

# Increasing the Nutrient Content in a Mine Soil Through the Application of Technosol and Biochar and Grown with *Brassica juncea* L.

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Received: 1 March 2017 / Accepted: 17 July 2017 / Published online: 21 July 2017  
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**Abstract** Mining is an anthropogenic activity that causes a profound environmental impact in many parts of the world, including soil degradation through physical, chemical and biological transformations. Mine soils are nutritionally deprived habitats characterized by unfertile soil with low pH values, a low cation exchange capacity (CEC), low nutrient availability, and poor organic matter. Today, techniques such as the use of technosols and biochar are starting to be used with the aim of recovering these soils. In this experiment we will compare the nutrient supply, increased pH, total carbon, total nitrogen (TN) and CEC of two treatments made of different amendments (technosol and biochar) on a mine soil. We will also determine the capacity of biochar to fix nutrients and enhance the positive effects of technosols in order to achieve the continuous growth of *Brassica juncea* L. The effects of the treatments were studied at three different depths over the 45-cm length of each cylinder. The study lasted a total of 11 months, using a settling pond from a depleted copper mine in Touro (Galicia, north-west Spain). The results of this experiment revealed that the treatments applied increased the pH, nutrient, total carbon, TN and CEC values. In turn, in the majority of the factors studied, the treatment combining the technosol and biochar was the most effective, with the *B. juncea* L. grown on this treatment having the highest biomass values.

**Keywords** Technosol · Biochar · Nutrients · Mining · Soil recovery · *Brassica juncea* L.

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## Introduction

Human-induced disturbance is pervasive among all ecosystems as the result of waste accumulation, industrial pollution, resource extraction, and urban sprawl [1]. Mining activities are an example of disturbance of ecosystems, mining is an anthropogenic activity that causes high environmental impact in many areas of the world, including soil modification and degradation through physical, chemical and biological transformations. The mining extraction process completely removes completely flora, fauna, and soils from the previous system. Following resource exhaustion, post-mine areas are typically characterized by low soil organic matter content, low fertility, and poor physiochemical and biological properties, permanent changes to the topography and geological structures, and disruption to the subsurface hydrologic regime. The reclamation process involves replacing the overburden, grading it to the original contour, and spreading the topsoil to a depth of about 30 cm [1–3]. Mining activities generate large amounts of waste materials and tailings that are deposited on the surface in the form of mine spoil dumps. These are nutritionally deprived habitats characterized by unfertile soil with alterations of pH values, a low cation exchange capacity (CEC), low nutrient availability, and poor organic matter [4].

Plant establishment and soil recovery in degraded habitats may be slow to recover by natural successional processes without human intervention [1]. The importance of a plant cover is related to the improvement of the physical (e.g. structure), chemical (e.g. increase of organic matter and nutrients, immobilization of contaminants, decreased leaching) and biological (e.g. increase of microbial activity and diversity) characteristics of soil or wastes [5]. For this reason, organic wastes such as sewage sludge and refuse or

manure compost can be used as soil amendments, and to a certain extent as a slow release nutrient source. The organic matter and nutrient content of some common organic materials can be used to reduce the availability of metals, in addition to remediating the physical and chemical properties of the spoils, and the provision of plant nutrients. The incorporation of organic amendments into contaminated mine soils has been proposed as a feasible, inexpensive and environmentally sound disposal practice [6, 7]. Recently, a number of studies have focused on technosols, some of them dealing with the restoration of degraded areas [2]. Technosols combine soils whose properties and pedogenesis are dominated by their technical origin. They contain a significant amount of artefacts (something in the soil recognizably made or strongly altered by humans or extracted from greater depths) or are sealed by technic hard material (hard material created by humans, having properties unlike natural rock) or contain a geomembrane. They include soils from wastes (landfills, sludge, cinders, mine spoils and ashes), pavements with their underlying unconsolidated materials, soils with geomembranes and constructed soils. Technosols are often referred to as urban or mine soils [8]. Furthermore, technosols could be elaborated from wastes and employed in the subsequent regeneration of degraded or polluted soils. Thereby, these materials are no longer considered as waste and a value-added product is generated [9]. The use of technosols increases the concentration of nutrients, the pH, CEC, and even duplicates the organic matter content [10, 11]. Authors such as [10] showed that the improvement provided by the technosols lasts more in the time in comparison with other traditional techniques.

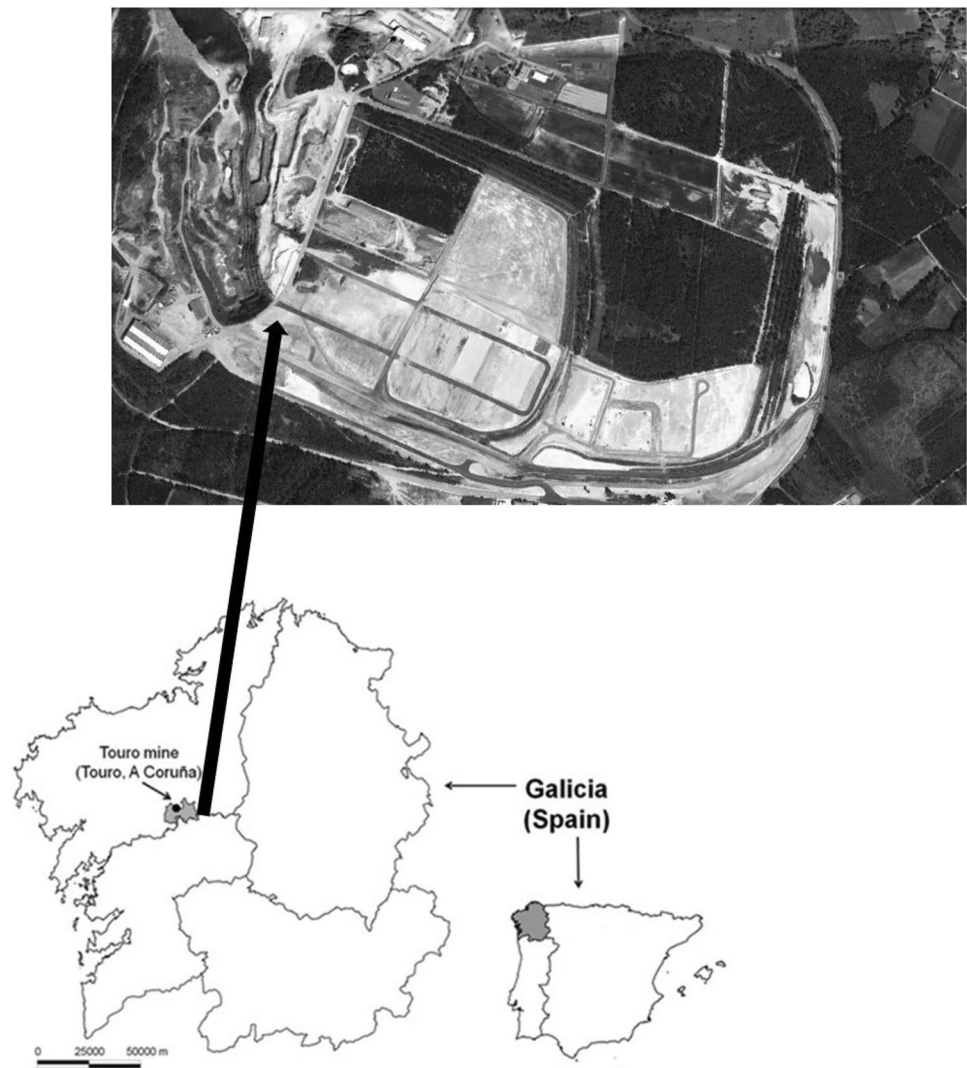
Today, researchers are beginning to study the use of biochar in the recovery of contaminated soils, as when biochar is mixed with amendments such as technosols, better results are obtained [12–14]. Also, using traditional amendments combined with biochar makes it possible to reduce costs. To create biochar, organic materials (i.e. feedstocks) are heated to temperatures between 300 and 800 °C in a low oxygen environment [15]. According to [1] the feedstocks may include agricultural wastes, forestry wastes, wood pellets, or manures. The high temperatures used in pyrolysis induce molecule polymerization within feedstocks to produce aromatic and aliphatic compounds. This creates a stable product demonstrated to be a potential sink for atmospheric CO<sub>2</sub> and beneficial soil amendment. Recent research [16, 17] has found that biochar is of great importance in increasing soil carbon storage, improving soil fertility, as well as maintaining the balance of soil ecosystems, and could act as a kind of soil fertilizer or amendment to increase crop yield and plant growth by supplying and retaining nutrients. According to authors such as [17] the increase on soil fertility may be due to the high surface area of feedstock biochar (200–300 m<sup>2</sup>/g) and high CEC

(27.7–222.4 mmolc/kg), which increases the water retaining capacity, nutrient sorption, and enhances plant growth by supplying and retaining nutrients. As biochar is highly recalcitrant, the effects of its application may be prolonged over a long period of time [18].

