FACT SHEET OVERVIEW

The Water Security Agency is the lead agency for water management in the province. The Water Security Agency has adopted a molybdenum water quality objective for the protection of aquatic life. The Ministry of Environment will adopt this water quality objective in the Saskatchewan Environmental Quality Guidelines.

MOLYBDENUM (Mo)

Molybdenum occurs naturally in the environment. It is a transition metal of Subgroup 6A in the periodic table, and has a molecular mass of 95.96 g/mol. The Chemical Abstracts Service (CAS) number for molybdenum is 7439-98-7. In mineral form, it is primarily observed as molybdenite (MoS₂), however other common forms include powellite (CaOMo₃) and wulfenite (PbMoO₄). It is also found in minerals containing iron, bismuth or copper, and may co-occur with other deposits. It has oxidation states that range between -2 and +6, however under typical environmental conditions molybdenum compounds are primarily in oxidation states ranging between +3 and +6 (Xu et al. 2013). The molybdate anion (MoO₄²⁻) is the predominate dissolved form of molybdenum in natural waters with pH values greater than 6 and is the species most commonly investigated in toxicity tests, typically supplied as sodium molybdate dihydrate (Na₂MoO₄·2H₂O).

The molybdenum water quality objective provides an update on current knowledge of the aquatic toxicity of molybdenum to freshwater organisms. Using these data, a long-term freshwater guideline has been produced using the fifth percentile of the species sensitivity distribution (SSD), following guidance provided in the CCME Protocol (2007). This has resulted in a new Surface Water Quality Objective (SWQO) that has been adopted by the Water Security Agency (WSA) in Saskatchewan for molybdenum in natural waters (Table 1).

<table>
<thead>
<tr>
<th></th>
<th>Long-Term Water Quality Objective for Molybdenum (µg/L)</th>
<th>Short-Term Water Quality Objective for Molybdenum (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater</td>
<td>31,000¹</td>
<td>NRG²</td>
</tr>
<tr>
<td>Marine</td>
<td>NRG³</td>
<td>NRG³</td>
</tr>
</tbody>
</table>

NRG = no recommended guideline

¹ This objective was derived based on total molybdenum concentrations.
² There were insufficient data available to derive a short-term freshwater benchmark with reasonable confidence due to the majority of available effect concentrations representing unbounded data points.
³ Data were not evaluated for marine species.
USES OF MOLYBDENUM
Mining of molybdenum is primarily performed on deposits of molybdenite (MoS$_2$) that contain between <0.1 and 0.25% molybdenum (Dorfler and Laferty 1981). However, by-product or co-product production, especially from copper circuits at selected porphyry copper mines, has been estimated to produce 79% of western and 55% of the worldwide molybdenum supply (Magyar 2004). Canada ranked as the sixth largest producer of molybdenum in 2013, behind China, the United States, Chile, Peru, and Mexico, with estimated production of 7,618 tonnes or 2.8% of the world supply (Marshall 2014).

Molybdenum is used primarily as an alloying agent in cast iron, steel, and superalloys to increase hardenability, strength, toughness, wear- and corrosion-resistance (Xu et al. 2013; Lasheen et al. 2015). It is also commonly used in the electronics industry (Xu et al. 2013).

MOLYBDENUM IN THE ENVIRONMENT
Molybdenum is an essential micro-nutrient for growth and development in both aquatic plants and animals. It enters aquatic systems naturally through the weathering of ores from igneous and sedimentary rock, and subsequent runoff to freshwater environments (Fletcher et al. 1998). Anthropogenic influences can accelerate molybdenum deposition to aquatic systems through: leaching processes due to mining activities, burning of fossil fuels, use of fertilizers that contain molybdenum as a growth promoter, wastewater treatment plant discharges, and chemical and industrial waste water discharges (Fletcher et al. 1998; Pyle 2000; Phillips and Russo 1978; McNeely et al. 1979).

