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Assesment of compost and Technosol as amendments to increase nutrient contents in a mine soil vegetated with *Brassica juncea*

Evaluación de enmiendas elaboradas con compost y un Tecnosol sobre el incremento del contenido de nutrientes en un suelo de mina vegetado con Brassica juncea
Avaliação ção de um composto e de um Tecnossolo como corretivos para aumentar o teor de nutrientes em um solo de mina vegetalizado com Brassica juncea

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ABSTRACT

Abandoned mines pose potential risks to the environment and human health, and the reclamation of these areas is difficult. Soils from mining areas are usually characterised by degraded structure, high concentration of potentially toxic elements and deficiencies in nutrients. A greenhouse experiment was carried out in cylinders with the mine soil from the settling pond of the depleted copper mine of Touro (Galicia, Northwest Spain) amended with compost or technosol made from organic and inorganic wastes, and planted with *Brassica juncea* for 11 months. The aim of the study was to evaluate the effect of compost and technosol amendments on nutrient concentrations at different depths in a mine soil planted with *Brassica juncea*. The results revealed that at depths 0-15 and 15-30 cm, soil+technosol+*Brassica juncea* (STP) and soil+compost+*Brassica juncea* (SCP) treatments had higher pH than untreated mine soil S at the end of experimental. At depths 0-15 and 15-30 cm, SCP had the highest carbon total content. The nitrogen was only detected at depth 0–15 cm and only in the treated settling pond soil. STP and SCP had higher percentage of base saturation (V%) and lower percentage of aluminum saturation (Al%) than S and SS (sand). At depth 0-15 cm, soil+technosol+*Brassica juncea* (STP) and soil+compost+*Brassica juncea* (SCP) did not show generally significant differences on the nutrients values. At time 3, *Brassica juncea* plants cultivated in soil+compost+*Brassica juncea* (SCP) had the highest biomass. Soil+technosol+*Brassica juncea* (STP) treatment was the most effective increasing soil pH. Soil+compost+*Brassica juncea* treatment was the one that produced the greatest increase in total carbon. The treatments increased the cation exchange capacity (CEC) at depth 0-15 cm. Both treatments corrected the CEC by increasing the V% and decreasing the Al%. The application of technosol and *Brassica juncea* plants, or compost and *Brassica juncea* to a mine soil improved the soil quality.

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RESUMEN

Las minas abandonadas suponen una serie de riesgos potenciales para el medio ambiente y la salud humana. La recuperación de este tipo de suelos es difícil. Los suelos de mina generalmente se caracterizan por una falta de estructura, una alta concentración de elementos potencialmente tóxicos y por ser deficientes en nutrientes. Este estudio se llevó a cabo en invernadero en cilindros en los cuales se introdujo el suelo de la balsa de decantación de la antigua mina de cobre de Touro (Galicia, Noroeste de España). Este suelo fue tratado con enmiendas elaboradas con residuos (orgánicos e inorgánicos), compost y un tecnosol, y se cultivó Brassica juncea *sobre ellos durante 11 meses. El objetivo del presente estudio fue evaluar el efecto de enmiendas elaboradas con compost y tecnosol sobre las concentraciones de nutrientes a diferentes profundidades en un suelo de mina vegetado con* Brassica juncea*. Los resultados revelaron que, al final del tiempo experimental, a las profundidades 0-15 y 15-30 cm el suelo enmendado presentaba un pH más alto que el suelo de la balsa de decantación sin tratar (S). En las profundidades 0-15 y 15-30 cm el tratamiento suelo+compost+*Brassica juncea *(SCP) presentó un contenido más alto de carbono total. El nitrógeno solo se detectó en la profundidad de 0-15 cm y solo en el suelo de la balsa de decantación donde se aplicaron las enmiendas. Suelo+tecnosol+*Brassica juncea *(STP) y SCP presentaron una saturación de bases (V%) más alta y una saturación de aluminio (Al%) más baja que S y SS (arena). En la profundidad 0-15 cm, generalmente SCP y STP no mostraron diferencias significativas en los valores de nutrientes. En el tiempo 3, las plantas de* Brassica juncea *cultivadas en SCP presentaron una mayor biomasa. El tratamiento con STP fue el más eficaz a la hora de aumentar el pH del suelo de la balsa de decantación. El tratamiento SCP fue el que produjo el mayor aumento en carbono total. Los tratamientos aumentaron la capacidad de intercambio catiónico (CEC) en la profundidad 0-15 cm. Ambos tratamientos corrigieron la CEC, aumentando la V% y disminuyendo el Al%. Los tratamientos generalmente incrementaron los nutrientes en el suelo de la balsa de decantación (S). La aplicación combinada de compost con* Brassica juncea *y tecnosol con* Brassica juncea *a un suelo de mina mejoraron la calidad de dicho suelo.*

RESUMO

As minas abandonadas representam um risco para o meio ambiente e para a saúde humana, e essas áreas são de difícil recuperação. Os solos em áreas mineiras têm, normalmente, a estrutura degradada, elevada concentração de elementos potencialmente tóxicos e deficiência de nutrientes. Foi realizado um ensaio em estufa, em cilindros preenchidos com solo de uma bacia de sedimentação procedente da mina de cobre abandonada de Touro (Galiza, noroeste de Espanha). O objetivo do presente estudo foi avaliar o efeito de tratamentos com aplicação de um composto e um Tecnossolo nas concentrações de nutrientes em diferentes profundidades num solo de mina (S) cultivado com Brassica juncea *L.. O solo foi tratado com um composto e com um Tecnossolo, ambos elaborados com resíduos (orgânicos e inorgânicos), tendo-se cultivado* Brassica juncea *durante 11 meses. Os resultados mostraram que, depois de 11 meses de ensaio, nas profundidades 0-15 e 15-30 cm, os solos dos tratamentos (solo+tecnosolo+*Brassica juncea*) STP e SCP (solo+composto+*Brassica juncea*) tinham pH mais elevado do que os solos sem tratamento (S). Nas profundidades 0-15 e 15-30 cm, SCP apresentou o maior teor de carbono total. O nitrogénio total foi detetado somente na profundidade 0-15cm e apenas nos solos tratados. Os solos dos tratamentos STP e SCP tiveram maiores valores de saturação de catiões alcalinos e alcalinoterrosos (V%) e menores de saturação de alumínio (Al%) do que S e SS (areia). Na profundidade 0-15 cm, o conteúdo de nutrientes em SCP e STP não apresentaram diferenças significativas. No tempo três, as plantas de* B. juncea *cultivadas no SCP tiveram a maior biomassa. O tratamento STP foi o mais eficaz para aumentar o pH do solo. O tratamento SCP foi o que mais aumentou o C total. Os tratamentos aumentaram a capacidade de troca catiónica (CTC) na profundidade 0-15 cm. Ambos os tratamentos corrigiram a CTC mediante o aumento da V% e a diminuição da Al%. De uma forma geral, os tratamentos aumentaram o conteúdo de nutrientes no solo de mina. A aplicação combinada de um Tecnossolo e plantas de* B. juncea*, ou composto e* B. juncea *a um solo de mina melhorou a sua qualidade.*

KEY WORDS
Soil quality, mining, biomass, waste recovery, total carbon.

