Modification of the availability of trace elements in contaminated mining soils by the use of additives

Modificación de la disponibilidad de elementos traza en suelos mineros contaminados mediante la aplicación de enmiendas

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RESUMEN

El experimento se realizó en el invernadero de la Universidad Autónoma de Madrid-España. El muestreo fue en Bustarviejo, en el Valle Alto del Lozoya. La mina Mónica se sitúa a dos kilómetros al noreste de Bustarviejo, en las faldas de la Sierra de Guadarrama, en la cara sur. Estos suelos mineros son fuentes de metales pesados y su capacidad de retención y movilidad dependerá de las características del suelo. Para la realización del experimento se evaluaron distintas enmiendas minerales ($E33P$, $FeSO_4 \times 7H_2O$ + $CaCO_3$, KH_2PO_4 y NPK) y orgánicas (compost) sobre la disponibilidad del elemento contaminante en diferentes tratamientos con la especie *Lolium perenne* como testigo vegetal. Las variables analizadas fueron: concentración total, concentración disponible y concentración total en plantas. Se encontraron diferencias significativas entre los distintos tratamientos, siendo el tratamiento con sulfato ferroso más carbonato cálcico eficaz en la reducción de la disponibilidad de elementos tóxicos. El diseño experimental que se utilizó es un análisis de varianza de un factor o one way.

Palabras claves: enmiendas, disponibilidad, fertilizantes, metales pesados, concentración.

ABSTRACT

The experiment was performed in the Universidad Autónoma de Madrid-España. Sampling was performed in Bustarviejo, in the Valle Alto del Lozoya. The Mónica mine is located two km northwest of Bustarviejo, in the southern foothills of the Sierra de Guadarrama. Mining soils are sources of heavy metals; their capacity for retention and mobility depends on the characteristics of the soil. The experiment evaluated different mineral additives ($E33P$, $FeSO_4 \times 7H_2O$ + $CaCO_3$, KH_2PO_4 and NPK), and an organic additive (compost) on the availability of the contaminating elements using *Lolium perenne* as the plant indicator. The variables analyzed were total concentration, available concentration and total concentration in plants, which were analyzed using one-way analysis of variance. We found significant differences among the treatments; the treatment with ferrous sulfate plus calcium carbonate was the most efficient in reducing the availability of toxic elements.

Key words: soil additives, availability, fertilizers, heavy metals, concentration.

Introduction

The potential danger for the environment and for humans due to heavy metals in the soil comes from the metallic minerals (Abrahams, 2002; Adriano, 2001). Studies have reported high amounts of metals in soils affected by the oxidation of pyritic materials (Álvarez *et al.*, 2003; Vázquez *et al.*, 2006), a type of residue frequent in metal mines. Once metals accumulate, physicochemical factors condition the transfer of each metal from the solid to liquid phase; this causes differences in the availability of the metals to be absorbed by plant species, entering the food chain and finally causing the toxicity of

the element. Heavy metals may reach critical levels in the soil; also the accumulation in plant tissues may produce an increase of the metals in the soil surface due to leaf fall, or create a way for the metals to enter in the trophic chain (Mertens *et al.*, 2007; Unterbrunner *et al.*, 2007).

Soils contaminated with heavy metals and metalloids frequently have low fertility, one of whose causes is the low organic metal content (Bernal *et al.*, 2009). There also tend to be few roots for the grown of microbial biomass, low nutrient availability and poor structure, frequently with scarce or no plant cover (Bernal *et al.*, 2009). This may lead to physical deterioration and possibly dissemination of the

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contaminants. Different additives may alleviate this problem, altering the distribution of heavy metals in the soil fractions and their availability for living organisms (Bernal *et al.*, 2009).

Materials and Methods

Sampling was conducted in Bustarviejo in the high valley of Lozoya. The mine Mónica is located two kilometers from Bustarviejo, in the foothills of the Sierra de Guadarrama, in the south face. The coordinates mine U.T.M. are 30T X = 438552, Y = 4524494.

We sampled in two points, a non-contaminated control and a site with remains of mine tailings, in January, 2009. These points were chosen taking into account possible dispersion routes of heavy metals (tailings) and the possibly uncontaminated areas (control). The majority of these are located in the margins of the canyon and in the tailing zones.

In the greenhouse of the Universidad Autónoma de Madrid the soil was dried in the air for 7 days. Soil samples were sieved at 2 mm and homogenized for analysis. We analyzed organic matter, pH, electrical conductivity (CE) and mineral elements (arsenic, cadmium, zinc, copper, lead and phosphorous), both total and available fractions.

