

REVEGETATION OF HEAVY METAL-CON-TAMINATED MINE TAILINGS (CHAT)

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ABSTRACT

Mined areas near the city of Galena, Kansas, are a continuing source of Pb, Zn, and Cd contamination that move off site in response to erosion by wind and running water. Revegetation of the mine tailings (chat) could limit the spread of these heavy metals. In this study, treatments that included the addition of manure, as well as inoculation with mycorrhizae or the addition of benomyl fungicide, were imposed on 24 test plots. Tall fescue grass was established in all seeded plots, and by the end of the third growing season, the vegetative cover for seeded treatments averaged 28.5%, and basal cover averaged 10.4%, indicating a decrease in vegetative and basal cover from a maximum during the course of the experiment. Zn, which the addition of manure had earlier significantly concentrated in the organic-bound fraction of the chat, has more recently been significantly concentrated in the more bioavailable exchangeable fraction of the manured plots. Together with the decrease of vegetative and basal cover, and with a significant decrease in available K in the manured plots, this may indicate a decrease in effectiveness of the manure treatments over time.

Key words: chat, heavy metals, revegetation, bioavailability

INTRODUCTION

From the mid-1800's to approximately 1970, the Tri-State district of southeastern Kansas, southwestern Missouri, and northeastern Oklahoma was one of the most important Pb and Zn mining areas of the world (McKnight and Fischer, 1970; Spruill, T., 1987). Surface mine spoils (also called chat) are still present in the city of Galena, Kansas, and adjacent areas (Figure 1), creating a source of heavy metal pollution that can spread to outlying areas by the action of wind and running water. Sources of the Pb and Zn are residual galena (PbS) and sphalerite (ZnS) ore, and Cd is also present where it substitutes for Zn in sphalerite (Berry and Mason, 1959; Klein and Hurlbut, 1977). Despite the passage of time, vegetation has had difficulty in establishing itself on the piles of chat. Revegetation has been shown to decrease the off-site spread of chat (Darmer, 1992), and would also decrease the possibility of off-site heavy metal pollution because of the association of galena and sphalerite with the chat. In this experiment, test plots were established in order to determine optimal conditions for revegetation with tall fescue grass. Previous mathematical modeling for the Galena area (Green et al.,1997) has indicated that grass buffers could reduce sediment loss by 18% to 25%, and that 100% grass cover would reduce sediment loss by nearly 70% compared to bare soil.

PROCEDURE

Six treatments with four replications were imposed on 24 plots on chat material within the city limits of Galena, Kansas. The treatments included a manure-amended and seeded control (SC);

two treatments that were manure-amended, seeded, and inoculated with mycorrhizae fungi (I-1 and I-2, one of which was originally planned to have been planted with poplar trees); and a manureamended, seeded treatment on which benomyl fungicide was applied (BF). Mycorrhizae inoculation was intended to assist the tall fescue in resisting Zn phytotoxicity by preventing its uptake by the plants, while by contrast the benomyl fungicide treatment was intended to prevent any mycorrhizae activity. Also included were an unseeded and manure-amended control (UMC), and an unseeded control which was not manure-amended (UC). After the tall fescue was established in satisfactory stands, Pb, Zn, and Cd in the chat were sequentially extracted according to the methodology of Tessier (1979), allowing the heavy metal concentration of the exchangeable, carbonate-bound, Fe/ Mn oxide-bound, organic-bound and residual fractions to be analyzed. Zn concentrations are reported here. The exchangeable fraction is considered to be the most bioavailable (most available to organisms), and the residual fraction the least, with the other fractions having intermediate degrees of bioavailability. The amount of vegetative and basal cover in the vegetated test plots and available soil nutrients were also measured. The SC, I-1 and I-2, and BF treatments were seeded and became vegetated with tall fescue. All treatments except UC had manure added to them to insure availability of plant nutrients for the fescue.

RESULTS

Figure 2 shows vegetative (crown) cover and Figure 3 shows basal ground cover for the test plots over a two-year period beginning in September 1996 and ending in October 1998. Vegetative cover (28.5%) for October 1998 was lower than previous point counts in May 1997, October 1997, and May 1998 (71.7%; 60.2%, and 51%, respectively), although not as low as reported in the initial vegetative cover point count following planting of the tall fescue (26.7% in September 1996). The October 1998 basal cover (10.4%) was actually the lowest recorded since planting the tall fescue, when compared with previous point counts from September 1996 (11.8%), May 1997 (35.7%), October 1997 (23.6%), and May 1998 (36.9%). These decreases may indicate that the manure is no longer supplying nutrients to the fescue, or possibly that it is no longer helping to alleviate problems with Zn phytotoxicity on the mine spoils material.

