

MINISTRY OF ENVIRONMENT AND PARKS  
PROVINCE OF BRITISH COLUMBIA

WATER QUALITY CRITERIA  
FOR  
MOLYBDENUM

TECHNICAL APPENDIX

L.G. Swain, P.Eng.  
Resource Quality Section  
Water Management Branch

Victoria, B. C.  
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## 1. OCCURRENCE IN THE ENVIRONMENT

Molybdenum is an essential element to all forms of life. The role of molybdenum in plants is to stimulate nitrogen fixation and nitrate reduction. This is accomplished by soil bacteria and by certain algae in water which convert molecular nitrogen to ammonia. Without this process, life would not exist.

Molybdenum has six valence states, but occurs naturally as  $\text{Mo}^{3+}$ ,  $\text{Mo}^{5+}$ , and  $\text{Mo}^{6+}$ .

### 1.1 SOURCES

Molybdenum does not occur in nature in its free or metallic state, but is found only chemically combined with other elements. Small deposits of molybdenum-bearing minerals occur throughout the world, but only molybdenite ( $\text{MoS}_2$ ) is of commercial importance<sup>(1)</sup>.

In the late 18th century, the first molybdenum-bearing ore was mined in Norway<sup>(1)</sup>. Mining in the United States first occurred in the early twentieth century in Colorado and New Mexico<sup>(1)</sup>. Canadian reserves of molybdenum are predominantly in porphyry copper ores in the Western Provinces, predominantly in British Columbia. Canadian molybdenum reserves account for about 15% of the world total<sup>(1)</sup>.

Canada is the second largest producer of molybdenum in the world<sup>(45)</sup>. Molybdenum is widely distributed in British Columbia as pure low-grade porphyry deposits of molybdenite. The Endako Mine in central British Columbia is one of the three largest molybdenum mines in the world<sup>(45)</sup>. The locations of mines in British Columbia with porphyry deposits are shown in Figure 1. Drainage from molybdenum-bearing mineral deposits and molybdenum mines is the only known source of molybdenum discharged to surface waters in British Columbia.

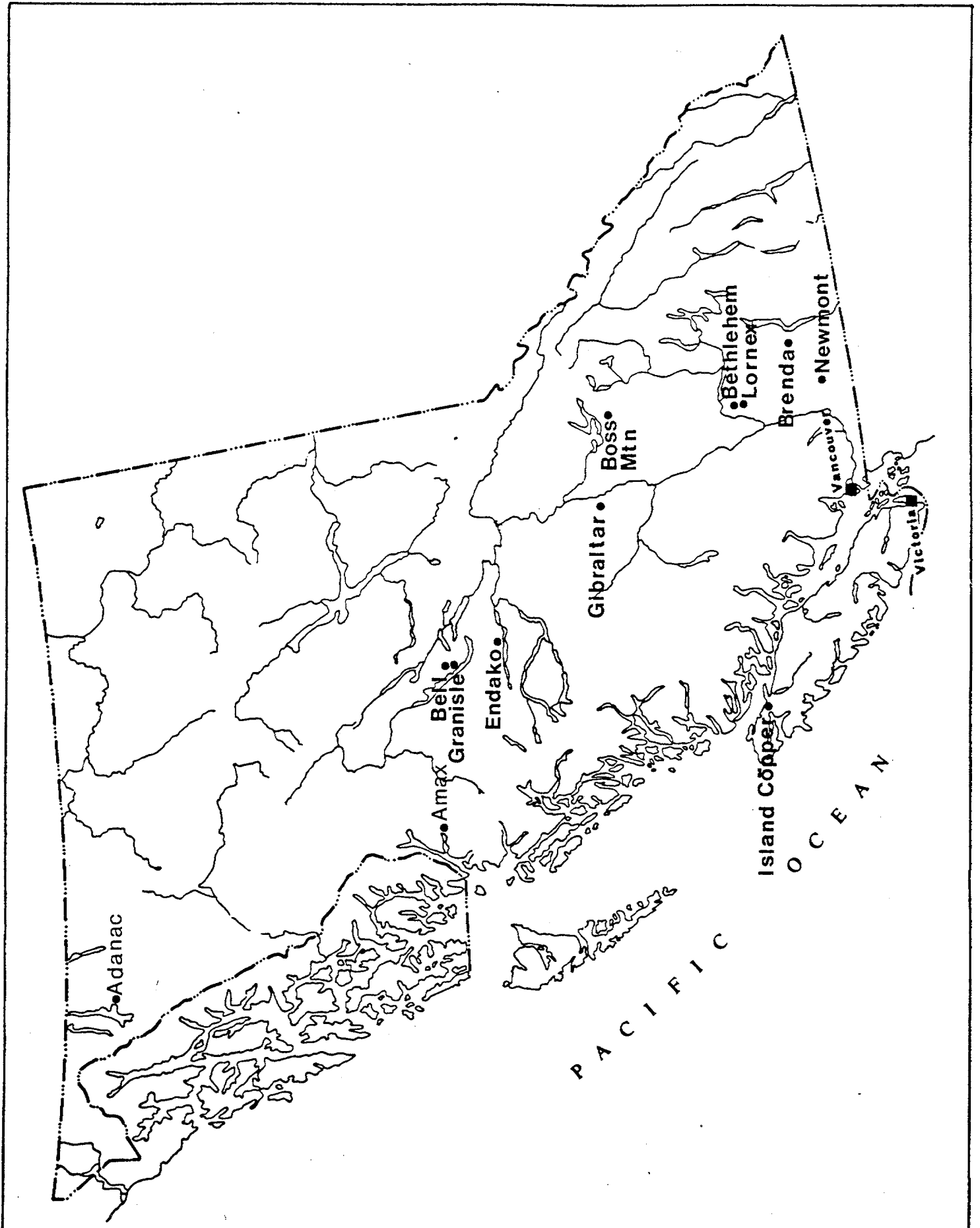


FIGURE I. Major Mines With Porphyry Deposits in B.C.

## 1.2 NATURAL LEVELS

The total concentration of molybdenum in soils averages 1 to 2 ppm. High molybdenum concentrations in soils have been associated with sedimentary materials<sup>(2)</sup>.

Molybdenum concentrations in rivers have been reported to be as high as 0.007 mg/L in parts of the United States and the Soviet Union, and as high as 0.0025 mg/L in some American lakes<sup>(2)</sup>.

For British Columbia, a mean value for rivers in the entire Province is not meaningful due to the heterogeneous geological nature of the Province. Values in rivers have been as high as about 0.0011 mg/L in the Fraser River near Mission<sup>(3)</sup>, 0.0005 mg/L in the Similkameen River<sup>(4)</sup>, 0.03 mg/L in the Nechako River near Vanderhoof<sup>(5)</sup>, and 0.0015 mg/L in tributary creeks to Stuart Lake<sup>(5)</sup>.

In a number of selected and generally pristine lakes, the mean value in British Columbia was <0.010 mg/L (Range: <0.01 to 0.04 mg/L). Only 34 of 262 samples had detectable molybdenum concentrations, the mean value of which was 0.019 mg/L<sup>(6)</sup>.

Analyses for molybdenum in sediments ranged between 5 and 10 µg/g (ppm) on a dry-weight basis in the Fraser River in the Lower Mainland area<sup>(7)</sup>. Regional stream surveys conducted throughout a number of large areas of British Columbia at a density of about one sampling site for every 14 km<sup>2</sup> reported values averaging < 2 ppm, with maximum values as high as 475 ppm in the Quesnel Lake area<sup>(8)</sup>. In lake sediments at selected sites in generally pristine areas, a mean molybdenum value of 14.2 ppm existed for a range from 1 to 183 ppm (n=202)<sup>(6)</sup>.

Singleton has reported that in a survey of fish in the Fraser River, from its headwaters to the Strait of Georgia, molybdenum could be detected (varying detection limits) in only 46 of 273 muscle tissue samples<sup>(9)</sup>.

The maximum concentration was 1.39  $\mu\text{g/g}$  (wet-weight) in a longnose sucker from the headwaters<sup>(9)</sup>. Most values in edible species were not detectable. A large number of the samples with detectable concentrations were from the upper reaches of the river which represented natural background levels. All fish muscle samples taken from the Columbia River near Trail had non-detectable molybdenum concentrations (detection limit ranged from about 0.4 to 1.5  $\mu\text{g/g}$ , assuming eighty percent moisture content)<sup>(9)</sup>.