Molybdenum is generally measured in water samples using inductively coupled plasma, combined with mass spectrometry (ICP-MS) or optical emission spectrometry (ICP-OES), or with graphite furnace atomic absorption spectrophotometry (GFAAS). Detection limits for these analyses typically range from 0.05 to 10 µg/L. Molybdenum concentrations are generally low in freshwater environments. In British Columbia, ambient molybdenum water concentrations collected from reference locations in areas that support molybdenum mining were reported between 3 and 22 µg/L, although concentrations as high as 11,400 µg/L have been reported in aquatic systems located in proximity to mine operations (Davies et al. 2005; Jones 1994).

Ambient molybdenum water concentrations were typically reported at or around the analytical detection limit in studies conducted in the Great Lakes (Rossman and Barres 1988) and in the Upper Gunison River drainage basin of Colorado (Colborn 1982), with median total molybdenum concentrations in the Great Lakes ranging between 0.15 and 2.8 µg/L. Mean total molybdenum concentrations in the Athabasca region of Canada were between 0.19 and 0.6 µg/L (Hatfield Consultants 2015) and average total molybdenum concentrations in the St. Lawrence River measured 1.4 µg/L between 2009 and 2011 (Rondeau 2015). Oxidation/reduction (redox) potential and pH in aquatic systems have been shown to significantly influence molybdenum solubility and mobility. At common environmental pH values (pH > 6) molybdenum tends to predominantly form the molybdate anion (MoO$_4^{2-}$) under aerobic conditions, which is highly soluble and, therefore, would be expected to be biologically available. The speciation of molybdenum influences how it interacts with organic ligands, anions, cations, oxides and hydroxides in the water column, or through the adsorption or absorption of molybdenum to particulate matter and sediments.

MOLYBDENUM IN BIOTA
Regoli et al. (2012) reviewed the available data on molybdenum bioaccumulation (BAFs) and bioconcentration factors (BCFs) for aquatic organisms. In general, BAFs and BCFs showed an inverse relationship to exposure concentration for molybdenum, which is consistent with data for a variety of other essential and non-essential metals (McGeer et al. 2003; DeForest et al. 2007). Regoli et al. (2012) showed that aquatic organisms apparently regulate internal concentrations of molybdenum to some extent. Molybdenum does
not appear to biomagnify in higher trophic levels; in fact, studies have reported higher bioaccumulation at the base of the food web (e.g., phytoplankton) relative to organisms in higher trophic levels (Muscatello and Janz 2009; Ikemoto et al. 2008; Saiki et al. 1993).

**UPTAKE AND MODE OF TOXIC ACTION**
There is limited information on the route of uptake of molybdenum in aquatic animals, however there is some evidence that molybdenum enters fish through the gill (Reid 2002). Tests with single celled organisms indicate that molybdenum is actively transported across cell membranes through similar anion channels as both sulphate and tungsten, which have similar size, charge and stereochemistry (Elliot and Mortenson 1975; Cole et al. 1993). However, data also exists that suggests that the uptake of molybdenum through these channels may also occur in a passive manner (Sakaguchi et al. 1981). Nevertheless, competition between molybdenum, sulphate and tungsten for cell binding sites has been well documented and sulphate, in particular, may represent an important toxicity modifying factor for molybdenum.

The mode of toxic action for molybdenum has been thought to be related to disruption of copper metabolism, resulting in copper deficiency. However, this has been primarily observed in ruminants and there is an absence of evidence of this mechanism of toxicity in aquatic organisms. In fact, there has been some evidence that acute toxicity to molybdenum may be related to gill irritation leading to respiratory distress in fish (Reid 2002). Furthermore, Barros et al. (2013) determined that molybdenum could cause reduced uptake of sulphate at higher molybdenum to sulphate ratios in the single-celled marine dinoflagellae *Lingulodinium polyedrum*, potentially resulting in oxidative damage to cells associated with disruption of cellular equilibrium.

**WATER QUALITY OBJECTIVE DERIVATION**
The SWQO for molybdenum for the protection of aquatic life was developed based on updated guidance provided in CCME (2007). It was derived using a species sensitivity distribution (SSD). Additional details are provided in the supporting scientific criteria document (Nautilus Environmental 2017). An objective was not derived for marine life.

