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Effects of Increasing Dosages of Acid Mining Wastes in Metal Uptake by *Lygeum spartum* and Soil Metal Extractability

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Abstract Mine tailings are an environmental problem in southern Spain because wind and water erosion of bare surfaces results in the dispersal of toxic metals over nearby urban or agricultural areas. Revegetation with tolerant native species may reduce this risk. We grew the grass *Lygeum spartum* under controlled conditions in pots containing a mine tailings mixed into nonpolluted soil to give treatments of 0%, 25%, 50%, 75%, and 100% mine tailings. We tested an acidic (pH 3) mine tailings which contained high concentrations of Cd, Cu, Pb, and Zn. Electrical conductivity and pH of the control soil were dramatically affected by the addition of the acid tailings (pH <4.5, electrical conductivity >2 dS m^{-1} in all treatments). Water extractable metal concentrations increased in proportion to the amount of tailings added (up to 1,000 mg kg^{-1} Zn). *L. spartum* survived, but only in the 25% treatment. In all treatments and for all metals, the plants accumulated higher concentrations in the roots than in shoots.

Keywords Phytostabilization · Phytomanagement · Mine tailings · Metal uptake · Metal tolerance

1 Introduction

The disposal of mining wastes can have deleterious effects on the environment. Tailings often have a low pH, high concentrations of heavy metals, a lack of nutrients, a low water retention capacity, high electrical conductivity, and steep slopes. These factors inhibit plant establishment and, consequently, their surfaces are exposed to wind and water erosion, which may result in the contamination of nearby waters and soils with toxic metals. The dispersal of contaminants may occur on local as well as regional scales.

Although natural revegetation of mine tailings is usually slow, a few species of metal and salt tolerant plants can survive in these extreme, but relatively competitor-free, environments (Macnair 1987). Annual species adapt faster to these conditions than perennial plants because their shorter life cycles allow them to produce a larger variety of genotypes in a shorter time (Wei et al. 2005).

The Cartagena–La Unión mining district (0–400 m above sea level; 37°37′20″ N, 0°50′55″ W–37°40′03″

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Fig. 1 Location of sampling area

N, 0°48′12″ W) is at the Southeast of the Iberian Peninsula and covers an area of 50 km^2 (Fig. 1). The semiarid climate of the zone is typically Mediterranean with an annual rainfall of 250–300 mm. The annual average temperature is 18°C. Mining occurred in this area for more than 2,500 years until it ceased in 1991 for economic and environmental reasons. Base metals were smelted from sulfide minerals that included galena and sphalerite. The wastes form mining refining operations were stockpiled into tailings. These tailings pose a risk to local ecosystems and human health, due to the dispersal of dust and sediments by erosion (Conesa et al. 2006). Some are near urban and agricultural areas, increasing the risk of human exposure to metals via wind-borne dust or consumption of contaminated garden and agricultural crops.

The aims of this work were to investigate the effect of increasing tailings dosages on metal solubility in an agricultural soil as well as the growth and metal uptake by a native grass species from the Cartagena–La Unión mining district.

2 Materials and Methods

2.1 Soil Samples

We studied the mine tailing called "Belleza", located near La Unión (U.T.M. X688 760 m; Y4165 700 m; Z190 m). Conesa et al. (2006) describe the sampling locations and local vegetation. Tailing samples were taken from the upper 40 cm of 15 separate soil pits that were dug at regular intervals, at least 8 m apart. Then, all samples were mixed to give one homogenized composite sample which was air dried, sieved to <2 mm, and stored in plastic bags prior to laboratory analysis and pot experiment. Control soil was taken from a forest site near Zürich (Switzerland). Soil samples characteristics are shown in Table 1.

2.2 Metal Extractability Studies

Tailings and agricultural soil were mixed at different proportions to give treatments of 0% (uncontaminated soil), 25%, 50%, 75%, and 100% (pure mine tailings). For each mixture, we measured pH at a soil/water ratio of 1:2.5 using a Metrohm (Omega) pH meter. Total metal concentrations were determined by X-ray fluorescence spectroscopy (Spectro X-Lab 2000). Soluble metals were extracted with H_2O at a 1:5 soil/water ratio (Ernst 1996). The filtered extracts were analyzed for Cu, Cd, Pb, Zn, K, Mg, Ca, and Na by flame atomic absorption spectrometry (SpectraAA 220/FS, Varian). Electrical conductivity was measured in the water extract (1:5 soil/water ratio) using a conductivity meter WTW LF318/SET.