Futer and Nassichuk<sup>(60)</sup> reported concentrations in muscle of eulachons from <0.3 to 3.1  $\mu\text{g/g}$  (dry weight) (95% of values were <0.3  $\mu\text{g/g}$ ). Values in livers ranged from <0.3 to 1.1  $\mu\text{g/g}$  (dry weight). The eulachons were from the Nass River.

A recent survey of biota in the lower Fraser River revealed molybdenum concentrations from <1 to 5  $\mu\text{g/g}$  (dry-weight)<sup>(7)</sup>. The few fish sampled all had molybdenum values < 1  $\mu\text{g/g}$  (dry-weight)<sup>(7)</sup>.

Farrell and Nassichuk reported molybdenum concentrations "were typically below detectable limits of 0.4  $\mu\text{g/g}$  dry weight" for cockles from Alice Arm (Davies Point)<sup>(61)</sup>.

## 2. DRINKING WATER SUPPLY

Human health appears to have been affected, in some isolated cases, by excess molybdenum intake in food. Some other effects may indirectly be drawn from research conducted on laboratory animals. Since drinking water is part of the intake of all elements to the human body, its role is discussed below.

### 2.1 EFFECTS OF EXCESS MOLYBDENUM

The primary toxic effect of molybdenum involves interference with copper metabolism, thus inducing a copper deficiency. Clinical disorders associated with copper deficiency, but not necessarily associated with molybdenum, are anemia, bone abnormalities, loss of pigmentation, reproductive failure, and cardiac lesions<sup>(10)</sup>. The synthesis of the enzyme xanthine oxidase increases with increased molybdenum intakes. This can increase the formation of uric acid, and can possibly lead to gout-type illness.

Molybdenum has been implicated in cases of gout-like diseases in the Soviet Union. The illness was characterized by pains in the joints. Medical examinations determined that 31% of the adults in one settlement, and 18% in a second settlement, displayed gout-type symptoms. This compares to a normal range from 1 to 4%<sup>(11)</sup>. The inhabitants of the settlements consumed between 10 and 15 mg of molybdenum and 5 to 10 mg of copper daily, compared to normal levels of 1 to 2 mg and 10 to 15 mg, respectively<sup>(11)</sup>.

A copper/molybdenum antagonism is known to exist for animals, and this will be discussed in further detail in other sections of this report. The Soviet findings just cited tend to confirm that this antagonism also may exist for humans<sup>(11)</sup>.

Chappell<sup>(10)</sup> reported that one clinical disorder of copper deficiency was cardiac lesions. In relation to coronary disorders, Underwood<sup>(12)</sup> cited Oster<sup>(46,47)</sup> who speculated that molybdenum was possibly linked to coronary heart disease in humans. The hypothesis put forth was that increased molybdenum leads to increased production of the enzyme, xanthine oxidase, which in turn leads to depletion of plasmalogens (phospholipids widely distributed in the body, particularly in cardiac tissue and other locations). Oster maintained that xanthine oxidase oxidized the plasmal moiety of plasmalogen which led to tissue necrosis and scar formation, and that cholesterol was deposited as a protective coating at these sites of tissue destruction. This initiated atherosclerosis. Consumption of homogenized cow's milk increased the biological availability of xanthine oxidase which can be absorbed directly through the intestinal mucosa and be deposited on the arterial wall or in the heart muscle<sup>(12)</sup>. More research is required to confirm the accuracy of this highly speculative hypothesis.

Molybdenum also has been implicated in cases of Genu Valgum deformity in India<sup>(13,14)</sup>. The syndrome affects predominantly males (10:1 ratio of males to females among children and 20:1 ratio among adolescents and young adults), and seems to be associated with a low dietary intake of calcium and a high intake of molybdenum. It is believed that the high molybdenum concentrations cause excretion of copper, resulting in poor formation of bone matrix and matrix osteoporosis<sup>(13,14)</sup>.

Laboratory studies on rats have also shown that molybdenum can affect the rate at which calcium is taken into the bones. The rate at which calcium is taken into the bones of rats was affected significantly ( $p < 0.05$ ) with 10 mg/L molybdenum in their drinking water<sup>(10)</sup>. Molybdenum concentrations in the bones increased from 0.71 ppm in the control group to 2.5 ppm in the rats receiving the 10 mg/L in their drinking water<sup>(10)</sup>. Chappell<sup>(10)</sup> cited the work of Davis<sup>(48)</sup> which showed a similar

increase in molybdenum content in bones of rats when dietary molybdenum increased from 1 to 30 ppm.

Other results from laboratory studies of molybdenum could have serious implications with respect to human health. Increased rates of young deaths and dead litters in mice over three generations was noted for a group receiving 10 mg/L molybdenum as sodium molybdenate in water compared to a control group receiving only 1 mg/L. Both groups were fed the same food containing 0.25 ppm molybdenum<sup>(10)</sup>.

Chappell<sup>(10)</sup> also referred to the work of Suttle<sup>(49)</sup> who had found significantly slower response in sheep fed 2 ppm molybdenum and guinea pigs fed 4.5 ppm molybdenum compared to controls fed 0.5 ppm. More importantly, he found the influence on copper utilization was not linear, and that the first increment of 4 ppm molybdenum gave as great a reduction in copper utilization as a change from 25 to 100 ppm<sup>(49)</sup>. "Thus, small increments seen to have disproportionately large effects. He (Suttle) suggested that the copper-molybdenum interaction may have a greater significance for nonruminants, including man, than has previously been realized"<sup>(10)</sup>.

Experience in the Soviet Union has shown a synergistic link between tungsten and molybdenum. At levels I believe (complete translation not available) were about 0.10 mg/L tungsten and 0.5 mg/L molybdenum, disturbances arose in the reproductive system of rats; "i.e., destruction of fertilized cells before their implantation, and disturbances in the development of embryos"<sup>(15)</sup>. The existence of a synergistic interaction contradicts the observation by others<sup>(59)</sup> that molybdate and tungstate interact competitively for transport across the intestinal wall.

## 2.2 CRITERIA FROM THE LITERATURE

The U.S.S.R. is the only nation known to have proposed surface water quality limits for molybdenum for public water supplies. A 1970 publication listed a value of 0.5 mg/L molybdenum as  $\text{Mo}^{6+}$  i.e., soluble molybdenate<sup>(16)</sup>. Recent experience related to the synergistic effect of tungsten has led to a reduction of the maximum permissible concentration to 0.25 mg/L<sup>(15)</sup>.

## 2.3 RECOMMENDED CRITERIA

Criteria developed for drinking water have to take into account the effect of molybdenum on human health, the quantity of molybdenum which can be safely consumed, and the amount of molybdenum taken into the body in other food.

Molybdenum is essential to all life, and it has been recommended that humans should consume a minimum of 0.2 mg per day<sup>(17)</sup>. Findings in India and Russia were that a dietary intake of more than 10 mg per day was dangerous to human health, whereas intakes of up to 1.5 mg per day had no noticeable effects<sup>(17)</sup>. "It would thus appear that in human subjects with a normal copper intake, a dietary molybdenum intake of 0.5 to 1 mg per day could be assumed as safe"<sup>(17)</sup>.

Schroeder et al.<sup>(18)</sup> found that the molybdenum content of food in the United States ranged from 100 to 500 ng/g<sup>(18)</sup>. An adult consuming 1000 grams of food per day at the maximum molybdenum content of 500 ng/g would take in 0.5 mg/d of molybdenum. Schroeder et al.<sup>(18)</sup> projected that adults might get 0.35 mg/d molybdenum from food when on good diets. This is high compared to values for England (0.13 mg/d) and New Zealand (0.1 mg/d)<sup>(18)</sup>.

Assuming 1 mg/d of molybdenum is safe (based upon work in the U.S.S.R. and that reported by Mertz<sup>(17)</sup>) and a maximum food intake of 0.5 mg/d, then 0.5 mg could be consumed safely in an adult's water intake. If the

maximum water consumption of an average adult is 2 L/day, the maximum total molybdenum content in water with no treatment should be (0.5 mg/d+2 L/d) or 0.25 mg/L. Smaller water consumptions would provide an added degree of safety.

This coincidentally is the value used by the U.S.S.R. as a criterion for drinking water due to concerns for tungsten synergism. It is expected that food intakes of over 1000 grams per day would be made up of foodstuffs not necessarily at the maximum 500 ng/g level. The calculated intake from food exceeds even the highest projections by Schroeder et al. As well, it is highly unlikely that this same individual would consume the maximum 2 litres of water per day.

