ENVIRONMENTAL MANAGEMENT CRITERIA FOR SELENIUM AND MOLYBDENUM: A REVIEW RELEVANT TO THE MINING INDUSTRY

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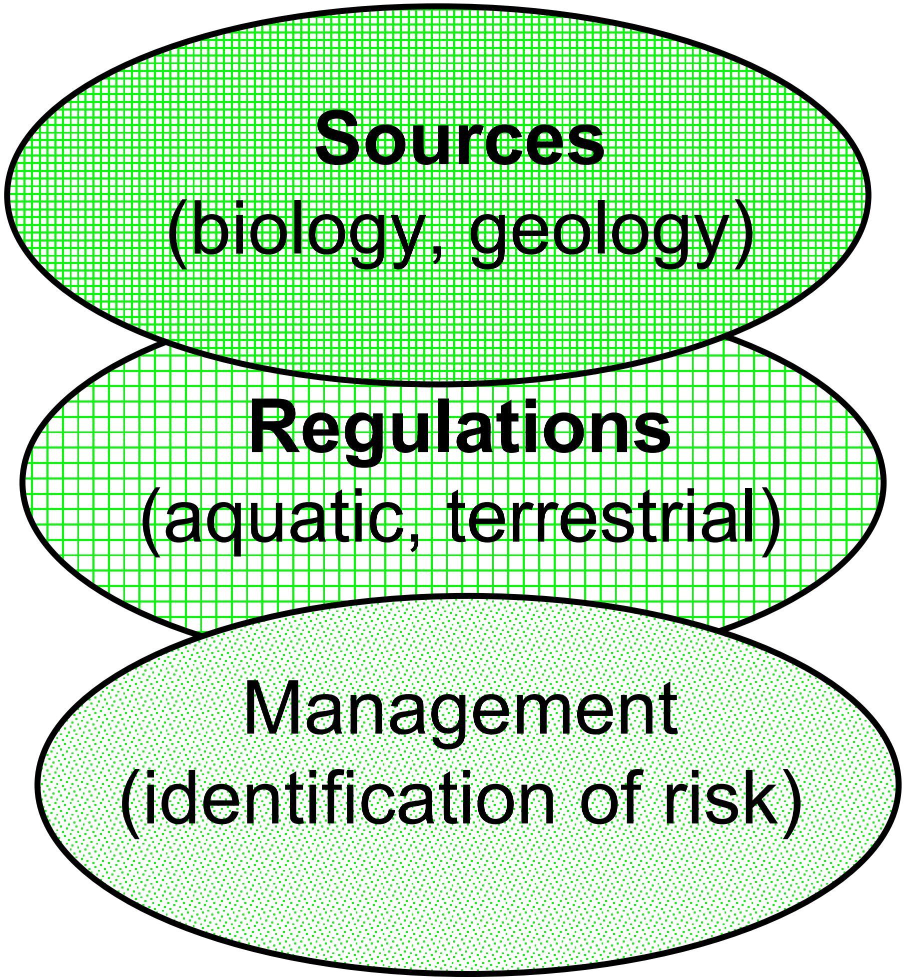
Management Criteria for Se and Mo



Assessment of **Sources** requires understanding of partitioning and monitoring of mine site activities.

Review the **Regulations** used to assess risk to aquatic and terrestrial environments near mines.

Management requires integration of awareness of sources and regulations to identify risk near mines.

Sources: biological context

Both Se and Mo essential elements for animals and plants.

Found throughout the aquatic and terrestrial environments.

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Both Se and Mo essential elements for animals and plants.

Found throughout the aquatic and terrestrial environments.

Selenium used in an amino acid (i.e., selenomethionine) produced by plants and required by animals.

Molybdenum used as a component in enzymes and hormones in plants and animals.

Sources: biological context

The difference between the required and toxic dose of Se and Mo is relatively small.

Thus, only somewhat higher exposure (environmental concentrations) can result in increased risk to biota.

Dust from mine operations can transport Se and/or Mo off site.

Sources: biological context

Some plants are hyperaccumulators of Se or Mo, and if animals consume such plants, they can receive high doses.

Such exposure particularly by terrestrial/aquatic animals to these plants is more relevant for Mo than Se.

Mendel, R. and G. Schwartz. 1999. Molybdoenzymes and molybdenum cofactor in plants. Critical Reviews in Plant Science 18:33-69.

Mikkelsen, R.L., G.H. Haghnia, A.L. Page and F.T. Bingham. 1988. The influence of selenium, salinity, and boron on alfalfa tissue composition and yield. Journal of\ Environmental Quality 17:85-88.

Retana, J., D.R. Parker, C. Amrhein, and A.L. Page. 1993. Growth and trace element concentrations of five plant species grown in a highly saline soil. Journal of Environmental Quality 22:805-811.

Sources: biological context

Studies indicate:

a) risk of Se exposure high to aquatic and terrestrial species,

b) risk of Mo exposure higher to terrestrial species over aquatic species,


Differences may exist between reservoirs and natural lakes.

Sources: biological context

Differences exist in Se and Mo dynamics between summer and winter.

Lemly, A.D. 1997. Role of season in aquatic hazard assessment. Journal Environmental Monitoring and Assessment 45:88-98.

Sources: biological context

Studies indicate:

a) risk of Se exposure high to aquatic and terrestrial species,

b) risk of Mo exposure higher to terrestrial species over aquatic species,

c) partitioning of Se differs between flowing (e.g., streams) and standing (e.g., lakes) waters,

d) partitioning of Mo does not differ between flowing and standing waters, and

e) chemical form of Se and Mo determines partitioning in the aquatic and terrestrial environments.

Morford and Emerson. 1999. The geochemistry of redox sensitive trace metals in sediments. Geochimica et Comochimica Acta 63:1735-1750.

Monitoring of Se and Mo in crops and livestock near base metal mine site in Peru.

Sources: geological context

Studies indicate:

Selenium commonly complexes with oxygen and exists in an anionic or negatively charged species in most environments.

In the water, sediment or soil of most natural environments, Se exists primarily in one of several inorganic forms:

selenate (SeO_4^{-2}),
selenite (SeO_3^{-2}),
elemental selenium (Se^0), or
selenide (Se^{-2}).

Hartikainen. 2005. Biogeochemistry of selenium and its impact on food chain quality and human health. Journal of Trace Elements in Medicine and Biology 18:309-318.

Sources: geological context

In the water, sediment or soil of most natural environments, Se exists primarily in one of several inorganic forms:

selenate (SeO_4^{-2}),
selenite (SeO_3^{-2}),
elemental selenium (Se^0), or
selenide (Se^{-2}).

In well-oxygenated waters, selenate is stable and the most common form under circum-neutral to alkaline pH conditions.

Selenite will form in less oxygenated waters, and is slightly less soluble and more reactive than selenate.

Frankenberger et al. 1998, Environmental Chemistry of Selenium. New York, Marcel Dekker, Inc., 713 p.

Sources: geological context

Under markedly acidic and reducing conditions, elemental Se^0 (insoluble and inert) is likely to form, and with further reduction, selenides can be generated.

Images of acid mine drainage from two different mine sites.

Simmons and Wallschläger. 2005. A critical review of the biogeochemistry and ecotoxicology of selenium in lotic and lentic environments. Environmental Toxicology and Chemistry 24:1331-1343.

Sources: geological context

Under markedly acidic and reducing conditions, elemental selenium (insoluble and inert) is likely to form, and with further reduction, selenides can be generated.

Selenides can be the precursor to organic selenides (e.g., methylated selenides and very soluble seleno-amino acids), and inorganic metal selenides, that are relatively insoluble.

Malisa, E.P. 2001. The behaviour of selenium in geological processes. Environmental Geochemistry and Health 23:137-158.

Sources: geological context

Selenite and selenate usually the dominant forms of soluble selenium in natural freshwaters. However, various physical or biological processes can change the selenium speciation and/or partitioning to other media.

Collectively, these factors identify why Se and Mo need to be considered explicitly for mine sites and adjacent environments.

Gupta, U.C. 1997. Soil and plant factors affecting molybdenum uptake by plants. Pages 71-92 *in* U.C. Gupta, (ed.) Molybdenum in agriculture. Cambridge University Press, Cambridge, U.K.

McDonald, B.G., and P.M. Chapman. 2007. Assessing selenium effects: A weight of evidence approach. Integr Environmental Assessment and Management 3: 129-136.

Sources: geological context

Different partitioning patterns and chemical complexes occur in marine waters but Se not regarded as a risk.

