

LIME AND TILLAGE EFFECTS ON SOIL COPPER AND ZINC PARTITIONING AND VEGETATIVE RESPONSE  
IN ACID CONTAMINATED AGRICULTURAL SOILS IN SOUTHWESTERN MONTANA<sup>1/</sup>

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Abstract: Agricultural soils in the Clark Fork valley of southwestern Montana have been contaminated by metals from historic mining. Liming, forage species and tillage were tested in an effort to develop cost-effective reclamation techniques. Soil chemical changes and vegetative response under different lime rates are discussed.

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## INTRODUCTION

The upper Clark Fork valley located in southwestern Montana has a legacy of mining dating from the 1860's when the region was first settled. The Clark Fork area served as an agricultural center for the growing mining towns of Virginia City, Bannack, and nearby Butte. Due to the arid climate (10-14 inch rainfall) much of the crop and livestock production was dependent upon irrigation from the abundant supplies of surface water in the basin.

With the wealth of the silver and then copper reserves discovered in Butte, just 20 miles upstream of the Clark Fork valley, came wholesale contamination of the surface waters vital to irrigated agriculture. Several million cubic yards of tailings may have been disposed directly into Silver Bow Creek, a major tributary of the Clark Fork River. The river was said to turn bright red during flood stage over 100 miles downstream in Missoula as late as the mid 1960's from the tailings. Continued use of Silver Bow Creek water for irrigation spread tailings and acid water over lands so that soils were acidified sufficiently to eliminate further agricultural uses.

The area contaminated, now an EPA superfund site, has several thousand acres of land where agricultural production is no longer possible, or where yields are reduced. In recent years, numerous landowners have experienced crop and livestock losses in the area due to metal contamination. Zinc toxicity has most often been cited as the cause of crop failure with copper toxicity occasionally cited.

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The purpose of this investigation was to develop and test cost-effective techniques for reclamation of contaminated lands for forage production. Evaluation of liming as a means of alleviating acid and metal solubility problems and selection of appropriate forage species were the objectives of the study.

Advantages of this reclamation approach include reduced metal solubility and reduced ground water recharge resulting in an abatement of metal movement to surface and ground water. Reduction in fugitive dust would also result from the enhanced vegetative cover. Finally, a productive agricultural use would be re-established helping bolster the local economy.

Primary disadvantages of the approach might include metal uptake by plants and accumulation in livestock, expense outweighing benefits, and solubilization of arsenic. Metal levels in plant tissue and soil arsenic levels were monitored in the investigation, treatments were chosen to keep overall reclamation costs as low as possible. Although treatments developed are not expected to be cost-effective for an individual farm enterprise, the additional public benefits justify payment of project costs by a public entity (State of Montana) or a responsible polluter (EPA-Superfund).

The area chosen for this investigation was said to have over 100 active dairy operations at the turn of the century. Now it is mostly barren ground contributing to a regional fugitive dust problem. Plants growing in the area are noxious weeds like leafy spurge, russian knapweed, canada thistle, field bindweed, and hoary cress.

## LITERATURE REVIEW

Generation of acidity from oxidation of sulfide-rich mine waste is a commonly observed environmental problem. (Caruccio 1968, Sobek and others 1978). Acidification of natural soils

through fluvial deposition of sulfidic materials has seldom been described, however the problem is identical in nature to other mine wastes. Although a number of potential remedies for acid generation have been proposed (Kabata-Pendias and Pendias 1984, Smith and others 1974), lime neutralization appears to be the most practical and cost-effective remediation technique for soils.

Several methods have been devised for determining the lime required to neutralize acidity. For most soils, the lime requirement is the amount necessary to neutralize the "active acidity" which is a function of the soil pH and its buffering capacity. Methods based on measurement of titratable acidity (McLean and others 1966, McLean 1982, Peech 1965) have been used to predict lime requirement for most natural soils. The SMP Buffer method (Shoemaker and others 1961) has received wide acceptance as a standard method for measuring titratable acidity.

Sulfide-rich soils also have "residual acidity" which may be released over many years. Oxidation of pyrite and other sulfides forms sulfuric acid. Research on coal overburden in the Eastern U.S. indicated that residual acidity is a function of sulfide sulfur and to an extent organic sulfur. Sulfate is already oxidized thus does not contribute to acid generation. More recently, organic sulfur was shown to be less acid-producing than inorganic sulfur (Sullivan and Sobek 1982). The pathway (Caruccio and Geidel 1984) and kinetics (Geidel 1979) of sulfide oxidation is complex. A number of factors have been shown to affect the rate of acid formation including crystalline form (Caruccio and others 1976), oxygen supply, moisture content, and microbial populations (Caruccio 1980). The "acid-base accounting" method has been used to calculate potential acid release from sulfide-rich materials (Smith and others 1976, Sobek and others 1978, Sturey and others 1982). These methods have often been criticized as overestimating lime requirement because coarse sulfide materials are not reactive or may be coated with iron oxides (Burt and Caruccio 1986). Artificial weathering chambers have been used to create accelerated weathering conditions to measure only those forms of sulfide most likely to react (Caruccio 1968, Sobek and others 1982). These tests are slow, costly and are difficult to extrapolate to field conditions.

Tailings material is unlike coal overburden in being low in organic sulfur. Therefore sulfide sulfur gives a good indication of maximum residual acidity. Sobek and others (1978) noted that lime required in tons per acre to neutralize residual acidity is percent sulfide sulfur times 31.25.

Most acid soils and overburden materials suppress plant growth due to increased bioavailability of manganese or aluminum ion in low pH soil solution (below 4.5). Reclamation of tailings contaminated soils is further complicated by the abundance of heavy metals like copper, zinc, cadmium, lead, and arsenic which often causes phytotoxic effects at higher pH levels (soil pH 5.5

to 6.0). Liming has often been recommended as the best technique for improvement of tailings and other metal-enriched mine waste because solubility of the metals decreases with increasing pH. Arsenic solubility, however, is much like phosphorus in having a maximum solubility at neutral pH and under reducing conditions.

