the substance. These approaches are:

- Statistical Derivation Approach This approach is the preferred approach, when data are adequate, and is based on the statistical distribution (i.e., a species sensitivity distribution [SSD]) of the available and acceptable toxicity data. Guidelines derived using this approach are called Type A Guidelines; and
- Lowest Endpoint Derivation Approach This approach is used if the data are inadequate for the Statistical Derivation Approach. This approach is based on extrapolation from the lowest available and acceptable toxicity data and application of uncertainty or safety factors, where warranted. This approach is based on the original federal guideline development protocol (CCME 1991). Guidelines derived using this approach are called Type B Guidelines, and are further divided into Type B1 and Type B2 guidelines based on the adequacy (availability and quality) of toxicity data.

Based on the CCME (2007) protocol, the general approach for development of the long-term SSWQO for arsenic followed a four-step process:

- 1) Toxicity data compilation Available freshwater chronic toxicity data for arsenic was compiled into a database with a focus on data for algae, aquatic plants, aquatic invertebrates, fish and amphibians;
- Toxicity data evaluation, categorization and endpoint selection The available toxicity data was evaluated
  for suitability and categorized as acceptable or unacceptable for developing a long-term SSWQO. Once the
  data were evaluated and categorized, preferred endpoints were selected;





- 3) Determination of the applicable SSWQO derivation approach Depending on the adequacy of the toxicity data, it was determined whether the Statistical Derivation Approach or the Lowest Endpoint Derivation Approach should be used to develop the SSWQO for arsenic; and
- 4) Development of the SSWQO for arsenic using the selected approach (Section 6.N-5).

These steps are described in detail in the sections below.

#### 6.N-3 TOXICITY DATA COMPILATION

Available toxicity data for arsenic were compiled into a database with a focus on long-term or chronic data for algae, aquatic plants, invertebrates, fish and amphibians in freshwater environments, per the recommendations of CCME (2007). The compilation of toxicity data began with the primary chronic toxicity data from the fact sheet used to derive the current CCME Canadian Water Quality Guideline for the Protection of Freshwater Aquatic Life (CWQG-PFAL) for arsenic (CCME 2001). The compilation included querying the ECOTOX Database administered by the United States Environmental Protection Agency (U.S. EPA 2016) and other journal databases (e.g., PubMed, Cambridge Scientific Abstracts) for the time period prior to, coinciding with and subsequent to the CWQG-PAL derivation (from the year 1915 to the year 2016). The query for the time period subsequent to the CWQG-PAL derivation was done to include recently generated freshwater toxicity data in the development of the SSWQO.

The definitions of long-term exposure durations provided by the CCME (2007) were followed in identifying chronic toxicity data. The definitions are:

- For fish and amphibians, exposure durations of ≥21 days for tests with juvenile or adult life stages and ≥7 days for tests with eggs and larvae.
- For short-lived invertebrates (e.g., *Ceriodaphnia dubia*), exposure durations of ≥96 hours for non-lethal effects measures (e.g., growth, reproduction) and <21 days for lethality on a case-by-case basis.
- For long-lived invertebrates (e.g., *Daphnia magna*), exposure durations of ≥7 days for non-lethal effects measures and ≥21 days for lethality.
- For aquatic and semi-aquatic plants, exposure must be through the water column. All tests for *Lemna* sp. following standard test protocols are generally considered long-term exposures. Data for other species is considered on a case-by-case basis.
- For algae, exposure durations of >24 hours or on a case-by-case basis (e.g., >72 hour tests with Pseudokirchneriella subcapitata were considered chronic).

Arsenic naturally occurs in several valence states: elemental arsenic (As<sup>0</sup>), trivalent arsenic (As<sup>3</sup> or As[III]), pentavalent arsenic (As<sup>5</sup> or As[V]) and arsenide (As<sup>3</sup>). The toxicity of arsenic is determined by its chemical form and valence state. In aquatic systems, As(III) and As(V) are the most common states, with As(V) dominating under oxidizing conditions (i.e., high pH, high redox potential (Eh), high dissolved oxygen [DO]) and As(III) dominating under reducing conditions (Eisler 1988). However, because the dissolved oxygen in an aquatic system varies both temporally and spatially, which affects the redox potential, the equilibrium position of the As(III) and As(V) reaction is constantly shifting (i.e., both As[III] and As[V] are thermodynamically unstable and interchangeable) (Fodor 2001; Smedley and Kinniburgh 2002). Consequently, aquatic biota are likely exposed to a mixture of As(III) and As(V), with the relative proportion dependent on, among other things, the dissolved oxygen concentration.





This coexistence of As(III) and As(V) has been observed in natural aquatic systems (Bright et al. 1994, Nagorski and Moore 1999). Some studies have demonstrated that As(V) is less toxic than As(III) in aquatic systems (Borgmann et al. 1980; Naumann et al. 2007).