**FRESHWATER LIFE**

**Short-term exposure toxicity data**
Acute (96 hour or less) LC$_{50}$ values for molybdenum were available for seven freshwater fish species; four salmonid, and three non-salmonid. Four of the seven reported endpoints had values that were greater than the highest concentration tested (Table 2). The fathead minnow (*Pimephales promelas*) was the most sensitive fish species that had a measured response concentration, which was a 96 hour LC$_{50}$ of 644 mg/L (GEI 2009). The least sensitive fish species was the white sucker (*Catostomus commersoni*) with a reported 96 hour LC$_{50}$ of >2,000 mg/L (Pyle 2000).

Acute LC$_{50}$ values were available for seven freshwater invertebrates. Measurable effect concentrations were available for seven of the eight data points (Table 2). The most sensitive species was the freshwater cladoceran, *Ceriodaphnia dubia*, with a 48 hour LC$_{50}$ of 1,015 mg/L (GEI 2009). The least sensitive species was the larval midge, *Chironomus dilutus*, with a geometric mean LC$_{50}$ of 7,533 mg/L (GEI 2009).

**Short-term freshwater objective**
A short-term objective was not calculated with these data due to the uncertainty associated with the large number of unbounded short-term endpoints.
Table 2. Toxicity data points determined to be of acceptable quality (based on CCME [2007]) for derivation of a short-term surface water quality objective for molybdenum.

<table>
<thead>
<tr>
<th>Species (Common name)</th>
<th>Duration</th>
<th>Endpoint</th>
<th>Reported</th>
<th>Species Geometric Mean</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fish</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Catostomus commersonii</em> (white sucker)</td>
<td>96 h</td>
<td>LC50</td>
<td>&gt;2,000</td>
<td>2,000</td>
<td>Pyle (2000)</td>
</tr>
<tr>
<td><em>Catostomus latipinnis</em> (flannelmouth sucker)</td>
<td>96 h</td>
<td>LC50</td>
<td>1,940</td>
<td>1,940</td>
<td>Hamilton and Buhl (1997)</td>
</tr>
<tr>
<td><em>Esox Lucius</em> (Northern pike)</td>
<td>96 h</td>
<td>LC50</td>
<td>&gt;128</td>
<td>128</td>
<td>Pyle (2000)</td>
</tr>
<tr>
<td><em>Oncorhynchus kisutch</em> (coho salmon)</td>
<td>96 h</td>
<td>LC50</td>
<td>&gt;1,000</td>
<td>1,000</td>
<td>Hamilton and Buhl (1990)</td>
</tr>
<tr>
<td><em>Oncorhynchus mykiss</em> (rainbow trout)</td>
<td>96 h</td>
<td>LC50</td>
<td>&gt;1,190</td>
<td>800</td>
<td>Pyle (2000)</td>
</tr>
<tr>
<td><em>Oncorhynchus tshawytscha</em> (Chinook salmon)</td>
<td>96 h</td>
<td>LC50</td>
<td>&gt;1,000</td>
<td>1,000</td>
<td>Hamilton and Buhl (1990)</td>
</tr>
<tr>
<td><em>Pimephales promelas</em> (fathead minnow)</td>
<td>96 h</td>
<td>LC50</td>
<td>644</td>
<td>644</td>
<td>GEI (2009)</td>
</tr>
<tr>
<td><strong>Invertebrates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Ceriodaphnia dubia</em> (cladoceran)</td>
<td>48 h</td>
<td>LC50</td>
<td>1,015</td>
<td>1,015</td>
<td>GEI (2009)</td>
</tr>
<tr>
<td><em>Chironomus dilutus</em> (midge)</td>
<td>48 h</td>
<td>LC50</td>
<td>7,533</td>
<td>7,533</td>
<td>GEI (2009)</td>
</tr>
<tr>
<td><em>Crangonyx pseudogracilis</em> (amphipod)</td>
<td>96 h</td>
<td>LC50</td>
<td>2,650</td>
<td>2,650</td>
<td>Martin and Holdich (1986)</td>
</tr>
<tr>
<td><em>Daphnia magna</em> (cladoceran)</td>
<td>48 h</td>
<td>LC50</td>
<td>1,728</td>
<td>502</td>
<td>GEI (2009)</td>
</tr>
<tr>
<td><em>Girardia dorotocephala</em> (flatworm)</td>
<td>96 h</td>
<td>LC50</td>
<td>1,226</td>
<td>1,226</td>
<td>GEI (2009)</td>
</tr>
<tr>
<td><em>Hyalella azteca</em> (amphipod)</td>
<td>96 h</td>
<td>LC50</td>
<td>&gt;741</td>
<td>741</td>
<td>Liber et al. (2011)</td>
</tr>
<tr>
<td><em>Tubifex tubifex</em> (oligochaete)</td>
<td>96 h</td>
<td>LC50</td>
<td>2,782</td>
<td>2,782</td>
<td>Lucas et al. (2017)</td>
</tr>
</tbody>
</table>