Several plant species have been evaluated for their adaptation to low soil pH or elevated soil metal levels (Bradshaw and Chadwick 1980). Locally, colonial bentgrass (*Agrostis tenuis*), tufted hairgrass (*Deschampsia caespitosa*) have been found to survive on acid tailings areas. Local seed sources have been documented to exhibit copper and zinc tolerance (Surbrugg 1982). Discussion with local farmers managing these grasses for hay and pasture indicated that toxic metal levels in forage, poor production, low palatability, and high water requirement all preclude the widespread use of these grasses if restoration of agricultural use is desired.

Traditional agricultural forage species vary in their ability to tolerate elevated metals or low pH (Bradshaw and Chadwick 1980). Plant species selected must also be drought tolerant and winter hardy to survive in the region. Additionally metal uptake by the plant must be determined so that toxic metal accumulation by livestock is prevented (NAS 1980). Fortunately, most species will die before accumulating sufficient metal to cause problems for livestock (Parr and others 1983). Some grasses may accumulate metals (especially copper and arsenic) in root and crown portions of the plant while maintaining moderate levels in plant tops. In some grazing systems, however, metal uptake by livestock can be partly or largely a function of metal in soil or root and crown tissue (Ian Thornton, personal communication) thus prevention of uptake by plant tops alone will not preclude livestock metal toxicity.

## METHODS

### Site Selection

The research area is located about 5 miles east of Anaconda, Montana on the Hazel Spangler ranch, a large dairy operation (Figure 1). Several thousand acres of contaminated soils are found in the vicinity where old surface irrigation systems brought Silver Bow Creek water onto low terraces and alluvial fans. Vegetative cover averages less than 10 percent and consists primarily of weedy species. Rainfall averages about 14 inches annually most of which falls from April to June, much of it as snow.

Soils in the area are in the Beaverell and Tally series. The Beaverell soils are loamy-skeletal, mixed, Aridic Argiborolls. These soils have loam to loamy-sand A1 horizons which are truncated by wind erosion in places. The argillic extends from 6 to 14 inches and is loam in texture. Rock fragments in the base of the argillic and in the C horizon average 40 to 50 percent by volume.

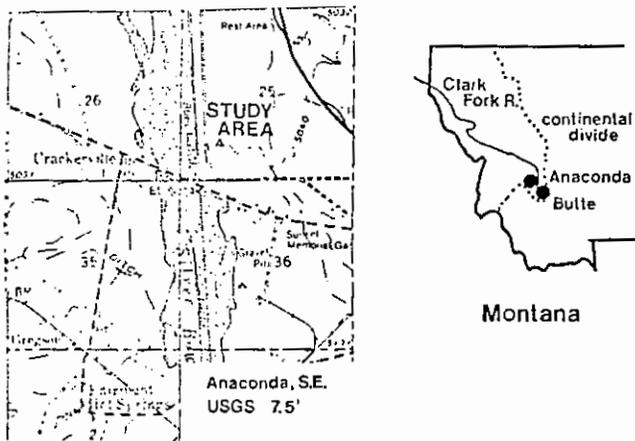


Figure 1. Location of the forage establishment study.

The Tully soils are coarse-loamy, mixed Typic Haploborolls. These soils are similar except in lacking a significant clay accumulation. A weak accumulation of carbonates are found below the argillic with some effervescence in the argillic observed occasionally. Both soils are cool variants (cryic) as mapped locally.

A uniform, barren area with measured soil pH of 5.5 to 5.7 and an EC of 0.3 to 0.4 mmhos/cm was selected for the plot location. Soil pH and EC was measured in each block of the study. The sodium bicarbonate extractable phosphorus was 64 ppm and extractable arsenic was 34 ppm.

#### Plot Layout and Experimental Treatments

The study was designed to test the effects of liming and species selection on forage establishment. A two-factor split block design was used so that species could be drill-seeded in one pass through an entire block (Little and Hills 1972).

Three lime rates and a control were used. Lime rates were designed at 0.5, 1.0, and 2.0 times the lime requirement adjusted for lime purity. An SMP buffer lime test (Shoemaker and others, 1961) predicted the lime rate necessary to raise the pH to 6.5 was 4.3 tons per acre. Preliminary soil analyses indicated that no measurable sulfide sulfur remained in the soils indicating that only the "active" acidity needed to be neutralized. Rates of 0, 2.15, 4.3, and 8.6 tons of lime per acre were used.

The four forage treatments included three perennial grasses and a grass/legume mixture. Ladak 65 alfalfa (*Medicago sativa*) and Nordan crested wheatgrass (*Agropyron cristatum*) were seeded in alternate rows. This treatment represented the traditional mixture used in the past by many area ranchers. Additional forage species included Yindall russian wildrye (*Elymus junceus*), Mandan 759 pubescent wheatgrass (*A. trichophorum*), and Sodar streambank wheatgrass (*A. riparian*). All seeding rates were adjusted for purity and germination to

yield 30 pure live seeds per foot of row.

A 0.6 acre site (132 feet by 196 feet) was sprayed in late 1984 with glyphosate to eradicate as many perennial weeds as possible. The research area was then staked into 64 plots (4 replicates). Agricultural lime (calcium carbonate) ground to less than 200 mesh was applied at a rate equivalent to 2.15, 4.3, and 8.6 tons per acre of pure calcium carbonate. Material used was rated at 94 percent effectiveness. Due to the powdery nature of the lime, and windy conditions encountered, lime was mixed with wet sandy soil from the plot prior to double spreading by hand over the plot area. Ammonium phosphate fertilizer (11-55-0) was surface applied to supply 80 pounds P<sub>2</sub>O<sub>5</sub> and 20 pounds of N. Phosphorus was added primarily to counteract an excessive level of arsenic. After spreading lime, the plots were plowed to a depth of 5 inches (moldboard), surface rocks were removed, and the seedbed packed before restaking.

