Proceedings of the 11th Annual British Columbia Mine Reclamation Symposium in Campbell River, BC, 1987.
The Technical and Research Committee on Reclamation

HEAVY METAL LEVELS IN GRASSES AND LEGUMES GROWN ON HIGHLAND VALLEY COPPER MINE TAILINGS AND THE EFFECT OF ARTIFICIAL WEATHERING ON TAILINGS GROWTH PRODUCTION CAPABILITY

by

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ABSTRACT

Samples of agronomic grasses and legumes grown on copper mine tailings under two surficial amendment regimes and two fertilizer treatments were analyzed for Ca, Cu, Fe, K, Mg, Mn, Mo, N, Ni, P, and Zn. These values were compared to National Research Council and Agriculture Canada diet recommendations for beef cattle. Foliar Ca, Fe, Mn, Ni and P concentrations were satisfactory. Copper and molybdenum concentrations were well above normal levels. Copper concentrations in the legumes and grasses averaged 63 and 44 mg/kg, respectively. Mean molybdenum concentrations were found to be 52 mg/kg in the grasses and 237 mg/kg in the legumes. Cu:Mo ratios in all species violated recommended dietary guidelines for beef cattle. Fluctuations in Cu:Mo ratios were attributable mainly to variations in foliar Cu. Most species were subjected to severe grazing by rodents, producing abnormal growth habits. As a result, assessment of relative species success was difficult. Grazing stress may also have affected foliar elemental levels.

Tailings material was artificially weathered by leaching with 0.3 N acetic acid for seven weeks in a Soxhlet extraction chamber. Leached and unleached samples were analyzed for pH, 0.1 N HCl available Cu, Fe, Mn, Ni, and Zn, acid ammonium oxalate extractable Mo, total elemental levels and mineralogical composition. As a result of leaching, the pH of the tailings was reduced from 6.6 to 3.5. Declines in available Cu, Fe, Mn, Zn, and Mo were noted after leaching. No qualitative changes in tailings mineralogy were detected after artificial weathering. During leaching, three general elemental release patterns were observed. These were attributed to the sequential dissolution of readily soluble salts and carbonates, followed by the degradation of micas, pyroxenes, amphiboles and host ore minerals. The relatively inert minerals, such as quartz, some aluminosilicates and oxyhydroxides of Fe and Al represented the third group. At present, the tailings are unsuitable as a forage production area for beef cattle as a result of toxic Cu:Mo ratios in the foliage. Based on chemical changes induced by artificial weathering, it *is* probable that forage grown on the tailings will become less toxic over time. Various management practices may be employed to accelerate improvement in growth medium parameters.

INTRODUCTION

This paper presents a cursory review of the author's masters degree thesis. For comprehensive coverage of the subject, the reader is referred to the thesis document of the same title. Thesis work was conducted in the Department of Soil Science at the University of British Columbia under the direction of Dr. L. M. Lavkulich. Funding for this project was provided by Cominco Copper Division and a post-graduate scholarship from the Natural Sciences and Engineering Research Council of Canada.

Background Information and Rationale

The study was carried out at the Cominco Valley Copper mine, now Highland Valley Copper (Figure 1), and was designed to explore the potential of rehabilitating the Main Tailing Pond for the purpose of producing forage for beef cattle. This end-use was considered for two reasons; (1) the mine is located in an area used primarily as beef cattle range, and (2) the tailings present a large, level surface which could be easily manipulated by cultivating machinery.

The realization of this reclamation goal would require prior knowledge of plant growth restrictions and forage quality, both at present and in the future. Research was designed to address these issues. Specifically, the objectives were to;

(1) identify forage species suitable for reclamation of the Main Tailings pond, with respect to growth adaptations and the nutritional requirements of beef cattle.