2.3 Pot Experiment

The pot experiment was performed with a native grass, *Lygeum spartum*. Plants of this species were grown from seed in plastic pots containing approximately 0.4 kg of the aforementioned mine tailings–soil mixtures. We used seeds of *L. spartum* collected from the mining area of Cartagena–La Unión. Two seeds were planted in each pot. Pots were irrigated with nutrient solution containing 400 mM $Ca(NO_3)_3$ $4H_2O$, 200 mM $MgSO_4$ $7H_2O$, 100 mM KH_2PO_4, and 500 mM KNO_3 (all chemicals from Merck). Soils

Table 1 Soil properties of the two soils employed in the experiment according to Conesa et al. (2006) and Menon et al. (2005)

Soil	pH	CEC (cmol (+) kg^{-1})	OC (%)	TN (%)	clay (%)	silt (%)	sand (%)
Acid tailing	3	16	0.5	0.035	12	33	55
Control soil	6.4	12	3.2	<0.03	5	8	87

CEC cation exchange capacity, *OC* organic carbon, *TN* total nitrogen were maintained near field capacity by adding 100–150 mL of solution per week. The plants were grown for 10 weeks in a climate chamber with a light cycle of 16:8 h light to dark under controlled humidity (50/90%) and temperature (16/23°C night/day).

The plants were harvested in the 11th week of the experiment, washed with deionized water, and dried at 65°C for 72 h. Shoots and roots were separated. Dry weights were determined for individual plants. Samples (0.050–0.200 g) were digested in Teflon tubes with 15 mL HNO_3 (65%) at 150°C for 1 h in a heating block DigiPREP MS (SCP Science). The digests were diluted to 20 mL with nanopure water. Copper, cadmium, lead, and zinc were measured by means of inductively coupled plasma optical emission spectrometry (Vista-MPX Varian). For quality assurance, we analyzed Certified Reference Material from the Community Bureau of Reference BCR No 62 (*Olea europaea*). We obtained recoveries of 80% for Pb and Cu and 90% for Zn.

We used SPSS 14.0.0 (SPSS, Chicago, IL, USA) for all statistical analysis (analysis of variance with least significant difference). Data that were log-normally distributed according to the Levene test were log-transformed before analysis. Differences at $P<0.05$ level were considered significant.

3 Results and Discussion

The addition of acid tailings material to the control soil significantly reduced the pH (from 7 to 4.2) already in the 25% treatment rate. All the mixtures with mine tailings had electrical conductivity values >2 dS/m (Table 2) and are thus *extremely saline* according to the classification of Alarcón-Vera (2004). Only salt tolerant species are able to grow under such conditions and one would expect that chickpeas, which are sensitive to salinity, would show reduced growth in the treatments with mine tailings.

The addition of tailing material to the control soil caused significant increases in extractable heavy metal concentrations (Fig. 2a). Some 20% of the total Zn and 60–90% of total Cd was water soluble in all acid tailing treatments. The water extractability of Pb and Cu increased in proportion to the percentage of tailing material added. The maximum values were 2% and 0.15%, respectively, in the 100% treatment. Water extractable Na concentrations were not affected by acid tailing addition (Fig. 2b), while soluble Ca and Mg concentrations increased significantly.

According to European legislation (European Communities Council 1986), the addition of the tailings materials used in this study to agricultural soils would be forbidden, because the metal concentrations exceeded limit values (>4,000 mg kg^{-1} Zn; >1,200 mg kg^{-1} Pb). Although at first view a mixture of 25% or 50% tailing with the surrounding soil may appear unlikely, some previous studies in the area have found that due to deposition of wind-eroded material, more than 50% of tailing materials had been incorporated into soil profiles of lands surrounding the tailings (García-García 2004).