Sources: geological context

The methylation of Se acts to increase the bioavailability and the toxicity to aquatic species in freshwaters, and this has been known since the 1970s.

In water, macrophytes and other plants (e.g., algae) can readily take up selenite and selenate from the water column and incorporate selenium in the tissue as selenomethionine.

Transfer of methylated selenium to higher trophic levels like amphibians, birds, reptiles, fish, mammals.

Hoffman, D.J. 2002. Role of selenium and toxicity and oxidative stress in aquatic birds. Aquatic Toxicology 57:11-26.

Sources: geological context

Anaerobic microbial reduction of selenate and selenite to insoluble elemental selenium can be a key mechanism for immobilizing and removing selenium from water.

Microbial production of methylated selenides occurs under reducing conditions in sediments, likely as a protective mechanism. Forms include dimethyl selenide, dimethyl diselenide, methane selanone, and dimethyl selenyl sulfide.

Chau *et al*. 1976. Methylation of selenium in the aquatic environment. *Science* 192:1130–1131.

Sources: geological context

The methylated selenides all tend to be short-lived in aquatic environments from volatilization losses to the atmosphere.

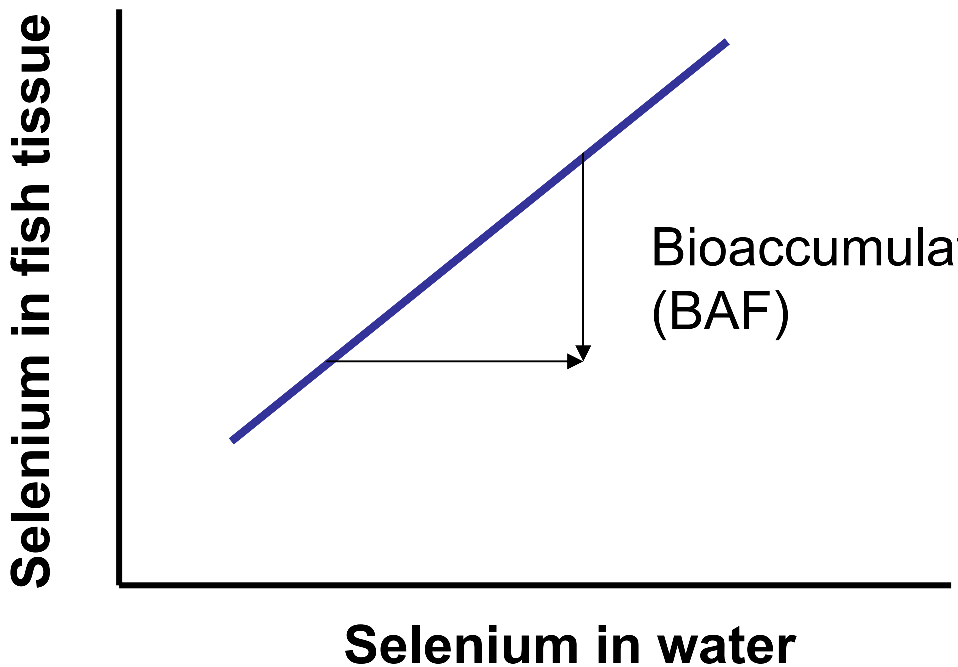
Regardless of environment or residence times, methylated forms of Se are quite bioavailable and may facilitate transfer of selenium to sediment-dwelling invertebrates or to other aquatic or terrestrial species that consume sediments and/or aquatic vegetation.

The species that consume sediment and/or vegetation can convey the Se to the higher trophic levels.

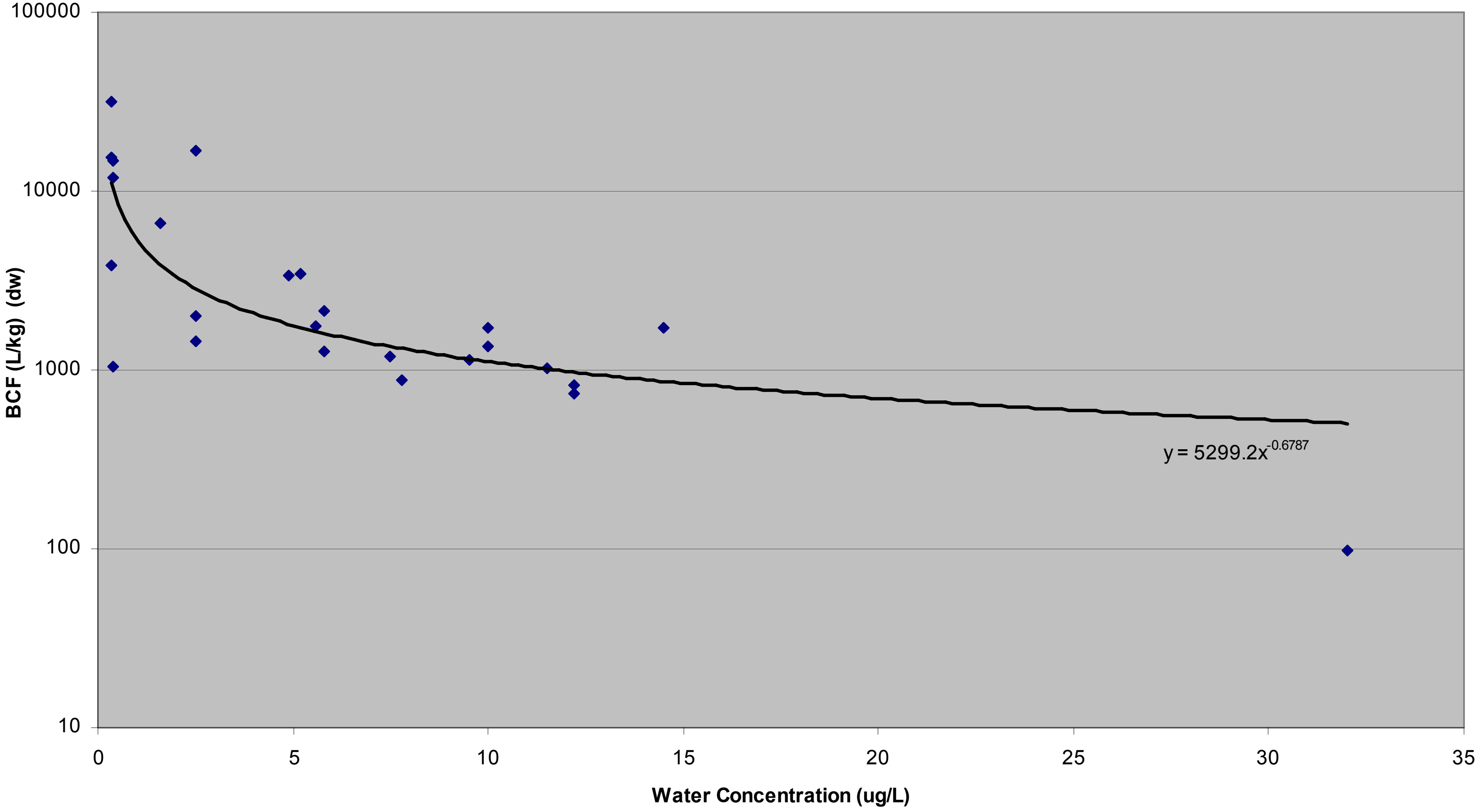
Canton, S.P. and W.D. Van Derveer. 1997. Selenium toxicity to aquatic life: An argument for sediment-based water quality criteria. *Environmental Toxicology and Chemistry* 16:1255-1259.

Sources: biological:geological context

Biota like fish usually show a linear relationship for selenium bioaccumulation based on water concentrations.



Lemly, A.D. 2004. Aquatic selenium pollution is a global environmental safety issue. Ecotoxicology and Environmental Safety 59:44–56.



Expected bioconcentration of Se in invertebrate tissue, adapted from U.S. EPA (2004).

U.S. EPA. 2004. Draft aquatic life water quality criteria for selenium. EPA-822-D-04-001

Sources: geological context

Molybdenum that is released from either natural sources (e.g., erosion of soil to surface waters) or mine site activities (e.g., dust from roads) will readily undergo transport and subsequent partitioning to various media in the environment.

Reduction of transport rate of Se and/or Mo via channel stabilization.

Sources: geological context

Molybdenum will readily undergo transport and subsequent partitioning to media in the receiving environment.

Molybdenum, like Se, does not break down in the environment, but its chemical form can change.

It is usually subject to differential partitioning to various media, and is widely recognized as bioavailable and readily assimilated into the food web.