Based on these considerations, arsenic speciation in lakes in the Project area likely includes both As (III) and As (V), and is likely somewhat variable depending upon the various modifying factors. As described above, it is possible that both oxic and anoxic conditions can potentially occur in freshwater systems and thus both As(V) and As(III) may occur in different areas or at different times in Mammoth Lake and downstream lakes. Thus, all available arsenic toxicity data, regardless of speciation were compiled in the database.

Aquatic organisms may be exposed to substances in water directly via uptake from the water or indirectly via diet. The SSWQO for arsenic is intended to be used in the assessment and management of arsenic in the water column. That is, the SSWQO is related to the concentration of arsenic in the water. The exposure pathway of greatest relevance to arsenic toxicity is via direct uptake from water, rather than through bioaccumulation or biomagnification into organism tissue (CCME 2001) supporting the development of an SSWQO rather than a tissue residue-based guideline. This approach is consistent with the CCME (2007) protocol, which indicates that while bioaccumulation is an important consideration, it is not part of the protocol for the derivation of a CWQG-PAL. Therefore, the compilation focussed on toxicity data where the route of uptake was directly from the water. Experiments in which test organisms were injected with arsenic or fed arsenic in the diet were not compiled because these types of exposure are not reflective of what would occur in the receiving environment.

## 6.N-4 TOXICITY DATA EVALUATION, CATEGORIZATION, AND ENDPOINT SELECTION

Once the available toxicity data were compiled in the database, the data were evaluated for suitability and categorized as acceptable (primary or secondary data) or unacceptable for developing a long-term SSWQO for consistent with CCME (2007) guidance. Data suitability was confirmed by consulting the original publication or report, reviewing the test methods and verifying the test results.

Consistent with CCME (2007) guidance, toxicity data for Canadian species were considered suitable for developing the long-term SSWQO for arsenic, and data for species non-resident to Canada were used if the species could be considered suitable surrogates for Canadian resident species (e.g., fall within the same taxonomic group) and the toxicity tests were conducted under exposure conditions representative of Canadian waters. The recalculation procedure for deriving SSWQOs provided in CCME (2003) allows removal of toxicity data from the data set on species that are known not to occur or do not have the potential to occur at a site; however, this was not done in the current assessment. This is because with removal of these data, the minimum data requirements for fish for development of an SSWQO would not be met. However, consideration was given to whether the species is known to occur or has the potential to occur in Nunavut. For example, Indian major carp (Catla catla) has not been identified in lakes in Mammoth Lake and downstream lakes; however, other fish species of this family (family Cyprinidae) are known to occur in Nunavut. Therefore, the toxicity data for this species were considered suitable for SSWQO development. Flagfish (Jordanella floridae) has not been identified Mammoth Lake and downstream lakes and other fish species of this family (family Cyprinodontidae) are not known to occur in Nunavut. Therefore, the toxicity data for this species were not considered to be suitable for SSWQO development.





Other criteria used to evaluate the suitability of the toxicity data included the following and are consistent with CCME (2007) guidance:

- The preferred test endpoints were measures of survival, growth, reproduction and development. Non-traditional endpoints, such as pathological changes or swimming speed were not considered suitable because the ecological relevance of these endpoints is uncertain.
- Appropriate documentation was required for test design/conditions (e.g., flow-through, renewal, static), test concentrations, environmental variables (e.g., temperature, hardness, pH, etc.), experimental design (controls, number of replicates) and description of statistics.
- Studies were considered suitable if they included control or reference organisms that have been exposed to similar conditions as the experimental organisms.
- Data generated from studies evaluating synergistic, antagonistic or compensatory responses of organisms, such as tolerance (acclimation, adaptation), were considered unsuitable.
- Tests using field-collected organisms were not considered suitable because the life history of these organisms and their rate of exposure to arsenic is not generally clearly defined.
- Tests using organic forms of arsenic were not considered suitable because inorganic arsenic is the form likely to be found in water.
- Tests were not considered suitable if the original publication or report could not be located because this prevented a review of the test methods and verification of the test results.

Once the data were evaluated and categorized, endpoints were selected. For the statistical derivation approach, the order of priority by which the endpoints are selected is as follows (CCME 2007):

- EC<sub>x</sub>/IC<sub>x</sub> representing a no-effects threshold:
- EC<sub>10</sub>/IC<sub>10</sub>;
- EC<sub>11-25</sub>/IC<sub>11-25</sub>;
- Maximum Allowable Toxicant Concentration (MATC), as defined below;
- No Observed Effect Concentration (NOEC);
- Lowest Observed Effect Concentration (LOEC);
- EC<sub>26-49</sub>/IC<sub>26-49</sub>; and
- Non-lethal EC<sub>50</sub>/IC<sub>50</sub>.

MATCs were calculated by taking the geometric mean of the NOEC and LOEC reported for a given test. The procedure can yield results that are comparable to  $IC_{25}$  results, as discussed for example in US EPA (2007).