PALABRAS CLAVE
Calidad del suelo, minería, biomasa, valorización de residuos, carbono total.

PALAVRAS-CHAVE
Qualidade do solo, atividade mineira, biomassa, valorização de resíduos, carbono total.

1. Introduction

Mine soils usually present unfavourable conditions for plant growth due to their physicochemical characteristics, such as extreme pH, high salinity, low water retention capacity, high metal(loid) concentrations, and deficiencies in soil organic matter and soil fertility (Wang et al. 2017). Mine residues can produce acid mine drainage (in our case: $FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$), a dangerous source of water contamination (Barrie and Hallberg 2005) and it has been demonstrated that those pose significant risks to the environment and human health (Yang et al. 2012; Sánchez-López et al. 2015). Therefore, there is a need to develop strategies to reduce the impact of mining residues spread on mine landscapes to guarantee ecosystem reclamation (Moreno-Barriga et al. 2017).

In the mine of Touro (Galicia, NW Spain) copper was extracted for 15 years, from 1973 to 1988. This zone belongs to the most important group of copper mineralization in Galicia, associated with the basic massif of Santiago de Compostela (Galicia, Spain). The Touro mine is located in a formation of granular Precambrian amphibolites mineralized with metal sulphides, pyrite and pyrrhotine, with significant levels of chalcopyrite and minor amounts of blende and other metal sulphides (Calvo de Anta et al. 1991). Once copper extraction ended, another company extracted material for road construction (Forján et al. 2014). The soils formed on the settling pond and on the mine tailing of the depleted copper mine of Touro have unfavourable conditions such as extremely acid pH values, high metal concentrations, low organic matter content, degraded structure and low nutrient contents (Asensio et al. 2014a; Rodríguez-Vila et al. 2017).

The stabilisation of metals in polluted soils is a promising research area for restoring degraded soils and reducing phytotoxicity of metals. However, the remediation process of mining areas is influenced by the presence of a variety of metals and soil characteristics (Ma et al. 2015; Ali et al. 2017a). Numerous amendments have been used to immobilise metals, reduce their bioavailability and increase the soil fertility to facilitate the establishment of plants in polluted soils. They include amendments made from waste such as compost and technosol. However, the application of these types of amendments can have problems such as high metal concentrations, the excess or deficiency of nutrients and the presence of non-biodegradable materials.

The creation of technosols using different organic and inorganic waste materials can be a sustainable strategy to reclaim mine areas and reduce the contamination spread on the environment. Technosol parent material is a material produced or exposed by human activity that otherwise would not occur at the Earth's surface (IUSS Working Group WRB 2015). Technosols are dominated by human made materials, and their properties and pedogenesis are highly influenced by their technical origin (Moreno-Barriga et al. 2017).

Badly managed organic waste can lead to serious sanitary and environmental problems such as soil, air, and water pollution (Pellejero et al. 2017). Composting of organic waste products is considered to be one of the most economical, practical, and environmentally beneficial management options (Arslan et al. 2016; Azim et al. 2017). The multiple benefits of adding compost to the soil include increasing the amount of nutrients, organic matter, microbial activity and soil vegetation (Rodríguez-Vila et al. 2016). Composting is a biooxidative process that involves the mineralization and partial humification of organic matter, giving rise to a stabilized final product, free of phytotoxicity and pathogens and with certain humic properties (Azim et al. 2017).

Phytoremediation is the use of plants and microorganisms associated with soil to eliminate or reduce pollutants in the different environmental matrices (air, soil and water) (Compant et al. 2010; Rascioa and Navari-Izzo 2011). It is a technology friendly to the environment and that can be used to extract or immobilize metals. Phytoremediation uses chemical, physical and biological processes to eliminate, degrade, transform, or stabilize the pollutants present in air, soil and water. In addition, through these processes, the mobility and bioavailability of metals and their entry into the food chain is considerably reduced (Chirakkara et al. 2016; Kushwaha et al. 2016; Pinto et al. 2015). *Brassica juncea* is a hyperaccumulator and fast growing plant member of the *Brassicaceae* family used for the phytoremediation of contaminated soils (Ali et al. 2017b).

A greenhouse experiment was carried out in cylinders with the mine soil from the settling pond of the depleted copper mine of Touro (Galicia, Spain) treated with compost or technosol made from waste, and planted with *Brassica juncea* (Indian mustard) plants for 11 months. The effects of the different treatments were studied at three depths. The aim of the study was to evaluate the effect of compost and technosol amendments on nutrient concentrations at different depths in a mine soil planted with *Brassica juncea*.

2. Materials and Methods

2.1. Soil sampling and amendments

The sampled zone is located at the depleted copper mine of Touro, north western Spain (8º 20' 12.06'' W 42º 52' 46.18'' N). The climate in this zone is oceanic with precipitation reaching 1886 mm per year (with an average of 157 mm per month) and a mean daily temperature of 12.6 ºC. In order to carry out the study, one soil and three amendments were selected. The soil was collected from the settling pond (S) at the Touro mine, and was comprised of waste material resulting from the flotation of sulphides during copper processing. The pool has been dry since 1988, and is considered to be soil according to the latest version of the IUSS Working Group WRB (2015). Samples were taken at 5 different zones of the settling pond and were mixed, at depths between 0-50 cm.

The three amendments were:

- Sand consisting of washed sea sand provided by the company Leboriz S.L.U. (control).
- Technosol (T) provided by the company Tratamientos Ecológicos del Noroeste (T.E.N.). The technosol (T) consisted of a mixture of 60% purification plant wastes, 10% aluminium company wastes (from Padrón, La Coruña, Spain) 5% ash (from Ence, a cellulose company in Pontevedra, Spain), 10% wastes from the agri-food industry (canning companies and Ecogal), and 5% purification plant sand (sand fraction). The percentages do not add up to 100%, due to the privacy policy of the companies. The company provided a few indicative percentages.
- Compost (C) was made from horse and rabbit manure mixed with grass cuttings, fruit and seaweed, which was provided by the company Ecocelta Galicia S.L. (Ponteareas, Pontevedra, Spain).