Howarth and Cole, 1985. Molybdenum availability, nitrogen limitation and phytoplankton growth in natural waters. *Science* 229:653-655.

Kufel, I. 1991. Lead and molybdenum in reed and cattail -- open versus closed type of metal cycling. *Aquatic Botany*. 40:275-288.

Sources: geological context

Integration of Mo in the food chain has been known since the 1960s and is partially explained by the essential requirement for this element, and due to the high water solubility of many molybdenum-containing compounds.

Foy, C., R. Chaney, and M. White, 1978. The physiology of metal toxicity in plants. Annual Review of Plant Physiology, 29, 511–566.

Opresko. 1993. Toxicity summary for molybdenum and molybdenum compounds. Report prepared for the Oak Ridge Reservation Environmental Restoration Program.

Sources: geological context

Molybdenum can exist in five oxidative states; the most common state in nature is the +6 ion.

Molybdenum typically complexes with other metal species and oxygen.

In water, the chemical form and availability of Mo varies with mixing patterns, pH, oxidation rates of organic sediments, reduction potential of sediments, and sedimentation patterns.

In circumneutral water that contains oxygen concentrations of at least 3 ppm, the common form will be the stable molybdate anion (MoO_4^{-2}).

Pais and Jones. 1997. *The Handbook of Trace Elements*. St. Lucie Press, Boca Raton, Florida.

Sources: geological context

At low pH (3-5), molybdate frequently shifts to hydrogen molybdate ($HMoO_4^{-1}$). In this lower pH range, molybdenum is commonly adsorbed to sediment particles composed of clay or other oxic minerals.

The molybdate anion can be reduced to molybdenum disulfide or molybdenite (MoS_2) in low redox environments.

Sources: geological context

Common metallic Mo species include molybdenite (the mineral mined to recover molybdenum) and ferrimolybdenite ($Fe_2[MoO_4]_3$) while the minor ones include powellite ($CaMoO_4$) and wulfenite ($PbMoO_4 \cdot 8H_2O$).

Overall, partitioning and accumulation of Mo is favoured in sediments with high Fe or Ca, and organic matter, and under low redox conditions and pH of 3 to 5.

Atmospheric transport of Mo and Se documented previously.

Schalscha *et al*. 1987. Lead and molybdenum in soils and forage near an atmospheric source. Journal of Environmental Quality 16:313-315.

Field of artichoke monitored for Se and Mo near proposed mine site in Peru.

Sources: geological context

The large majority of Mo observed in rain collected in Japan was present as soluble molybdate. Further, all of the rain samples also contained molybdenum bound to iron-containing particulate matter (e.g., Kawakubo *et al*., 2001).

It is also likely that variable quantities of Mo and Se deposited in habitats (e.g., lakes) along with other elements in ash from forest fires (e.g., Allen *et al*., 2003).

Various diffuse sources need to be <u>included in risk assessments</u> of Mo and Se across watersheds.

Allen *et al*. 2003. Surface water chemistry of burned and undisturbed watersheds on the Boreal Plain: an ecoregion approach. Journal of Environmental Engineering Science 2:S73-86.

Kawakubo *et al*. 2001. Physiochemical speciation of molybdenum in rain water. *Water Research* 35:2489-2495.

Episodic event: Forest fire all around a mine in north Saskatchewan.

Sources: geological context

The abundance of molybdenum in the ocean suggests the biological reactivity and toxicity is low.

This low reactivity of molybdenum, as molybdate in sea water, is due to chemical antagonism or interference with sulfate anions.

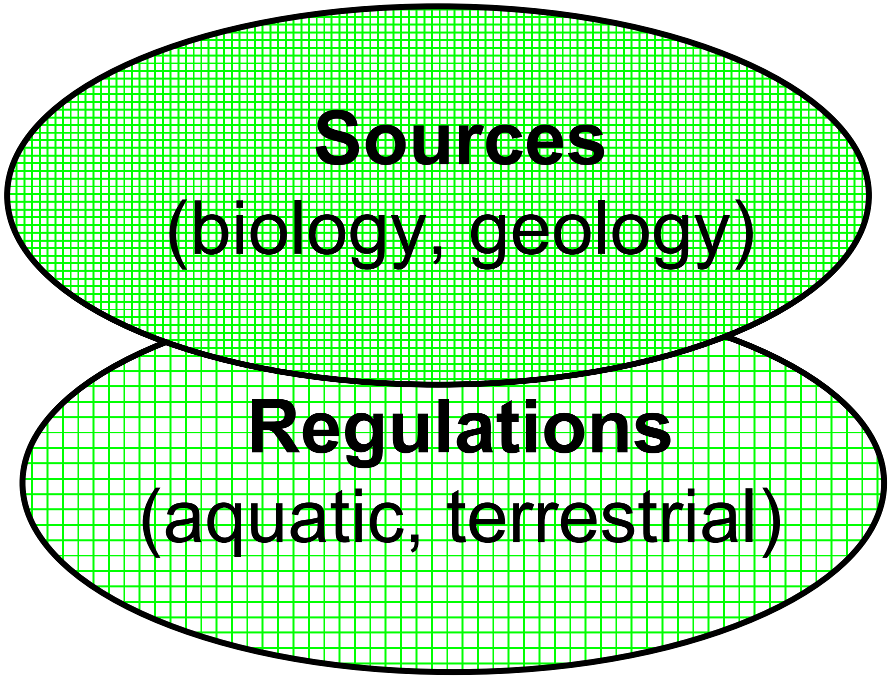
Specifically, the similarity in effective size and stereochemistry between sulfate and molybdate make it difficult for enzymes to preferentially uptake molybdate unless high specificity exists for this compound.

Also, the chemical form of molybdenum changes with salinity concentrations and this can shape microorganism and phytoplankton production rates.

These reasons explain why disposal of waste rock in marine environments is regarded as environmentally safe.

Howarth, R.W. 1988. Nutrient limitation of net primary production in marine ecosystems. Annual Reviews of Ecology and Systematics 19:89-110.

Management Criteria for Se and Mo



Assessment of **Sources**

Review the **Regulations** used to assess risk to aquatic and terrestrial environments near mines.

Regulations: general

Regulations for concentrations of Se and Mo in media and biota reflect observed environmental partitioning and toxicity.

Assessments usually include local lakes and rivers and biota.

Regulations: general

Regulations for concentrations of Se and Mo in media and biota reflect observed environmental partitioning and toxicity.

➡ integrate guidance provided from the Canadian Council for Ministers of Environment (CCME),

reflect past experience with Se and Mo from sites particularly in western North America and the Arctic,

regarded as conservative for Se due to observed consequences on biota in well known settings,

similarly conservative for Mo primarily due to **one set** of studies from 1970s that is currently under scrutiny.

Regulations: general

Generally, the toxic potential of Se and Mo linked to the form in the water column.

Variety of factors can lead to environmental antagonism and reduce the potential for toxicity of Se and Mo.

Presence of environmental factors not always considered when regulations established for mine sites.

Lemly, A.D. 2002. Symptoms and implications of selenium toxicity in fish: the Belews Lake case example. Aquatic Toxicology 57, 39-49.

Gailer. 2002. Reactive selenium metabolites as targets of toxic metals/metalloids in mammals: a molecular toxicological perspective. *Environment, Biology and Toxcicolog*y 16:701-707.

Regulations: monitoring at mine sites

Routine monitoring of Se and Mo for ecosystems at some mines.

Primarily a requirement at uranium mines, some base metal and coal mines with expectation of application to other sectors of industry in near future.

Mussel field exposures downstream of site in eastern Canada.

Regulations: monitoring at mine sites

Active and routine monitoring of Se and Mo for different components of the aquatic and terrestrial ecosystem occurs at some mine sites.

Primarily a requirement at uranium mines and some base metal and coal mines with expectation of application to other sectors of industry in near future.

Such monitoring varies across sites but usually involves the following components: surface water, groundwater,

sediment, soil,
aquatic and terrestrial vegetation,
aquatic and terrestrial invertebrates,
different species of fish,
vertebrates that use aquatic ecosystems
top predators

Regulations: aquatic

The environmental guidelines for Se in water (CCME) are :

- 1 µg/L (i.e., 0.001 mg/L) for aquatic life protection;

  20 - 50 µg/L for irrigation water; and

  50 µg/L for livestock watering.

Useful to contrast guidelines with toxicity thresholds for different aquatic species.

For fish, acute toxicity, as LC50, range:1,000 to 100,000 µg/L.

Chronic toxicity for fish about 10-fold lower, typically in range of 100 to 10,000 µg/L, with the lowest at 5 µg/L.

