

# RECLAMATION OF COPPER MINE TAILINGS USING BIOSOLIDS AND GREEN WASTE<sup>1</sup>

by

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**Abstract.** Field experiments were conducted to determine the efficacy of applications of municipal biosolids and green waste (shredded plant material) for copper mine tailings reclamation. The study was established in southern Arizona on an area of fresh tailings with neutral pH. Two levels of green waste addition (0, 220 Mg/ha) and four levels of biosolids addition (0, 67, 134, 200 Mg dry matter/ha) were applied to the tailings. The tailings were seeded with a mixture of annual and perennial grasses and small shrubs. Plant biomass and tailing core samples (0-1.2m) were taken every six months during a two year period to determine plant establishment and growth, tailing N concentrations, microbial activity, total and available metals, and tailing NO<sub>3</sub>-N concentrations. Biosolids and green waste amendments significantly ( $p \leq 0.05$ ) enhanced plant growth, canopy cover, soil N concentrations, and soil basal respiration. Biosolids applications did not significantly ( $p \leq 0.05$ ) increase metal concentrations in soil or plant matter, and did not result in significant NO<sub>3</sub><sup>-</sup> movement.

## INTRODUCTION

Successful reclamation of copper mine tailing impoundments in Arizona will require the establishment of a self-sustaining plant and microbial community adapted to conditions at the site. Mine tailings possess a number of physical and chemical properties hostile to plant and microbial life, such as lack of organic matter, low available nutrients, low water retention, and high bulk density (Hue, 1995). Addition of organic materials can stimulate microbial activity, increase water holding capacity, and promote the formation of stable soil structure within the tailings (Hue, 1995). Municipal biosolids are a potentially useful amendment for use on mine tailings because of their ability to neutralize acidity, their organic matter content, and their content of N, P, and other plant nutrients (Hue, 1995). Furthermore, application to mine tailings represents a productive

disposal method for municipal biosolids.

The dry portion of biosolids is almost entirely organic, and rich in complex organic compounds with functional groups capable of chelating metals and reducing their phytoavailability and leachability (Knox, et al. 2001). Biosolids also contain high N and P concentrations, essential for plant growth. Organic N in the biosolids will be converted (mineralized) by microorganisms to NH<sub>4</sub><sup>+</sup>. Ammonium can be converted by microorganisms to NO<sub>3</sub><sup>-</sup>, which is highly mobile in soil and may percolate downward to contaminate groundwater (Hue, 1995). Therefore, it will be very important to monitor nitrate movement to determine potential negative impacts on groundwater quality. Adding plant material high in carbon (C) and low in N, such as sawdust or green waste (shredded plant material), may help prevent NO<sub>3</sub><sup>-</sup> loss (Hue, 1995). These amendments may stimulate microbial activity, resulting in the assimilation of mineralized nitrogen into the microbial biomass. This temporarily immobilizes inorganic N in the soil and limits NO<sub>3</sub><sup>-</sup> leaching.

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## OBJECTIVES

The objectives of this project were to i) determine the appropriate combinations of biosolids and green waste amendments for reclamation of fresh, pH neutral copper mine tailings in semi-arid environments such as found in southern Arizona, and ii) determine the effects

of the reclamation treatments on plant establishment and growth, soil organic matter and N, soil microbial activity, metal phytoavailability, and NO<sub>3</sub><sup>-</sup> concentrations.

### **MATERIALS AND METHODS**

Plots were established in October 1998 at BHP's San Manuel Copper Mine located just north of Tucson, Arizona. Amendments were incorporated into a leveled area of freshly-deposited tailings with neutral pH. The Class B biosolids were obtained from a City of Phoenix wastewater treatment plant and the green waste came from a landscaping company in Tucson. Prior to incorporation of the amendments, the tailings were analyzed for total metals by ICP (Soon and Abboud, 1993), and DTPA-extractable metals (Liang and Karamanos, 1993) (Table 1). The biosolids were analyzed for total K, P and total metal content by ICP (Soon and Abboud, 1993), and total N and C concentrations by combustion (Gavlak and Horneck, 1994) (Table 2). Total N and C content of the green waste was also determined by combustion (Gavlak and Horneck, 1994) (Table 2). The experiment was a complete factorial with two levels of green waste addition (0, 220 Mg/ha), four levels of biosolids addition (0, 67, 134, 200 Mg dry matter/ha), and three replications. The biosolids application rate of 67 Mg/ha is the maximum rate allowed by the Arizona Department of Environmental Quality for agronomic use. Currently there are no regulations for biosolids application on mine spoils, so 134 and 200 Mg/ha are simply multiples of this agronomic rate. The green waste application rate of 220 Mg/ha was used to achieve a minimum C:N ratio of 30:1 in those plots where green waste was applied. The treatments were arranged in a split-plot design.

