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Effect of waste mixed with biochar as soil amendment on trace element solubility in a mine soil

Efecto de residuos mezclados con biochar como enmienda del suelo en la solubilidad de elementos traza en un suelo de mina
Efeito de resíduos misturados com biochar como emenda do solo na solubilidade de elementos traço em um solo de mina

AUTHORS

Rodríguez-Vila A.[1,@]
fonso@uvigo.es

Forján R.[1]

Guedes R. S.[2]

Covelo E. F.[1]

[@] Corresponding Author

[1] Department of Plant Biology and Soil Science, Faculty of Biology, University of Vigo. Lagoas, Marcosende, 36310 Vigo, Pontevedra, Spain.

[2] Institute of Agricultural Sciences, Federal Rural University of Amazonia (ICA-UFRA). 2501, Belém-PA, 66077-830, Brazil.

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ABSTRACT

Abandoned mining sites often cause contamination of surface and subsurface waters. A 3-month pot experiment was performed to evaluate the influence of waste mixed with biochar as a soil amendment on a series of chemical characteristics and trace element solubility in a mine soil. Trace element concentrations were measured in pore water of the mine soil reclaimed with different proportions of waste-biochar amendment (20, 40, 80 and 100%) and grown with *Brassica juncea*. The results showed that amendment application improved soil conditions such as pH, total carbon, dissolved organic carbon, total nitrogen, and strongly reduced the concentration of Al (99.99%), Co (99.95%), Cu (99.97%), Fe (99.79%) and Ni (99.91%) in pore water, compared to the unamended soils. Waste and biochar also promoted the establishment of *B. juncea* in the mine soil. These results highlight the importance of mitigating the impacts from abandoned mines sites on water quality. The use of waste and biochar as soil amendment combined with *B. juncea* plants was effective in reducing metal concentrations in pore water and the associated toxicity risk.

RESUMEN

Las minas abandonadas suelen causar la contaminación de las aguas superficiales y subsuperficiales. Se llevó a cabo un experimento con macetas durante 3 meses para evaluar la influencia de la mezcla de residuos y biochar como enmienda en una serie de características químicas y en la solubilidad de elementos traza en un suelo de mina. La concentración de los elementos traza se midió en el agua de poro del suelo de mina enmendado con distintas proporciones de la mezcla de residuos-biochar (20, 40, 80 y 100%) plantado con Brassica juncea. *Los resultados mostraron que la aplicación de enmienda mejoró las condiciones del suelo como el pH, carbono total, carbono orgánico disuelto, nitrógeno total, y disminuyó la concentración de Al (99,99%), Co (99,95%), Cu (99,97%), Fe (99,79%) y Ni (99,91%) en el agua de poro, comparado con los suelos sin enmienda. Los residuos y biochar también promovieron el establecimiento de* B. juncea *en el suelo de mina. Estos resultados destacan la importancia de mitigar los impactos de las minas abandonadas en la calidad del agua. El uso de residuos y biochar como enmienda combinado con* B. juncea *fue efectivo para reducir las concentraciones de metales en el agua de poro y el riesgo de toxicidad asociado.*

RESUMO

As minas abandonadas geralmente causam a contaminação das águas superficiais e subterrâneas. Um experimento com vasos durante três meses foi realizado para avaliar a influência da mistura de resíduos e biochar como emenda em uma série de características químicas e na solubilidade de elementos traço num solo de mina. A concentração dos elementos traço foi medida na água de poro do solo de mina emendado com diferentes proporções da mistura de resíduos-biochar (20, 40, 80 e 100%) plantado com Brassica juncea. *Os resultados mostraram que a aplicação de emenda melhorou as condições do solo como pH, carbono total, carbono orgânico dissolvido, azoto total, e disminuiu a*

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concentração de Al (99,99%), Co (99,95%), Cu (99,97 %), Fe (99,79%) e Ni (99,91%) em água de poro em relação ao solos sem emenda. Resíduos e biochar também promoverom o estabelecimento de B. juncea *no solo de mina. Estes resultados destacam a importância da mitigação dos impactos das minas abandonadas na qualidade da água. O uso de resíduos e biochar como emendas combinado com* B. juncea *foi eficaz na redução das concentrações de metais na água de poro e o risco de toxicidade associada.*

1. Introduction

Mining areas are characterised by young, poorly developed soils often with scarce or absent vegetation cover due to extreme pH values, poor fertility conditions, low organic matter contents and degraded soil structures, usually with high metals and another potential hazardous elements (Mench et al. 2010). The mobility and bioavailability of metals such as Cu, Pb and Zn in contaminated soils is of global concern (Uchimiya et al. 2010). Reducing trace element contamination in mine soils, especially in the soil pore water, is important due to its impact on surface and subsurface waters (Beane et al. 2016). Techniques for measuring the mobility of trace elements such as the sampling of interstitial pore water could have significant potential for ecotoxicology testing (Beesley et al. 2010a). The examination of element behaviour and movement in soils should be as representative as possible of processes occurring in the soil (Beesley et al. 2010a). The presence of a vegetation cover in mine soils reduces the potential transport of contaminants to surface and ground waters (Beesley et al. 2014; Ruttens et al. 2006). However, these soils often have important limitations for revegetation due to their extremely degraded conditions (Thakur et al. 2016).