Regulations: aquatic

The environmental guidelines for Se in water (CCME) are :

1 μg/L (i.e., 0.001 mg/L) for aquatic life protection;

20 -50 μg/L for irrigation water; and

50 μg/L for livestock watering.

Useful to contrast guidelines with toxicity thresholds for different aquatic species.

Invertebrates appear slightly more sensitive than fish.

The ranges of both acute and chronic values overlapped largely with those of fish but more variability in tolerances.

The lowest chronic value for invertebrates was 2 μg/L.

Regulations: aquatic

Useful to contrast guidelines with toxicity thresholds for different aquatic species.

Challenging to measure low concentrations of Se in water.

Thus, mine site assessments sometimes use tissue from exposed local animals or fish and measure concentrations of methylated selenate in the tissue.

Regulations: aquatic

Fish tissue selenium as surrogate of environmental exposure.

Fish muscle U.S. EPA (2004) draft criterion as 7.91 µg/g (dw).

Suggests that effects on fish could occur when fish tissue concentrations in range of ~10 to 20 µg/g (dw).

Toll *et al*. 2005. Setting site-specific water quality standards using tissue residue criteria and bioaccumulation data. Part 1: Methodology. Environmental Toxicology and Chemistry 24:224-230.

Site specific study for SK, Canada: Toll, J.E. 2005. Statistical regression model for setting site-specific selenium water quality objectives. Report prepared for the Canadian Nuclear Safety Commission. Toll Environmental, Seattle, WA. Contract No. 877055-05-0179.

Regulations: aquatic

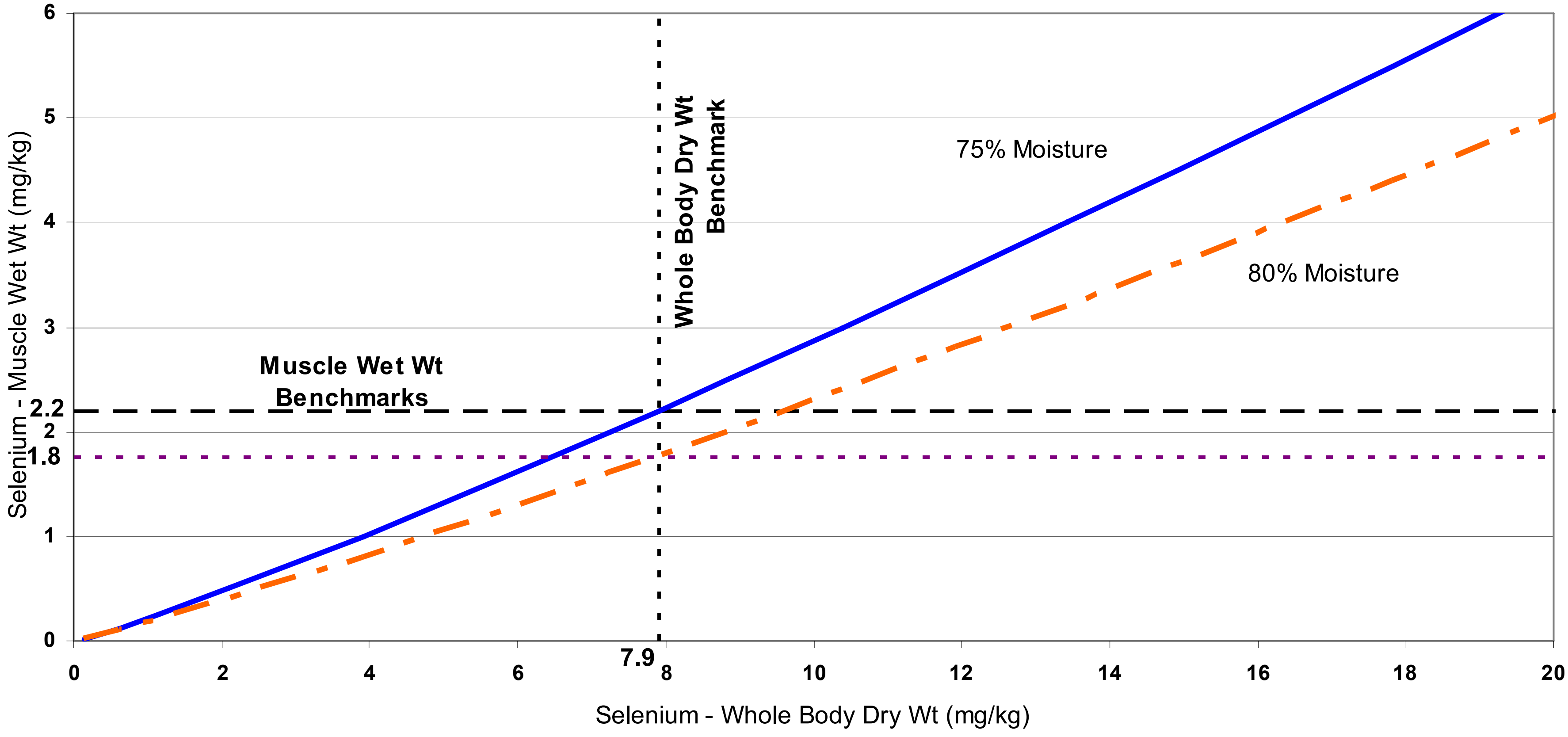
Fish tissue selenium as surrogate of environmental exposure.

Fish muscle U.S. EPA (2004) draft criterion as 7.91 µg/g (dw).

Suggests that effects on fish could occur when fish tissue concentrations in range of ~10 to 20 µg/g (dw).

Review of literature confirmed this inference on concentrations that lead to effects in fish as related to tissue concentrations,

Sometimes requires the conversion of wet weight values to dry weight estimates.



Selenium conversion relationship for fish wet to dry weight, U.S. EPA method.

Regulations: aquatic

The environmental guidelines for Mo in water (CCME) are :

➡ 73 µg/L (i.e., 0.073 mg/L) for aquatic life protection;

10 µg/L for irrigation water; and

500 µg/L for livestock watering.

Guidelines reflect seminal studies by

Birge (1978): LC_{50} = 0.73 mg/L

Birge *et al*. (1980): LC_{50} = 0.78 mg/L

Regulations: aquatic

The environmental guidelines for Mo in water (CCME) are :

- 73 µg/L (i.e., 0.073 mg/L) for aquatic life protection;
  10 µg/L for irrigation water; and
  500 µg/L for livestock watering.

British Columbia guidelines:

- 2000 µg/L for aquatic life protection;
  Absent for irrigation;
  80 µg/L for livestock watering; and
  50 µg/L for wildlife watering

Regulations: aquatic

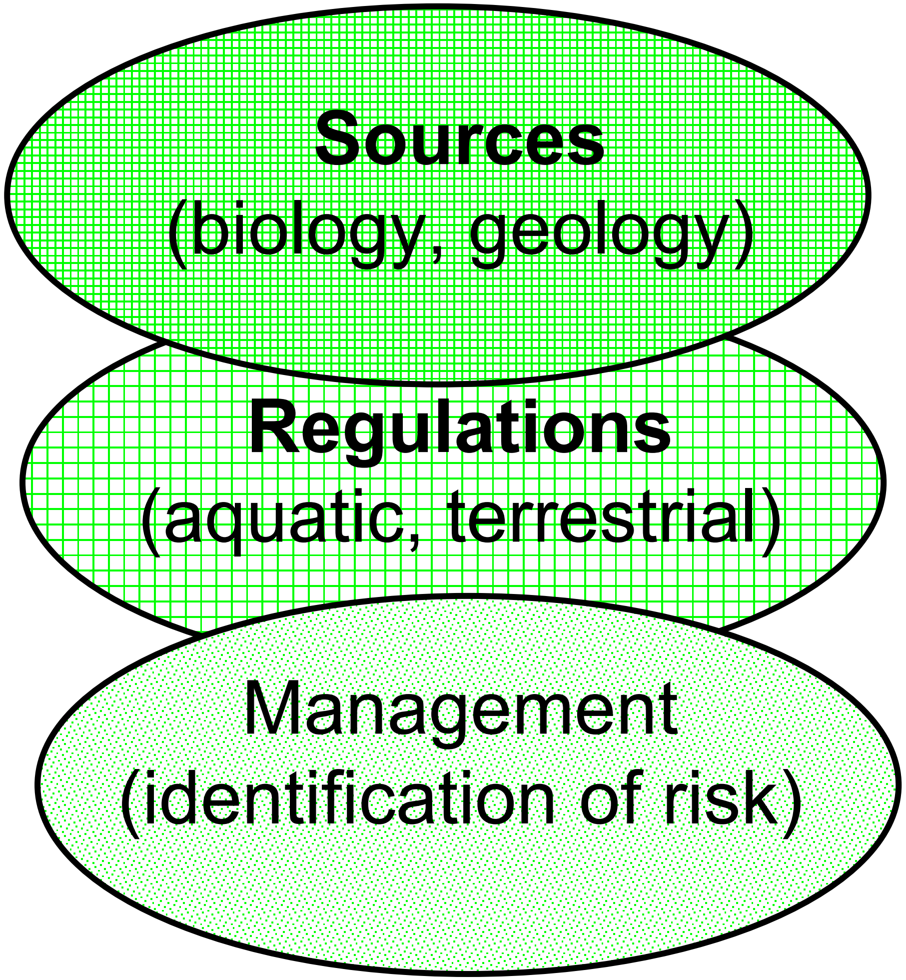
Controversy over the Mo guidelines due to recent studies and much higher estimates of LC_{50} for fishes and other species.