Extractable nitrate nitrogen, ammonium nitrogen, P, and K concentrations in soil samples collected during the spring of 1998 are shown in Table 1. Soil nitrogen in the test plots averaged 3.4 mg/kg, up from an average 2.3 mg/kg in the spring of 1996 (not shown), and soil ammonium nitrogen averaged 2.4 mg/kg (down from an average 7.0 mg/kg in the spring of 1996). There is no significant difference in soil nitrate nitrogen and ammonium nitrogen between the first five treatments listed in Table 1 (SC; I-1; I-2; BF, and UMC, all of which had added manure), and the unseeded (and non-manured) control (UC). Soil P is significantly higher in the first five treatments listed in Table 1 (an average 130.2 mg/kg, up from an average 91.8 mg/kg in the spring of 1996) than it is in the unseeded control UC (14.1 mg/kg). Soil K in Table 1 is significantly higher in the first five

(manured) treatments (an average 43.1 mg/kg) than it is in the non-manured, unseeded control UC (23.2 mg/kg), but is considerably below what it was in the spring of 1996 (281.6 mg/kg). Therefore, although there have not been major changes in soil nitrate nitrogen and ammonium nitrogen in the manured test plots, and soil P has actually increased over time as it apparently continues to be released from the manure, there has been a significant decrease in the effectiveness of the manure in releasing K. As suggested earlier, the manure may no longer be supplying essential nutrients to the fescue.

Chaney (1983) considered Zn concentrations of 500 to 1,500 mg/kg Zn in plant tissue to be phytotoxic. Levy, Redente, and Uphoff (1999) grew switchgrass and big bluestem in chat collected from the Tri-State mining district in southwestern Missouri, and concluded that there was little evidence of Zn or other heavy metal phytotoxicity. However, tall fescue plant tissue Zn concentrations from vegetated test plots in the present study (not shown) averaged 490 mg/kg in the summer of 1996, and 706 mg/kg in the spring of 1997. Zinc phytotoxicity would therefore appear to have become a problem during the course of the experiment and may be related to the loss of effectiveness of the manure in concentrating soil Zn.

The sequential extraction scheme of Tessier et al., 1979, should allow the influence of vegetation and manure amendments on the fractionation of the Pb, Zn, and Cd in the chat to be evaluated. In the spring of 1996, the presence of vegetation (first four treatments in Table 2) had not influenced the distribution of Zn. However, the presence of manure in the SC; I-1; I-2; BF, and UMC treatments had significantly reduced exchangeable and residual Zn concentrations (an average 218 and 7562 mg/kg, respectively) compared to the non-manured UC treatment (where exchangeable and residual Zn concentrations were 338 and 12,725 mg/kg, respectively). Meanwhile, the organicbound Zn concentration in the five manured treatments (which averaged 683 mg/kg) was significantly greater than in the non-manured UC treatment (324 mg/kg). The presence of manure, therefore, had the effect of moving Zn from the exchangeable and residual fractions into the organicbound fraction. By the fall of 1997, vegetation still did not influence the distribution of Zn, but the influence of the presence of manure on Zn distribution had changed (Table 3). Exchangeable Zn in the unseeded (and nonmanured) control (UC) was lower than in the manured treatments (357 mg/ kg versus an average of 714 mg/kg for the manured treatments). Because exchangeable Zn in the unseeded control was essentially the same in the fall of 1997 as it was in the spring of 1996 (357) mg/kg versus 338 mg/kg), this may be another indication that the manure treatments have lost their effectiveness over time. Further, the increase in bioavailable exchangeable Zn have been the cause of phytotoxic levels of Zn in the tall fescue plant tissue. Residual Zn in the unseeded control remained higher than in the manured treatments during the fall of 1997 (6,498 mg/kg versus an average 4,295 mg/kg, respectively), but was no longer significantly higher. Total Zn concentration for all test plots in this study averaged 19,819 mg/kg in the spring of 1996, and 21,539 mg/kg in the

fall of 1997 (Tables 2 and 3), within 8% agreement. Total Zn concentrations for individual treatments at the two sampling times agreed within 13%, except for treatment I-1 (15,460 mg/kg in the spring of 1996, and 19,649 mg/kg in the fall of 1997, for a 21% difference), and I-2 (14,140 mg/kg in the spring of 1996, and 19,494 mg/kg in the fall of 1997, for a 28% difference).