The high cost of physical and chemical soil remediation techniques prompted the development of alternative techniques that are cost-effective and less disruptive to the environment (Sakaguchi et al. 2015). Remediation technologies increasingly focus on environmentally friendly techniques, such as phytostabilization, often primed by the addition of soil amendments (Kumpiene et al. 2008). In contrast to physical and chemical metal remediation strategies, which involve the physical removal of contaminated soil, chemical washing and reburial, it is estimated that phytoremediation could reduce operational costs and reduce environmental harm (Wood et al. 2016). Phytoremediation is often complicated in contaminated environments due to phytotoxicity by metals, and other factors such as extreme pH values, low fertility, low water holding capacity and poor soil structure which prevent plant establishment (Puga et al. 2016). Advantages of phytoremediation include low cost, environmentally friendly techniques, large scale operation, conservation of soil structure and prevention of erosion and leaching of metals (Azubuike et al. 2016). Phytostabilization deals with the decrease in the bioavailability and mobility of metals in the soil due to their stabilization from off site transport with the help of plants (Mahar et al. 2016). Certain plant species, such as *Brassica juncea* L., grows in soils with high concentrations of metals and tolerates these contaminants in its roots and shoots (Mourato et al. 2015; Neilson and Rajakaruna 2012) without severe damage to plant growth and vital physiological processes (Rascio and Navari-Izzo 2011) and have been successfully used in phytostabilization in the recent years (Ma et al. 2015; Thakur and Sharma 2016).

KEYWORDS
Metals, organic materials, remediation, pore water

PALABRAS CLAVE
Metales, materiales orgánicos, recuperación, agua de poro

PALAVRAS-CHAVE
Metais, materiais orgânicos, recuperação, água de poro

Organic materials, such as waste and biochar have been used as soil amendments to enhance the condition of degraded soils (Peña et al. 2015; Zhang et al. 2014; Zong et al. 2016). Organic amendments prepared from wastes used in soil reclamation can be dominated by human made materials and contain a significant amount of artefacts (FAO 2014). Biochar is a carbon-rich solid material resulting from the pyrolysis of biomass in a limited oxygen environment (Beesley et al. 2011). Biochar is biologically and chemically more stable than the organic matter from which it is made (Mosley et al. 2015). Biochar contains various functional groups, has a highly porous structure, and has been shown to be effective in the adsorption of metals, especially in aquatic systems (Liu and Zhang 2009). Biochar has an even greater ability than other soil organic matter to adsorb cations per unit carbon (Sombroek et al. 2003), due to its greater surface area, negative surface charge, and charge density (Lehmann 2007).

Several previous studies have investigated the influence of adding organic amendments to contaminated soils (Fresno et al. 2016; Liu et al. 2016a; Mingorance et al. 2014; Yin et al. 2016), but only a few authors have evaluated the effect of organic amendments on trace element concentration in pore water (Beesley and Dickinson 2011; Manzano et al. 2014). And there is a lack of understanding over the influence of the combination of waste mixed with biochar as soil amendment on trace element solubility. The objective of the present study was to evaluate the effect of waste and biochar mixture on trace element soil pore water concentrations in a mine soil from the depleted copper mine of Touro (Spain). The authors aim to demonstrate that the combination of this amendment and *B. juncea* can reduce the potential toxic trace element concentrations in pore water through the decrease of contaminant solubility in the mine soil.

2. Materials and methods

2.1. Soil collection

The mine soil used in the experiment (M) was collected from the settling pond of the depleted copper mine of Touro (Galicia, Spain) (Lat/Lon (Datum ETRS89): 8°20′12.06″W 42°52′46.18″N). Copper was extracted from Touro mine between 1973 and 1988 and this activity produced a settling pond and mine tailings. The settling pond was created by the accumulation of waste from the copper flotation process, and today it is completely emerged and dry. There is an active oxidation zone near the surface where vegetation does not grow. Since copper ceased to be mined, other companies extracted material for road construction. The former mining area was partially reclaimed by planting trees (*Pinus pinaster* Aiton and *Eucalyptus globulus* Labill) in some locations. Later, some mine sites were amended using organic materials such as sewage sludge and paper mill residue.