Establishment of the vegetation, site colonization with ambient plant species and recovery of the ecosystem is considered an indication of remediation success. A reclaimed soil is necessary for it to be able to sustain a stable vegetation cover, as this is very effective in reducing surface erosion because the roots bind the substrate. Also, vegetation can return a large proportion of percolating water to the atmosphere through transpiration, thus reducing the concentrations of soluble metals entering water courses [19]. Vegetation cover also goes a long way towards reducing the visual scars in the landscape caused by large-scale mining operations. Successful revegetation may allow for recreational use of the land, and even agriculture or forestry if conditions are favourable [19, 20]. It is very difficult to achieve a stable vegetation layer in these types of soils, as apart from containing metals, they usually have unfavourable properties such as a lack of nutrients, virtually no organic matter, and an extreme pH [21]. In order to achieve a stable vegetation cover on a degraded soil, such as a mine, it is necessary to remedy these deficiencies. Site preparation practices have the potential to modify the physical and chemical properties of the soil, thereby influencing nutrient availability for the establishing plants. For this reason, the early stage of vegetation establishment is particularly crucial and requires good site preparation practices to maximise the chance of success of the revegetation process [22].

The novelty of this work is to know the effect of the application of amendments made from residues to a degraded soil along 45 cm of depth. To know these effects we proposed the following objectives. The main objective of this study is compared the nutrient supply, increased pH, total carbon, total nitrogen (TN), and CEC of two treatments made using different amendments (technosol, biochar) on a mine soil. One treatment only contained technosol, while the second treatment contained technosol and biochar. Another objective of this study was to determine the capacity of biochar to retain nutrients and enhance the positive effects of technosols in order to be able to establish a permanent crop of *Brassica juncea* L. *B. juncea* L. has been used successfully in polluted mine soils [23–25]. With this aim, in this study we used soil from the settling pond of a copper mine into 50-cm cylinders in order to mimic as closely as possible the first few centimetres of the settling pond in the field. The settling pond soil was treated with different combinations of technosol and biochar, and *B. juncea* L. was planted. This study lasted a total of 11 months. The settling pond belongs to the depleted soil copper mine located in Touro (Galicia, north-west Spain).

**Fig. 1** Location of the sampled area in Touro mine



## Materials and Methods

### Soil Sampling and Amendments

The sample zone is located in an old copper mine in Touro, north western Spain ( $8^{\circ}20'12.06''W$   $42^{\circ}52'46.18''N$ ) (Fig. 1). The climate in this zone is Atlantic (oceanic) with precipitation reaching 1886 mm per year (with an average of 157 mm per month) and a mean daily temperature of  $12.6^{\circ}C$ . The average of relative humidity is 77% (AEMET 2015). In order to carry out the study, one soil and three amendments were selected. The soil that was chosen belongs to the settling pond (S) at the Touro mine, S 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 FAO [8].

The three amendments were:

- Sand (SS) consisted in 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. For this reason the sum of the percentages is not 100%. The technosol was elaborated with the aforementioned residues.
- The biochar (B) provided by the company PROININSO S.A., the biochar (B) used was made from *Quercus ilex* wood with a pyrolysis temperature of  $400^{\circ}C$  for 8 h.

## 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 (Fig. 2). The cylinders are filled with: settling pond soil (S, negative control), settling pond soil and sand (SS, neutral control), and the treatments:

- settling pond soil + technosol (ST)
- settling pond soil + technosol + vegetated with *B. juncea* L. (STP)
- settling pond soil + technosol + biochar (STB)
- settling pond soil + technosol + biochar + vegetated with *B. juncea* L. (STBP).

In the elaboration of the treatments STB and STBP, the technosol and the biochar were mixed, later the mixture was deposited in the surface of the soil. The amendment ratios used are detailed in Table 1. The total weight of each cylinder was 3.5 kg.

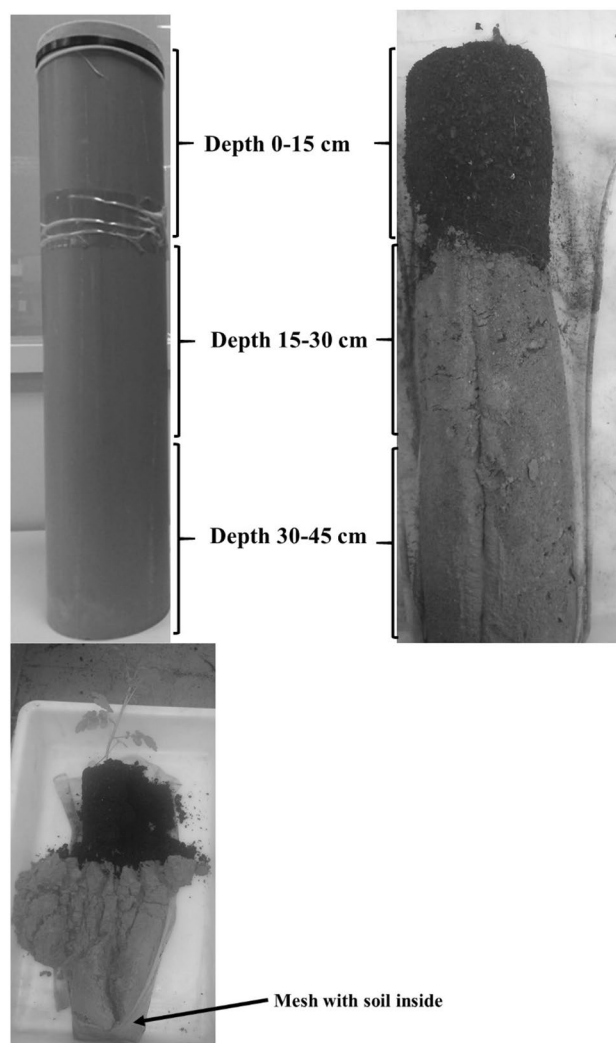
The experiment was carried out over 11 months at a controlled temperature and humidity (temperature of  $22 \pm 2$  °C, and  $65 \pm 5\%$  relative air humidity). A total of 90 cylinders, 15 cylinders of each treatment were prepared and distributed randomly (S, SS, ST, STP, STB, STBP). Three cylinders of each type were withdrawn at three 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 three different depths: the first from 0 to 15 cm, the second from 15 to 30 cm, and the third from 30 to 45 cm (Fig. 2). The cylinders were watered to field capacity throughout the experiment.

## Soil, Technosol and Biochar Analysis

The settling pond soil samples collected from the cylinders were air dried, passed through a 2 mm sieve and

**Table 1** Proportions used to make the controls and the different treatments

	Soil (%)	Sand (%)	Technosols (%)	Biochar (%)
S	100			
SS	85	15		
ST	85		15	
STP	85		15	
STB	85		11	4
STBP	85		11	4



**Fig. 2** Cylinder design and the different depths

homogenized prior to analysis. Soil pH was determined using a pH electrode in 1:2.5 water to soil extracts [26]. Total soil carbon (TC) and TN were determined in a LECO CN-2000 module using solid samples. Exchangeable cations were extracted with 0.1 M BaCl<sub>2</sub> [27] 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). Pseudototal concentrations were compared with the generic reference level (GRL) established for Galician soils [28].

A series of critical values were assigned to each of the chemical parameters, based on the model of the soil fertility capability classification (SFCC) proposed by [29] and adapted by [30–32]. These were used to evaluate the limiting factors for plant production.

## Harvested Biomass and Height of *Brassica juncea* L.

The *B. juncea* L. were pre-germinated in seedbeds until they grew two fully expanded leaves, and were then transferred to the cylinders (STP, STBP). The plants were harvested in the same state of maturity, for comparison in the same 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  $22 \pm 2^\circ\text{C}$  and  $65 \pm 5\%$  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  $80^\circ\text{C}$  and cooling at room temperature.

## 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. Principal component analysis (PCA) was also

carried out. Student *t* test was using to compare the results of biomass and height between STP and STBP.