CONCLUSIONS

While the presence of the tall fescue does not in itself appear to reduce Zn content of the Galena mine tailings, models that incorporate vegetative buffers have shown a reduction in the redistribution of the mine tailings by wind and water, thereby reducing the spread of heavy metal contamination. Adding manure to test plots not only aids in the growth of the tall fescue planted there, it also tends to cause the redistribution of the Zn into the organic fraction and away from the more bioavailable exchangeable fraction. This effect decreases over time as the manure treatments become less effective.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of a grant from the Great Plains/Rocky Mountain Hazardous Substance Research Center.

REFERENCES

- Berry, L., and B. Mason, 1959, Mineralogy, W. H. Freeman and Company, San Francisco, 612 p.
- Chaney, R., 1983, Potential Effects of Waste Constituents on the Food Chain, In:J. Parr, *et al.*, (Eds.), Land Treatment of Hazardous Wastes, Noyes Data Corporation, Park Ridge, New Jersey, pp. 152-240.
- Darmer, G., 1992, Surface Mining: Ecological Guidelines for Reclamation, Van Nostrand Reinhold, New York, 201 p.
- Green, R., L. Erickson, R. Govindaraju, and P. Kalita, 1997, Modeling the Effects of Vegetation on Heavy Metals Containment, 12th Conference on Hazardous Waste Research, Kansas City, Missouri, pp. 476-487.
- Levy, D., E. Redente, and G. Uphoff, 1999, Evaluating the Phytotoxicity of Pb-Zn Tailings to Big Bluestem (*Andropogon gerardii* vitman) and Switchgrass (*Panicum virgatum* L.), Soil Science, vol. 164, pp. 363-375.
- McKnight, E., and R. Fischer, 1970, Geology and Ore Deposits of the Picher Field, Oklahoma and Kansas, United States Geological Survey Professional Paper 588, 165 p.
- Moore, J., 1998, Maps of the U.S.A., Evan-Moore, Monterey, California, 63 p.
- Klein, C., and C. Hurlbut, 1977, Manual of Mineralogy, 21st edition, John Wiley & Sons, Inc., New York, 681 p.
- Spruill, T., 1987, Assessment of Water Resources in Lead-Zinc Mined Areas in Cherokee County, Kansas, and Adjacent Areas, United States Geological Survey Water-Supply Paper, No. 2268, 68 p.

Tessier, A., P. Campbell, and M. Bison, 1979, Sequential Extraction Procedure for the Speciation of Particulate Trace Metals, Analytical Chemistry, vol. 51, pp. 884-851.

Table 1. Extractable nitrate nitrogen, ammonium nitrogen, P, and K concentrations for soil samples collected in the spring of 1998. Numbers within a column followed by the same letter are not significantly different at P=0.05.

| TREATMENT | NO-3-N | NH ⁺ ₄ -N | P | | K | | |
|--------------------------------|----------|---------------------------------|------------|------------|-----------|-----------|--|
| Seeded Control (SC) | 4.2a | 2.4a | 116.4ab | | 43.2a | | |
| Inoculated-1 (I-1) | 2.7a | 2.1a | 161.4a | | 44.2a | | |
| Inoculated-2 (I-2) | 2.1a | 2.9a | 145.5ab | 130.2 ave. | 39.5a | 43.1 ave. | |
| Benomyl Fungicide (BF) | 5.0a | 2.3a | 124.4ab | | 48.0a | | |
| Unseeded Manured Control (UMC) | 3.4a | 2.4a | 103.3b | | 40.7a | | |
| Unseeded Control (UC) | 2.8a | 2.2a | 14.1c | | 23.2b | | |
| | 3.4 ave. | 2.4 ave. | 111.0 ave. | | 39.8 ave. | | |

Table 2. Fractionation of Zn in soil collected during the spring of 1996 into exchangeable, carbonate, Fe/Mn, organic-bound, and residual fractions (in mg/kg). Numbers within a column followed by the same letter are not significantly different at P=0.05.