2.2. Experimental set-up

A mixture of wastes supplied by Tratamientos Ecológicos del Noroeste S.L. (Santiago de Compostela, Spain) and biochar provided by PROININSO S.A. (Málaga, Spain) were used for producing an amendment mixture in the greenhouse experiment. The mixture of wastes (W) was composed of sewage sludge (60%), waste from food industries (canning and rabbit farms) (10%), sludge from an aluminium company (10%), ashes from a paper mill (5%) and sands from treatment plants (5%). A 10% of the wastes have unknown origin.

The biochar (B) was derived from holm oak wood branches with a pyrolysis temperature of 400 ºC for 8 hours. The combined use of biochar and other organic materials as a soil amendment has been shown to successfully improve the condition and reduce the availability of metals in contaminated soils (Karami et al. 2011).

A greenhouse experiment was performed in pots; and the mine soil was mixed with a combination of waste and biochar and vegetated with *Brassica juncea* plants. An unamended treatment called S, with 0% amendment was also used. The plastic pots were filled with a dry weight of 200 g of the corresponding soil mixture.

The mine soil was mixed with 20%, 40%, 80% and 100% of an amendment mixture (95% amendment made from waste and 5% biochar) before filling the pots with the corresponding soil mixture: T1 = 20% amendment + 80% mine soil; T2 = 40% amendment + 60% mine soil; T3 = 80% amendment + 20% mine soil, and T4 = 100% amendment. Unamended pots were supplemented with plastic drinking straws cut into 1 cm pieces, in order to minimize the difference between the substrate volume of the unamended soils and the amended soils (Puig et al. 2013). Six pots were filled with each type of mixture: three were used for planting *B. juncea*, and the other three were left unplanted. The soil samples with *B. juncea* plants were labelled with the letter P (e.g., T1P). Soil treatments description is shown in **Table 1**.

Three seedlings of *B. juncea*, previously germinated from seeds until they grew two fully expanded leaves, were transferred to each pot. After 45 days, the plants were thinned to one per pot. The plants, with three replicates per treatment, were irrigated with tap water at field capacity (approximately two times a week, as required) to maintain a proper moisture level, were not fertilized and were harvested 90 days after transplanting. The greenhouse was maintained at temperature of 15 ± 3 °C and 75 ± 5% relative air humidity.

Table 1. Soil treatments description for the different soil samples

Soil treatment	Pots without *B. juncea*	Pots with *B. juncea*
Control: mine soil	S	SP
80% mine soil + 20% amendment*	T1	T1P
60% mine soil + 40% amendment*	T2	T2P
20% mine soil + 80% amendment*	T3	T3P
100% amendment*	T4	T4P

*Amendment mixture is made of 95% waste + 5% biochar.

2.3. Analytical methodology

Soil samples collected from the field (mine soil) and from the pots were air dried, passed through a 2 mm sieve and homogenized in a vibratory homogeniser for solid samples (Fritsch Laborette 27 rotary sampler divider) prior to analysis. The determination of soil pH was performed with a pH electrode (CRISON pH & ION-Meter GLP 22+) in 1:2.5 water or KCl to soil extracts (Porta 1986). Soil total carbon (TC), total nitrogen (TN) and inorganic carbon (IC) were measured in a LECO CN-2000 module using solid samples. Total organic carbon (TOC) contents were calculated from the difference TC — IC. Dissolved organic carbon (DOC) was extracted with bidistilled H_2O according to Sánchez-Monedero et al. (1996). Pseudototal concentrations of Cu, Ni, Pb and Zn were extracted with *aqua regia* by acidic digestion (1:3 v/v) in a microwave oven (Milestone ETHOS 1). Metal concentrations were determined by ICP-AES (PerkinElmer Optima 4300 DV). At the end of the greenhouse experiment, plants were washed with deionised water and dry biomass was weighed in a laboratory scale (METTLER PJ400) after oven-drying (Memmert Beschickung-Loading Model 100-800) at 80 °C for 48 h and cooling at room temperature. The plant tissues were ground and the total concentrations of Cu, Ni, Pb and Zn extracted by acid digestion using a mixture of H_2O_2 and HNO_3 (1:6 v/v) in a microwave oven. Metal concentrations in *B. juncea* were determined by ICP-AES (PerkinElmer Optima 4300 DV).

One week before harvesting the *B. juncea* plants, a “Rhizon” soil pore water sampler (Eijkelkamp

Agrisearch Equipment, The Netherlands) was carefully inserted into the soil of each treatment replicate pot at an angle of approximately 45º. Vacuum tubes (10 mL) were attached through a Luer lock system with hypodermic needles to extract pore water. Pore water samples were analysed for Al, Ca, Co, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb and Zn concentrations by ICP-AES (PerkinElmer Optima 4300 DV), carried out in triplicate.

2.4. Statistical analysis

The data obtained in this study were statistically treated using the software SPSS 19.0. Analysis of variance (ANOVA) and a test for homogeneity of variance were performed. In case of homogeneity, a post-hoc least significant difference (LSD) test was carried out. If there was no homogeneity, Dunnett's T3 test was carried out. Correlated bivariate analyses and a principal component analysis (PCA) were also performed. All the experimental measurements were performed in triplicate ± CI (confidence interval).