## Results

### General Characteristics of the Settling Pond Soil (S), Sand (SS), Technosol (T), and Biochar (B)

Technosol and biochar (T and B) had higher pH values than soil from the settling pond (S) and sand neutral control (SS) ( $P < 0.05$ ) (Table 2). The biochar had the highest pH (Table 2). Total carbon (TC) was significantly higher in the biochar and technosol (T) compared to the soil from the settling pond and sand ( $P < 0.05$ ) (Table 2). The technosol had the highest TN content ( $P < 0.05$ ) (Table 2). S had the highest Fe concentration (Table 2). With regard to the concentration of the different nutrients studied, the technosol had the highest concentration of Ca, Mg, Mn and Na (Table 2). The biochar had the highest concentration of K ( $P < 0.05$ ) (Table 2). On the other hand, in relation to the cation exchange, the  $\text{Al}^{3+}$  content in S was significantly higher than in the amendments ( $P < 0.05$ ) (Table 2). The amendments had higher concentrations of  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  than S and SS. The CEC of T and B was significantly higher than in the controls (S and SS). The settling pond soil had the highest pseudototal concentration of Cu ( $P < 0.05$ ) (Table 2). The technosol had the highest

**Table 2** Characteristics of the mine tailing (S), sand (SS), technosols (T) and biochar (B)

		S	SS	T	B
pH		$2.73 \pm 0.07\text{d}$	$3.83 \pm 0.55\text{c}$	$6.04 \pm 0.05\text{b}$	$9.90 \pm 0.02\text{a}$
TC	$\text{g kg}^{-1}$	$1.93 \pm 0.15\text{c}$	$2.76 \pm 0.60\text{c}$	$256 \pm 2.51\text{b}$	$676 \pm 4.58\text{a}$
TN	$\text{mg kg}^{-1}$	u.d.	$0.10 \pm 0.01\text{c}$	$17.6 \pm 0.50\text{a}$	$5.34 \pm 0.22\text{b}$
Ca	$\text{mg kg}^{-1}$	$13.3 \pm 0.02\text{c}$	$9.65 \pm 0.05\text{c}$	$7785 \pm 15.9\text{a}$	$531 \pm 8.48\text{b}$
Fe		$323 \pm 8.97\text{a}$	$0.42 \pm 0.02\text{b}$	0.05b	u.d.
K		$6.40 \pm 0.89\text{c}$	u.d.	$2687 \pm 87.8\text{b}$	$3243 \pm 23.1\text{a}$
Mg		$216 \pm 2.10\text{c}$	1.83d	$1997 \pm 25.1\text{a}$	$548 \pm 11.6\text{b}$
Mn		$5.71 \pm 0.22\text{b}$	0.18c	$93.3 \pm 0.16\text{a}$	0.12c
Na		$27.4 \pm 0.22\text{c}$	$7.95 \pm 0.05\text{c}$	$2805 \pm 13.3\text{a}$	$65.4 \pm 1.29\text{b}$
$\text{Al}^{3+}$	$\text{cmol}_{(+)} \text{kg}^{-1}$	$2.32 \pm 0.02\text{a}$	0.02b	u.d.	u.d.
$\text{Ca}^{2+}$		0.07c	0.05c	$38.9 \pm 0.01\text{a}$	$2.66 \pm 0.02\text{b}$
$\text{K}^+$		0.02c	u.d.	$6.88 \pm 0.01\text{b}$	$8.30 \pm 0.05\text{a}$
$\text{Mg}^{2+}$		$1.78 \pm 0.01\text{c}$	0.01d	$16.3 \pm 0.05\text{a}$	$4.51 \pm 0.09\text{b}$
$\text{Na}^{2+}$		$0.14 \pm 0.02\text{c}$	0.04d	$14.0 \pm 0.15\text{a}$	$0.34 \pm 0.04\text{b}$
ECC	$\text{cmol}_{(+)} \text{kg}^{-1}$	$4.33 \pm 0.05\text{c}$	$0.12 \pm 0.01\text{d}$	$76.0 \pm 4.80\text{a}$	$15.8 \pm 17.8\text{b}$
Cu	Pseudototal ( $\text{mg kg}^{-1}$ )	$637 \pm 2.08\text{a}$	$46.4 \pm 1.14\text{c}$	$226 \pm 5.13\text{b}$	$27.1 \pm 1.24\text{d}$
Pb		$16.1 \pm 1.00\text{b}$	$10.4 \pm 0.56\text{c}$	$89.6 \pm 1.52\text{a}$	u.d.
Ni		$16.4 \pm 1.10\text{b}$	$8.26 \pm 1.05\text{c}$	$26.3 \pm 0.57\text{a}$	$25.0 \pm 2.00\text{a}$
Zn		$65.4 \pm 2.51\text{b}$	$18.9 \pm 1.20\text{c}$	$340 \pm 5.50\text{a}$	$62.6 \pm 1.95\text{b}$

For each row, different letters in different samples means significant differences ( $n=3$ , ANOVA;  $P < 0.05$ ). u.d. undetectable level. Typical deviation is represented by  $\pm$

pseudototal concentration of Pb and Zn. The biochar and technosol had a higher pseudototal concentration of Ni than S and SS (Table 2).

### Evolution of the pH at the Three Depths and Over the 11-Month Period

At depth 0–15 cm, treatments STB and STBP (the settling pond soil treated with technosol and biochar) had the highest pH over time (Fig. 3A). At depth 15–30 cm, at 3 and 7 months, the treatments ST and STB had a significantly higher pH than the untreated settling pond soil ( $P < 0.05$ ) (Fig. 3B). At depth 30–45 cm, the ST at 3 months and the STB at 7 months had a higher pH than the negative control (S); at 11 months, STB, STBP and the STP had a significantly higher pH than the untreated settling pond soil ( $P < 0.05$ ) (Fig. 3C).

### Evolution of Total Carbon (TC) at Three Depths and Over the 11-Month Period

At depth 0–15 cm, treatments STB and STBP had the highest TC concentration over time (Fig. 4A). At depth 15–30 and 30–45 cm, at 3 and 7 months, treatments STB and STBP had a significantly higher TC concentration than the untreated settling pond soil ( $P < 0.05$ ) (Fig. 4B, C). At 11 months, at depth 15–30 and 30–45 cm, the settling pond soil treated with the different treatments had a higher TC concentration than S (Fig. 4B, C).

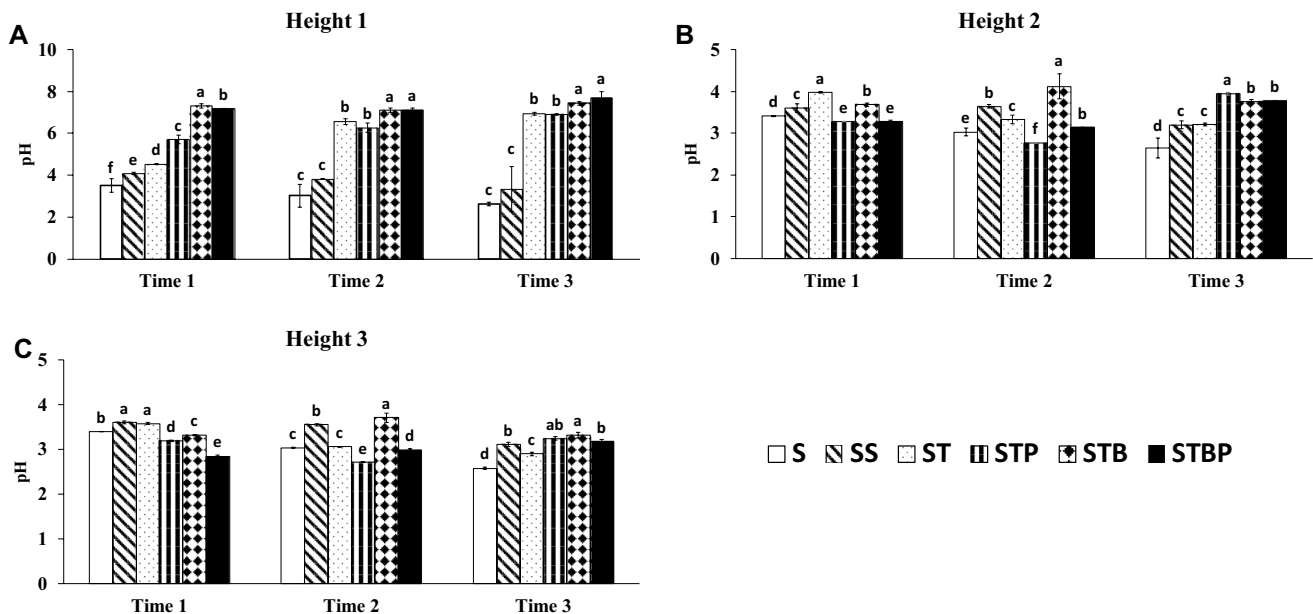
### Evolution of Total Nitrogen (TN) at Three Depths and Over the 11-Month Period

The TN was only detected at depth 0–15 cm and only in the treated settling pond soil. At 3 and 11 months, the treated settling pond soil only with technosol had the highest TN concentration (Fig. 5). At 7 months, the treatments that were made with technosol and biochar had the highest TN concentration ( $P < 0.05$ ) (Fig. 5).

