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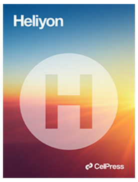

Research article

Assessment of the application of two amendments (lime and biochar) on the acidification and bioavailability of Ni in a Ni-contaminated agricultural soils of northern Colombia

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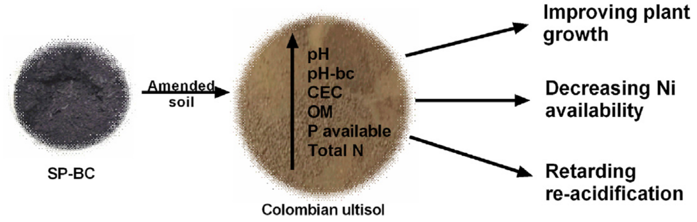
GRAPHICAL ABSTRACT



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ABSTRACT

Soil acidification and increased bioavailability of Ni are problems that affect agricultural soils. This study aims to compare the effects of both lime and biochar from corn stover in soil acidity correction, improving soil physicochemical properties and soil re-acidification resistance. As well as assesseing the impacts on human health risk caused by bioavailability of nickel. A greenhouse pot experiment was conducted for 30 days to determine the effect of biochar and lime on soil physicochemical properties and nickel bioavailability. Afterwards, a laboratory test was carried out to determine the repercussions of both amendments on soil resistance to re-acidification and re-mobilization of nickel. Human health risk was determined using nickle bioavailable concentration. Overall, the results of this study showed that biochar application significantly reduced soil acidity from 8.2 ± 0.8 meq 100 g^{-1} to 1.9 ± 0.3 meq 100 g^{-1}, this reduction markedly influenced the bioavailability of nickel, which decreased significantly. Moreover, soil physicochemical properties and soil resistance to acidification were improved. Furthermore, biochar significantly reduced human health risk compared to lime application, even under a re-acidification scenario. It was possible to verify that Ni immobilization in the soil was increased when biochar was used. Soil Ni immobilization is associated with co-precipitation and chemisorption. Hence, it was demonstrated that biochar is more effective than lime in reducing soil acidity and remedying nickel-contaminated agricultural soils.

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1. Introduction

Acidification of soils is a global issue, since suitable land for crop production is lost due to the toxicity generated by content of Al and Mn in soils, as well as the low bioavailability of mineral nutrients such as Ca, Mg, K, P and Mo, which adversely affects crop yields and farmers economies (Fageria and Baligar, 2008). In addition, reduction in soil pH increases the bioavailability of potential toxic metals (PTM's) generating risks to human health (Bolan et al., 2003; Wang et al., 2015). Recent studies have identified that, among all PTM's, Ni is an important pollutant in agricultural soils (Hassan et al., 2019) and there is evidence that soil acidification increases its bioavailability (Wang et al., 2015). Thus, restoration of Ni contaminated soils is recognized as an important task to reduce Ni mobility and bioavailability in agricultural lands, thereby human health risks associated to Ni pollution are minimized. However, studies related to bioavailability and health risks of Ni in soils are limited compared to others PTM's, such as Cd, Pb, As, Hg.

Application of liming materials is the most widely applied agronomic practice to ameliorate soil acidification. Which, in parallel, decreases the bioavailability of PTM's (Bolan et al., 2003). Lime application is a strategy that increases soil pH and reduces the bioavailability of metals through precipitation mechanisms (e.g., by forming carbonates) (Ali et al., 2020; López et al., 2022; Sumalatha et al., 2022). However, it has been demonstrated that the incorporation of these materials is not effective in increasing soil resistance to acidification, thereby lime soils treated can be susceptible to re-acidification (Shi et al., 2018). Besides, throughout this process, PTM's can be re-mobilize to bioavailable fractions (Du et al., 2018; Guo et al., 2018). This means that a constant application of liming materials is necessary to keep their beneficial effect on soil, which is not economically attractive to farmers (Alonso-Gómez et al., 2016; Cooper et al., 2020). Considering the problems related to current methods to improve soil acidity, it is necessary to develop long-term alternatives that provide a better management of soil acidity and the risks associated to PMTs bioavailability.

Currently, biochar has been proposed as amendment to ameliorate soil acidity (Dai et al., 2017; Kizito et al., 2019). Biochar is the result of pyrolisis, which is a process of thermal decomposition in the abscense of oxygen (López et al., 2020). It has been reported that the application of biochar to agricultural soils increases soil physicochemical properties, soil fertility and crop yield (Dai et al., 2017; Jeffery et al., 2017; Sarfraz et al., 2017; Kizito et al., 2019). Likewise, the capability of biochar to remediate soils contaminated with PTM's has been extensively studied (Houben et al., 2013; Ahmad et al., 2014; Palansooriya et al., 2020). However, the comparative effect of biochar and other amendments (e.g., lime) in correcting soil acidity, as well as its influence on reducing the bioavailability of Ni and human health risks associated to it have been poorly studied, especially considering the effects of soil re-acidification. Biochar is characterized by its great capability to immobilize soil contaminants through electrostatic interaction, complexation, ion exchange, precipitation and chemisorption mechanisms. Due to its physical and chemical attributes such as alkalinity, specific surface area, cation exchange capacity, porosity, and functional groups (Ali et al., 2020; López et al., 2020, 2022; Haider et al., 2022).

Colombia is a tropical country with a large presence of acidic soils (Oxisol, Ultisol, and acidic Entisols) representing the 47% of territory, equivalent to 54 million ha, approximately. Significant Ni enrichment has been reported in soils of northern Colombia, associated to mining activities. These soils are often used for farming, therefore, increase in Ni concentration represents a risk to human health (Marrugo-Negrete et al., 2017). Therefore, in this study a greenhouse pot experiment and simulated re-acidification tests were conducted, using a Colombian acidic Ultisol. To evaluate the efficiency of both biochar and lime as amendments to mitigate soil acidification, improve plant growth and decrease human health risks produced by Ni bioavailability. We hypothesize that biochar can provide an alkalinizing capability equal to or greater than that of lime, in addition to increasing the soil's capability to resist re-acidification. This would be a more effective amendment for the remediation of acidic soils contaminated by Ni.