If a study yielded multiple results for a single endpoint, then the results were reduced to a single measurement to avoid biasing the database towards the results of a single study. For example, if inhibition concentrations (ICs) to





10%, 25% and 50% of the test population were reported for the growth of fathead minnow exposed to arsenic, then only the most protective of the three values (i.e., the  $IC_{10}$  value) was included in the database.

The CCME (2007) protocol allows for the incorporation of exposure and toxicity modifying factors (ETMFs) in the development of water quality guidelines. As noted previously, chemical speciation of arsenic (i.e., valency) is an important ETMF; however, there is uncertainty as to whether As(V) or As(III) predominates Mammoth Lake and downstream lakes. Therefore, endpoints for both As(V) and As(III) were included in the database. If a toxicity study tested both arsenic species for a given test species, then the lower of the two endpoints was included in the database. For example, Naumann et al. (2007) reported EC<sub>10</sub>s of 11,600 and 1,270  $\mu$ g/L for growth of *Lemna minor* exposed to As(V) and As(III), respectively. The lower EC<sub>10</sub> of 1,270  $\mu$ g/L for *Lemna minor* exposed to As(III) was included in the database.

The bioavailability (and toxicity) of arsenic is reduced by the presence of phosphorus, organic matter and clays, metal sulfides, and iron, aluminum, and manganese oxides and oxyhydroxides (Eisler 1988; Senn and Hemond 2003; Sharma and Sohn 2009). Additionally, an increase in As(V) toxicity has been observed with increasing temperatures (ANZECC and ARMCANZ 2000; McGeachy and Dixon 1989). However, these parameters were reported in very few studies and their potential influence on arsenic toxicity could not be readily quantified. As such, the influence of these parameters were not incorporated into the development of the SSWQO for arsenic.

## 6.N-5 DETERMINATION OF THE APPLICABLE SSWQO DERIVATION APPROACH

The minimum data set requirements for the derivation of a long-term guideline for freshwater environments outlined in CCME (2007) were used to determine whether the statistical derivation approach or the lowest endpoint derivation approach should be used to develop the SSWQO for arsenic. The available chronic toxicity data for arsenic in freshwater met the minimum data set requirements for the derivation of a long-term guideline using the statistical derivation (SSD) approach. Therefore, the statistical derivation approach was used to derive a long-term SSWQO for arsenic.

# 6.N-6 DEVELOPMENT OF THE SSWQO FOR ARSENIC USING THE STATISTICAL DERIVATION APPROACH

The chronic toxicity data used in the SSD are summarized in Table 6-N-1. Table 6-N-1 provides only the chronic toxicity data that were used in the SSD to develop the SSWQO. It does not include all of the studies and data that were compiled and evaluated for suitability for developing the long-term SSWQO. A full description of how the data provided in Table 6-N-1 were selected was provided in Section 6.N-4. Therefore, all of the data presented in Table 6-N-1 are categorized as acceptable (i.e., primary or secondary data as per CCME [2007]).



Table 6-N-1: Chronic Toxicity Data used in the Development of the SSWQO for Arsenic

Test Species	Common Name	Taxa Group	Arsenic Species	Test Duration (days)	Biological Measurement	Endpoint	Effect Concentration (µg As/L)	Source	Rank
Daphnia pulex	Water Flea	Invertebrate	As(V)	26	Reproduction	LOEC	10	Chen et al. 1999	1
Scenedesmus obliquus	Green Algae	Aquatic Plant/Algae	As(V)	14	Growth	EC <sub>50</sub>	48	Vocke et al. 1980; See note (a)	2
Melosira granulata	Algae	Aquatic Plant/Algae	As(V)	8-24	Growth	IC35/LOEC	75	Planas and Healey 1978; See note (a)	3
Ochromonas valesiaca	Algae	Aquatic Plant/Algae	As(V)	8-24	Growth	IC <sub>20</sub> /LOEC	75	Planas and Healey 1978; See note (a)	4
Monoraphidium arcuatum	Freshwater Algae	Aquatic Plant/Algae	As(V)	3	Growth	LOEC	81	Levy et al. 2005	5
Gammarus pseudolimnaeus	Scud	Invertebrate	As(III)	14	Survival	LC <sub>15</sub>	88	Spehar et al. 1980	6
Lemna gibba	Inflated Duckweed	Aquatic Plant/Algae	As(V)	21	Growth	MATC	224	Mkandawire et al. 2006; See note (b)	7
Cryptomonas erosa	Algae	Aquatic Plant/Algae	As(V)	8-24	Growth	IC <sub>22</sub>	225	Planas and Healey 1978	8
Ankistrodesmus falcatus	Green Algae	Aquatic Plant/Algae	As(V)	14	Growth	EC <sub>50</sub>	256	Vocke et al. 1980	9
Baetis tricaudatus	Mayfly	Invertebrate	As(III)	12	Survival	MATC	300	Irving et al. 2008	10
Cyclops vernalis, C. bicuspidatus thomasi, Diaptomus sp.	Copepods	Invertebrate	As(III)	14	Growth	EC <sub>20</sub>	320	Borgmann et al. 1980; See note (a)	11
Ceriodaphnia dubia	Water Flea	Invertebrate	As(III)	7	Reproduction	EC <sub>19</sub>	891	Spehar and Fiandt 1986	12
Pimephales promelas	Fathead Minnow	Fish	As(V)	30	Growth	MATC	892	De Foe 1982; see Note (b)	13
Daphnia magna	Water Flea	Invertebrate s	As(III)	28-31	Survival/Growth /Reproduction	MATC	914	Lima et al. (1984)	14
Pteronarcys dorsata	Stonefly	Invertebrate	As(III)	28	Survival	NOEC	961	Spehar et al. 1980	15
Helisorna campanulata	Snail	Invertebrate	As(III)	28	Survival	LC <sub>10</sub>	973	Spehar et al. 1980	16
Stagnicola emarginata	Snail	Invertebrate	As(V)	28	Survival	LC <sub>10</sub>	973	Spehar et al. 1980	16