### Evolution of the Cation Exchange Capacity (CEC), Base Saturation (%), and Aluminium Saturation (%) at Three Depths and Over the 11-Month Period

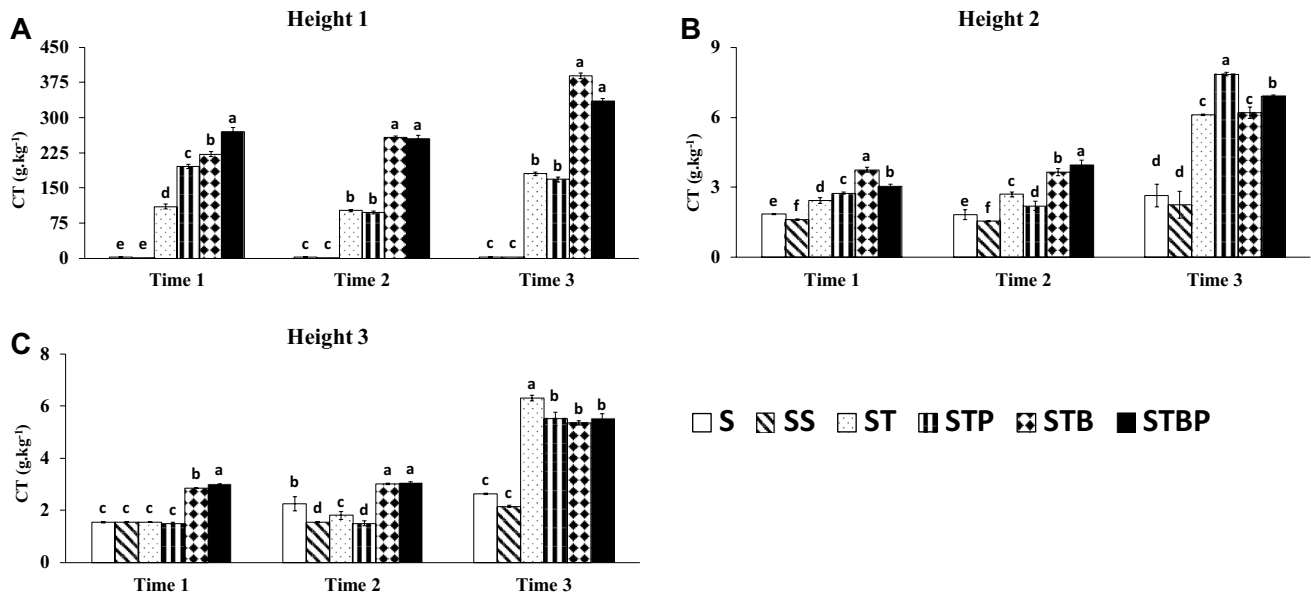
At depth 0–15 cm, the treated settling pond soil had the highest CEC over time ( $P < 0.05$ ) (Table 3). At 11 months the STB and STBP treatments had the highest CEC respectively (Table 3). The base saturation (V%) was higher in the treated soil than in the controls (S, SS). The settling pond (S) and the neutral control (SS) had a higher aluminium saturation (Al%) than the treated settling pond soil (ST, STP, STB, STBP) (Table 3).

At depth 15–30 cm, at 11 months, S had the highest CEC ( $P < 0.05$ ) (Table 3). The highest level of V% at the three times was provided by the treated settling pond soil (ST, STP, STB, STBP) (Table 3). The settling pond soil (S) had the highest aluminium saturation (Al%) over time (Table 3).



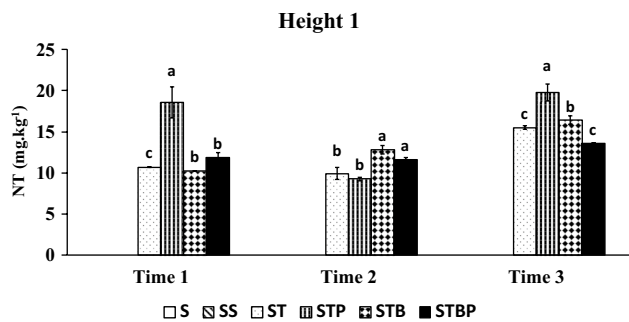
**Fig. 3** Evolution of the pH at three heights and over the 11-month period. Height 1 = 0–15 cm, Height 2 = 15–30 cm, Height 3 = 30–45 cm. For each row, differ letters in different samples means

significant differences ( $n=3$ , Student's  $t$  test:  $P < 0.05$ ). Error bars represent standard deviation



**Fig. 4** Evolution of the total carbon (TC) at three heights and over the 11-month period. Height 1 = 0–15 cm, Height 2 = 15–30 cm, Height 3 = 30–45 cm. For each row, differ letters in different samples

means significant differences (n=3, Student's *t* test:  $P < 0.05$ ). Error bars represent standard deviation



**Fig. 5** Evolution of the total nitrogen (TN) at height 1 and over the 11-month period. Height 1 = 0–15 cm. For each row, differ letters in different samples means significant differences (n=3, Student's *t* test:  $P < 0.05$ ). Error bars represent standard deviation

At depth 30–45 cm, at 11 months, the untreated settling pond soil had the highest CEC ( $P < 0.05$ ) (Table 3). The treatment STB had the highest base saturation at 3 and 7 months, but at 11 months the highest V% was corresponded to ST (Table 3). At 3 and 7 months, the settling pond soil (S) had the highest aluminium saturation (Al%) (Table 3). At 11 months, the treated settling pond soil (ST, STP, STB, STBP) had the highest Al% (Table 3).

**Evolution of Nutrients in Three Depths and Over the 11-Month Period**

At depth 0–15, the settling pond soil had the highest Fe concentration over time. The settling pond soil treated with

the different treatments had higher Ca, K, Mg, Mn, Na concentrations than S over time, except at 11 months where Mn concentrations were lower in STB and STBP than in S ( $P < 0.05$ ) (Table 4).

At depth 30–15 cm, at 3 months the treatments with technosol and biochar had the highest nutrients concentration except for Na concentration. STP had the highest Na concentration ( $P < 0.05$ ) (Table 4). At 7 months, STB and STBP had higher concentrations of Ca and K than the controls (S, SS) (Table 3). The highest Mn concentrations were shown by the ST, STP and STBP. The STBP and STB had the highest Na concentrations. The settling pond soil had the highest Fe concentration (Table 4). At 11 months, S had the highest Ca, Mg and Mn concentrations. The ST and STP had the highest K and Na concentrations respectively. The neutral control (SS) had the highest Fe concentration (Table 4).

At depth 30–45 cm, at 3 months the treated settling pond soil with STBP had the highest Ca, Fe, Mg and Mn concentrations. The highest K concentrations were shown by STB and STBP. The ST and STB had the highest Na concentrations ( $P < 0.05$ ) (Table 4). At 7 months, the settling pond soil had higher Fe concentrations than the treated settling pond soil. The neutral control (SS) had the highest Ca concentrations. The highest K concentrations were shown by the STB. The settling pond soil treated with the different treatments had higher Ca concentrations than the controls (Table 4). At 11 months, the settling pond soil (S) had higher Ca, Mg and Mn

**Table 3** Evolution of the cation exchange capacity (CEC), base saturation (V%), and aluminium saturation (Al%) at three depths and over the 11-month period