Plots were seeded in mid-April of 1985. A 7 foot double-disk drill was used. All species were seeded at 12 inch row spacing except for russian wildrye which had 24 inch spacing. Unseasonably windy, hot, and dry conditions followed during the summer of 1985 making the months of January through July the driest on record. Wind erosion filled in and crusted over many of the drill rows causing patchy germination due to trapping of seedlings below the crust. The fall of 1985 had above-normal rainfall while 1986 was a near average rainfall year.

Germination was measured in early July of 1985. The inside 5 seeded rows of grass, all rows of alfalfa, and inside 2 rows of crested wheatgrass were used to randomly select four one foot row segments to count seeded plants. All row segments were permanently staked. Establishment was measured in the same row segments in June of 1986. At the same time vegetation was clipped from the pubescent wheatgrass and crested wheatgrass treatments where sufficient plant material was available.

On 5 June 1986, a qualitative estimate of plant stand and vigor was made of each plot. The rankings ranged from 1 for an excellent stand or excellent vigor to 9 for very poor stand or vigor. Plant material was clipped from the upper two-thirds of the aboveground portion of the plant for elemental analysis. Grasses were in the early to late boot stage at clipping.

#### Soil and Plant Tissue Analyses

Soil samples were collected from each plot in mid June of 1985. Each sample was taken from the 0 to 5 inch layer, which was the depth of lime incorporation, and was expected to be the zone most affected by metal contamination. Samples were a composite of six subsamples taken from the central portion of each plot. All samples had pH and EC measured in a saturation extract. Samples from Block 4 (plots 49 to 64) had a number of additional

analyses performed (Table 1). Soluble calcium, magnesium, and sodium were also measured in a saturation extract. An ammonium acetate extraction buffered at pH 5.5, which was close to the original soil pH, was used for analysing cadmium, copper, lead, and zinc levels. A Bray extraction was used for arsenic and phosphorus analysis.

Samples were again collected from all plots using the same protocol on 5 June 1986 at the same time that plant material was collected. These samples were all measured for soil pH and EC. Samples from plots seeded with pubescent wheatgrass or crested wheatgrass also had extractable metals analysed including: saturation extractable, 1 N ammonium acetate pH 5.5 extractable, DTPA extractable, and total (nitric acid, hydrogen peroxide) copper, zinc, cadmium, iron, and in some cases aluminum (Table 1). Bray extractable phosphorus and arsenic and total arsenic were also measured. Plant tissue samples were oven-dried and digested in a combination of nitric and perchloric acid. Determinations of elemental concentrations in plant tissue included copper, zinc, iron, arsenic, and cadmium.

Table 1. Methods of analysis for soil analyses.

Parameter	Procedure	Reference
pH	paste	U.S. Salinity Lab
EC	satn. paste	Sandoval & Power
Cu,Zn,Cd,Fe	satn. extract	U.S. Salinity Lab
Cu,Zn,Cd,Fe, Al	NH <sub>4</sub> OAc extract	Thomas
Cu,Zn,Cd,Fe	DTPA-TEA extract	Baker and Amacher
Cu,Zn,Cd,Fe, Al,As	Total/HNO <sub>3</sub> -H <sub>2</sub> O <sub>2</sub>	
As, P	NaHCO <sub>3</sub> extract	Ganje & Rains
lime reqt.	titratable acid.	Shoemaker & others

### Statistics

Analysis of variance for a split-block design was used to verify the significance of forage response to lime treatments, and response of soil chemical parameters to lime or species. For analysis of the soils data from plots 49 to 64, the design is a randomized complete block when species treatments are considered replicates of the lime treatments (Snedecor and Cochran 1978).

For species or chemical properties indicating a significant response in the analysis of variance, a Neuman-Keuls mean separation test was used to evaluate differences between treatments. Further, simple linear regression was also used to show significant data trends especially between soil and plant metal levels.

## RESULTS AND DISCUSSION

**Soil Chemistry:** Results of soil pH sampling from all plots indicated that the lime-species study area thought to be uniform in pH based on preliminary field pH measurements in each block, was quite variable in pH. Soil pH from all control plots was used to contour map original pH (Figure 2). Original pH on the south half of the plots was much higher in general than the north half of the plots. Soil pH from block 1 and 2 averaged near 7.0 and blocks 3 and 4 averaged near 5.6. A map of lime response at the design SMP rate (Figure 2) indicated that lime application tended to raise pH most on the low pH plot areas thus reducing the overall variability in soil pH across all plots.

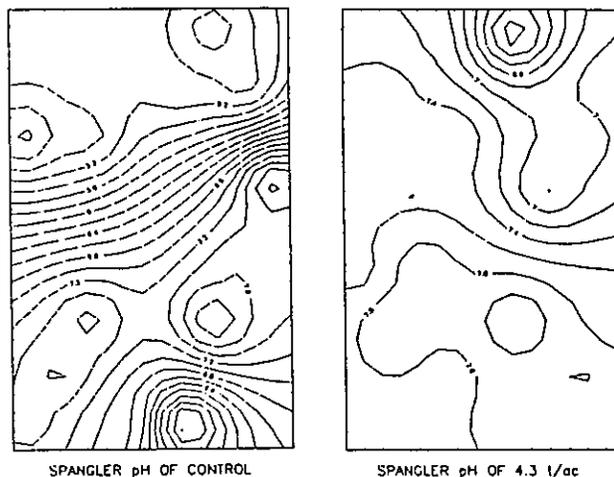


Figure 2. Spangler site soil pH at 0 and 4.3 tons of lime per acre.

Due to the variability in original soil pH, soil chemical data available from all plots (pH, EC) were analysed separately for the south half of the study (blocks 1 and 2) than for the more acid north half (blocks 3 and 4). Tables 2 and 3 show the significance of the analysis of variance (ANOVA) and comparison of mean values for each lime rate. The ANOVA design was a two factor split-block with only two replicates. Due to the reduced number of replicates caused by analysing the high and low pH blocks separately, significant differences in soil chemistry would tend to be masked.

