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Proposed Soil Quality Guidelines
Molybdenum
Environmental and Human Health Effects

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Table of Contents

List of Tables

Page

List of Figures

List of Appendices

Distribution List

Client	1 copy(ies)
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1.0 INTRODUCTION

Soil quality guidelines are numerical soil concentrations intended to be protective of human and environmental health for current and potential future uses of land. They are frequently used for the assessment and remediation of contaminated sites.

The Canadian Council of Ministers of the Environment (CCME) published "A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines" (CCME 2006) to provide a framework and methodology for developing risk-based soil quality guidelines protective of human health and the environment; the guidelines developed using this protocol have been published in the Canadian Soil Quality Guidelines (CCME 1999) and also formed the basis for some provincial guidelines, including the Alberta Tier 1 Soil and Groundwater Remediation Guidelines (ESRD 2010). The current Alberta guidelines for molybdenum, however, date back to the earlier Interim Canadian Environmental Quality Criteria for Contaminated Sites (CCME 1991), which did not use modern risk-based approaches.

This report provides the basis for proposed soil quality guidelines for molybdenum based on the CCME (2006) protocol. It includes a review of sources of molybdenum, concentrations in the environment, fate and behaviour, and toxicological effects on soil microorganisms, plants, animals and humans. Guidelines are derived for the agricultural, residential/parkland, commercial and industrial land uses as defined by CCME (2006), as well as the natural area land use defined by ESRD (2010).

2.0 BACKGROUND INFORMATION

2.1 Physical and Chemical Properties

Molybdenum (Mo; CAS # 7439-98-7) is a silver metal that comprises approximately 0.0015% of the earth's crust (Chappell et al. 1979). Mo is a Group VI transition element with an atomic number of 42, an atomic weight of 95.96, a melting point of 2622°C, a boiling point of 4639°C, and a specific density of 10.222 g/cm^3 (CRC,2011). The most common molybdenum mineral is molybdenite (MoS), but it also occurs as powellite ($CaMoO_4$) and wulfenite ($PbMoO_4$) (CCME 1999). The most commonly encountered molybdenum oxidation states are 0, 2, 3, 4, 5, and 6.

Physical and chemical properties of molybdenum and some molybdenum compounds are presented in Table 1.

Table 1 Physical and Chemical Properties of Molybdenum and Select Molybdenum Compounds

Property	Molybdenum	Molybdenite[a]	Molybdenum Trioxide
Chemical formula	Mo	MoS_2	MoO3
CAS Registry Number	7439-98-7	1309-56-4	1313-27-5
Molecular weight (g/mol)	95.96	128.02	143.94
Physical state at 25°C	Solid	Solid	Solid
Melting point (°C)	2622	-	795
Boiling point (°C)	4639	-	1155
Density (g/cm3)	10.222	4.73	4.69
Water solubility (g/100mL)	Insoluble	-	0.49

a – values from (NIST 2013)

2.2 Analytical Methods

Molybdenum in environmental media is most commonly analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES) or inductively coupled plasma-mass spectrometry (ICP-MS), although atomic absorption spectrophotometry (AAS) can also be used.

The first step in both ICP-OES and IOCP-MS is conversion of an analyte solution into ions by passing it though a plasma source. ICP-OES measures the emission of light from the heated ions, which occur at a specific wavelength and which has an intensity correlated to the concentration in the original analyte solution. ICP-MS directs these ions into a magnetic field, which deflects their path based on their mass to charge ratio, and onto a detector. This allows for identification and quantification of chemical species in the original analyte solution (Harris 2003).

AAS involves conversion of an analyte solution into a gaseous state within a flame or furnace. A light source is then directed through the flame, and the concentration of the analyte is determined by the absorption of the light source at specific frequencies characteristic of individual elements (Harris 2003).

Typical soil sample preparation techniques are intended to indicate the environmentally available concentration of molybdenum, using strong acid leachate (CCME 2013). Water samples are field filtered and preserved in solutions with pH values less than 2 (CCME 2013). Relevant US EPA methods for extraction of molybdenum include method 3005A *Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy* (US EPA 1992), and method 3050B *Acid Digestion of Sediments, Sludges, and Soils* (US EPA 1996); the extraction method is critical for determining concentrations and needs to be consistent.

US EPA recommends analysis using either FLAA/ICP-AES or GFAA/ICP-MS using either method 6010C *Inductively Coupled Plasma-Atomic Emission Spectrometry* (US EPA 2007a) and method 6020a *Inductively Coupled Plasma-Mass Spectrometry* (US EPA 2007b).

CCME (1993) previously recommended method 3120B *Inductively Coupled Plasma (ICP) Method* (CCME 1993) for determination of metals in water samples, and US EPA method 6010 for determination from metals in soils, sludges, sediments. Current CCME (2013) draft recommendations are for ICP-OES, ICP-MS, or AAS with no standard methodology recommended, but with a requirement that analytical standards be matrix matched to samples.

2.3 Production and Uses in Canada

An estimated 9005 tonnes of Molybdenum were produced in Canada in 2009, entirely mined from British Columbia (NRCan 2011). Molybdenum in Canada is mined from molybdenite ore and as a by-product of copper mining.

1871 tonnes of molybdenum were used in Canada in 2007 (NRCan 2013), and Canada supplied 8% of ferromolybdeum and 16% of the molybdenum ore demand in the United States between 2008 and 2001, totaling over 10,000 tonnes of material (USGS 2013). Estimated reserves of molybdenum in Canada have been on an increasing trend since 2005 and were predicted to be greater than 250,000 tonnes as of 2010 (Natural Resources Canada 2013).

Global molybdenum demand is currently increasing, with the majority of molybdenum use occurring in China and Europe (IMOA 2013). Uses of molybdenum include specialist steel alloys, petroleum desulphurisation catalysts, adhesives, lubricants, corrosion inhibitors, flame retardants and medical isotopes. Global demand for molybdenum is primarily related to production of steel alloys, but molybdenite is seeing increasing use in electronics and as catalysts. Molybdenum ferroalloy was produced in Canada as of 2007 (Didaleusky et al. 2010), and it is estimated that over 75% of molybdenum is used for production of steel alloys (IMOA 2013). Molybdenum-99 is also used to produce Tc-99, which is a commonly used medical radioactive tracer used for diagnostic procedures and is produced at the Natural Research Universal reactor in Ontario.

Releases of molybdenum trioxide were reported from 23 facilities in Canada during 2011, with 0.034 tonnes of on-site releases and 202 tonnes of offsite disposal (Environment Canada 2012).

2.4 Sources and Concentrations in the Canadian Environment

The assessment of soil quality for naturally occurring metals must take into consideration regional variations in background concentrations in Canada. Background concentrations and environmental fate of metals strongly depends on geological and biological characteristics and therefore, any assessment of potential risks should take into consideration regional differences in metal content in the natural environment (Chapman and Wang 2000).

Relatively high concentrations of metals can occur naturally in Canadian soils, stream sediments, and water, blurring the distinction between anthropogenic pollution versus naturally occurring geological formations and natural bodies of ore. In 2004, Canadian companies produced 9500 tonnes of contained molybdenum in the form of molybdenum ore, all of which were mined in British Columbia (Natual Resources Canada 2004). Soils and sediments reflect the composition of parent material, resulting in higher metal concentrations in mineralized areas (Wilson, Murray, and Huntington 1998). Mining districts are characterized by naturally occurring metals in soil, sediment, rock, and water at concentrations that could result in their classification as "contaminated sites" if background concentrations are not properly evaluated (Painter et al. 1994). In the determination of anthropogenic metal contamination of soils, no single guideline concentration can adequately represent the variance in background concentrations across Canada (Painter et al. 1994; Chapman and Wang 2000).

Data on concentrations in environmental media are summarized in Appendix A.

2.4.1 Atmosphere

Natural molybdenum emissions to the atmosphere have been estimated to range between 140 and 5,800 tonnes per year globally (Nriagu 1989). Atmospheric molybdenum concentrations in Canada were monitored through the federal National Air Pollution Surveillance (NAPS) over a two year period from May 2004 to December 2006. Median atmospheric molybdenum concentrations in fine particulate matter ($PM_{2.5}$) at seven sites in eastern and western Canada ranged from 0.06 to 0.35 ng/m^3 (Celo and Dabek-Zlotorzynska 2010).

Seasonal chemical composition of fine particulate matter was measured at rural locations in Alberta (Cheng et al. 2000). Molybdenum concentrations of $PM_{2.5}$ at Ester and Swann Hills showed little seasonal variation and were approximately 0.04 (Swan Hills) and 1.0 (Ester) ng/m^3.

Measurements of airborne molybdenum were obtained from four distinct urban environments in Calgary (Lane et al. 2013). Air particulates were collected on teflon filters and molybdenum concentrations were measured after sample preparation using MC-ICP-MS. Molybdenum concentrations ranged from 0.07 ng/m^3 (laboratory setting) to 19.0 ng/m^3 (bus garage).

2.4.2 Soil and Dust

Molybdenum is a ubiquitous natural constituent in soil, originating from rocks in the earth's crust (Chappell et al. 1979), with world-wide levels being reported at 0.1-7.35 mg/kg (Kabata-Pendias and Pendias 1992). It is highest in organic rich sediments (2.0-2.6 mg/kg), shales (0.7-2.6 mg/kg) and felsic rocks (1-2 mg/kg); and lowest in limestones (0.16-0.40 mg/kg) (Kabata-Pendias and Pendias, 1992).

A comparison of total elemental concentrations in garden soil, house dust and street dust in the city of Ottawa reported geometric means for molybdenum of 0.59 mg/kg for garden soil, 1.96 mg/kg for house dust and 1.29 mg/kg for street dust (Rasmussen, Subramanian, and Jessiman 2001).

The molybdenum content of Manitoba soils ranged from 1 to 31 mg/kg, with a median concentration of 3 mg/kg (Haluschak et al. 1998). Molybdenum concentrations for these soils were found to generally increase with clay content, with an average molybdenum concentration of 2 ppm in coarse-textured soils and 4 ppm in fine-textured soils. Areas of greatest molybdenum concentration in southern Manitoba appear to occur in the Saskatchewan Plain, especially in soils with higher shale content.

Mean molybdenum concentrations for seven ecoregions within Alberta ranged from 0.013 to 0.067 mg/kg at depths of 0 to 15 cm, and from 0.011 to 0.056 mg/kg at depths of 15 to 30 cm (Penney 2004). The study concluded there were significant differences for molybdenum concentrations for the 0 to 15 cm soil samples between the different ecoregions. The concentrations in this survey were based on a hot water soluble analysis rather than total molybdenum.

Grunsky et al. (2012) reported a concentration range for molybdenum of <1 to 206 mg/kg based on soil and till surveys covering parts of nine Canadian provinces and territories. More than 50% of the reported data were less than the detection limit of 1 mg/kg for samples prepared using total/near total digestion techniques. The mean concentration was 1.4 mg/kg with a standard deviation of 3.71 mg/kg. Elevated molybdenum values occurred within survey areas located in central BC, central Baffin Island and New Brunswick (Grunsky, Rencz, and Adock 2012).

2.4.3 Water

Natural sources of molybdenum in the aquatic environment include runoff from the weathering of igneous and sedimentary rock (especially shale) into streams and lakes. Leaching processes from molybdenum mines and burning of fossil fuels may also introduce molybdenum to aquatic environments (Phillips and Ruso 1978). Molybdenum-containing fertilizers may be an important anthropogenic source for aquatic environments (McNeely, Neimanis, and Dwyer 1979).

Molybdenum concentrations in Canadian freshwater sources range from less than 0.1 µg/L to 500 µg/L (Ontario Ministry of Environment and Energy 1995). In British Columbia, surface water concentrations of molybdenum ranged from less than 0.1 µg/L to 57 µg/L (CCME 1999). Approximately 13% of 262 samples taken from lakes assumed to be pristine in British Columbia had molybdenum concentrations above the method detection limit, with a maximum reported molybdenum concentration of 40 µg/L (Swain 1986). An average concentration of 70 µg/L was reported for surface waters in areas associated with human and industrial activity (Chappell et al. 1979). (Rossmann and Barres 1988) found median dissolved molybdenum concentrations ranging between 0.15 µg/L to 2.8 µg/L in the Great Lakes.

In the United States of America, surface water molybdenum concentrations from a survey of 15 major river basins ranged between 2 to 1500 µg/L, with a mean concentration of 60 µg/L (Kopp and Kroner 1967)(National Academy of Sciences) 1977). Groundwater molybdenum levels in the USA were reported to range from undetectable to 270 µg/L (Kehoe, Cholak, and Largent 1944). Levels of molybdenum in drinking water do not usually exceed 10 µg/L but may be significantly higher in areas near mining sites (World Health Organization (WHO) 2011). A survey of wells in Wisconsin found molybdenum was only detected in 20% of samples, with 98% of concentrations less than 20 µg/L (Webb, Thornton, and Fletcher 1968). A British survey indicated that molybdenum in drinking water is generally less than 1 µg/L and often consistent with source water concentrations (Smedley et al. 2008).

2.4.4 Sediments

Substantial variability has been reported for molybdenum levels in aquatic sediments, ranging from 2 to 400 mg/kg (Chappell, 1975). Stream sediments were reported to contain an average concentration of 2 mg/kg of molybdenum (Webb et al., 1968). Molybdenum concentrations in sediment from the Fraser River in the Lower Mainland area ranged between 5 and 10 mg/kg (Swain 1986). In lake sediments of generally pristine areas of British Columbia, a mean molybdenum value of 14.2 mg/kg was reported, with a range of 1 to 183 mg/kg (Swain, 1986). Three sediment samples from background areas in Grand Lake, New Brunswick and two from East River, Nova Scotia showed median molybdenum concentrations of 5.6 and 1.75 mg/kg, respectively (Lalonde, Ernst, and Comeau 2011).

2.4.5 Aquatic Organisms

Molybdenum is an essential trace element for aquatic organisms and serves as a growth promoter for phytoplankton, periphyton and macrophytes (CCME 1999). A study with trout from Cayuga Lake in Ontario showed the highest concentrations (8.5 and 8.2 µg per kg fresh weight, respectively) occurred in fish that were one and two years old, with a gradual decrease (2.2 and 2.8 µg per kg fresh weight, respectively) for fish that were eleven and twelve years old (Tong et al. 1974). In a survey of benthic organisms and fish in the Fraser River, molybdenum levels in invertebrates were less than 5 µg/g and approximately half of these had values of less than 1 µg/g of dry weight (Singleton, 1983). Only 46 of 273 muscle tissue samples from fish in the Fraser River had detectable levels of molybdenum, with a maximum concentration of 1.39 µg/g of wet weight. (Futer and Nassichuk 1983) reported molybdenum concentrations between less than 0.3 to 3.1 µg/g (dry weight) in the muscle of eulachons from Nass River in British Columbia, 95% of which were below 0.3 µg/g. Molybdenum concentrations were typically below detection limits (less than 0.4 µg/g of dry weight) in cockles from Alice Arm in British Columbia (Farrell and Nassichuk 1984).

2.4.6 Plants

Molybdenum is an essential component of plant enzymes (nitrogenase and nitrate reductase). Molybdenum content in plants is affected by the soil molybdenum concentration and pH, with the highest concentrations in plants grown in molybdenum-rich alkaline to neutral soils (Schulte 2004).

Limited information is available on the variability of molybdenum content between plant species. Molybdenum concentration is generally highest in seeds and nodules of nitrogen fixing plants (Swain 1986). When molybdenum is limiting, it is preferentially accumulated in root nodules. Molybdenum concentrations of 0.03 to 0.15 mg/kg are generally adequate for plant physiological requirements, with concentrations in plant leaves being in the order of 1 mg/kg (Jones 1994).

Foods from above ground plant material, such as legumes and leafy vegetables, generally contain higher concentrations of molybdenum compared to foods from tubers (Clark et al. 2007). In the area of the former Soviet Union, where molybdenum has been implicated in gout-like diseases, the highest molybdenum concentrations were found in beans (82 µg/kg), mint (57 µg/kg), eggplant (13 µg/kg) and potatoes (11 µg/kg), in dry weight. In comparison, normal levels were reported to be 5.1 µg/kg for beans and between 1 and 5 µg/kg for vegetables (Kovalskii, Yarovaya, and Shmavonyan 1961).

2.4.7 Animals

A survey of slaughtered bovine, porcine and avian specimens in Ontario reported two to three fold higher levels of molybdenum in kidney than in muscle (R. Frank et al. 1986). Mean molybdenum concentration ranged from 253 to 429 µg per kg (wet weight) in bovine muscle and from 799 to 886 µg/kg in bovine kidney. Porcine muscle and kidney contained an average of 214 and 854 µg/kg and avian muscle and liver contained an average of 474 to 562 µg/kg and 1490 to 1750 µg/kg of molybdenum, respectively.

2.4.8 Humans

Molybdenum is an essential cofactor of several human enzymes. The major source of molybdenum for most people is from their diet. Daily intake can range from 100 to 500 µg of molybdenum; however, the contamination of water by industrial activities may result in a daily intake of up to 1000 µg (Barceloux 1999). Shortly after ingestion and gastrointestinal absorption, molybdenum concentrations increase in the blood and other organs, with the highest concentrations in the liver, kidney and bone (WHO 2011). Molybdenum is primarily excreted in the urine, with urinary levels being a direct reflection of dietary intake (IOM 2001).

Based on the Second National Health and Nutrition Examination Survey (NHANES II) in the U.S., daily intake for molybdenum was between 75 to 250 µg for adolescents and adults with an average American diet (NRC 1989).