	S	SS	ST	STP	STB	STBP
<b>Depth 0–15 cm</b>						
<b>3 Months</b>						
CEC (cmol <sub>(+)</sub> kg <sup>-1</sup> )	2.58 ± 0.16c	0.26 ± 0.01c	21.5 ± 2.31b	35.3 ± 1.07a	23.6 ± 0.87b	23.4 ± 1.45b
V%	39.4	43.7	99.9	99.9	99.9	99.9
Al%	60.5	56.2	0	0	0	0
<b>7 Months</b>						
CEC (cmol <sub>(+)</sub> kg <sup>-1</sup> )	5.06d	0.50 ± 0.01d	25.3 ± 0.40b	23.2 ± 0.04c	26.0 ± 0.17b	31.0 ± 1.17a
V%	36.1	52.9	99.9	99.9	99.9	99.9
Al%	63.8	47.0	0	0	0	0
<b>11 Months</b>						
CEC (cmol <sub>(+)</sub> kg <sup>-1</sup> )	5.86c	0.54 ± 0.07c	30.0 ± 1.79ab	25.2 ± 0.26b	31.9 ± 0.08a	29.1 ± 0.96b
V%	41.8	44.2	99.9	99.9	99.9	99.9
Al%	58.1	55.7	0.06	0	0	0
<b>Depth 15–30 cm</b>						
<b>3 Months</b>						
CEC (cmol <sub>(+)</sub> kg <sup>-1</sup> )	4.78 ± 0.46a	0.84 ± 0.03d	1.32 ± 0.10c	2.25 ± 0.07b	1.52 ± 0.02c	2.85 ± 0.77b
V%	36.3	27.8	75.7	76.3	77.3	62.8
Al%	63.6	72.1	24.2	23.6	22.6	37.1
<b>7 Months</b>						
CEC (cmol <sub>(+)</sub> kg <sup>-1</sup> )	4.12 ± 0.83a	1.21 ± 0.08b	3.46 ± 0.08a	1.30 ± 0.06b	1.62 ± 0.18b	4.43 ± 0.06a
V%	37.5	47.6	43.5	50.7	75.5	47.9
Al%	62.2	51.6	56.4	49.2	24.4	52.0
<b>11 Months</b>						
CEC (cmol <sub>(+)</sub> kg <sup>-1</sup> )	11.0 ± 0.12a	5.00 ± 0.12b	3.14 ± 0.03c	2.49 ± 0.02d	1.20 ± 0.18e	1.19 ± 0.18e
V%	38.3	39.0	41.0	52.1	73.0	71.3
Al%	61.6	60.9	58.9	47.8	26.9	28.6
<b>Depth 30–45 cm</b>						
<b>3 Months</b>						
CEC (cmol <sub>(+)</sub> kg <sup>-1</sup> )	2.26 ± 0.52b	0.69 ± 0.08b	0.56 ± 0.10b	0.78 ± 0.05b	0.49 ± 0.10b	5.38 ± 0.33a
V%	41.1	26.8	60.1	54.7	66.3	34.6
Al%	58.8	73.11	39.8	45.2	33.6	65.3
<b>7 Months</b>						
CEC (cmol <sub>(+)</sub> kg <sup>-1</sup> )	4.60 ± 0.09b	1.53 ± 0.02c	4.06 ± 0.18b	1.38 ± 0.01c	1.65 ± 0.01b	6.11 ± 0.34a
V%	32.8	59.5	42.9	52.0	58.7	35.4
Al%	67.1	40.4	57.0	47.9	41.2	64.5
<b>11 Months</b>						
CEC (cmol <sub>(+)</sub> kg <sup>-1</sup> )	11.5 ± 0.01a	7.29 ± 1.71b	3.93 ± 0.12c	3.19 ± 0.068c	0.90 ± 0.07d	0.93 ± 0.02d
V%	40.2	33.9	39.9	37.4	35.6	38.4
Al%	59.7	66.0	60.0	62.5	64.3	61.5

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

concentrations than the treated settling pond soil and the neutral control. SS had the highest Fe concentrations, and ST had higher Na concentrations than the controls and the other treated settling pond soils (P < 0.05) (Table 4).

### Limiting Factors for Plant Production in Depth 0–15 cm

All of the factors and values detailed above are shown in Table 5. The high acidity of the settling pond soil, over time, is a limiting factor for plant production (Factor c).



**Table 4** Evolution of nutrients concentration (mg kg<sup>-1</sup>) in three depths and along the 11 months

	S	SS	ST	STP	STB	STBP
Depth 0–15 cm						
3 Months						
Ca	6.53±0.26b	4.61±0.81b	2837±310a	3847±330a	3282±100a	2771±161a
Fe	8.71±0.57a	1.49±0.61b	0.18±0.04c	0.49±0.17c	0.53±0.05b	0.06±0.05c
K	7.89±0.41c	6.46±0.23c	593±56.2b	1048±27.1a	643±42.1b	991±62.7a
Mg	11.4±0.09c	2.07±0.29d	551±61.4b	996±1.19a	587±25.0b	581±35.9b
Mn	0.94±0.02d	0.14±0.01e	70.6±5.78a	95.9±7.75a	5.72±0.22b	4.11±0.19c
Na	21.7±0.51d	7.69±0.75e	247±21.9b	1043±129a	141±12.9c	458±37.5a
Time 2						
Ca	38.7±1.05c	16.5±2.20d	3690±64.6ab	2992±13.9b	3740±24.0a	3607±135b
Fe	696±42.9a	6.01b	0.92±0.29b	0.84±0.11b	0.07b	0.06±0.01b
K	2.12±0.51e	0.67±0.05e	481±4.56c	301±4.85d	615±1.27b	790±32.6a
Mg	184±0.57c	7.49±0.20d	612±7.19b	645±2.89b	621±6.17b	904±39.9a
Mn	4.10±0.14d	0.51 f	54.4±1.62b	59.5±0.35a	2.58±0.02e	5.53±0.05c
Na	17.8±1.24e	19.9±2.41e	130±1.57d	432±15.4b	138±0.99c	701±17.4a
7 Months						
Ca	58.4c	13.4±4.31d	4488±260.0a	3790±28.0b	4951±19.5a	4441±148.29ab
Fe	143±3.00a	4.88±1.52b	0.85±0.08c	0.36c	0.10±0.09c	u.d.
K	u.d.	u.d.	500±34.1a	191±1.23d	331±3.60b	225±5.42c
Mg	253±1.63c	15.5±2.95d	698±45.4ab	628±12.4b	720±1.08a	704±22.8a
Mn	6.82±0.13c	0.72±0.08e	35.9±1.75b	42.3±0.16a	2.34±0.07d	2.32±0.15d
Na	11.9±0.48c	6.15±0.44d	115±7.60a	122±3.17a	84.7±0.50b	110±3.74a
Depth 15–30 cm						
11 Months						
Ca	8.18±0.80e	10.4±0.19e	57.0±5.12d	115±3.58b	98.1±3.61c	138±4.10a
Fe	6.09±0.32b	6.32±0.95b	3.73±0.36c	5.63±0.11b	7.32±0.16b	22.7±1.95a
K	14.7±0.29c	10.0±0.21d	58.0±6.35b	72.2±3.98b	95.9±1.21a	58.1±2.24b
Mg	9.18±0.53d	9.82±0.77d	32.9±2.88c	56.8±2.10b	29.8±0.024c	82.3±3.44a
Mn	0.96c	0.86±0.06c	2.04±0.15b	4.29±0.20a	1.63±0.13b	3.69±0.10a
Na	23.8±1.79d	10.8±0.67e	54.8±3.84b	93.3±4.53a	34.9±0.72c	50.3±1.42b
7 Months						
Ca	45.5±9.96b	50.2±9.54b	72.9±2.65b	48.9±0.46b	133±28.8a	98.6±1.25ab
Fe	487±110a	25.6±6.04c	108±0.54b	5.12±0.94c	3.79±0.35c	143±3.21b
K	0.54±0.42d	1.57±0.20d	7.45±0.24c	25.5±1.08b	88.8±3.06a	33.7±5.56b
Mg	148±32.2a	21.6±0.49c	124±0.80b	17.4±0.64c	24.5±1.52c	152±1.38a
Mn	3.64±0.79bc	1.62±0.04b	6.74±0.038a	1.79±0.02b	1.11±0.07b	5.57a
Na	16.7±2.33b	26.8ab	16.4±0.81b	36.7±1.39a	21.2±4.63b	53.9±8.62a
11 Months						
Ca	123±7.29a	34.1±0.66c	63.9±6.06c	128±13.5a	112±25.6b	115±26.3ab
Fe	47.7±0.80c	268±9.36a	62.4±0.01b	65.2±0.35b	8.26±0.54d	9.39±0.29d
K	u.d.	u.d.	1.22±0.06a	u.d.	1.56±1.06a	u.d.
Mg	430±3.45a	207±1.72b	108±0.63c	69.7±0.89d	30.4±3.74e	25.3±2.98e
Mn	16.1±0.46a	4.68±0.06b	5.32±0.07b	4.99b	1.85±0.17c	2.52±0.33c
Na	11.5±0.58b	11.5±0.23b	10.7±0.08b	13.4±0.07a	8.93±1.07b	10.0±0.83b
Depth 30–45 cm						
3 Months						
Ca	5.38±0.75c	11.5±0.06c	38.0±9.54b	66.4±0.40b	47.2±11.3b	118±0.42a
Fe	4.65±0.82b	6.12±1.28b	3.16±0.56b	6.06±0.02b	4.99±1.14b	300±3.18a
K	7.26±0.40c	9.98±1.95c	40.4±6.05ab	31.0±0.97b	72.5±21.0a	63.1±2.30a
Mg	6.72±2.12c	12.7±0.01c	31.6±5.90b	36.1±0.47b	30.3±9.60b	231±9.13a
Mn	0.63±0.20c	1.42bc	1.97±0.33b	2.87±0.08b	1.09±0.24c	12.7±0.41a