On low pH plots there was a significant increase in pH due to liming with the design lime rate (4.3 tons per acre) raising the pH to 7.01, above the target pH level of 6.5. The same pattern of pH response was noted two months and one year after liming. The pH seemed to climb slightly after the two month measurement especially on the two lower lime rates.

On the high pH plots, the effect of liming was masked as expected though there was an apparent increase in pH (from 7.3 to 8.0) due to liming. On all plots there was a trend for EC to increase with increasing lime rate. The soil salinity never

Table 2. Analysis of variance for soil pH and EC in the high pH plots (block 1 and 2).

Lime Rate (tons/acre)	Soil pH 6/85	Soil pH 6/86	E.C. (mmhos/cm)
0	7.33 a	6.91 a	0.66 a
2.1	7.87 a	7.42 a	0.63 a
4.3	7.91 a	7.62 a	0.82 a
8.6	8.03 a	7.69 a	0.78 a
ANOVA prob. of F	.15	.15	.02

numbers followed by the same letter are not significantly different at  $p=.05$

Table 3. Analysis of variance for soil pH and EC in the low pH plots (block 3 and 4).

Lime Rate (tons/acre)	Soil pH 6/85	Soil pH 6/86	E.C. (mmhos/cm)
0	5.19 a	5.22 a	0.61 a
2.1	6.25 ab	6.69 ab	0.59 a
4.3	7.01 ab	7.16 b	0.63 a
8.6	7.47 b	7.44 b	0.69 a
ANOVA prob. of F	.006	.13	.50

numbers followed by the same letter are not significantly different at  $p=.05$

reached a high enough level to have an effect on vegetation, however.

Elevated levels of water soluble metals in the soil solution may constitute a threat to ground water if the metals leach from the system without being precipitated. Soluble levels of metals in soil solution are often used to predict the types of minerals potentially controlling solubility (Lindsay 1979). Often, trace metal solubility is thought to be controlled by adsorption reactions with clay minerals and organic matter. However, in polluted soils metal solubility can be elevated (Kubota-Pendias and Pendias 1984) which may indicate saturation of the soil adsorption sites and formation of solid phase minerals.

Zinc and copper concentrations on a soil weight basis were converted to a soil solution molar concentration by using the saturation percentage as an approximation of water content at saturation and then multiplying by atomic weight. Concentrations were corrected to activities using the extended Debye-Huckel coefficient. Stability diagrams for water soluble zinc and copper levels in soils were plotted (Figure 3 and 4).

Zinc stability indicated that solubility decreased at increasing pH ( $r=-.96$ ) as is commonly observed, however, the relative difference in solubility was not as great as expected. Normally, solubility drops by two orders of magnitude for each unit increase in pH (Lindsay 1979). At low pH, zinc values were close to or slightly above the published stability of soil zinc. At higher pH, however stability was close to Willemite in unlimed soils, but was closer to Smithsonite ( $ZnCO_3$ ) in limed soils. Mattigod and others (1986) identified smithsonite in the Shipham area of Great Britain in a soil impacted by mining.

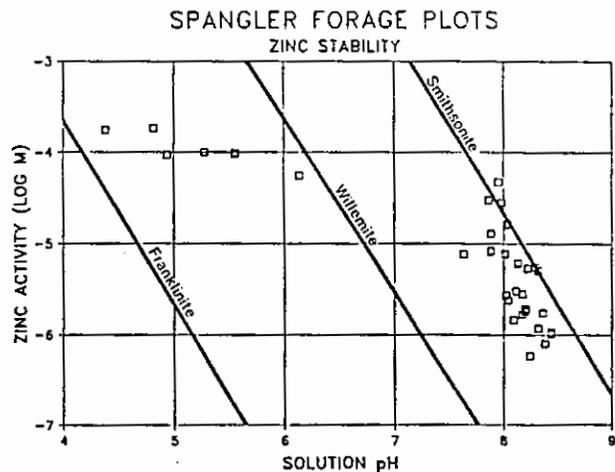


Figure 3. Stability diagram for zinc at Spanglers.

Soil copper solubility varied little at varying pH ( $r=-.65$ ) (Figure 6). At low pH, copper stability was intermediate between cupric ferrite ( $CuFe_2O_4$ ) and malachite ( $Cu_2(OH)_2CO_3$ ) or azurite ( $Cu_3(OH)_2(CO_3)_2$ ). At pH near 8, the solubility was intermediate between malachite/azurite and copper carbonate. The lack of change in copper solubility at increasing pH indicates that a single solid phase mineral does not control solubility. However, copper solubility exceeds the proposed limit for several known copper minerals. It may be that the kinetics of forming these complex minerals is very slow. The opportunity exists for decreasing solubility of copper by increasing the levels of ligands (phosphate, sulfate, hydroxide, carbonate) in solution which typically precipitate copper.

Several soil solution extracts were analysed in 1985 and 1986 to determine how liming affected the solubility and plant-availability of selected metals. A saturation extract (distilled water) was analysed to provide a measure of the difference in potential ground water pollution hazard of lime-treated soils. Ammonium acetate (pH 5.5), and DTPA (pH 8.0) extracts were analysed to indicate the "bioavailable" fraction of metals. The bioavailable fraction includes soluble plus weakly adsorbed or moderately soluble phases of metals.

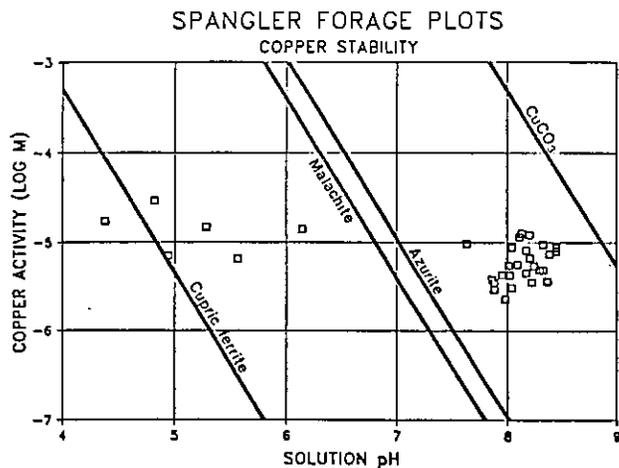


Figure 4. Stability diagram for copper at Spanglers.