| TREATMENT | EXCHANG. | | CARBONATE | | Fe/Mn OXIDE | | ORGANIC | | RESIDUAL | | TOTAL Zn | |
|---|----------|------|-----------|------------------|-------------|--------------|---------|-------------|----------|----------------|----------|---------------|
| Seeded Control (SC) | 239 b | | 8068bc | . 8069 . ave. | 1557ab | 1661 ave. | 788a | 683 ave. | 7499bcd | . 7562 ave. | 18151 | 19819 ave. |
| Inoculated-1 (I-1) | 194bc | | 6491c | | 1130b | | 661ab | | 6984cd | | 15460 | |
| Inoculated-2 (I-2) | 243b | 218 | 6080c | | 1325b | | 747a | | 5745d | | 14140 | |
| Benomyl Fungicide (BF) | 174c | ave. | 9512b | | 2112a | | 669ab | | 8253b | | 20720 | |
| Unseeded Manured Control (UMC) | 242b | | 10194ab | | 2182a | | 548b | | 9331b | | 22497 | |
| Unseeded Control (UC) | 338a | | 12500a | | 2060a | | 324c | | 12725a | | 27947 | |

Table 3. Fractionation of Zn in soil collected during the fall of 1997 into exchangeable, carbonate, Fe/Mn oxide, organic-bound, and residual fractions (in mg/kg). Numbers within a column followed by the same letter are not significantly different at P=0.05.

| TREATMENT | EXCHANG. | | CARBONATE | | Fe/Mn OXIDE | | ORGANIC | | RESIDUAL | | TOTAL Zn | |
|--------------------------------------|----------|-------------|-----------|--------------|-------------|-------------|---------|--------------|----------|--------------|----------|---------------|
| Seeded Control (SC) | 677ab | | 6767a | | 5852a | | 1969a | | 3676c | | 18941 | |
| Inoculated-1 (I-1) | 556bc | | 7570a | | 5836a | | 1574a | | 4113b | | 19649 | |
| Inoculated-2 (I-2) | 793ab | 714 ave. | 7021a | 7843 ave. | 5781a | 6390 ave | 1709a | 1744 ave. | 4190b | 4295 ave. | 19494 | 21539 ave. |
| Benomyl Fungicide (BF) | 712ab | | 8935a | | 6874a | | 1789a | | 4687ab | | 22997 | |
| Unseeded Manured Control (UMC) | 831a | | 8923a | | 7605a | | 1677a | | 4807ab | | 23843 | |
| Unseeded Control (UC) | 357c | | 7247a | | 9398a | | 813a | | 6498a | | 24313 | |



Figure 1. Map showing the location of the city of Galena, Kansas, in the Tri-State mining district of southeastern Kansas, southwestern Missouri, and northeastern Oklahoma (base map of the United States after Moore, 1998).

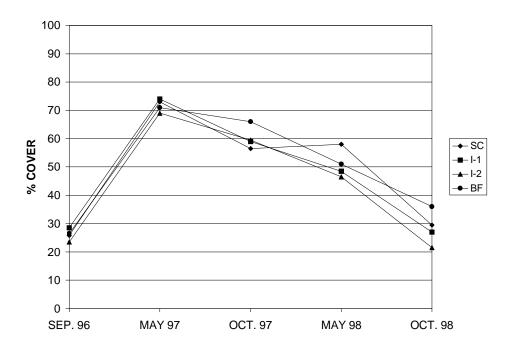


Figure 2. Average vegetative cover over time. SC = Seeded Control; I-1 =Inoculated-1; I-2 = Inoculated-2; and BF = Benomyl Fungicide.

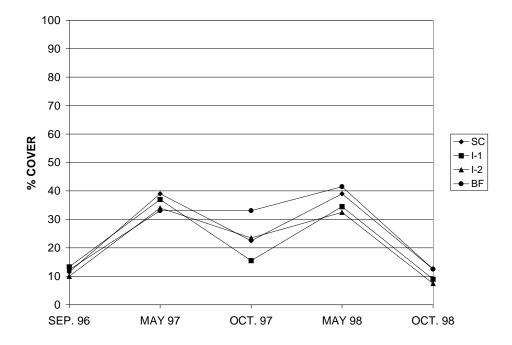


Figure 3. Average basal cover over time. SC = Seeded Control; I-1 = Inoculated-1; I-2 = Inoculated-2; and BF = Benomyl Fungicide.