Higher molybdenum levels could be permitted in the raw water supply depending upon the success of water treatment. It has been found that as much as 98% of molybdenum was removed from solution in an industrial wastewater which contained 1 to 11 mg/L. This was accomplished by adding  $\text{FeCl}_3$  at a pH of 3.1<sup>(10)</sup>. This would be advanced water treatment (i.e. acidification, coagulation, flocculation, neutralization) as opposed to conventional treatment. The effect that the removal of molybdenum can have on concentrations is not well documented, thus no allowance has been made for treatment. Allowance could be made on a site-specific basis if information on treatment efficiency were available.

### 3. AQUATIC LIFE

Little information is available in the literature, probably due to the low concentrations of molybdenum in nature (see Section 1.0), and the relatively low toxicity of molybdenum to aquatic life.

#### 3.1 ALGAE

Several species of algae can concentrate molybdenum from water by a factor of two to fifteen<sup>(19)</sup>. The minimum requirement for molybdenum in dry tissues of green algae ranges from 0.1 to 1 ppm<sup>(18)</sup>.

"Molybdenum appears to be essential for the growth of Scenedesmus, and indeed the threshold concentration for deleterious effect upon this alga occurs at 54 mg/L"<sup>(19)</sup>.

#### 3.2 MACROPHYTES

No information on the relationship of molybdenum to macrophytes was available. However, it generally can be stated that aquatic macrophytes grow over a wide range of water quality conditions, that there are certain upper and lower limits beyond which plants won't live, but no information exists on these upper and lower limits.

#### 3.3 INVERTEBRATES

No information on the relationship of molybdenum to invertebrates was available. However, molybdenum values measured recently in invertebrates in the lower Fraser River Estuary area were less than 5  $\mu\text{g/g}$ <sup>(7)</sup>. Approximately one-half of these invertebrates had values  $<1$   $\mu\text{g/g}$  (dry-weight)<sup>(7)</sup>.

McKee and Wolf<sup>(19)</sup> reported that Daphnia tolerated molybdenum concentrations of 1000 mg/L without perceptible injury. The hardness of the water was not cited.

### 3.4 FISH AND OTHER AQUATIC LIFE

Little work has been done on molybdenum toxicity to fish. McConnell<sup>(20)</sup> cited the work of Tarswell and Henderson<sup>(50)</sup> which established a 96 h LC50 for the fathead minnow of 70 mg/L as MoO<sub>3</sub> in water with hardness of 20 mg/L as CaCO<sub>3</sub>, and 360 mg/L as MoO<sub>3</sub> in water with hardness of 400 mg/L as CaCO<sub>3</sub>. These LC50's convert to about 42 mg/L and 216 mg/L, respectively, when expressed as Mo.

McConnell<sup>(20)</sup> also cited the work of Easterday and Miller<sup>(51)</sup> who determined a 96 h LC50 of 1320 mg/L of sodium molybdate to the bluegill (Lepomis macrochirus). The water hardness was not cited. This is equivalent to a 96 h LC50 of about 615 mg/L as Mo. Another study cited by McConnell<sup>(20)</sup> discussed LC50's (time not indicated) for molybdenum as sodium molybdate from 2500 to > 10 000 mg/L for bluegill, rainbow trout, fathead minnow and catfish<sup>(20)</sup>. This range was equivalent to 1165 mg/L to >4660 mg/L when expressed as Mo.

McConnell<sup>(20)</sup> has carried out by far the most intensive studies of toxicity of molybdenum to aquatic organisms. In his work, rainbow trout were used as the test species, and McConnell tried to determine if long-term exposure to molybdenum levels similar to environmental levels was harmful.

"The long-term experiment was initiated with 330 eyed rainbow trout eggs placed in plastic trays suspended in each of six aquaria. The eggs were allowed to hatch and after the yolk sacs were assimilated, the fry were released into the aquaria. Fish were fed a standard dry ration. Amounts fed daily were adjusted by means of computerized growth rate projections, based on weight data obtained approximately every month.

Total numbers of fish in each aquaria were reduced at appropriate intervals to prevent overcrowding. Fish were randomly sacrificed, at which time hematocrits and fish length data were collected. All mortalities were removed from tanks and counted daily"<sup>(20)</sup>.

McConnell<sup>(20)</sup> reported that: "after one year of exposure no significant biological differences were noted in mortality, growth or hematocrits for fish exposed to molybdenum concentrations as high as 17 ppm". In the long-term toxicity tests, molybdenum at environmental levels did not exert a toxic effect on eyed eggs, sac-fry, or fingerling stages of development. Molybdenum concentrations of 0, 0.05, 0.3, 1, 4 and 17 ppm as Mo were used in the test. Hardness values ranged from 14 to 32 mg/L (average 25 mg/L). The pH of the water ranged from 6.9 to 7.2, temperatures ranged from 5.5 to 17.5°C, and dissolved oxygen was from 6.4 to 9.2 mg/L.

McConnell<sup>(20)</sup> also performed two static acute tests, one on rainbow trout 20 mm in length and a second on fish 55 mm long. The 96 h LC50 values were 800 mg/L and 1320 mg/L as Mo, respectively. The water temperature for the test was 12°C. It is assumed that the hardness was about 25 mg/L.

A summary of toxicity data for molybdenum is given below.

Toxicity Data for Molybdenum

Organism Tested	Concentration (mg/L) Mo	Hardness (mg/L) CaCO <sub>3</sub>	Response
Alga ( <u>Scenedesmus</u> ) <sup>19</sup>	54	-	Threshold of deleterious effects
Invertebrate ( <u>Daphnia</u> ) <sup>19</sup>	1000	-	No perceptible injury
Fish:fathead	42	20	96 h LC50
minnow <sup>50</sup>	216	400	96 h LC50
:bluegill <sup>51</sup>	615	-	96 h LC50
:bluegill, rainbow	1165 -	-	LC50's (time not indicated)
trout, fathead	>4660		
minnow, catfish <sup>20</sup>			
:rainbow trout 20 mm <sup>20</sup>	800	25	96 h LC50
:rainbow trout 50 mm <sup>20</sup>	1320	25	96 h LC50
:rainbow trout, eyed eggs, sac-fry and fingerlings to one year <sup>20</sup>	0-17	14-32	No effect on mortality, growth and hematocrits over one year

### 3.5 CRITERIA FROM THE LITERATURE

No specific official criteria to protect aquatic life have been found in the literature. The National Academy of Sciences<sup>(21)</sup>, in discussing molybdenum values in sea water, recommended a maximum value equal to 0.05 of the 96 h LC50 for the most sensitive species, and 0.02 of the 96 h LC50 for a 24-hour average value.

The Canadian Council for Resource and Environment Ministers (CCREM) recommends the use of an application factor of 0.01 if data are extremely limited, or 0.05 for materials that are nonpersistent or have noncumulative effects.

### 3.6 RECOMMENDED CRITERIA

Not a great deal of information has been gathered on the toxicity of molybdenum to aquatic life. This is likely due to the fact that a concern has never existed for the toxic effects of this metal; i.e., no problems have been apparent at levels in the environment. We do have information from one long-term study which found no effects on growing rainbow trout at various molybdenum levels. These salmonids are important throughout British Columbia. Usually the most sensitive resident fish species is a salmonid and is representative of the response of other salmonids to contaminants.

Any criterion proposed should protect the most sensitive aquatic life for which information is available, while protecting those more sensitive life forms for which information is not available. In Section 3.1, a threshold concentration of 54 mg/L for an alga was cited. No information was available on molybdenum toxicity to macrophytes. The lowest 96 h LC50 for other aquatic life was 70 mg/L for fathead minnows, expressed as MoO<sub>3</sub>, or 42 mg/L when expressed as Mo. This species is not native to British Columbia; however, due to the small data base, these data are useful.

Strict adherence to the CCREM guidelines would suggest that the application factor of 0.01 should be used. However, it is believed that the work of McConnell is extensive enough to provide justification for the use of the higher factor of 0.05. The use of the application factor of 0.02 to define an average value tempers the impact that potentially could exist if only the 0.05 factor were used.

The data for acute toxicity to the fathead minnow which is not native to British Columbia are not significantly different from the data for the alga which is found in British Columbia, especially when application factors are used. Since the data base is not large, the inclusion of these data for species not native to British Columbia is not deemed to be a problem.

Using the factors of 0.02 and 0.05 cited in Section 3.5 for application to 96 h LC50 values, and rounding-off these values using 42 mg/L Mo as the lowest 96 h LC50, the proposed criteria for total molybdenum to protect sensitive aquatic life are an average value over thirty days not to exceed 1 mg/L, and a maximum value not to exceed 2 mg/L. These criteria easily should protect most aquatic life, including salmonids.