2. Materials and methods

2.1. Soil sampling

Acidic soil was collected from Ayapel municipality in north of Colombia (8°11′51.46 ″N, 74°59′51.79″ W). The soil was classified as Ultisol as per USDA soil taxonomic classification (IGAC, 2015). It was selected due to the potential contamination by Ni that has been previously reported in this area, with pseudototal Ni concentrations between 8.3 and 1757 mg kg^{-1} (Marrugo-Negrete et al., 2017). Soil samples were collected from the top layer (0–20 cm) using a zig-zag sampling scheme (500 kg), obtaining a composite soil sample. Soil was air-dried, ground, sieved (<2mm), and stored for physicochemical analysis and experiments (Table 1).

2.2. Biochar production

Corn stover was used as feedstock for biochar production. First, the biomass (initial moisture content 35.83%) was air-dried at room temperature (28 °C ± 2 °C) for 48 h. Subsequently, the air-dried biomass was dried at 80 °C for 48 h. Then ground to pass through a 2 mm sieve and placed in ceramic crucibles. The crucibles were covered with a close-fitting lid and pyrolyzed under limited oxygen supply in a muffle furnace. The pyrolysis temperature was raised to 500 °C at a rate of 20 °C min^{-1} and held constant for 3 h, followed by cooling to room temperature inside a furnace. The biochar was aerated for 24 h at room temperature (25 °C), then sieved (<2mm) and stored in airtight containers (Morales et al., 2021; Sepúlveda-Cadavid et al., 2021; Herrera et al., 2022). The biochar obtained was named as SP-BC. The pH and electrical conductivity (EC) of SP-BC was estimated in a suspension of 1:10 SP-BC:deionized water (DW) ratio using adigitial pH meter (WTW™ 2AA210, Berlin, Germany) and conductivity meter (HANNA™ HI8033, Woonsocket, USA) (López et al., 2020). Ash content was measured as the weight of the residue after a SP-BC sample was heated at 700 °C in an open crucible (López et al., 2020). The C and N content were determined using an elemental analyzer (Elemental Analyzer, Germany) (Sepúlveda-Cadavid et al., 2021). Total concentration of Ni was determined by acid digestion and quantified by ICP-OES (Inductively coupled optical emission spectrometry, Agilent Technologies 5100 ICP-OES equipment,

Table 1. Properties of acidic soil and corn stover derived biochar (SP-BC).

Properties	Soil	SP-BC
pH	5.1	9.7
EC (ds/m)	0.54	9.8
CEC (meq 100 g^{-1})	8.5	-
Ash (%)	-	22.2
P-Olsen (mg kg^{-1})	9.4	84.7
Soil N (g kg^{-1})	3.2	-
Soil OC (%)	1.2	-
N (%)	-	2.2
C (%)	-	65.1
Pseudo-total Ni (mg kg^{-1})	110.4	ND
Bioavailable Ni (mg kg^{-1})	35.2	-
Soil Texture	Clay loam soil	
Sand (%)	15	
Silt (%)	38	
Clay (%)	47	

ND: undetected. Data are presented as mean values of three replicates ±standard error of the mean (SEM). EC: electrical conductivity. Soil OC: soil organic carbon. CEC: cation exchange capacity.

Santa Clara, USA). In brief, 1.0 g of solid sample underwent acid digestion (1:3 Suprapur® HCl:HNO_3) at 90 °C for 1 h and 140 °C for 3 h. After digestion, sample was diluted with Milli-Q water and passed through a 0.45μm membrane (López et al., 2020). Subsequently, the filtrate was used for the determination of elements by ICP-OES (Table 1). Superficial functional groups were determined by FTIR (Fourier-transform infrared spectroscopy) analysis using an infrared spectrometer (Thermo scientific Smart iTR Nicolet iS10, Waltham, USA), which was operating in a 4000-400 cm^{-1} spectral range with a resolution of 4 cm^{-1} (Sepúlveda-Cadavid et al., 2021).

2.3. Greenhouse experiment

An experiment of two stages was performed to assess the effect of SP-BC and lime on ameliorating soil acidity, improving plant growth, and decreasing soil Ni bioavailability. Two application doses (0 and 1%) (Fig. S1) and two soil amendments (SP-BC and lime) were implemented. Lime characteristics are shown in Table S1. First, pots with soil were amended with SP-BC and lime at a dose of 1% (w/w), equivalent to 25 t/ha. The dose per hectare was calculated using tillage depth of 0.2 m and bulk density of 1250 kg/m^3. The soil without amendment was used as control. The pots were incubated for eight days, maintaining 50% of soil water holding capacity (WHC) using DW to avoid leaching. Incubation experiment was maintained at room temperature (28 °C±2 °C) for 30 days.

After the incubation period, a greenhouse experiment was established at Institución Universitaria Colegio Mayor de Antioquia (6°16′23.83″ N, 75°35′31.23″ E) (Medellín, Colombia). Certified seeds of bean cargamanto mocho (*Phaseolus vulgaris* L) (AgroSemillas®, Colombia) were used. They were germinated on peat (Sustitutos Ecológicos®, Antioquia, Colombia) moistened with deionized water at 70% WHC for 5 days (Sepúlveda-Cadavid et al., 2021). Then, one pre-germinated seed was planted in a plastic bag that contained 700 g of pre-incubated amended soils. The pots were irrigated to maintain 70% of their WHC to avoid leaching and then distributed randomly in the greenhouse. Experiments were performed in triplicate.

The photoperiod was 12 h light and 12 h dark. The temperature fluctuated between 25 to 30 °C and humidity fluctuated between 60 to 65% during the study. After 30 days of growth, the *P. vulgaris* plants were harvested and divided into roots and shoot, and then their lengths were measured. Plant's biomass was air-dried to a constant weight and the dry weight of shoot and root were measured, respectively.