The ratios of exchangeable Ca/Mg and K/Mg ratios were within the normal range in soils, indicating that neither excess nor deficiencies should occur. According to Alarcón-Vera (2004), ratios of exchangeable Ca/Mg (in meq 100 g^{-1}) around 5 are

Table 2 Mean values of pH, electrical conductivity, and concentrations of Cu, Zn, Cd, and Pb in the mine tailing/soil mixtures (treatments) at the beginning of the experiments

Treatment	pH[a]	EC 1:5 (dS m^{-1})	Total metals			
			Cu (mg kg^{-1})	Zn (mg kg^{-1})	Cd (mg kg^{-1})	Pb (mg kg^{-1})
100% acid tailing	3.0	4.47 (0.03)	379 (8)	5,420 (90)	9.2 (1.1)	7,240 (90)
75% acid tailing	3.2	3.83 (0.06)	299 (6)	4,130 (20)	6.6 (0.1)	5,670 (20)
50% acid tailing	3.6	3.22 (0.01)	202 (7)	2,530 (30)	3.3 (0.6)	3,920 (20)
25% acid tailing	4.2	2.27 (0.17)	108 (3)	1,390 (10)	2.3 (0.3)	2,160 (20)
Control soil	7.0	0.12 (0.01)	9 (1)	35 (1)	<1.0	12 (1)

Values in brackets are standard deviation of three replicate treatments

EC electrical conductivity

[a] Geometric mean. The differences between the samples were <0.1, the detection limit of our apparatus

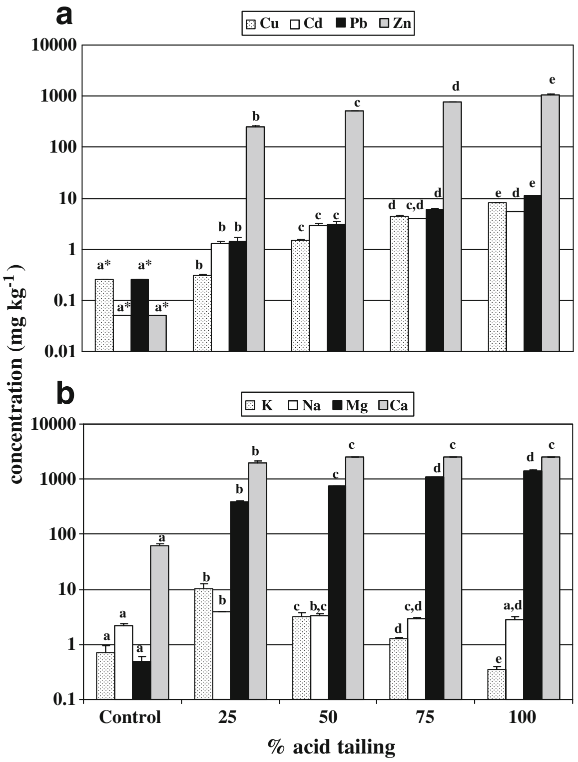
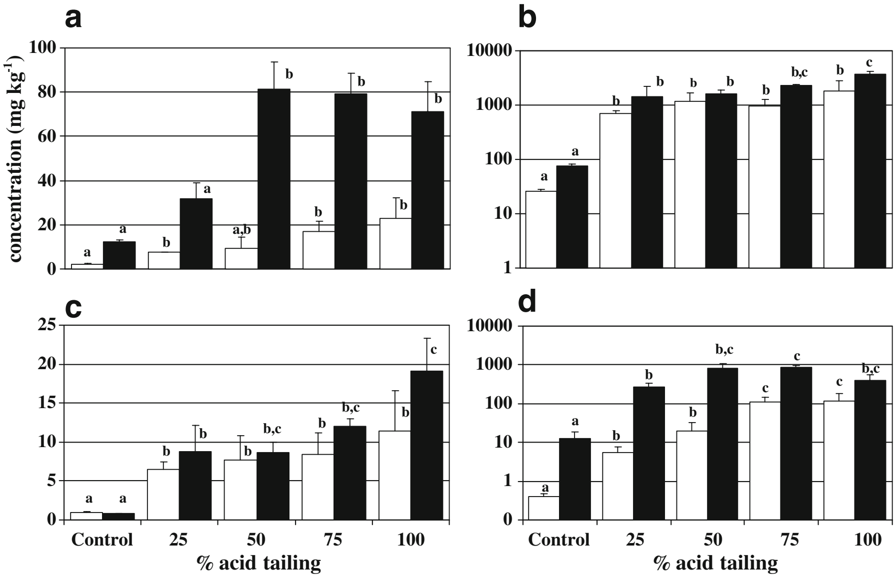