Molybdenum concentrations in whole blood from 19 collection sites in the United States showed mean values of 0.50 to 15.73 µg per 100 mL (Allaway et al. 1968). Whole blood concentrations up to 150 µg/mL have been noted for people from areas rich in molybdenum or from molybdenum mining areas (Forrer, Gautschi, and Lutz 2001).

Analysis of NHANES survey data for the years 2003 to 2010 found a significant difference between molybdenum levels of pregnant and nonpregnant females in urine; with a geometric mean of 48.8 µg/L in pregnant females compared to a geometric mean of 43.3 µg/L in nonpregnant females (Jain 2013).

The geometric means for trace element concentrations in non-smoking adults (aged 33 to 64) from the west coast of Canada were reported to be 15.36 nmol/L in blood and 58.41 umol per mol of creatinine in urine (Clark et al. 2007). Smokers were reported to have significantly lower levels of molybdenum than non-smokers (Jain 2013).

Molybdenum concentrations in the blood and urine of participants aged 6 to 79 years were measured in the Canadian Health Measures Survey in two cycles, Cycle 1 in 2007 to 2009 and the Cycle 2 in 2009 to 2011 (Health Canada 2013). The geometric means for molybdenum concentrations in the two cycles were 0.67 and 0.65 µg/L in whole blood and 36 and 44 µg/L in the urine of the study groups.

The average molybdenum concentration in breast milk has been reported to be 2 µg/L (National Health and Medical Research Council 2006).

2.5 Existing Soil and Water Quality Criteria and Guidelines

Soil and water quality criteria and guidelines for molybdenum have been developed by several agencies, and are summarized in Appendix B.

3.0 ENVIRONMENTAL FATE AND BEHAVIOUR IN SOIL

In the natural environment molybdenum occurs with oxidation states ranging of +6, in molybdate (MoO_4^{2-}) and +4 in molybdenum disulphide (Pyrzynska 2007). The fate of molybdenum is dependent on a series of physiochemical and biological factors that influence cycling among biotic and abiotic components of the environment. Molybdenum is an essential element for plants and animals (Florence 1982) with an estimated natural concentration range of 0.05-40 mg/kg (Das et al. 2007).

3.1 Atmosphere

Molybdenum does not volatilize except under extreme conditions; however, volatile molybdenum compounds have been detected in landfill gas (Feldmann and Cullen 1997).

3.2 Water

In aquatic ecosystems molybdenum only weakly interacts with particulate matter, and tends to be adsorbed or complexed onto humic iron aggregates (Das et al. 2007). Molybdenum also forms water-soluble complexes with some organic compounds, most notably with organo-oxygen compounds such as polyols, carboxycilic acids and sugars). Molybdenum can adsorp, absorb, or co-precipitate with oxides of iron and aluminium at pH values under 5, while tending to remain in solution at pH values greater than five (CCME 1999).

3.3 Soil

Soil solution metal concentrations and metal bioavailability of molybdenum are controlled by sorption-desorption reactions at the surfaces of soil colloids, and is generally controlled adsorption to iron oxides and clays (Wichard et al. 2008). Molybdenum in soil is primarily in oxoanion form and sorbed to oxides and organic matter (Pyrzynska 2007); however, soluble forms are susceptible to leaching (Wichard et al. 2009). Molybdenum can bind to organic and inorganic compounds in soil and is often present in the nitrogenase enzyme in nitrogen fixing bacteria (Wichard et al. 2009), but molybdenum also adsorbs to mineral surfaces under acidic conditions and becomes less bioavailable (Wichard et al. 2009).

3.4 Biota

Marine plankton and some plant species bioconcentrate trace molybdate (Das et al. 2007), but bioavailability of molybdenum varies significantly. Bioconcentration factors of less than 100 have been suggested in aquatic biota and in some cases may not be much greater than 1 (CCME 1999). Molybdenum is necessary in the fixation of nitrogen (Pyrzynska 2007), but intake of molybdenum is antagonistic with copper. Formation of thiomolybdates reduces copper absorption by forming insoluble cupric thiomolybdate (Spears 2003).

4.0 BEHAVIOUR AND EFFECTS IN TERRESTRIAL BIOTA

The available information on the toxicological effects of molybdenum on soil microbial processes, terrestrial plants, invertebrates, as well as mammals and birds have been reviewed and summarized below. Detailed data are provided in Appendix C.

Plants and animals may accumulate contaminants over time if the amount to which they are directly exposed is greater than the amount they can eliminate through excretion and metabolic processes. Bioconcentration is the transfer of contaminants directly from a medium to an organism and the transfer of contaminants to an organism through the consumption of contaminated food is referred to as bioaccumulation (CCME 2006).

Molybdenum is not found naturally as a free metal but rather in various oxidation states from +2 to +6. Of the possible oxidation states; +6 is the most common in the environment. Unlike a number of other metals, the solubility of molybdenum increased with increasing pH (Zimmer and Mendel 1999; Gupta, Chipman, and Mackay 1978). In dilute solutions at neutral pH, the predominant form of soluble molybdenum is MoO_4, reported as the only bioavailable form for plants (Kaiser et al. 2005). Molybdenum is typically found adsorbed to soil colloids, held in crystal lattices of minerals and bound in organic matter.

4.1 Soil Microbial Processes

Microorganisms are a critical component of terrestrial ecosystems and changes to the structure and function of microbial populations may have adverse effects on the function on the ecosystem. Molybdenum is required for the synthesis of bacterial enzymes, notably those utilized to fix atmospheric nitrogen by bacteria and essential to global nitrogen cycling. These enzymes either use molybdenum within the active site, which is the case for the nitrogenase enzyme, or utilize molybdenum in molybdenum cofactors or molybdoenzymes (Hernandez, George, and Rubio 2009). The effect of molybdenum on enzyme production has become a routinely used toxicity assessment metric for bacteria. The results of available literature related to molybdenum toxicity to soil microbial organisms, enzyme activities or soil microbial processes are presented below.

4.1.1 Toxicity

Molybdenum added as a salt solution ($MoCl_5$) to forest topsoil negatively affected the respiration of the microbial community at concentrations of 460 mg/kg, but produced no significant measurable effect on the community structure (Åkerblom et al. 2007). An effect concentration resulting in a 10% reduction in cumulative respiration (EC_{10}) of 77.5 mg/kg was calculated. A concentration of 250 mg/kg molybdic acid had no statistically significant effect on soil ethylene production relative to the control (Arshad and Frankenberger 1991). Yanni (1990) reported no negative effect on root nodule numbers for soybeans at concentrations of 2 and 4 mg/kg of sodium molybdate.

Concentrations of 5 µmol/g of molybdenum in soil had no effect on the amidase activity in soils, a ubiquitous microbial enzyme (Frankenberger and Tabatabai 1981). Concentrations of 2.5 µmol/g molybdenum inhibited the nitrate reductase activity by 20% in acid and neutral soils (Fu and Tabatabai 1989). Alluvial soils amended with 1000 mg/kg sodium molybdate had no observed inhibitory effect on nitrification and ammonification (Ueda, Kobayashi, and Takahashi 1988). The effect of molybdic acid on nitrogen mineralization varied between 10 to 54% in soils amended with a concentration of 480 mg/kg molybdic acid (Liang and Tabatabai 1977). Arylsulphatase activity after amending soil with 2,400 mg molybdic acid was inhibited between 14 and 79% (Al-Khafaji and Tabatabai 1979). Acid and alkaline phosphatase activity was also inhibited between 41 and 93% and 22 and 25% respectively after amending soil with 2,400 mg/kg molybdic acid (Juma and Tabatabai 1977). Urease production was inhibited between 4 and 16% in soil amended with 480 mg/kg molybdic acid (Tabatabai 1977). Stott et al (1985) measured pyrophosphatase activity in soil after amending with 2,400 mg/kg molybdic acid, buffered tests resulted in an inhibition of between 75 and 83 %. L-glutaminase and L-asparaginase activity was measured after amending soil with 480 mg/kg molybdic acid, inhibition of between 4 and 6% and 3 and 6% respectively was measured relative to controls (Frankenberger Jr and Tabatabai 1991b; Frankenberger Jr and Tabatabai 1991a).

The International Molybdenum Association (IMOA) commissioned a literature review and effects assessment of molybdenum in the terrestrial environment (ARCHE 2012). This review identified the majority of these studies outlined above as unreliable due to only one or two test doses and that extracellular enzymatic activity is not considered a relevant metric for microbial toxicity. To derive a reliable data set consistent with accepted toxicity testing protocols, three microbial toxicity assays were conducted including nitrification, glucose induced respirations and mineralization of plant residues in 10 topsoils with contrasting properties. Results from these microbial process assays produced 18 usable EC_{10} values that ranged from 10 mg/kg for glucose induced respiration to 3841 mg/kg for substrate induced nitrification (ARCHE 2012). EC_{20}, EC_{30} and EC_{50} were later generated from the same data. A summary of the microbial ecotoxicity data from the literature reviewed and the ARCHE generated data is presented in Appendix C.

4.2 Terrestrial Plants

Molybdenum is an essential nutrient required for plant growth and necessary in nitrate assimilation, sulfite detoxification, and plant hormone synthesis (Baxter et al. 2008; Chatterjee and Nautiyal 2001; Gupta and Lipsett 1982). Molybdenum is often added to crops as a micro-nutrient to protect against deficiency and to ensure the effectiveness of nitrogen assimilation, essential for plant growth (Gupta and Lipsett 1982). Molybdenum turnover in ecosystems has been linked to its distribution and availability for plant uptake, molybdenum content in the organic detritus layer correlates with environmental levels and ensures this essential nutrient remains accessible in the root horizon (Lang and Kaupenjohann 2000).

4.2.1 Uptake, Metabolism and Fate

Molybdenum in either deficiency or excess can inhibit plant growth (Kaiser et al. 2005). Controlled plant uptake is regulated by the mitrochondrially localized molybdenum transporter (MOT1) that belongs to the sulfate transporter superfamily; deletion of the promoter for this transporter has been associated with low molybdenum uptake in roots and shoots (Baxter et al. 2008). Deficiency is characterized by chloroplast disorganization, as well as protein, RNA and starch effects, and is noted to resemble nitrogen deficiency in several plant species (Chatterjee and Nautiyal 2001). Molybdenum deficiency is common in acidic soils, as is the case for agricultural areas in south-western Australia. Increasing soil pH through soil liming can be effective at ameliorating this deficiency (Brennan 2006). Conversely, environmental liming to combat acid rain has been linked to molybdenosis in moose in northern Sweden (A. Frank et al. 2000). Increased molybdenum plant uptake is also noted in alkaline sloughs, in areas where industrial contamination may have reduced the soil pH, or where activities have elevated the concentration of molybdenum and other metals in the soil.

Uptake has been demonstrated to increase with the use of fertilizers, with increasing soil pH, with increasing copper, in phosphorus deficient soils, in soils with a high clay content, with the age of the plant and be positively correlated to anthocyanin content (water soluble vacuolar pigments) and stomata openings (Brenchley 1948; Gupta, Chipman, and Mackay 1978; Basak, Mandal, and Haldar 1982; Heuwinkel et al. 1992; Hale et al. 2001; McBride 2005; Stout and Meagher 1948; Tyler and Olsson 2001). Forage grasses have also been found to uptake molybdenum at higher concentrations at contaminated sites where other metals are elevated, uptake has however been shown to be both species- and site-specific (McBride 2005; Neuman and Munshower 1984; McBride and Cherney 2004). The labile pool of molybdenum available for plant uptake is noted to decrease as soil and associated molybdenum age (Kirby et al. 2012). Energy dispersive x-ray analysis has shown that molybdenum accumulates predominately in the vacuoles of epidermal plant cells (Hale et al. 2001).

Uptake varies among species and is strongly influenced by soil type and competing ions (Connick et al. 2010); however, the fate of molybdenum in plant tissues is more defined. The leaves of vegetables and leafy plants including tobacco, tomatoes, alfalfa, red clover, broccoli, brussel sprouts, cauliflower, rutabaga and soybean plants have been found to contain higher concentrations than stems (Smith, Brown, and Deuel 1987; Gupta and Lipsett 1982; Gupta 1991). Roots were found to have higher concentrations relative to shoots in rice (Basak, Mandal, and Haldar 1982). Corn and bromegrass grown on soils amended with sewage sludge containing 12 to 39 mg/kg molybdenum have been noted to increase the dry weight concentration of molybdenum by 2 to 3 times (Eisler 1989). Leaf and above ground biomass concentrations can generally be correlated to soil concentrations (Tyler 2000).

4.2.2 Bioconcentration

Bioconcentration has also been documented in plants after several years of lime-treated sludge application but rates are noted to vary widely and be dependent on a variety of soil and plant factors (Tyler and Olsson 2001). Overall the literature demonstrated that plants uptake molybdenum relative to the soil concentration in which they were grown but do not bioconcentrate molybdenum above these levels.

4.2.3 Toxicity

Data on the toxicity of molybdenum to field-grown crops or terrestrial plants grown outdoors is lacking and has been noted to rarely occur. Toxicity can only generally be induced under experimental conditions (Zimmer and Mendel 1999). Numerous studies have shown no effect on plant yield after amending soil with molybdenum and even a beneficial effect on dry matter yield, seed yield, chlorophyll content, and nitrogen fixation (Moraes et al. 2009; Mulder 1954; Valenciano, Boto, and Marcelo 2011; Xia and Xiong 1991; Yu, Hu, and Wang 1999). In one study (de Iorio et al. 1998), researchers applied sodium molybdate at a maximum concentration of 1 mg/kg producing no measurable effect on plant yield. Yanni (1990) reported no negative effect on soybean seed yield after applying 4 mg/kg sodium molybdate and an increase in nitrogen fixing root nodule bacteria after treatment. Low level molybdenum (0.3 mg/kg Mo) and phosphorus (160 mg/kg P) fertilizer addition was shown to increase the molybdenum uptake in the leaves and shoots of *Brassica napus* seedlings, growth and photosynthesis was positively affected with the addition of both but not with molybdenum alone (Liu, Probst, and Liao 2010). The application of molybdenum and phosphorus was found to have synergistic effects on wheat seed protein content, seed yield and seedling vigor (Modi 2002).

Growth experiments with higher molybdenum concentrations demonstrated reduced dry weight production in a number of vegetable species (Brenchley 1948). Another study (Nautiyal and Chatterjee 2004) demonstrated reduced biomass production, seed yield and leaf chlorosis growing chickpeas in sand with a 2.0 mg/L solution of sodium molybdate. Reduced seed viability and vigor has been reported in cereal grains with elevated molybdenum (Chatterjee and Nautiyal 2001). Kevresan et al. (2001) showed that young pea seedlings were significantly negatively affected at 9.6 mg/kg sodium molybdate, while root growth was most sensitively affected at 0.096 – 0.00096 mg/kg. Growth experiments with young spring barley grown with sodium molybdate (Davis, Beckett, and Wollan 1978) established an EC_{10} for dry matter yield of 70 mg/kg for soil and 135 mg/kg in the tissue of the leaves and shoots. Buekers et al. (2010) investigated the toxicity of sodium molybdate and molybdenum trioxide on the nitrification process in soil and on wheat (*Triticum aestivum* L.) growth. Results indicated that molybdenum salt (sodium molybdate) had less of an effect on toxicity than the pH (molybdenum trioxide); sodium molybdate was suggested to be the preferred species for toxicity testing. A plant yield EC_{10} of 15 mg/kg as total molybdenum was produced. Despite this data the majority of studies presented above provided insufficient detail on how total molybdenum was added to soils to create a homogeneous mixture and rarely tested a sufficient range of concentrations to produce a dose-response effect.

Total carbon content, or ammonium oxalate extractable iron concentrations, were found to be the best predictors of toxicity threshold values for soluble molybdate (MoO_4^{-2}) among four tested plant species (McGrath, Micó, Zhao, et al. 2010). Sulphate concentrations in soil were found to ameliorate molybdenum toxicity, possibly due to the competition at uptake sites. Further research (McGrath, Micó, Curdy, et al. 2010) established that plant bioavailability of molybdenum in soil was highly dependent on molybdenum solubility and to a lesser extent dependent on soil properties.

To create a more robust molybdenum plant toxicity data set that followed accepted toxicity testing protocols ARCHE (2012) conducted dose-response testing on canola (*Brassica naps),* red clover *(Trifolium pretense),* ryegrass *(Lolium perenne),* tomato (*Lycopersicon esculentrum)* and barley (*Hordeum vulgare)* in soil with a range of chemical and physical properties. This testing resulted in 45 applicable EC_{10} values ranging from 5 mg/kg for canola and red clover to 3,479 mg/kg for ryegrass; EC_{20}, EC_{30} and EC_{50} values were later generated from the same data. A summary of the plant ecotoxicity data from the literature reviewed and the ARCHE generated data is presented in Table 2.

4.3 Terrestrial Invertebrates

Limited data is available on the toxicity or bioaccumulation of molybdenum in terrestrial invertebrates. A total of four papers specifically studying the effects of molybdenum on invertebrate species were identified in the literature. Invertebrate toxicity texting was also conducted by ARCHE (2012) for this receptor group. A summary of this work and the available literature is presented below. A summary of the ecotoxicity data generated by ARCHE is presented in Table 3.

4.3.1 Uptake, Metabolism and Fate

Molybdenum uptake and excretion was demonstrated in the earthworm, reaching equilibrium after 10-12 days, followed by efficient molybdenum excretion when transferred to uncontaminated soils (Díez-Ortiz et al. 2010). Uptake increased with increasing soil concentration and while some molybdenum may be utilized in biological process, molybdenum did not appear to be metabolized. Excretion was demonstrated to be intrinsic to the organism and independent of soil properties, the rate of excretion was comparable to other essential metals in different invertebrate species (Díez-Ortiz et al. 2010).

