Metal mobility assessment in semiarid mine tailings amended with biochar and urban compost: results of a bioassay employing a pioneer plant species
Movilidad de metales en balsas mineras enmendadas con biochar y compost urbano: resultados de un bioensayo empleando una especie vegetal pionera

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Abstract

Phytomanagement allows to reduce the environmental risks of abandoned mine tailings. The aim of this work was to assess metal mobility in mine tailings amended with biochar and/or urban compost and the effectiveness of these amendments for reducing the toxicity of soil solution to a pioneer plant species (*Zygophyllum fabago*). A mesocosm experiment was performed (20 months) with mine wastes with and without amendment. Mesocosms were maintained at field capacity with tap water and drained at different times. Soil solution was regularly monitored (pH, electrical conductivity, dissolved organic carbon –DOC-, dissolved total nitrogen –TDN- and metals -Mn, Zn-), as well as drainage. A bioassay with seeds of *Z. fabago* was performed with midterm soil solution (seed germination, seedling performance). Treatments containing urban compost showed higher initial DOC and metal concentrations in solution. A decrease of DOC and metal concentrations in soil solution with time occurred due to their lixiviation in the drainage water. In spite of the higher metal pool, urban compost favoured root length due to its greater content of DOC and TDN in soil solution.

Keywords: Metal availability; mining impacts; organic amendment; soil contamination

Resumen

El fitomanejo permite reducir el riesgo ambiental de balsas mineras abandonadas. El objetivo del trabajo fue evaluar la movilidad de metales en balsas mineras enmendadas con biochar y/o compost urbano y la efectividad de las enmiendas reduciendo la toxicidad de la solución edáfica para una planta pionera (*Zygophyllum fabago*). Se llevó a cabo un experimento en mesocosmos (20 meses) con residuo minero con y sin enmienda. Los mesocosmos se mantuvieron a capacidad de campo con agua de la red y se drenaron en diferentes momentos. Se monitorizó la solución edáfica regularmente (pH, conductividad eléctrica, carbono orgánico soluble –COS--, nitrógeno total soluble –NTS- y metales -Mn, Zn-), al igual que el drenaje. Se realizó un bioensayo con semillas de *Z. fabago* con la solución edáfica de mitad del experimento (germinación de semillas, crecimiento de plántulas). Los tratamientos con compost urbano mostraron mayor concentración inicial de COS y metales en solución. Se observó un descenso temporal de la concentración de DOC y metales en la solución edáfica debido a su lixiviación en el drenaje. A pesar del mayor contenido de metales, el compost urbano favoreció la elongación de la raíz debido al mayor contenido de COS y NTS en solución.

Palabras clave: Disponibilidad de metales; impactos de la minería; enmiendas orgánicas; contaminación del suelo

1. INTRODUCTION

Phytomanagement is considered a suitable tool to reduce the environmental risks of abandoned mine tailings [1]. Plant roots can fix soil preventing the migration of metal-enriched particles from tailings bare surfaces. However, phytomanagement long-term success requires the monitoring and assessment of metal mobility since some practices employed to improve soil fertility at tailings (*e.g.* amendments) may modify metal availability, changing the toxicity risks to biota [2]. In addition, some of the amendments employed in environmental practices, such as urban composts, may contain high metal pool that needs to be assessed before their application [3]. The aim of this work was to assess metal mobility in mine tailings amended with biochar and/or urban compost and the effectiveness of the amendments for reducing the toxicity of the soil solution to a pioneer plant species (*Zygophyllum fabago*).

2. MATERIALS AND METHODS

A mesocosm experiment was performed in a greenhouse during 20 months using mine wastes from tailings of the Cartagena-La Unión mining district (Murcia, SE Spain). Environmental problems related to the presence of metal-enriched mine tailings have been previously reported in this area [4]. The mine wastes employed in the experiment showed neutral pH (~7.3, 1:5 soil:water), high electrical conductivity (EC ~2.4 dS m^{-1}, 1:5 s:w), sandy texture, low content of total organic carbon (~1.4 g kg^{-1}) and total nitrogen (~0.7 g kg^{-1}), and high total concentrations of Zn, Mn and Pb (~6,500-10,000 mg kg^{-1}). The mine wastes were mixed with biochar and/or urban compost, resulting four treatments (n=4): mine wastes (T), mine wastes + 4% biochar (TB), mine wastes + 4% urban compost (TC), and mine wastes + 4% urban compost + 4% biochar (TCB). The urban compost employed was taken from Cartagena Municipal Waste Treatment Plant: pH ~7.9 (1:5 s:w); EC ~8.6 dS m^{-1} (1:5 s:w); dissolved organic carbon -DOC- ~25,000 mg kg^{-1} (1:5 s:w); dissolved total nitrogen (DTN) ~3,000 mg kg^{-1} (1:5 s:w); total Zn, Mn, Pb and Cu concentrations ~500-1,300 mg kg^{-1}. The biochar was provided by Piroeco S.L. (pyrolysis temperature 900 ˚C): pH ~9.9 (1:5 s:w); EC ~2.65 dS m^{-1} (1:5 s:w); DOC ~790 mg kg^{-1} (1:5 s:w); DTN ~8 mg kg^{-1} (1:5 s:w); total Zn, Mn and Cu concentrations ~67-960 mg kg^{-1} (Pb was not detected). All the treatments were irrigated with tap water (pH ~7.5-8.0, EC ~0.45 dS m^{-1}, DOC ~2 mg L^{-1}, metal(loid)s concentrations <2μg L^{-1} except for Zn that was ~15 μg L^{-1}) and maintained at field capacity. Mesocosms were let to drain at different time points.