2.4. Simulated soil re-acidification experiment

With the aim of evaluating the effect of SP-BC and lime on soil acidification and Ni bioavailability with acid input, a simulated soil re-acidification experiment was performed. Before the re-acidification experiments, SP-BC was incorporated in 150 g soil sample at a dose of 1% (w/w). Afterwards, it was incubated as previously described (30 days at 50% of WHC using DW), and then soil pH was determined. A soil sample of 150 g without SP-BC was amended with lime at a dose (2.4 % w/w) that allowed it to reach the same soil pH value obtained with SP-BC after incubation period. The dose of lime needed was calculated using the equation obtained from the liming curve ($pH = 1.007*(dose\%) + 4.221$). The soil sample was mixed with lime and subjected to an incubation period (30 days at 50% of WHC using DW), after which each soil sample was air-dried. The soil samples were called “ameliorated soil samples”. As for the re-acidification experiment, this was carried out using HNO_3 solutions as acid input (Shi et al., 2020). Where, ameliorated soil samples (100 g) were placed in airtight plastic bags. Then the soil was moistened with HNO_3 solutions at different concentrations (0–4.0 mM) up to 80% of WHC, equivalent to 36 ml of HNO_3 solutions. Then, the initial weight of each bag was measured. The bags were moistened daily with the same solutions for 7 days adding 1 ml of HNO_3 solution to maintain the soil humidity as similar as possible to the initial weight. Afterwards, the soil samples were air-dried to determine pH, exchangeable Al^{3+}, CEC, and Ni bioavailability.

2.5. Soil analyses

Soil and post-haverst soil samples were collected, air-dried, ground, and sieved (<2 mm). Soil pH, soil pH buffer capacity (pH-bc), and EC analyzes have been carried out in DW using a 1:2 soil:DW ratio with a digital pH meter according to ISO 10390:2005 (WTW™ 2AA210, Berlin, Germany) and conductivity meter (HANNA™ HI8033, Woonsocket, USA). Particle size distribution was determined by hydrometer method (Beverwijk, 1967). The SOM was measured by Walkley-Black method (Diaz-Zorita, 1999). Total N was determined for Kjeldhal method (ISO 11261:1995). Bioavailable P concentration was extracted with Olsen method and estimated using a spectrophotometer (Sepúlveda-Cadavid et al., 2021). Exchangeable base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) were extracted with 1 M NH_4-acetate at pH 7.0 and quantified by ICP-OES according to ISO 11260:2018. Soil cation exchange capacity (CEC) was determined as the sum of exchangeable basic cations according to ISO/DIS 22171, 2020. Soil exchangeable acidity (H^+ and Al^{3+}) was measured using extraction with 1 M KCl and titration with 0.1 M NaOH (ISO 14254:2018). Exchangeable aluminium was determined using 1 M KF and titration with 0.025 M HCl (Pansu and Gautheyrou, 2006). Total concentration of Ni was determined by acid digestion. In brief, 1.0 g of soil sample was weighed and underwent acid digestion (1:3 HCl:HNO_3) in an Ethos One Milestone Chemist microwave, following the USEPA Method 3050B (da Silva et al., 2020; Ma et al., 2022). After digestion, the sample was diluted with Milli-Q water and passed through a 0.45μm membrane, subsequently the filtrate was used for the determination of elements by ICP-OES. A soil reference material (NITS® SRM® 2709a, Sigma-Aldrich) was used to validate the method of extraction and quantification of Ni. The recovery percentages were between 95 and 102%. Soil samples pH-bc was determined using a titration technique (Shi et al., 2018). Titration curves were established by adding incremental amounts of HCl or NaOH to soil suspensions with 1:5 soil:liquid ratio. Finally, after equilibrium time the solutions pH was measured. The geochemical fractionation of Ni was determined using Tessier sequential extraction method (Tessier et al., 1979) (see supplementary information. Supplementary description S1). For re-acidification experiment, bioavailable concentration of Ni in soil samples was determined by the first step of Tessier method, which is associated with more metal bioavailability. The concentration of Ni in all fractions was determined by ICP-OES.

2.6. Health risk assessment (HRA)

Human exposure to impacts of PTM's may occur through three major pathways, i) direct oral ingestion, ii) inhalation, and iii) dermal absorption (Luo et al., 2012). Exactly, chronic Daily Intake (CDI) (mg/kg day) is predictive of estimating health risks through ingestion, inhalation, and dermal contact routes in both children and adults (Kusin et al., 2018). Reference exposure factors used for a soil with properties like the soil used in this study for the estimation of CDIs are provided (Table 2). Bioavailable concentration of Ni in soil samples obtained from greenhouse experiment and re-acidification experiment were used to calculate CDIs values. The following are the equations used to determine CDIs values for human exposure to toxic metals by ingestion, inhalation, and dermal contact (Kusin et al., 2018).

$$CDI_{Ingest} = \left[\frac{(C*IngR*EF*ED)}{BW*AT}\right]*CF \tag{1}$$

$$CDI_{Inhale} = \left[\frac{(C*InhR*EF*ED)}{PEF*BW*AT}\right]*CF \tag{2}$$

$$CDI_{Dermal} = \left[\frac{(C*SA*AF_{soil}*ABS*EF*ED)}{BW*AT}\right]*CF \tag{3}$$

The HRA was determined calculating the carcinogenic risk exposures for both children and adults using the total lifetime cancer risk (LCR). In

Table 2. Reference exposure factors for CDIs calculation (USEPA 2012).