The average value, based on the application factor of 0.02 (from the National Academy of Sciences), reflects a value for thirty days and not twenty-four hours as originally intended. This modification is believed to be acceptable since long-term tests on rainbow trout at concentrations seventeen times greater than the proposed criterion indicated no ill effects on the test species. The criteria are believed to be conservative, but should not create hardship in British Columbia. A conservative approach is reasonable since there are so few data available, particularly for invertebrates and plants. The maximum molybdenum concentration measured in British Columbia was 1.6 mg/L based on nearly 3 600 measurements from stream, lake, and marine stations in natural and contaminated areas in the period 1965 to 1976<sup>(57)</sup>.

Criteria for marine aquatic life have not been proposed. No toxicity data are available for marine species in saline water.

#### 4. WILDLIFE

There is virtually no information in the literature related to the sensitivity of wildlife to molybdenum. It is known that ruminants are more susceptible to molybdenosis than monogastric animals. Therefore molybdenosis could be a potential problem to wild ruminants such as deer, elk, moose, cariboo, sheep, and goats.

"Six mule deer were fed diets containing about 50, 200, and 1000 ppm Mo to determine their susceptibility to molybdenosis. No clinical symptoms were observed after 33 days intake of 1000 ppm. One animal died that received 500 ppm Mo for 15 days after 22 days on the 200 ppm Mo diet. Deer appear to be far more tolerant of molybdenum than sheep or cattle"<sup>(23)</sup>. The reason why deer respond to molybdenum more like non-ruminants is not clear.

Apart from this consideration, it is likely that, under favourable conditions (i.e. no drought, severe winter, etc.), wildlife would be less susceptible to molybdenosis than domesticated animals because the former are not confined to one area. Therefore wildlife potentially can acquire a more balanced diet; i.e., they can offset molybdenum-rich diets with food-stuffs which have less molybdenum. The exception to this would be forage crops grown on tailings piles and available to wildlife.

##### 4.1 CRITERIA FROM THE LITERATURE

There are no known criteria published in the literature.

##### 4.2 RECOMMENDED CRITERIA

It is suspected that as with domesticated animals, the largest amount of molybdenum would enter wildlife through their food, rather than directly through their drinking water.

Wildlife have the advantage over domesticated animals of not being confined to restricted areas for food. This roaming nature allows them to obtain a diet lower in molybdenum.

It is recommended that the criterion developed for livestock watering in Section 5.3 also apply to wildlife. It is therefore recommended that the criterion to protect wildlife from excess total molybdenum be that the maximum concentration in water should not exceed 0.05 mg/L. The criterion for livestock is applicable to wildlife so that wild ruminants can be protected, since some of these may be more sensitive than deer. There is no evidence that criteria derived for aquatic life (Section 3.6) will protect sensitive ruminants.

## 5. LIVESTOCK WATERING

Livestock can consume molybdenum in forage and in water. The primary toxic effect of molybdenum involves interference with copper metabolism, inducing a copper deficiency when inadequate sulphate is present. Molybdenum toxicity is frequently observed among animals when the Cu/Mo ratio of their diet is low.

### 5.1 EFFECTS OF EXCESS MOLYBDENUM

Molybdenum accumulates in the absence of sulphate. Sulphate can decrease gastrointestinal absorption of molybdenum and can mobilize stored molybdenum, leading to increased molybdenum excretion. Inhibition of molybdenum toxicity by sulphate might be explained by mass displacement of molybdate by sulphate<sup>(18)</sup>. Ruminants, as opposed to non-ruminants, are particularly subject to copper deficiency and a copper-molybdenum-sulphur imbalance.

Molybdenosis is a disease which has been reported in ruminants in Ireland<sup>(24)</sup>, England<sup>(25)</sup>, Nevada<sup>(26)</sup>, Colorado<sup>(27)</sup>, Oregon<sup>(28)</sup>, California<sup>(29)</sup>, and Manitoba<sup>(30)</sup>. This disease is associated with extreme molybdenum levels, and is characterized by diarrhea (scouring), discolouration of hair, loss of appetite, joint abnormalities, osteoporosis, reproductive difficulties, lack of sexual activity, testicular degeneration, and occasionally death in cattle and sheep<sup>(10)</sup>. Cattle are the most sensitive ruminant animals. Molybdenosis is in part a copper deficiency since signs and lesions of molybdenosis are almost identical to copper deficiency. As well, the condition can be successfully prevented and treated with copper supplements.

Reid and Horvath<sup>(31)</sup> reported that normal values of copper, molybdenum, and sulphate in plants were 2 to 15 ppm, 0.1 to 4 ppm, and 0.2 to 0.45%, respectively. Hansen and Chaney<sup>(32)</sup> reported that induced copper deficiency can occur if forages contain 5 to 10 µg/g molybdenum and

if the copper to molybdenum ratio is less than two. Dietary copper levels less than 10 ppm will lead to deficiency, regardless of the molybdenum level. The minimum copper to molybdenum ratio of 2:1 was first cited by Miltimore and Mason<sup>(33)</sup> in relation to plants growing in British Columbia.

## 5.2 CRITERIA FROM THE LITERATURE

Only one criterion to protect livestock existed in the literature. The Australian Water Resources Council<sup>(34)</sup> identified a level of 0.01 mg/L; however, this was simply due to a feeling that the value should be the same as in irrigation water. The Council had stated that the "possibility of molybdenum in water producing a direct hazard to the health of livestock appears remote"<sup>(34)</sup>.

## 5.3 RECOMMENDED CRITERIA

Two criteria are proposed for livestock watering based upon protection of cattle, the most sensitive ruminant; the first to be applied to areas where the forage crops consumed by cattle are not irrigated or fertilized with molybdenum-containing fertilizer; and the second to be applicable where forage irrigation and/or fertilizer is applied.

Forages containing 5  $\mu\text{g/g}$  molybdenum can cause a copper deficiency. If it is assumed that forage with normal molybdenum concentrations can contain as much as 4  $\mu\text{g/g}$ , the minimum balance which can be safely consumed in drinking water is equivalent to 1  $\mu\text{g/g}$ . Lactating cows can consume as much as 16 kg/d of dry matter<sup>(31)</sup>. Therefore, the maximum amount of molybdenum which could be taken in safely by watering would be 16 mg (16 kg/d x 1  $\mu\text{g/g}$ ).

In British Columbia, the maximum daily water consumption for a dairy cow would be about 205 litres<sup>(35)</sup>; however, the normal daily water consumption for dairy cattle would be about 75 litres<sup>(55)</sup>. Based upon

this maximum daily water consumption and the maximum amount of molybdenum which can be consumed by cattle, it is recommended that the maximum molybdenum concentration in water used for livestock should not exceed 0.08 mg/L (16 mg ÷ 205 L). This criterion applies when the forage is not irrigated or when no molybdenum-containing fertilizer is applied to the forage.

When water used for irrigation of forage crops is also consumed by livestock, or when fertilizers containing molybdenum are used on the forage crops, molybdenum in the livestock water should not exceed the criterion for irrigation water (see Section 6.4), i.e., a maximum of 0.05 mg/L.

## 6. IRRIGATION WATER SUPPLY

The principal problem related to irrigating with water which has high molybdenum concentrations is that molybdenum is absorbed and concentrated by plants. High molybdenum concentrations seldom retard plant growth, but the high concentrations in the plants can be toxic to ruminant animals that feed on the plants.

### 6.1 EFFECTS OF EXCESS MOLYBDENUM

Forage with molybdenum concentrations of 10 ppm has caused molybdenosis in ruminants, although problems also have been associated with forage containing as little as 5 ppm<sup>(52)</sup>.

### 6.2 FACTORS TO CONSIDER

Reid and Horvath<sup>(31)</sup> reported that "the supply of ions to plant roots is controlled by processes of convection, diffusion, and interception, and the root produces exudates of organic complexing anions to dissolve fixed metals for absorption". All of these processes can be influenced by the soil environment, including soil acidity, moisture content, temperature, and type of plant.

#### 6.2.1 SOIL DRAINAGE

Kubota et al.<sup>(37)</sup> found that the response of plants to molybdenum concentrations depended upon soil type. Soils tested were a poorly-drained, fine, gravelly loam, an excessively-drained, fine, gravelly, loamy sand, and a well-drained, fine, sandy loam. However, for all soils, a wet soil condition increased the molybdenum concentration in the soil and plant compared to similar soils under dry conditions.