AGNICO EAGLE



June 2016 Project No. 1541520

Test Species	Common Name	Taxa Group	Arsenic Species	Test Duration (days)	Biological Measurement	Endpoint	Effect Concentration (μg As/L)	Source	Rank
Lithobates pipiens	Leopard Frog	Amphibian	As(V)	113	Growth	NOEC	1026	Chen et al. 2009	17
Chlorella sp.12	Green Algae	Aquatic Plant/Algae	As(V)	3	Growth	MATC	1243	Levy et al. 2005; See note (b)	18
Lemna minor	Duckweed	Aquatic Plant/Algae	As(III)	7	Growth	EC <sub>10</sub>	1270	Naumann et al. 2007	19
Anabaena variabilis	Algae	Aquatic Plant/Algae	As(V)	8-24	Growth	IC <sub>10</sub>	2250	Planas and Healey 1978	20
Chlamydomonas reinhardtii	Algae	Aquatic Plant/Algae	As(V)	8-24	Growth	MATC	3182	Planas and Healey 1978; See note (b)	21
Oncorhynchus mykiss	Rainbow Trout	Fish	As(III)	21	Growth	MATC	4243	Speyer 1975; See note (b)	22
Catla catla	Indian Major Carp	Fish	As(V)	35	Survival	NOEC	4378	Kavitha et al. 2010	23
Microcystis sp.	Blue-Green Algae	Aquatic Plant/Algae	As(V)	14	Growth	NOEC	7492	Gong et al. 2009	24
Selenastrum capricornutum	Green Algae	Aquatic Plant/Algae	As(V)	14	Growth	EC <sub>50</sub>	30761	Vocke et al. 1980	25
Scenedesmus quadricauda	Algae	Aquatic Plant/Algae	As(V)	12	Growth	EC <sub>50</sub>	61000	Fargasova 1994	26
Microcoleus vaginatus	Green Algae	Aquatic Plant/Algae	As(V)	14	Growth	NOEC	100000	Vocke et al. 1980	27

<sup>(</sup>a) Data used in the development of the current CWQG-PFAL for arsenic (CCME 2001).



June 2016 Project No. 1541520

<sup>(</sup>b) MATCs were calculated by Golder by taking the geometric mean of the NOEC and LOEC reported for a given study.

 $<sup>\</sup>mu$ g As/L = micrograms arsenic per litre; MATC = maximum acceptable toxicant concentration; As(V) = pentavalent arsenic; LOEC = lowest observed effect concentration; IC<sub>X</sub> = X% inhibitory concentration; As(III) = trivalent arsenic; LC<sub>X</sub> = X% lethal concentration; NOEC = no observed effect concentration; EC<sub>x</sub> = X% effect concentration.



There were some studies that were included by the CCME in the development of the current CWQG-PFAL for arsenic that were not included in the SSD for the Project. These include the following:

- 28-d LC<sub>50</sub> of 550 μg/L for rainbow trout (Birge et al. 1978);
- 7-d LOEC of 500 µg/L and a 72-h LOEC for survival for climbing perch (Jana and Sahana 1989);
- 7-d LOEC of 970 μg/L for catfish (Jana and Sahana 1989);
- 21-d EC<sub>16</sub> (reproduction) of 520 μg/L for *Daphnia magna* (Biesinger and Christensen 1972);
- 96-h EC<sub>50</sub> (immobility) of 850 μg/L for *Bosmina longirostris* (Passino and Novak 1984);
- 7-d LC<sub>80</sub> of 960 µg/L for Gammarus pseudolimnaeus (Spehar et al. 1980);
- T-d LOEC (immobilization) of 1000 μg/L for Ceriodaphnia dubia (Spehar and Fiant 1986); and
- 20-d VSUE (very severe unfavourable effect) of 960 µg/L for Scenedesmus obliquus (Fargasova 1993).