4.3.2 Bioaccumulation

Experimental data suggest that molybdenum can accumulate in tissues but is not magnified relative to external concentrations; once the source of molybdenum was removed biological concentrations reduced (Díez-Ortiz et al. 2010). This linear bioaccumulation of environmental concentrations has been documented in the earthworm *Eisinia andrei*, suggesting that earthworms may not be capable of regulating their internal molybdenum concentrations (van Gestel et al. 2011).

4.3.3 Toxicity

High concentrations of molybdenum have been used as termite control agents, with effective lethal concentrations around 1,000 mg/kg (Yoshimura, Tsunoda, and Nishimoto 1987). However, concentrations as high as 5,000 mg/kg did not affect various ant, beetle and cockroach species (Brill, Ela, and Breznak 1987).

No relevant literature was identified for invertebrates in the effects assessment conducted by ARCHE (2012), laboratory based toxicity testing was conducted in support of generating an effects database for these receptors and published in a paper by van Gestel et al. (2011). Three species of invertebrates (*Enchytraeus crypticus*, *Eisinia andrei* and *Folsomia candida)* were used to generate 23 usable EC_{10} reproduction values. These values range from a molybdenum concentration in soil of 8.88 mg/kg for *Eisinia andrei* to 1,865 mg/kg for *Folsomia candida* (ARCHE, 2012). Overall, molybdenum addition affected survival in only three low pH sand soils and in all other soil the LC_{50} was >3200 mg/kg. Soil properties were noted to have a strong but species-specific effect on molybdenum toxicity.

4.4 Livestock and Terrestrial Wildlife Species

Available avian toxicity testing is limited to chickens. Minor growth inhibition has been reported at a dietary concentration of 200 mg/kg (Underwood 1971). Higher dietary doses of 500 mg/kg reduced the growth rate of chicks after 4 weeks, hens laid 15% fewer eggs and this dietary concentration was found to be embryolethal in all eggs (Friberg et al. 1975). Higher dietary doses ranging from 1,000 to 4,000 mg/kg resulted in spleen lesions, injury to immune function, as well as lymphocyte and renal cell apoptosis (Yang et al. 2011; Xiao et al. 2011b; Xiao et al. 2011a). Oak Ridge National Laboratory has published an avian LOAEL of 35.3 mg/kg-bw/day, based on a study by (Lepore and Miller 1965) documenting embryo death and other adverse reproductive effects in chickens (Oak Ridge National Laboratory, 1997).

Available livestock toxicity testing includes data on horses, goats, rabbits, guinea pigs, sheep and cattle. Horses are generally considered to be more tolerant of molybdenum excesses and copper deficiencies than ruminants (Eisler 1989). Horses exposed to dietary concentrations of 107 mg/kg molybdenum for 14 days had no observable effects (Cymbaluk et al. 1981). Symptoms of molybdenosis resulted after oral exposure at doses of 20 mg/kg-bw/d in goats (Kusum et al. 2010). Rabbits fed a diet amended with 40 mg/kg molybdenum produced no significant growth differences relative to controls. Rabbits ingesting molybdenum in feed mainly excreted this metal in the urine (57%), however tissues of the kidney and liver had elevated concentrations after exposure (Bersényi et al. 2008). Higher dietary concentrations of 500 mg/kg for 12 weeks resulted in rabbit growth retardation, and concentrations of 2,000 mg/kg were found to be lethal (Friberg et al. 1975). Adverse effects in guinea pigs were noted at doses of 250 mg/kg-bw (Chappell et al. 1979).

Molybdenosis in ruminants and the associated broad-spectrum effects associated with this disease are the outcomes most often documented in the literature from elevated molybdenum exposure, and/or low copper exposure. A molybdenum content of more than 12 mg/kg dry weight can induce problems associated with moyldensosis in cattle, and to a lesser extent sheep (Friberg et al. 1975). Symptoms of molybdenosis including joint and bone effects were noted in sheep after dietary exposure of 5.5 to 12.5 mg/kg dry weight (M. Pitt, Fraser, and Thurley 1980). A lower molybdenum range between 2 to 20 mg/kg for both cattle and sheep is more problematic in copper-deficient pastures (copper-molybdenum ratio less than 3).

Comparatively more data are available on the effects of dietary molybdenum exposure in cattle than sheep. Mild symptoms of molybdenosis have been noted in cattle grazing pastures or fed diets amended with molybdenum at concentrations as low as 5 mg/kg and copper of 4 mg/kg (Phillippo, Humphries, and Garthwaite 1987; Phillippo et al. 1987). Total daily intake for cattle approaching 140 mg has produced molybdenum-associated problems, and body weight residues of 10 mg/kg have been shown to be fatal (Lloyd, Hill, and Meerdink 1976). Doses of 4.11 to 7.84 mg/kg-d have resulted in molybdenosis in bulls (Thomas and Moss 1951). Adverse effects other than molybdenosis have also been documented in cattle. Dietary molybdenum at concentrations of 40 mg/kg and 6 mg/kg of copper resulted in a reduction in dairy cow milk production and reduced growth in nursing calves (Wittenberg and Devlin 1987). Concentrations of between 15 to 20 mg/kg in feed have also resulted in adverse reproduction effects including abnormal embryo development (O'Gorman et al. 1987).

Limited toxicity testing for terrestrial wildlife is available but suggests that domestic livestock are at greater risk to molybdenosis than wildlife species. Female mule deer exposed to concentrations of 200 mg/kg in feed showed no visible effects after 8 days, or after 8 days of exposure to 1,000 mg/kg; concentrations of 5,000 to 7,000 mg/kg for 3 to 15 days elicited signs of molybdenosis

Oak Ridge National Laboratory published a mammalian chronic-lowest observed adverse effect level (LOAEL) of 2.58 mg/kg-bw/day, based on study by Shroeder and Mitchner (1971) resulting in reduced reproductive success in mice given molybdate in food and water for three generations (ORNL (Oak Ridge National Laboratory) 1996).

4.4.1 Uptake, Metabolism and Fate

Ruminants excrete molybdenum through feces, whereas other more tolerant mammals such as pigs and rats excrete molybdenum in urine and at a much faster rate (Underwood, 1971; Pitt, 1976). Excretion rates for cattle are also slower, 67% of administered molybdenum in 7 day, whereas guinea pigs excreted 100% in 8 days, and swine excreted 75% in 5 days (Penumarthy and Oehme 1978). In ruminants, molybdates and sulfides are metabolized by bacteria to form thiomolybdates which are not formed in monogastric digestion. Produced thiomolybdates react with copper forming a poorly absorbed complex, often resulting in a copper deficiency (MERCK 2013).

4.4.2 Bioaccumulation

Accumulation of molybdenum in the testes, epididymides and seminal vesicles of rats after high exposure doses orally was observed (Pandey and Singh 2002). Molybdenum in wild duck tissue was found highest in the liver and kidney tissues (Mochizuki et al. 2002). Other evidence of bioaccumulation was not presented in the literature for livestock or terrestrial wildlife species.

4.4.3 Toxicity

Molybdenosis, thought to be a copper-deficiency that occurs through exposure to molybdenum, is characterized by scouring, weight loss, anemia, joint and bone deformities, reproductive impairment and death. This condition has been documented in ruminants, notably sensitive are cattle, sheep and moose (Erdman, Ebens, and Case 1978; Eisler 1989; A. Frank 1998; A. Frank et al. 2000; M. A. Pitt 1976). Cattle appear to be the most sensitive and were adversely affected when grazing on pastures with a copper to molybdenum ratio <3, or when fed diets containing 2 to 20 mg/kg molybdenum in the diet, or when total daily intake approaches 141 mg (Eisler 1989). A lethal dose of 10 mg/kg body weight has been established for cattle (Eisler 1989). Molybdenum poisoning in ruminants, referred to as teart disease, is proportional to the molybdenum content in the pasture feed. Concentrations of more than 12 mg/kg dry weight have been shown to produce molybdenum associated effects in cattle (Friberg et al. 1975). Other mammal species including horses, pigs, small laboratory animals and mammalian wildlife are comparatively tolerant to higher dietary doses of molybdenum (Eisler 1989; McCarter, Riddell, and Robinson 1962). The Merck Veterinary Manual (2013), reports that species other than cattle and sheep are at least 10 times less sensitive to molybdenum.

The toxicity of molybdenum in ruminants is noted to be influenced by a number of factors that include:

- the dose of copper the animal receives,
- the dose of inorganic sulfate the animal receives,
- the dose of molybdenum the animal receives relative to the above doses,
- the proportion of water soluble forms of molybdenum,
- the presence of sulfur-containing amino acids, and
- the age of the animals.

5.0 BEHAVIOUR AND EFFECTS IN HUMANS AND EXPERIMENTAL ANIMALS

5.1 Overview

Molybdenum is an essential nutrient, although molybdenum deficiency is rare and normally only associated with biochemical abnormalities.

5.2 Pharmacokinetics

5.2.1 Absorption

Adsorption of molybdenum following oral exposure depends on the chemical form; hexavalent molybdenum is more readily absorbed than tetravalent molybdenum (WHO 2011). The limited human data suggests absorption of 30-70% of ingested molybdenum (Engel, Price, and Miller 1967; Robinson et al. 1973). No data on absorption after inhalation or dermal contact were identified.

5.2.1.1 Relative Absorption Factors

Health Canada has published a relative dermal absorption factor of 0.01 for molybdenum (Health Canada 2010) compared to oral absorption. This value was adopted from the Ontario Ministry of the

Environment, who in turn based it on extrapolation from other inorganic substances (Ontario Ministry of the Environment 2011). In the absence of other values from reputable agencies, this factor is adopted herein.

An oral relative absorption factor of 1 is recommended due to the lack of sufficient data to quantify differences in gastrointestinal absorption between soil and other media. Similarly, an inhalation relative absorption factor of 1 is also recommended.

5.2.2 Distribution

Within the human body, molybdenum is found at highest concentrations in the liver, kidneys and bones, but is also found in blood and other organs. It does not appear to bioaccumulate (Schroeder, Balassa, and Tipton 1970). Animal studies have suggested that at high doses the liver reaches a saturation point, beyond which increased molybdenum dose does not increase the molybdenum concentration in the liver (Cox et al. 1960).

5.2.3 Metabolism

Molybdenum, in the form of molybdopterin, is a cofactor for certain enzymes, including sulfite oxidase, xanthine oxidase and aldehyde oxidase (Institute of Medicine (U.S.). Panel on Micronutrients and Institute of Medicine (U.S.). Standing Committee on the Scientific Evaluation of Dietary Reference Intakes 2001). It has been shown to play a role in the metabolism of phosphorus and copper (Comar, Singer, and Davis 1949).

5.2.4 Elimination

Elimination of molybdenum from humans is primarily in urine (Schroeder, Balassa, and Tipton 1970; WHO 2011). Concentrations of molybdenum in urine have been found to increase at high levels of molybdenum exposure (Chappell et al. 1979).

5.2.5 Physiologically-based Pharmacokinetic Models

No physiologically-based pharmacokinetic models for molybdenum were identified.

5.3 Essentiality

As noted above, molybdenum, in the form of molybdopterin, is a cofactor for certain enzymes. Molybdenum deficiency is not common, but can occur with some medical conditions. In one case a Crohn’s disease patient on long-term parenteral nutrition exhibited numerous adverse effects including tachycardia, tachypnea, central scotomas, night blindness, irritability, and eventual coma, along with several biochemical abnormalities relating to sulphur amino acid metabolism. These effects were improved with ammonium molybdate (Abumrad et al. 1981).

5.4 Acute and Sub-Chronic Exposure

5.4.1 Human

No data on acute or subchronic toxicity of molybdenum to humans were identified.

5.4.2 Animal

Subchronic oral median lethal doses in rats range from 101 mg/kg/d to 330 mg/kg/d, depending on the species of molybdenum (Fairhall et al. 1945, cited in WHO 2011).

A 6-week dietary study using Holtzman rats fed hydrogen molybdate at 75 or 300 ppm in diet found that molybdenum inhibited growth at both doses, but that this effect was eliminated (at 75 ppm) or reduced (at 300 ppm) by sulphate supplementation at 2200 ppm. A second experiment using 100 ppm sodium molybdate found that sulphate between 800 and 2200 ppm alleviated most of the growth inhibition (Miller, Price, and Engel 1956).

A series of experiments using guinea pigs exposed to sodium molybdate, copper sulphate or both (Arthur 1965). Molybdenum added to the diet at 1000 ppm to 8000 ppm for 8 weeks adversely affected weight gain and survival, and at 5000 ppm and higher caused weight loss. Above 2000 ppm, graying of the hair was also observed. In the second experiment, molybdenum at 2000 ppm and copper at 10 or 20 ppm for 8 weeks showed a reduction in the greying effect with 20 ppm copper, but weight gain was still affected.

Long-Evans rats were fed a diet supplemented by copper (5 or 20 ppm) and molybdenum (<1, 20, 80 or 140 ppm) for 13 weeks (Jeter and Davis 1954). Molybdenum treatments of 20 ppm or higher in the lower copper group resulted in reduced average weight gain, with the effect greater in males than females. The 80 and 140 ppm molybdenum groups also exhibited achromotrichia and alopecia.

Two experiments conducted on Long-Evans rats (Cox et al. 1960) involved adding molybdenum to a mineralized whole milk diet at 0, 500 and 800 pm for 5 weeks (males) or 8 weeks (females), or to a synthetic diet at 0, 250 and 800 ppm for 7 to 8 weeks (males) or 9 weeks (females). In the first experiment, both exposed groups exhibited decreased growth, diarrhea and emaciation, as well as increased molybdenum in the liver, reduced xanthine oxidase activity, and reduced liver respiration. In the second experiment, the growth rate was still reduced at both exposure doses and liver molybdenum concentrations increased; there was a slight but not statistically significant decrease in xanthine oxidase, liver respiration and blood uric acid in the 800 ppm group.

The same authors fed calves diets with 0, 200 or 400 ppm molybdenum added for three to six months; while molybdenum concentrations in the liver increased, there were no observed effects on liver enzymes (Cox et al. 1960).

Another study (Huber, Price, and Engel 1971) involved feeding lactating dairy cows molybdenum in their diet at concentrations ranging from 53 ppm to 300 ppm for up to 6 months, combined with low copper (6 ppm). Signs of molybdenum toxicity including diarrhea and reduced growth were observed at 173 ppm and above, but not at concentrations 100 ppm and lower. All molybdenum treatments resulted in decreased liver copper and increased copper levels in milk and kidneys, along with increased molybdenum concentrations in liver, blood and milk.

Molybdenum was added to drinking water of calves at 0, 1, 10 and 50 ppm for 21 days (Kincaid 1980). At 50 ppm, the copper concentration in the liver was reduced, while the copper concentration in plasma increased; no effects were observed at lower concentrations.

In another study (Thomas and Moss 1951), two male Holstein calves were fed a molybdenum-supplemented diet for 129 days. The amount of molybdenum increased from 2.6 g/day to 5.0 g/d over the course of the experiment. This resulted in doses ranging from 4.11 to 7.84 mg/kg-bw/day. Reported results included reduced growth rates, and brief diarrhea. In one calf there were reports of stiffness, and the black hair on this calf began to turn white/grey after 6 weeks. The calves exhibited a lack of libido, and a histological examination showed degeneration of the seminiferous tubules and an absence of sperm or spermatids in the tubules. Autopsies found erosion of cartilage in the metatarsal joints. There were only 2 exposed calves and no controls in this study, however.

Fugnwe et al (1990) exposed 5 groups of 21 female Sprague-Dawley rats to a diet containing 0.025 mg/kg molybdenum and drinking water supplemented with sodium molybdate at 0, 5, 10, 50 or 100 mg/L molybdenum. After 6 weeks, 6 rats from each group were sacrificed while the remaining rats were mated and allowed to gestate for 21 days. Mated dams were observed to gain less weight during gestation than controls at concentrations of 10 mg/L and higher; this was attributed to reduced fetal sizes. Fewer pups were also observed at 10 mg/L and higher concentrations, and the fetuses were significantly smaller and showed evidence of a less mature hepatic structure. Macroscopic evidence of fetal resorption was observed at 10 mg/L and higher. The length of the estrous cycle was also increased in these rats, and plasma Cp activity was increased in gestating rats. Significant effects were observed on sulphur oxidase and xanthine oxidase/dehydrogenase activity in all treatment groups.

A recent study involved exposing 4 goats to ammonium molybdate (20 mg/kg-bw/d) or ammonium molybdate (20 mg/kg-bw/d) plus copper sulphate (II) pentahydrate (7.9 mg/kg-bw/d) for 30 days in water (Kusum et al. 2010). Blood samples were collected throughout the treatment period, as well as 7 and 14 days after treatment, for evaluation of hematological parameters. The group exposed to ammonium molybdate alone showed evidence of inappetence, weight loss, decreased ruminal motility, rough hair coat, diarrhea, alopecia, sway back, anemia, achromotrichia and emanciation, as well as significant reductions in hemoglobin and packed cell volume on the 30th day, reduced total erythrocyte and total leukocyte counts from 28 days on, and reduced mean corpuscular hemoglobin from 7 days on (compared to pre-exposure values), along with an increase in mean corpuscular volume and neutrophils level. These effects appeared to be ameliorated in the goats also exposed to copper salt, and were attributed by the authors to secondary copper deficiency.

A 56-day study on steers (Kessler et al. 2012) involved providing water with low sulphur (375 mg/L SO_4), high sulphur (2,218 mg/L SO_4) or high sulphur plus molybdenum (187.5 mg/L). There were 32 steers in each group. The authors hypothesized that molybdenum would bind excess sulphur in the rumen, reducing sulphur toxicity without causing molybdenum toxicity. However, the group with molybdenum supplementation showed signs of molybdenum toxicity, including severe diarrhea, loss of body condition, anorexia, changes in hair colour and stiff joints.