	Unit	Adult	Children
IngR	mg day^{-1}	100	200
EF	day year^{-1}	350	350
ED	years	24	6
BW	kg	70	15
AT	days	8760	2190
CF	kg mg^{-1m}	1E10^{-6}	1E10^{-6}
InhR	mg cm^{-2}	20	20
PEF	m^3 kg^{-1}	1.36E10^9	1.36E10^9
SA	cm^2	5700	5700
Afsoil	mg cm^{-2}	0,07	0,07
ABS	-	0,001	0,001

turn, LCR was determined by estimating the total value of cancer risk for each exposure pathway (intake, inhalation, and dermal contact) (Kusin et al., 2018). The acceptable threshold value for LCR used was 1.0E^{-04} (USEPA 2012). The following are the equations used to determine LCRs values (Kusin et al., 2018).

$$Cancer\ risk_{Ingest} = CDI_{Ingest} * CSF_{Ni} \tag{4}$$

$$Cancer\ risk_{Inhale} = CDI_{Inhale} * CSF_{Ni} \tag{5}$$

$$Cancer\ risk_{Dermal} = CDI_{Dermal} * CSF_{Ni} \tag{6}$$

$$LCR = Cancer\ risk_{Ingest} + Cancer\ risk_{Inhale} + Cancer\ risk_{Dermal} \tag{7}$$

Where CDI is the chronic daily intake (Ingest, Inhale or Dermal) (mg/kg day), AT is the average time (days), AFsoil is the skin-to-soil adhesion factor (mg/cm^2), ABS dermal absorption factor, BW average body weight (kg), C metal concentration in soil (mg/kg), CF conversion factor (kg/mg), EF exposure frequency (days/years), ED exposure duration (years), IngR soil ingestion rate (mg/day), InhR inhalation rate (mg/cm^2), PEF particle emission factor (m^3/kg), SA surface of the skin that is in contact with the ground (1/cm^2). LCR is the total life-time cancer risk and CSF is the cancer slope factor, the CSF value used for Ni was 0.84 mg/kg day (CSF_{Ni}) (Mohammadi et al., 2019). The acceptable threshold value of the cancer risk is 1.0E-04 (USEPA 2012).

2.7. Data analysis

All data are presented as mean values and standard error of three replicates. Graph's plotting was done with Python and the statistical analysis was carried out with Statgraphics® Centurion XVIII software. Values of $p \leq 0.05$ were considered statistically significant (ANOVA), and pairwise comparisons were performed with the Tukey post hoc test. Prior to analysis, Bartlett's test and the Shapiro–Wilk test were applied to verify the assumptions of homogeneity of variance and data normality, respectively.

3. Results

3.1. Biochar application ameliorates soil acidity and improves soil quality

The changes in soil physicochemical properties after 30 days are shown in Table 3. In general, the application of SP-BC and lime significantly improved soil physicochemical properties compared to the control, except for pH-bc, SOM and exchangeable Mg^{2+}, K^+, and Na^+ values in the lime treatment. Soil pH increased by 1.6 and 2.3 units in the SP-BC and lime treatments, respectively. The CEC increased by 62% when SP-BC was applied compared to the control, while when lime was applied CEC increased by 28% compared to the control. Likewise, SP-BC increased bioavailable P by 36% (as Olsen-P) while lime increased this parameter by 14% compared to the control. Other soil physicochemical parameters were favored to the same extent by both treatments compared to the control. Exchangeable acidity and Al^{3+} decreased an average of 83% in both SP-BC and lime treatments. Application of SP-BC increased by 80, 70, 79, and 18% the pH-bc, SOM, Mg^{2+}, and N, respectively. Also, SP-BC increased 16- and 2-fold the concentration of K^+ and Na^+, respectively, compared to the control. While the application of lime did not generate significant changes in these parameters. Content of Ca^{2+} was the only parameter that was favored by the application of lime compared to SP-BC, increasing by 45% compared to the control. On the other hand, SP-BC increased Ca^{2+} by 15% compared to the control.

3.2. Plant growth

The changes in plant growth parameters after 30 days are shown in Figure 1. Dry weight of shoot showed no significant differences between SP-BC and lime treatments compared to the control. However, SP-BC treatment showed a superior tendency. Compared to lime, the application of SP-BC showed a significant increase in shoot dry weight. For both length and root dry weight, no significant statistical differences were found between the treatments. Although the changes in biometric parameters in plants were not so significant, it was possible to observe a trend that indicates that the application of SP-BC is favorable for promoting plant growth.

3.3. Biochar application delays soil re-acidification

Application of SP-BC significantly retarded the effects of acid inputs on soil parameters (Figure 2). With SP-BC addition, the decrease in soil was lower compared to lime. As can be seen in Figure 2 soil pH in SP-BC treatment was higher than in soil amended with lime at the same HNO_3 added level. The exchangeable Al^{3+} increased with HNO_3 concentration, related to decreasing of soil pH. Compared to the lime treatment, the increase in exchangeable Al^{3+} during re-acidification experiment was inhibited by the application of SP-BC.

Table 3. Soil properties with corn stover derived biochar (SP-BC) and lime incubated for 30 days with greenhouse scale bean cultivation.

	pH	pH-bc (mM HNO_3/kg pH)	SOM (%)	Soil exchangeable (m_{eq}/100 g)							CEC (m_{eq}/100 g soil)	Total N (g/kg)	Bioavailable P (mg/kg)
				Acidity	Al^{3+}	H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+			
Control	4.7 ± 0.2c	11.8 ± 0.6b	2.6 ± 0.3b	8.2 ± 0.8a	8.0 ± 0.8a	0.3 ± 0.0a	6.6 ± 0.3c	2.6 ± 0.4b	0.2 ± 0.0b	0.2 ± 0.0b	9.6 ± 0.3c	2.6 ± 0.1b	9.7 ± 0.3c
SP-BC	6.6 ± 0.1b	22.3 ± 0.0a	7.1 ± 0.4a	1.9 ± 0.3b	1.7 ± 0.4b	0.2 ± 0.1a	7.7 ± 0.1b	5.4 ± 0.3a	3.9 ± 0.1a	0.4 ± 0.0a	17.3 ± 0.3a	3.0 ± 0.1a	13.2 ± 0.3a
Lime	7.4 ± 0.3a	14.5 ± 1.4b	3.5 ± 0.4b	0.8 ± 0.2b	0.6 ± 0.2b	0.3 ± 0.1a	9.7 ± 0.3a	2.4 ± 0.4b	0.2 ± 0.0b	0.2 ± 0.0b	12.4 ± 0.3b	2.5 ± 0.1b	11.2 ± 0.7b

ND: undetected. Data are presented as mean values of three replicates ±standard error of the mean (SEM) followed by the same letter are not significantly different (Tukey at $p \leq 0.05$). EC: electrical conductivity. SOM: soil organic matter. CEC: cation exchange capacity.