2.2. Greenhouse experiment

The greenhouse experiment was carried out in cylinders to try to reflect the top 45 cm of soil; the cylinders are made of PVC with a depth of 50 cm and a diameter of 10 cm. A porous mesh was introduced into the cylinders, and the settling pond soil into the inner. Mesh was used for the settling pond soil was not in contact with the PVC for a long period of time. The cylinders are filled with: i) Settling pond soil (S, negative control), ii) Settling pond soil and sand (SS, neutral control), iii) and the treatments:

- Settling pond soil + technosol + vegetated with *Brassica juncea* (STP).
- Settling pond soil + compost + vegetated with *Brassica juncea* (SCP).

Technosol, compost and sand were deposited in the surface of the soil. The total weight of each cylinder was 3.5 kg. The experiment was carried out over 11 months at a controlled temperature and humidity (temperature of 22 ± 2 °C, and 65 ± 5% relative air humidity). A total of 48 cylinders, 12 cylinders of each treatment were prepared and distributed randomly (S, SS, STP, SCP). Randomly, three cylinders of each type were withdrawn at 3 different times: Time 1 = 3 months, Time 2 = 7 months, Time 3 = 11 months. The meshes were removed from the cylinders and processed for analysis at 3 different depths: the first from 0-15 cm, the second from 15-30 cm, and the third from 30-45 cm. The cylinders were watered to field capacity throughout the experiment.

2.3. Soil, technosol and compost analysis

The settling pond soil samples collected from the cylinders were air dried, passed through a 2 mm sieve and homogenized prior to analysis. Soil pH was determined using a pH electrode in 1:2.5 water to soil extracts (Porta 1986). Total soil carbon (TC) and total nitrogen (TN) were determined in a LECO CN-2000 module using solid samples. Exchangeable cations were extracted with 0.1 M $BaCl_2$ (Hendershot and Duquett 1986) and their concentrations determined by ICP-OES (Optima 4300 DV; Perkin-Elmer). Pseudototal metal contents were extracted with aqua regia by acid digestion in a microwave oven (Milestone ETHOS 1, Italy). Metal concentrations were determined by ICP-AES (Optima 4300 DV; Perkin-Elmer)

2.4. Harvested biomass and height of *Brassica juncea*.

Brassica juncea plants were pre-germinated in seedbeds until they grew two fully expanded leaves, and were then transferred to the cylinders (STP, SCP). The plants were harvested in the same state of maturity (the state of maturity chosen was before flowering), for comparison in the same physiological state of development in the three times (Time 1 = 3 months, Time 2 = 7 months, Time 3 = 11 months). Growth was allowed under greenhouse-controlled conditions, with a photoperiod of 11:13 light/dark, temperature of 22 ± 2 °C and 65 ± 5% relative air humidity. At the end of each time period, the height of the plants was measured, and they were carefully washed with deionised water. Fresh biomass was weighed immediately, and dry mass was assessed after oven-drying for 48 h at 80 °C and cooling at room temperature.

2.5. Statistical analysis

All of the analytical determinations were performed in triplicate. The data obtained were statistically treated using version 19.0 of the programme SPSS for Windows. Analysis of variance (ANOVA) and a test of homogeneity of variance were carried out. 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 performed. A correlated bivariate analysis was also carried out between TC and the content of Ca, K, Mg, and Na.

3. Results

3.1. General characteristics of the settling pond soil (S), sand (SS), compost (C) and technosol (T)

The compost (C) had higher pH values, total carbon (TC) and total nitrogen (TN) contents than S, SS and T ($P < 0.05$) (**Table 1**). The technosol (T) had higher CEC than S, SS and C (**Table 1**).

The pseudototal Cu concentration in the settling pond soil was higher than in T, C and SS ($P < 0.05$) (**Table 1**). The technosol had the highest pseudototal concentration of Pb (**Table 1**). The compost had higher pseudototal concentration of Ni and Zn than S, SS and T (**Table 1**).

3.2. Evolution of pH at three depths and over the 11-month period

On the one hand, at depths 0-15 and 15-30 cm, STP and SCP had higher pH than S at the end of experimental time (**Figures 1A, 1B**). On the other hand, at depth 0-15 and 15-30 cm, STP had higher pH values than SCP at the end of experimental time (**Figures 1A, 1B**). At depth 30-45 cm at time 3, STP and SCP had higher pH than S, moreover these treatments did not show significant differences in the pH values ($P < 0.05$) (**Figure 1C**).

Table 1. Characteristics of the mine tailing (S), sand (SS), technosol (T) and compost (C)

		S	SS	T	C
pH		2.73 ± 0.07d	3.78 ± 0.14c	6.04 ± 0.05b	6.47 ± 0.02a
TC	g kg^{-1}	1.93 ± 0.15c	2.76 ± 0.60c	256 ± 2.51b	276 ± 2,49a
TN	mg kg^{-1}	u.l.	0.10 ± 0.01c	17.67 ± 0.50b	21.33 ± 1.02a
Ca	mg kg^{-1}	13.3 ± 0.02c	9.65 ± 0.05d	7785 ± 0.15a	6455 ± 153b
K		6.40 ± 0.89c	u.l.	2687 ± 0.08b	3041 ± 46.5a
Mg		216 ± 2.10c	1.82 ± 0.02d	1997 ± 0.25a	1038 ± 14.9b
Na		27.4 ± 0.90c	7.95 ± 0.05d	2805 ± 0.03a	987 ± 12.4b
CEC	$cmol_{(+)}$ kg^{-1}	6.11 ± 0.05c	0.13 ± 0.05d	76.61 ± 0.04a	53.54 ± 1.07b
Cu	Pseudototal (mg kg^{-1})	637 ± 2.08a	46.6 ± 0.96d	226 ± 5.13b	193 ± 1.14c
Pb		16.10 ± 1.00c	10.10 ± 0.27d	89.65 ± 1.52a	26.67 ± 0.96b
Ni		16.41 ± 1.01c	8.41 ± 0.52d	26.32 ± 0.57b	49.70 ± 1.71a
Zn		65.40 ± 2.51c	18.75 ± 0.85d	340 ± 5.50b	403 ± 3.33a

Means ± SD. For each row, different letters in different samples means significant differences (n = 3, P < 0.05). u.l.: undetectable level.

3.3. Evolution of total carbon (TC) at three depths and over the 11-month period

At depths 0-15 and 15-30 cm at time 1, STP had higher total carbon contents than SCP, SS and S (P < 0.05) (**Figures 2A, 2B**). At times 2 and 3, SCP had the highest TC contents (**Figures 2A, 2B**). At depth 30-45 cm at times 1 and 2, SCP had the highest TC contents (**Figure 2C**). At time 3 SCP and STP did not show significant differences in the pH values (**Figure 2C**), but the treatments had higher TC contents than S and SS (**Figure 2C**).