3. Results

3.1. Characteristics of the mine soil, biochar and waste

Characteristics of the mine soil and amendments are shown in **Table 2**. The soil from the settling pond at the mine of Touro had an extremely acid pH (2.96), pseudototal Cu concentration of 452 mg kg^{-1} (above the generic reference level established for Galician soils, 50 mg kg^{-1}) and soil total carbon (TC), soil total nitrogen (TN) and dissolved organic carbon (DOC) contents were below the detection limit (TC content < 4.0 g kg^{-1}, TN content < 1.5 kg^{-1}) (**Table 2**). In contrast, the biochar used contain a TC content of 667 g kg^{-1}, TN content of 5.8 g kg^{-1} and DOC content of 1.59 g kg^{-1}, and the pH of biochar was strongly alkaline (9.93) according to the USDA (1998) (**Table 2**). The amendment made from waste showed a TC content of 218 g kg^{-1}, TN content of 22.9 g kg^{-1} and DOC content of 12.63 g kg^{-1} (**Table 2**). The pH of this material was moderately acid (5.55) according to the USDA (1998) (**Table 2**). The waste mixture contained high Cu, Ni, Pb and Zn pseudototal concentration probably due to components such as sewage sludges (Bolan et al. 2014).

Table 2. Chemical characteristics and pseudototal concentration of metals in the mine soil (M) and in the two organic materials: biochar (B) and waste (W)

	M	B	W
pH H_2O	2.96 ± 0.07c	9.93 ± 0.22a	5.55 ± 0.07b
pH KCl	2.73 ± 0.02c	9.64 ± 0.05a	5.48 ± 0.05b
TC (g kg^{-1})	u.l.	667 ± 57.22a	218 ± 15.85b
TN (g kg^{-1})	u.l.	5.8 ± 0.87b	22.9 ± 3.16a
C/N	-	115a	9b
SOC (g kg^{-1})	u.l.	599a	193b
IC (g kg^{-1})	u.l.	68.28 ± 9.31a	25.25 ± 4.39b
DOC (g kg^{-1})	u.l.	1.59 ± 0.07b	12.63 ± 0.84a
Cu (mg kg^{-1})	452 ± 52.56b	28.69 ± 2.76c	656 ± 47.55a
Ni (mg kg^{-1})	18.9 ± 3.40b	27.92 ± 8.69b	82.43 ± 17.84a
Pb (mg kg^{-1})	20.89 ± 3.20b	u.l.	186 ± 11.69a
Zn (mg kg^{-1})	65.35 ± 20.77b	85.82 ± 11.38b	1446 ± 91.52a

Mean ± CI (confidence interval) values (n = 3). Values followed by different letters differ significantly with P < 0.05. u.l.: undetectable level; TC: total carbon; TN: total nitrogen; TOC: total organic carbon; IC: inorganic carbon; DOC: dissolved organic carbon.

3.2. Characteristics of the greenhouse soil samples

3.2.1. Chemical characteristics

The unamended soils (S and SP) presented extremely acid pH values according to the USDA (1998), after 3 months of greenhouse experiment (**Table 3**). The pH of soil increased significantly after waste and biochar application (from extremely acidic values (2.7) to slightly acid values (6.18)) (**Table 3**). The TC and TN concentrations were below the detection limit in the unamended soils and the addition of waste and biochar significantly increased TC and TN contents with increasing amount of amendment (**Table 3**). The DOC concentrations were below the detection limit in the untreated soils and increased significantly after amending with waste and biochar and planting *B. juncea* plants. The DOC concentrations ranged between 1.35 – 8.04 g kg^{-1} in the greenhouse soil samples and the highest concentration was observed in T4P (**Table 3**).

3.2.2. Soil pore water concentrations

The influence of waste and biochar amendment and *B. juncea* plants on the immobilization of metals was examined by analysing trace element pore water concentration in soils treated with this amendment mixture. The addition of waste and biochar amendment to the mine soil was very effective in reducing Al and Cu concentration in soil pore water, indicating metal immobilization (**Table 4**). Waste and biochar reduced Al and Cu pore water concentrations from 1406 and 344 mg L^{-1} to 0.07 (99.99%) and 0.09 (99.97%) mg L^{-1}, respectively (**Table 4**). The application of waste and biochar as soil amendment reduced Fe concentration in pore water from 37.25 to 0.08 (99.79%) mg L^{-1} after amendment application (**Table 4**). The solubility of Co and Ni in soil was clearly affected by the addition of waste and biochar amendment mixture. The concentration of Co and Ni in pore water decreased from 21.96 and 21.50 mg L^{-1} to 0.01 (99.95%) and 0.02 (99.91%) mg L^{-1}, respectively (**Table 4**). The waste and biochar amendment reduced Zn concentration in pore water from 40% amendment application, compared to the unamended soils (**Table 4**). Manganese concentration in pore water significantly decreased from 80% amendment application in the soils without *B. juncea* plants, and from 40% amendment application in the soils with *B. juncea* plants, compared to the unamended soils (**Table 4**). However, Pb and Mg concentration in soil pore water did not showed a specific trend after waste and biochar application, compared to the unamended soils (**Table 4**).