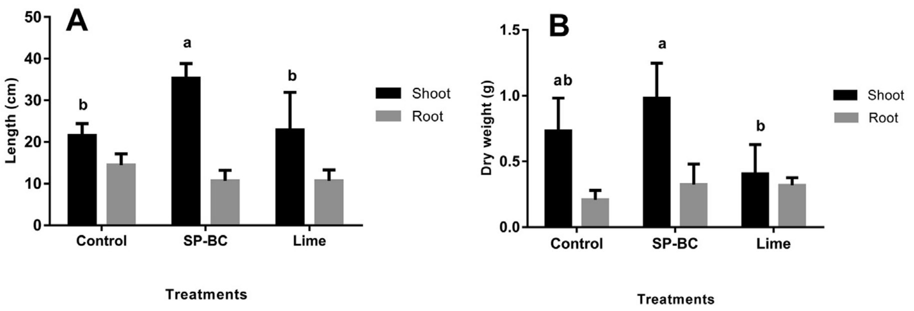

Figure 1. Length and dry weight of *Phaseolus vulgaris* after 30 days of greenhouse growth. Means (n = 3) followed by different letter within columns are significantly different (Tukey at $p \leq 0.05$). Absence of letters indicates no significant statistical difference (Tukey at $p \leq 0.05$). Vertical bars represent the standard error of the mean (SEM). SP-BC: corn stover derived biochar.

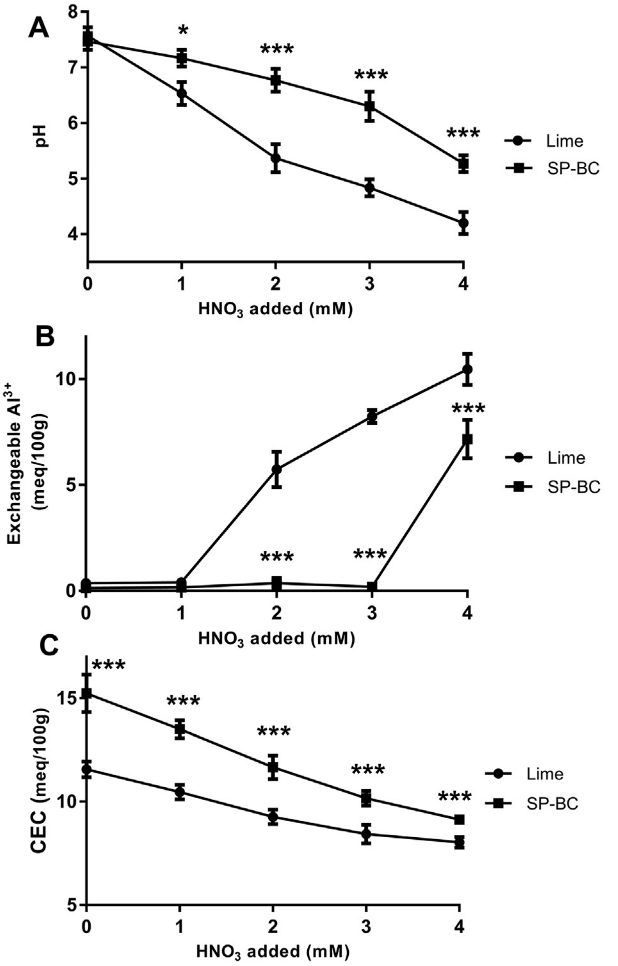

Figure 2. Soil properties with corn stover derived biochar (SP-BC) and lime after re-acidification. Means (n = 3) followed by *, **, *** present significant differences (ANOVA test $*p \leq 0.05$ $**p \leq 0.01$, $***p \leq 0.001$). Vertical bars represent the standard error of the mean (SEM).

3.4. Biochar application reduces Ni bioavailability and Ni re-mobilization by acid inputs

Distribution of Ni in soil geochemical fractions after 30 days of the greenhouse experiment are shown in Figure 3. Concentrations of Ni in the five Tessier's fractions are shown in Table S1 (see supplementary information). Compared to control, the application of SP-BC and lime significantly decreased in 12- and 3-fold the distribution of Ni in exchangeable fraction (F1), respectively. On the other hand, both SP-BC and lime treatments significantly increased in 1- and 1.2-fold the distribution of Ni in bound to Fe/Mn oxides fraction (F3), respectively and significantly increased in 2.3- and 1.3-fold the Ni concenten in the bound to organic matter fraction (F4), respectively. The distribution of Ni in bound to carbonates fraction (F2) improved significantly (2.3-fold) only in the soil treated with lime. The residual fraction (F5) had no significant changes compared to the control. The results of the re-acidification test showed that as the soil pH decreases Ni bioavailability increases, regardless of the treatment applied. However, the application of SP-BC resulted in a lower remobilization of Ni to the bioavailable fraction compared to lime treated soil.

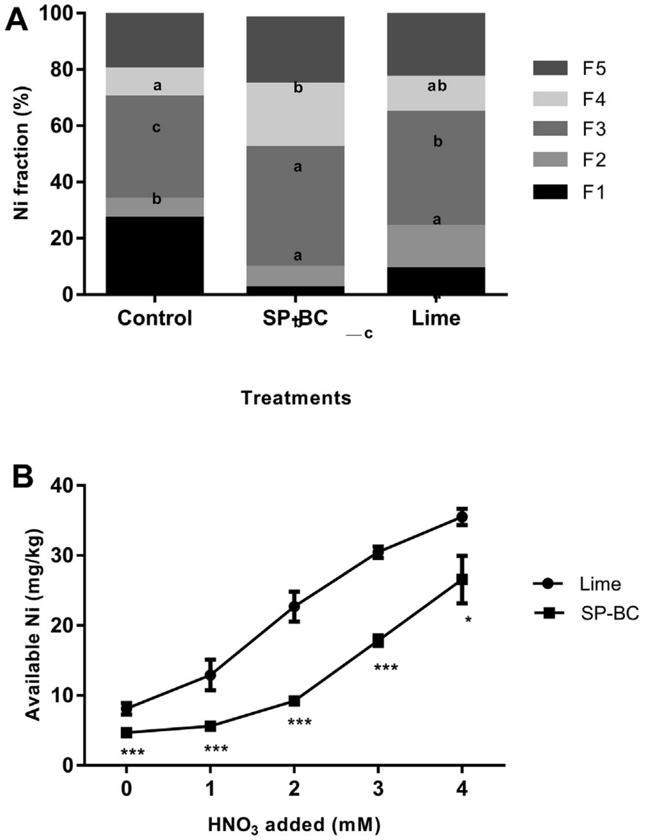

Figure 3. Soil Ni fractionation affected by corn stover derived biochar (SP-BC) and lime. Fractions: Water soluble and exchangeable (F1), Carbonates (F2), Mn and Fe oxides (F3), Organic matter (F4) and Residual (F5). Means (n = 3) followed by the same letter within columns are not significantly different (Tukey at $p \leq 0.05$). Vertical bars represent the standard error of the mean (SEM).