Plot size was 7.3 m x 12.2 m. The green waste amendment was added first using a front-end loader to achieve the appropriate rates. Next, dewatered biosolids (70% solids) were applied at the appropriate rates also using a front-end loader. The amendments were spread evenly using a tractor drawn spreader, and then incorporated by disking. Plots were seeded with a mixture of annual and perennial plants including productive *Setaria leucopila*, *Sporobolus wrightii*, *Eragrostis lehmaniana*, *Atriplex lentiformis*, *Atriplex canescens*, and *Cynodon dactylon*. A sprinkler system uniformly irrigated the plot as needed until the stand was established, and then usually weekly after that. Irrigation was intended primarily as a supplement to rainfall, and irrigation frequency and amount were based upon weather conditions and plant needs.

Table 1. Metal concentrations in fresh, unamended

tailing material used in field experiment.

	<b>Total (ppm)</b>	<b>Avail. (ppm)</b>
Cu	1190	45
Zn	150	1.4
Cd	N/D*	0.03
Cr	8.7	0.08
Fe	27,260	33
Ni	12	N/D
Se	2.5	N/D
As	1.7	N/D
Pb	16	1.3

\* N/D= Not detected at a minimum detection limit

**Table 2. Total metal, K, P, C and N concentrations in biosolids and green waste amendments.**

	<b>Biosolids</b>	<b>Green waste</b>
C(%)	25	34
N(%)	4.4	1.1
K(%)	0.16	ND*
P(%)	2.8	ND
Fe(%)	3.4	ND
As(ppm)	9.8	ND
Cr(ppm)	74	ND
Cu(ppm)	520	ND
Ni(ppm)	49	ND
Pb(ppm)	44	ND
Se(ppm)	8.5	ND
Zn(ppm)	640	ND

\* ND= Not determined

Germination, percent plant canopy cover, stand density, species present, and their relative proportions were monitored regularly. Plant biomass production was determined by sampling all above-ground biomass in several 1m<sup>2</sup> rings within randomly selected areas of each plot in May 1999, December 1999, and October 2000. Composite plant samples (all species present in rings) collected from each plot were ground to pass through a 30-mesh sieve and analyzed for total N and C by CNS analyzer (Gavlak and Horneck, 1994). Plant total metal concentrations were determined following procedures described in USEPA Methods 3052 (USEPA, 1996). The Daubenmire Method (Daubenmire, 1959) was used to make visual estimates of the percent canopy cover (the projection of all plant parts vertically onto the ground) of each plot on the three sampling dates mentioned above.

Tailing core samples were collected from each plot using a 5- cm- diameter auger in October 1998, June 1999, December 1999, and October 2000. Several

cores were collected per plot in a random manner, and the cores were composited by depth (0-30 cm, 30-60 cm, 60-90 cm, 90-120 cm). Samples were analyzed for total C and N by CNS analyzer (Gavlak and Horneck, 1994), for extractable  $\text{NH}_4^+$  and  $\text{NO}_3^-$  by 2MKCl extraction and steam distillation (Keeney and Nelson, 1982), and for DTPA-extractable metals (Soon and Abbound, 1993).

Soil basal respiration measurements were made to assess the activity of belowground biomass using the procedure described by Anderson (1982). Twenty ml of 1.0M NaOH were pipetted into glass jars which were placed on the surface of the tailings. Over each jar an airtight, confining cylinder was pressed 2 cm into the soil. The NaOH acted as a trap for evolving  $\text{CO}_2$  over a period of 24 hours. The jars were then sealed and transported to the laboratory where the alkali solutions were first treated with excess  $\text{BaCl}_2$  to precipitate the carbonate as insoluble  $\text{BaCO}_3$ , and then titrated with HCl to determine the quantity of NaOH that had not reacted with  $\text{CO}_2$ .