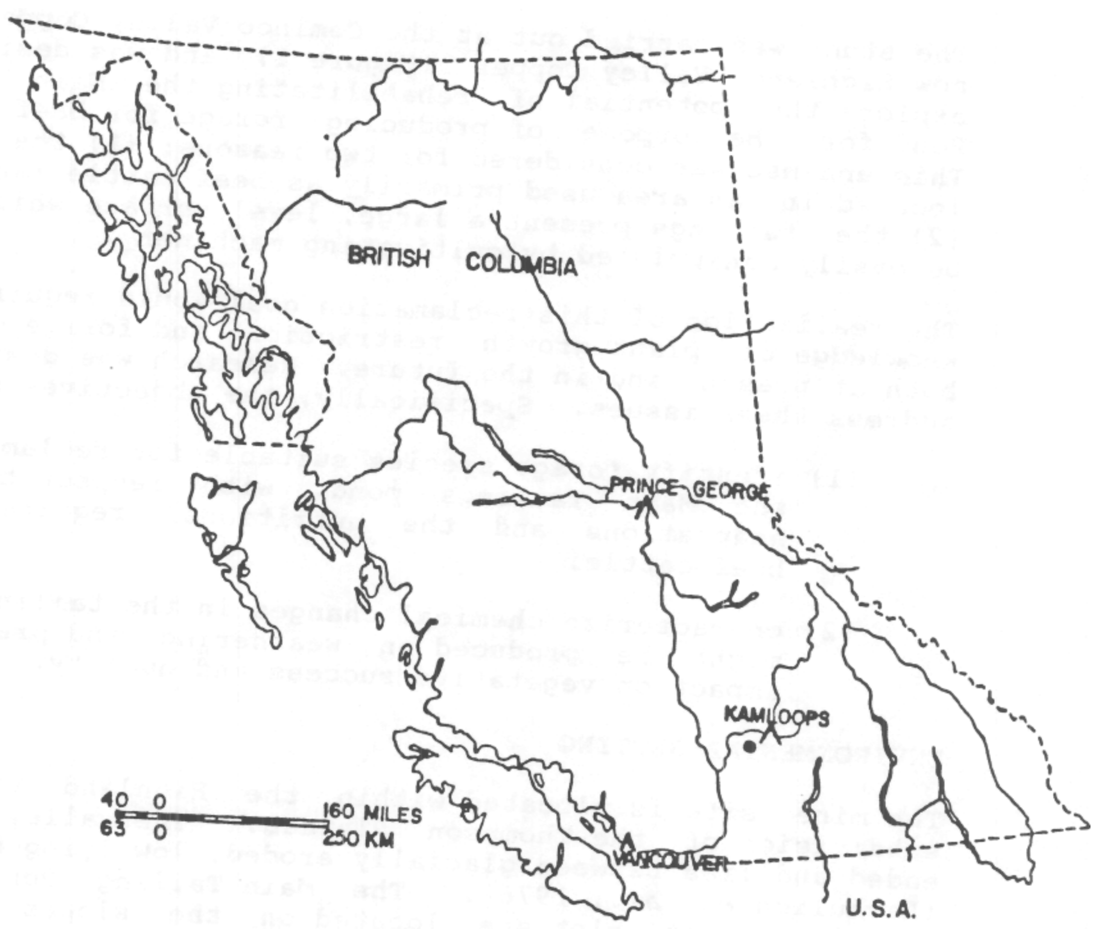
(2) characterize chemical changes in the tailings which might be produced on weathering and predict the impact on vegetative success and quality.

ENVIRONMENTAL SETTING

The mine site is located within the Highland Valley, a subdivision of the Thompson Plateau. The valley is open-ended and lies between glacially eroded, low lying mountains (Lavkulich *et al.,* 1976). The Main Tailing Pond and the actual research plot are located on the slopes of this valley at elevations ranging from 1300 m to 1600 m.

The area is located at the transition between the Interior Douglas-fir and Montane Spruce biogeoclimatic zones

FIGURE 1: LOCATION OF STUDY SITE



Highland Valley •

(Mitchell and Green, 1981).

Overall precipitation in the area is low, averaging about 300 nun annually, however, variation in yearly precipitation patterns can be substantial.

The mill tailings received by the Main Tailing Pond have been derived from a variety of orebodies. The roost recent discharges into this pond were tailings from the Lake Zone orebody. This orebody has been characterized as the Bethsaida phase of the Guichon batholith. Host rocks vary from porphyritic granodiorite to quartz monzonite. Primary sulphide minerals include bornite, chalcopyrite, molybdenite and pyrite. Copper minerailization is associated with a network of quartz veins which fill fractures and joints within the host rocks. Molybdenite is usually present as coatings on fault planes bordering quartz veins. Pyrite tends to form a halo around the periphery of the orebody and is scarce within the actual deposit (Cominco Copper Division, 1982, internal report).