A 14-day study used 5 New Zealand white rabbits (Bersényi et al. 2008) fed carrots grown in soil with high molybdenum concentrations (270 mg/kg) resulting in an approximate concentration in carrots of 39 mg/kg dry matter, plus 5 controls. A second experiment involved feeding 5 rabbits a commercial pellet diet supplemented with 40 mg/kg dry matter molybdenum, with 5 rabbits in a control group, also for 14 days. Body weights were not significantly affected. Rabbits ingesting the carrots (daily molybdenum ingestion estimated at 1.4 mg/day) did not show any effect on daily dry matter intake or nutrient digestibility. Concentrations of molybdenum were elevated in tissues, and were 5 times as high in the kidneys of exposed rabbits as control rabbits. Serum alanine aminotransferase activity was decreased, while creatine kinase activity and malondialdehyde concentrations were increased. Rabbits ingesting the pellet diet with molybdenum added showed decreased dietary intake, a non-significant decrease in digestibility of crude protein, crude fibre and nitrogen-free extract. Triclyceride concentrations in serum were decreased while malondialdehyde levels increased. Histological examination of the testes showed a reduction in germ cells and mature spermatocytes.

A sub-acute mouse study (Zhai et al. 2013) involved providing groups of 10 male ICR mice water with molybdenum concentrations of 0, 12.5, 25, 50, 100 and 200 mg/L for 14 days and examining the testes for sperm quality and other reproductive effects. Sperm quality was reported to be improved at 25 mg/L, but decreased at 100 mg/L and 200 mg/L. Accompanying changes in superoxide dismutase and glutathione peroxidase activities and malondialdehyde levels were also observed.

A related study using female mice (Zhang et al. 2013) in groups of 25 exposed to molybdenum concentrations in water of 0, 5, 10, 20 or 40 mg/L for 14 days examined effects on ovaries. An improvement in M II oocyte morphology, ovary index and ovulation was observed at 5 mg/L; at 40 mg/L these parameters were adversely affected, and at 20 mg/L abnormal ovarian mitochondria were observed. Superoxide dismutase activity was increased at 10 mg/L but decreased at 20 mg/L and 40 mg/L; glutathione peroxidase activity was increased at 5 and 10 mg/L and decreased at 40 mg/L; malondialdehyde levels were increased at 20 and 40 mg/L. The authors concluded that low molybdenum exposures improve fertility while high exposure decrease fertility.

5.5 Chronic Exposure

5.5.1 Oral Toxicity

5.5.1.1 Human

Chappell et al. (1979) evaluated 42 people from Denver, Colorado exposed to molybdenum in drinking water at 1 to 50 µg/L compared to 13 college students in Golden, Colorado with drinking water molybdenum concentrations of 200 µg/L or greater for 2 years. Concentrations of molybdenum and copper in urine, and uric acid in ceruloplasmin were affected by molybdenum exposure, but no adverse effects were observed in either group. A follow up with the students from Golden 2 years later, with molybdenum concentrations in water reduced to 40 µg/L, the effects on serum ceruloplasmin and urinary copper were no longer apparent.

An association between high molybdenum content in cereals and lower-limb osteoporosis was suggested in one study in India (Krishnamachari & Krishnaswamy 1974, cited in WHO 2011).

Another study was conducted in two areas of the former Soviet Union with significantly elevated molybdenum in soil and plants (Kovalskiy 1961). An unusually high incidence of a gout-like disease was observed in these areas, as high as 31% of the population in one of the provinces. The molybdenum content of food was 2 to 10 times higher than in control areas; the estimated molybdenum intake from food was 10 to 15 mg per day combined with reduced copper intake of 5 to 10 mg/day (compared to control intakes of 1 to 2 mg molybdenum and 10 to 15 mg copper per day).

5.5.1.2 Animal

Charles River CD mice were exposed to 10 mg/L molybdenum in water for six months (Schroeder and Mitchener 1971), resulting in increased fetal mortality in the F1 and F2 generations.

A dietary study involved supplementing pregnant Cheviot ewes with 0 or 50 mg/day molybdenum. Three of four lambs born to the exposed group exhibited ataxia, which was associated with degenerative changes and demyelination in the cerebral cortex and spinal cord (Mills and Fell 1960).

Long-Evans rats were fed a diet supplemented by copper (5 or 20 ppm) and molybdenum (<1, 20, 80 or 140 ppm) for 13 weeks (Jeter and Davis 1954). At 80 and 140 ppm, male infertility was observed, caused by seminiferous tubule degeneration. No significant effects on birth weight or pup weight gain were observed, but stillbirths were increased at 140 ppm. Molybdenum-exposed rats (180 and 140 ppm) showed reduced lactation and lower weaning weights.

A 6-month lamb feeding study (Al-Kirshi, Alimon, and Ivan 2011) supplemented diet for groups of 4 lambs with ammonium molybdate (20.8 g/kg Mo), ammonium molybdate (20.8 g/kg Mo) plus sodium sulphate (3 mg/kg S), or zinc (560 mg/kg), with an additional 4 lambs in a control group. The diet was based on dietary palm kernel cakes, which pose a risk of copper toxicity and had an approximate molybdenum concentration of 0.8 g/kg, sulphur concentration of 2 g/kg and zinc concentration of 60 g/kg. All three supplements affected copper concentrations in the liver and blood; the molybdenum plus sulphur reduced it below safe ranges. The primary intent of this experiment was to evaluate the effects of supplements on reducing copper toxicity, and doses were not well characterized.

5.5.2 Inhalation Toxicity

The data on inhalation toxicity are very limited. One cross-sectional study (Walravens et al. 1979) was conducted on 25 molybdenum smelter workers in Denver, Colorado. Concentrations of molybdenum in respirable dust ranged from 3.04 to 33.28 mg/m^3 in different locations within the facility; the estimated daily intake of molybdenum was 10.2 mg. Workers exhibited higher molybdenum concentrations in blood and urine than a control population, along with higher serum ceruloplasmin and uric acid. Several workers indicated they had health complaints such as joint pain, back pains, headaches, or unspecified skin/hair changes; six workers indicated they had an upper respiratory tract infection within the past two weeks and two exhibited signs of mild obstructive lung disease. The authors considered the reports to be non-specific and difficult to assess scientifically.

5.6 Carcinogenicity and Genotoxicity

5.6.1 Human Data

No human data on molybdenum carcinogenicity and genotoxicity were identified.

5.6.2 Animal Data

There is some evidence that molybdenum may inhibit the formation of certain cancers in animal studies. One rat study found that 2 or 20 ppm molybdenum added to drinking water along with N-nitrososarcosine ethyl ester (NSEE) significantly reduced the incidence of esophageal and forestomach cancers compared to NSEE alone (Luo, Wei, and Yang 1983). Another study by the same group using virgin female rats exposed to 10 ppm molybdenum in water after treatment with N-nitroso-N-methylurea (NMU) found a significantly lower incidence of mammary carcinoma than rates treated with NMU only (Wei, Luo, and Yang 1985).

5.6.3 Genotoxicity/Mutagenicity

Mutation induction experiments using a rec-assay with three strains of *Bacillus subtilis* and mutation induction assays with three *E. coli* strains (Nishioka 1975) found ammonium molybdate to be positive in the rec-assay; potassium molybdate was negative in the *B. Subtilis* test, while potassium molybdate was mildly positive. The mutation induction assay was performed for ammonium molybdate only and showed reduced survival and increased tryptophan reversions compared to a control. A screening for induction of gene conversion and reverse mutation in *Saccharomyces cervisiae* (yeast) yielded negative responses for both ammonium molybdate and sodium molybdate (Singh 1983).

5.6.4 Carcinogenic Classification

Health Canada, US EPA, and the International Agency for Research on Cancer (IARC) have not classified molybdenum with respect to carcinogenicity. The available data do not suggest molybdenum carcinogenicity.

5.7 Toxicological Limits

5.7.1 Toxicological Limits Developed by Health Canada

(Health Canada 2010) has identified molybdenum as an essential trace element and defined age-specific tolerable upper limits of 0.023 mg/kg-bw/d for ages 0 to 11, 0.027 mg/kg-bw/d for ages 12 to 19, and 0.028 mg/kg-bw/d for adults 20 years or older. These values were adopted from the Institute of Medicine (IOM 2001) upper limits, adjusted for Health Canada age groups and default body weights.

The IOM ULs were based on a subchronic (9-week) rat drinking water study (Fungwe et al. 1990) with doses of 0, 5, 10, 50 and 100 mg/L in water plus 0.025 mg/kg in diet (equivalent doses were 0, 0.91, 1.6, 8.3 and 16.7 mg/kg-bw/d). A NOAEL of 0.9 mg/kg-bw/d and LOAEL of 1.6 mg/kg-bw/d were established based on reproductive effects. Uncertainty factors of 10 for interspecies variability and 3 for intraspecies variability were applied.

5.7.2 Toxicological Limits Developed by Other Regulatory Agencies

5.7.2.1 US EPA

US EPA (United States Environmental Protection Agency (US EPA) 1993) published an oral reference dose (RfD) for molybdenum of 0.005 mg/kg-bw/d. This RfD was based on a cross-sectional epidemiological study in Armenia (Kovalskii, Yarovaya, and Shmavonyan 1961) in a region with a high molybdenum content in soil and plants and a high incidence of gout-like sickness in the adult population. A molybdenum intake of 0.14 mg/kg-bw/d was associated with elevated serum uric acid levels compared to the general population. This intake was designated as the LOAEL; an uncertainty factor of 3 was applied for sensitive humans (since a large human population was included in the study) and 10 for use of a LOAEL to derive the RfD. The confidence in the RfD was considered to be medium. US EPA (1993) did not classify molybdenum with respect to carcinogenicity.

5.7.2.2 World Health Organization

(World Health Organization (WHO) 2011) evaluated molybdenum toxicity for a drinking water guideline. They determined that a formal guideline was unnecessary, but suggested a health-based value of 0.07 mg/L based on the NOAEL of 0.2 mg/L established by Chappell et al. (1979), with a factor of 3 for intraspecies variation.

5.7.3 Toxicity Reference Values Selected for SQG Development

The tolerable upper limits specified by Health Canada are adopted as TRVs herein: 0.023 mg/kg-bw/d for ages 0 to 11, 0.027 mg/kg-bw/d for ages 12 to 19, and 0.028 mg/kg-bw/d for adults 20 years or older. These values are higher than the US EPA value; however, they are more recent, reflect a larger database and more current approaches, and consider the essentiality of molybdenum. Furthermore, there is some uncertainty in the actual exposures in the epidemiological study used for the US EPA RfD.

6.0 DERIVATION OF ENVIRONMENTAL AND HUMAN HEALTH SOIL QUALITY GUIDELINES

6.1 Environmental Soil Quality Guidelines

Canadian Soil Quality Guidelines are derived for four different land uses: agricultural, residential/parkland, commercial and industrial. Alberta also adds guidelines for the natural area land use.

All data for use in the following derivations have been screened for ecological relevance and are presented in the preceding sections. For the soil contact pathway, data were not selected from soils that are outside the typical conditions found in Canada (e.g. pH <4), or from studies that did not use soil or artificial soil, did not record soil texture and pH, did not use appropriate statistical analyses, did not use controls, or involved sewage sludge or mixtures of toxicants.

6.1.1 Soil Quality Guidelines for Soil Contact

Soil quality guidelines for soil contact (SQG_{SC}) are based on toxicological data for plants and soil invertebrates. The preferred approach is to use a weight of evidence method using EC_{25} or similar values; if the data do not meet the requirements for this method, then additional approaches using other data points can be applied, such as effects/ no effects data, lowest observed effects concentrations, and median effects.

The data requirements for the preferred weight of evidence approach include:

- At least 10 discrete data points from at least 3 studies.

- A minimum of 2 soil invertebrate and 2 crop/plant data points.

The plant and invertebrate data available for molybdenum meet the minimum requirements for this approach and therefore the weight of evidence approach is applied.

In some cases it is prudent to combine data points to eliminate redundancy by calculating the geometric mean of individual data points (CCME 2006). For example, data points representing the same type of response in the same species under highly similar exposure conditions, or different responses that are known to be directly, causally connected should be combined. Consideration can also be given to combining data for different soil types – in general variations in toxicity due to exposure conditions such as soil type are considered to be a valid part of the sensitivity distribution, but in some cases it may be appropriate to combine data points to prevent a significant bias of the sensitivity distribution to a single species. Where multiple response levels are available for the same species and response type (e.g. EC_{20} and EC_{50}), the value closest to the EC_{25} is used rather than combining the data points.

Plant and invertebrate toxicity data from McGrath et al. (2010b) and ARCHE (2012) met the minimum requirements. Data from Bueker et al. (2010) also meet minimum data requirements; however this study was done to examine the effects of different These data include 6 different plant species and 3 invertebrate species. For most species, 10 different soil types are included in the data set; since the different soil types have been evaluated for 5 plant species and 3 invertebrate species there is no need to combine data points for different soil types. Multiple response levels are available; EC_{20} values were used from McGrath et al. (2010b) and ARCHE (2012), and EC_{10} values from Bueker et al. (2010) as the values closest to EC_{25}. Inclusion of the Bueker et al. (2010) data with EC values further from EC_{25} than the remaining data is conservative since the values from this study were all at the lower end of the resulting species sensitivity distribution. Where only an unbounded NOEC was observed, the data were not used. A total of 49 plant data points and 23 invertebrate endpoints were retained.

As specified by CCME (2006), the selected data were ranked and rank percentiles determined for each data point. The protocol allows plant and invertebrate data to be either combined or treated separately; both approaches have been examined herein. The resulting species sensitivity distributions were found to be similar, and therefore the combined data set was used for greater statistical power.

The resulting species sensitivity distribution is shown on Figure 1 below.

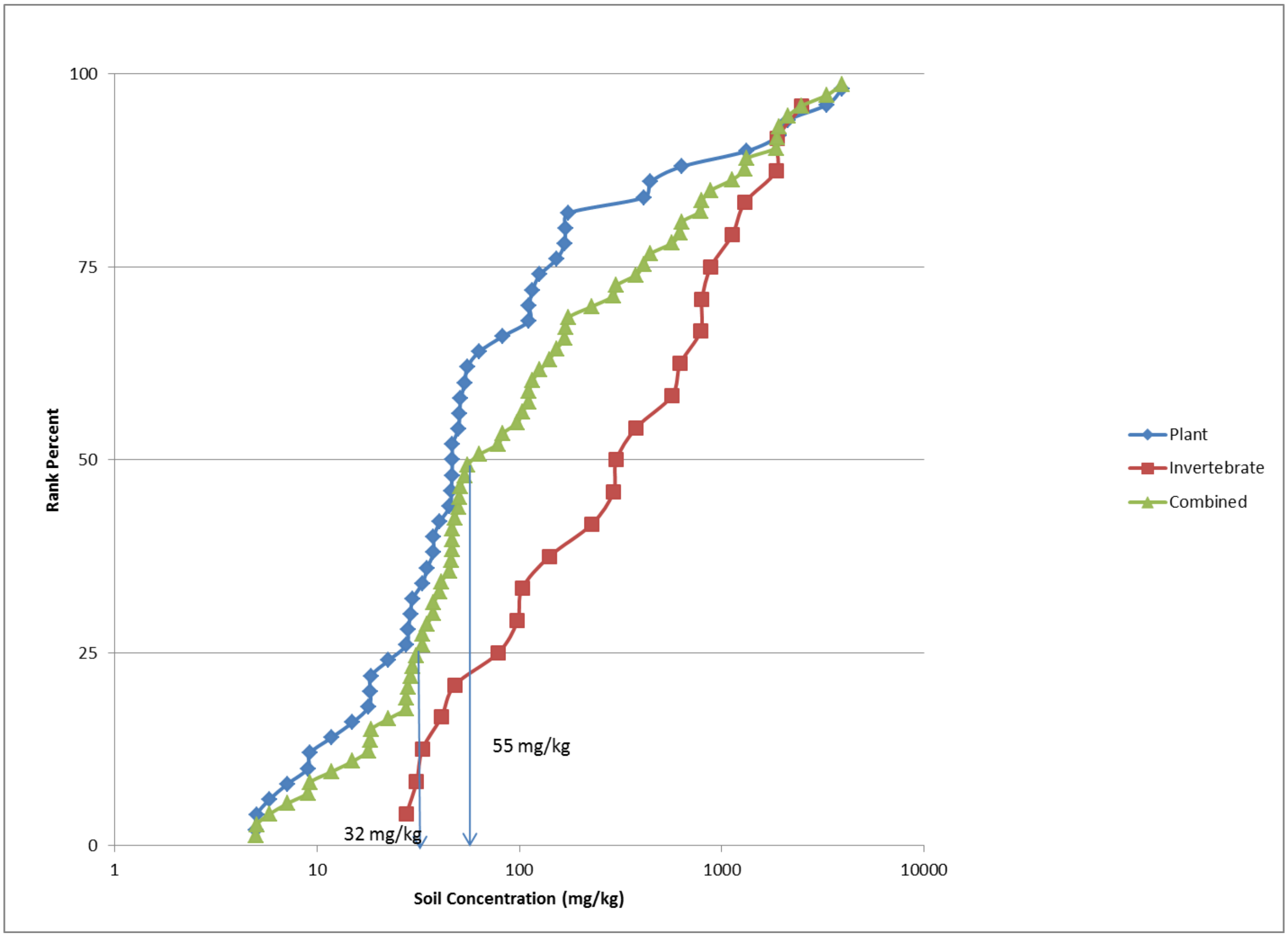

Figure 1: Species Sensitivity Distribution for Ecological Soil Contact

6.1.1.1 Guidelines for the Agricultural, Residential/Parkland and Natural Area Land Uses

The soil contact guidelines are calculated from the 25th percentile of the estimated species sensitivity distribution ($ESSD_{25}$). The $ESSD_{25}$ has been calculated at 32 mg/kg.