## **RESULTS AND DISCUSSION**

All dependent variables in the split-plot design were analyzed by means of analysis of variance (ANOVA) with Statistix for Windows, Version 2.0 (Analytical Software, 1998). There were significant ( $p < 0.05$ ) effects of both biosolids and green waste on biomass production (Fig. 1). At the first sampling date in June 1999, significantly more growth was observed on plots with green waste. This is most likely due to higher soil moisture in plots amended with green waste. Additional measurements collected at the site

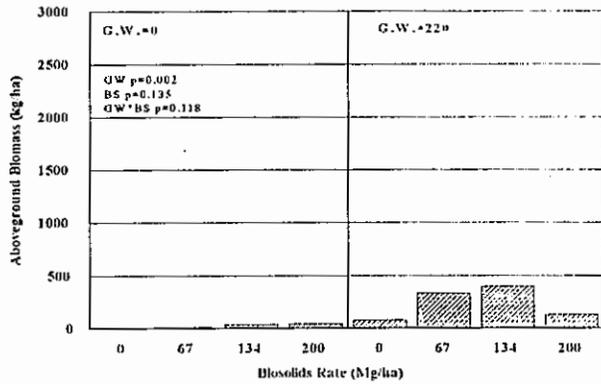
show consistently higher soil moisture with green waste (data not shown), due no doubt to a mulching effect. By the second sampling date in Dec. 1999 (Fig. 1) differences between plots with and without green waste were less obvious than at the first sampling date, but still evident. The same trend was evident in the Oct. 2000 sampling (Fig. 1). Seaker and Sopper (1988-II) found similar trends. Aboveground biomass on sludge amended minespoils increased with age during their five year study from 4.1 Mg/ha the first year, to 16.6 Mg/ha the fifth year. Canopy cover estimates (Fig. 2) also confirm the positive effects of biomass and green waste additions. Addition of green waste alone, or the minimum biosolids rate of 67 Mt/ha, resulted in more than 50% canopy cover compared to the control plots. The data from the October 2000 sampling (Fig. 2) confirm these trends. To date, it is clear that, 1) untreated tailings supported very little plant growth, 2) biosolid rates in excess of 67 Mt/ha did not significantly improve plant growth, and 3) the addition of green waste in addition to biosolids significantly increased biomass production. Based upon

these results, it appears that a biosolids rate as low as 67 Mt/ha is sufficient for successful revegetation of these non-acidic tailings. The addition of green waste will further increase plant growth.

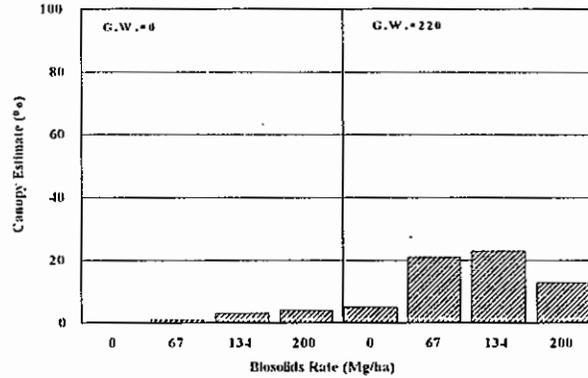
Addition of biosolids or green waste had no significant effects on DTPA-extractable soil metals (Fig. 3). Statistically significant ( $p \leq 0.05$ ) but small increases in extractable soil Fe, Ni, and As, were observed at the higher biosolids rates in samples collected immediately after biosolids application in October 1998 (data not shown). However, these differences disappeared by June 1999. We can conclude that the biosolids applications in this study resulted in little increase in phytoavailable metals. Analysis of plant tissue showed that addition of biosolids or green waste did not significantly increase the uptake of metals into plant biomass (Fig. 4). Addition of biosolids or green waste did, however, significantly decrease the uptake of Cd into plant biomass. There is some evidence that applications of organic matter to contaminated soils may decrease the phytoavailability of heavy metals. Metals can be inactivated by sorption onto exchange sites or complexation with the organic material (Berti and Cunningham, 2000). This may explain the decreased phytoavailability of Cd when amendments were added to the soil. Alberici et al. (1989) monitored trace metal concentrations in soil and vegetation on sewage sludge amended minespoils, and found similar trends. Trace metal concentrations did not significantly increase in the soil or vegetation.