METHODS

Research was carried out in three phases; the analysis of tailings, vegetation and reclaim water.

Tailings Analyses

Analyses conducted on the mill tailings from the Main Tailing pond included pH, total elemental levels, available heavy metals, mineralogical composition, phosphate adsorption, and an artificial weathering study. Artificial weathering was carried out using a Soxhlet apparatus. Columns of tailings were leached with 0.3 N acetic acid at high temperature (about 100 ^{0}C) for a total of seven weeks. On a weekly basis, the leachates were removed and replaced with fresh acid. After seven weeks, the leached tailings were recovered. This procedure, with some modifications, has been used by other researchers to mimic mineral degradational processes which might occur in time in a natural setting (Singleton, 1978; Lavkulich *et al,* 1976).

Vegetation Analyses

A tailings test plot was constructed and seeded with various agronomic forage species under different amendment regimes; these included surficial applications of overburden and mulch, with a control plot of unamended tailings. In addition, trials of no fertilizer, a split application and a single application were tested. This produced a total of nine plots. Foliage produced under each regime was analyzed for elemental content after two growing seasons.

Reclaim Water Analyses

Water samples were collected from three tailing ponds. At the time of sampling, pH was determined colorimetrically. Solution concentrations of 24 elements were determined using inductively coupled argon emission spectroscopy (ICP).

RESULTS AND DISCUSSION

Tailings

Total concentrations of the 20 elements examined were within ranges normally encountered in soils, with the exception of Ti, Zn, Ni, Cu and Mo. Ti, Zn and Ni were at, or below, the lower limits of normal and Cu and Mo were well above the usual range found in soils (Table 1).

Plant available Cu [diethylenetriaminepentaacetic acid (DTPA) extraction] and Mo (acid ammonium oxalate extraction) levels were found to be well above normal values, and far in excess of plant growth requirements when compared to critical nutrient ranges (Table 2). Levels of DTPA-available Zn and Mn, however, indicated a potential plant deficiency. DTPA-available Fe appeared normal. DTPA-extractable Ni and Cd were below the detection limit of the flame spectrophotometer at less than 0.2 and 0.06 mg/kg, respectively.

Artificial Weathering Study

Over the course of the seven week leaching period, the pH of the tailings dropped from 6.7 (in $CaCl_2$) to 3.5.

There was no apparent qualitative change in mineralogy after leaching. Minerals identified by x-ray diffraction included kaolinite, montmorillonite, vermiculite, mica, a montmorillonite-mica interstratified mineral, amphibole, K-feldspar, plagioclase, pyroxene and quartz.

There was a general trend for available heavy metals to decline after leaching. The effect of leaching on available Cu, however, appeared to vary with the sample. It was hypothesized that the form of Cu, i.e. reduced (as in

TABLE 1: TOTAL LEVELS OF TITANIUM, ZINC, NICKEL, COPPER AND MOLYBDENUM IN NORMAL AGRICULTURAL SOILS AND TEST PLOT TAILINGS

ELEMENT	TOTAL CONCENTRATION (mg/kg)			
	TAILINGS		"NORMAL" SOILS[s]	
	Mean	Range	Mean	Range
Ti	1000	900 - 1000	-	3000 - 6000
Zn	26	23 - 28	100	10 - 250
Ni	7	5 - 9	100	5 - 500
Cu	754	640 - 830	50	5 - 150
Mo	23	16 - 30	2	0.2 - 5

[s] After Brady (1974) and Swaine (1955)

TABLE 2: PLANT AVAILABLE COPPER, MOLYBDENUM, ZINC, IRON, AND MANGANESE IN NORMAL AGRICULTURAL SOILS AND TAILINGS AS COMPARED TO MINIMUM PLANT REQUIREMENTS

ELEMENT	TAILINGS (mg/kg)	"NORMAL" SOILS (mg/kg)	C.N.R.[s] (mg/kg)
Cu[ss]	17	1.3[a]	0.2[b]
Mo	0.7	0.2[c]	0.1[c]
Zn	0.4	0.3 - 11[b]	0.5 - 1.0[b]
Mn	4	20 - 110[d]	3 - 5[d]
Fe	15	20 - 250[d]	3.0 - 4.5[d]

[s] C.N.R. = Critical Nutrient Range. Extractable levels below the C.N.R. would indicate a plant deficiency for that element.
[ss] DTPA-extractable Cu, Zn, Mn, and Fe; acid ammonium oxalate-extractable Mo.