Waste and biochar amendment significantly increased Ca, K and Na concentrations in soil pore water from 322 mg L^{-1} to 1242 mg L^{-1}, from 4.14 mg L^{-1} to 622 mg L^{-1}, and from 34.86 mg L^{-1} to 1040 mg L^{-1}, respectively (**Table 4**). Phosphorus concentration in pore water increased from values below the detection limit to 0.76 mg L^{-1} in the amended soils, but the P values were generally low in all the greenhouse soil samples (**Table 4**). The concentration of Ca, K, Na and P in the treatments without *B. juncea* plants was generally higher than in the treatments with *B. juncea* plants.

3.2.3. *Brassica juncea* growth

B. juncea plants did not survive in the mine soil (SP), dying 1 week after being planted. *B. juncea* plants grew in all the soils with amendment (from 20 to 100% of amendment). The biomass produced by *B. juncea* plants in the different soil treatments was 0.74 ± 0.12 (T1P), 2.4 ± 0.23 (T2P), 2.95 ± 0.25 (T3P), 2.55 ± 0.67 (T4P). The treatment T3P showed the highest biomass of *B. juncea* plants. The concentration of metals in *B. juncea* plants grown in the different soil treatments after 3 months of experiment is showed in **Table 5**.

3.2.4. Principal component analysis (PCA) in the soil samples

Pore water concentrations of the analysed trace elements were selected to perform a principal component analysis (PCA) (**Table 6**). The two principal components obtained accounted for 84% of the total variance. According to the position of the soil samples in the scatter plot (**Figure 1**), the amended soils significantly changed their trace element concentration in comparison to the unamended soils (S and SP). The component score coefficients matrix obtained (**Table 6**) showed that S and SP were positively influenced by Al, Co, Cu, Fe, Mn, Ni and Zn (**Figure 1**). The scatter plot showed that soils T1, T2, T3, T4 and T3P were positively influenced by the concentration of Ca, K, Mg and Na, but they were not negatively influenced by any trace element (**Figure 1**). In addition, the soils T1P, T2P and T4P were not influenced by any of the trace element contents (**Table 6**, **Figure 1**).

Table 3. Selected chemical properties in soil samples at 3 months of experiment

Soil sample	pH H_2O	pH KCl	TC (g kg^{-1})	TOC (g kg^{-1})	IC (g kg^{-1})	DOC (g kg^{-1})	TN (g kg^{-1})	C/N
S	2.83 ± 0.08g	2.72 ± 0.04g	u.l.	u.l.	u.l.	u.l.	u.l.	-
SP	2.70 ± 0.17g	2.60 ± 0.18h	u.l.	u.l.	u.l.	u.l.	u.l.	-
T1	4.56 ± 0.11f	4.49 ± 0.11f	26.23 ± 0.99e	21.83e	4.4 ± 0.7d	1.35 ± 0.28f	2.6 ± 0.35e	10b
T2	5.16 ± 0.13e	5.12 ± 0.15e	56.53 ± 2.48d	46.8d	9.73 ± 0.7d	1.6 ± 0.36f	5.5 ± 1.76d	10b
T3	5.97 ± 0.28c	5.94 ± 0.26c	131 ± 4.85b	105b	25.73 ± 3.69c	4.25 ± 0.22d	11.4 ± 3.69b	11a
T4	6.02 ± 0.1bc	5.98 ± 0.1c	238 ± 2.54a	190a	47.93 ± 5.8a	6.78 ± 0.15b	20.23 ± 2.81a	11a
T1P	4.58 ± 0.05f	4.54 ± 0.07f	21 ± 2.45e	17.2e	3.8 ± 0.35d	1.49 ± 0.23f	1.97 ± 0.35e	10b
T2P	5.56 ± 0.26d	5.52 ± 0.21d	59.1 ± 3.34d	49.37d	9.73 ± 0.35d	2.51 ± 0.26e	5.03 ± 0.7d	11a
T3P	6.18 ± 0.24a	6.17 ± 0.23a	110 ± 2.12c	90.13c	19.87 ± 2.46c	5.82 ± 0.77c	9.5 ± 1.23c	11a
T4P	6.07 ± 0.1b	6.06 ± 0.07b	236 ± 1.24a	195a	40.6 ± 0.88b	8.04 ± 0.31a	20.5 ± 0.88a	11a

Mean ± CI (confidence interval) values (n = 9). Values followed by different letters in each column differ significantly with $P < 0.05$. u.l.: undetectable level; TC: soil total carbon; TOC: total organic carbon; IC: soil inorganic carbon; DOC: dissolved organic carbon; TN: soil total nitrogen.