Both biosolids and green waste additions resulted in significant increases in total soil N (Fig. 5). Total N concentrations were more than eight times higher in plots with the highest biosolids rate and green waste, compared to unamended tailings. The chemical composition of these amendments can vary substantially, and we found that the C:N ratio of the green waste was lower than expected. The green waste amendments added more N to the soil than expected and the higher total N concentrations in these plots reflect this. These increases may be temporary, however. Increased microbial respiration may remove significant amounts of organic matter. In June, 2000 we measured  $\text{CO}_2$  evolution from the tailings as an index of soil + plant respiration (Fig. 6.). Green waste significantly increased  $\text{CO}_2$  evolution, but biosolids did not. Carbon dioxide evolution was more than 4 times greater in plots receiving both green waste and the highest biosolids rate compared to the unamended control plots. Just two years after the incorporation of

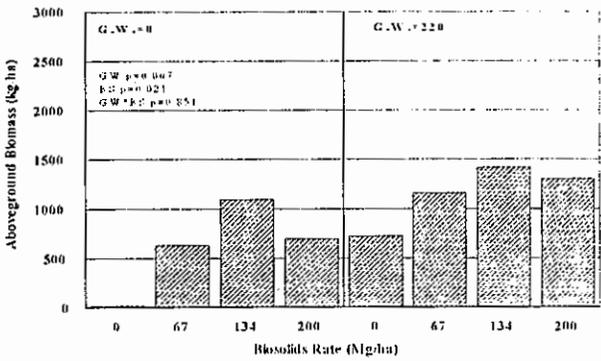
### June 1999 Sampling



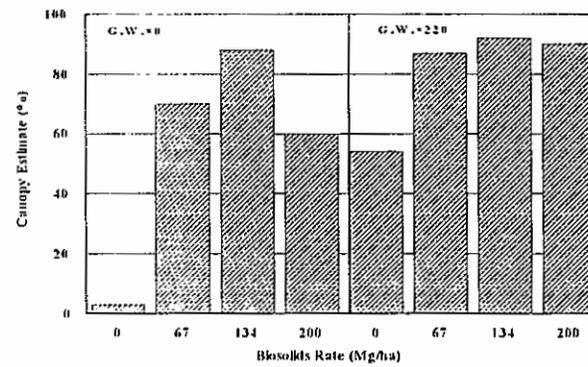
### June 1999 Sampling



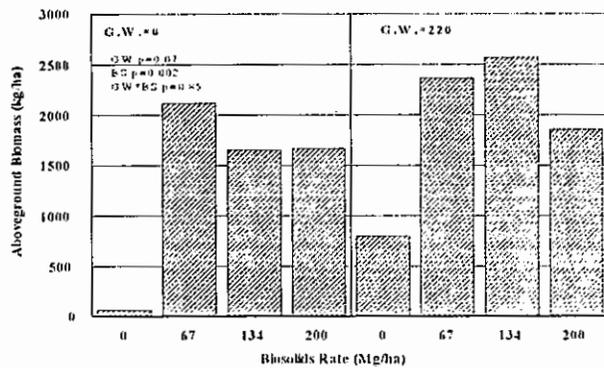
### Dec. 1999 Sampling



### Dec. 1999 Sampling



### Oct. 2000 Sampling



### Oct. 2000 Sampling

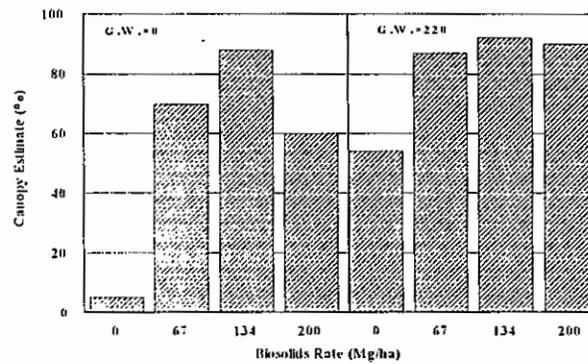


Fig. 1. Aboveground biomass production in plots receiving 0 and 220 Mg/ha of green waste