3.4. Evolution of Total Nitrogen (TN) at the three different depths over the time

The TN was only detected at depth 0–15 cm and only in the treated settling pond soil. At time 1, the settling pond soil amended with technosol and vegetated with *Brassica juncea* (STP) had the highest TN values (**Figure 3**). At time 2, the settling pond soil treated with compost and *Brassica juncea* (SCP) had the highest TN values (**Figure 3**). At time 3, these treatments did not show significant differences in the TN values (**Figure 3**).

3.5. Evolution of the cation exchange capacity (CEC), base saturation (V%), and aluminium saturation (Al%) at three depths and over the 11-month period

At depth 0-15 cm, the treatment STP had generally the highest CEC over the time (P < 0.05) (**Table 2**). STP and SCP had higher V% and lower Al% than S and SS (**Table 2**).

At depth 15-30 cm, at time 1 SCP had the highest CEC (P < 0.05) (**Table 2**). At times 2 and 3, S and SS had higher CEC than STP and SCP (P < 0.05) (**Table 2**), but SCP had generally higher V% over the time at this depth (**Table 2**).

At depth 30-45 cm, at time 1 the SCP had the highest CEC (P < 0.05) (**Table 2**). At time 2, STP had the highest CEC (**Table 2**). However, at time 3, S was the treatment with the highest CEC, but STP and SCP had the highest V% (**Table 2**).

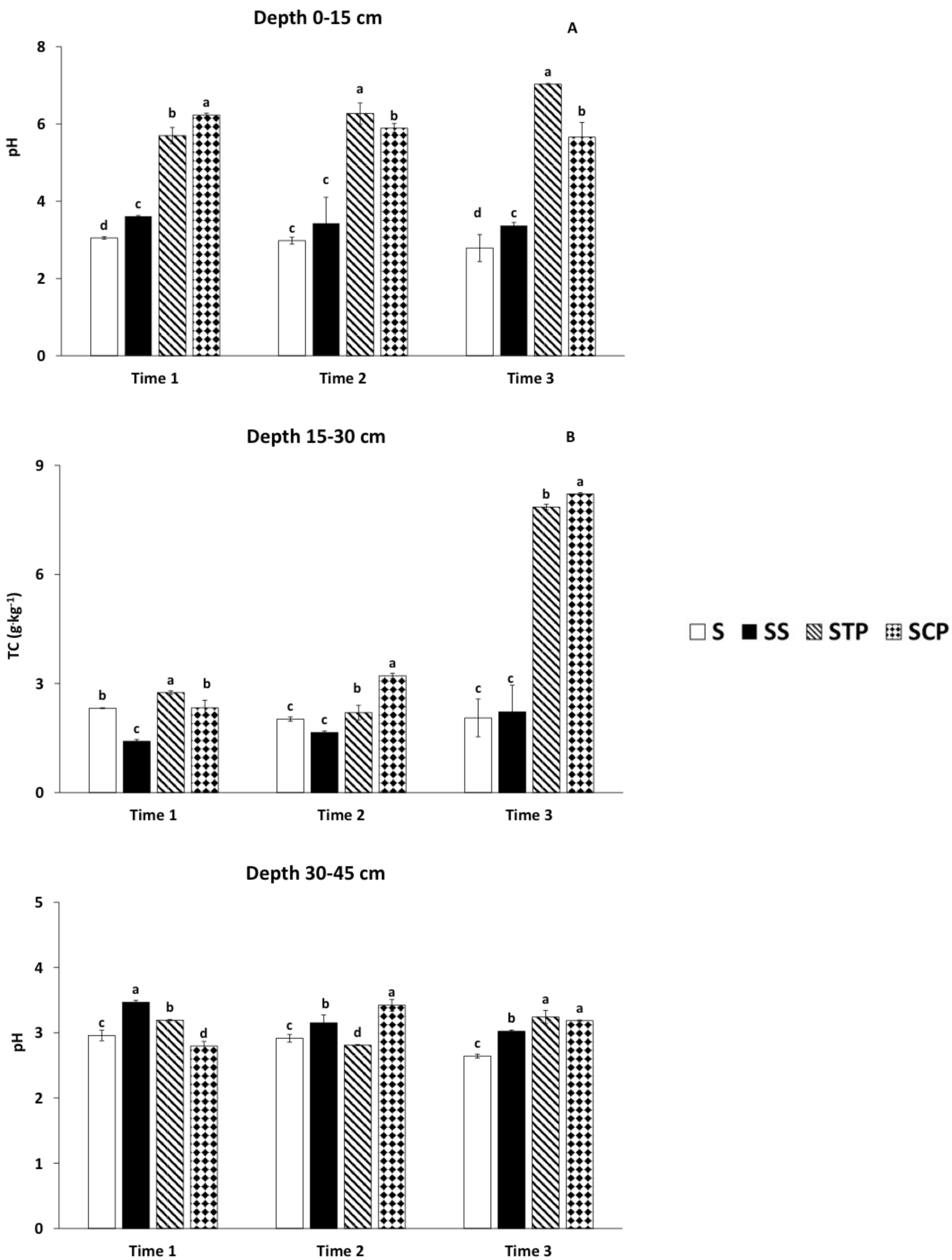

Figure 1. Evolution of the pH at three depths and over the 11-month period of experiment. S (settling pond soil), SS (settling pond soil + sand), STP (Settling pond soil + technosol + *Brassica juncea*), SCP (settling pond soil + compost + *Brassica juncea*). For each time, different letters in different samples mean significant differences (n = 3, ANOVA; P < 0.05). Error bars represent standard deviation.