[a] Dolar and Keeney (1971)
[b] Viets and Lindsay (1973); Lindsay and Norvell (1978)
[c] Cheng and Ouellette (1973)
[d] Lindsay and Norvell (1978)

chalcopyrite) or oxidized (as in malachite) was critical in determining the effect of leaching on Cu availability.

During leaching, three general elemental release patterns were observed. Initially adsorbed cations, soluble salts and carbonates were leached producing maximum alkali and alkaline earth leachate concentrations early in the artificial weathering process. Week 2 and 3 were characterized by peak concentrations of Cu, Zn, Mn and Mg in the leachate. This observation was probably a result of the degradation of micas, pyroxenes, amphiboles and host ore minerals. Fe, Al and Si produced maximum peaks after 4 to 5 weeks of leaching. Concentrations then remained stable or declined slightly. These patterns were probably due to the degradation of the relatively inert minerals, such as quartz, some aluminosilicates, and oxyhydroxides of Fe and Al.

Vegetation

Foliar elemental content may be altered dramatically by variation in growing conditions, such as climatic and tailings variability and degree and rate of defoliation by grazers. The values and trends reported here may not be representative of foliar levels in a well established stable stand.

Foliar Copper

Copper concentrations in the grasses ranged from 24 to 79 mg/kg with a mean value of 44 mg/kg (Table 3). Within the grasses, significant differences in copper concentrations were observed between species. It would therefore appear that the efficiency of the physiological mechanisms which restrict copper uptake and translocation within the plant, vary across species. There was no difference in mean copper concentrations across plots. This would suggest that copper availability did not differ significantly between plots.

In the legumes, foliar copper concentrations ranged from 57 to 70 mg/kg, with a mean value of 63 mg/kg. Statistical comparisons of foliar concentrations between legume species within plots, and within species across plots, was not possible due to limited sample sizes.

TABLE 3: FOLIAR CONCENTRATIONS OF COPPER AND MOLYBDENUM AND COPPERrMOLYBDENUM RATIOS IN GRASSES AND LEGUMES GROWN ON TAILINGS AS COMPARED TO NORMAL LEVELS AND BEEF CATTLE REQUIREMENTS

SAMPLE	FOLIAR CONCENTRATIONS (mg/kg dry weight)		RATIO
	Cu	Mo	Cu:Mo
"Normal"	5 - 20[a]	1 - 5[b]	-
Grasses			
Mean	44	52	1.0
Range	24 - 79	18 - 113	0.7 - 1.4
Legumes			
Mean	63	237	0.3
Range	57 - 70	141 - 304	0.2 - 0.4
Cattle Requirement			
Desirable	4 - 10[c]	-	4 - 6[d]
Toxic	>115[c]	>6[c]	<3[d]

[a] Jones (1972)
[b] Sillanpaa (1977)
[c] National Research Council (1984)
[d] Agriculture Canada (1981)

Foliar Molybdenum

Molybdenum concentrations in the grasses ranged from 19 to 113 mg/kg, with an overall mean value of 52 mg/kg (Table 3). There was no significant difference in mean Mo concentration across species, considering all plots combined. Mean molybdenum concentrations did vary across plots, however, indicating that levels of plant available Mo were not consistent over all treatments.

The legumes, as expected, contained higher concentrations of molybdenum than the grasses. The average Mo concentration was found to be 237 mg/kg, with *a* sample range of 141 to 304 mg/kg.

Copper/Molybdenum Ratios

In the grasses, copper to molybdenum ratios ranged from 0.7:1 to 1.4:1, with *a* mean value of 1:1 (Table 3). Fluctuations in Cu:Mo ratios were attributable mainly to variations in foliar Cu.

Copper/molybdenum ratios in the legumes ranged from 0.2:1 to 0.4:1, with a mean ratio of 0.3:1.

All ratios were well below the minimum level of 3:1 recommended by Agriculture Canada (1981). Ratios below this guideline level are considered hazardous to ruminants. Vegetation produced under the conditions of this study would therefore not be suitable forage for beef cattle.