Fig. 2. Plant canopy cover estimates

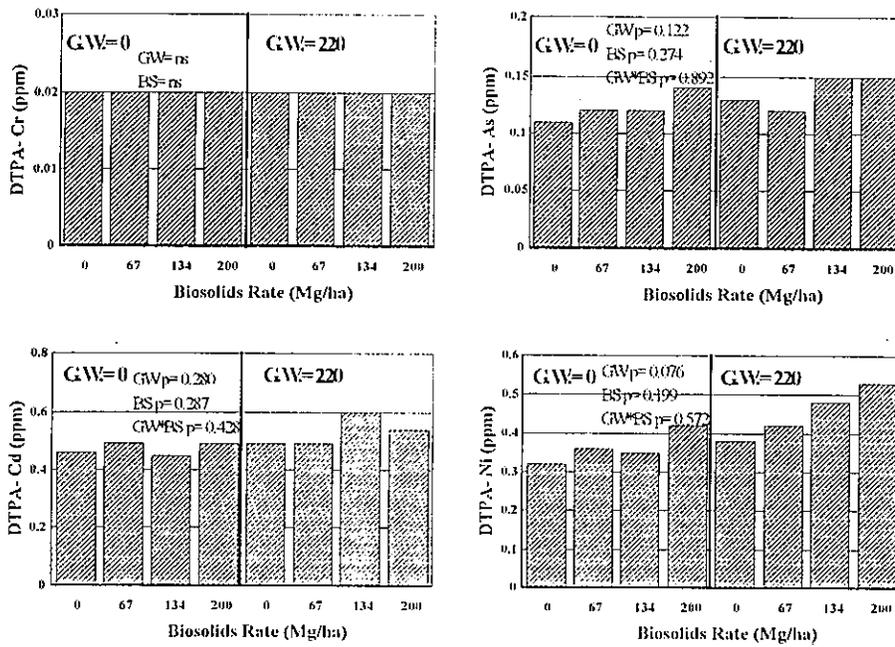


Fig. 3. Available metal concentrations in Dec. 1999 tailing samples (0-60cm)