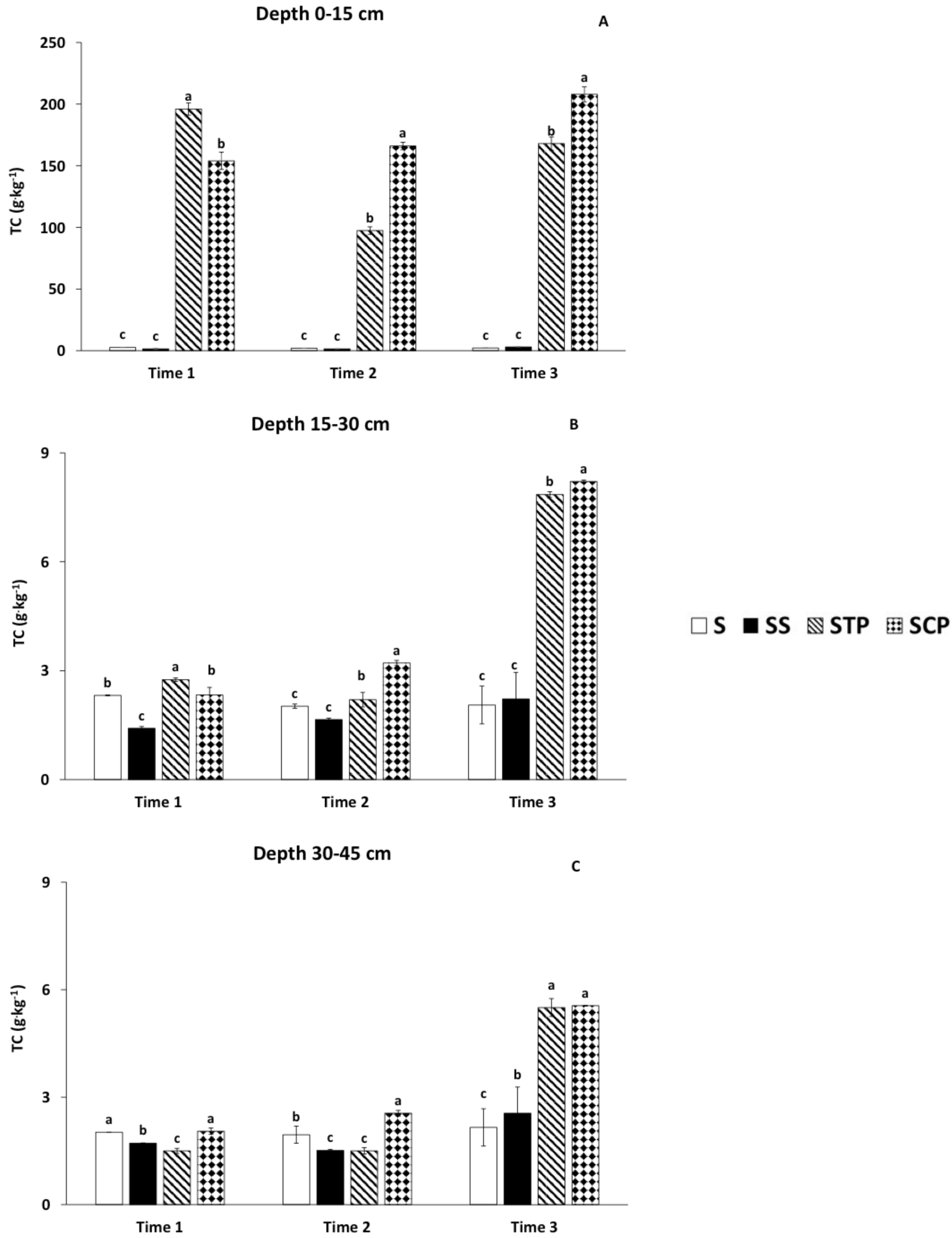

Figure 2. Evolution of Total Carbon (TC) at the three depths and over the 11-month period of experiment. S (settling pond soil), SS (settling pond soil + sand), STP (Settling pond soil + technosol + *Brassica juncea*), SCP (settling pond soil + compost + *Brassica juncea*a). For each time, different letters in different samples mean significant differences (n = 3, ANOVA; P < 0.05). Error bars represent standard deviation.

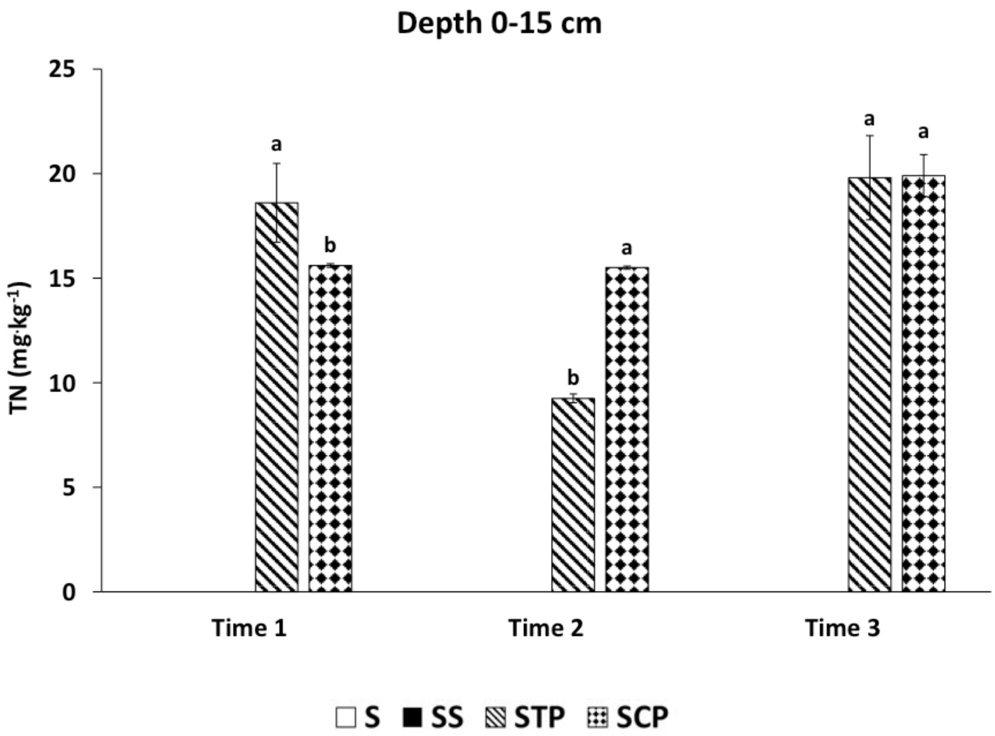

Figure 3. Evolution of Total Nitrogen (TN) at the three depths and over the 11-month period of experiment. S (settling pond soil), SS (settling pond soil+sand), STP (Settling pond soil + technosol + *Brassica juncea*), SCP (settling pond soil + compost + *Brassica juncea*). For each time, different letters in different samples mean significant differences (n = 3, ANOVA; $P < 0.05$). Error bars represent standard deviation.

3.6. Evolution of nutrients at three depths and over the 11-month period

At depth 0-15 cm, at the end of experimental time the treated soils had higher nutrient content (Ca, K, Mg, Na) than S, but SCP and STP did not show generally significant differences in the nutrients values (**Table 3**).

At depth 15-30 cm, at time 3 SCP had the highest K values (**Table 3**). STP and SCP had higher Ca values than S and SS (**Table 3**). S had the highest Mg values (**Table 3**). S, SS and SCP did not show significant differences in the Na values, which were higher than in STP (**Table 3**).

