

Compost amendment of Cu–Zn minespoil reduces toxic bioavailable heavy metal concentrations and promotes establishment and biomass production of *Bromus carinatus* (Hook and Arn.)

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Organic amendment decreased toxic bioavailable heavy metal concentrations in metalliferous minespoil, thereby promoting plant growth.

Abstract

A series of lab and greenhouse studies were undertaken to understand how Cu and Zn toxicity influences *Bromus carinatus* (Hook and Arn.) growth, to what degree an organic amendment (yard waste compost) may reduce Cu and Zn bioavailability in Cu–Zn minespoil and promote plant growth in combination with fertilizer, and how the vertical distribution of compost in the minespoil influences rooting depth. Root Cu and Zn toxicity thresholds were determined to be 1 mg L^{-1} and 10 mg L^{-1} in solution, respectively. The compost amendment had exceptionally high Cu and Zn binding capacities (0.17 and $0.08 \text{ g metal g C}^{-1}$, for Cu and Zn, respectively) that were attributed to high compost humic and fulvic acid concentrations. Maximum plant biomass was achieved when minespoil was amended with compost and fertilizer in combination. Fertilizer alone had no effect on plant growth. Mixing compost into the minespoil was essential to promote adequate rooting depth.

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1. Introduction

Mine wastes represent the greatest total proportion of waste generated globally by industrial activity, with an estimated 15–20 billion metric tons produced annually (Lottermoser, 2003). Mining activities in the United States alone produce approximately 1 billion metric tons of mine wastes annually in addition to the 50 billion tons that have already been generated (Thomas, 1985). Approximately 50% (0.5 billion metric tons) of the total mine wastes produced annually in the US are associated with Cu recovery. Metal ores, like Cu and Zn, are frequently associated with sulfur-bearing minerals including

FeS₂ (pyrite) (Evangelou, 1995; Lottermoser, 2003). Microbially-mediated oxidation of sulfur-bearing minerals generates acid mine drainage (AMD) laden with toxic levels of trace elements including Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, and Cd (Evangelou, 1995). The US Forest Service has estimated that acid mine drainage from up to 50,000 mines is impacting over 23,000 km (0.4%) of the approximately 5,600,000 km of rivers and streams in the US (Matlock et al., 2002). An example of one such mine is the abandoned Penn Cu–Zn mine in central California, USA.

The Penn mine is located within the 250 km long Cu–Zn belt of the western Sierra Nevada foothills, in Calaveras County, California (Sections 3 and 4, T.4N., R.10E, and Section 33, T.5N., R.10E, Mount Diablo base meridian). Nearly a century of mining activity at the Penn mine resulted in the deposition of 275,000 m³ of pyrite- and heavy metal-rich

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tailings within a 10 ha drainage to the Mokelumne River and adjacent Camanche Reservoir and has left the site devoid of vegetation (Jenkins, 1948). Historically, toxic AMD run-off from the mine resulted in frequent fish kills in the Mokelumne River (Finlayson and Rectenwald, 1978). Penn mine AMD has a pH ~ 3 and contains toxic concentrations of heavy metals including Al, Fe, Cd, Cu, and Zn. Penn mine seasonal AMD chemistry and watershed hydrology have been characterized in detail previously by Hamlin and Alpers (1995), Hamlin et al. (1999), Bambic et al. (2006), and Silk et al. (2006).

Coarse minespoil, such as that found at the Penn mine, is inhospitable to plant establishment and growth due to poor water-holding capacity, low organic matter content, nutrient deficiency, heavy metal toxicity, and low microbiological activity. Revegetation of mine wastes is desirable to reduce erosion and increase evapotranspiration, thereby reducing the generation of AMD. Additionally, revegetation can improve habitat for wildlife and the overall aesthetics of the site. Current approaches to the revegetation of metalliferous mine wastes include (1) direct seeding into mine wastes with metal-tolerant species, (2) amendment of mine waste with organic (sewage sludge, peat, compost) and/or inorganic amendments (fertilizer, lime), and (3) isolating the mine waste under a cap overlain with an adequate depth of growth medium to provide adequate rooting depth (80 cm as cited by Williamson et al. (1982) and Tordoff et al. (2000)). While most mineral capping materials, such as gravel, sand, and clay, merely provide an inert barrier between the revegetation community and the underlying toxic mine waste, organic amendments actively increase water-holding capacity and cation exchange capacity of the substrate, provide a slow-release nutrient source, complex toxic heavy metals, and boost microbial activity (Tordoff et al., 2000).