Reid and Horvath<sup>(31)</sup> reported that the soils often associated with a copper/molybdenum problem in ruminants are peats, and other poorly drained

soils with high organic matter content. Thornton<sup>(53)</sup> found that molybdenum uptake increased with pH (5.3-7.8) and the soil's organic carbon content.

Most soils contain between 0.6 and 3.5 ppm of molybdenum. Water soluble molybdenum can be extracted by plants, but so can adsorbed molybdenum in alkaline or low copper soils<sup>(11)</sup>. A metal can be retained in roots if chelates are formed in the root-cell's sap and cannot be transported<sup>(32)</sup>. Molybdenum is weakly chelated<sup>(32)</sup>.

### 6.2.2 SOIL pH

The following is cited from Barrow<sup>(38)</sup>. Soil pH, the organic matter in soil, copper, iron, manganese, phosphorus, and sulphur can influence the assimilation of molybdenum by plants. Adsorption of molybdenum to soil particles is pronounced at lower pH values. Molybdenum fixation in soils is increased with acidity to pH 2.2 due to the formation of insoluble molybdates of iron and aluminum. The maximum release of retained molybdenum from soil occurred in the pH range 5.0 to 8.5.

W.R. Chappell<sup>(10)</sup> illustrated the effect of soil pH on the concentration of molybdenum in a plant in the following table.

Soil pH	Molybdenum Content (ppm)	
	Soil	Plant
5.5 - 5.7	24	<1
5.9 - 7.9	<24	60

Barshad<sup>(39)</sup> reported that in slightly alkaline, neutral or acid soils the greater the amount of water soluble molybdenum in the soil, the

greater the molybdenum content of the plant. He also reported a decrease in plant molybdenum content at soil pH above 8 or below 7 (i.e., the highest plant molybdenum content was in the range from pH 7-8)<sup>(34)</sup>.

The relationship of high molybdenum in plants to soil wetness was closer than the relation to soil pH<sup>(40)</sup>. The reason for this is that in poorly-drained soils it is not possible to lose dissolved molybdenum to deep percolating waters. This permits soluble molybdenum to remain in the root zone until it is removed by cropping. Allaway<sup>(40)</sup> cited Jackson et al.<sup>(54)</sup>: "...that on well-drained soils, even alkaline soils, irrigation waters of relatively high molybdenum concentration can be used without hazard of producing high molybdenum forages, even though these same waters might pose a hazard on poorly-drained soils". And from the National Academy of Sciences: "For any given molybdenum content, organic soils and those with impeded drainage are the most toxic"<sup>(42)</sup>. This confirms information reported by Kubota et al.<sup>(28)</sup>, who found that although the molybdenum content of both well-drained and poorly-drained soils was the same and both were alkaline, the plants grown on poorly-drained soils had higher molybdenum concentrations.

### 6.2.3 MOLYBDENUM IN SOILS AND PLANTS

Molybdenum accumulates in the absence of sulphate. Its uptake by plants can be reduced by increasing sulphate levels in the soil<sup>(36)</sup>.

Molybdenum in soil is particularly immobile in an oxidizing iron-rich environment<sup>(42)</sup>. The movement or retention of molybdenum and consequent levels in soils are influenced by the amount of clay present (which can influence the exchange capacity)<sup>(42)</sup>.

Chappell<sup>(10)</sup> reported that soil applications of molybdenum increased plant concentrations as follows:

Soil Type/Description	Type of Plant	Application Rate of Molybdenum (kg/ha)	Increase in Molybdenum in Plant ppm (dry-weight basis assumed)
Neutral Sandy Loam	Alfalfa	1	5.2*
Neutral Sandy Loam	Tall Fescue	1	3.5*
Peat Soil	White Clover	0.22	10.5
Unknown	Alfalfa	1.79	1.7
Unknown	Alfalfa	7.17	11.7
Clay Loam	Lotus corniculatus	20	148
Calcareous (pH > 6.5)	Alfalfa	1	2.9
Sandy Loam (pH 5.6-6.1)	Carpet Grass	2.2	>10 (after 5 yrs)
Acid Peaty Soil	-	0.84	98 (after 1 yr) declined to 11 (after 3 years)

\*Correlation coefficient of 0.952 for alfalfa and 0.959 for tall fescue.

The concentrations of molybdenum in the alfalfa and tall fescue confirmed the findings of other authors who found that the molybdenum content of herbage varied with species on the same soil. Generally, legumes absorb considerably more molybdenum than do non-legumes<sup>(29,41)</sup>. Animals will select a diet high in legumes when grazing under pasture conditions<sup>(41)</sup>.

Applications of sewage sludge with 5 ppm molybdenum to an alkaline soil on which white clover and rye grass were planted caused no appreciable change in plant molybdate; however, the application of 103 ppm molybdenum to the same type soil with white clover and rye grass caused excessive molybdenum uptake by white clover<sup>(32)</sup>.

Kubota et al. reported that legumes with molybdenum concentrations which were toxic were grown on wet soils with  $\geq 1$  ppm molybdenum<sup>(28)</sup>. Most legumes with molybdenum concentrations  $\geq 10$  ppm in Oregon were from wet

soils on flood plains<sup>(28)</sup>. Interestingly, well-drained soils had as much molybdenum as poorly-drained soils; however, molybdenum concentrations in legumes from the former were lower than those from the latter<sup>(28)</sup>. Kubota *et al.* found that molybdenum concentrations in plants grown on well-drained soils were not high, regardless of soil pH or soil parent material<sup>(28)</sup>.

If forage crop production on high molybdenum areas is required, harvesting and drying of the forage for feeding as hay will reduce the hazard of molybdenum toxicity below that occurring when the forages are grazed as green plants<sup>(40)</sup>. The mechanism that allows this to happen is not fully understood. However, it appears that it has to do with a change in the chemical form of the molybdenum<sup>(58)</sup>.

#### 6.2.4 COPPER TO MOLYBDENUM RATIOS

The copper to molybdenum ratio in plants is an important factor in determining if problems will occur in ruminants. Miltimore and Mason<sup>(33)</sup> analyzed ruminant feeds from throughout British Columbia. These authors deemed a copper to molybdenum ratio of 2:1 to be critical since scouring did not occur with a ratio of 4.3:1 while some scouring occurred with a 2.3:1 ratio and severe scouring took place at a 1.0:1 ratio<sup>(33)</sup>. It was assumed in this analysis that sulphate concentrations were distributed at random even though these concentrations are critical. Miltimore and Mason<sup>(33)</sup> found "a trend for relatively high Mo concentrations to be associated with the lowest Cu concentrations, resulting in unfavorable Cu/Mo ratios". Miltimore *et al.*<sup>(44)</sup> had found about 95% of all feeds had <10 ppm copper, the recommended minimum for cattle. Thus copper supplements will be necessary if molybdenum is present in significant amounts.

#### 6.3 CRITERIA FROM THE LITERATURE

"The Federal Water Pollution Control Administration (1968) has suggested an irrigation water standard of 5 ppb of Mo for continuous use on soils

and 50 ppb for short-term use. This standard is based on a greenhouse investigation by Kubota *et al.* (1963) in which 5 ppb of Mo in the soil solution was associated with alsike clover (*Trifolium hybridum* L.) containing 10 ppm of Mo. This standard is open to question because a soil solution concentration is related to the labile pool of Mo in the soil and not directly to a level of 5 ppb in irrigation water. However, the labile pool may be influenced by the level of Mo in applied irrigation water"<sup>(27)</sup>.

An updated set of criteria<sup>(21)</sup> proposed 0.01 mg/L for continued use of water on all soils and 0.05 mg/L for short term use on soils that "react with this element"<sup>(21)</sup>. This was also based on the work of Kubota *et al.*<sup>(37)</sup> who found that "molybdenum concentrations of 0.01 mg/L or greater in soil solutions were associated with animal toxicity levels of this element in alsike clover"<sup>(21)</sup>.

No other criteria based upon independent analysis are known to exist.

#### 6.4 RECOMMENDED CRITERIA

Poorly-drained soils allow most applied molybdenum to remain within the root zone. Therefore all the applied molybdenum potentially is available. It therefore is desirable to have two sets of criteria as a minimum, one for well-drained soils and one for poorly-drained soils.

Copper is the most important element related to the effects of molybdenum. It has been suggested that for plants in British Columbia, a copper to molybdenum ratio of 2:1 is critical<sup>(33)</sup>. Therefore copper to molybdenum ratios higher than 2:1 are desirable. It seems reasonable that to achieve this ratio in plants, it should also be present in the soil and irrigation water.

Sulphate is also an extremely important element in relation to molybdenum uptake. Sulphate to molybdenum ratios have not been suggested in the literature. Further research is required to determine the critical sulphate to molybdenum ratio.