Normally, the amount of adsorbed metals decreases with increasing pH because the number of soil adsorption sites increases. Total metals in soil were also measured so that partitioning of metals into selected phases (soluble, available, and unavailable) could be determined.

As expected soluble cadmium, copper, and zinc decreased with increasing lime rate in response to the decline in average pH. Soluble iron had no clear pattern. An ANOV indicated only slight significance ( $p=.07$ ) for saturation zinc, but no significant decline for soluble copper. This low probability is attributed to the high variability in chemistry.

Effects of liming on extractable metal levels were less predictable. The buffering of DTPA and ammonium acetate could be expected to eliminate pH differences caused by liming, but the increase in binding to pH-dependent adsorption sites should still cause a reduction in extractable metals. Extractable iron and aluminum consistently decreased due to liming as expected. The significance of the ANOV was low, however. The lack of strong observed correlation of extractable iron and aluminum with liming may have been due in part to the limited sample number. Only plots 49 to 64 had a complete suite of metal determinations which could be used in an ANOV. Sixteen additional plots which were sampled for plant tissue had extractable metals determined. Means listed below are from all available data ( $n=8$ ), though the ANOV was only performed on data from plots 49 to 64. (Table 4).

Extractable cadmium and zinc showed no apparent change due to liming, while extractable copper appeared to increase as a result of liming. Extractable arsenic did not change with increasing lime rate. Formation of soluble oxides, poor carbonates, slow kinetic response to pH change, or competition of iron and aluminum for adsorption sites may explain the apparent anomalous behavior of

these elements.

As expected, liming had no effect on total metal levels.

Regression analysis of soils data supported the trends identified above. Of all soil parameters, only saturation extractable zinc ( $r=-.96$ ) and copper ( $r=-.65$ ) were correlated with pH or lime rate. Extractable levels for specific metals were highly correlated with total levels and with other extractions.

Table 4. Average concentration of extractable metals for differing lime rates.

Parameter	Lime Rate (tons/acre)			
	0.0	2.1	4.3	8.6
pH	6.07	7.06	7.39	7.56
Saturation extract (concentration mg/l extract)				
cadmium	.028	.026	.010	.008
copper	.446	.325	.241	.259
iron	.102	.126	.084	.253
zinc	2.89	1.29	.403	.153
Ammonium acetate (concentration mg/kg soil)				
cadmium	1.49	1.51	1.36	1.58
copper	74.4	87.8	66.0	94.1
iron	2.08	1.96	1.43	1.29
zinc	144	146	121	148
aluminum	16.3	14.9	9.8	8.4
DTPA				
cadmium	2.71	2.96	2.51	2.71
copper	141	171	135	170
iron	101	85.5	78.0	80.2
zinc	193	202	169	192
Total				
cadmium	3.97	4.35	3.68	4.10
copper	332	366	309	391
iron	13485	13004	12576	13370
zinc	272	281	249	295
aluminum	16656	16206	15803	16216
Bray phosphorus	239	270	233	231
Bray arsenic	18.6	17.1	14.9	16.9
Total arsenic	72.9	99.1	86.9	96.9

On plots 49 to 64, samples were extracted with ammonium acetate both in 1985 and 1986 to identify temporal changes in extractable metal levels. Extractable copper changed little from 1985 (83.3 micrograms per gram) to 1986 (77.1 micrograms per gram). Zinc, however, increased during the same period from 67.6 to 141 micrograms per gram.

Liming appears to have either little effect on or may increase the extractable levels of potentially phytotoxic metals (Zn, Cu, Cd). This observation

was discussed previously.

Comparison of extractable metal levels to the total amount in soil gives an idea of the "partitioning" of metals into various forms of varying availability. "Soluble" is available both to ground water and to plants and is the most available in the system. "Extractable" is the soluble plus weakly adsorbed phase which may be available to plants. The remaining fraction is mostly unavailable and represents metals in primary minerals or coprecipitated with insoluble oxide minerals.

The soluble fraction (Figure 5) of both copper and zinc decreased with increasing pH and lime rate, but copper changed less than zinc. The soluble fraction varied from 0.01 to 3.7 percent.

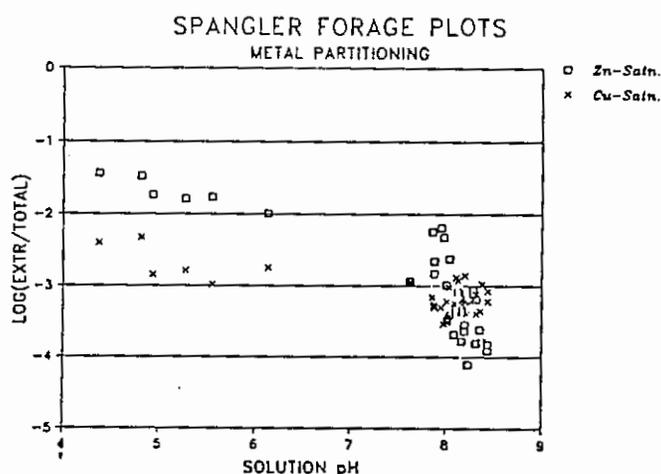


Figure 5. Log of soluble metals divided by total metals at the Spangler site.

Extractable metals (Figure 6) were less changeable with changing pH than the soluble fraction which may be due largely to the buffered nature of the soil extracts. The DTPA and ammonium acetate levels of zinc averaged 80 and 60 percent of total zinc respectively. The fraction decreased slightly with increasing pH, and was lowest for those plots that originally had a pH above 7.0. The DTPA and ammonium acetate copper was 50 and 30 percent of total and varied little with increasing pH. Again, plots with pH above 7 before liming had lower percent extractable copper. This indicates that extractable copper and zinc may decrease slightly with time as the system adjusts to a new equilibrium pH.