At depth 30-45 cm, at time 3 the K content was not detectable at this depth (**Table 3**). The soil from the settling pond had the highest Ca and Mg contents (**Table 3**). Finally, the treated soils (STP and SCP), SS and S did not show significant differences in the contents of Na (**Table 3**).

3.7. Harvested biomass of *Brassica juncea* over the 11-month period

The *Brassica juncea* plants were not capable of growing in the settling pond soil (S) and in the neutral control (SS), so these treatments were not represented in the **Figure 4**. At time 1 and 2, *Brassica juncea* plants cultivated in STP had higher biomass than *Brassica juncea* cultivated in SCP, but at time 3 *Brassica juncea* cultivated in SCP had the highest biomass (**Figure 4**).

Table 2. Evolution of the cation exchange capacity (CEC), base saturation (V%), and aluminium saturation (Al%) at three depths and over the 11-month period of experiment. S (settling pond soil), SS (settling pond soil + sand), STP (Settling pond soil + technosol + *Brassica juncea*), SCP (settling pond soil + compost + *Brassica juncea*)

			S	SS	SCP	STP
Depth 0-15 cm	Time 1	CEC	0.84 ± 0.05b	0.94b	34.7 ± 0.08b	36.5 ± 0.77a
		V%	35.7	27.8	100	100
		Al%	65.4	72.3	0	0
	Time 2	CEC	3.61 ± 0.04c	5.05b	28.7 ± 0.69a	28.4 ± 1.28a
		V%	37.5	36.2	99.9	100
		Al%	64.7	64.0	0.01	0
	Time 3	CEC	10.78 ± 0.47c	5.86c	31.4 ± 3.40b	39.3 ± 0.08a
		V%	43.4	41.8	99.9	100
		Al%	57.1	58.1	0.01	0
			S	**SS**	**SCP**	**STP**
Depth 15-30 cm	Time 1	CEC	0.94 ± 0.02b	1.10 ± 0.02b	4.61 ± 2.35a	2.91 ± 0.15ab
		V%	26.9	26.1	81.8	92.3
		Al%	73.1	73.9	18.2	7.70
	Time 2	CEC	3.06 ± 0.49ab	4.12 ± 0.84a	2.87 ± 0.02b	2.74 ± 0.25b
		V%	36.9	37.7	87.0	56.6
		Al%	63.1	62.3	13.0	43.4
	Time 3	CEC	10.6 ± 0.12a	11.0 ± 0.13a	4.46 ± 0.28b	4.18 ± 0.26b
		V%	41.0	38.5	63.7	62.5
		Al%	59.0	61.5	36.3	37.5
Depth 15-30 cm	Time 1	CEC	1.09 ± 0.01c	1.15 ± 0.10c	5.03 ± 0.61a	2.03 ± 0.10b
		V%	23.1	42.1	55.7	69.8
		Al%	76.9	57.9	44.3	30.2
	Time 2	CEC	3.23 ± 0.16b	4.61 ± 0.10a	1.58 ± 0.02c	4.73a
		V%	38.4	32.8	55.9	47.7
		Al%	61.6	67.2	44.1	52.3
	Time 3	CEC	15.6 ± 0.47a	11.5 ± 0.01b	4.70 ± 0.24c	2.86 ± 0.18d
		V%	38.3	40.0	42.5	42.9
		Al%	61.7	60.0	57.5	57.1

For each row, different letters in different samples mean significant differences (n = 3, ANOVA; P < 0.05). u.d. undetectable level. Standard deviation is represented by ±.

Table 3. Evolution of nutrients (mg.kg-1) in three depths and along the 11 months of experiment. S (settling pond soil), SS (settling pond soil + sand), STP (Settling pond soil + technosol + *Brassica juncea*), SCP (settling pond soil + compost + *Brassica juncea*)

Depth 0-15 cm		S	SS	STP	SCP
Time 1	Ca	9.51 ± 1.74b	6.53 ± 0.26b	4349 ± 3.04a	4818 ± 93.11a
	K	9.18 ± 0.07d	7.89 ± 0.41c	1888 ± 21.90a	1511 ± 37.89b
	Mg	12.01 ± 2.66b	11.4 ± 0.09b	655 ± 0.65a	662 ± 13.75a
	Na	25.75 ± 2.20c	21.75 ± 0.51c	553 ± 9.46b	615 ± 19.93a
Time 2	Ca	30.60 ± 0.31c	38.73 ± 1.05c	3870 ± 93.39b	4358 ± 208a
	K	1.68 ± 0.69c	2.12 ± 0.51c	1210 ± 25.24a	699 ± 16.74b
	Mg	128 ± 1.10c	184 ± 0.57b	533 ± 10.42a	479 ± 21.40a
	Na	22.36 ± 0.14c	17.81 ± 1.24c	366 ±1 2.10a	176 ± 2.43b
Time 3	Ca	94.84 ± 4.29b	58.40 ± 0.01c	4942 ± 533a	5647 ± 194a
	K	u.d	u.d	495 ± 61.31a	596 ± 18.71a
	Mg	496 ± 24.10a	253 ± 1.63b	594 ± 62.79a	556 ± 16.30a
	Na	14.20 ± 0.92b	11.90 ± 0.48b	101 ± 12.46a	125 ± 3.53a
Depth 15-30 cm		**S**	**SS**	**STP**	**SCP**
Time 1	Ca	6.47 ± 0.14c	8.18 ± 1.13c	324 ± 21.36a	228 ± 1.26b
	K	8.30 ± 0.87b	14.76 ± 0.42b	205 ± 12.75a	209 ± 17.10a
	Mg	8.64 ± 0.56c	9.18 ± 0.76c	120 ± 40.91a	44.60 ± 3.08b
	Na	21.22 ± 1.21b	23.87 ± 2.54b	123 ± 66.50a	124 ± 8.98a
Time 2	Ca	28.85 ± 4.60d	45.53 ± 9.96c	229 ± 3.81a	105 ± 13.01b
	K	1.59 ± 0.70c	0.54 ± 0.42c	210 ± 4.33a	51.56 ± 2.17b
	Mg	103 ± 18.61a	148 ± 32.21a	40.79 ± 0.06c	88.49 ± 8.13d
	Na	20.60 ± 0.54c	16.70 ± 2.33d	91.84 ± 0.70a	28.27 ± 1.57b
Time 3	Ca	110 ± 2.71b	123 ± 7.29b	333 ± 31.11a	248 ± 21.50a
	K	u.d	u.d	u.d	10.72 ± 0.83a
	Mg	452 ± 4.74a	430 ± 3.45b	135 ± 4.54c	112 ± 8.74c
	Na	10.60 ± 0.13a	11.50 ± 0.58a	8.71 ± 0.32b	11.81 ± 0.02a
Depth 30-45 cm		**S**	**SS**	**STP**	**SCP**
Time 1	Ca	7.01 ± 0.18c	5.38 ± 0.75c	160 ± 40.99a	80.40 ± 6.50b
	K	7.50 ± 0.19c	7.26 ± 0.40c	70.35 ± 10.94b	109 ± 4.59a
	Mg	13.90 ± 0.03c	6.72 ± 2.12d	168 ± 23.76a	32.01 ± 1.91b
	Na	20.89 ± 0.62b	23.11 ± 2.70b	82.07 ± 24.75a	90.11 ± 2.36a
Time 2	Ca	55.44 ± 1.79b	54.19 ± 10.12b	47.03 ± 1.20c	95.77 ± 0.39a
	K	1.00 ± 0.37c	0.27 ± 0.27c	96.49 ± 1.74a	71.12 ± 0.08b
	Mg	102 ± 4.67b	144 ± 4.57b	17.70 ± 0.15c	165 ± 2.56a
	Na	19.69 ± 1.36b	6.09 ± 3.10c	46.81 ± 1.67a	42.80 ± 4.71a
Time 3	Ca	184 ± 5.66a	150 ± 0.26b	71.01 ± 0.26c	34.20 ± 1.63d
	K	u.d	u.d	u.d	u.d
	Mg	606 ± 18.54a	465 ± 0.49b	192 ± 0.49c	109 ± 8.59d
	Na	10.31 ± 0.56a	11.30 ± 0.19a	9.34 ± 0.19a	10.45 ± 1.07a