The threshold effects concentration is then calculated as:

$$TEC = ESSD_{25}/UF$$

Where:

TEC	=	threshold effects concentration (mg/kg)
$ESSD_{25}$	=	estimated species distribution – 25th percentile (mg/kg)
UF	=	uncertainty factor (if needed)

An uncertainty factor is only applied if the data are borderline, such as if only the minimum number of studies is available, fewer than three taxonomic groups are represented, greater than 50% of either the plant or invertebrate toxicity data are in the lower 25th percentile of the combined distribution, short-term toxicity studies were used, or more than 50% of the data reflect low bioavailability conditions (CCME 2006). None of these conditions apply, and therefore an uncertainty factor is not considered to be warranted.

The SQG_{SC} for the agricultural, residential/parkland and natural area land uses is set at the TEC, or 32 mg/kg.

6.1.1.2 Guidelines for the Commercial and Industrial Land Uses

The soil contact guidelines are calculated from the 50th percentile of the estimated species sensitivity distribution ($ESSD_{50}$). The $ESSD_{50}$ has been calculated at 55 mg/kg.

The effects concentration - low is then calculated as:

$$ECL = ESSD_{50}$$

Where:

ECL	=	threshold effects concentration (mg/kg)
$ESSD_{50}$	=	estimated species distribution – 50th percentile (mg/kg)

An uncertainty factor is not normally applied to the ECL. The SQG_{SC} for the commercial and industrial land uses is set at the ECL, or 55 mg/kg.

6.1.1.3 Confidence Ranking for the Soil Contact Guideline

CCME (2006) uses a ranking system to indicate the confidence in the guideline, based on the method used and whether there were enough data to evaluate plants and invertebrates separately.

For molybdenum, the preferred weight of evidence approach using EC_X data was used. While the plant and invertebrate data were combined, there were sufficient data to evaluate both groups separately. Therefore, a confidence ranking of ‘A’ is assigned.

6.1.2 Nutrient and Energy Cycling

The nutrient and energy cycling guideline (SQG_{NEC}) is used to evaluate biological processes in the soil that are expected to affect the overall soil ecosystem performance. Professional judgment is applied as to whether this guideline should be used in the overall soil quality guideline calculation (CCME 2006).

The preferred data for the calculation of guidelines for this pathway are nitrification and nitrogen-fixation data. Only two nitrification studies were identified, and one of these had an unbounded no effects concentration only; therefore the data are not considered adequate for guideline calculation. The limited effects concentration values identified are significantly higher than the SQG_{SC} calculated above.

In the absence of sufficient nitrification and nitrogen fixation values, the data set can be supplemented with decomposition, respiration and nitrogen mineralization data. With the incorporation of these data, an adequate data set is available. Specifically, nitrification data from Bueker et al. (2010), nitrogen mineralization data from Liang and Tabatabai (1977), and nitrification and respiration data from University of Leuven, 2009 were used to generate a species sensitivity distribution, shown in Figure 2.

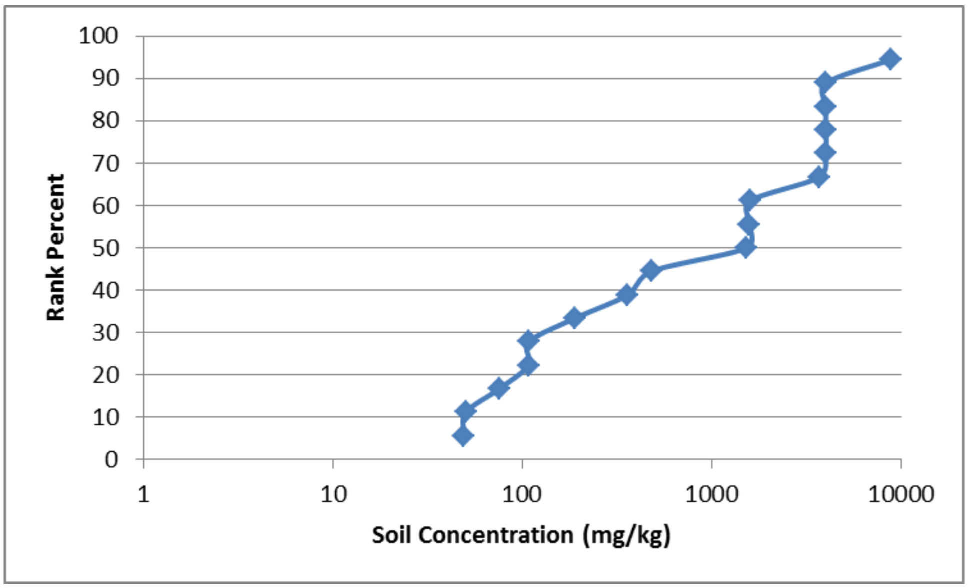

Figure 2: Species Sensitivity Distribution for Nutrient and Energy Cycling

The data appear to exhibit a potential multi-modal distribution. The $ESSD_{25}$ is 108 mg/kg and the $ESSD_{50}$ is 1522 mg/kg. Since these values are higher than those calculated for ecological soil contact and due to the limitations of the data set, the SQG_{NEC} is not calculated as part of the overall soil quality guideline.

6.1.3 Soil Quality Guidelines for Soil and Food Ingestion

Soil and food ingestion guidelines (SQG_I) are calculated for the agricultural and natural area land uses to protect domestic animals and wildlife.

The CCME (2006) process normally evaluates grazing herbivores on agricultural lands, although other species can be considered if identified as being particularly sensitive to the contamination. The first step is to identify the species most at threat based on oral toxicological data for grazing/foraging species. The minimum data requirements include at least two oral mammalian studies, only one of which can be a laboratory rodent study and at least one of which should reflect a grazing herbivore, and one oral avian study.

As discussed in Section 4.4, several grazing herbivore studies have been identified, along with a smaller number of avian studies.

6.1.3.1 Development of the Daily Threshold Effect Dose (DTED)

Several toxicity studies have been conducted using livestock species, including cattle, goats and sheep. In nearly all cases the studies resulted in unbounded NOAELs and LOAELs due to the small number of treatment groups. Furthermore most of these studies involved very small numbers of animals in each treatment group.

A mammalian LOAEL of 2.58 mg/kg-bw/d was developed by Oak Ridge National Laboratory based on a mouse study (ORNL (Oak Ridge National Laboratory) 1996). However, there is evidence that cattle and other livestock may be particularly sensitive to molybdenum. A review by the US Fish and Wildlife Service (Eisler 1989) suggested that molybdenum is toxic to cattle at a concentration of 15 to 30 mg/kg dry weight in feed, and recommended a maximum tolerable level of 6 mg/kg dry weight. For a 550 kg cow with a typical food ingestion rate (approximately 2.5% of body weight per day, or 13.75 kg/d dry weight), this would correspond to a dose of 0.15 mg/kg-bw/d, which is applied as a daily threshold effects dose (DTED) for livestock. The Oak Ridge value is applied for wildlife for the Alberta natural area calculation.

6.1.3.2 Receptor Parameters

A cattle body weight of 550 kg and soil ingestion rate of 0.747 kg/d have previously been used for soil quality guideline derivation (CCME 2008), (ESRD 2010). A typical cattle food ingestion rate is 2.5% of body weight per day or 13.75 kg/d dry weight. This value is slightly higher than what would be calculated using the allometric equation recommended by CCME (2006).

For Alberta natural area land use calculations, a vole with a body weight of 0.017 kg and soil ingestion rate of 0.000058 kg/d is used (ESRD 2010). A food ingestion rate of 0.00241 kg/d is calculated using the CCME (2006) allometric equation.

6.1.3.3 Bioavailability

There is no information on the relative bioavailability of molybdenum in natural food/soil compared to bioavailability in the critical toxicity studies. A bioavailability factor of 1 is therefore assumed.

6.1.3.4 Bioconcentration Factors

In general the bioconcentration of molybdenum in plants appears to be low. Many of the available studies where plant uptake do not contain sufficient information to calculate a meaningful bioconcentration factor – often available instead of total molybdenum concentrations are reported, or molybdenum is provided in solution. Several studies also involve mine tailings or sewage sludge instead of soil. US EPA have previously endorsed a literature-derived bioconcentration factor of 0.25 (US EPA 2013), which has also been previously proposed by Oak Ridge National Laboratory (Baes et al. 1984); since this is the only BCF that was identified it is adopted herein.

6.1.3.5 Calculation of the Soil Quality Guideline for Ingestion

The guideline for soil and food ingestion can be calculated for a primary consumer using the following equation (CCME 2006):

$$SQG_I = \frac{0.75 \times DTED \times BW}{(SIR \times BF) + (FIR \times BCF)}$$

Where,

SQGI	=	soil quality guideline for food and soil ingestion (mg/kg)
DTED	=	daily threshold effects dose (mg/kg-bw/d)
BW	=	body weight (kg)
SIR	=	soil ingestion rate (kg/d)
FIR	=	food ingestion rate (kg/d dry weight)
BF	=	bioavailability factor
BCF	=	bioconcentration factor (mg/kg plant per mg/kg soil)

The resulting SQG_I for the agricultural land use is 15 mg/kg. For the Alberta natural area land use, the wildlife SQGI is 50 mg/kg.

6.1.4 Guidelines for the Protection of Groundwater

No guidelines for protection of groundwater (freshwater life, livestock water and irrigation water) were derived for molybdenum due to restrictions on the mathematical model when applied to metals (CCME 2006).

6.1.5 Off-site Migration Guidelines for Commercial and Industrial Land Uses

The guideline for offsite migration (SQG_{OM-E}) is calculated for the commercial and industrial land uses to protect against transfer of contaminated soil to a more sensitive nearby property through processes such as wind and water erosion. CCME (2006) derived the following equation to evaluate this pathway, based on the Universal Soil Loss Equation and Wind Erosion Equation:

$$SQG_{OM-E} = 14.3 \times SQG_A - 13.3 \times BSC$$

Where,

SQG_{OM-E}	=	environmental soil quality guideline for off-site migration (mg/kg)
SQG_A	=	soil quality guideline for agricultural land use (15 mg/kg)
BSC	=	background concentration of chemical in receiving soil (1 mg/kg)

The resulting SQGOM-E for commercial and industrial land uses is 200 mg/kg.

6.1.6 Summary and Selection of the SQG_E

The lowest ecological guideline for the agricultural land use is the SQG_I of 15 mg/kg. For all other land uses, the soil contact guideline is lowest. All mandatory pathways have been evaluated and therefore a SQG_E can be established.

6.1.7 Data Gaps in the Derivation of Environmental Soil Quality Guidelines

The data set for the direct soil contact pathway is considered to be robust, with several different plant and invertebrate species evaluated in multiple soil types using standard test protocols.

The nutrient and energy cycling guideline could not be calculated reliably, but the available data suggested it would likely be higher than the direct contact guideline.

Uncertainty in the soil and food ingestion pathway arises in part from limited information on bioaccumulation of molybdenum in plants. Furthermore, effects on livestock are not solely a function of molybdenum, but rather of the ratio of molybdenum to copper in diet. In areas where, due to geochemistry or plant species, high bioaccumulation of molybdenum occurs, the proposed guideline may not be protective. Therefore, when molybdenum contamination is present within topsoil on agricultural lands potentially used for grazing, site-specific evaluation of molybdenum concentrations in plants/feed may be warranted.

6.2 Human Health Soil Quality Guidelines

6.2.1 Estimated Daily Intakes

A background molybdenum concentration in soil of 1 mg/kg was selected based on the Geological Survey of Canada soil and till surveys (Grunsky, Rencz, and Adock 2012). These data represent a Canada-wide survey with extensive prairies soil data. The mean concentration was 1.4 mg/kg, but since more than 50% of concentrations were less than the detection limit of 1 mg/kg this value is considered to represent typical background exposure conditions. Areas with high background molybdenum should be evaluated on a site-specific basis.

Data on molybdenum concentrations in drinking water are limited as discussed in Section 2.4.3. Overall, it appears that concentrations are most often less than 1 µg/L, which is frequently the detection limit; this concentration would also be consistent with those measured in the Great Lakes. Therefore 1 µg/L is selected as a reasonable and likely slightly conservative background concentration.

Data on molybdenum in air published by Celo and Dabek-Zlotorzynska (2010) and Cheng et al. (2000) are considered to be representative of typical ambient air concentrations in Canada. The median or mean values at the study locations ranged from 0.03 to 1.0 ng/m^3. The geometric mean of these measurements, approximately 0.16 ng/m^3, is used for estimating typical background exposures. The same value is applied for indoor air due to the absence of actual indoor air data.

Molybdenum was included in the Canadian Total Diet Study between 1993 and 1999 (Health Canada 2011). Concentrations are summarized in Appendix D.

Receptor characteristics used for the Estimated Daily Intake (EDI) calculations are summarized in Table 2 below. The calculated EDI for molybdenum is summarized in Table 3. Background exposure to molybdenum is almost entirely dietary.

Table 2 Receptor Characteristics for EDI Calculation[a]

Age Group / **Characteristic**	**0-6 months**	**0.5 – 4 yr**	**5 – 11 yr**	**12 – 19 yr**	**20 – 64 yr**	**65+ yr**
Inhalation Rate (m3/day)	2.1	9.3	14.5	15.8	16.2	14.3
Water Ingestion Rate (L/day)	0.2	0.2	0.4	0.4	0.4	0.4
Soil & Dust Ingestion Rate (mg/day)	30	100	65	30	30	30
Body Weight (kg)	7.5	15.5	31	59.4	70.9	72
Time Spent Outdoors (day/day)	0.125	0.125	0.125	0.125	0.125	0.125

Table 2 Receptor Characteristics for EDI Calculation[a]						
Age Group / **Characteristic**	**0-6 months**	**0.5 – 4 yr**	**5 – 11 yr**	**12 – 19 yr**	**20 – 64 yr**	**65+ yr**
Time Spent Indoors (day/day)	0.875	0.875	0.875	0.875	0.875	0.875

a – values provided by Health Canada for EDI calculation (may not match values used for guideline calculation)

Table 3 Estimated Intake (µg/kg-bw/d) of Molybdenum						
Age Group / **Route of Exposure**	**0-6 months**	**0.5 – 4 yr**	**5 – 11 yr**	**12 – 19 yr**	**20 – 64 yr**	**65+ yr**
Ambient Air	5.6×10^{-6}	1.2×10^{-5}	9.4×10^{-6}	5.3×10^{-6}	4.6×10^{-6}	4.0×10^{-6}
Indoor Air	3.9×10^{-5}	8.4×10^{-5}	6.6×10^{-5}	3.7×10^{-5}	3.2×10^{-5}	2.8×10^{-5}
Drinking Water	0.027	0.013	0.013	0.0067	0.0056	0.0056
Food and Beverages[a]	10.8	8.3	6.0	3.4	2.5	2.3
Soil	0.004	0.0065	0.0021	0.00051	0.00042	0.00042
Total Intake	10.9	8.3	6.0	3.4	2.5	2.3

a – see Appendix C

6.2.2 Soil Guideline for Direct Contact with Soil

Direct human contact with soil is calculated for the agricultural, residential/parkland, commercial and industrial land uses. Since molybdenum is treated as a threshold substance a toddler is considered to be the most sensitive human receptor, except for the industrial land use where only adults are assumed to spend significant amounts of time (CCME 2006).

The direct contact guideline includes 3 separate exposure pathways: incidental soil ingestion, dermal contact with soil, and soil particulate inhalation. In the absence of separate TRVs for each exposure route, the pathways are combined into a single guideline calculation:

$$SQG_{DH} = \frac{(TDI - EDI) \times SAF \times BW}{[(AF_G \times SIR) + (AF_S \times SR) + (AF_L \times IR_S) \times ET_2] \times ET_1} + BSC$$

Where:

SQG_{DH}	=	direct contact human health soil quality guideline (mg/kg)
TDI	=	tolerable daily intake (mg/kg-bw/d)
EDI	=	estimated daily intake (mg/kg-bw/d)
SAF	=	soil allocation factor (dimensionless)
BW	=	body weight (kg)
BSC	=	background soil concentration (mg/kg)
AF_G	=	relative absorption factor for the gut (dimensionless)
AF_L	=	relative absorption factor for the lung (dimensionless)
AF_S	=	relative absorption factor for the skin (dimensionless)
SIR	=	soil ingestion rate (kg/d)
IRS	=	soil inhalation rate (kg/d)
SR	=	soil dermal contact rate (kg/d)
	=	(hand surface area x hand soil adherence factor) + (arm/leg surface area x arm/leg adherence factor) x events/day
ET_1	=	exposure term 1 (dimensionless) – days per week/7 x weeks per year/52
ET_2	=	exposure term 2 (dimensionless) – hours per day/24

Input values are summarized in Table 4 below for each land use, along with the calculated guidelines.