3.5. Biochar application reduces human health risk

The values of CDIs and cancer risk are shown in Tables S3, S4 and S5 (Supplementary material). In accordance with the results found for soil

Ni bioavailability, the application of SP-BC and lime significantly reduced the LCR value compared to control soil, both for adults and children (Figure 4). The results of LCR shows that the most vulnerable population is children, since it exceeds the acceptable LCR by 228.1% while the adult is 64.8% below the acceptable LCR. Although the adult LCR decreased significantly when using lime and SP-BC compared to the control, SP-BC had the greatest decrease in health risk in adults. The results of children LCR decreased significantly when using lime and SP-BC, but only the application of SP-BC resulted in a decrease below the acceptable LCR. As for re-acidification process, adult LCR does not exceed the acceptable LCR, although significant differences were found when comparing lime and SP-BC. Since the increase in LCR was greater with lime (Figure 4). Figure 4 shows children LCR in the re-acidification process, where the acceptable LCR is overcomed from the beginning when using lime. As analyzing the effect of SP-BC, LCR would exceed the acceptable one when it has a pH lower than 6.8, associated to the addition of HNO_3 concentrations greater than 2 mM.

4. Discussion

Amelioration of soil acidity and decrease in bioavailability of Ni are an important research topic worldwide. Particularly in areas where Ni contamination occurs, e.g., near to a smelter or mining activity (Gonnelli and Renella, 2013; Marrugo-Negrete et al., 2017). In acidic soil this situation is even more serious because of greater bioavailability of Ni and likelihood of Ni leaching into the ground water compared to alkaline soil (Ali et al., 2020). The results of this study show five relevant aspects: i) in comparison to lime, application of biochar is more effective in reducing soil acidity, improving soil physicochemical properties and promoting plant growth, ii) the use of biochar increases soil resistance to re-acidification, iii) application of biochar reduces Ni bioavailability and Ni re-mobilization during soil re-acidification, and iv) human health risks are reduced with the application of biochar, even when the soil is re-acidified. The implications of these findings are herein discussed to support further practical applications of biochar in Ni-contaminated soil remediation under field conditions. The findings of this study support the hypothesis that biochar is superior as a soil amendment in acidic soils contaminated by Ni in comparison to lime, under evaluated experimental conditions.

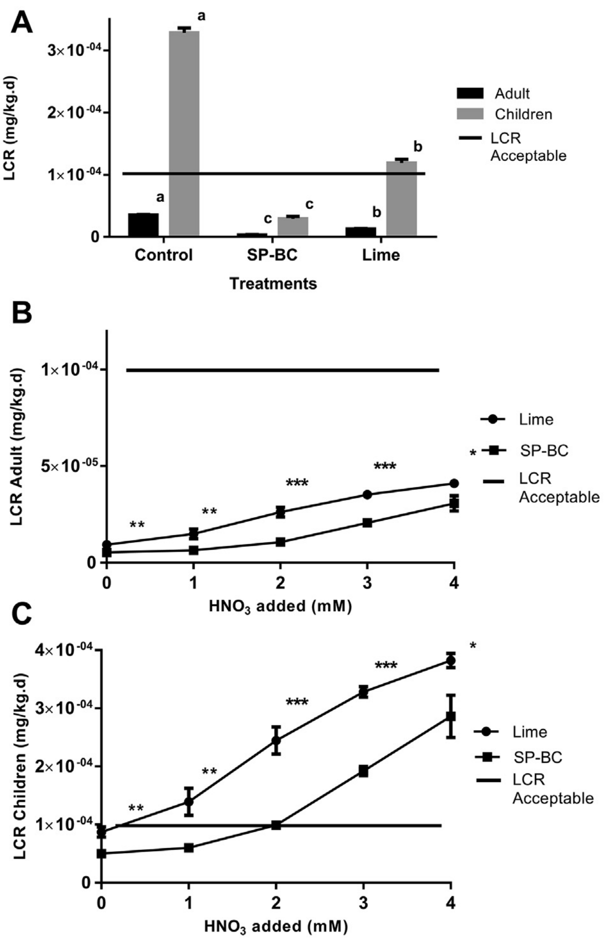

Figure 4. LCR of adults and children with corn stover derived biochar (SP-BC) and lime. Means (n = 3) followed by the same letter within columns are not significantly different (Tukey at $p \leq 0.05$). Vertical bars represent the standard error of the mean (SEM). horizontal line indicates the threshold value (USEPA 2012).

4.1. *Changes in soil physicochemical properties*

Compared to lime, the application of SP-BC increased soil pH and pH-bc (Table 3). The capability of biochars for increasing soil pH and pH-bc can be attributed to their alkalinity, base cations concentration, abundant organic functional groups on biochars surface and their proton consumption capability (Chintala et al., 2014; Shi et al., 2018). These results suggest that SP-BC incorporation increased the resistance of the Ultisol to acidification and that the pH rise could be maintained in the long term. However, this should be evaluated in long-term trials and under field conditions (e.g., considering the effect of precipitation and leaching). Therefore, the use of biochar is desirable, since the results indicate that the need for reapplication over time would be lesser, being practical, efficient, and cost-effective for farmers. Soil pH is the key factor controlling exchangeable soil acidity. It has been determined that as soil pH increases the exchangeable Al^{3+} precipites as insoluble hydroxyl Al-species (Bolan et al., 2003; Fageria and Baligar, 2008). Additionally, biochars can release into soil their base cations, which can participate in exchange reactions and replace the exchangeable Al^{3+} and H^+ on soil surface. Also, biochars contain oxygen functional groups that can form surface complexes with Al^{3+} (Masud et al., 2014; Chintala et al., 2014).