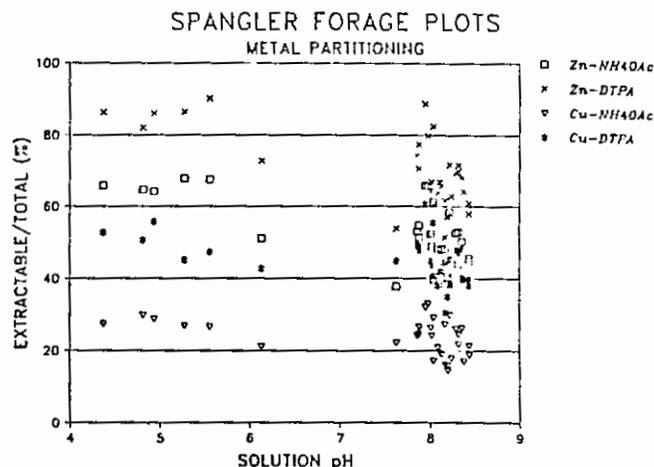


Figure 6. Metal partitioning of copper and zinc at the site near Anaconda, Montana.

Vegetation: As discussed previously, original soil pH of the plots varied more than was expected from an initial evaluation. Vegetation response on most plots with original pH above 6.5 was very good in most cases. Response on the lower pH plots was much poorer. As a result, separate analysis of variance tests were performed for the low and high pH plots (Table 5 and 6).

Table 5. Analysis of variance results for vegetation response in the high pH plots (block 1 and 2).

Species	Germ. (plants/ft)	Estab. (plants/ft)	Stand (rating 1/)	Vigor
Crested Wh.	24.3	10.4	5.6	4.8
Russian Wild.	11.2	5.7	7.6	5.5
Pubescent Wh.	22.1	7.5	5.6	4.8
Streambank Wh.	16.8	7.2	6.6	6.1

1/. Stand and vigor are a numerical rating ranging from 1=excellent to 9=very poor. No differences are significant in the ANOV.

Individual species appeared to differ in response on the plots but the ANOV did not show significant trends most likely due to the lack of replication caused by splitting the plots. All species except russian wildrye, and alfalfa had germination above 50 percent (30 pure live seeds per foot were planted). Alfalfa performance was so poor that it will not be discussed further in this report. Survival of grasses was much lower ranging from above 30 percent for crested wheatgrass on the

Table 6. Analysis of variance results for vegetation response in the low pH plots (block 3 and 4).

Species	Germ. (plants/ft)	Estab. (plants/ft)	Stand (rating 1/)	Vigor
Crested Wh.	22.2	2.1	8.1	5.8
Russian Wild.	8.0	1.2	8.0	6.9
Pubescent Wh.	24.8	1.5	8.1	6.3
Streambank Wh.	22.3	0.8	8.4	6.0

1/. Stand and vigor are a numerical rating ranging from 1=excellent to 9=very poor. No differences are significant in the ANOV.

high pH plots to less than 3 percent for streambank wheatgrass on the low pH plots. The harsh climate of the site and low rainfall in 1985 account in part for the low survival. Establishment clearly differed between the low and high pH plots, however, indicating that site chemistry was an important factor in determining survival. Many workers have noted a slow kinetic response to lime application especially when CaCO<sub>3</sub> is used. The poor stand and establishment on the low pH plots may have been due in part to slow pH correction on these plots.

In no case did lime rate affect vegetation performance. Thus, liming did not appear to statistically improve the chances for vegetation to become established.

Though plant vigor and establishment were not correlated with solution pH, low pH did seem to limit vegetation response. For example, establishment never exceeded 3 to 4 plants per foot unless soil pH was raised to 6 or higher. Not all plots with pH above 6 achieved a good stand, however. A similar trend was noted for vigor. The most vigorous plants (rating of 5 or lower) were only achieved at pH levels above 6. Roughly half of all plots with pH above 6 had vegetation with low vigor presumably due to high uptake of zinc and copper. High pH alone though did not assure adequate vegetation performance.

Plant tissue samples were collected in June, 1986 and analysed for heavy metals. Regression analysis indicated that metal levels in plant tissue often correlated with vegetation performance. In crested wheatgrass, vigor was correlated with plant zinc ( $r=.69$ ,  $p<.05$ ). Vigor was also correlated with DTPA copper ( $r=.69$ ) and ammonium acetate extractable copper ( $r=.74$ ). Establishment (plants per foot) was inversely correlated with DTPA zinc ( $r=-.64$ ,  $p<.05$ ) and ammonium acetate extractable zinc ( $r=-.64$ ). In pubescent wheatgrass establishment was inversely correlated with zinc in vegetation ( $r=-.64$ ). These observations all indicate that excessive copper and zinc uptake is suppressing plant establishment and vigor. Soil pH does not seem to affect zinc uptake or extractable soil zinc levels.

Further evidence of the tendency for excess zinc or zinc and copper to suppress plant growth was suggested through paired sampling and analysis of healthy and chlorotic appearing vegetation in the same plots (Table 7). All plots had an apparent mosaic of vigorous, and stunted grasses, with patches of bare ground. Differential deposition from irrigation water or redistribution of contaminants by wind may best account for this small-scale variability. Chlorotic plants had elevated zinc, iron, and copper with zinc within limits identified as phyto-toxic in the literature.

Table 7. Comparison of elemental concentrations in neighboring healthy and chlorotic pubescent wheatgrass.

Plot Type	As	Cd	Cu	F	Fe	Zn
----- (mg/kg plant tissue) -----						
22 healthy	<.01	<.50	13.5	-	380.	78.2
chlorotic	.21	<.50	15.6	6.1	649.	182.
26 healthy	<.01	<.50	10.8	-	368.	61.9
chlorotic	<.01	.58	17.3	-	753.	249.
toxic levels *	5-20	5-30	20-100	50-500	-	100-400

\* toxic levels from Kabata-Pendias and Pendias (1984).