Table 4. Pore water trace element concentrations (mg L^{-1}) in soil samples at 3 months of experiment

	S	SP	T1	T2	T3	T4	T1P	T2P	T3P	T4P
Al (mg L^{-1})	1406±357a	874±85.04b	1.02±0.39c	0.16±0.02c	0.07±0.02c	0.23±0.02c	1.18±0.23c	0.07±0.02c	0.08±0.02c	0.08±0.02c
Ca (mg L^{-1})	337±14.56f	322±10.02f	607±61.11d	841±75.46b	1242±179a	1234±205a	427±22.52e	296±57.26f	775±76.91bc	719±68.18c
Co (mg L^{-1})	21.96±4.36a	13.14±1.79b	0.46±0.05c	0.10±0.03c	0.01±0c	0.02±0c	0.44±0.12c	0.02±0c	0.02±0c	0.01±0c
Cu (mg L^{-1})	344±95.91a	220±9.12b	0.19±0.05c	0.14±0.02c	0.09±0.02c	0.09±0.03c	0.20±0.04c	0.09±0.02c	0.14±0.02c	0.07±0.03c
Fe (mg L^{-1})	37.25±8.35a	31.71±3.02a	0.12±0.03b	0.24±0.02b	0.10±0.03b	0.10±0.02b	0.08±0.03b	0.10±0.01b	0.12±0.02b	0.11±0.02b
K (mg L^{-1})	4.14±0.19f	5.80±0.95f	293±61.23c	456±83.55b	622±60.24a	623±183a	159±50.99d	102±14.35e	340±110c	314±71.32c
Mg (mg L^{-1})	536±46.59a	331±23.81cd	368±41.57c	458±45.45b	529±54.86a	503±85.4ab	252±58.64e	131±17.62f	344±37.43c	282±78.64de
Mn (mg L^{-1})	41.54±4.89a	25.48±2.31b	37.62±4.9a	26.38±3.79b	8.42±2.22c	8.89±1.61c	27.44±2.52b	5.02±0.59c	5.91±0.65c	4.85±1.17c
Na (mg L^{-1})	38.19±1.17f	34.86±2.93f	453±66.27d	733±25.95b	1040±110a	1038±140a	284±56.76e	260±67.5e	741±64.63b	623±50.3c
Ni (mg L^{-1})	21.5±3.52a	13±1.76b	0.24±0.02c	0.06±0.01c	0.03±0c	0.02±0c	0.27±0.07c	0.02±0c	0.03±0c	0.03±0c
P (mg L^{-1})	u.l.	u.l.	0.56±0.02e	0.57±0.03e	0.76±0.04c	1.29±0.3a	0.65±0.02d	0.37±0.04g	0.44±0.02f	0.83±0.06b
Pb (mg L^{-1})	0.09±0.02ab	0.07±0.01b	0.10±0.02a	0.09±0.03ab	0.07±0.02b	0.08±0.02ab	0.07±0.01b	0.08±0.01b	0.09±0.02ab	0.07±0.02b
Zn (mg L^{-1})	8.2±0.95a	5.55±0.65b	5.12±0.61b	2.01±0.23c	0.34±0.05d	0.41±0.06d	4.98±1.12b	0.41±0.03d	0.35±0.05d	0.32±0.04d

Mean ± CI (confidence interval) values (n = 3). Values followed by different letters in each row differ significantly with $P < 0.05$. u.l.: undetectable level.

Table 5. Concentration of Cu, Ni, Pb y Zn in *B. juncea* plants grown in the different soil treatments at 3 months of experiment

Soil sample	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
T1P	223 ± 8.69a	55.19 ± 8.12a	6.67 ± 0.87b	1113±33.36a
T2P	67.08 ± 8.92b	25.01 ± 0.9b	u.l.	716±9.41b
T3P	47.05 ± 2.67c	4.26 ± 0.02d	11.78 ± 2.59a	729±23.77b
T4P	34.45 ± 3.55d	19.07 ± 4.28c	11.72 ± 2.48a	922±44.78a

Mean ± CI (confidence interval) values (n = 9). Values followed by different letters in each column differ significantly with $P < 0.05$. u.l.: undetectable level.