Birge (1978): LC_{50} = 0.73 mg/L for fishes
Davies *et al*. (2005) as >400 mg/L LC_{50} for fishes
Pickard *et al*. (1999) as >90 mg/L LC_{50} for fishes
Hamilton and Buhl (1990) as >1000 mg/L LC_{50} for fishes
Diamantino *et al*. (2000) as >2,000 mg/L LC_{50} for zooplankton

Davies *et al*. 2005. Acute molybdenum toxicity to rainbow trout and other fish. Journal of Environmental and Engineering Science 4:481-485.

Hamilton, S.J., and Buhl, K.J. 1990. Acute toxicity of boron, molybdenum, and selenium to fry Chinook salmon and coho salmon. *Archives of Environmental Contamination* 19:366-373.

Management Criteria for Se and Mo



Assessment of **Sources**

Review the **Regulations**

Management requires integration of awareness of sources and regulations to identify risk near mines.

Management: case studies

Case studies

1. Selenium

    Precious metal mine predicted effluent release scenario in NT

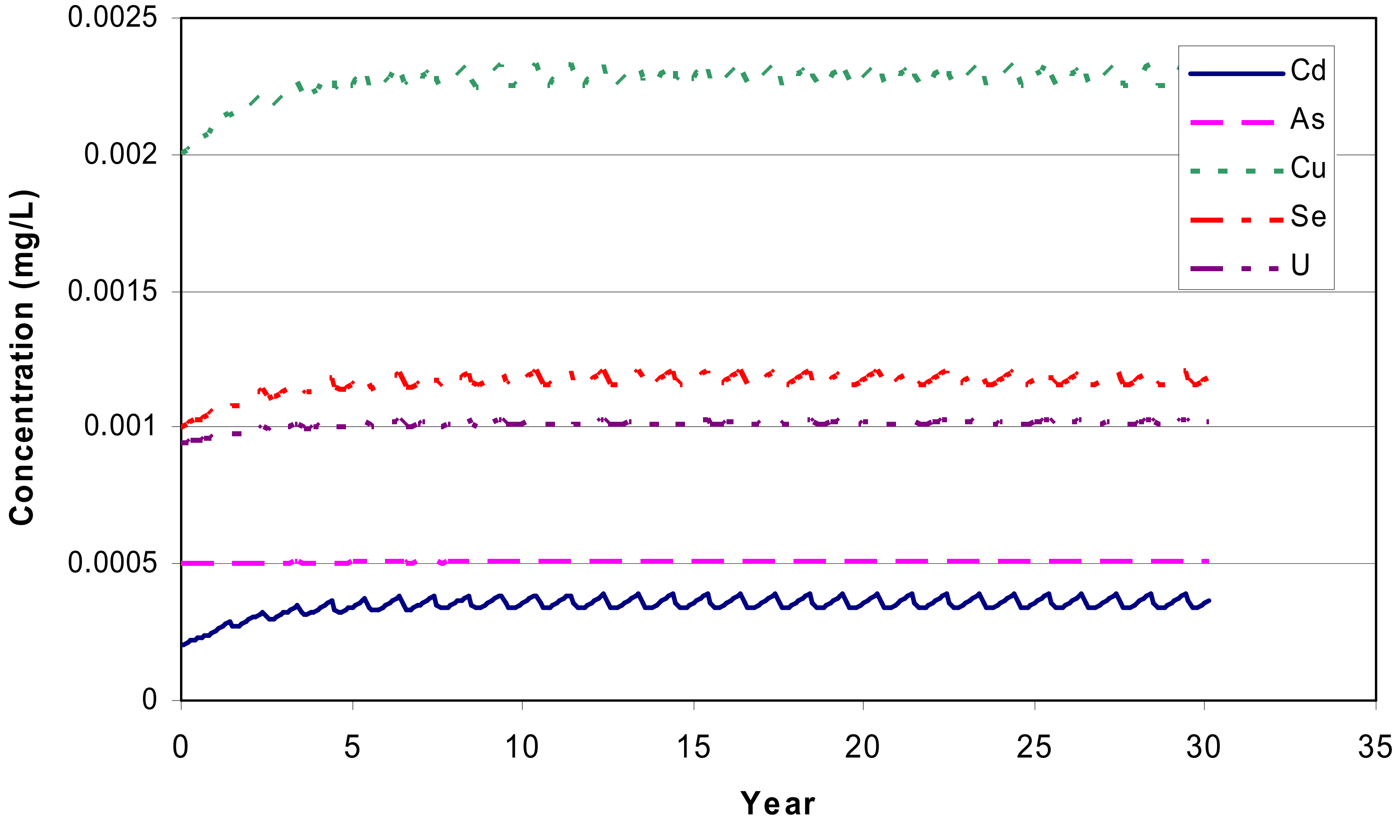
    Assessment of fish from SK

2. Molybdenum

    Brenda Mine example involving aquatic:terrestrial linkages in BC

3. Complication factor: Climate change and fluctuations of temperature and precipitation patterns.

Management: case study in NT

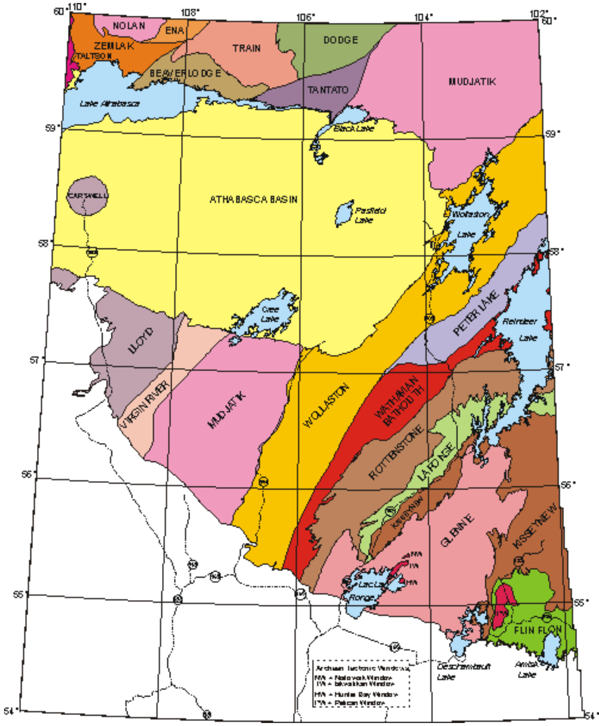


Example of scenario of predicted metals in effluent from precious (i.e., U) metal mine in NT based on ore characteristics in baseline study.

Management: case study in SK

Northern Saskatchewan is ideal for aquatic field studies.