**Table 4** (continued)

	S	SS	ST	STP	STB	STBP
Na	23.1 ± 2.70b	9.05 ± 0.67c	54.2 ± 11.3a	43.9 ± 1.76ab	55.3 ± 19.9a	33.3 ± 1.11b
7 Months						
Ca	54.1 ± 10.1c	120 ± 1.47a	74.5 ± 1.25b	58.6 ± 1.76bc	44.7 ± 0.36c	75.9 ± 0.47b
Fe	830 ± 34.5a	20.6 ± 0.95d	363 ± 13.2b	8.12 ± 0.57e	5.57 ± 0.65e	276 ± 15.1c
K	0.27 ± 0.27d	2.01 ± 1.70d	2.87 ± 1.37d	18.9 ± 0.68b	120 ± 1.99a	14.1 ± 1.07c
Mg	144 ± 4.57a	22.1 ± 0.48b	150 ± 6.26a	19.4 ± 0.57c	17.5 ± 0.16c	187 ± 13.3a
Mn	3.42 ± 0.06c	2.15 ± 0.04d	4.07 ± 0.14b	1.76 ± 0.04e	0.68 f	10.9 ± 0.50a
Na	6.09 ± 3.10c	20.6 ± 6.19b	21.1 ± 3.49ab	39.1 ± 8.90a	55.2 ± 0.74a	37.5 ± 5.05a
11 Months						
Ca	150 ± 0.26a	51.0 ± 3.75b	32.7 ± 1.59c	22.8 ± 0.32d	18.7 ± 2.05de	16.8 ± 0.32e
Fe	218 ± 7.40b	637 ± 201a	105 ± 3.15b	68.3 ± 1.37b	14.1 ± 0.57b	22.6 ± 0.07b
K	u.d.	u.d.	u.d.	u.d.	u.d.	u.d.
Mg	465 ± 0.49a	260 ± 40.1b	161 ± 2.85c	122 ± 0.58d	20.2 ± 0.45e	26.6 ± 0.07e
Mn	12.7 ± 0.12a	6.30 ± 0.74b	3.99 ± 0.10c	2.99d	1.53e	1.73 ± 0.01e
Na	11.3 ± 0.19b	12.0 ± 0.77ab	12.6 ± 0.25a	11.1 ± 0.64b	9.10 ± 0.95b	8.39 ± 0.11c

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

The controls (S, SS) had deficient amounts of Ca that gave rise to the limiting Factor Ca. The CEC values are below the limit set by the Factor e at 3 months for the controls, and at 7–11 months only for the neutral control (SS). The K values were a limiting factor (Factor K) in

S and SS over time. The neutral control (SS) had a deficiency in Mg<sup>2+</sup> over time; this resulted in the presence of a limiting factor for plant production (Factor Mg). Only SS at 3 and 7 months exceeds the limit set by the Factor n. The settling pond soil and the neutral control are

**Table 5** Limiting factors for crop production linked to the content of bases in the complex change at depth 0–15 cm

	Factor c	Factor Ca	Factor e	Factor K	Factor Mg	Factor n	N
3 Months							
S	3.51	0.34	2.58	0.02	0.53	4.58	0
SS	4.08	0.02	0.26	0.02	0.01	17.9	0
ST	4.53	14.1	21.5	1.52	4.54	5.78	1.07
STP	5.70	19.2	35.3	2.68	8.20	14.7	1.86
STB	7.31	16.4	23.6	1.65	4.84	3.03	1.02
STBP	7.17	13.8	23.4	2.54	4.79	9.7	1.19
7 Months							
S	3.02	0.19	5.06	0.01	1.52	1.95	0
SS	3.81	0.08	0.50	0	0.06	21.8	0
ST	6.55	18.4	25.3	1.23	5.04	2.59	0.99
STP	6.27	14.9	23.2	0.77	5.31	9.33	0.92
STB	7.10	18.7	26.0	1.58	5.11	2.67	1.28
STBP	7.11	18.0	31.0	2.02	7.44	11.3	1.16
11 Months							
S	2.63	0.29	5.86	0	2.08	1.18	0
SS	3.33	0.07	0.54	0	0.12	7.43	0
ST	6.93	22.4	30.0	1.28	5.74	1.94	1.55
STP	7.03	18.9	25.2	0.49	5.17	2.46	1.98
STB	7.14	24.7	31.9	0.85	5.92	1.35	1.64
STBP	7.48	22.2	29.1	0.58	5.79	1.93	1.36

Factor c pH<3.5; Factor Ca<1.5 cmol<sub>(+)</sub> kg<sup>-1</sup>; Factor e ECC<4 cmol<sub>(+)</sub> kg<sup>-1</sup>; Factor K<0.2 cmol<sub>(+)</sub> kg<sup>-1</sup>; Factor Mg<0.4 cmol<sub>(+)</sub> kg<sup>-1</sup>; Factor n Na>15%; N total content <0.1%

severely limited for plant production according to the Factor N over time.

### Harvested Biomass of *Brassica juncea* L.

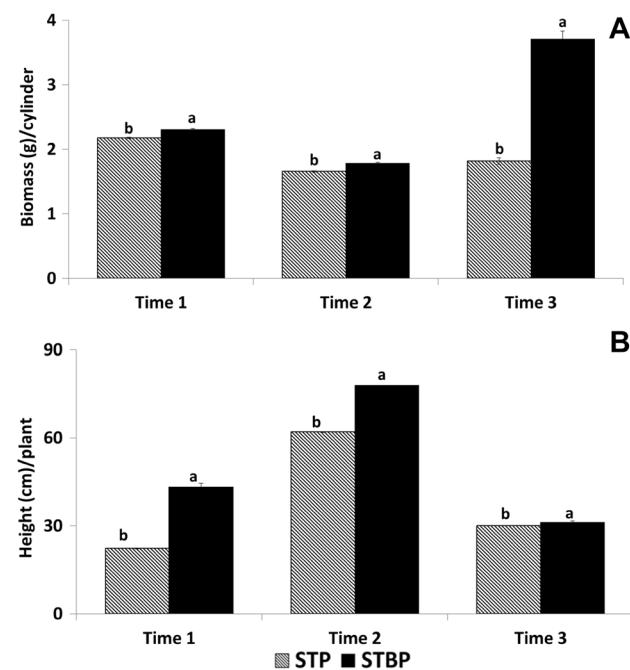
The *B. juncea* L. was not capable of growing in the settling pond soil (S) and in the neutral control (SS), and so it is not represented in Fig. 6A, B. The biomass of *B. juncea* L. harvested in treatment STPB was higher than in STP over time (Fig. 6A,  $P < 0.05$ ). The *B. juncea* L. harvested in treatment STPB was the highest over time (Fig. 6B,  $P < 0.05$ ).

## Discussion

### Evolution of the pH at Three Depths and Over the 11-Month Period

The low pH of the settling pond soil (S) is due to its origin, as sulphide minerals in contact with water and air produce sulphuric acid [33], and also this soil has a predominance of wastes resulting from the flotation of sulphides during copper processing. At depth 0–15 cm, after applying the treatments (ST, STP, STB, STBP) it was possible neutralize the acidity of the soil throughout the entire experiment. This was possibly due to the high pH of the amendments used in producing the treatments that were applied. The

treatments that increased the pH the most were those that combined technosol and biochar (STB, STBP). This is due, on the one hand, to the high pH of the elements used to create this technosol, something that has already been demonstrated by various authors, who have indicated that the types of waste used in this study have high concentrations of basic cations [34, 35]. This high pH of the technosol was increased by the biochar, which causes an increase in the pH of the soils where it is applied, as demonstrated by authors such as [36, 37]. At depths 15–30 and 30–45 cm, it was found that in the settling point soil (S) where the two different treatments were applied, the pH increased as time progressed. This is important, as it shows that these treatments do not only increase the pH in the top few centimetres, but also at depth. As occurred with depth 0–15 cm, in depths 15–30 and 30–45 cm a trend was observed in which treatments STB and STBP were more effective, further increasing the pH values. Soils with pH below 3.5 are strongly limited for plant production [38]. So the increase of pH in these soils is very important when carrying out the revegetation, and biochar could be used as a liming amendment for enhancing nutrient availability and plant survival during the early stages of vegetation establishment productivity [3, 22, 37]. In general, the combined application of technosol and biochar increases pH values more than the direct application of technosol, being evident the effectiveness of mixing technosol and biochar.



**Fig. 6** Harvested biomass and height of *Brassica Juncea* L. over the 11-month period. For each row, different letters in different samples means significant differences ( $n=3$ , Student's  $t$  test;  $P < 0.05$ ). Error bars represents standard deviation

### Evolution of the Total Carbon (TC) at the Three Depths and Over the 11-Month Period

As previously mentioned, one of the most important problems when recovering mine soils is their low organic matter content [4]; we also observed this low TC content in the settling pond soil. As a result, we applied the different treatments in an attempt to increase it. After applying the different treatments to soil S, the TC increased considerably. This increase of carbon content in the soil is very important because according to authors such as [39] carbon is an indicator associated with soil quality, fertility and health.