(Nautilus Environmental 2017)
**Long-term exposure toxicity data**

Chronic toxicity values for molybdenum were available for three fish species (two salmonid and one non-salmonid; Table 3). The most sensitive species was rainbow trout (*Oncorhynchus mykiss*) with an EC$_{10}$ value for biomass of 43.2 mg/L (De Schamphelaere et al. 2010). The least sensitive fish species was brown trout (*Salmo trutta*) with an EC$_{10}$ for growth of 202 mg/L (Lucas et al. 2017).

Chronic toxicity values for molybdenum were available for aquatic life stages of six freshwater invertebrate species, with nine data points represented (Table 3). The most sensitive species was the amphipod, *Hyalella azteca*, which had an EC$_{10}$ for reproduction in a 42-day test of 44.6 mg/L. The second most sensitive species was the cladoceran, *Ceriodaphnia dubia*, with a geometric mean EC$_{10}$/IC$_{10}$ for reproduction of 51.3 mg/L (De Schamphelaere et al. 2010, Naddy et al. 1995, GEI 2009). This mean includes an IC$_{12.5}$ value (34 mg/L; Naddy et al. 1995), as it was more sensitive than the other data points, and is close to an IC$_{10}$ value. The least sensitive species was the snail, *Lymnaea stagnalis*, with a 28-day growth EC$_{10}$ of 221.3 mg/L (De Schamphelaere et al. 2010).

Data were available for two species of algae or plants (Table 3). The green alga, *Pseudokirchneriella subcapitata*, was the more sensitive of the two, with a 72-hour geometric mean EC$_{10}$ for growth of 110.4 mg/L (De Schamphelaere et al. 2010). Duckweed (*Lemna minor*) had a 7-day EC$_{10}$ for growth rate of 241.5 mg/L (De Schamphelaere et al. 2010).

One chronic data point was available for the African clawed frog, *Xenopus laevis* (Table 3); an EC$_{10}$ of 116 mg/L for malformations was reported (De Schamphelaere et al. 2010). Although this species is not native to North America, it was included in the distribution since it reflected the only available data point for an amphibian.
Table 3. Toxicity data points used in the species sensitivity distribution to determine the long-term surface water quality objective for molybdenum.