T0 treatment used 100% control soil; T1 used a mixture of 60% control soil and 40% tailings soil. Treatments T2-T6 also used the T1 mixture, but with additives. T2 used 18 g E33P; T3 used 43,92 g $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ + 15,75 g CaCO_3 (calculations based on Lepp *et al.*, 2002); T4 used 162 g KH_2PO_4 ; T5 used 0,36 g NPK (these were calculated according to the nutritional needs of the test plant, *Lolium perenne*); T6 used 90 g compost (5%). Treatments were prepared in 1.5 L pots; there were 4 replicas per treatment.

Pots were watered to field capacity for 3 weeks to equilibrate the soil (aging), in order to obtain more realistic conditions. After this period, the experiment began with homogeneous seedlings in three replicas of each treatment; the fourth was left without plants. Germination took approximately one week; the vegetative period lasted 6 weeks. During this period, pots were watered to field capacity.

To determine total element concentrations weighed 1 g of each of the soil samples. then added 6 ml of distilled water, 6 ml of nitric acid and 4 ml of H_2O_2 and was digested at 1.5 kg/cm² pressure for 30 min in an autoclave. Samples were then filtered

(Whatman N° 38) and filled up to 50 ml (Wenzel *et al.*, 2001; Wenzel *et al.*, 2002). To determine available element concentrations, to 1.5 g of homogenized soil was added 20 mL $(\text{NH}_4)_2\text{SO}_4$ 0.1 M and distilled water. The mixture was agitated for 4 h at 180 rpm at 20° C and then filtered (Whatman N° 42) (Wenzel *et al.*, 2001; Wenzel *et al.*, 2002; Vázquez *et al.*, 2007). For both methods blanks without soil were prepared. In the soil extracts we measured As, Cd, Zn, Cu, P and Mn using ICP-MS (inductively coupled mass spectrometry).

We analyzed the organic material of the soils by oxidation with potassium dichromate in the presence of sulfuric acid (MAPA, 1994). The excess of oxidant was evaluated with Mohr's salt (ferrous-ammonium sulfate) and the quantity of organic material was estimated by the amount of dichromate reduced. We analyzed the pH of the samples using a 1:2.5 soil-water suspension. We mixed 5 g of soil and 12.5 ml distilled water. The sample was agitated for 10 min at 200 rpm and left to stand for 30 min, then measured with a pH meter (MAPA, 1994). The pH was determined in the same way at the end of the test, in the pots and in the pore water. The CE measurements of the samples were performed in a 1:5 soil water suspension. 5 g of soil were mixed with 25 ml distilled water, then agitated for 1 h at 200 rpm and filtered (Whatman N° 38), and finally measured with a conductivity meter. The CE of the pore water was determined similarly.

Results and Discussion

Characterization of the soil and tailings

Organic material (OM), Electrical conductivity (EC) and pH. Figure 1a shows the increase of EC in T1 (differences were significant) due to the content of metal and metalloid ions present in the contaminated soil. Figure 1b shows that there were no differences in pH between the soils with and without tailings; soils were acid in both cases. Figure 1c shows significant differences due to a decrease in OM in T1 produced by the mixture with contaminated soil low in OM.

Initial concentrations of total and available metals in T0 and T1

The total initial concentrations of four metals in T0 and T1 are shown in Table 1. There was an increase

Figure 1a. Values of EC in soils. Mean±S.E. (N=5)

Figure 1b. pH for control and mixed soils. Mean±S.E. (N=5).

Figure 1c. Percentage of organic material in control and mixed soils. Mean±S.E. (N=4)

in the concentration of heavy metals and metals due to the mixture with tailings. Concentrations in T0 were below the reference levels of the Comunidad de Madrid, thus it is not considered a contaminated

soil. However, the concentration of As in T1 was above the reference level. It is also clear that the available elements increased when mixed with tailings (Table 2).

Table 1. Initial concentrations of total elements (mg/kg) in T0 and T1. Mean±S.E. (n=3).

	As	Cd	Zn	Cu
T0	6.96±0.2	0.07±0.015	37.14±2.8	6.40±0.1
T1	2721.73±93.05	13.14±0.45	3627.5±92.23	798.50±11.1

Table 2. Initial concentrations of available elements (mg/kg) in T0 and T1. Mean±S.E. (n=3).