Table 4 SQG_{DH} Input Values for Each Land Use

Parameter	Agricultural	Residential / Parkland	Commercial	Industrial
TDI (mg/kg-bw/d)	0.023	0.023	0.023	0.028
EDI (mg/kg-bw/d)	0.0083	0.0083	0.0083	0.0025
SAF	0.2	0.2	0.2	0.2
BW (kg)	16.5	16.5	16.5	70.7
BSC (mg/kg)	1	1	1	1
AF_G	1	1	1	1
AF_L	1	1	1	1
AF_S	0.01	0.01	0.01	0.01
SIR (kg/d)	0.00008	0.00008	0.00008	0.00002

Table 4 SQG_{DH} Input Values for Each Land Use

Parameter	Agricultural	Residential / Parkland	Commercial	Industrial
IRS (kg/d)	7.07×10^{-9}	7.07×10^{-9}	7.07×10^{-9}	1.20×10^{-8}
SR (kg/d)	0.000069	0.000069	0.000069	0.00011
ET_1	1	1	0.66	0.66
ET_2	1	1	0.42	0.42
SQG_{DH}	**600**	**600**	**910**	**26000**

6.2.3 Guideline for the Protection of Potable Groundwater

No guideline for protection of potable groundwater was derived for molybdenum due to restrictions on the mathematical model when applied to metals (CCME 2006).

6.2.4 Guideline for the Protection of Indoor Air Quality

Molybdenum is not a volatile chemical and therefore a guideline for the protection of indoor air quality is not required.

6.2.5 Produce, Meat and Milk Ingestion Check

The produce, meat and milk ingestion check is not normally calculated for inorganics (CCME 2006). Bioaccumulation of inorganics in food is highly affected by soil chemistry as well as specific plant species and can vary significantly between sites.

This pathway should be evaluated on a site-specific basis if food crops are grown in molybdenum-contaminated soils.

6.2.6 Off-site Migration Guidelines for Commercial and Industrial Land Uses

The guideline for offsite migration (SQG_{OM-HH}) is calculated for the commercial and industrial land uses to protect against transfer of contaminated soil to a more sensitive nearby property through processes such as wind and water erosion. CCME (2006) derived the following equation to evaluate this pathway, based on the Universal Soil Loss Equation and Wind Erosion Equation:

$$SQG_{OM-HH} = 14.3 \times SQG_A - 13.3 \times BSC$$

Where,

SQG_{OM-HH} = human health soil quality guideline for off-site migration (mg/kg)

SQG_A	=	soil quality guideline for agricultural land use (600 mg/kg)
BSC	=	background concentration of chemical in receiving soil (1 mg/kg)

The resulting SQG_{OM-HH} for commercial and industrial land uses is 8600 mg/kg.

6.2.7 Discussion of Uncertainties Associates with the Human Health Soil Quality Guidelines

The human health soil quality guidelines were derived using tolerable upper limits established by IOM and adopted by Health Canada. These values were based on a subchronic rat water ingestion study. There is some uncertainty associated with the extrapolation from subchronic to chronic exposures and rats to humans, although this is addressed through the use of uncertainty factors. Combined with the essentiality of molybdenum and the limited data on human toxicity, overall the tolerable upper limits are believed to be protective.

Further conservatism is introduced by the assumption that gastrointestinal absorption from soil is equivalent to gastrointestinal absorption in the critical toxicity study (i.e. from water). It is likely that absorption is lower from soil than water, but this has not been quantified.

Some components of the EDI are relatively uncertain due to the limited data on molybdenum concentrations in the environment. However, the EDI is dominated by food ingestion, which has been characterized as part of Canada's Total Diet Study; exposure from other environmental media appears to be negligible. The EDI is also significantly lower than the toxicity benchmarks. Therefore the uncertainty in the EDI is not expected to affect the resulting soil quality guidelines.

Soil guidelines have not been calculated based on uptake by plants and subsequent ingestion by humans. This pathway is not normally quantitatively evaluated for inorganics (CCME 2006), but can be a significant source of exposure if crops are grown directly in contaminated soils. If food crops are grown directly in soils with molybdenum contamination in the rooting zone, then this pathway may need to be evaluated on a site-specific basis.

7.0 DERIVATION OF THE FINAL SOIL QUALITY GUIDELINE

The final soil quality guideline (SQG_F) considers both environmental and human health.

7.1 Considerations Other than Toxicity

If there is evidence that a contaminant may cause significant adverse effects other than toxicity to human and ecological receptors, this evidence may be used to derive a soil quality guideline for management considerations (SQG_M). This may include aesthetic concerns, damage to infrastructure, explosive hazards, or mobile free-phase liquid formation.

There is no indication that significant adverse effects other than toxicity are of concern for molybdenum, and no SQG_M is proposed.

7.2 Evaluation Against Plant Nutritional Requirement, Geochemical Background and Practical Quantitation Limits

While molybdenum is an essential plant nutrient, the proposed guidelines are above minimum levels for plant growth. Similarly the proposed guidelines are above geochemical background at the majority of locations within Canada, and also above practical quantitation limits. Therefore no adjustment of the guidelines for these factors is necessary.

7.3 Final Soil Quality Guidelines

The guidelines are summarized in Table 5 below.

Table 5 Soil Quality Guidelines for Molybdenum

Pathway	Natural Area	Agricultural	Residential/ Parkland	Commercial	Industrial
Guideline (SQG_F)	**32**	**15**	**32**	**55**	**55**
Human health guidelines					
SQG_{HH}	***NA***	***600***	***600***	***910***	***8,600***
Direct Contact (SQG_{DH})	NA	600	600	910	26,000
Protection of Indoor Air Quality (SQG_{IAQ})	NA	NA	NA	NA	NA
Protection of Potable Water (SQG_{PW})	NA	NA	NA	NA	NA
Off-site migration check (SQG_{OM-HH})	NA	NA	NA	8,600	8,600
Produce, meat & milk check (SQG_{FI})	NC	NC	NC	NC	NC
Environmental health guidelines					
SQG_E	***32***	***15***	***32***	***55***	***55***
Soil contact (SQG_{SC})	32	32	32	55	55
Soil and food ingestion (SQG_I)	50	15	NA	NA	NA
Protection of freshwater life (SQG_{FL})	NA	NA	NA	NA	NA
Livestock watering (SQG_{LW})	NA	NA	NA	NA	NA
Irrigation water (SQG_{IR})	NA	NA	NA	NA	NA
Nutrient and energy cycling (SQG_{NEC})	NC	NC	NC	NC	NC
Off-site migration check (SQG_{OM-E})	NA	NA	NA	200	200
SQG_M (non-toxicity considerations)	NA	NA	NA	NA	NA
Interim soil quality criterion (CCME 1991)	4 (Alberta Tier 1)	5	10	40	40

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APPENDIX A: CONCENTRATIONS OF MOLYBDENUM IN THE CANADIAN ENVIRONMENT

Table A-1 Background Concentrations of Molybdenum in the Atmosphere

Location		Number of Samples	Sampling Duration	Concentration	Analytical Technique	Reference
7 Sites in Eastern and Western Canada		>1000	24 hr	Approximately 0.06 to 0.35 ng/m3[a]	ICP-MS	Celo and Dabek-Zlotorzynska, 2010, Canadian National Air Pollution Surveillance Program
Rural locations in Alberta	Ester Summer	136	24 hr	0.95 ng/m3[b]	PIXE	Cheng et al., 2000
	Ester Winter		24 hr	1.00 ng/m3[b]	PIXE	
	Swan Hills Summer	1	1 month	0.04 ng/m3	ICP-MS	
	Swan Hills Winter	1	1 month	0.03 ng/m3	ICP-MS	
Urban environments in the City of Calgary	Residential	2	1000-2000 hr	0.2-2.0 ng/m3	ICP-MS	Lane et al., 2013
	Weather Station	3	800-2000 hr	0.7-0.9 ng/m3	ICP-MS	
	Laboratory	2	340-1400 hr	0.07-0.3 ng/m3	ICP-MS	
	Bus Garage	8	100-330 hr	0.88-19.0 ng/m3	ICP-MS	

[a]Median concentration

[b]Not specified

PIXE - particle induced X-ray emission

ICP-MS - inductively coupled plasma mass spectrometry

Table A-2 Background Concentrations of Molybdenum in Soil and Dust

Location		Number of Samples	Concentrations	Analytical Technique	Reference
City of Ottawa	Garden Soil	50	0.30 to 1.70 mg/kg, 0.64 mg/kg[a], 0.59 mg/kg[b], 0.60 mg/kg[c], 1.26 mg/kg[d]	ICP-MS	Rasmussen et al., 2000
	House Dust	48	0.66 to 28.64 mg/kg, 3.16 mg/kg[a], 1.96 mg/kg[b], 1.70 mg/kg[c], 14.22 mg/kg[d]	ICP-MS	
	Street Dust	45	0.38 to 2.68 mg/kg, 1.39 mg/kg[a], 1.29 mg/kg[b], 1.38 mg/kg[c], 2.16 mg/kg[d]	ICP-MS	
Manitoba		619	1 to 31 mg/kg, 3.2 mg/kg[a],3 mg/kg[c], 5 mg/kg[d] for all soils, 2 mg/kg[a] in coarse-textured soils, 4 mg/kg[a] in fine-textured soils	NR	Haluschak et al., 1998
43 benchmark sites within agricultural regions of Alberta across seven ecoregions	Peace Lowlands	129 for each sampling depth	0.020 mg/kg[a] for 0-15 cm, 0.029 mg/kg[a] for 15-30 cm	ICP-MS	Penney, 2004, Alberta Environmentally Sustainable Agriculture
	Mixed Boreal Upland		0.067 mg/kg[a] for 0-15 cm, 0.056 mg/kg[a] for 15-30 cm	ICP-MS	
	Boreal Transition		0.013 mg/kg[a] for 0-15 cm, 0.011 mg/kg[a] for 15-30 cm	ICP-MS	
	Aspen Parkland		0.022 mg/kg[a] for 0-15 cm, 0.025 mg/kg[a] for 15-30 cm	ICP-MS	
	Moist Mixed Grassland		0.025 mg/kg[a] for 0-15 cm, 0.022 mg/kg[a] for 15-30 cm	ICP-MS	
	Fescue Grassland		0.018 mg/kg[a] for 0-15 cm, 0.023 mg/kg[a] for 15-30 cm	ICP-MS	
	Mixed Grassland		0.015 mg/kga for 0-15 cm, 0.053 mg/kg for 15-30 cm	ICP-MS	
Soil and till surveys covering parts of nine Canadian provinces and territories		12496	0.5 to 206 mg/kg, 1.4 mg/kg[a], 0.50 mg/kg[c], 4 mg/kg[d]	AAS, ICP-OES, ICP-MS	Grunsky et al., 2012

[a]Arithmetic mean

[b]Geometric mean

[c]Median

[d]95th percentile

NR-not reported

ICP-MS - inductively coupled plasma mass spectrometry

AAS - atomic absorption spectroscopy

ICP-OES - inductively coupled plasma optical emission spectrometry

Table A-3 Background Concentrations of Molybdenum in Water

Location		Number of Samples	Concentrations	Analytical Technique	Reference
Canadian rivers and lakes, compilation of benchmarks			<0.1 µg/L to 500 µg/L		OMOEE, 1995 as referenced in CCME, 1999
British Columbia Surface Waters		NR	<0.1 µg/L - 57 µg/L	NR	CCME, 1999
British Columbia Lakes		NR	<0.010 - 0.04 mg/L, <0.010 mg/L[a]	NR	Swain, 1986
Great Lakes	Lake Huron	1	0.62 µg/L[b]	AAS	Rossman and Barres, 1988
	Lake Erie	10-11	1.5 µg/L[b]		
	Lake Michigan	11	1.3 µg/L[b]		
	Lake Superior	20-22	0.14 µg/L[b]		
	Lake Ontario	23	1.9µg/L[b] (1981), 1.5µg/L[b] (1985)		

[a]Arithmetic mean

[b]Median

NR-not reported

AAS - atomic absorption spectroscopy

Table A-4 Background Concentrations of Molybdenum in Sediments

Location		Number of Samples	Concentrations	Analytical Technique	Reference
Stream sediments			2 mg/kg[a] of molybdenum		Webb et al., 1968 as referenced in Swain, 1986
Fraser River sediment, Lower Mainland			5 and 10 mg/kg		Swain, 1985 as referenced in Swain, 1986
British Columbia, lake sediments		202	1 to 183 mg/kg, 14.2 mg/kg[a]	NR	Swain, 1986
Grand Lake, New Brunswick and East River, Nova Scotia	Grand Lake	3	5.6 mg/kg (dw)[b]	ICP-MS	Benoit, et al., 2011
	East River	2	1.75 mg/kg (dw)[b]	ICP-MS	

[a]Arithmetic mean concentration

[b]Median concentration

NR - not reported

ICP-MS - inductively coupled plasma mass spectrometry

Table A-5 Background Concentrations of Molybdenum in Aquatic Organisms

Location	Number of Samples	Concentrations	Analytical Technique	Reference
Cayuga Lake, Ontario	36 total (3 per age group)	8.5 and 8.2 µg per kg fresh weight for fish one and two years old, respectively. 2.2 and 2.8 µg per kg fresh weight for fish eleven and twelve years old, respectively	MS	Tong et al., 1974
Fraser River	273 muscle and 43 liver tissues	<1 to 1.39 µg/g of wet weight in muscle tissue; less than DL to 1.23 µg/g in liver tissue	ICP-MS	Singleton, 1983
Nass River, British Columbia	10	<0.3 to 3.1 µg/g (dry weight) in the muscle of eulachons	ICP-ES	Futer and Nassichuk, 1983
Alice Arm, British Columbia	30	<0.4 µg/g of dry weight in cockles	ICP-ES	Farrell and Nassichuk, 1984

ICP-MS - inductively coupled plasma mass spectrometry

MS - spark source mass spectrometry

ICP-ES - inductively coupled optical emission spectrometry

Table A-6 Background Concentrations of Molybdenum in Plants

Location	Number of Samples		Concentrations	Analytical Technique	Reference
Not specified			Concentrations of 0.03 to 0.15 mg/kg are generally adequate for plant physiological requirements, plant leaves have concentrations in the order of 1 mg/kg		Jones, 1994 (review)
Former Soviet Union	NR	Molybdenum-rich areas	82 µg/kg in beans, 57 µg/kg in mint, 13 µg/kg in eggplant, 11 µg/kg in potatoes (dry weight)	NR	Kovalskiy et al., 1961
		Control areas	5.1 µg/kg in beans, 1.4 µg/kg in mint , 0.97 µg/kg in eggplant, 3.3 µg/kg in potatoes (dry weight)		

NR-not reported

Table A-7 Background Concentrations of Molybdenum in Animals

Location	Number of Samples	Concentrations	Analytical Technique	Reference
Ontario	197 bovine	253 to 429 µg per kg (wet weight) in bovine muscle, 799 to 886 µg/kg in bovine kidney	AAS	Frank et al., 1986
	33 porcine	214 µg/kg[a] porcine muscle, 854 µg/kg[a] porcine kidney		
	115 avian	474 µg/kg[a] (under 14 weeks) to 562 µg/kg[a] (over 14 weeks)in avian muscle and 1490 µg/kg[a] (under 14 weeks) to 1750 µg/kg[a] (over 14 weeks) in avian liver.		

[a]Arithmetic mean concentration

AAS - Atomic Absorption Spectrometery

Table A-8 Background Concentrations of Molybdenum in Humans

<table>
<tr><th>Location</th><th colspan="2">Number of Samples</th><th>Concentrations</th><th>Analytical Technique</th><th>Reference</th></tr>
<tr><td>19 blood collection sites in the United States</td><td colspan="2">229</td><td>0.50 to 15.73 µg per 100 mL in whole blood</td><td>NA</td><td>Allaway et al., 1968</td></tr>
<tr><td>Zurich, Switzerland</td><td colspan="2">110</td><td>0.44 µg/L[a], 3.00 µg/L[b] in whole blood</td><td>ICP-MS</td><td>Forrer et al., 2001</td></tr>
<tr><td rowspan="4">United States</td><td rowspan="4">1565</td><td>233 pregnant</td><td>44.4 to 53.4 µg/L 48.8 µg/L[c] in urine</td><td rowspan="4">ICP-MS</td><td rowspan="4">Jain, 2013 (NHANES)</td></tr>
<tr><td>1323 nonpregnant</td><td>41.7 to 44.9 µg/L, 43.3 µg/L[c] in urine</td></tr>
<tr><td>nonsmoker-NR</td><td>43.6 to 47.1 µg/L, 45.3 µg/L[c] in urine</td></tr>
<tr><td>smoker-NR</td><td>37.1 to 43.1 µg/L, 40.0 µg/L[c] in urine</td></tr>
<tr><td rowspan="2">Non-smoking adults (aged 33 to 64) from the west coast of Canada</td><td colspan="2">61</td><td>8.03 to 37.00 nmol/L, 16.14 nmol/L[a], 15.36 nmol/L[d], 25.64[b] in whole blood</td><td rowspan="2">ICP-MS</td><td rowspan="2">Clark et al., 2007</td></tr>
<tr><td colspan="2">59</td><td>11.54 to 247.1umol per mol, 72.06 umol per mol[a], 58.41 umol per mol[d], 188.4 umol per mol[b] of creatinine in urine</td></tr>
<tr><td rowspan="2">Canadians living at home and residing in the 10 provinces and 3 territories</td><td colspan="2">5319 for whole blood, 5492 for urine (cycle 1, 2007-2009)</td><td>0.67 µg/L[d], 1.3 µg/L[b] in whole blood; 36 µg/L[d], 130 µg/L[b] in urine</td><td rowspan="2">ICP-MS</td><td rowspan="2">Health Canada, 2013 (Canadian Health Measures Survey)</td></tr>
<tr><td colspan="2">5575 for whole blood; 5738 for urine (cycle 2, 2009-2011)</td><td>0.65 µg/L[d], 1.4 µg/L[b] in whole blood; 44 µg/L[d], 170 µg/L[b] in urine</td></tr>
</table>