The 96-h LC<sub>50</sub> for rainbow trout, the 7-d LC<sub>80</sub> for *Gammarus pseudolimnaeus* and the 20-d VSUE for *Scenedesmus obliquus* were not included in the SSD because lethal effect levels of 50% or greater are not acceptable for guideline development using the SSD approach as per the CCME (2007) protocol. The data for climbing perch and catfish were not included in the SSD because the Jana and Sahana (1989) reference could not be located for review and verification of test methods and results. The 96-h EC<sub>50</sub> for *Bosmina longirostris* was not included in the SSD because the exposure duration is considered to be short-term based on current CCME (2007) guidance. The 21-d EC<sub>16</sub> for reproduction in *Daphnia magna* was not included in the SSD because a more applicable endpoint was identified for this species. While the 7-d LOEC for immobilization for *Ceriodaphnia dubia* from Spehar and Fiandt (1986) was not included in the SSD, the 7-d EC<sub>19</sub> for reproduction of 819 μg/L from the same study was included. The EC<sub>19</sub> rather than the LOEC was included in the SSD because an EC<sub>11-25</sub>/IC<sub>11-25</sub> endpoint is preferred over a LOEC endpoint based on CCME (2007) guidance.

Overall, 28 species were included in the SSD. The species list consisted of:

- three fish species (one salmonid and three non-salmonids);
- one amphibian species;
- nine aquatic invertebrate species (including crustaceans, insects [mayflies and stoneflies] and gastropods),
- two aquatic plant species; and
- 13 algal species.

The CCME (2007) protocol specifies that if multiple comparable records for the same endpoint are available for a species, they are to be combined by the geometric mean of the records to represent the averaged effects endpoint for that species. The determination of which records are "comparable" is subject to professional judgement; ideally, comparable records would have identical life stage, test duration, exposure protocol, biological endpoint, statistical response measure, and water quality characteristics. However, in practice, obtaining perfect concordance among toxicity data collected by different investigators is rare. There were no suitably comparable records identified in the arsenic toxicity dataset; therefore, no geometric means were calculated for the SSD.





The software package, SSD Master Version 3.0 (CCME 2013), was used to generate the SSD. In brief, the software ranks each species according to sensitivity to arsenic (from lowest effect concentration to highest effect concentration) and its centralized position on the SSD (Hazen plotting position) is determined using the following equation (Alderberg et al. 2002; Newman et al. 2002):

Percent Species Affected = (X - 0.5) / N

Where X is the species rank, with 1 being the most sensitive species (lowest effect concentration), and N is the total number of species included in the SSD. The percent species affected and the corresponding effect concentrations are then plotted in the SSD. Several cumulative distribution functions (Normal, Logistic, Extreme Value and Gumbel) are fit to the data (both in arithmetic and log space) using regression methods. One of the models is then chosen as the best fit to the data based on a goodness-of-fit test (Anderson-Darling Goodness-of-Fit) and an overall visual assessment of model fit.

Of the models tested, the Normal model was considered to provide the best fit of the data. The equation of the Normal model is:

$$F(x) = \frac{1}{2\left(1 + erf\left(\frac{x - \mu}{\alpha\sqrt{2}}\right)\right)}$$

Where:

F(x) = proportion of taxa affected at the given arsenic concentration; 0.05;

 $x = arsenic concentration (\mu g/L);$ 

 $\mu$  = mean or expectation of the distribution (also its median and mode); 2.9; and

 $\alpha$  = standard deviation; 0.86.

The long-term SSD is shown on Figure 6-N-1.





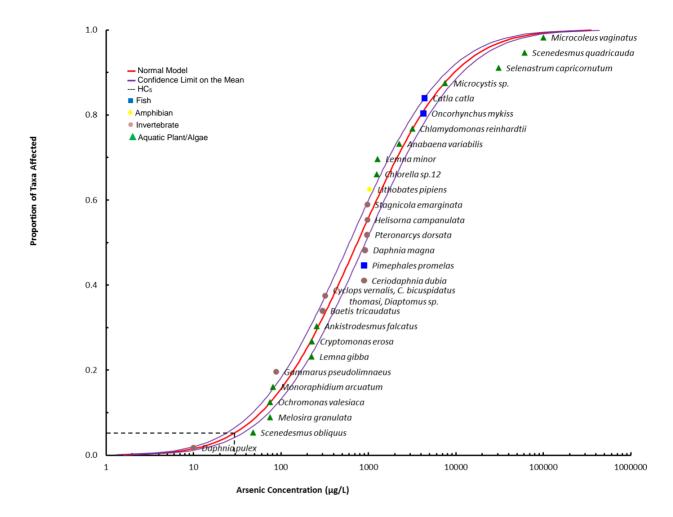


Figure 6-N-1: Species Sensitivity Distribution for Arsenic

CCME (2007) defines the long-term guideline as the intercept of the  $5^{th}$  percentile of the y-axis with the fitted SSD curve (or the HC<sub>5</sub>, or hazardous concentration to 5% of species). The  $5^{th}$  percentile on the long-term SSD (HC<sub>5</sub>) and the SSWQO for arsenic is  $28 \,\mu\text{g/L}$ . The lower confidence limit on the mean is  $22 \,\mu\text{g/L}$  and the upper confidence limit on the mean is  $35 \,\mu\text{g/L}$ .