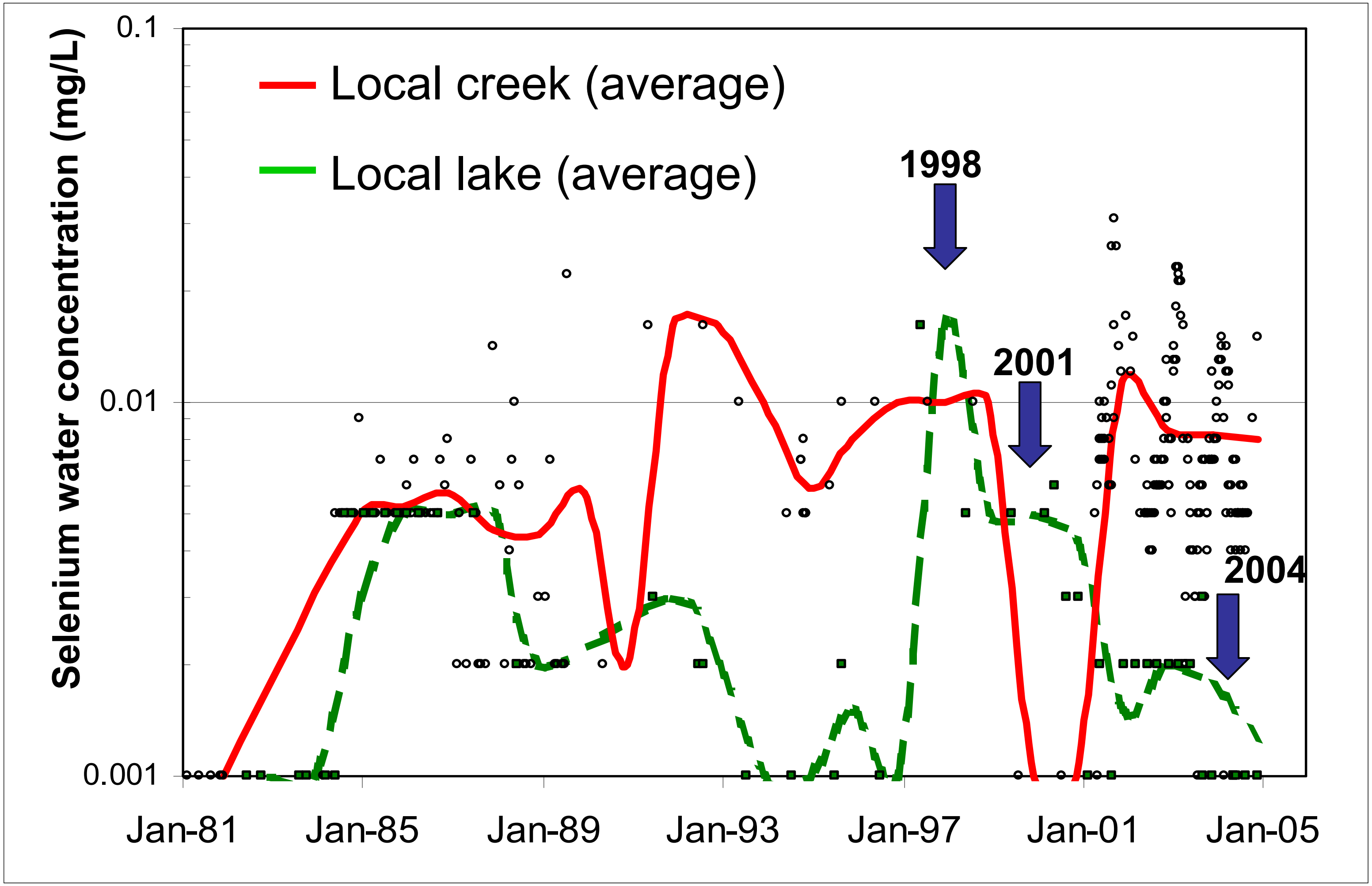
Management: case study in SK



Athabasca basin is unique mostly due to sandstone.
(www.ir.gov.sk.ca/)

International Atomic Energy Agency (IAEA). 1988. *A World Atlas of Uranium Occurrences and Deposits*. Vienna, Austria.

Management: case study in SK



This creek and lake near one mine site show disparity in lake and creek selenium and rapid changes in concentration due to mine operations.

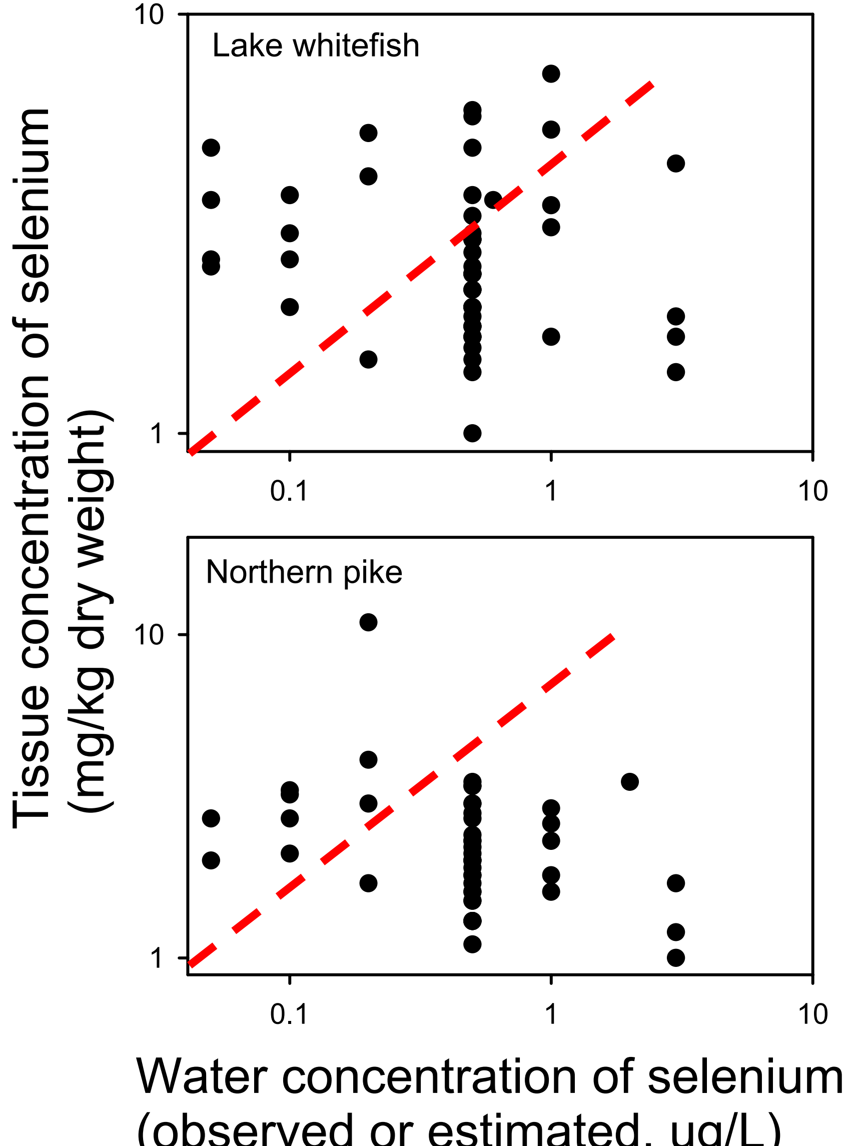
Management: case study in SK

Species used in monitoring near mine:

Northern pike
(*Esox lucius*)