	As	Cd	Zn	Cu
T0	0.02±0.003	0.02±0.0001	0.02±0.019	nd
T1	6.92±0.2	0.15±0.01	4.21±0.31	0.39±0.035

nd: not detectable.

Changes in pH during plant growth

pH values at the end of the study are shown in Figure 2. There was a significant increase in the pH of T3 due to the incorporation of CaCO_3 in the soil. The other treatments were not significantly different from T1. Comparison with the pH at the beginning of the study (Figure 1b) shows that there was no change in soil pH.

Concentration of toxic elements in the soil and plants

Concentration of As

The total concentration of As in soil with tailings did not show differences between treatments (Figure 3a). However, the available As of T3 was significantly different from T1, (3.68 mg/kg); there was a decrease in the available As (Figure 3b). This was due to the formation of oxides of Fe *in situ* in soils, which reduces the bio-availability of As (Adriano, 2001), due to the co-precipitation and absorption of the element. The total concentration of As in the plants of T3 was significantly lower (46 mg/kg) than in T1 (Figure 3c). This effect may be attributed to a greater capacity to co-precipitate and retain As by the Fe oxides formed *in situ*, while in T2, in spite of the capacity of Fe oxides to retain As in liquid media, this was not effective in the soil. T6 (4.75 mg/kg) did not show a significant difference with T1 (3.68 mg/kg) with respect to the concentration of available As (Figure 3c), however, it was significantly different from T1 (122.72 mg/

kg) in the quantity in plant material (T6: 40 mg/kg) (figure 3c). Adding compost to the soil probably increased the concentration of available As due to interchange with phosphates and organic complexes, and to the increase in the pH (Bernal *et al.*, 2009). The increase of the concentration of P in T6 (0.34 mg/kg) compared to T1 (0.02 mg/kg) showed a decrease in As absorption (antagonism), since the phosphate-arsenate transporter has more affinity for P (Esteban *et al.*, 2003). There was a much greater increase in As availability in T6 (compost) compared to T4 and T5, which received phosphate fertilizers and thus must have mobilized more As.

Concentration of Cd

There was a significant decrease in the total Cd concentration in T6 compared to T1 (Figure 4a). The concentrations of available Cd were significantly different in T2 (0.11 mg/kg) and T3 (0 mg/kg). The concentration in T3 was even lower than the control T0 (0.01 mg/kg) (Figure 4b), which was also significant compared to T1. This effect in T3 may be attributed to the increase in pH due to the incorporation of CaCO_3 and probably to the precipitation of CdCO_3 , the increase in pH controls the solubility of Cd (Alloway, 1995). There was also a decrease in the absorption of Cd by the plants in T3 (0.28 mg/kg) (Figure 4c), which had the lowest concentration of Cd in plant material and was significantly different from T1 and T2, 0.95 and 0.66 mg/kg, respectively. The difference between T1 and T2 was not significant, indicating that Fe oxides were not efficient in the co-precipitation of Cd, leaving

Figure 2. pH values at the end of the study Mean±S.E. (n=3).

Figure 3a. Concentration of total As in the soil of the different treatments Mean±S.E. (n=3).

Figure 3b. Concentration of available As in the soil of the different treatments Mean±S.E. (n=3)

Figure 3c. Total As concentration in the above-ground plant material of the different treatments Mean±S.E. (n=3)

this element available in the soil. T6 had an elevated concentration of available Cd similar to T1 (0.10 and 0.11 mg/kg, respectively) (Figure 4b); however, the concentration in the plant material was significantly lower in T6 (0.29 mg/kg) than in T1 (0.95 mg/kg) (Figure 4c). This effect was probably due to the

concentration of Mn in the soil of T6 (30 mg/kg), significantly greater than that of T1 (15 mg/kg), causing a Cd/Mn antagonism which decreased the absorption of Cd by the roots and increased its concentration in plant material (239 mg/kg). Studies have demonstrated that the accumulation of Cd is

Figure 4a. Concentration of total soil AS in the different treatments distintos tratamientos Mean±S.E. (n=3).

Figure 4b. Concentration of available Cd in soil in the different treatments Mean±S.E. (n=3)

Figure. 4c. Total Cd concentration in plants of the different treatments Mean±S.E. (n=3).

decreased in plant tissues when the concentration of Mn is greater (Hernández *et al.*, 1998).