Most important, however, is whether the land to which irrigation water is being applied will be used to produce feed for ruminant animals. Irrigation waters high in molybdenum can be used more safely on land used for crops other than forage production. It also is likely that rural areas used for other crops will not revert to forage production, since forage crops are usually grown on more marginal lands in foodstuff producing areas.

Therefore drainage, copper present, and types of crops are most important in assessing criteria for irrigation. It is proposed that the following maximum and average total molybdenum concentrations should be applicable for the stated situations:

Mo Concentration		Application
0.01 mg/L	average*—	poorly-drained soils used for forage crops with Cu/Mo ratio <2:1 in irrigation water
0.05 mg/L	maximum*—	
0.02 mg/L	average*—	well-drained soils used for forage crops, or, poorly-drained soils used for forage crops with Cu/Mo ratio $\geq$ 2:1 in irrigation water
0.05 mg/L	maximum*—	
0.03 mg/L	average*	irrigation of non-forage crops

\* Maximum and average values apply during the irrigation season, with average values being calculated from samples collected at a minimum of once per week for five weeks in a period no longer than thirty days.

#### RATIONALE

These values have been chosen for the following reasons:

### Poorly-Drained Fields with Forage Crops

This is virtually the exact situation for which criteria have been proposed by the National Academy of Sciences<sup>(21)</sup>. Poorly-drained fields will allow applied molybdenum to be available at virtually any time. As more molybdenum is applied, molybdenum in the soil mantle will tend to increase unless taken up by plants. If the plants are forage crops, they will concentrate the applied molybdenum to levels which are toxic to ruminants. This classification will also cover areas where the Cu:Mo is <2:1.

Since no data are available to refute the criteria of 0.01 mg/L (continued use) or 0.05 mg/L (short-term use), these criteria should be adopted for poorly-drained fields used to grow forage crops. These values will be adopted as average and maximum values, respectively.

### Well-Drained Fields or Poorly-Drained Fields with High Copper to Molybdenum Ratios in Irrigation Water with Forage Crops

A second level has been added to cover situations where the potential for a build-up of molybdenum is less.

The discussion has already pointed out that in well-drained soils with molybdenum concentrations identical to poorly-drained soils, plants will contain relatively safe levels of molybdenum. Kubota et al.<sup>(37)</sup> reported molybdenum concentrations in clover increased from a maximum of 12 ppm to 20 ppm (1.7 times) under greenhouse conditions going from a well-drained soil to a poorly-drained soil (average increase was 6 ppm to 20 ppm or 3.3 times). Alsike clover grown in a hay-pasture field had increased molybdenum concentrations from 9 to 135 ppm (15 times)<sup>(37)</sup>. It seems likely that average molybdenum values can be doubled over those proposed for a situation with poorly-drained soils. The lack of data, and the desire to take a conservative approach to establishing criteria, would suggest that the maximum permitted molybdenum concentration in irrigation water should not be increased over that applicable to poorly-drained fields.

The importance of an adequate Cu:Mo ratio has been documented. Ratios for Cu:Mo have been proposed in the literature. The minimum Cu:Mo ratio of 2:1 in plants found under British Columbia conditions is suggested as a cutoff for irrigation waters.

#### Irrigation of Non-Forage Crops

Higher molybdenum concentrations in irrigation waters used in urban areas or for non-forage crops likely are acceptable since ruminants will not consume the crops. To be properly developed, the criteria should examine existing levels of molybdenum in vegetables from non-contaminated areas, the quantity consumed on a maximum daily basis, and the maximum molybdenum anticipated which can be passed along from irrigation waters to the crop. Such data are not available at present. Therefore a conservative approach has been taken to this question.

Since non-forage crops are consumed by humans, not ruminants, some higher albeit relatively arbitrarily chosen criteria are proposed. The average value is three times the criterion put forth to protect ruminants from crops grown on poorly-drained soils. These values have been determined based upon the following rationale.

A concentration of about 10 ppm in plants is an approximate value above which molybdenosis can occur in ruminants. Potential effects of excess molybdenum on humans has been documented in Section 2.1. Therefore it is conceivable, but very unlikely, that humans can be at risk from excessive molybdenum in their diets. Vegetables can accumulate molybdenum.

The concentration in plants which would be a concern to humans is not known; however, a conservative estimate would be about 5 ppm. In the area of the Soviet Union where molybdenum has been implicated in gout-like diseases (Section 2.1), the highest molybdenum concentrations were found in beans (82 ppm), mint (57 ppm), chavak (18 ppm), eggplant (13 ppm) and potatoes (11 ppm)<sup>(11)</sup>. The most significant increases between regions

with normal molybdenum concentrations and those enriched in molybdenum occurred for cabbage (130 times higher, to 5.2 ppm), sedge (127 times higher, to 9.3 ppm), mint (52 times higher, to 57 ppm) and tarragon (36 times higher, to 8.3 ppm)<sup>(11)</sup>. No problems were encountered in the region with normal molybdenum when beans had 5.1 ppm molybdenum and several other vegetables had between 1 and 5 ppm. Therefore, based upon this latter fact, upon the high concentrations in areas with problems, and upon those vegetables which had the highest increases in concentrations between regions, a value of 5 ppm in vegetables probably is safe for human consumption.

The criteria were determined using the following procedure. Actual details are in the Appendix. The yield per hectare of ten vegetables grown in British Columbia was calculated for 1981 from available statistics. This figure was then adjusted by the ratio of 1980-1984 production to 1981 production, since crops in 1981 were poor due to weather conditions and some fields were not planted. Assuming that the safe molybdenum value in vegetables of 5 ppm came solely from irrigation water, the yield (kg/ha) was multiplied by the safe molybdenum level in vegetables (5 ppm or 0.005 mg/g) and then divided by the required irrigation flow for each crop on different soils. This resulted in molybdenum concentrations in irrigation water ranging from 0.006 mg/L for peas to 0.064 mg/L for onions, or an average for the ten crops of 0.035 mg/L. The criterion for an average molybdenum value therefore was established at 0.03 mg/L.

In the application of these criteria, it may be desirable to measure molybdenum concentrations in peas or broccoli where such crops are irrigated with water at or near these criteria, since these two crops could be the most susceptible to concentrating molybdenum.

## 7. INDUSTRIAL WATER SUPPLY

Water is used by several industries for a variety of processes. Industries of particular relevance to British Columbia are those which use steam generation and cooling. Industries in British Columbia which require high quality water are those producing paper and allied products, mining and cement industries, primary metals industries, food canning, chemical products, petroleum refining and lumber and wood products.

Molybdenum normally is not considered as an element of concern in any of these industries<sup>(21)</sup>. All these industries would have the capability to treat the raw water supply if it had too much molybdenum for their particular requirements.

### 7.1 EFFECT OF EXCESS MOLYBDENUM

There are no known effects of excess molybdenum on industrial processes. However, in the production of chemicals, a general "rule of thumb" is that the characteristic in question should fall in the range of drinking water standards.

### 7.2 CRITERIA FROM THE LITERATURE

There are no water quality criteria known to exist for industrial water supplies.

### 7.3 RECOMMENDED CRITERIA

A criterion for molybdenum in industrial water supplies is not recommended, since there is no evidence as to what industries need.

## 8. RESEARCH AND DEVELOPMENT NEEDS

In preparing this document, we found that research data were usually lacking except in the area of agricultural production. The reasons for this are that there have been no problems with molybdenum in water for aquatic life, wildlife, humans, or industrial processes. Therefore research on these topics would be secondary to research on agricultural production. For all these non-agricultural topics, the applicability of the proposed criteria should be verified in field studies.

Other research needs are:

1. Irrigation - determine whether total and dissolved molybdenum are available equally to forage crops.
  - determine a minimum  $\text{SO}_4$ :Mo ratio, to correspond to the Cu:Mo ratio.
  - refine the definition of "poorly-drained" fields, i.e., are soils predominantly silt and clay of equal concern to peat-type soils?
2. Aquatic Life - determine the effects of molybdenum on algal species typical to British Columbia.
  - determine the effects of molybdenum on aquatic macrophytes and invertebrates other than daphnia.
  - determine effects on aquatic life in salt water.
3. Wildlife - determine the effects of molybdenum on wildlife, other than deer.