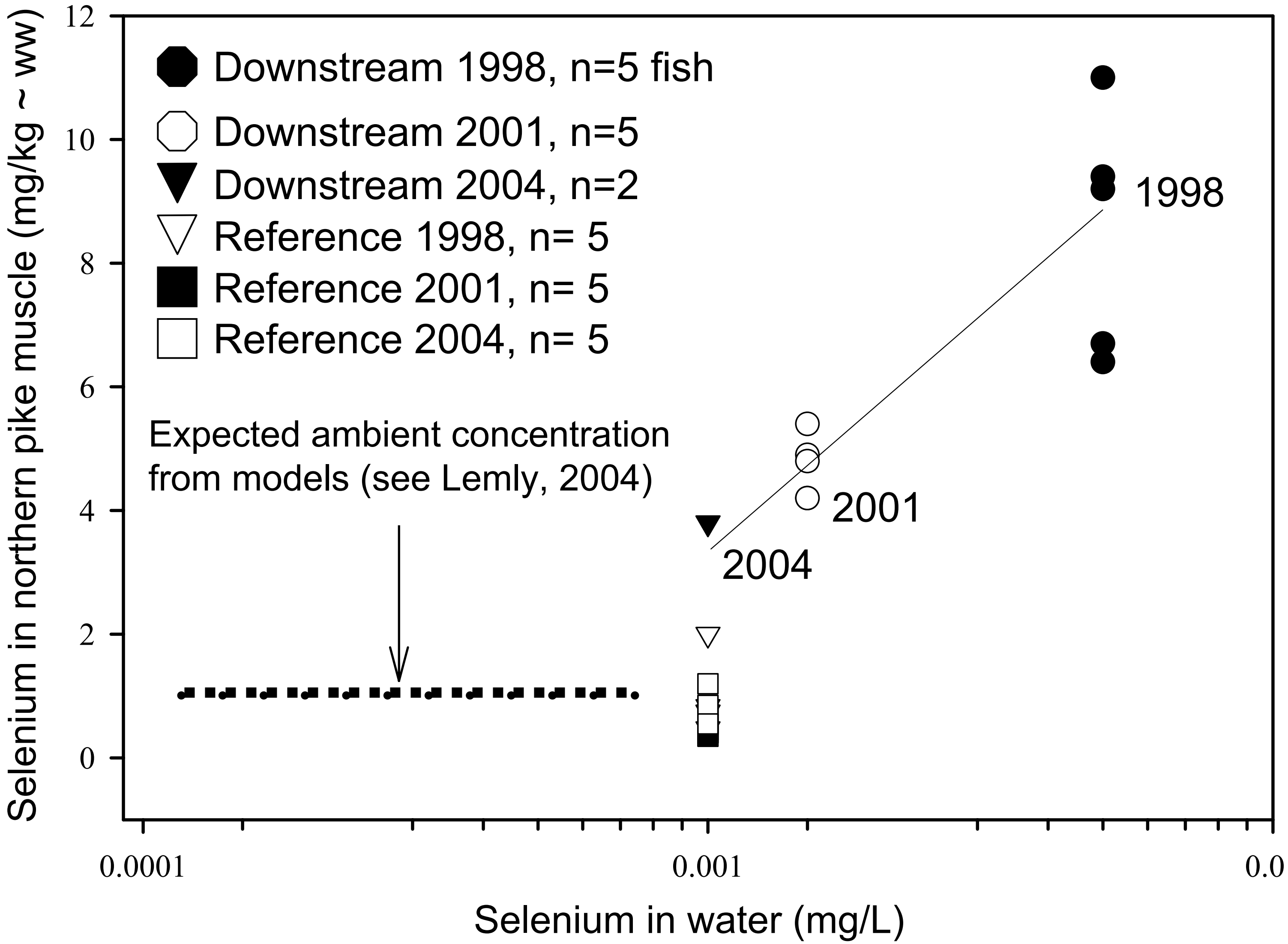
Lake whitefish
(*Coregonus clupeaformis*)

Management: case study in SK

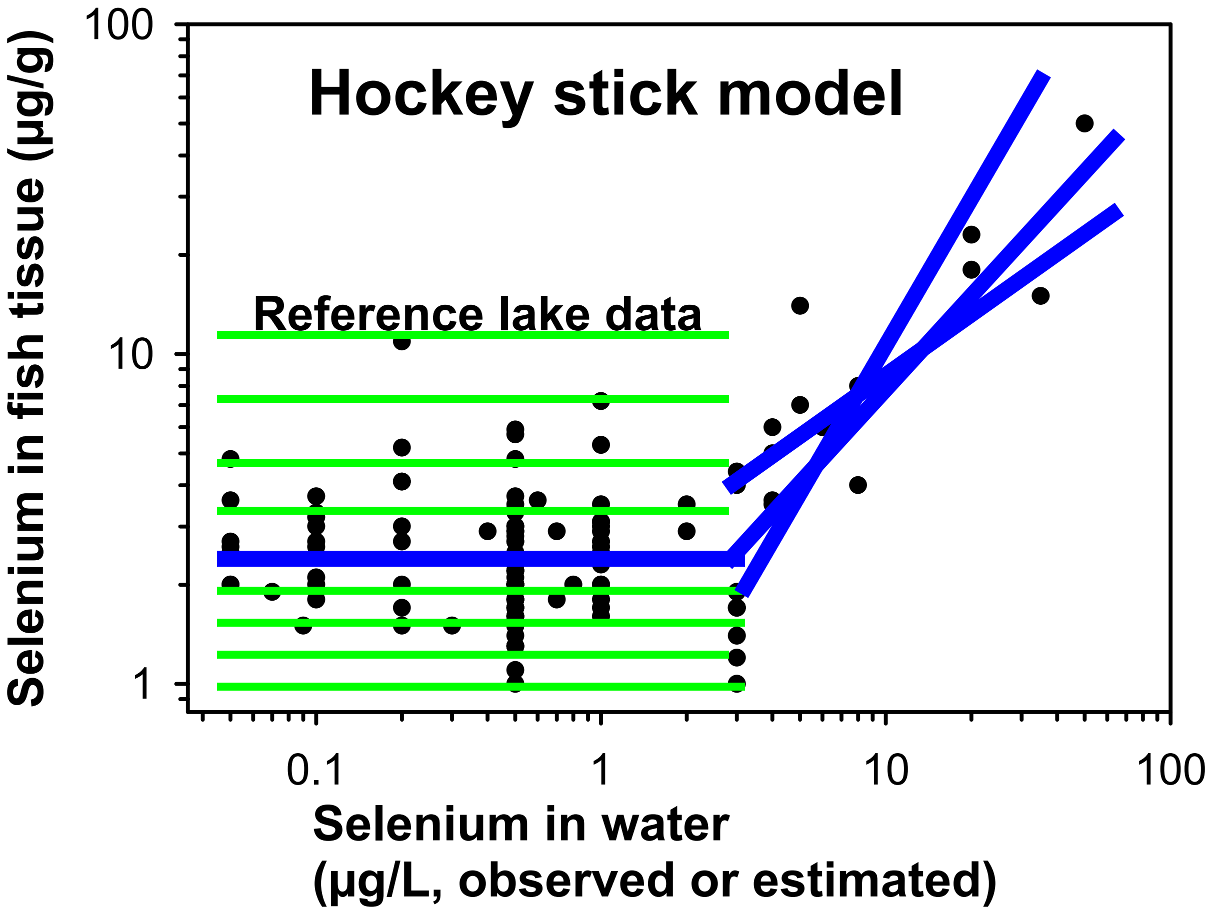


Expected linear relationship <u>not</u> observed for reference lakes.

Management: case study in SK



Management: case study in SK



Difficult to identify both ends of the `hockey stick` model due to natural variation in fish tissue Se concentrations.

Management: case study in SK

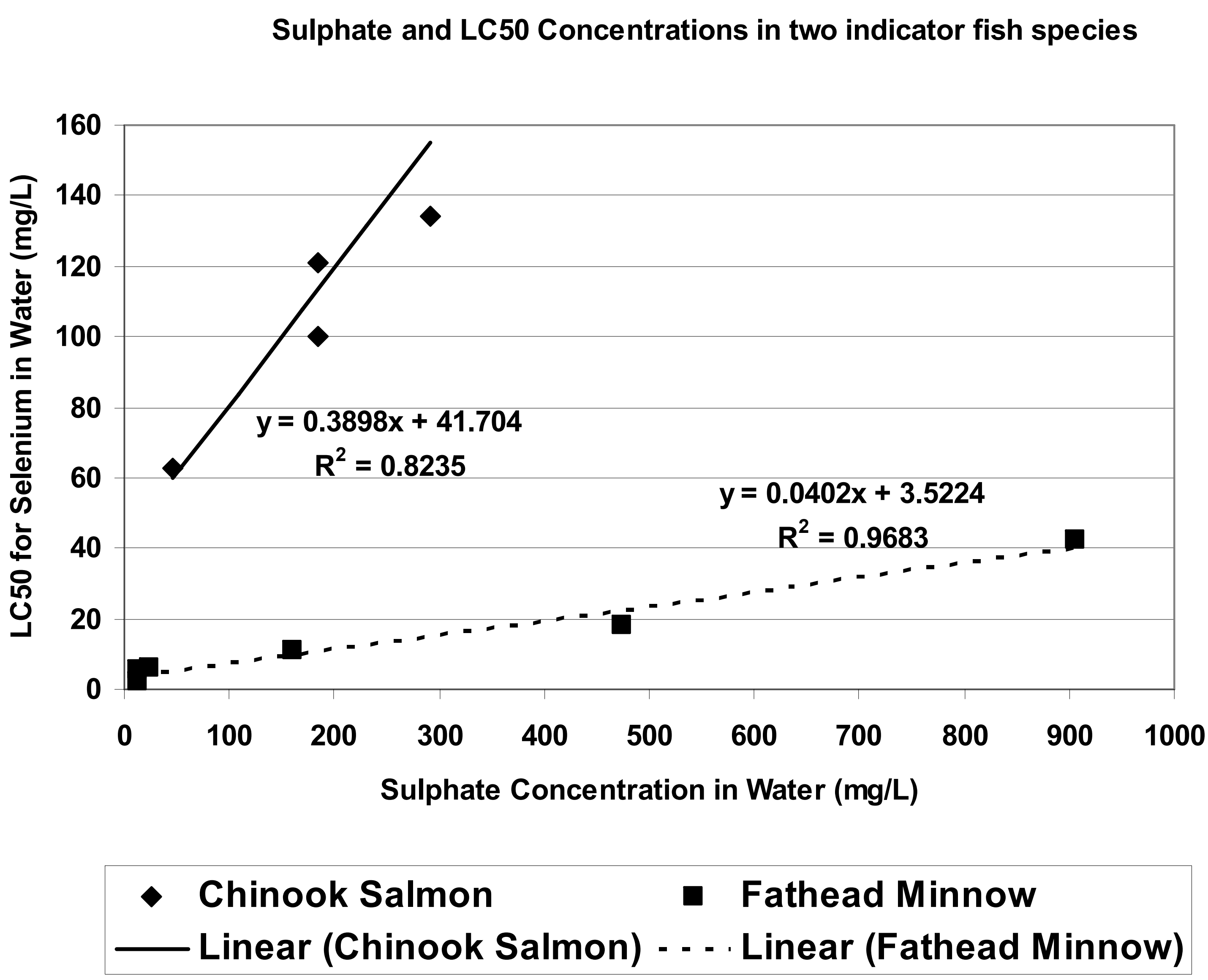
Field data for reference lakes confirm relationship of accumulation of Se, is <u>NOT</u> fully consistent with expected relationship suggested by Toll.