[a]Arithmetic mean

[b]95th percentile

[c]adjusted geometric mean

[d]geometric mean

NA-not available

ICP-MS - inductively coupled plasma mass spectrometry

NR-number not reported

APPENDIX B: EXISTING ENVIRONMENTAL GUIDELINES FOR MOLYBDENUM

Jurisdiction	Guideline	Application	Receptors	Narrative Protection Goal	Operational Protection Goal	Reference
Soil	mg/kg					
Canada	**5; 10; 40; 40**	Agricultural; Residential/Parkland; Commercial;Industrial	Ecosystem function & human health	No unacceptable effects to key ecological receptors	Interim guideline	CCME, 1999-2006
Netherlands	**39**	MPC	All species	Minimal effects to most species	5th percentile of NOEC distribution	Verbuggen, et.al., 2001
Netherlands	**190**	Serious Risk Concentration	All species	Protective against serious harm to ecosystems	50th percentile of NOEC distribution	Verbuggen, et.al., 2001
New York	**2**	Soil Cleanup Objective	Ecological Resources	Protection of Ecological Resources	N/A	NYDEC, 2010
Ontario	**6.9; 40**	Surface soil, Residential/Parkland; Industrial/Commercial	Ecosystem function & human health	Protective of human health, groundwater leaching, migration to air, plants, soil-dwelling organism, mammals and avian	Lowest values selected from all receptor routes	MOE, 2011
Ontario	**1200**	Subsurface soils	Ecosystem function & human health	Protective of human health, groundwater leaching, migration to air, plants, soil-dwelling organism, mammals and avian	Lowest values selected from all receptor routes	MOE, 2011
Quebec	**40; 10**	Industrial/Non-Residential Commercial/Non-sensitive-use Recreational;Residential/Residential district Commercial/Sensitive-use Recreational/Institutional	Wildlife, flora, and the environment	To preserve the health of future users and protect the environment. May not be adequate for environments critical or sensitive for biodiversity, protected areas, and threatened or vulnerable species or those likely to be so designated, and their habitats	N/A	MDDEP, 2002
USA	**2**		Plants	Minimal phytotoxic effects to plant biota	10th percentile of LOEC distribution	ORNL, 1997b; EPA, 2001; Bachman, 2008; EPA, 2003
USA - DOE	**200**		Microbes	Minimal effects to microbial processes	10th percentile of LOEC distribution for microbial processes	ORNL, 1997a; Bachman, 2008
Sediment	mg/kg dw					
Netherlands	**25**	Maximum Permissible Concentration	Ecosystem Health	Minimal effects to most species	5th percentile of NOEC distribution	Verbuggen, et.al., 2001
Netherlands	**23**	Serious Risk Concentration	Ecosystem Health	Protective against serious harm to ecosystems	50th percentile of NOEC distribution	Verbuggen, et.al., 2001
Groundwater	μg/L					
British Columbia	**10000**		Aquatic life	No effects on important commercial species	Lowest EC20 for fish species with UF	BC Regs 375/96, 1996
British Columbia	**10- 30**		Irrigated crops- Standard varies with crop, soil drainage and Mo:Cu ratio.	N/A	N/A	BC Regs 375/96, 1996
British Columbia	**50**		Livestock	N/A	N/A	BC Regs 375/96, 1996
Canada	**0.073**	Interim Guideline	Ecosystem function & human health	No unacceptable effects to key ecological receptors	CCME SQG converted to water concentration with exposure estimate	Environment Canada, 2010
Michigan	**73**	Screening level	Human Health/Drinking Water	Concentrations of hazardous substances in drinking water that are safe for long-term consumption	Cancer risk 1 in 100,000 or Hazard Quotient < 1	MDEQ, 2012
Ontario	**9.20E+03**		Ecosystem health	No effects to aquatic or terrestrial receptors, including human health	Lower of GW concentration modeled to meet safe indoor air quality objectives and aquatic protection objectives	MOE, 2011
Quebec	**2000**	Seepage in to surface waters or infiltration into sewers	Aquatic life and piscivorous terrestrial fauna	N/A	The lowest of the following: 1X Acute aquatic life toxicity criterion, 100X Chronic aquatic life toxicity criterion, 100X Contamination of aquatic organisms prevention criterion, or 100X Piscivorous terrestrial fauna criterion, as derived Québec's surface water quality criteria (2001).	MENV, 2001
USA	**70**	Max Contaminant Level	Human Health/Drinking Water	No known or anticipated effects on persons	Relative water contribution to result in Hazard Index = 1	EPA, 2009
Porewater	mg/L					
USA	**0.5**		Plants	Minimal phytotoxic effects to plant biota	10th percentile of LOEC distribution	ORNL, 1997
Surface Water	μg/L					
British Columbia	**2000**	Acute	Freshwater aquatic organisms	Protect all forms of aquatic life and all aspects of aquatic life cycle	Acute LOAEL + UF	BC MOE, 2010
British Columbia	**1000**	Chronic	Freshwater aquatic organisms	Protect all forms of aquatic life and all aspects of aquatic life cycle	Chronic LOAEL + UF	BC MOE, 2010
British Columbia	**500**	Chronic	Irrigated crops	No effects to sensitive crop species at any life stage	Geometric mean of LOAEL and NOEC divided by UF for sensitive species (i.e.: lowest calculated)	BC MOE, 2010
British Columbia	**10**	Chronic	Irrigated crops	No effects to sensitive crop species at any life stage	Geometric mean of LOEC and NOEC divided by UF for sensitive species (i.e.: lowest calculated)	BC Regs 375/96, 1996
British Columbia	**10,000**	Chronic	Aquatic life	No effects to commercially important species	Lowest EC20 for fish species with UF	BC Regs 375/96, 1996
British Columbia	**50**	N/A	Livestock	N/A	N/A	BC Regs 375/96, 1996
Canada	**500**	Chronic	Livestock	No effects to sensitive livestock species and life stages	Lowest Tolerable Daily Intake (geomean of LOAEL and NOAEL divided by UF) for sensitive species	CCME, 1993; BC MOE, 2010; Saskatchewan MOE, 2006
Canada	**73**	Chronic	Freshwater aquatic organisms	Protect all forms of aquatic life and all aspects of aquatic life cycle	5th percentile of EC10/no-effect SSD	CCME, 2007; AE, 1999; EPA, 2005
Michigan	**3,200**	Chronic	Aquatic life	No injurious or debilitating effects to aquatic life	N/A	MDEQ, 2008
Michigan	**29,000**	Acute	Aquatic life	No unacceptable effects to aquatic life	N/A	MDEQ, 2008
Ontario	**40**	Chronic	Freshwater aquatic life & recreation	Protect from effects to human, aquatic or plant life and esthetic qualities	Lowest NOEC of aquatic toxicity, mutagenicity or bioaccumulation endpoints	MOE, 1994
USA/Canada (Great Lakes Initative)	**16,000**	Acute	Freshwater aquatic organisms	No unacceptable effects to aquatic organisms with less than 1 hour exposure	One half of the geometric mean of genus EC50 values divided by UF (data dependant)	EPA, 1995
USA/Canada (Great Lakes Initative)	**370**	Chronic	Fershwater aquatic organisms	No unacceptable effects to aquatic organisms	Geometric mean of genus EC50 values divided by UF and Acute to chronic ratio	EPA, 1995
Air	$\mu g/m^3$					
Ontario	**120**	24 hour average	Environmental and human health	No expected adverse health or environmental effects	NOAEL from animal study with uncertainty factors applied	MOE, 2008
Idaho	**500; 250**	24 hour average, acceptable ambient concentration for insoluble; soluble	Human health	No effects to human health	Hazard Index <1	IDEQ, n.d.a

APPENDIX C: ECOLOGICAL TOXICITY DATA

Table C-1 Plant Toxicity Data

Species	Endpoint	Soil	pH	Organic C %	Clay %	Sand %	Silt %	Fe oxides (mg/kg)		Added (mg Mo/kg)	Total (mg Mo/kg)	Reference	Qualification
Triticum aestivum L.	Plant yield	Haplic luvisol	6.4						EC10/EC50		15/42	Bueker et al., 2010	Sodium molybdate
											5/28	Bueker et al., 2010	Molybdenum oxide
											9/35	Bueker et al., 2010	Molybdenum oxide + CaCO3 for pH stabilization
Hodreum vulgare L.	Dry matter leaves and shoots	Silver sand							EC10	70	70	Davis et al., 1978	Molybdenum oxide
Bradyrhizobium japonicum	Seed yield and legume root nodule number and weight	Clay-loamy alluvial soil	8.05	0.84	54				NOEC	≥4		Yanni, 1990	Sodium molybdate, unbound NOEC
Pisum sativum, pea	Root yield	Calcareous chenozem	8.1	2.5					NOEC	0.1		Kevresan et al., 2001	Sodium molybdate, unbound NOEC. Application of Mo during plant growth without mixing, inconsistent dose spacing
	Shoot yield	Calcareous chenozem	8.1	2.5					NOEC	0.001			
Elytrigia elongata , wheat grass	Shoot yield	Halomorphic soil (typic natraquoll), poorly drained with high salt content	7.1	1.32					NOEC	≥1		De Iorio et al., 1998	Sodium molybdate, unbound NOEC, correlated uptake with soil Cu content
Molybdenum Consortium Research Data (McGrath et al., 2010b)													
Brassica napus	Shoot yield	Zegveld	4.4	30.7	20	9	5	11.7	EC20		3301.5	Rothamsted Research, 2009	
		Kovlinge	5	2	3	78	9	1.9	EC20		51.32		
		Kasterlee	5.2	2.8	2	79	9	1.5	EC20		27.641		
		Zwijnaarde	5.2	1.8	2	81	8	1	EC20		46.361		
		Woburn	6.3	3.6	27	43	16	15.3	EC20		126.35		
		Ter Munck	6.7	0.9	12	8	70	2.2	EC20		11.758		
		Souli	6.8	0.6	33	51	11	0.7	EC20				below lowest added Mo dose, not used
		Rots	7.3	1.3	10	20	50	1.2	EC20		29.689		
		Nagyhorcsok	7.6	2.1	18	54	54	0.5	EC20		7.1248		
		Guadelajara	7.8	0.8	11	16	16	0.1	EC20		5.0208		
Trifolium pratense		Zegveld	4.4	30.7	20	9	5	11.7	EC20		1917.1		
		Kovlinge	5	2	3	78	9	1.9	EC20		49.932		
		Kasterlee	5.2	2.8	2	79	9	1.5	EC20		33.166		
		Zwijnaarde	5.2	1.8	2	81	8	1	EC20		46.122		
		Woburn	6.3	3.6	27	43	16	15.3	EC20		169.04		
		Ter Munck	6.7	0.9	12	8	70	2.2	EC20		45.374		
		Souli	6.8	0.6	33	51	11	0.7	EC20				below lowest added Mo dose, not used
		Rots	7.3	1.3	10	20	50	1.2	EC20		22.503		
		Nagyhorcsok	7.6	2.1	18	54	54	0.5	EC20		5.8226		
		Guadelajara	7.8	0.8	11	16	16	0.1	EC20		9.2143		
Lolium perenne		Zegveld	4.4	30.7	20	9	5	11.7	EC20		3917.3		
		Kovlinge	5	2	3	78	9	1.9	EC20		50.673		
		Kasterlee	5.2	2.8	2	79	9	1.5	EC20		152.75		
		Zwijnaarde	5.2	1.8	2	81	8	1	EC20		116.21		
		Woburn	6.3	3.6	27	43	16	15.3	EC20		444.52		
		Ter Munck	6.7	0.9	12	8	70	2.2	EC20		46.707		
		Souli	6.8	0.6	33	51	11	0.7	EC20		167.17		
		Rots	7.3	1.3	10	20	50	1.2	EC20		55.288		
		Nagyhorcsok	7.6	2.1	18	54	54	0.5	EC20		28.202		
		Guadelajara	7.8	0.8	11	16	16	0.1	EC20		40.516		
Lycopersicon esculentum		Zegveld	4.4	30.7	20	9	5	11.7	EC20		2118.2		
		Kovlinge	5	2	3	78	9	1.9	EC20		35.087		
		Kasterlee	5.2	2.8	2	79	9	1.5	EC20		37.64		
		Zwijnaarde	5.2	1.8	2	81	8	1	EC20		18.445		
		Woburn	6.3	3.6	27	43	16	15.3	EC20		175.45		
		Ter Munck	6.7	0.9	12	8	70	2.2	EC20		46.746		
		Souli	6.8	0.6	33	51	11	0.7	EC20		111.79		
		Rots	7.3	1.3	10	20	50	1.2	EC20		18.014		
		Nagyhorcsok	7.6	2.1	18	54	54	0.5	EC20		18.392		
		Guadelajara	7.8	0.8	11	16	16	0.1	EC20				below lowest added Mo dose, not used
Hordeum vulgare	root elongation	Zegveld	4.4	30.7	20	9	5	11.7	EC20		632.76		
		Kovlinge	5	2	3	78	9	1.9	EC20		28.926		below lowest added Mo dose, not used
		Kasterlee	5.2	2.8	2	79	9	1.5	EC20		82.642		
		Zwijnaarde	5.2	1.8	2	81	8	1	EC20		111.56		
		Woburn	6.3	3.6	27	43	16	15.3	EC20		411.68		
		Ter Munck	6.7	0.9	12	8	70	2.2	EC20		63.23		
		Souli	6.8	0.6	33	51	11	0.7	EC20		1323.5		
		Rots	7.3	1.3	10	20	50	1.2	EC20		37.728		
		Nagyhorcsok	7.6	2.1	18	54	54	0.5	EC20		53.8		
		Guadelajara	7.8	0.8	11	16	16	0.1	EC20				below lowest added Mo dose, not used

Underlined values were used for guideline calculation

Table C-2 Invertebrate Toxicity Data

Species	Soil	pH	Organic C %	Clay %	Sand %	Silt %	Fe oxides (mg/kg)		Added (mg Mo/kg)	Total (mg Mo/kg)
Enchytraeus crypticus	Zegveld	4.4	30.7	20	9	5	11.7	EC20	>2719[a]	>2722
	Kovlinge	5	2	3	78	9	1.9	EC20	227.56	178
	Kasterlee	5.2	2.8	2	79	9	1.5	EC20	103.06	67
	Zwijnaarde	5.2	1.8	2	81	8	1	EC20	291.23	273
	Woburn	6.3	3.6	27	43	16	15.3	EC20	883.31	708
	Ter Munck	6.7	0.9	12	8	70	2.2	EC20	784.84	617
	Souli	6.8	0.6	33	51	11	0.7	EC20	2489.747259	1663
	Rots	7.3	1.3	10	20	50	1.2	EC20	1127.6	922
	Nagyhorcsok	7.6	2.1	18	54	54	0.5	EC20	>2816[a]	>2817
	Guadelajara	7.8	0.8	11	16	16	0.1	EC20	1889.396921	1239
	OECD	7	5.8	20				EC20	567.02	413
Eisenia andrei	Zegveld	4.4	30.7	20	9	5	11.7	EC20	624.38	455
	Kovlinge	5	2	3	78	9	1.9	EC20	78.52	60
	Kasterlee	5.2	2.8	2	79	9	1.5	EC20	97.726	72
	Zwijnaarde	5.2	1.8	2	81	8	1	EC20	140.68	113
	Woburn	6.3	3.6	27	43	16	15.3	EC20	301.38	174
	Ter Munck	6.7	0.9	12	8	70	2.2	EC20	33.121	8.88
	Souli	6.8	0.6	33	51	11	0.7	EC20	1300.2	917
	Rots	7.3	1.3	10	20	50	1.2	EC20	31.06	9.21
	Nagyhorcsok	7.6	2.1	18	54	54	0.5	EC20	41.091	79
	Guadelajara	7.8	0.8	11	16	16	0.1	EC20	27.628	25
	OECD	7	5.8	20				EC20	378.01	244
Folsomia candida	Zegveld	4.4	30.7	20	9	5	11.7	EC20	>2719[a]	>2722
	Kovlinge	5	2	3	78	9	1.9	EC20	47.999	39
	Kasterlee	5.2	2.8	2	79	9	1.5	EC20	1860.8	1865
	Zwijnaarde	5.2	1.8	2	81	8	1	EC20	798.75	728
	Woburn	6.3	3.6	27	43	16	15.3	EC20	>3395[a]	>3396
	Ter Munck	6.7	0.9	12	8	70	2.2	EC20	>2895[a]	>2896
	Souli	6.8	0.6	33	51	11	0.7	EC20	>2742[a]	>2744
	Rots	7.3	1.3	10	20	50	1.2	EC20	>2843[a]	>2844
	Nagyhorcsok	7.6	2.1	18	54	54	0.5	EC20	>2816[a]	>2817
	Guadelajara	7.8	0.8	11	16	16	0.1	EC20	>2820[a]	>2821
	OECD	7	5.8	20	-	-	-	EC20	>2628[a]	>2628

a - no effect at largest Molybdenum dose tested
Underlined values were used for guideline calculation
Data produced by ARCHE (2012), all testing applied reproduction as the effect endpoint.