For each row, different letters in different samples mean significant differences (n = 3, ANOVA; P < 0.05). u.d. undetectable level. Standard deviation is represented by ±.

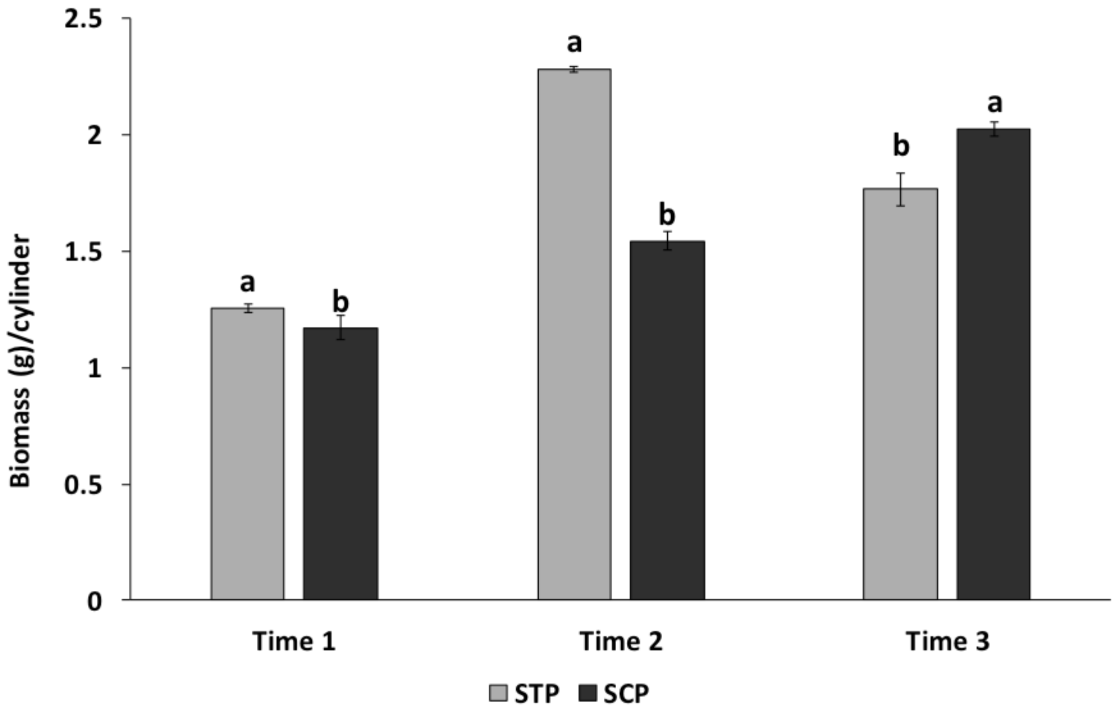

Figure 4. Harvested biomass of *Brassica juncea* over the 11-month period of experiment. STP (Settling pond soil + technosol + *Brassica juncea*), SCP (settling pond soil + compost + *Brassica juncea*). For each time, different letters in different samples mean significant differences (n = 3, Student's t test: $P < 0.05$). Error bars represents standard deviation.

4. Discussion

4.1. Evolution of the pH at three depths and over the 11-month period

The sulphide minerals in contact with water and air produce sulphuric acid (Pataca 2004), This process begins with the oxidation of pyrite, key in the oxidation-leaching process, which generates Fe^{3+} ions and sulfuric acid, which in turn contributes sulfate ions (SO_4^{-2}) and H^+ to the system. At the same time, ferric sulfate [$Fe_2(SO_4)_3$] is a key element in the oxidation processes that occur in the rest of the sulphides (Johnson and Hallberg 2005). The soil S has a predominance of waste resulting from the flotation of sulphides during copper processing and this was the origin of the low pH of the settling pond soil.

At depth 0-15 cm and 15-30 cm, at time 3 STP had the highest pH values. This might be due to the fact that although the technosol had a lower pH than the compost (Table 1) the technosol presented a higher CEC. This higher CEC of the technosol could influence the increase of pH values in STP. The lower pH increase in SCP treatment at these depths may be due to compost losing its effect before the other types of amendments since compost has a less recalcitrant effect than other amendments such as technosols or biochar, as demonstrated by Walker et al. (2004). At depth 30-45 cm, SCP and STP increased the pH in the settling pond soil but the treatments did not present significant differences on the pH values.

The increase of the pH values produced by the treatments in all the studied depths is important because soils with pH below 3.5 are strongly limited for plant production (Bendfeldt et al. 2001).

4.2. Evolution of the Total Carbon (TC) at the three depths and over the 11-month period

At depths of 0-15 cm and 15-30 cm, SCP treatment increased the TC more than the treatment STP, because compost had a higher TC content than technosol (**Table 1**). In addition, as compost loses stability over time (Walker et al. 2004), this can produce an increase on TC at lower depths by the migration of carbon due to leaching. At depth 30-45 cm pH showed a similar trend and there were no significant differences between the treatments. The improvement in carbon content through the application of STP and SCP treatments is very important since the carbon content is an important factor in the quality of a soil (Bendfeldt et al. 2001; Vega et al. 2005). This improvement in quality was reflected in the SCP treatment where a positive correlation (0.97, $P < 0.01$) between TC and *Brassica juncea* biomass was obtained.