The SP-BC was not only effective in controlling soil acidity, also, the application of SP-BC improved the concentration of basic cations (Table 3). This can be explained by the fact that lime application generates an important contribution of Ca^{2+}, but not of other nutrients (Masud et al., 2014; Wu et al., 2020). On the other hand, when SP-BC is incorporated, Ca^{2+}, Mg^{2+}, K^+, and Na^+ are released from biochar to the soil, increasing the concentration of these elements. In parallel with the increase in pH and the concentration of exchangeable bases, the soil treated with SP-BC show a significantly higher CEC compared to soils treated with lime (Table 3), those findings are in line with results of this study (Chintala et al., 2014). The increase in CEC is explained by the increment in soil pH, which enhances the amount of negative soil surface charges, plus the contributions of surface functional groups in the biochar (Wan et al., 2014; Shi et al., 2018; Dong et al., 2019). As expected, the SP-BC increased the SOM (Table 3), which is related to organic carbon inputs from SP-BC (Shi et al., 2020). In relation to P and N contents, the incorporation of SP-BC improved them in comparison with lime (Table 3). Masud et al. (2014) propose that biochars contained relatively more P than others liming materials and, therefore, amendment with biochars directly increased soil bioavailable P. Another important factor that improves bioavailability of P is soil pH (Zhang et al., 2016), since P has its greatest bioavailability in soil at pH between 6 – 7. Therefore, the increase in Ultisol pH increased the bioavailability of P. Biochar's capacity to adsorb N due to its high porosity could have generated a controlled release of this element, avoiding its loss. In addition, possible effects on microbial diversity, abundance and activity could be involved in this phenomenon (Dai et al., 2017; Xia et al., 2020). Overall, the application of SP-BC improved soil health, therefore it was able to improve the growth of *P. vulgaris* plants, as evidenced by the results (Figure 1). This is related to the control of acidity and the improvement of soil chemical environment.

4.2. Biochar increases soil resistance to acidification

On the other hand, the findings of this study showed that the application of SP-BC reduced soil re-acidification (Figure 2). Which may be related to the liming effect of SP-BC, in addition to the ability of biochar to retain Al^{3+} in surface functional groups (Shi et al., 2020). The result indicates that compared to lime, biochar proved to be a more stable amendment than lime in maintaining soil pH and reducing Al^{3+} concentration under acidic conditions. The CEC is a representation of the negative charges on surface of soil colloids and strongly depends on soil pH and the type of colloids it contains. The decline in soil CEC was related to protonation of the SP-BC that contains oxygen functional groups (Fig. S2). Which is associated with the contribution of biochars to soil pH-bc (Shi et al., 2018). The results show that compared to lime, biochar increases the resistance of soils to acidification. Which is related to SP-BC capability to increase soil pH-bc, as discussed above. Therefore, SP-BC can be a promising alternative to increase soil resistance to acidification. It could be a practice that counteracts the negative effects of the use of chemical synthesis fertilizers and acid rain on soil acidity. This is fundamental in the agronomic management of tropical soils, which naturally tend to be of acidic nature.

4.3. Biochar reduces Ni bioavailability

In line with the reduction of soil acidification, SP-BC application significantly reduced Ni bioavailability compared to lime and the control (Figure 3). In this study, SP-BC reduced the bioavailability of Ni over 80%, while lime reduced the most bioavailable fraction of this element by 60%. Other studies such as Turan et al. (2018) report a 47% reduction in Ni bioavailability with the application of rice straw biochar at 1%. In this line, Ali et al. (2020) used rice husk derived biochar at doses of 1 and 2%, found Ni immobilization percentages of 73 and 78%, respectively. Comparing the high percentage reduction in bioavailability of Ni by SP-BC at a conservative dose of 1% shows that this material has potential for use in soil remediation.

The reduction in the bioavailability of Ni by biochar is explained by direct and indirect mechanisms. The direct mechanisms are related to the absorption of metals by biochar and indirect mechanisms with changes in soil physicochemical properties that cause the soluble fraction of Ni to decrease and transform into less mobile species (Gong et al., 2022; Haider et al., 2022). Directly, oxygen-containing functional groups (e.g., O–H and C–O) in biochar are involved in Ni immobilization mechanisms by complexation (Fig. S2). Also, these functional groups are related to ion exchange phenomena, where Ni^{2+} is exchanged with other cations such as Ca^{2+} and Na^{+}, as demonstrated by Zhu et al. (2021). By the other hand, to investigate the indirect possible mechanisms associated with the reduction of Ni bioavailability, in this study the Tessier's fractions are determined (Figure 3), which are F1 (exchangeable), F2 (bound to carbonates), F3 (bound to Fe/Mn oxides), F4 (bound to organic matter), and F5 (residual). Fractions F1 and F3 represent metals concentration that are readily bioavailable, fractions F3 and F4 represent the concentration of potentially less bioavailable metals, and F5 represent the concentration of metals in the residual fraction (e.g., associated with silicates) (Tessier et al., 1979; Adamo and Zampella, 2008). The results indicated that SP-BC was more effective than lime in lowering Ni concentration in the soluble and easily exchangeable fraction (F1). The largest increase of Ni in F3 is related to the Ni sorption at the surface of the soil Fe and Mn oxides, due to the increase of the negative charges and the rise of the soil pH (Haider et al., 2022). Thus, Ni may be attracted to Fe and Mn oxides (variable-charge coloids) under formation of mononuclear, monodentate binding ($FeOH + Ni^{2+} - > FeOHNi^{+} + H^{+}$) (Borggaard et al., 2019). The increase of F4 in the treatment SP-BC is related to the Ni sorption in surface functional groups (e.g., oxygen-containing functional groups) present SOM, in addition to the functional groups present in the SP-BC (Fig. S2). This would favort the formation of Ni-ligand complexation ($Ni^{2+} + R\text{-}OH - > Ni\text{-}RO + H^{+}$) (Hamid et al., 2020).