Plant metal levels were strongly correlated with extractable soil metal levels (Table 8). Saturation extractable levels of metals did not correlate well with plant response. Total levels correlated highly with plant uptake in a few, but not all cases. The ammonium acetate and DTPA extractable metal levels were most highly correlated with plant uptake. The DTPA extraction performed slightly (but not significantly) better overall.

Crested wheatgrass tended to take up slightly more copper and nearly twice as much zinc as pubescent wheatgrass at similar soil levels of copper and zinc.

Typical ranges of copper in plant tops varies widely (Kubota-Pendias and Pendias 1984) but seldom exceeds 20 ppm. Many plants have a tendency to reduce transport of copper to plant tops at excess copper levels making it difficult to assign a toxic plant level for copper. The tendency for plant and soil copper levels to correlate with plant performance indicates that copper may inhibit vegetation. Based on this observation, a likely maximum tolerable level of plant copper would be 15 ppm. This plant level would equate to a maximum tolerance of 130 ppm DTPA extractable copper for crested wheatgrass. A prudent "caution" level of DTPA extractable copper would be 100 ppm.

Table 8. Correlation of plant metal levels with soil extractable levels.

crested wheatgrass (n=9)

Cu = 17.13 - 1.12	Cu-sat	R2 = .001
Cu = 8.18 + 0.11	Cu-NH <sub>4</sub> OAc	R2 = .48 *
Cu = 5.36 + .073	Cu-DTPA	R2 = .51 *
Cu = 1.65 + .038	Cu-total	R2 = .84 *
Zn = 234 + 124	Zn-sat	R2 = .06
Zn = -46.7 + 2.33	Zn-NH <sub>4</sub> OAc	R2 = .69 *
Zn = -109.7 + 2.03	Zn-DTPA	R2 = .71 *
Zn = 56.4 + 0.67	Zn-total	R2 = .28

pubescent wheatgrass (n=12)

Cu = 13.7 - 1.92	Cu-sat	R2 = .02
Cu = 9.2 + .047	Cu-NH <sub>4</sub> OAc	R2 = .25
Cu = 8.3 + .291	Cu-DTPA	R2 = .35 *
Cu = 9.4 + .0099	Cu-total	R2 = .22
Zn = 105.8 + 16.6	Zn-sat	R2 = .20
Zn = -121.2 + 1.69	Zn-NH <sub>4</sub> OAc	R2 = .51 *
Zn = -164.3 + 1.44	Zn-DTPA	R2 = .52 *
Zn = 168.1 - .18	Zn-total	R2 = .02

\* significant at p<.05.

Typical ranges of zinc in plant tissue varies widely by species and season (Kubota-Pendias and Pendias 1984) but seldom exceeds 40 ppm for grasses and cereals. Many plants exhibit tolerance for excessive zinc and many do not translocate Zn to plant tops. Based on the tendency for excess zinc to reduce plant performance, maximum allowable plant zinc levels in this study could best be generalized at 75 for pubescent wheatgrass to 150 ppm for crested wheatgrass. These values translate into allowable DTPA concentrations in soil of 160 ppm for pubescent wheatgrass and 125 ppm for crested wheatgrass. A prudent "caution" level of DTPA Zinc would be 120 ppm.

CONCLUSIONS AND RECOMMENDATIONS

A two-year study was conducted to develop techniques for re-establishing forages on lands disturbed by mining. Affected soils had been irrigated with tailings-contaminated water through the early 1900's and though it was once productive farm ground it was mostly barren of vegetation.

Experimental treatments included trials of a number of forage species, and use of three rates of lime. Plant performance on the plots was variable. Poor performance may be attributed in part to the dry hot year that plants were established (1985).

Use of lime to correct acid problems was necessary to allow plant establishment. Prediction of lime requirement on contaminated agricultural soils requires extensive sampling to characterize both the average and range in lime requirement. Lime rates should be targeted to improve 85 to 95

percent of soils to a target pH (6 to 6.5).

Liming alone did not insure adequate plant performance on copper and zinc enriched soils. Zinc and perhaps copper toxicity reduced plant vigor on plots with pH of 7 or above. Other soil amendments like manure and phosphorus may be required to further reduce zinc and copper availability to plants. No plants sampled appeared to accumulate levels of metals that could be toxic to livestock.

Broadcast seeding at high seeding rates may best utilize suitable soil areas, though protection from wind erosion would be required. Additional conclusions are listed below:

1. Liming can be used to raise the pH of acid-contaminated agricultural soils. The SMP buffer lime test accurately predicts the lime requirement indicating little if any sulfide sulfur.
2. Plant vigor and establishment is limited unless pH is raised to at least 6.1 or higher.
3. Liming reduces soluble levels of zinc, copper, and cadmium which should reduce the potential of treated soils to pollute ground water. Extractable arsenic levels were not affected by liming.
4. Poor stands on low pH plots may have been due to slow attainment of pH thus causing damage to seedlings. Vegetation was spotty in each plot with healthy vigorous plants adjacent to stunted chlorotic ones. In order to take advantage of all suitable seedbed area, broadcast seeding with increased seeding rates may be desirable. Erosion protection will have to be provided.
5. Raising pH does not guarantee successful plant performance. Plant uptake correlates with extractable metal levels. Elevated levels of extractable zinc and copper are not reduced by liming. Other soil amendments like phosphate or organic matter may further reduce extractable metal levels by forming less available minerals or adsorbed phases.
6. Soil DTPA and ammonium acetate extractable copper and zinc correlated well with plant uptake. Based on the observation that vigor was reduced by elevated plant copper and zinc, tolerable soil levels can be generalized for this site. In order to avoid reduced plant performance, DTPA zinc should not exceed 120 ppm and DTPA copper should not exceed 100 ppm.

LITERATURE CITED

Baker, D.E. and M.C. Amacher. 1982. Nickel, copper, zinc, and cadmium. Pages 323-336 in A.L. Page, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 2, 2nd.