Soil solution from the upper 20cm was taken periodically using Rhizon® samplers and pH, EC, DOC, TDN and metals (e.g. Mn, Zn) concentrations were measured. Drainage water was quantified and analysed. At the middle of the experiment (ninth month), soil solution from each treatment was used to perform a bioassay with seeds of *Z. fabago* in which seed germination and seedlings performance (length of roots, hypocotyl and cotyledon) were evaluated. Seeds were collected from the same mine tailing site than the mine wastes employed in the mesocosm experiment and they were cleaned and disinfected (NaClO 5%). After that, Petri dishes were prepared with filter paper and 25 seeds each, and irrigated with 5 mL of the corresponding soil solution (n=4). Then, they were incubated in a climate room (24 °C during 14 hours light -4 lux-; 20 °C during 10 hours darkness). Distilled water was used as a control. The percentage of germination was registered after 15 days, the average time for germinating was calculated, and vigour was registered after 30 days by measuring the seedling length.

3. RESULTS AND DISCUSSION

In all the treatments, the pH of the soil solution ranged between ~7.7 and ~7.9 and the EC between ~2.5 and ~4.5 dS m^{-1} (data not shown). The DOC concentrations (Fig. 1C) were higher in TC and TCB treatments than in those without urban compost (T and TB), which could be attributed to the greater labile organic materials contained in this amendment. A tendency to decrease DOC concentrations was observed in all the treatments (from ~43 to ~1.9 mg L^{-1} for TC and TCB treatments; from ~6.7 to ~1.3 mg L^{-1} for T and TB treatments). The treatments containing urban compost showed higher metal concentrations in the initial soil solution than the treatment without amendment or only biochar (1.5-2.5-fold higher for Mn and 1.5-2.0-fold higher for Zn) (Figs. 1A and 1B), probably because it contained a higher labile metal pool. In all the treatments, a decrease of metal concentrations in soil solution with time occurred. The decrease of DOC, Zn and Mn concentrations in soil solution throughout the experiment could be related to their lixiviation in the drainage water, as shown in Table 1.

Seed germination (Fig. 2A) significantly decreased when comparing distilled water (control) with soil solution treatments (from ~47% to ~10%), but no differences occurred among the tested treatments. The treatments containing urban compost showed a delay in the germination time (Fig. 2B). Urban compost improved root length: ~3.3 cm for control; ~1.9 cm for T; ~1.0 cm for TB; ~4.9-5.0 cm for TC and TCB (Fig. 2C). This could be related to the higher presence of DOC and TDN contained in this amendment: soil solution DOC concentration in the ninth month (~6-7 mg L^{-1} in T and TB vs ~10-13 mg L^{-1} in TC and TCB); soil solution TDN concentration in ninth month (~1-4 mg L^{-1} in T and TB vs ~13-37 mg L^{-1} in TC and TCB) (data not shown). No clear patterns were observed for hypocotyl and cotyledon (Fig. 2C).

4. CONCLUSIONS

Initial soluble metal concentrations in mine wastes were affected by the amendment added, although a general decrease with time occurred for all the treatments due to metal lixiviation. Urban compost favoured higher metal concentrations in soil solution than biochar, which could lead to changes in the toxicity risks to biota. However, the greater labile organic carbon and nitrogen pool of urban compost had a positive effect on the development of plant roots, which could favour its establishment in tailings.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

[1] Robinson, B.H., Bañuelos, G., Conesa, H.M., Evangelou, M.W.H., Schulin, R., 2009. The phytomanagement of trace elements in soil. Crit. Rev. Plant Sci. 28:240-266.

[2] Parraga-Aguado, I., Álvarez-Rogel, J., González-Alcaraz, M.N., Conesa, H.M. 2017. Metal mobility assessment for the application of an urban organic waste amendment in two degraded semiarid soils. J. Geochem. Explor. 173:92-98.

[3] Kohler, J., Caravaca, F., Azcón, R., Díaz, G., Roldán, A. 2014. Selection of plant species–organic amendment combinations to assure plant establishment and soil microbial function recovery in the phytostabilization of a metal-contaminated soil. Water Air Soil Poll. 225:1930.