The HC $_5$  for arsenic is almost three times higher than the current CCME water quality guideline for the protection of freshwater aquatic life of 5 µg/L (CCME 1999/2016). The HC $_5$  is higher than the most sensitive species used in the SSD derivation. The most sensitive species used in the SSD was *Daphnia pulex*, with a 26-day LOEC for reproduction of 10 µg/L (Chen et al. 1999). Other daphnids were considerably less sensitive, with effect concentrations of 891 µg/L for *Ceriodaphnia dubia* (Spehar and Fiandt 1986) and 914 µg/L for *Daphnia magna* (Lima et al. 1984). The likelihood of an endpoint on an SSD falling below the 5<sup>th</sup> percentile increases with sample size, and is therefore inherent in the SSD approach.





In cases where an endpoint falls below the 5<sup>th</sup> percentile (or SSWQO), consideration may be given to applying the protection clause which was developed by the CCME (2007) to ensure that the long term guideline is sufficiently protective. The clause is invoked under the following circumstances:

- If an acceptable single (or, if applicable, geometric mean) no-effect or low-effect level endpoint (e.g., EC<sub>x</sub> for growth) for a species at risk is lower than the proposed guideline, then that endpoint becomes the recommended guideline value. If the endpoint is a moderate- or severe-effect level endpoint (i.e., EC<sub>x</sub> with x ≥50 or a lethality endpoint [LC<sub>x</sub>]), then the guideline value is determined on a case-by-case basis (e.g., by using an appropriate safety factor).
- If an acceptable single (or, if applicable geometric mean) lethal-effects endpoint (i.e., LC<sub>x</sub>, where x ≥15) for any species is below the proposed guideline, then that endpoint becomes the recommended guideline value.
- Special consideration is required if multiple endpoints for a single taxon (e.g., fish, invertebrates, plant/algae) and/or an elevated number of secondary studies are clustered around the 5<sup>th</sup> percentile.
- If it can be demonstrated that an endpoint below the 5<sup>th</sup> percentile is for a species at risk within a given province/territory or region/site, for a species of commercial or recreational importance, or for an "ecological important" species, than that data point may be used for deriving the guideline.

In considering the long-term acceptable dataset, only one endpoint fell below the 5<sup>th</sup> percentile on the SSD; the 26-d LOEC for reproduction in *Daphnia pulex* of 10 µg/L. The dataset did not contain any acceptable endpoints below the 5<sup>th</sup> percentile that represent effects to either species at risk or lethal effects, or for species of commercial, recreational or ecological importance. Multiple endpoints for a single taxon and an elevated number of secondary studies were not clustered around the 5<sup>th</sup> percentile. Therefore, the protection clause was not invoked in the development of the SSWQO for arsenic.

#### 6.N-7 UNCERTAINTY

The main sources of uncertainty associated with the development of the long-term SSWQO for arsenic for the protection of freshwater aquatic life were:

- Inclusion of Data for Both As(V) and As(III) Arsenic speciation is an important ETMF; however, arsenic speciation in lakes in Mammoth Lake is not well understood. It is possible that both oxic and anoxic conditions can potentially occur in freshwater systems and thus both As(V) and As(III) may occur in different areas or at different times. As a result, endpoints for both As(V) and As(III) were included in the development of the SSWQO. Some studies have demonstrated that As(V) is less toxic than As(III) in aquatic systems (Borgmann et al. 1980; Naumann et al. 2007). The SSWQO may be conservative if one species (e.g., As(V)) predominates Mammoth Lake and downstream lakes.
- Lack of Incorporation of other ETMFs —The toxicity of arsenic is ameliorated by the presence of phosphorus, organic matter and clays, metal sufides, and iron, aluminum and manganese oxides and oxyhydroxides. Given the limited data, it was not possible to quantify the effect of these ETMFs on arsenic bioavailability and toxicity. It is possible that these ETMFs are lower in concentration in laboratory toxicity tests relative to Mammoth Lake and downstream lakes; therefore, toxicity may be overestimated in the laboratory-based studies. As a result, the SSWQO may be conservative for the Project.





Selected SSD Model – The Normal model was selected as the best fit to the toxicity data based on the Anderson-Darling Goodness-of-Fit test (A² = 0.456) and an overall visual assessment of model fit. It is noted that the Logistic model also provided a good fit to the data and yielded an HC₅ of 22 μg/L. For the Logistic Model, the Anderson-Darling Goodness-of-Fit test provided an A² of 0.370 which was lower than that for the Normal model; however, model fit in the lower tail of the distribution which determines the HC₅ was not as good as for the Normal model based on the visual assessment. This was supported by a slightly higher mean square error in the lower tail for the Logistic model (0.0386 versus 0.0374 for the Normal model). As well, the confidence limit on the mean was wider for the Logistic model (from 16.29 to 30.41 μg/L) than for the Normal model (from 22.96 to 35.06 μg/L).