At depth 0–15 cm we saw the same behaviour as with the pH, in other words, in the settling soil where we applied the treatments STB and STBP, there was a greater increase in the TC. This is not only due to contribution of TC provided by the elements used to make the technosol, such as solid urban waste, sewage sludge and remnants from agri-food industries [40–44], but also from the carbon provided by the biochar, as previously demonstrated by [16, 17]. Fowles [14] already showed a better behavior of the amendments when they are combined with the biochar. The carbon contribution is important for the recovery of degraded soils, as the increase in organic carbon in the soil increases its possibility to retain the water that is available,

increases the concentration of nutrients in bioavailable form, and improves the structure of the soil and other physical properties [45]. At depths 15–30 and 30–45 cm, the increase in TC after applying the different treatments was very clear, especially at 11 months. This shows that these treatments increase the TC at depth, and not only in the first few centimetres of the soil, in the same way as the pH. The comparison between treatment at these depths (15–30 and 30–45 cm) at the end of the time the treatment without biochar STP presented the highest contents of TC. This may be due to the carbon being fixed in the superficial depth in the treatments elaborated with technosol and biochar. On the other hand, the higher carbon content in STP compared to ST may be due to the action of the roots of plants.

### Evolution of the Total Nitrogen (TN) at the Three Depths and Over the 11-Month Period

Settling pond soil has undetectable amounts of TN, which is a significant problem when attempting to grow stable plant cover on its surface. The inflow of nitrogen is very low in a mine soil compared to forested or agricultural land [46]. At depths 15–30 and 30–45 cm, the contents were low (below TN < 0.1%), possibly due to the lower effect of the treatments both in terms of their capacity to provide TN and their retention, as the nitrogen is lost quickly by leaching. After applying the different treatments, it was not possible to increase the TN content. This increase is important, as the availability of N to plants is a universally important aspect of soil quality, and nitrogen often represents an immediate limitation to plants [47].

The treatment that raised the nitrogen content the most was the one made with technosol and which had *B. juncea* L. cultivated on it (STP). The fact that this treatment increased the nitrogen content more than the treatments that combined technosol and biochar (STB, STBP) is due to several factors; the first is that this treatment (STP) was made of 15% technosol, containing an average of  $17.6 \pm 0.50$  mg/kg of N. In turn, the treatments that combined technosol and biochar were made of 11% technosol and 4% biochar (STB, STBP), which means they contained a lower proportion of technosol and included biochar, which contained  $5.34 \pm 0.22$  mg/kg of nitrogen. In this case, the biochar has a diluting effect in terms of the nitrogen content. The higher nitrogen content in the technosol is due to the fact that it was made using purification plant sludge and remnants from agri-food industries, which are rich in nitrogen [44, 48, 49].

In turn, the fact that the treatment with compost and *B. juncea* L. (STP) had a higher N content in comparison with the treatment only using compost (ST) at the end of the experiment is probably due to the effect of the *Brassicaceae* on the rhizosphere. Root exudates are important factors

that structure the bacterial community of the rhizosphere. It is established that seed/root exudates of plants can be processed as nutrients leading to enhanced growth and a higher prevalence of degrading strains of bacteria [50]. Some non-symbiotic nitrogen-fixing bacterial communities are usually associated with certain species of *Brassicaceae*; this proliferation of bacteria is the result of various exudates released by the root [51, 52]. Due to these factors, *B. juncea* L. is capable of providing significant amounts of nitrogen to the soil, as demonstrated by [53].

### Evolution of the Cation Exchange Capacity (CEC) ( $\text{cmol}_{(+)} \text{kg}^{-1}$ ), Base Saturation (V%), and Aluminium Saturation (Al%) at the Three Depths Over the 11-Month Period

As previously discussed, at depth 0–15 cm, both controls had a low CEC, especially the neutral control (SS). This is a major obstacle to recovering a degraded soil, as a low CEC means the soil has a low resistance to changes in soil chemistry that are caused by land use [54]. At depth 0–15 cm, all of the treatments were able to increase the CEC, although as time passed the treatments that combined technosol and biochar (STB, STBP) had higher values. These results agree with those found by authors such as [55] who showed that the application of amendments made with residues increases the CEC. On the other hand, [1] have already shown that amended soils benefit from the large, oxidized surface area of biochar and its porous structure. Soils amended with biochar have an increased soil charge density (potential CEC, per unit surface area) in comparison to non-amended soils. According to [56] the retention of nutrients in terms of CEC increase when applying biochar to the soil. This is important, as the CEC is a major controlling agent of nutrient availability for plant growth, soil pH, and the soil reaction to fertilisers and other ameliorants [54]. If we break down the CEC at depth 0–15 cm, we can see that the base saturation in the treatments (V%) is 99%, but that the aluminium saturation (Al%) is 0%, indicating that the binding sites of the soil in these treatments are saturated with  $\text{Ca}^{2+}$ ,  $\text{K}^{+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^{+}$ . This saturation of basic cations is important when it comes to increasing the pH, but also because they are nutrients for plants. The treatments we applied that combined technosol and biochar (STB, STBP) had a higher CEC in the final months, due to the higher cation retention capacity of the biochar, as demonstrated by [36, 54], as the biochar has a high aromaticity, high surface area, and a negative charge. At depth 15–30 cm and all at of the times, the treatments applied, while not always having a higher CEC, did always have a higher base saturation (V%) and lower aluminium saturation (Al%). This indicates that at this depth, the treatments

that were applied were still effective. At depth 30–45 cm at 3 and 7 months, this trend was maintained, although in time three the V% decreased and the Al% increased in the treatments. This may be due to a decreased effectiveness of the treatments, or that they still needed more time to act. At depths 15–30 and 30–45 cm in 3 and 7 months, treatments STB and STBP had a higher CEC and base saturation, once again clearly revealing the positive effect of biochar in combination with technosol [1, 14].

### Evolution of Nutrients at the Three Depths and Over the 11-Month Period

At all of the depths and in all of the times studied, it was found that in general, all of the treatments increased the contents of macronutrients such as Ca, Na and K. The application of soil amendments improves soil nutrient content. This is due to the increase of organic matter which improves the EC and it has an effect on the increase of nutrient contents [55]. The nutrient content at depth 0–15 cm was higher in the soil amended with the different treatments, due to the contribution made by the elements used to make the technosol and biochar. The contribution of nutrients by technosols to soils degraded by activities such as mining has already been demonstrated by [10]. Biochar contributes a smaller amount of nutrients at first, although because of its high capacity to retain nutrients, as time passed it retains the nutrients provided by the technosol, and releases them slowly [57]. This is why the nutrient content at 7 and 11 months was generally higher in treatments STB and STBP. As a result, the benefits of applying biochar to these highly weathered systems include the prevention of nutrient loss by leaching, and the retention of nutrients in the root zone [56].

This retention of nutrients is clearer at depth 15–30 cm at 3 and 7 months, in which the treatments combining technosol and biochar (STB, STBP) generally had higher contents of the nutrients studied, while at 11 months this effect was no longer visible. Depth 30–45 cm, the retaining effect of the biochar was observed at 11 months. It is possible that this retaining effect of the biochar did not become apparent until at 11 months at depths 15–30 and 30–45 cm due to the fact that the biochar had still not taken effect at depth in a constant manner. This is perhaps because the acidic pH and lack of organic matter in the final depths did not allow it to act within the timescale of the experiment.

### Limiting Factors for Plant Production at Depth 0–15 cm

With regard to the limiting factors for plant production, we will focus on depth 0–15 cm because is the root range zone and discuss the most interesting aspects. The mine soil was

affected by the *c Factor* due to its low pH, which is a limiting factor for the growth of plant life, as most plants and trees cannot grow in a soil with such a low pH. However, the pH that was achieved once the treatments were applied, especially those that combined technosol and biochar (STB, STBP), was an optimum pH for the growth of the majority of plants. Both the mine soil and the neutral control (SS) were affected by the *Ca Factor*, possibly due to the fact that the low pH of S and SS reduces the availability of Ca to plants. However, the pH range of the soil after treatment is optimal for both the solubility and bioavailability of Ca for plants [54]. Despite the fact that according to [29, 30] the settling pond soil would only be affected by the *e Factor* in time 1, several authors have demonstrated that soils with a CEC with values of less than six are considered as very low, meaning that the soil has a low resistance to changes in soil chemistry that are caused by land use. This is one of the reasons why vegetation is not able to establish in settling pond soil without being treated [54]. With regard to K, both S and SS were affected by the *k Factor* throughout the entire duration of the experiment, and its values are critical for plant growth. After applying the different treatments, the critical values for K were exceeded. Although it was found to be a nutrient whose concentration decreased over time in all of the treatments, despite this decrease the values were always found to be well above the value of  $0.2 \text{ cmol}_{(+)} \text{ kg}^{-1}$  considered to be critical [29, 30]. Due to the starting material of the settling pond soil, and in the case of the treatments because of the elements used to make them, none of them were affected by the *Mg Factor*. Only the neutral control SS had a deficit of Mg, possibly due to its origin and the processing of the sand. The settling pond soil and the neutral control (S, SS) were seriously affected by the *N Factor* as their TN content was not detectable. None of the treatments that were applied were affected by this factor. This increase in the nitrogen content is significant, as it is a highly important aspect in recovering the quality of a soil. It is also a nutrient that plays a crucial role in plant production, as when it does not reach a given value, it becomes a limiting factor for plant production [47].