[4] Conesa, H.M., Schulin, R. 2010. The Cartagena-La Unión mining district (SE Spain): a review of environmental problems and emerging phytoremediation solutions after fifteen years research. J. Environ. Monit. 12:1225-1233.

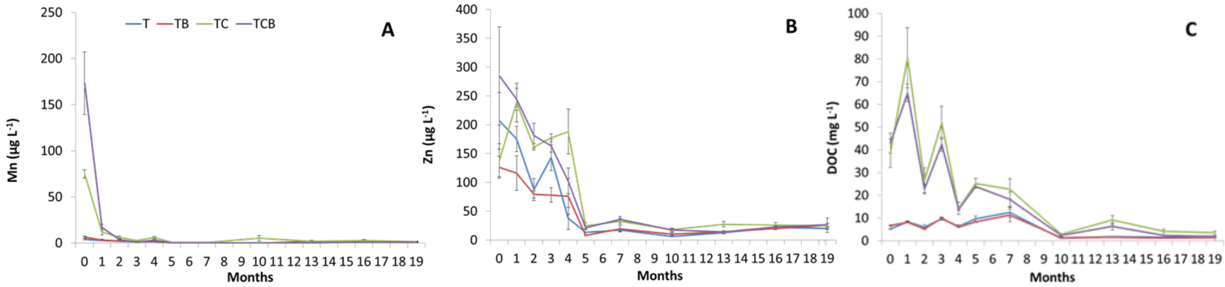

Figure 1. Evolution of soil solution concentration of Mn (A), Zn (B) and dissolved organic carbon – DOC – (C) during the experiment. Treatment codes as it follows: T (mine wastes); TB (mine wastes + 4% biochar); TC (mine wastes + 4% urban compost); TCB (mine wastes + 4% urban compost + 4% biochar). Data are average ± standard error (n=4).

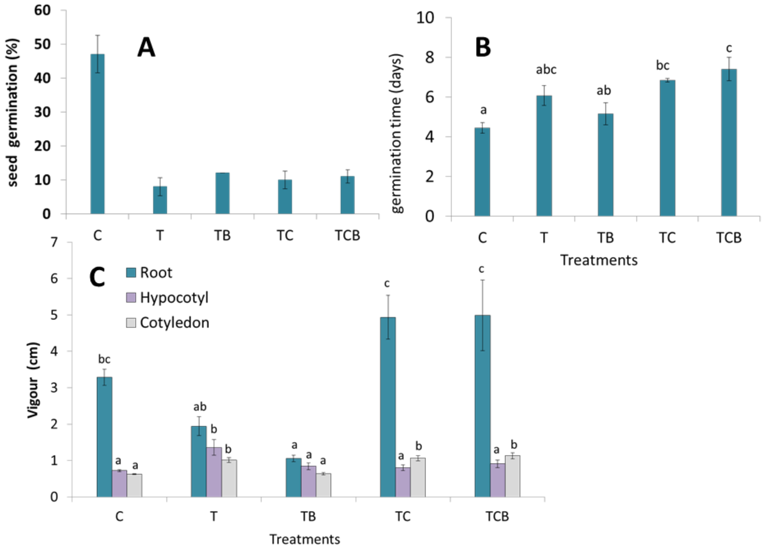

Figure 2.-Percentage of germination (A), average time for germinating (B), and the results from vigour test (C). Different letters in each column group mean significant differences among treatments (one-way ANOVA with Tukey post-hoc test, $p < 0.05$). Treatments codes as it follows: C (control with distilled water); T (mine wastes);, TB (mine wastes + 4% biochar); TC (mine wastes + 4% urban compost); TCB (mine wastes + 4% urban compost + 4% biochar). Data are average ± standard error (n=4).

Table 1. Concentrations of dissolved organic carbon (DOC), Zn and Mn in drainage water at different time points during the experiment (months 0, 10 and 19). Concentrations are expressed in relation to the drainage volume collected: DOC in mg; metals in µg. Treatment codes as it follows: T (mine wastes); TB (mine wastes + 4% biochar); TC (mine wastes + 4% urban compost); TCB (mine wastes + 4% urban compost + 4% biochar). Data are average ± standard error (n=4). No drainage was collected for TB treatment at 10th month.

Parameter	Month	Treatment			
		T	TB	TC	TBC
DOC	0	9.72±2.60	1.66±0.46	143±37	122±15
	10	1.20±0.25	-	10.6±6.36	4.86±0.75
	19	1.48±0.26	1.25±0.27	1.85±0.65	1.33±0.27
Zn	0	80.3±5.95	18.9±4.90	224±54	124±13
	10	2.48±1.30	-	10.9±1.95	5.66±1.15
	19	10.4±2.43	10.1±2.82	8.21±2.35	6.38±1.58
Mn	0	7.28±0.65	3.16±0.78	15.9±4.20	12.6±2.53
	10	0.48±0.16	-	0.86±0.08	0.70±0.17
	19	1.65±0.25	1.04±0.38	0.92±0.36	1.06±0.22