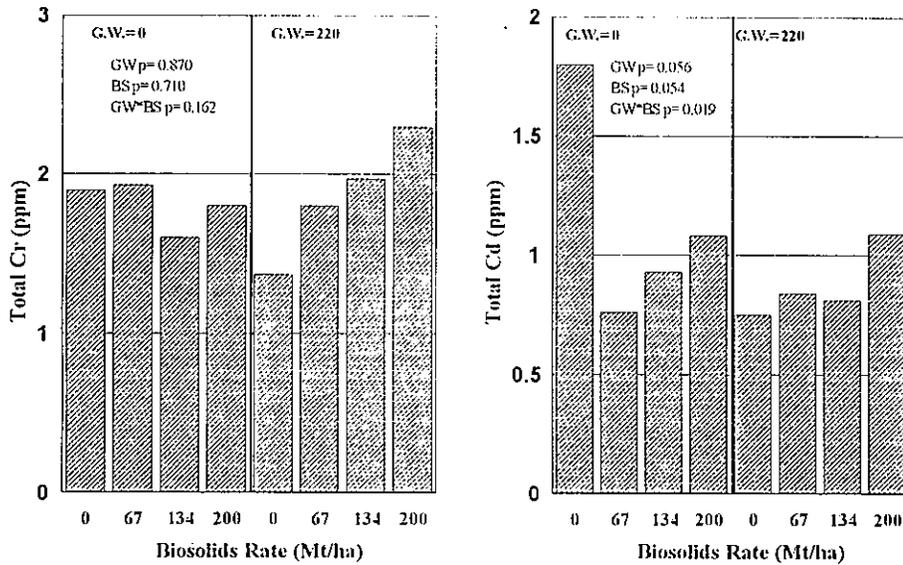


Fig. 4. Metal concentrations in plant aboveground biomass sampled Dec. 1999

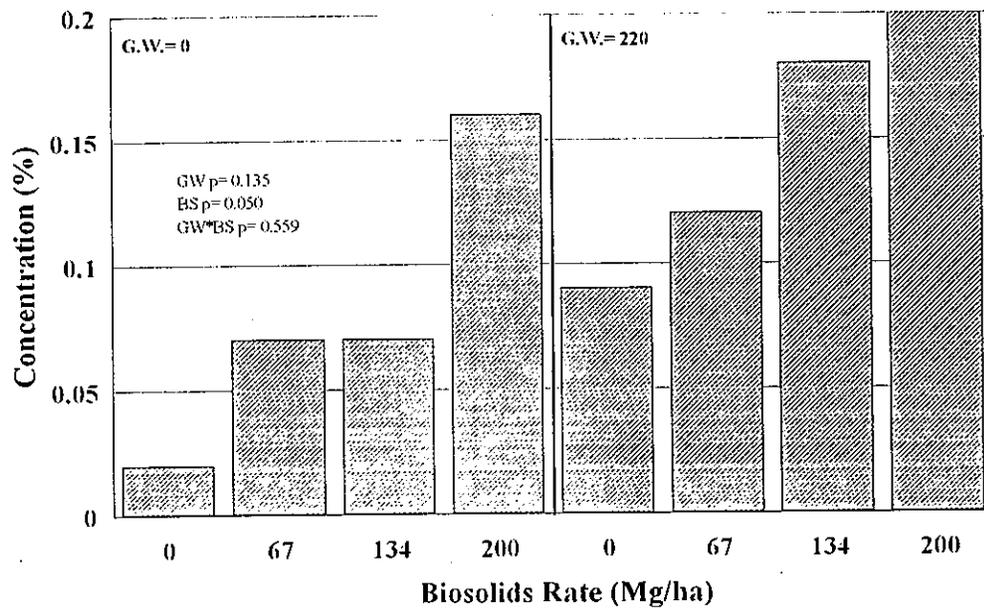


Fig. 5. Total N in Dec. 1999 tailing samples (0-60cm)

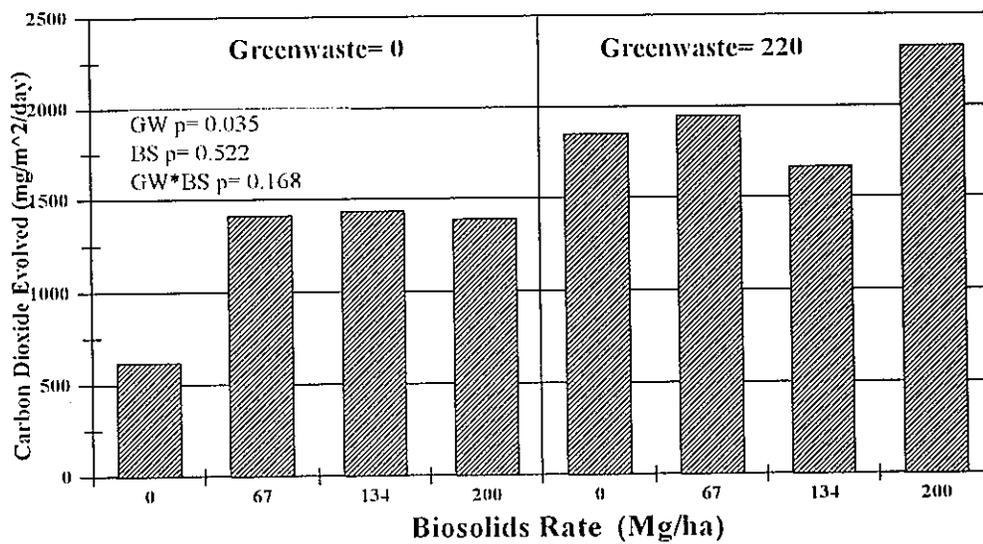


Fig. 6. Soil respiration measurements in June 2000

the amendments into the soil, most of the organic matter has been broken down and is difficult to identify. Seaker and Sopper (1988-I) studied the effects sludge applications have on microbial populations and activity in minespoils. They point out that microbial processes are important in ecosystem recovery, and that biosolids applications can quickly increase the numbers and activity of microorganisms. In their study, they found that recovery of normal soil microbial populations within the top 5-cm occurred within 2 years of sludge incorporation and does not appear to deteriorate.