Concentration of Zn

There were significant differences between T3 (0.57 mg/kg) and the other treatments with tailings

(2.57-3.56 mg/kg) in the amount of Zn available (Figure 5b); T3 immobilized the Zn best. Zn extraction decreases in calcareous soils (Adriano, 2001), and the availability of Zn diminishes in calcareous soils with high pH; it is absorbed by CaCO_3 forming nearly insoluble compounds such as $\text{Zn}(\text{OH})_2$ and ZnCO_3 (Marschner, 1995), and

Figure 5a. Total concentration of Zn in the soil of the different treatments. Mean $\pm$ S.E. (n=3). Figure 5b. Concentration of Zn available in the soil of the different treatments. Mean $\pm$ S.E. (n=3). Figure 5c. Concentration of Zn in the plants of the different treatments. Mean $\pm$ S.E. (n=3).

probably the co-precipitation by iron oxides decreased the concentration of the element available. Thus the absorption by plants was significantly reduced in T3 (58 mg/kg) compared to T1 (143.53) (Figure 5c). The difference between T1 and T2 was

not significant for plant material, thus the synthetic iron oxides used to purify the water were not efficacious in retaining Zn, leaving this element available in the soil. There was also no difference in the concentration of available Zn between T4

and T5 (Figure 5b). However, the concentration in plant material was significantly different between them, probably due to the dilution of the element in the greater growth of the plants (Figure 5c). T6

was not different from T1 in the concentration of available Zn (3.42 and 3.56 mg/kg respectively) (Figure 5b), however, the total plant concentration of Zn was (significantly) much lower in T6 (48.1 mg/

Figure 6a. Total Cu concentration in the soil of the different treatments, Mean±S.E. (n=3).

Figure 6b. Available Cu concentration in the soil of the different treatments, Mean±S.E. (n=3).

Figure 6a. Total Cu concentration in the soil of the different treatments, Mean±S.E. (n=3).

kg) than in T1 (143.53 mg/kg) (Figure 5c). High concentrations of Mn in T6 (29.88 mg/kg) induced the low absorption of Zn by plants, produced by a Zn/Mn antagonism Mn (Marschner, 1995) and an increase of Mn in the plants.

Concentration of Cu

There were significant differences of available Cu in T3 compared to the other treatments (Figure 6b), indicating a high immobilization of this element (0.14 mg/kg). Cu deficiency is found in basic soils, decreasing its bio-availability (Marschner, 1995); the presence of iron oxides also controls the absorption of Cu (Adriano, 2001), probably by its co-precipitation as occurs with Zn and Cd. Khan and Jones (2008) reported that the application of lime reduced the availability of Cu and Zn for plants. The difference between T1 and T2 was not significant for available Cu, thus the synthetic iron oxides used to purify the water were not efficient in retaining Cu, leaving this element available in the soil. The total Cu concentration in plants was significantly different between T3 and T1 (18.40 and 32.84 mg/kg respectively) (Figure 6c). There was a significant difference in the available Cu (Figure 6b) between T6 and T1 (0.27 and 0.68 mg/kg respectively); its concentration in soil decreased with compost. Stevenson and Fitch (1981) reported the formation of Cu-MO complexes in soil, being retained in the matrix, especially with humic acids, which also decreased the concentration in plants

(Figure 6c), with a significant difference compared to T1 (8.57 and 32.84 mg/kg, respectively).

Biomass and visual symptoms

There were significant differences in the aerial biomass of *Lolium perenne* between T3 and T6 with respect to the rest of the treatments and the control. During the 6 weeks of vegetative growth there was a tendency to less biomass in treatments T1, T2, T4 and T5.

Conclusions

In terms of the use of additives based on iron oxides to reduce the availability of contaminant soil elements, the treatment with ferrous sulfate and calcium carbonate reduced efficiently the availability of toxic elements and thus the toxicity of the tailings, allowing plant grown comparable with the control. However, treatment with ferric oxide (E33P) was not effective in reducing bio-availability. The use of compost did not reduce the bio-availability of toxic elements efficiently, although it reduced the concentrations of elements in the plants and allowed more vegetative growth than the control, thus it might cause some mobilization of toxic elements in the soil. The additives based on phosphate did not have significant effects in the mobility of the toxic elements or on plant growth. Among the tested soil additives, T3 (calcium carbonate and ferrous sulfate) was the most efficient.

Figure 7. Fresh aerial plant weight at the end of the experiment. Mean±S.E. (n=3).

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