In 1999, barren Penn minespoil piles were graded to restore landscape contours and drainage patterns to pre-mining conditions. The minespoil was then revegetated by spreading a fertilizer- and manure-amended subsoil layer of approximately 15 cm depth over most of the site followed by seeding with a commercial mix of deep-rooted, drought-tolerant, California native grasses and forbs, including *Bromus carinatus* (Hook and Arn.; California brome) (M. Busnardo, HT Harvey and Associates, personal communication). Although native grasses, including *B. carinatus*, composed a significant portion of the revegetation community in the first growing season following seeding, the revegetation community rapidly became dominated by shallow-rooted, invasive annuals including *Lolium multiflorum* (Lam.; Italian ryegrass) and *Bromus diandrus* (Roth.; ripgut brome) from annual grasslands surrounding the site (D. Bambic, Larry Walker Associates, personal communication). Approximately 10% of the site that did not receive subsoil application during the revegetation project continues to remain barren seven years later.

A series of lab and greenhouse studies were undertaken to understand how Cu and Zn toxicity influences *B. carinatus* growth, to what degree an organic amendment (yard waste compost) may reduce Cu and Zn bioavailability in Cu–Zn minespoil and promote plant growth in combination with

fertilizer, and how the vertical distribution of compost in the minespoil influences rooting depth. The objective of study 1 was to determine the Cu and Zn binding capacity of the compost used in amendment trials. The focus of study 2 was to determine the Cu and Zn toxicity thresholds of the study species *B. carinatus*. Study 3 examined the biomass production and nutrient content of *B. carinatus* grown in compost-amended, barren Penn minespoil. Study 4 investigated how the vertical distribution of compost amendment in barren Penn minespoil influenced the rooting depth of *B. carinatus*. The findings from these component studies can be integrated to guide the design of treatments for mined land revegetation projects.

2. Materials and methods

2.1. Study 1. Humic, humic acid, and fulvic acid content and Cu (II) and Zn (II) binding capacity of compost

Yard waste compost consisting of decomposed grass clippings, leaves, and wood chips (US EPA 503; thermophilic process followed by a 90-day aerobic curing period) was obtained from the city of Redding municipal compost facility, Redding, California. The compost was air-dried and screened to less than 2 mm particle size. Compost humic acid (HA) and fulvic acid (FA) content was determined using the methods of Schnitzer (1982).

For the compost Cu (II) and Zn (II) binding capacity determination, separate Cu and Zn stock solutions were prepared from deionized water and reagent-grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Fisher Scientific, Fairlawn, New Jersey, USA) at the following Cu or Zn molar concentrations (pH 7.0): 0.001, 0.01, 0.1, 0.3, and 0.5. The Cu and Zn stock solutions were standardized by analysis on ICP-MS (Agilent 7500i, Palo Alto, California, USA). The Cu and Zn stock solutions were measured to be within 5% of their original target values. The actual concentration of the stock solutions was used in metal compost binding calculations.

Three gram compost samples were weighed into 50 mL conical centrifuge tubes and 15 mL of either Cu or Zn solution was added for three replicates of each treatment. After shaking for 2 h at 250 rpm, the tubes were centrifuged for 10 min at 8000 rpm to separate the solution phase from the solid phase. The supernatant was then filtered to remove any remaining suspended compost particles and then analyzed for Cu or Zn concentration by ICP-MS along with samples of the Cu and Zn stock solutions. Dissolved organic carbon (DOC) content in each sample was determined with a TOC-V_{CSH} total organic carbon analyzer (Shimadzu Corporation, Kyoto, Japan). Total Cu and Zn bound to compost was calculated as the concentration difference between the solution-treated compost sample and its corresponding stock solution. Metal binding capacity was identified as the treatment solution concentration where the percentage of metal bound dropped significantly below that of the next lower treatment solution concentration.

2.2. Study 2. Cu and Zn toxicity thresholds of *B. carinatus*

Cu and Zn thresholds of *B. carinatus* seedlings were determined based on the modification of methods described by Wilkins (1978). Rhizotrons were constructed from 10 cm $\times$ 10 cm $\times$ 1.5 cm clear polystyrene petri dish plates (Fisher Scientific International, New Hampshire, USA) by cutting away one of the 1.5 cm sidewalls. The two halves of the petri dish plates were bound together with rubber bands and oriented vertically to provide a narrow container with wide horizontal dimensions that was ideal for root growth observations. Rhizotrons were filled with silica sand and moistened to field capacity with Cu (as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, pH 7.0) or Zn (as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, pH 7.0) solutions at the following concentrations (mg L^{-1}): 0.1, 0.5, 1.0, 5, 10.0, 20.0, 30.0, 40.0, 50.0, 100.0, and 200.0. No other nutrients were supplied. Since no site-collected *B. carinatus* seed was available from the Penn mine, seed was acquired from a commercial producer (Hedgerow Farms, Winters, California,

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