## REFERENCES CITED

- (1) Kuklis, A. Molybdenum. In Mineral Facts and Problems. Bureau of Mines, U.S. Dept. Int. Bulletin 667. pp 669-714. 1975.
- (2) Jarrell, W.M., A.L. Page, and A.A. Elsewi. Molybdenum in the Environment. Residue Reviews: Residues of Pesticides and Other Contaminants in the Total Environment. 74:1-43. 1980.
- (3) Swain, L.G. and G.B. Holms. Fraser Delta Area, Fraser River Sub-Basin from Hope to Kanaka Creek, Water Quality Assessment and Objectives. B.C. Ministry of Environment. Victoria, B.C. November 1985.
- (4) Swain, L.G. Okanagan Area, Similkameen River Sub-basin, Water Quality Assessment and Objectives. B.C. Ministry of Environment. Victoria, B.C. November 1985.
- (5) Swain, L.G. and R. Girard. Takla-Nechako Area, Nechako River Sub-basin. Water Quality Assessment and Objectives. B.C. Ministry of Environment. Victoria, B.C. July 1985 (draft report).
- (6) Personal Communication. Mr. C. McKean, Water Management Branch to Mr. L.G. Swain. May 29, 1985.
- (7) Swain, L.G. A 1985 Survey of Metals, PCB's and Chlorophenols in the Sediments, Benthic Organisms and Fish of the Lower Fraser River. B.C. Ministry of Environment. Victoria, B.C. (June 1986).
- (8) British Columbia Ministry of Energy, Mines and Petroleum Resources. Victoria, B.C. National Geochemical Reconnaissance 1:250 000 Map Series. 1981-1982.
- (9) Singleton, H.J. Trace Metals and Selected Organic Contaminants in Fraser River Fish. MOE Technical Paper 2. B.C. Ministry of Environment. Victoria, B.C. April 1983.
- (10) Chappell, W.R. Transport and Biological Effects of Molybdenum in the Environment. In Heavy Metals in the Aquatic Environment. Proceedings of the International Conference held in Nashville, Tennessee. December 1973.
- (11) Koval'skiy, V.V., G.A. Yarovaya and D.M. Shmavonyan. Changes of Purine Metabolism in Man and Animals Under Conditions of Molybdenum Biochemical Provinces. Zhurnal obshchey biologii. 22(3). 1961.
- (12) Underwood, E.J. Molybdenum in Animal Nutrition. In: Molybdenum in the Environment, Volume 1, The Biology of Molybdenum. (W.R. Chappell and K.K. Peterson, Editors). Marcel Dekker Inc., Publishers. 1976.
- (13) Agarwal, A.K. Crippling Cost of India's Big Dam. New Scientist. 65(934):260. 1975.

- (14) Krishnamachaeri, K.A.V.R. and K. Krishnaswamy. An Epidemiological Study of the Syndrome of Genu Valgum Among Residents of Endemic Areas for Fluorosis in Andhra Pradesh. Indian Journal of Medical Research. 62:1415. 1974.
- (15) Nadeenko, V.G., V.G. Lenchenko, A.N. Oshchepkova and N.A. Polykovskaya. Novye dannye k normirovaniyu vol'frama i molibdena pri razdel' nom i odnovremennom prisutstvii v vodoemakh. Gigiena I Saniteriya. Number 3. 1977.
- (16) Union of Soviet Socialist Republics. Maximum Permissible Concentrations (MPC) of Toxic Substances in Water for Sanitary Household Use. 1970.
- (17) Mertz, W. Defining Trace Element Deficiencies and Toxicities in Man. In Molybdenum in the Environment, Volume 1, The Biology of Molybdenum. (W.R. Chappell and K.K. Peterson, Editors). Marcel Dekker Inc., Publishers. 1976.
- (18) Schroeder, H.A., J.J. Balassa and I.H. Tipton. Essential Trace Metals in Man: Molybdenum. J. Chron. Dis. 23:481-499. 1970.
- (19) McKee, J.E. and H.W. Wolf. Water Quality Criteria. California State Water Resources Control Board. Publ. 3-A. 24, 220-221. 1963.
- (20) McConnell, R.P. Toxicity of Molybdenum to Rainbow Trout Under Laboratory Conditions. In: Molybdenum in the Environment, Volume 2, The Geochemistry, Cycling and Industrial Uses of Molybdenum. (W.R. Chappell and K.K. Petersen, Editors). Marcel Dekker Inc., Publishers. 1976.
- (21) Environmental Studies Board, National Academy of Sciences. Washington, D.C. Water Quality Criteria, 1972. 1972.
- (22) Personal Communication. Dr. P. Warrington, Water Management Branch to Mr. L.G. Swain. June 5, 1985.
- (23) Ward, G.M. and J.G. Nagy. Molybdenum and Copper in Colorado Forages, Molybdenum Toxicity in Deer, and Copper Supplementation in Cattle. In: Molybdenum in the Environment, Volume 2, The Geochemistry, Cycling, and Industrial Uses of Molybdenum. (W.R. Chappell and K.K. Petersen, Editors). Marcel Dekker Inc., Publishers. 1976.
- (24) Webb, J.S. and W.J. Atkinson. Regional Geochemical Reconnaissance Applied to Some Agricultural Problems in County Limerick, Eire. Nature 208: 1056-1059. 1965.
- (25) Ferguson, W.S., A.H. Lewis and S.J. Watson. The Teart Pastures of Somerset: (1) The Cause and Cure of Teartness. Journal of Agriculture Science. 33: 44-51. 1943.

- (26) Kubota, J., V.A. Lazar, L.N. Langan, and K.C. Beeson. The Relationship of Soils to Molybdenum on Toxicity in Cattle in Nevada. Soil Science Society of America Proceedings. 25:227-232. 1961.
- (27) Jackson, D.R., W.L. Lindsay and R.D. Heil. The Impact of Molybdenum-Enriched Irrigation Water on Agricultural Soils Near Brighton, Colorado. Journal of Environmental Quality. 4(2):223-229. 1975.
- (28) Kubota, J., V.A. Lazar, G.H. Simonson, and W.W. Hill. The Relationship of Soils to Molybdenum Toxicity in Grazing Animals in Oregon. Soil Science Society of America Proceedings. 31(5):667-671. 1967.
- (29) Barshad, I. Molybdenum Content of Pasture Plants in Relation to Toxicity to Cattle. Soil Science. 66:187-195. 1948.
- (30) Cunningham, H.M., J.M. Brown and A.E. Edie. Molybdenum Poisoning of Cattle in the Swan River Valley of Manitoba. Canadian Journal of Agriculture Science. 33:254-260. 1953.
- (31) Reid, R.L. and D.J. Horvath. Soil Chemistry and Mineral Problems in Farm Livestock: A Small Review. Animal Feed Science and Technology. 5:95-167. 1980.
- (32) Hansen, L.G. and R.L. Chaney. Environmental and Food Chain Effects of the Agricultural Use of Sewage Sludge. In Reviews in Environmental Toxicology I. (Ernest Hodgson, Editor). Elsevier Publishers. 1984.
- (33) Miltimore, J.E. and J.L. Mason. Copper to Molybdenum Ratio and Molybdenum and Copper Concentrations in Ruminant Feeds. Canadian Journal of Animal Science. 51:193-200. 1971.
- (34) Australian Water Resources Council. A Compilation of Australian Water Quality Criteria. Technical Paper No. 7. 1974.
- (35) Personal Communication. Mr. P. Johnson, B.C. Ministry of Agriculture and Food, Abbotsford, to Mr. L.G. Swain. June 6, 1985.
- (36) Olsen, S.R. and F.S. Watanabe. Interaction of Added Gypsum in Alkaline Soils with Uptake of Iron, Molybdenum, Manganese and Zinc by Sorghum. Soil Science Society of America Journal. 43:125-130. 1979.
- (37) Kubota, J., E.R. Lemon and W.H. Allaway. The Effect of Soil Moisture Content Upon the Uptake of Mo, Cu, and Co by Alsike Clover. Soil Science Society of America Proceedings. 27:679-683. 1963.
- (38) Barrow, N.J. Factors Affecting the Molybdenum Status of Soils. In: Molybdenum in the Environment, Volume 2, The Geochemistry, Cycling, and Industrial Uses of Molybdenum. (W.R. Chappell and K.K. Petersen, Editors). Marcel Dekker Inc., Publishers. 1977.