Table 6. The component score coefficients matrix from the PCA for the soil samples after 3 months of experiment

Indicators	PC1	PC2
Al	0.92	-0.32
Ca	-0.24	0.96
Co	0.92	-0.32
Cu	0.92	-0.33
Fe	0.88	-0.36
K	-0.37	0.92
Mg	0.63	0.77
Mn	0.71	-0.23
Na	-0.43	0.89
Ni	0.92	-0.32
P	-0.57	0.63
Pb	0.46	0.09
Zn	0.78	-0.43

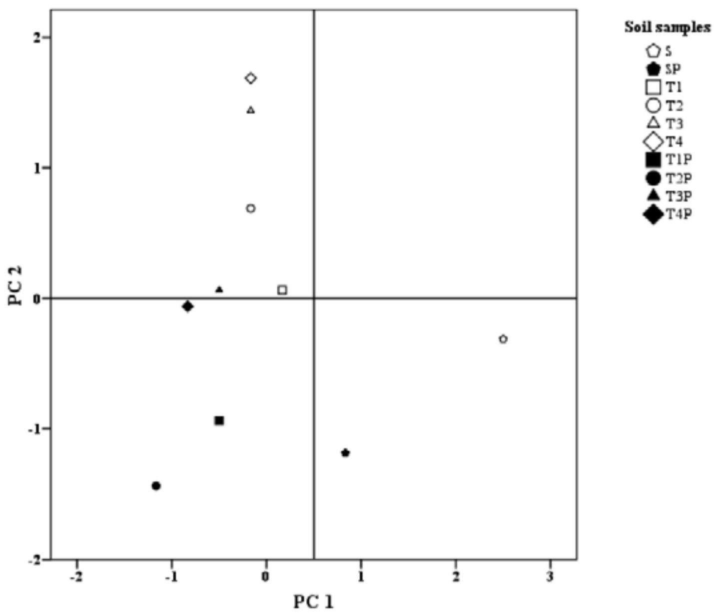

Figure 1. Scatter plot with the two principal components obtained in the PCA (PC 1 and PC 2) referred to the soil samples after three months of experiment.

4. Discussion

4.1. Effect of waste mixed with biochar as soil amendment, and *B. juncea* plants on soil chemical characteristics

The soil pH values increased significantly after waste and biochar application to the mine soil (Table 3). The pH of the amended soils ranged 4.6–6.2 and the pH of the unamended soils remained extremely acidic according to the USDA (1998), after three months of experiment (Table 3). These results agree with those found in previous works by Zornoza et al. (2016) and Hansen et al. (2016). Zornoza et al. (2016) reported an increase of soil pH in acid mine soils after addition of different amendments (pig manure and pyrogenic carbonaceous material) for soil reclamation. Hansen et al. (2016) observed that application of straw and wood biochar as soil amendment increased soil pH values. Soils with amendment and *B. juncea* plants showed generally higher pH values than the soils with amendment and without *B. juncea* plants (Table 3). The TC, TOC and IC contents significant increased after the application of the waste and biochar amendment to the mine soil (Table 3). Agegnehu et al. (2015) observed a significantly increase of TOC after biochar and compost application to the soil and Peltre et al. (2015) reported an increase of TOC after the use of organic waste products as soil amendment. Amendment incorporation into the mine soil significantly increased soil DOC content (Table 3). The addition of organic waste materials (e.g. sewage sludge, poultry and animal manures) increases the amount of DOC in soils (Sherene 2009). Liu et al. (2016b) also reported an increase of DOC after biochar application as soil amendment.