#### 6.N-8 SUMMARY

In summary, there were sufficient chronic toxicity data to derive a long-term SSWQO for arsenic for the protection of aquatic life using an SSD. In total, 28 aquatic species were included in the long-term SSD. The Normal model provided the best fit to the toxicity data and was used to derive the long-term SSWQO of 28 µg/L.

#### 6.N-9 REFERENCES

- Aldenberg T, Jaworska TS, Traas JP. 2002. Normal species sensitivity distributions and probabilistic ecological risk assessment. In Posthuma L, Suter II GW, Traas TP (eds), Species Sensitivity Distributions in Ecotoxicology. CRC Press, Boca Raton, FL, USA, pp 49-102.
- ANZECC (Australian and New Zealand Environment and Conservation Council) and ARMCANZ (Agriculture and Resource Management Council of Australia and New Zealand). 2000. Aquatic Ecosystems Rationale and Background Information (Chapter 8). Australian and New Zealand Guidelines for Fresh and Marine Water Quality Vol. 2.
- Biesinger KE, Christensen GM. 1972. Effects of various metals on survival, growth, reproduction, and metabolism of *Daphnia magna*. J Fish Res Bd Can 29: 1691-1700.
- Birge, W.J., J.E. Hudson, J.A. Black, and A.G. Westerman. 1979. Embryo-larval bioassays on inorganic coal elements and *in situ* biomonitoring of coal-waste effluents. In: Surface mining and fish/wildlife needs in the eastern United States, D.E. Samuel, J.R. Stauffer, C.H. Hocutt, and W.T. Mason Jr., eds., pp. 97-104. Fish and Wildlife Service, Office of Biological Services. FWS/OBS-78/81. U.S. Government Printing Office, Washington, DC.
- Borgmann U, Cove R, Loveridge C. 1980. Effects of metals on the biomass production kinetics of freshwater copepods. Can J Fish Aquat Sci 37: 567-575.
- Bright DA, Coedy B, Dushenko WT, Reimer KJ. 1994. Arsenic transport in a watershed receving gold mine effluent mear Yellowknife, Northwest Territories, Canada. Sci Total Environ 155: 237-252.
- CCME (Canadian Council of Ministers of the Environment). 1991. Appendix IX— A protocol for the derivation of water quality guidelines for the protection of aquatic life (April 1991). In: Canadian water quality guidelines, Canadian Council of Resource and Environment Ministers, 1987. Prepared by the Task Force on Water Quality Guidelines. [Updated and reprinted with minor revisions and editorial changes in Canadian environmental quality guidelines, Chapter 4, Canadian Council of Ministers of the Environment, 1999, Winnipeg, MB].





- CCME. 2001. Canadian water quality guidelines for the protection of aquatic life: Arsenic. Updated. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
- CCME. 2003. Canadian water quality guidelines for the protection of aquatic life: Guidance on the Site-Specific Application of Water Quality Guidelines in Canada: Procedures for Deriving Numerical Water Quality Objectives. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
- CCME. 2007. A protocol for the derivation of water quality guidelines for the protection of aquatic life 2007. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, 1999, Winnipeg.
- Chen CY, Sillett KB, Folt CL, Whittemore SL, Barchowsky A. 1999. Molecular and demographic measures of arsenic stress in *Daphnia pulex*. Hydrobiologia 401: 229-238.
- Chen TH, Gross JA, Karasov WH. 2009. Chronic Exposure to Pentavalent Arsenic of Larval Leopard Frogs (*Rana pipiens*): Bioaccumulation and Reduced Swimming Performance. Ecotoxicology 18(5): 587-593.
- DeFoe DL. 1982. Arsenic (V) Test Results. U.S. EPA, Duluth, MN (Memo to R.L. Spehar, U.S. EPA, Duluth, MN): 9 p.
- Eisler R. 1988. Arsenic Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. United States Fish and Wildlife Service Contaminant Hazard Reviews Report No. 12.
- Fargasova, A. 1993. Effect of five toxic metals on the alga *Scenedesmus quadricus*. Biologia (Bratislava) 48(3):301–304.
- Fargasova A. 1994. Comparative toxicity of five metals on various biological subjects. Bull Environ Contam Toxicol 53: 317-324.
- Fodor P. 2001. Arsenic speciation in the environment. In Ebdon L, Pitss L, Cornelius R, Crews H Donard OFX, Quevuviller PH, eds, Trace Element Speciation for Environment, Food, and Health. MPG Books, Cornwall, UK, pp 196-210.
- Gong Y, Chou HN, Tu C, Liu X, Liu J and Song L. 2009. Effects of arsenate on the growth of microcystin production of Microcystis aeruginosa isolated from Taiwan as influenced by extracellular phosphate. J Apply Phycol 21: 225-231.
- Irving EC, Lowell RB, Culp JM, Liber K, Xie Q. 2008. Effects of arsenic speciation and low dissolved oxygen condition on the toxicity of arsenic to a lotic mayfly. Environ Toxicol Chem 27(3):583–590.
- Jana, S., and S.S. Sahana. 1989. Sensitivity of the freshwater fishes *Clarias batrachus* and *Anabas testudineus* to heavy metals. Environ. Ecol. 7(2):265–270.
- Kavitha C, Malarvizhi A, Senthil Kumaran S, Ramesh M. 2010. Toxicological effects of arsenate exposure on hematological, biochemical and liver transaminases activity in an Indian major carp, *Catla catla*. Food Chem Toxicol. 48: 2848-2854.