- edition. Madison, WI. 1159 pp.
- Bradshaw, A.D. and M.J. Chadwick. 1980. The Restoration of Land. University of California Press, Berkeley and Los Angeles. 317p.
- Burt, R.A. and F.T. Caruccio. 1986. The effect of limestone treatments on the rate of acid generation from pyritic mine gangue. *Environ. Geochem. and Health*. 8:71-78.  
<http://dx.doi.org/10.1007/BF02311025>
- Caruccio, F.T. 1968. An evaluation of factors affecting acid drainage production and ground water interactions in selected areas of western Pennsylvania. Pages 107-151 in *Second Symposium on Coal Mine Drainage Research*. Bituminous Coal Research, Inc.
- Caruccio, F.T., G. Geidel and J.M. Sewell. 1976. The character of drainage as a function of the occurrence of framboidal pyrite and ground water quality in eastern Kentucky. Pages 1-16 in *Sixth Symposium on Coal Mine Drainage Research*. Bituminous Coal Research, Inc.
- Caruccio, F.T. 1980. Estimating the acid production potential of coal mine refuse. Pages 437-443 in Chadwick and Goodman, eds. *The Ecology of Resource Degradation and Renewal*. Blackwell Scientific Pub. London.
- Caruccio, F.T. and G. Geidel. 1984. The prediction of acid mine drainage from coal strip mines. *Proceedings of the Conference on Reclamation of Abandoned Acid Spoils*. Missouri Dept. of Natural Resources, Land Reclamation Commission.
- Ganje, T.J. and D.W. Rains. 1982. Arsenic. Pages 385-402 in A.L. Page, ed. *Methods of Soil Analysis*. American Society of Agronomy Monograph No. 9, Part 2, 2nd edition. Madison, WI. 1159 pp.
- Geidel, G. 1979. Alkaline and acid production potentials of overburden material: the rate of release. *Reclamation Review*. 2:101-107.
- Kabata-Pendias, A., H. Pendias. 1984. Trace Elements in Soils and Plants. CRC Press, Inc. Boca Raton, Florida. 292p.
- Lindsay, W.L. 1979. Chemical Equilibria in Soils. Wiley Interscience. New York. 449p.  
<http://dx.doi.org/10.2136/sssai1982.03615995004600060045x>
- Little, T.M. and F.J. Hills. 1972. Statistical Methods in Agricultural Research. University of California, Davis. 242p.
- Mattigod, S.V., A.L. Page, and I. Thornton. 1986. Identification of some trace metal minerals in a mine-waste contaminated soil. *Soil Sci. Soc. Am. J.* 50:254-258.  
<http://dx.doi.org/10.2136/sssai1986.03615995005000010050x>
- McLean, E.O., S.W. Dunford and F. Coronel. 1966. A comparison of several methods of determining lime requirements of soils. *Soil Sci. Soc. Am. Proc.* 30:26-30.  
<http://dx.doi.org/10.2136/sssai1966.03615995003000010015x>
- McLean, E.O. 1982. Soil pH and lime requirement. Pages 199-224 in A.L. Page, ed. *Methods of Soil Analysis*. American Society of Agronomy Monograph No. 9, Part 2, 2nd edition. Madison, WI. 1159 pp.
- National Academy of Sciences. 1980. Mineral Tolerance of Domestic Animals. Committee on Animal Nutrition, National Research Council. Washington, D.C.
- Parr, J.F., P.B. Marsh, J.M. Kla. 1983. Land Treatment of Hazardous Wastes. Noyes Data Corporation, Park Ridge, New Jersey. 418p.
- Peech, M. 1965. Lime requirement. Pages 927-932 in C.A. Black, ed. *Methods of Soil Analysis*. American Society of Agronomy Monograph No. 9, Part 2. Madison, WI. 1572 pp.
- Rice, P.M. and G.J. Ray. 1984. Floral and faunal survey and toxic metal contamination study of the Grant-Kohrs ranch national historic site. Final report to National Park Service, Deer Lodge, MT.
- Sandoval, F.M. and J.R. Power, 1977. Laboratory methods recommended for chemical analysis of mined-land spoils and overburden in western United States. U.S. Dept. of Agric., Agric. Handbook No. 525.
- Shoemaker, H.E., E.O. McLean, and P.F. Pratt. 1961. Buffer methods for determining lime requirement of soils with appreciable amounts of soluble aluminum. *Soil Sci. Soc. of Amer. Proc.* 19:164-167.
- Smith, R.M., W.E. Grube Jr., T. Arkele Jr. and A.A. Sobek. 1974. Mine spoil potentials for soil and water quality. West Virginia University. EPA-670/2-74-070.
- Snedecor, G.W. and W.G. Cochran. 1978. *Statistical Methods*. Iowa State University Press. Ames, Iowa. 593 p.
- Sobek, A.A., M.A. Bambenek, and D. Meyer. 1982. Modified soxhlet extractor for pedologic studies. *Soil Sci. Soc. of Amer. J.* 46:1340-1342
- Sobek, A.A., W.R. Schuller, J.K. Freeman and R.M. Smith. 1978. Field and laboratory methods applicable to overburdens and mine soils. U.S. Environmental Protection Agency. EPA-600/2-78/054.
- Sturey, A.S., J.R. Freeman, T.A. Keeney and J.W. Strumm. 1982. Overburden analyses by acid-base accounting and simulated weathering studies as a means of determining the probable hydrological consequences of mining and Sedimentology and Reclamation, Univ. of Kentucky, Lexington. pp. 163-179.
- Sullivan, P.J. and A.A. Sobek. 1982. Laboratory

weathering studies of coal refuse. Miner.  
Environ. 4:9-16.

<https://doi.org/10.1007/BF02093338>

Surbrugg, J.E. 1982. Copper and zinc tolerance in two  
Montana grass species growing on copper mill  
tailings. Unpubl. M.S. thesis, Montana State  
University, Bozeman, MT. 56p.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and  
improvement of saline and alkali soils.  
Agricultural Handbook No. 60. U.S. Dept. of  
Agriculture. Washington D.C.