Other Micronutrients

The potential Zn deficiency indicated by DTPA extractable values was confirmed by foliar levels which were generally less than 25 mg/kg; the critical concentration for many plants (Chapman, 1966). Zn concentrations in the grasses ranged from 7 to 34 mg/kg with a mean of 15 mg/kg. Zinc concentrations in the legumes averaged 30 mg/kg.

Zinc requirements for beef cattle, as suggested by the National Research Council (1.984), are met by foliage with concentrations of 20 to 40 mg/kg. Agriculture Canada (1981) recommendations are higher, with adequate levels ranging from 50 to 100 mg Zn/kg dry matter. Zn content in most species-plot groups were below both dietary guidelines. Therefore, Zn may be deficient for both plants and cattle.

Foliar manganese ranged from 101 to 711 mg/kg with a mean value of 253 rag/kg. Legume Mn concentrations averaged 232 mg/kg. Most groups were well within the sufficient range (20 to 500 mg/kg) for plant nutrition.

Several plant species were consistently above the adequate Mn range for beef cattle, but did not approach excessive levels. All other groups met beef cattle Mn requirements.

The mean foliar nickel concentration was 39 mg/kg in the grasses. Values ranged from 3 to 102 mg/kg. The average Ni concentration in the legumes was 9 mg/kg.

The National Research Council (1984) does not list nickel as a required nutrient for beef cattle. Based on Agriculture Canada (1981) guidelines, foliar Ni levels may be considered adequate to high.

Reclaim Water

Although sampling was not rigorous, analysis of the tailing pond water indicated that this water would not be suitable for irrigation purposes as a result of excessive Mo levels. Mo levels were also well above desirable limits for wildlife and livestock drinking water. The use of this water source for irrigation would, therefore, be contraindicated if the reclamation goal is to produce beef cattle forage.

The reaction of the tailings water is critical to heavy metal solution levels. The present neutral to basic situation, restricts Cu from coming into solution and promotes the dissolution of Mo compounds. This is apparent in the relative solution levels of each element (Mo » Cu), as compared to total levels in the tailings (Cu » Mo). In fact, reconnaissance of Mo levels in stream water has been used as a means of locating Cu ore bodies, since the two elements are often associated in geological deposits and Mo is much more mobile than Cu under basic conditions (Huff, 1970).

CONCLUSIONS

Foliar molybdenum levels were one to two orders of magnitude higher than normal. Copper : molybdenum ratios were below the critical level of 3:1 in all samples. Consequently, vegetation produced under the conditions of the study would not be suitable for beef cattle forage. It may be possible to modify the copper : molybdenum ratios in plants growing on the tailings. Rather than increase copper levels, it would seem prudent to attempt to reduce molybdenum concentrations in the forage. The results *of* this study show that species selection would not be effective, since within the grasses, molybdenum concentrations did not vary significantly. Alternatively, modification of molybdenum availability in the medium may be attempted by reducing the pH of the tailings. The target pH for optimal plant growth and minimal Mo uptake would be very near 6. As shown in the artificial weathering study, declines in pH will probably occur naturally, but may take considerable time. This process may be accelerated through the application of acid forming fertilizers or elemental sulphur. Irrigation of the area would also promote acidification through leaching of the basic cations, which are at present, maintaining tailings reaction in the neutral to alkaline range. The use of reclaim water for this purpose would not be recommended for two reasons. Firstly, this water contains relatively high levels of soluble molybdenum, which would be readily available to plants, compounding the molybdenum problem. Secondly, the addition of bases from the reclaim water, would retard pH decline.

Aside from the copper molybdenum issue, zinc levels appear to be inadequate for both plants and cattle. Stand quality would probably benefit from zinc fertilization.

In the long term, weathering of the tailings may be expected to provide a more suitable medium for vegetative success and improved quality. This situation would be affected by the decline in pH and synthesis of clays, through mineral degradation and recombination processes, which would improve the nutrient and water holding capacities of the tailings. Incorporation of organic matter would also be beneficial in this respect. Organic content would also provide a template for microbiological organisms and allow the cycling of nutrients, particularly nitrogen. Nitrogen and phosphorus inherent in the tailings are not adequate to maintain plant growth and must be provided until such time that the tailings environment approaches a natural soil system.

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