- Levy JL, Stauber JL, Adams M, Maher W, Kirby JK, Jolley DF. 2005. Toxicity, biotransformation, and mode of action of arsenic in two freshwater microalgae (*Chlorella* sp. and *Monoraphidium arcuatum*). Environ Toxicol Chem 24: 2630-2639.
- Lima AR, Curtis C, Hammermeister DE, Markee TP, Northcott CE and Brooke LT. 1984. Acute and chronic toxicities of arsenic (III) to fathead minnows, flagfish, daphnids, and an amphipod. Arch Environ Contam Toxicol 13: 595-601.
- McGeachy SM, Dixon DG. 1989. The impact of temperature on the acute toxicity of arsenate and arsenite to Rainbow Trout (*Salmo gairdneri*). Ecotoxicol Env Safety 17: 86-93.
- Mkandawire M, Taubert B, Dudel EG. 2006. Limitations of growth-parameters in *Lemna gibba* bioassays for arsenic and uranium under variable phosphate availability. Ecotoxicol Environ Saf 65: 118-128.
- Nagorski SA, Moore JN. 1999. Arsenic mobilization in the hyporheic zone of a contaminated stream. Water Resourc Res 35: 3441-3450.
- Naumann B, Eberius M, Appenroth K-J. 2007. Growth rate based dose-response relationships and EC-values of ten heavy metals using the duckweed growth inhibition test (ISO 20079) with *Lemna minor* L. Clone St. J Plant Physiol 164: 1656-1664.
- Newman, M. C., Ownby, D. R., Mezin, L. C. A., Powell, D. C., Christensen, T. R. L., Lerberg, S. B. et al. 2002. Species sensitivity distributions in ecological risk assessment: Distributional assumptions, alternate bootstrap techniques, and estimation of adequate number of species. *In* Species Sensitivity Distributions in Ecotoxicology. Posthuma, L., Suter, G. W. I., and Traas, T. (ed.) Boca Raton, FL, CRC Press LLC, pp. 119-132.
- Passino, D.R.M., and A.J. Novak. 1984. Toxicity of arsenate and DDT to the cladoceran *Bosmina longirostris*. Bull. Environ. Contam. Toxicol. 33:325–329.
- Planas D, Healey FP. 1978. Effects of arsenate on growth and phosphorus metabolism of phytoplankton. J Phycol 14: 337-341.
- Senn DB, Hemond HF. 2004. Particulate arsenic and iron during anoxia in a eutrophic, urban lake. Environ Toxicol Chem 23: 1610-1616.
- Sharma VK, Sohn M. 2009. Aquatic Arsenic: Toxicity, Speciation, Transformations, and Remediation. Env Internat 35: 743-759.
- Smedley PL, Kinniburgh DG. 2002. A review of the source, behavior, and distribution of arsenic in natural waters. Appl Geochem 17: 517-568.
- Spehar RL, Fiandt JT, Anderson RL, DeFoe DL. 1980. Comparative toxicity of arsenic compounds and their accumulation in invertebrates and fish. Arch Environ Contam Toxicol 9: 53-63.
- Spehar RL, Fiandt JT. 1986. Acute and chronic effects of water quality criteria–based metal mixtures on three aquatic species. Environ Toxicol Chem 5:917–931.
- Speyer MR. 1975. Some effects of chronic combined arsenic and cyanide poisoning on the physiology of rainbow trout. M.S. Thesis, Concordia University, Montreal, Canada.





- U.S. EPA (United States Environmental Protection Agency). 2007. Aquatic Life Ambient Freshwater Quality Criteria Copper. 2007 Revision. Washington, DC, USA. Available online: http://www.epa.gov/waterscience/criteria/aqlife.html. Accessed on February 27, 2012.
- U.S. EPA. 2016. ECOTOX User Guide: ECOTOXicology Database System. Version 4.0. Available: http://www.epa.gov/ecotox/.

Vocke RW, Sears KL, O'Toole JJ, Wildman RB. 1980. Growth responses of selected freshwater algae to trace elements and scrubber ash slurry generated by coal-fired power plants. Water Res 14: 141-150.