A significant increase in the F5 fraction in the SP-BC treatment indicates Ni co-precipitation mechanisms, as new mineral faces are formed that increase the % of the residual fraction (F5). Considering these results, the immobilization of Ni by SP-BC is related to chemisorption mechanisms. However, it is important to note that the bioavailability data obtained by chemical extractions do not represent the complex dynamics between soil-Ni-plants, therefore it will be necessary to perform Ni bioaccumulation tests to determine if the transfer of the metal to the plant is really decreased, according to the results found in this study regarding bioavailability in soils.

Soil re-acidification increased Ni bioavailability for both SP-BC and lime treatments (Figure 3). Indicating that the processes of Ni immobilization by the amendments depend on soil pH. The application of lime reduced the concentration of Ni in F1 fraction and presented a significant increase in F2 fraction. Nevertheless, this fraction associated with carbonates is very susceptible to changes in pH (Tessier et al., 1979; Xian, 1989), and possibly this is associated with a greater remobilization of Ni in this treatment. On the contrary, the application of SP-BC increased the concentration of Ni in F3 and F4 fractions. Which can be associated with more stable Ni immobilization processes. Xian (1989) reported that the metals associated with the F1 and F2 fractions represent a higher bioavailability and are dependent on changes in soil pH. While the metals associated with the F3 and F4 fractions are less bioavailable and more stable. Therefore, the SP-BC proved to be a more suitable candidate than lime for stabilizing Ni and remediating Ni-contaminated acidic soils. This study provides evidence to support the use of biochar for the control of Ni contamination in tropical soils, which are acidic and susceptible to re-acidification.

Considering these results, it is possible that chemisorption is involved in a higher resistance of the SP-BC treated soil to release Ni to soil solution under re-acidification conditions. The increase in concentration of Ni in F2 for the lime treatment is explained by the formation of complexes with CO_3 from lime (Ali et al., 2020). Possibly, Ni co-precipitates with carbonate ions to form stable and poorly bioavailable compounds. However, these compounds are removed when the soil pH decreases again (re-acidification) and Ni becomes bioavailable once again. This may explain the results of the Ni remobilization experiment in this study (Figure 3). In general, in this study, SP-BC and lime application reduced Ni bioavailability. Nevertheless, SP-BC generated a greater decrease in Ni bioavailability. In addition, SP-BC slowed down Ni re-mobilization when the soil was re-acidified, due to more stable metal immobilization processes such as chemisorption (Figure 3).

4.4. Biochar improves the physicochemical properties and health of soils

The ecotoxicological risk of accumulation of toxic elements in soils has been studied using indicators such as LCR, which is included in the human health risk assessment (Cüce et al., 2022; Ustaoğlu, 2021; Zulkafflee et al., 2019). Human health risk assessments due to environmental hazard exposures are considered as characterization of the adverse health effects of humans. LCR represents the lifetime cancer risk values for adults and children. The acceptable value recommended by the USEPA is 1×10^{-4}, which means that values above this threshold represent a potential carcinogenic risk to human health (USEPA, 2012). LCR values exceeded the acceptable value in the control and lime treatment, indicating that both adults and children may experience some adverse health effects in the future. Therefore, lime is not a good amendment to control risk under the conditions evaluated. By the other hand, the results of this study indicate that regarding the risk scenarios associated with Ni bioavailability, the potential risk to human health, especially for children, was decreased by the application of SP-BC (Figure 4). This is related to the increased capability of soil to immobilize Ni once the SP-BC treatment was applied. Children have been identified as a special population to consider in risk assessment because of their immature physiology a metabolism (USEPA, 2012). An important finding of this study was that the risk was attenuated by the addition of SP-BC when the soil was re-acidified. Therefore, the application of SP-BC will achieve a better effect in reducing health risk than lime, since it is more resistant to acidification processes. These results indicate that under a soil re-acidification process, biochar can effectively decrease the bioavailability of Ni and delay its remobilization, which is reflected in a lower risk to human health. On the other hand, the application of lime was not effective in controlling the risk to human health when soil pH decreases. Therefore, SP-BC is a better amendment to reduce the risk to human health due to the decrease of Ni bioavailability in acidic soils. Biochar could be incorporated into agricultural practices in soils surrounding Ni contamination hotspots, such as ferronickel mining. Which could lead to reduce potential human exposure (e.g., ingestion, respiratory or dermal) to this metal. The results obtained in this study may encourage stakeholders and environmental authorities to take measures focused on better environmental and risk management for Ni-contaminated soils.

5. Conclusion

A biochar with adequate physical and chemical conditions to reduce soil acidity and Ni bioavailability was obtained. Biochar is a better amendment than lime for soil remediation, even though lime is widely used to correct soil acidity. This study showed that Ni immobilization by biochar is associated with co-precipitation and chemisorption, which is favored by the physicochemical properties of the biochar used. It was also found that the use of biochar increases soil resistance to acidification and, at the same time, the re-mobilization of Ni. Likewise, it was possible to verify that the application of biochar from the pyrolysis of corn stover significantly avoids risks to human health due to the decrease in the bioavailability of Ni. Likewise, it was possible to verify that the application of biochar from the pyrolysis of corn stover improves some physicochemical properties of the soil, leading to an increase in its health. The foregoing could suggest that healthy soils bring healthy crops that can positively impact people's health, due to the decrease in Ni bioavailability in the soils of the study area. However, it is important to conduct Ni bioaccumulation studies using plant models, as well as ecotoxicological studies, to verify the effects of biochar on the chemical bioavailability used in this study. Field trials under real environmental conditions should be applied for the development of a remediation technology for Ni contaminated soils using biochar.

Declarations

Author contribution statement

Evelyn Becerra-Agudelo: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Julián E. López: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Héctor Betancur-García; Jaiber Carbal-Guerra; Maicol Torres-Hernández: Performed the experiments; Analyzed and interpreted the data.

Juan F. Saldarriaga: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest's statement

The authors declare no conflict of interest.

Additional information

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