Fig. 2 Metals extracted with water from the different combinations of acid tailing material with control soil. *Error bars* represent standard errors ($n=3$). *Different letters* indicate significant differences among treatments for the corresponding element ($p<0.05$). An *asterisk* means that the detection limit is given, as the measurements did not exceed the respective detection limits that were 0.25 mg kg^{-1} for Cu and Pb and 0.05 mg kg^{-1} for Cd and Zn

ideal for healthy plant growth. If this ratio is <1, deficiencies of Ca may occur and if it is >10, then deficiencies of Mg may take place. Following this criteria, our control soil had deficiencies of Mg (ratio Ca/Mg >10), while all the treatments with acid tailing had deficiency of Ca (ratio Ca/Mg <1). Furthermore, Alarcón-Vera (2004) considers ratios of K/Mg (in meq 100 g^{-1}) below 0.2 as an indicator of K deficiencies. In all the treatments except the control soil, the K/Mg ratio was 0.4 and thus above this value. For K, solubility increased in the 25% treatment compared to the control, then decreased at higher rates of mine tailing additions. Total K in control soil is 14,000 mg kg^{-1} while in acid tailing is 2,000 mg kg^{-1} (data not shown). The addition of acid tailing enhanced mobility of K due to acidification in the 25% treatment. Further addition of acid tailing decreased of the pool of total K and consequently the water extractable concentrations were lower. Calcium and magnesium increased significantly as mine tailing is added. This may be produced by higher cation availability in the control soil as pH decreases and the high content of these two cations in the tailing soil.

L. spartum plants died in 50%, 75%, and 100% tailing treatments and only those in the 25% treatment showed signs of growth. These plants (Fig. 3) had higher Pb (100 mg kg^{-1} in shoots; 800 mg kg^{-1} in roots) and Zn (1,000–1,800 mg kg^{-1} in shoots, up to 3,500 mg kg^{-1} in roots). Differences were larger between controls and acid tailing treatments than

Fig. 3 Metal uptake in acid tailing treatments *L. spartum* for **a** Cu, **b** Zn, **c** Cd, and **d** Pb. $3<n<6$. *White columns* are shoots and *black columns* are roots. *Black bars on columns* are standard error. *Different letters* indicated significant differences among treatments for the shoots or roots ($p<0.05$). $3<n<5$



among the various acid tailings treatments possibly because of having reached in the latter one the phytotoxic levels. Conesa et al. (2006) reported levels ~150 mg kg^{-1} for Zn, ~50 mg kg^{-1} for Pb, and ~5 mg kg^{-1} for Cu in *Pipthaterum miliaceum* and *L. spartum* plants growing in situ in tailings from the Cartagena–La Unión mining area. These concentrations were lower than the values obtained in our study (even in relation to the lowest polluted treatment). Conesa et al. (2007) showed how the growth of certain plant species under controlled conditions resulted in significantly higher metal uptake compared to plants sampled in the field due to the changes in growing conditions. These changes were especially important when plants from arid environments are oversupplied with water.

Cattle should be prevented from grazing on *L. spartum* growing on soils affected by deposition of mine tailings material. Although the concentrations of metals taken up through roots and accumulated in plant tissues are low, metal-rich dust particles adhering to the surfaces of plants must also be taken into account. Furthermore, factors such as the direct ingestion of soil by cattle may play an important role for the transfer of the metals into the food chain.

4 Conclusions

Adding mine tailings to nonpolluted soil affects soil properties, plant growth, and metal accumulation by plants differed. Acid mine tailings addition had a greater affect on soil properties (pH, electrical conductivity) and inhibited plant growth in all treatments except at 25% dosage.

Our experiment indicate that *L. spartum* grow in polluted mine tailing polluted soils and accumulate high concentrations of metals without being showing visible symptoms under low dosages of polluted tailings. Therefore, plant metal uptake may pass unnoticed by farmers and constitute risk for food chain. On the other hand, revegetating bare mine tailings is important to stabilize the surfaces of these polluted soils and to reduce the migration of polluted materials to the adjacent fields. Future scientific studies could investigate soil amendments that decrease metal bioavailability in polluted areas near tailings.

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