4.2. Effect of waste mixed with biochar as soil amendment, and *B. juncea* plants on soil pore water concentrations

Amendment made from waste and biochar significantly decreased Cu concentrations in pore water compared to the unamended soils (Table 4). This was confirmed by significantly negative correlations between the concentration of Cu and pH ($P < 0.01$, $r = -0.853$), TC ($P < 0.01$, $r = -0.487$), TOC ($P < 0.01$, $r = -0.500$) and DOC ($P < 0.01$, $r = -0.561$). With increasing pH of the soil, the solubility of Cu will decrease. Binding of Cu by soils is related to the formation of organic complexes and is highly dependent on soil pH (Kabata-Pendias 2011). Karami et al. (2011) observed that the application of biochar as soil amendment was an effective treatment to reduce pore water Cu concentrations. Zeng et al. (2015) also reported that Cu concentration in pore water was significantly reduced after adding compost and biochar to the soil. The application of combine mixture of waste and biochar significantly reduced Al and Fe concentration in pore water (Table 4). Significant negative correlations were found between the concentration of Al and pH ($P < 0.01$, $r = -0.851$), TC ($P < 0.01$, $r = -0.486$), TOC ($P < 0.01$, $r = -0.499$) and DOC ($P < 0.01$, $r = -0.559$), and the concentration of Fe and pH ($P < 0.01$, $r = -0.773$), TC ($P < 0.01$, $r = -0.437$), TOC ($P < 0.01$, $r = -0.449$) and DOC ($P < 0.01$, $r = -0.504$). Waste and biochar significantly increased Co and Ni immobilization in soil (Table 4). This was confirmed by significant negative correlations between the concentration of Co and pH ($P < 0.01$, $r = -0.856$), TC ($P < 0.01$, $r = -0.497$), TOC ($P < 0.01$, $r = -0.510$) and DOC ($P < 0.01$, $r = -0.569$), and the concentration of Ni and pH ($P < 0.01$, $r = -0.853$), TC ($P < 0.01$, $r = -0.491$), TOC ($P < 0.01$, $r = -0.504$) and DOC ($P < 0.01$, $r = -0.564$). Similarly, Hattab et al. (2015) reported that fresh ramial chipped wood and composted sewage sludge amendments significantly decreased Co concentration in pore water, compared to the unamended soil. Waste and biochar amendment significantly reduced Zn concentration in pore water (Table 4). It was found significantly negative correlations between the concentration of Zn and both pH ($P < 0.01$, $r = -0.910$) and TC ($P < 0.01$, $r = -0.732$). Significant negative correlations between the concentration of Zn and both TOC ($P < 0.01$, $r = -0.747$) and DOC ($P < 0.01$, $r = -0.783$) were also observed. Beesley et al. (2010b) studied the effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of trace elements in a multi-element contaminated soil. These authors observed that Zn concentration in soil pore water decreased after adding both amendments to the soil. Zeng et al. (2015) and Puga et al. (2015) also observed that Zn concentration in pore water significantly decreased after compost and biochar application. Nevertheless, waste and biochar application to the mine soil had no significant effect on Mg and Pb concentration in soil pore water (**Table 4**). Solubility of Pb in soils is usually very restricted (Kabata-Pendias 2004).

Soil application of waste and biochar as soil amendment resulted in an increase of Ca, K, Na and P concentrations in pore water (**Table 4**). The treatments T4 and T3 had generally the highest concentrations of Ca, K, Na and P in soil pore water (**Table 4**). These results agree with those found by other authors in previous studies. Novak et al. (2009) determined the impact of biochar additions on soil fertility characteristics and water leachate chemistry. Biochar additions to the soil increased soil pH, soil organic carbon, Ca, K, and P concentrations in soil, and K and Na concentrations in leachates. Roberts et al. (2015) reported that biochar contributed essential trace elements to soil pore water. The concentrations of K and P in the leachates increased significantly when the biochar was added to the soil.

In our study, it was found that waste and biochar amendment was generally effective in the immobilization of metals (**Table 4**). Reduced metal concentration in soil pore water resulting from waste and biochar application can be attributed to both the immobilization of bioavailable metals and dilution effect due to increasing amount of amendment (Kumpiene et al. 2008). The incorporation of organic waste into contaminated soils can change soil pH, increase water holding capacity and nutrient content, stimulate the humification process and carbon cycle, increase microbial biomass and activity, and form immobilized complexes between humic acids and metals (Kumpiene et al. 2008; Pardo et al. 2014). It has often been reported that the addition of biochars to the soil improves cation exchange capacity, specific surface area, water retention, total nitrogen and organic carbon (Laird et al. 2010). Biochars have high surface area, thereby enhancing the sorption of metals when incorporated into soils (Park et al. 2011).

Additional benefits of applying a waste and biochar amendment were observed in the growth of the *B. juncea* plants. Waste and biochar optimized soil properties and helped to sustain *B. juncea* plants in the mine soil. These plants did not survive in the unamended settling pond soil, probably due to the extreme acidity and the high levels of Cu in the mine soil (**Table 2**). The use of waste and biochar as amendment promoted plant growth and *B. juncea* plants were capable of growing in all of the amended soils. Similar results were reported by Lamb et al. (2012) and Bolan et al. (2013). These authors reported that the growth of *B. juncea* plants increased after the application of organic waste materials (biosolids collected from wastewater treatment plants) as soil amendment. The selection of an adequate plant species is a very important fact for the successful phytostabilization of degraded soils. The plant species selected (*Brassica juncea*) can tolerate high levels of metals and can produce a large amount of biomass in reasonable periods of time (Pérez-Esteban et al. 2014).

5. Conclusions

The results presented in this study suggested that a mixture of wastes and biochar have the potential to significantly affect the behavior of trace elements in a mine soil by altering their solubility in the soil. This study clearly showed that waste and biochar application improved soil properties (pH, TC, DOC, TN) and had the potential of generally increase the immobilization of metals, such as Al, Co, Cu, Fe, Mn, Ni and Zn, compared to the unamended soils. The results did not show great differences on soil-pore water metal concentrations between the planted and the unplanted pots. This waste and biochar amendment was also effective in promoting the revegetation of the mine soil, as *B. juncea* plants did not survive in the unamended mine soil. Therefore, the use of waste and biochar amendment combined with *B. juncea* plants could be an efficient strategy to enhance the phytostabilization process and reduce the metal solubility on contaminated soils.

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