Indicates that natural variation exists in Se content of fish tissue and no evidence of deformities etc. in lakes with naturally high Se concentrations.

Such processes suggest that local processes influence the ability of fish to accumulate and then depurate Se. Suggests local adaptation or tolerance.

Toll, J.E. *et al*. 2005. *Environ Toxicol Chem* 24:224-

‘Toll-Brix accumulation model’



Other factors can influence toxicity of Se, like sulphate.

Management: case study in BC

Analysis of risk of Mo transfer to moose (*Alces alces*) at now closed Brenda Mine in BC.

Assessed Mo in different components of aquatic ecosystem along with direct observations on moose.

Water treatment plant and small stream at Brenda Mine.

Management: case study in BC

Assessed Mo in different components of aquatic ecosystem along with direct observations on moose.

Three main issues with Mo toxicity in wildlife associated with aquatic environments at Brenda Mine, and elsewhere:

First, a high dietary intake of molybdate can be toxic to mammals and can cause copper deficiency.

Second, copper supplementation in the diet can limit or reverse the effects of Mo toxicity.

Third, high dietary intake of sulfur can exacerbate toxicity from Mo and important for ruminants.

Frank, A. 1998. Mysterious moose disease in Sweden. Similarities to copper deficiency and/or molybdenosis in cattle and sheep. Biochemical background of clinical signs and organ lesions. Science of the Total Environment 209:17-26.

Management: case study in BC

Mo from site activities

Mo transfer to water, soil and sediment

Mo in terrestrial vegetation

Mo in macrophytes

Management: case study in BC

Analyses estimated 332 mg/L of molybdate in macrophytes, and ≤ 1 mg/L in terrestrial browse, sediment, and water.

Analyses show moose consume ≤ 5% of annual diet as macrophytes.

Weighted average of Mo in diet estimated as ~10.7 mg/Kg.

Revealed little risk of Mo to moose in habitat.

Field studies confirmed this interpretation.

It is feasible to quantify movement of Mo and Se with computer model developed by EcoMetrix called IMPACT®

Taylor and McKee. 2003. Wild ruminant study at Brenda Mines. Presented at the 27th Annual British Columbia Mine Reclamation Symposium. Kamloops, B.C. Sept. 15-18, 2003.

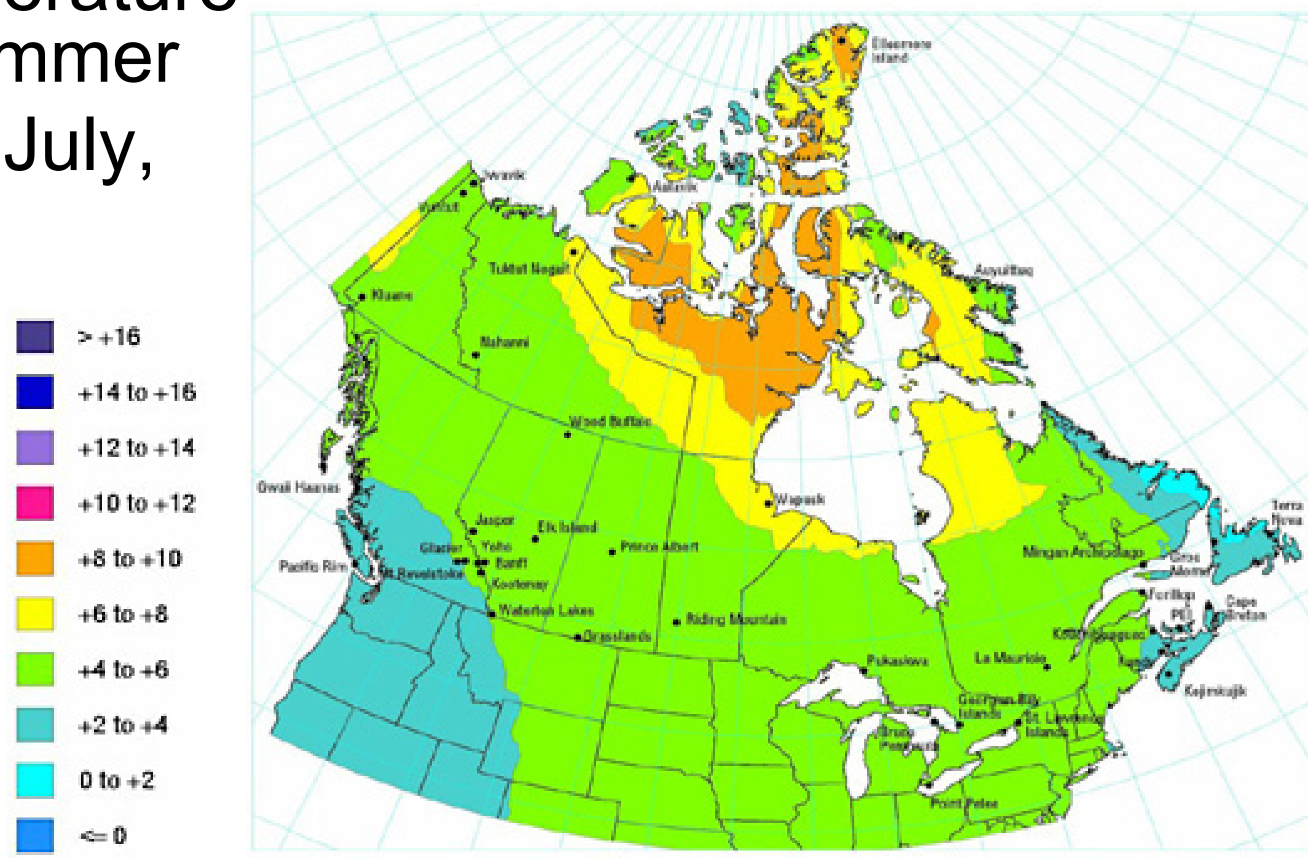
Management: case study general

Influence of climate change will require
direct management action
within the area of neutral mine drainage.

Process relevant in northern and southern locales

“By the end of the 21st century, Arctic temperatures will be at least 5 degrees warmer than today”

Projected temperature increase - summer 2090 (June, July, August)



Adaptation & Impacts Research (AIR) Group, Environment Canada, 1999

Climate change will likely strongly influence hydrological cycles and the movement of Se and Mo in northern ecosystems.

Lake Erie:

Spring of 1998

Autumn of 1999

➡ Low water levels can occur even in very large lakes.

Summary: Sources and Regulations

Small concentrations of Se and Mo above background can lead to biomagnification and risk to exposed species.

Toxicity of Se and Mo varies across ecosystem habitats.

Tolerance to Se and Mo varies across species.

Aquatic toxicity thresholds reasonably well described for Se but not for Mo, and justify reconsideration.

Summary: Management

Available case studies identify convincing examples that site-specific and species-specific processes exist for Se and Mo across ecosystems.

The site and species-specific processes of Se and Mo toxicity identify that site-specific risk assessment is justified.

Methods for site-specific risk assessment well known.

Also feasible to apply computer models to quantify ecosystem components and predict accumulation of Se or Mo in exposed species, and assess risk.


Thanks for your involvement!
Questions?