- (39) Barshad, I. Factors Affecting the Molybdenum Content of Pasture Plants. I. Nature of Soil Molybdenum, Growth of Plants and Soil pH. Soil Science. 71:297-313. 1951.
- (40) Allaway, W.H. Perspectives on Molybdenum in Soils and Plants. In Molybdenum in the Environment, Volume 2, The Geochemistry, Cycling and Industrial Uses of Molybdenum. (W.R. Chappell and K.K. Petersen, Editors). Marcel Dekker Inc., Publishers. 1977.
- (41) Lesperance, A.L. and V.R. Bohman. Effect of Inorganic Molybdenum and Type of Roughage on the Bovine. Journal of Animal Science. 22(3): 686-693. 1963.
- (42) National Academy of Sciences. Copper and Molybdenum. In Geochemistry and the Environment, Volume 1, The Relation of Selected Trace Elements to Health and Disease. 1974.
- (43) Jensen, E.J. and A.L. Lesperance. Molybdenum Accumulation by Forage Plants. Agronomy Journal. 63(2): 201-204. 1971.
- (44) Miltimore, J.E., J.L. Mason, and D.L. Ashby. Copper, Zinc, Manganese and Iron Variation in Five Feeds For Ruminants. Canadian Journal of Animal Science. 50:293-300. 1970.
- (45) Gunn, A.G. Minerals in British Columbia. British Columbia Ministry of Mines and Petroleum Resources. Victoria, B.C. (undated).
- (46) Oster, K.A. American Journal of Clinical Research 2, pp30-35. 1971. Cited in Underwood, Reference 12.
- (47) Oster, K.A. Medical Counterpoint. 5 p.26. 1973. Cited in Underwood, Reference 12.
- (48) Davis, G.K. The Influence of Copper on the Metabolism of Phosphorus and Molybdenum. In Symposium on Copper Metabolism. pp. 216-229. (McElroy, W.D. and Glass, B., eds.), Johns Hopkins Press, Baltimore. 1950.
- (49) Suttle, N.F. The Nutritional Significance of the Cu:Mo Interrelationship to Ruminants and Non-Ruminants. In Trace Substances in Environmental Health VII. University of Missouri. D.D. Hemphill, Editor.
- (50) Tarswell, C.M. and C. Henderson. Transactions of Seminar on Sanitary Engineering Aspects of the Atomic Energy Industry. Sanitary Engineering Center, TID-8517. 1956. Cited in McConnell, Reference 20.
- (51) Easterday, R.L. and R.F. Miller. Proceedings of the Virginia Journal of Science. pp.199-200. 1963. Cited in McConnell, Reference 20.

- (52) Vlek, P.L.G. and W.L. Lindsay. Molybdenum Contamination in Colorado Pasture Soils. In Molybdenum in the Environment, Volume 2, The Geochemistry, Cycling and Industrial Uses of Molybdenum. (W.R. Chappell and K.K. Petersen, Editors). Marcel Dekker Inc., Publishers. 1977.
- (53) Thornton, I. Biogeochemical Studies on Molybdenum in the United Kingdom. In Molybdenum in the Environment, Volume 1, The Geochemistry Cycling and Industrial Uses of Molybdenum. (W.E. Chappell and K.K. Petersen, Editors). Marcel Dekker Inc., Publishers. 1977.
- (54) Jackson, D.R., W.L. Lindsay and R.D. Heil. In Transport and Biological Effects of Molybdenum in the Environment, Progress Report to NSF (W.R. Chappell, ed.). The Molybdenum Project, University of Colorado, Boulder. 1974.
- (55) Federal Water Pollution Control Administration. Water Quality Criteria. Report of the National Technical Advisory Committee to the Secretary of the Interior. April 1, 1968.
- (56) Personal Communication. Dr. W.T. Buckley, Research Branch, Agriculture Canada, Agassiz, B.C. to Mr. L.G. Swain. Letter Dated December 4, 1985.
- (57) Clark, M.J.R. A Statistical Overview of Water Quality Analyses for British Columbia: 1965-1976. B.C. Ministry of Environment, Pollution Control Branch. Victoria, B.C. Report No. 78-4. May 1978.
- (58) Personal Communication. Dr. W.T. Buckley, Research Branch, Agriculture Canada, Agassiz, B.C. to Mr. L.G. Swain. March 19, 1986.
- (59) Cardin, C.J. and J. Mason. Molybdate and Tungstate Transfer by Rat Ileum: Competitive Inhibition by Sulphate. Biochimica et Biophysica Acta. 455: 937-946. 1976.
- (60) Futer, P. and M. Nassichuk. Metals in Eulachons from the Nass River and Crabs From Alice Arm, B.C. Canadian Manuscript Report of Fisheries and Aquatic Sciences No. 1699. Vancouver, B.C. March 1983.
- (61) Farrell, M.A. and M.D. Nassichuk. Trace Metal Levels in Bivalves and Crabs From Alice Arm, Hastings Arm and Observatory Inlet, B.C. Canadian Data Report of Fisheries and Aquatic Sciences No. 467. Vancouver, B.C. June 1984.

APPENDIX  
Calculation of Irrigation Criteria for Non-Forage Crops

1. Initial Production Data

Vegetable	1981 <sup>1</sup> Production 1000 kg	1981 <sup>2</sup> Acreage (ha)	1981 <sup>3</sup> Yield (kg/ha)	Adjusted <sup>4</sup> Yield kg/ha
Broccoli	3 758	765	4 913	4 618
Cabbage	5 491	350	15 704	20 368
Carrots	4 646	273	17 008	20 341
Cauliflower	3 104	564	5 502	7 692
Cucumbers	2 761	133	20 800	20 800
Lettuce	5 495	298	18 449	22 877
Onions	4 644	238	19 550	26 099
Peas	5 522	1 609	3 432	5 127
Potatoes	50 264	unknown	19 054	22 560
Sweet Corn	12 080	1 571	7 689	12 156

- (1) Source: Ministry of Agriculture and Food. Agriculture Statistics Profile 1984. Victoria. November 1985.
- (2) Source: Ministry of Agriculture and Food. Agriculture Statistics Yearbook, British Columbia, 1981. Victoria. 1982. (Figures converted by author from acres to hectares).
- (3) Production divided by acreage, except for potatoes, which is from source (2) above.
- (4) "Vegetable crops suffered in 1981 when 526 mm of rain fell on the Lower Mainland between March 8 and July 31, the area where over 75% of B.C.'s vegetables are produced. A lot of crops went in much later than normal or they did not go in at all which was the case in large low-lying areas. Acreage was down, crops matured late and unevenly" (Reference 2). To compensate for this atypical year, the author used average production figures for each vegetable (from Reference 1) for the period 1980-1984, and adjusted the 1981 yield by the ratio of average production rate (1980-1984) to 1981 production rate. This resulted in an increased yield for all crops except broccoli.

2. Irrigation water requirements

The amount of irrigation water required is crop and site specific. More irrigation water is required for sandy soils, as opposed to loams or organic soils. As well, the root zone for each crop will determine irrigation water requirements, since plants with shallow root zones require more water than those with deeper root zones. The location within British Columbia is another factor. Since the majority of vegetables are grown in the Lower Mainland, this consideration was ignored in preparing the criteria. In

areas of British Columbia requiring more irrigation water, such as the Okanagan Valley, measurement should be made of molybdenum in vegetables irrigated with molybdenum enriched waters. Site specific water quality objectives may have to be more stringent in such cases than the criteria developed herein.

Vegetable	Adjusted Yield kg/ha	Average Concentration <sup>1</sup> (mg/L) in Irrigation Water if Grown on	
		Muck Soil <sup>2</sup>	Loam <sup>3</sup>
Broccoli*	4 618	0.011	-
Cabbage*	20 368	0.050	-
Carrots*	20 341	0.050	-
Cauliflower*	7 692	0.019	-
Cucumbers*	20 800	0.051	-
Lettuce*	22 877	0.056	-
Onions*	26 099	0.064	-
Peas	5 127	-	0.006
Potatoes	22 560	-	0.026
Sweet Corn	12 156	-	0.021
Average: 0.035 mg/L			

\* Generally grown on muck-type soils near the Serpentine-Nicomekl River in the Lower Mainland (Source: Dr. J. Wiens. Waste Management Branch)

(1) Sample Calculation:

$$\begin{aligned}
 \text{Molybdenum concentration} &= \frac{\text{Safe Plant Content} \times \text{Adjusted Yield}}{\text{Irrigation water}} \\
 &= \frac{(0.005 \text{ mg/g}) \times (4618 \text{ kg/ha})}{0.203 \text{ m/ha} \times (1 \text{ ha}) \times 10\,000 \text{ m}^2/\text{ha}} \\
 &= 0.011 \text{ mg/L}
 \end{aligned}$$

(2) Irrigated with average of 0.203 m per ha per year.

(3) Irrigation with: 0.533 m per ha per year for peas and potatoes  
: 0.305 m per ha per year for sweet corn