Tailing  $\text{NH}_4^+$  concentrations were initially very high following biosolids addition (data not shown). However, these concentrations decreased significantly by June 1999, while  $\text{NO}_3^-$  concentrations increased. Excessive  $\text{NO}_3^-$  movement was not expected in this study because of limited irrigation and the semi-arid conditions in southern Arizona.

The pattern of tailing  $\text{NO}_3^-$  accumulation suggests that little  $\text{NO}_3^-$  movement below 30 cm depth had occurred by June 1999. Additional samples collected in December 1999 (Fig. 7.) also suggested that very little  $\text{NO}_3^-$  had leached below 30 cm depth, except in plots receiving the highest biosolids rate, where  $\text{NO}_3^-$  concentrations were only slightly elevated. The lower than expected C:N ratio of the green waste suggests that immobilization of inorganic nitrogen was probably limited. Despite this, it appears that  $\text{NO}_3^-$  movement below 30 cm has been minimal. At the biosolids rate of 67 Mg/ha, which is adequate for the reclamation of these tailings, there is little danger of excessive nitrate leaching.

### CONCLUSIONS

Biosolids and green waste amendments have excellent potential for enhancing mine tailings reclamation in semi-arid environments such as southern Arizona. These amendments represent a long term source of mineralizable N, and also provide the soil with other nutrients essential for plant growth. Additions of organic matter also improve the physical conditions of the soil by increasing water holding capacity, and decreasing the bulk density. These qualities are important in the establishment of a vegetative cover on tailings impoundments. Establishment of vegetation will dramatically reduce the erosion of tailings impoundments by wind and water, thereby limiting the potential for metal contamination of nearby natural and inhabited areas. This field scale experiment at BHP's San Manuel

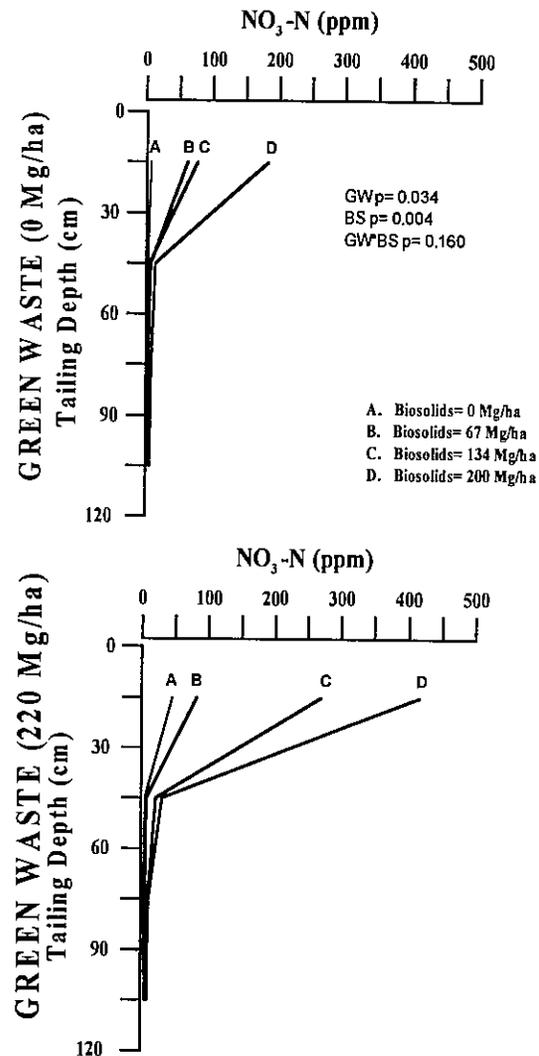


Fig. 7. Depth profile of tailing  $\text{NO}_3\text{-N}$  concentrations sampled Dec. 1999

copper mine on biosolids and green waste amendments has been very successful. With minimal irrigation, a dense vegetative cover has been established on otherwise sterile mine tailings. Addition of 67 Mg/ha (dry matter basis) of biosolids resulted in much-increased biomass production compared to control plots. Biosolids additions in excess of 67 Mg/ha did not result in significant increases in biomass production. Biosolids addition has resulted in little or no increase in soil extractable metals or plant metal uptake. Total N has increased in the tailings where biosolids or green waste have been added. Soil  $\text{NO}_3^-$

increased greatly where biosolids were added, but so far there is little evidence of excessive  $\text{NO}_3^-$  movement

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