In this experiment, a positive correlation was obtained between TC and the content of Ca (0.97, $P < 0.01$), K (0.78, $P < 0.01$), Mg (0.83, $P < 0.01$), Na (0.67, $P < 0.01$). These data coincide with those obtained by Lal et al. (2006) who concluded that the soil carbon is important for the recovery of degraded soils, as the increase of the soil organic carbon produce an increase on the concentration of nutrients in bioavailable form.

4.3. Evolution of the Total Nitrogen (TN) at the three depths and over the 11-month period

On mine degraded soils, nitrogen is a major limiting factor and addition of TN fertilizer becomes a common practice to maintain healthy growth and persistence of vegetation (Li 2006). The S soil presented a not detectable TN content, for this reason the treatments STP and SCP were applied and they increased those contents in the depth 0-15 cm. However, there were no significant differences on nitrogen contents between the treatments.

This increase of TN content is due to the residues from which the treatments were assembled. In the case of technosols, these were residues from purification plant waste, ash, and waste from the agri-food industry (Canet et al. 2007; Pérez-Esteban et al. 2012; Smith 2009; Weber et al. 2007). In the case of compost, these were residues from horse and rabbit manure mixed with grass cuttings, fruit and seaweed, which have high TN contents (Canet et al. 2007; Khan et al. 2009; Pérez-Esteban et al. 2012; Miller et al. 2003).

In addition, this increase of TN caused by the treatments can be influenced by the presence of *Brassica juncea* plants. Some non symbiont nitrogen-fixing bacterial communities are usually associated with certain species of *Brassica*; this proliferation of bacteria is the result of various exudates released by the root (Germida et al. 1998; Misko and Germida 2002). Due to these factors, *Brassica juncea* plants can provide significant amounts of nitrogen to the soil, as demonstrated by Zhou et al. (2012).

4.4. Evolution of the cation exchange capacity (CEC) ($cmol_{(+)}$ kg^{-1}), base saturation (V%), and aluminium saturation (Al%) at the three depths over the 11-month period

At depth 0-15, in general the treatment STP improved the CEC more than the treatment SCP. This is possibly due to the technosol having a higher CEC than compost, and compost is an amendment that can lose stability after 31 days (Walker et al. 2004). At depth 0-15 cm, STP and SCP had an average base saturation (V%) of 100%, which indicates that the binding sites of the soil in these treatments are saturated with Ca^{2+}, K^{+}, Mg^{2+}, and Na^{+}. Authors such as Pérez-Esteban et al. (2012) showed that the application of amendments made from residues increases the cation exchange capacity.

At depths 15-30 cm and 30-45 cm, at the end of the experimental time the treatments did not increase the CEC in comparison with S. However, the V% is higher in SCP and STP than in S, which indicates that the treatments increased the basic cations. This improvement of the CEC increasing the V% and decreasing the Al% is important since CEC can be an obstacle to recovering a degraded soil because CEC is a major controlling agent of nutrient availability for plant growth, soil pH, and the soil reaction to fertilisers and other ameliorants (Hazelton and Murphy 2007).

4.5. Evolution of nutrients at the three depths and over the 11-month period

The treatments SCP and STP increased the nutrients in S, but this effect in the depths 15-30 cm and 30-45 cm was lost by deepening the profile and over the time. The increase of nutrients provided by amendments made from residues in degraded mine soils was previously reported by Asensio et al. (2014b). At depth 0-15 cm, there were no significant differences on nutrient content between the treatments. This increase in nutrient content was due to the residues used to produce the amendments. On the one hand, technosol whose residues contain high levels of Ca, K and Mg (Canet et al. 2007; Pérez-Esteban et al. 2012; Smith 2009; Weber et al. 2007) and on the other hand, compost made from waste (Canet et al. 2007; Khan et al. 2009; Pérez-Esteban et al. 2012; Miller et al. 2003). The increase of nutrients at depths 15-30 cm and 30-45 cm was lower, this could be due to the acidic pH and lack of organic matter at greater depths. Authors such as Pérez-Esteban et al. (2012) already detailed the relationship between nutrient increase with CEC and organic matter. In addition, in this experiment the positive effect of the increase of the nutrient contents on the biomass of *Brassica juncea* was reflected on positive Pearson correlations with values of $r = 0.99$ ($P < 0.01$), $r = 0.88$ (0.05), $r = 0.99$ ($P < 0.01$) for K, Mg and Na, respectively.

4.6. Harvested biomass of *Brassica juncea*

Brassica juncea cultivated in S and in SS did not grow over time. These treatments showed deficiencies in TN, TC, nutrient content and low pH or CEC. Wong (2003) studied this difficulty in establishing stable plant cover in mine soils, and states that degraded mine soils are human-made habitats which experience a wide range of problems for establishing and maintaining vegetation. In STP and SCP the *Brassica juncea* plants grew throughout the entire experimental period. The application of the treatments SCP and STP amended with residues improved the conditions of S allowing the development of *Brassica juncea* plants. The improvement of soil condition by organic amendments was already demonstrated by authors such as Wong (2003). At the end of the experiment time, the biomass produced by *Brassica juncea* plants was higher in SCP than in STP. The highest biomass of the *Brassica juncea* harvested in the SCP treatment may be due to the higher TC content of the SCP treatment compared to the STP treatment, since in the other parameters analysed there are practically no significant differences between treatments. In addition, in the SCP treatment, a positive correlation was obtained between the TC and the *Brassica juncea* biomass (0.97, $P < 0.01$).

5. Conclusions

The application of technosol and *Brassica juncea* plants, or compost and *Brassica juncea* to a mine soil improved the soil quality. At the end of the experimental time, STP treatment was more effective than SCP increasing the pH values. In general, SCP treatment produced a greater increase of TC content. Both treatments increased TN content but there were no significant differences between the two treatments. Both treatments increased CEC at depth 0-15 cm. However, throughout the experimental time both treatments corrected the CEC by increasing the V% and decreasing the Al%. The treatments SCP and STP increased the nutrients in S, but this effect in the depths 15-30 cm and 30-45 cm was not observed over the time. At the end of experimental time *Brassica juncea* plants cultivated in SCP had higher biomass than *Brassica juncea* grown in STP. The application of technosol and *Brassica juncea* plants, or compost and *Brassica juncea* to a mine soil improved the soil quality.

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