### Harvested Biomass of *Brassica juncea* L.

*Brassica juncea* L. planted in the settling pond soil (S) and in the control soil (SS) did not grow over time. These soils showed deficits in certain factors, such as low nutrient content and low pH. This difficulty in establishing stable plant cover in mine soils has already been studied by [7], who states that degraded mine soils are a man-made habitat which experience a wide range of problems for establishing and maintaining vegetation. The plants grew without any problems throughout the whole

of the experimental period both in the treatment made only using technosol (STP) and in the treatment using technosol and biochar (STBP). The fact that the plants grew once the different treatments were applied to the soil was also demonstrated by [7], who states that the use of organic amendments to improve the soil helps to consolidate vegetation in settling pond soils. However, the STPB treatment proved to be more effective than STP. In the STPB treatment, the *Brassicas* had a larger biomass, which increased over time. The larger biomass that was harvested is possibly due to the characteristics the biochar provides to this treatment. Biochar is capable of reducing the leaching of nitrates, allowing plants to use nutrients more efficiently, increasing the pH of the soil, and improving its structure [58]. The nutrients provided by the technosol and the retention capacity of the same by the biochar are a good combination for the vegetal growth. Apart from the larger biomass found in the plants growing in STBP, it was found that the plants in this treatment were higher, indicating that they grew more vigorously. The good development of *B. juncea* L. plants is important because vegetation improves the soil physical, chemical, and biological condition of mine soils [39].

### Principal Component Analysis (PCA) of the Soil Samples

The concentrations of the nutrients analysed at depth 0–15 cm were selected to perform a PCA (Table 6). The two principal components obtained accounted for 97% of the total variance, according to the position of the soil samples in the scatter plot (Fig. 6). In the case of the PCA in the soil samples we focused on the evolution of these components in the first depth over time, as this had the greatest influence on the plants used in this experiment.

At 3 months, the treated soils significantly changed their nutrient concentration in comparison to the controls (S and SS). The component score coefficients matrix obtained (Table 6) showed that S and SS are not influenced by any of the nutrient contents. Nevertheless, the soils that were only treated with technosol (ST, STP) were positively influenced by the concentration of most of the nutrients that were analysed (Ca, K, Mg, Mn, Na), while the soils treated with technosol + biochar (STB, STPB) were positively influenced by the concentrations of Mg, Mn, and Na (Fig. 7). The scatter plot shows that treated soils were negatively influenced by Fe. (Table 6; Fig. 7). At 7 months, the nutrient concentration remained higher in the treated soils. However, in this case the soils treated with technosol and biochar were also positively influenced by the concentration of Ca and K, as well as by the concentration of Mg

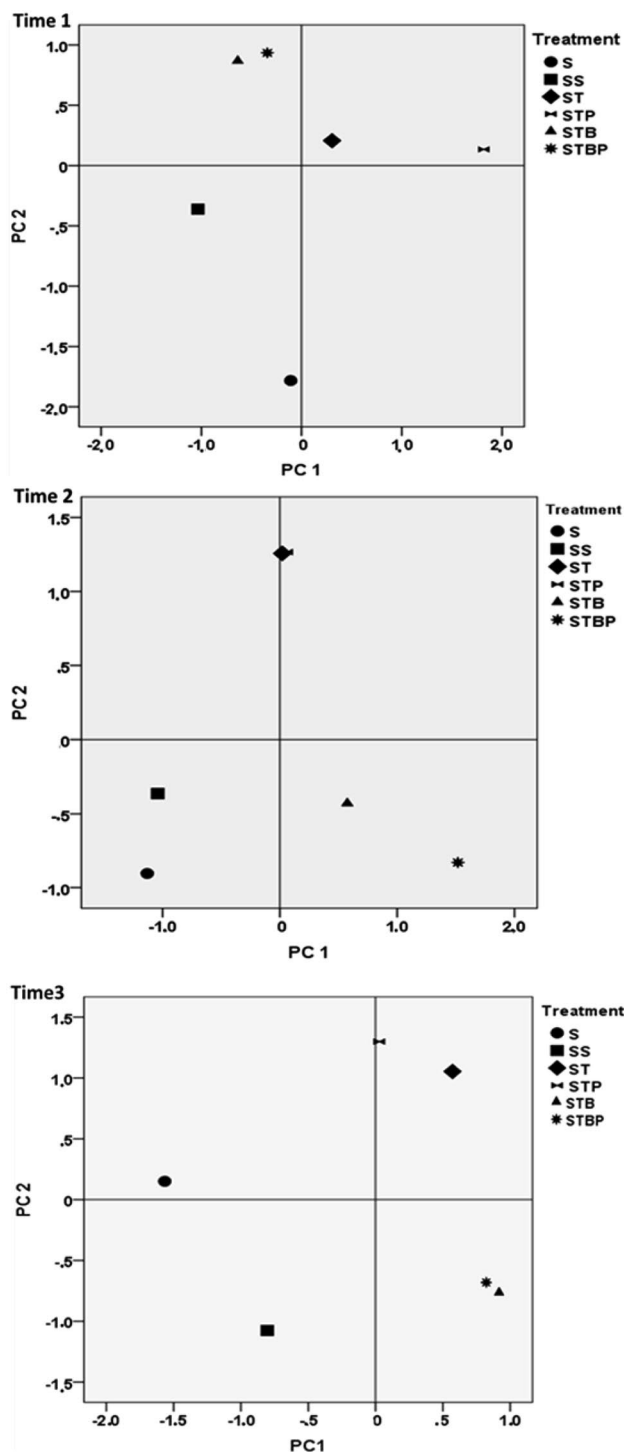
**Table 6** The component score coefficients matrix from the PCA depth 0–15 cm

	Indicators	PC1	PC2
3 Months	Ca	0.57	0.77
	Fe	−0.11	−0.91
	K	0.58	0.75
	Mg	0.73	0.66
	Mn	0.89	0.16
	Na	0.87	0.35
7 Months	Ca	0.86	0.41
	Fe	−0.56	−0.44
	K	0.97	0.04
	Mg	0.94	0.24
	Mn	0.06	0.96
	Na	0.83	0.03
11 Months	Ca	0.95	0.25
	Fe	−0.78	0.06
	K	0.81	0.38
	Mg	0.85	0.37
	Mn	0.15	0.95
	Na	0.82	0.52

and Na, while the soil that was only treated with technosol behaved in the same way as in time 1 (Table 6; Fig. 7). Finally, at 11 months (Table 6; Fig. 7), the treated soils significantly changed their nutrient concentration in comparison to S and SS, continuing to be positively influenced by the concentration of most of the nutrients that were analysed in the same way as in time 2.

### Conclusions

The application of designed treatments improved soil quality. The treatment developed with the combination of technosol and biochar showed in general the best results over the experimental time. Once the treatments were applied the improvement of the pH values and TC content was maintained throughout the experimental time. After treatment, the settling pond soil in depth 0–15 cm experienced a considerable increase of its TN, with the highest values in STP. The CEC increased in nearly all of the cases once the settling pond soil had been treated: the CEC was highest in STBP. After analysing the CEC, it was found that the base saturation was higher in the settling pond soil where these treatments were applied, and that also the aluminium saturation was lower in the settling pond soil where these treatments were applied, especially in STB. This improvement of the CEC is due to the characteristics of the biochar. The high capacity of biochar to retain nutrients was crucial



**Fig. 7** Scatter plot with the two principal components obtained in the PCA (PC 1 and PC 2) in height 1

for the treatment made with technosol and biochar to present the highest nutrient contents. Once the settling pond soil was treated, the critical values for the limiting factors for plant production were exceeded. These factors

were exceeded to a greater extent in the treatments that combined technosol and biochar. Finally, the PCA in the samples confirmed the effectiveness of the treatments in increasing the nutrient content of the settling pond soil. The capacity of the biochar to improve the settling pond soil was clearly indicated on analysing the biomass of the *B. juncea* L., as the biomass and vigour of the plants was greater in the treatments that combined technosol and biochar.

**Acknowledgements** This work was supported by the Spanish Ministry of Economy and Competitiveness under project CGL2016-78660-R.

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