<table>
<thead>
<tr>
<th>Species</th>
<th>Duration</th>
<th>Endpoint</th>
<th>Observed Effect</th>
<th>Effects Concentration (mg/L Mo)</th>
<th>Species Geometric Mean</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oncorhynchus mykiss (rainbow trout)</td>
<td>78 d</td>
<td>EC10</td>
<td>Biomass</td>
<td>43.2</td>
<td>43.2</td>
<td>De Schamphelaere et al. (2010)</td>
</tr>
<tr>
<td>Pimephales promelas (fathead minnow)</td>
<td>34 d</td>
<td>EC10</td>
<td>Biomass</td>
<td>39.3</td>
<td>59.8</td>
<td>De Schamphelaere et al. (2010)</td>
</tr>
<tr>
<td>Salmo trutta (brown trout)</td>
<td>86 d</td>
<td>EC10</td>
<td>Growth</td>
<td>202.0</td>
<td>202.0</td>
<td>Lucas et al. (2017)</td>
</tr>
<tr>
<td>Brachionus calyciflorus (rotifer)</td>
<td>48 h</td>
<td>EC10</td>
<td>Reprod.</td>
<td>193.6</td>
<td>193.6</td>
<td>De Schamphelaere et al. (2010)</td>
</tr>
<tr>
<td>Ceriodaphnia dubia (cladoceran)</td>
<td>7 d</td>
<td>EC10</td>
<td>Reprod.</td>
<td>78.2</td>
<td>34.0</td>
<td>De Schamphelaere et al. (2010)</td>
</tr>
<tr>
<td>Chironomus riparius (midge)</td>
<td>14 d</td>
<td>EC10</td>
<td>Biomass</td>
<td>121.4</td>
<td>121.4</td>
<td>De Schamphelaere et al. (2010)</td>
</tr>
<tr>
<td>Daphnia magna (cladoceran)</td>
<td>21 d</td>
<td>EC10</td>
<td>Reprod.</td>
<td>105.6</td>
<td>89.4</td>
<td>De Schamphelaere et al. (2010)</td>
</tr>
<tr>
<td>Hyalella azteca (amphipod)</td>
<td>42 d</td>
<td>EC10</td>
<td>Reprod.</td>
<td>44.6</td>
<td>44.6</td>
<td>Heijerick and Carey (2017)</td>
</tr>
<tr>
<td>Lymnaea stagnalis (snail)</td>
<td>28 d</td>
<td>EC10</td>
<td>Growth</td>
<td>221.3</td>
<td>221.3</td>
<td>De Schamphelaere et al. (2010)</td>
</tr>
<tr>
<td>Pseudokirchneriella subcapitata</td>
<td>72 h</td>
<td>EC10</td>
<td>Growth rate</td>
<td>74.3</td>
<td>110.4</td>
<td>De Schamphelaere et al. (2010)</td>
</tr>
<tr>
<td>Lemna minor (duckweed)</td>
<td>7 d</td>
<td>EC10</td>
<td>Growth rate</td>
<td>241.5</td>
<td>241.5</td>
<td>De Schamphelaere et al. (2010)</td>
</tr>
<tr>
<td>Xenopus laevis (African clawed frog)</td>
<td>4 d</td>
<td>EC10</td>
<td>Malformation</td>
<td>115.9</td>
<td>115.9</td>
<td>De Schamphelaere et al. (2010)</td>
</tr>
</tbody>
</table>

(Nautilus Environmental 2017)
**Long-term freshwater objective**

The long-term freshwater SWQO for molybdenum for the protection of aquatic life was developed based on CCME guidance (CCME 2007) using the statistical derivation approach (Type A), since the minimum data requirements for a Type A guideline were met. A total of 18 data points, for 12 different species were used in derivation of the guideline. Of the 18 data points, 17 were EC$_{10}$ values and 1 was an IC$_{12.5}$ value. The Normal model produced the best fit for the SSD, based on the Anderson-Darling goodness of fit test. The equation for the Normal model is:

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

Where, for the fitted model: $x = \log$ (concentration) of molybdenum (mg/L), $f(x)$ is the proportion of species affects, $\mu = 2.0257$ and $\sigma = 0.3213$.

The fifth percentile (HC$_5$) of the long-term SSD was 31 mg/L of molybdenum (Table 4; Figure 1).

**Therefore, the long-term SWQO for molybdenum for the protection of aquatic life is 31 mg/L or 31,000 µg/L.**

**Table 4. Long-term surface water quality objective for molybdenum.**

<table>
<thead>
<tr>
<th></th>
<th>Mo (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSD 5$^{th}$ Percentile</td>
<td>31,000</td>
</tr>
<tr>
<td>SSD 5$^{th}$ Percentile; 95% lower fiducial limit</td>
<td>25,000</td>
</tr>
<tr>
<td>SSD 5$^{th}$ Percentile; 95% upper fiducial limit</td>
<td>40,000</td>
</tr>
</tbody>
</table>

(Nautilus Environmental 2017)

**Figure 1** Long-term species sensitivity distribution (SSD) for molybdenum in freshwater using data for 12 freshwater species (Nautilus Environmental 2017).
REFERENCES


Pyle GG. 2000. The toxicity and bioavailability of nickel and molybdenum to standard toxicity-test fish species and species found in Northern Canadian Lakes. Thesis. Department of Biology, University of Saskatchewan, Saskatoon, SK.


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