Table C-3 Microbial Toxicity Data

Table 1: Microbial Ecotoxicity data

Species	Endpoint	Soil	pH	Organic C %	Clay %	CEC pH soil (cmol$_c$/kg)	Al$_{ox}$ (g/kg)	Fe$_{ox}$ (g/kg)	Mn$_{ox}$ (g/kg)	Cb (mg Mo/kg)		Added (mg Mo/kg)	Total (mg Mo/kg)	Reference	Qualification
Native microbial biomass	Basal respiration, reduced respiration	Mor layer of forest soil amended with Scot pine needles	unknown							2.5	EC10	75	77.5	Akerblom et al., 2007	Mo salt as $MoCl_5$
	Basal respiration, reduced respiration	Mor layer of forest soil amended with Scot pine needles	unknown							2.5	NOEC	4.5	7		
Native microbial biomass	Arylsulfatase activity	Natural soil (Nicollet)	6.2	2.73	29						EC63	2400		Al-Khafaji and Tabatabai, 1979	H_2MoO_4, only two test concentrations, cannot qualify EC
		Natural soil (Harps)	7.6	3.24	30						EC26	240			
		Natural soil (Harps)	7.6	3.24	30						EC60	2400			
		Natural soil (Webster)	6.5	2.91	26						EC40	240			
		Natural soil (Webster)	6.5	2.91	26						EC79	2400			
		Natural soil (Okoboji)	7	5.32	34						EC14	2400			
Native microbial biomass	Ethylene production	Handford soil	7.15	0.48	18	5.9					NOEC	0.5		Arshad and Frankenberger, 1991	
											LOEC	1			
											EC50	5			
	Nitrification	Haplic Luvisol	6.2								EC10/50	1522/3129		Buekers et al. 2010	sodium molybdate
												188/638			molybdenum oxide
												Stimulation			MoO3 + CaCO3 for pH stabilization
Native microbial biomass	Nitrate reductase	Typic Albaqualf (Ames)	6.7	2.99	10						EC20	240		Fu and Tabatabai, 1989	
		Typic Haplaquoll (Canisteo)	7.8	4.66	32						EC0	240			
		Cumulic Haptaquoll (Oboboji)	7.1	5.59	36						EC26	240			
		Cumulic Haptaquoll (Oboboji)	7.1	5.59	36						EC70	2400			
Native microbial biomass	L-glutaminase activity	Natural soil (Harps)	7.6	3.24	30						EC5	480		Frankenberger and Tabatabai, 1991a	
		Natural soil (Muscatine)	5.6	2.63	28						EC6	480			
		Natural soil (Okoboji)	7	4.7	34						EC6	480			
Native microbial biomass	L-asparaginase activity	Natural soil (Harps)	7.6	3.24	30						EC3	480		Frankenberger and Tabatabai, 1991b	
		Natural soil (Muscatine)	5.6	2.63	28						EC4	480			
		Natural soil (Okoboji)	7	4.7	34						EC6	480			
Native microbial biomass	Amidase activity	Natural soil (Harps)	7.6	3.24	30						EC2	480		Frankenberger and Tabatabai, 1991c	
		Natural soil (Muscatine)	5.6	2.63	28						EC0	48			
		Natural soil (Muscatine)	5.6	2.63	28						EC2	480			
		Natural soil (Okoboji)	7	4.7	34						EC4	480			
Native microbial biomass	Acid phosphatase activity	Clay loam (Harps)	7.8	3.74	30						EC41	2400		Juma and Tabatabai, 1977	H_2MoO_4
		Silty clay loam (Okoboji)	7.4	5.45	34						EC68	2400			
		Loam soil (Webster)	5.8	2.58	23						EC69	240			
		Loam soil (Webster)	5.8	2.58	23						EC93	2400			
		Clay loam (Harps)	7.8	3.74	30						EC25	2400			
		Silty clay loam (Okoboji)	7.4	5.45	34						EC12	240			
		Silty clay loam (Okoboji)	7.4	5.45	34						EC22	2400			
Native microbial biomass	Nitrogen mineralization	Loam soil (webster)	5.8	2.58	23						EC10	480		Liang and Tabatabai, 1977	H_2MoO_4, single dose tested, unable to qualify effect concentration
		Judson soil	6.6	2.95	45						EC22	480			
		Clay loam (Harps)	7.8	3.74	30						EC22	480			
		Silty clay loam (Okoboji)	7.4	5.45	34						EC54	480			
Native microbial biomass	Pyrophosphatase activity	Natural soil (Clarion)	4.6	1.99	24						EC62	480		Stott et al., 1985	
		Natural soil (Clarion)	4.6	1.99	24						EC75	2400			
		Natural soil (Nicollet)	6.2	2.73	29						EC83	2400			
		Natural soil (Okoboji)	7	5.32	36						EC81	2400			
		Natural soil (Clarion)	4.6	1.99	24						EC62	50			
		Natural soil (Nicollet)	6.2	2.73	29						EC31	50			
		Natural soil (Okoboji)	7	5.32	36						EC19	50			
Native microbial biomass	Urease activity	Natural soil (Weller)	5.1	1.51	17						EC7	480		Tabatabai, 1977	
		Natural soil (Nicollet)	6.1	3.32	30						EC16	480			
		Loam soil (Webster)	5.8	2.58	23						EC14	480			
		Clay loam (Harps)	7.8	3.74	30						EC11	48			
		Clay loam (Harps)	7.8	3.74	30						EC12	480			
		Natural soil (Luton)	6.8	4.35	42						EC4	480			
		Silty clay loam (Okoboji)	7.4	5.45	34						EC9	48			
		Silty clay loam (Okoboji)	7.4	5.45	34						EC16	480			
Native microbial biomass	Nitrification	Alluvial loamy soil	4.7	1.1							NOEC	≥466		Ueda et al., 1988	Na_2MoO_4
	Ammonification	Alluvial loamy soil	4.7	1.1							NOEC	≥466			
Bradyrhizobium japonicum	Nodulation	Clay-loamy alluvial soil	8.05	0.84	54						NOEC	≥4		Yanni, 1990	
Molybdenum Consortium Research Data															
Native microbial biomass	Substrate induced nitrification	Zegveld	4.4	30.7	58.8	41.7	3.5	11.7	0.09	3	EC20		1591	University of Leuven, 2009	
		Kovlinge	5	2	3.3	4.2	2.1	1.9	0.04	1	EC20		49		
		Kasterlee	5.2	2.8	2.2	6.3	0.6	1.5	0.06	<1	EC20		75		
		Zwijnaarde	5.2	1.8	2.2	4.1	1.2	1	0.06	1	EC20		108		
		Woburn	6.3	3.6	31.4	30	0.6	15.3	0.17	1	EC20		>10000		
		Ter Munck	6.7	0.9	13.3	12.2	0.6	2.2	0.35	1	EC20		3981		
		Souli	6.8	0.6	34.7	14.2	0.7	0.7	0.47	2	EC20		3990		
		Rots	7.3	1.3	12.5	14.3	0.4	1.2	0.21	1	EC20		3987		
		Nagyhorcsok	7.6	2.1	21.2	24.8	1.5	0.5	0.45	1	EC20		>10000		
		Guadelajara	7.8	0.8	18	14.1	0.3	0.1	0.05	1	EC20		3981		
	Substrate induced respiration	Zegveld	4.4	30.7	58.8	41.7	3.5	11.7	0.09	3	EC20		>10000		
		Kovlinge	5	2	3.3	4.2	2.1	1.9	0.04	1	EC20		>10000		
		Kasterlee	5.2	2.8	2.2	6.3	0.6	1.5	0.06	<1	EC20		50		
		Zwijnaarde	5.2	1.8	2.2	4.1	1.2	1	0.06	1	EC20		107		
		Woburn	6.3	3.6	31.4	30	0.6	15.3	0.17	1	EC20		>10000		
		Ter Munck	6.7	0.9	13.3	12.2	0.6	2.2	0.35	1	EC20		359		
		Souli	6.8	0.6	34.7	14.2	0.7	0.7	0.47	2	EC20		3660		
		Rots	7.3	1.3	12.5	14.3	0.4	1.2	0.21	1	EC20		1575		
		Nagyhorcsok	7.6	2.1	21.2	24.8	1.5	0.5	0.45	1	EC20		>10000		
		Guadelajara	7.8	0.8	18	14.1	0.3	0.1	0.05	1	EC20		8786		
	Plant residue mineralisation	Zegveld	4.4	30.7	58.8	41.7	3.5	11.7	0.09	3	EC20		>10000		
		Kovlinge	5	2	3.3	4.2	2.1	1.9	0.04	1	EC20		4107		
		Kasterlee	5.2	2.8	2.2	6.3	0.6	1.5	0.06	<1	EC20		1161		
		Zwijnaarde	5.2	1.8	2.2	4.1	1.2	1	0.06	1	EC20		1018		
		Woburn	6.3	3.6	31.4	30	0.6	15.3	0.17	1	EC20		>10000		
		Ter Munck	6.7	0.9	13.3	12.2	0.6	2.2	0.35	1	EC20		6102		
		Souli	6.8	0.6	34.7	14.2	0.7	0.7	0.47	2	EC20		>10000		
		Rots	7.3	1.3	12.5	14.3	0.4	1.2	0.21	1	EC20		>10000		
		Nagyhorcsok	7.6	2.1	21.2	24.8	1.5	0.5	0.45	1	EC20		>10000		
		Guadelajara	7.8	0.8	18	14.1	0.3	0.1	0.05	1	EC20		>10000		

Underlined values were used for guideline calculation

Table C-4 Livestock and Wildlife Toxicity Data

Species	Study Notes	Molybdenum Food Concentration	Copper Food Concentration	Total Daily Exposure	Endpoint	Toxicity Metric	Reference	Notes
Livestock Species								
Horse	12 fillies fed pasture amended with molybdenum for 84 days	0.6 to 1.2 mg/kg dry weight 8 to 15 mg/kg dry weight	6 to 9 mg/kg		copper deficiency	unbounded NOAEL	Pearce et al., 1998	
Horse	4.5 diet trial	20 mg/kg dry weight			blood plasma coppe content	unbound NOAEL	Strickland et al., 1987	
Horse	14 day	107 mg/kg				unbound NOAEL	Cymbaluk et al., 1981	
Goat	36 cashmere goats (1.5 yr) fed wild rye and alfalfa amend with copper and molybdenum for 84 days	0.16 mg/kg	4.72 mg/kg		serum lipid profiles	unbouned NOAEL	Zhang et al., 2012	
Goat	Oral administration, 30 days			20 mg/kg-bw/d	molybdenosis	unbounded LOAEL	Kusum et al., 2010	
Rabbit	Commercial pellets and carrots amended with molybdenum for 14 days	39, 40 mg/kg dry matter			growth	unbounded NOAEL	Bersenyi et al., 2008	
Rabbit	52 lab rabbits, oats and alfalfa amended with molydbenum (Na_2MoO_4) and 37 control rabbits	2,000 mg/kg	copper concentration not quantified		molybdenosis	unbounded LOAEL	McCarter et al., 1962	
Rabbit	12 week	500 mg/kg			growth retardation at 500 mg/kg deaths above 2000 mg/kg	LOAEL	Friberg et al., 1975	
Guinea pig		250 mg/kg - bw			mortality	unbound LOAEL	Chappell et al., 1979	calcium molybdate
Sheep		50 mg/d	5 ug/g		molybdenosis	unbounded LOAEL	Mills and Fell, 1960	
Sheep	Molybdenum amended pasture	5.5 - 12.5 g/kg dry weight	6 - 8.7		cartilage lesions and bone changes	unbound LOAEL	Pitt and Thurley, 1980	
Sheep	193 days	20, 40, 60 mg/kg	82 mg/kg		Renal effect: at 40 and 60 mg/kg both metals accumulated in kidney cortex no damage observed	unbound NOAEL	Van Ryssen et al., 1986	
Cattle	Aerial deposition onto pasture, 5000 grazing cows	2 to 20 mg/kg dry weight	pasture had slight copper deficiency (concentration unknown)		40% had molybdenosis	unbound LOAEL	Alary et al., 1981	
Cattle	84 weeks	5 mg/kg dry weight	4 mg/kg dry weight		decereased food intake, puberty onset delayed 10 weeks, decreased conception	unbound LOAEL	Phillippo et al., 1987a, b	
Cattle		15 to 20 mg/kg			84% of embryos developed abnormally	unbound LOAEL	O'Gorman et al., 1987	
Cattle	lactating cows for 9 weeks	40 mg/kg	6 mg/kg		30% reduction in milk yield, growth reduction nursing calves	unbound LOAEL	Wittenberg and Devlin, 1987	
Cattle		60 mg/kg dry weight		1,360 mg molybdate	brittle bones	unbound LOAEL	Penumarthy and Oehme, 1978	
Cattle	diary cow	140 mg/kg fresh weight	10 mg/kg fresh weight		molybdenosis	unbound LOAEL	Lloyd et al., 1976	
Cattle				141 mg	Anorexia, weight loss	unbound LOAEL	Friberg and Lener, 1986	
Cattle	96 yearling steers fed high fibre diets amended with Mo and drinking water amended with sulfur	187.5 mg/kg dry matter			Signs of Mo toxicity observed including anorexia, changes in hair colour, stiffness in joints	unbound LOAEL	Kessler et al., 2012	effects of sulfur addition on Mo toxicity hard to quantify
Cattle	dairy cow	173 ppm and higher in diet			reduced body weight gains	LOAEL	Huber et al., 1971	
Cattle	bull, n=2, increasing concentrations of molybdenum with age	4.11 to 7.84 mg/kg/d			molybdenosis	unbound LOAEL	Thomas and Moss, 1951	no controls
Wildlife Species								
Mule deer		2,500 mg/kg			reduced food intake	LOAEL	Nagy et al., 1975	
		200 to 1,000 mg/kg			no effect	NOAEL		
Bird Species								
Chicken	300, 1 day old broilers, fed diets amended with molybdenum for 6 weeks	13, 500, 1,000, 1,500			renal cell apoptosis at 1,000 mg/kg and higher	LOAEL	Xiao et al., 2011	
Chicken	300, 1 day old broilers, fed diets amended with molybdenum for 42 days	500, 1,000, 1,500			Concentrations of 1000 mg/kg and higher induced splenic lesions and lymphocyte apoptosis	LOAEL	Yang et al., 2010	
Chicken	300, 1 day old broilers, fed diets amended with molybdenum for 42 days	500, 1,000, 1,500 mg/kg sodium molybdate dihydrate			Concentrations of 1000 mg/kg and higher induced a decrease in t-cells, serum IL-2 contents and thymic lesions - cellularl immune function was injured.	LOAEL	Xiao et al., 2011	
Chicken	16 - 20 ppm resulted in embryo death	35.3 mg/kg/d			embyro death	LOAEL	Lepore and Miller, 195	dose used by ORNL to set their avian limit
Chicken	Increasing concentrations above 500 reduced egg laying, growth depression, anmeia at 4,000 mg/kg, and mortality at 6,000 mg/kg	500 mg/kg			reduced chick growth rate, 15% fewer eggs and all eggs has embryo death	LOAEL	Friberg et al., 1975	

APPENDIX D: DIETARY INTAKE OF MOLYBDENUM

Average dietary intakes (µg/kg bw/day) of trace elements for Canadians in different age/sex groups for Total Diet Study from 1993 to 1999

Trace element	0 - 1	2 - 3	4 - 6	7 - 9	10 - 12	1 - 4	5 - 11	12 - 19	20 - 39	40 - 64	65+	12 - 19	20 - 39	40 - 64	65+	All ages
	months	months	months	months	months	years	years	years	years	years	years	years	years	years	years	Canadians
	M & F	M & F	M & F	M & F	M & F	M & F	M & F	M	M	M	M	F	F	F	F	M & F
Al	96.946	121.207	99.659	87.582	93.432	237.775	264.349	225.129	139.743	137.017	102.417	191.669	131.045	119.163	102.002	134.71
Ba	20.760	23.350	21.414	21.213	22.823	25.251	18.741	11.759	9.704	8.976	7.839	9.280	8.418	7.855	7.546	8.817
Bi	0.054	0.090	0.122	0.086	0.076	0.046	0.034	0.024	0.018	0.015	0.012	0.019	0.014	0.012	0.010	0.016
Cd	0.590	0.676	0.569	0.621	0.649	0.908	0.738	0.518	0.394	0.322	0.283	0.388	0.324	0.270	0.248	0.339
Ce	0.146	0.194	0.136	0.130	0.119	0.114	0.086	0.059	0.043	0.037	0.029	0.046	0.036	0.031	0.028	0.039
Co	0.674	0.821	0.697	0.653	0.625	0.656	0.493	0.350	0.279	0.240	0.202	0.263	0.231	0.211	0.184	0.241
Cu	62.025	77.494	41.391	49.592	39.785	45.742	36.309	25.084	21.140	17.496	14.289	18.831	17.423	14.961	13.364	17.651
La	0.154	0.190	0.118	0.115	0.090	0.075	0.054	0.036	0.027	0.023	0.019	0.029	0.023	0.021	0.018	0.025
Mn	76.538	91.589	72.986	80.851	104.231	127.875	105.304	71.094	67.182	73.376	66.731	54.769	63.098	63.921	64.501	61.344
Mo	9.228	12.451	10.848	9.172	8.002	8.223	5.994	3.779	2.867	2.524	2.269	2.970	2.409	2.248	2.251	2.659
Pb	0.445	0.543	0.418	0.454	0.496	0.492	0.368	0.250	0.223	0.205	0.162	0.198	0.185	0.168	0.144	0.189
Rb	156.820	142.767	201.120	149.987	155.188	133.094	84.136	56.661	50.712	44.012	35.630	43.406	43.560	40.298	32.704	43.458
Sr	101.716	106.707	82.014	79.161	76.888	72.784	52.430	33.660	32.202	29.182	24.264	29.032	29.230	29.725	23.669	28.276
Tl	0.026	0.024	0.024	0.043	0.061	0.088	0.067	0.044	0.032	0.028	0.024	0.034	0.027	0.022	0.019	0.029
Y	0.274	0.339	0.166	0.171	0.109	0.096	0.070	0.057	0.044	0.035	0.030	0.040	0.039	0.031	0.026	0.037
Zn	751.553	803.220	649.428	602.037	503.511	558.553	398.213	310.047	272.150	205.189	155.394	208.705	190.871	160.170	122.645	203.94