

ORIGINAL RESEARCH

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Biochar derived from invasive plants improved the pH, macronutrient availability and biological properties better than liming for acid rain-affected soil

Yazheng Li^{1†}, Ahmed I. Abdo^{1,2,3,4†}, Zhaoji Shi^{1,4,5}, Abdel-Rahman M. A. Merwad³ and Jiaen Zhang^{1,4,5*}

Abstract

Rapid development in industrialization and urbanization causes serious environmental issues, of which acid rain is one of the quintessential hazards, negatively affecting soil ecology. Liming has been investigated for a long time as the most effective amendment to alter the adverse effects of soil acidity resulting from acid rain. Herein, this study tested the biochar produced from invasive plants as an alternative amendment and hypothesized that biochar can maintain better availability of macronutrients under acid rain than liming by improving soil chemical and biological properties. Therefore, a pot experiment was conducted to compare the effects of lime and biochar at two rates (1% and 3%) on soil available nitrogen (N), phosphorous (P) and potassium (K) under simulated acid rain of two pH levels (4.5: pH_{4.5} and 2.5: pH_{2.5}) as compared with tap water (pH_{7.1}) as a control treatment. Biochar was produced using different invasive plants, including Blackjack (*Biden Pilosa*), Wedelia (*Wedelia trilobata*) and Bitter Vine (*Mikania micrantha Kunth*). Liming decreased the availability of soil N, P, and K by 36.3% as compared with the control due to the great increment in soil pH and exchangeable calcium (Ca²⁺) by 59% and 16-fold, respectively. Moreover, liming reduced the alpha diversity of soil bacteria and fungi by 27% and 11%, respectively. In contrast, biochar at different types and rates resulted in a fourfold increment in the available N, P, and K as an average under acid rain (pH_{4.5} and pH_{2.5}) owing to maintaining a neutral pH (6.5–7), which is the most favorable level for soil microbial and enzymatic activities, and the bioavailability of soil nutrients. Furthermore, biochar caused balanced increments in Ca²⁺ by threefold, cation exchange capacity by 45%, urease activity by 16%, and fungal diversity by 10%, while having a slight reduction in bacterial diversity by 2.5%. Based on the path, correlation, and principal component analyses, the exchangeable aluminum was a moderator for the reductions in macronutrients' availability under acid rain, which decreased by 40% and 35% under liming and biochar, respectively. This study strongly recommended the use of biochar from invasive plants instead of lime for sustainable improvements in soil properties under acid rain.

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Handling editor: Yilai Lou

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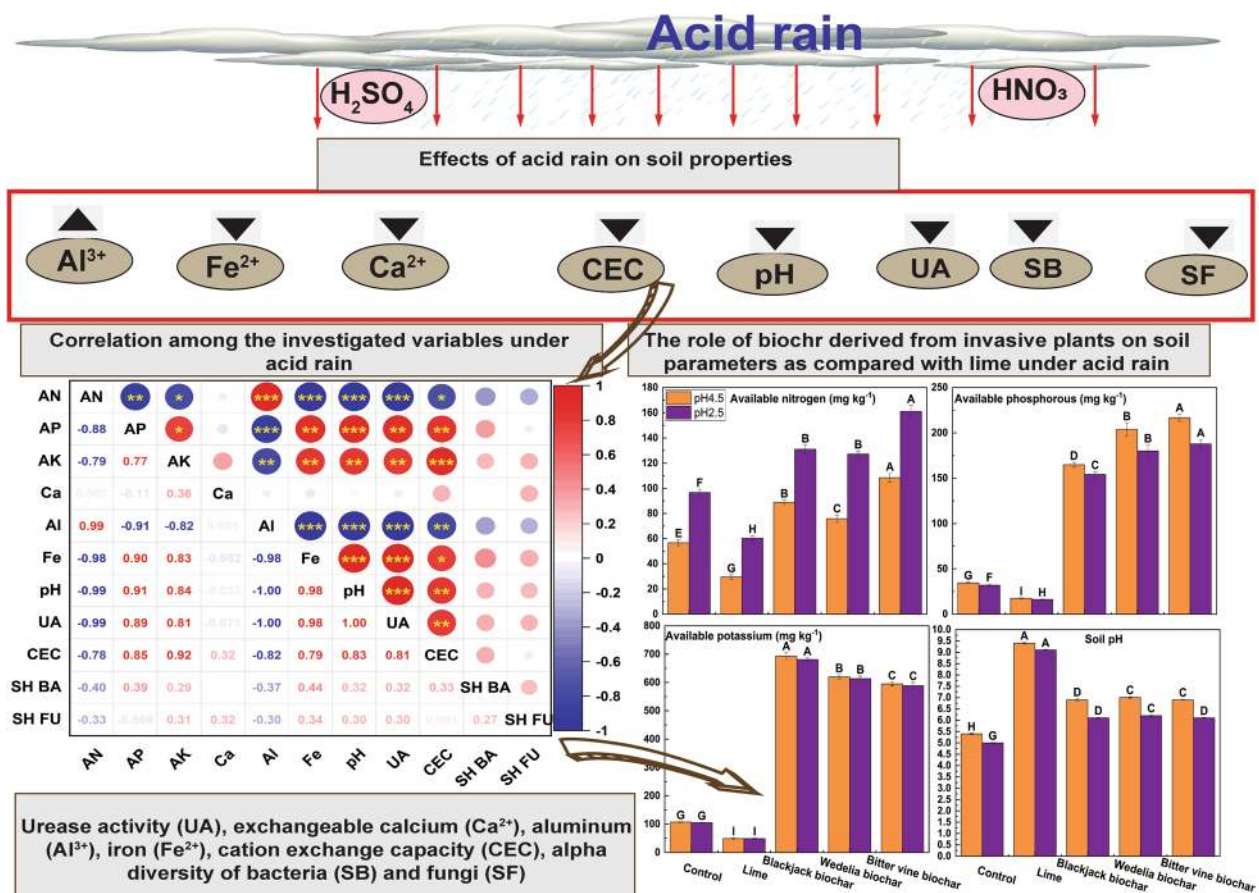
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Highlights

- Biochar of invasive plants maintained a neutral soil pH under acid rain, while liming alkalized the soil pH to 9.5.
- Biochar caused a four-fold increment in soil available N, P higher than liming.
- BJ-biochar increased soil available P and K higher than other two types, while BV-biochar maximized soil available N.

Keywords Acidic soil, Liming, Invasive plants, Biochar feedstock, Soil chemical properties

Graphical Abstract



1 Introduction

Serious environmental and economic problems have resulted from the global expansion of the invasive plants (Lian et al. 2020). More than eight hundred of invasive plants were identified in China, of which 50% are among the top 100 dangerous species according to World Conservation Union statistics (Zhou et al. 2020). Invasive plants have been investigated to affect soil microbial diversity and functionality, soil physical and chemical

properties, and nutrients' cycle (Lian et al. 2020; Sanon et al. 2012, Weidenhamer and Callaway 2010). The present study used three invasive plants as a new feedstock for biochar production, including Blackjack (*Biden Pilosa*), Wedelia (*Wedelia trilobata*) and Bitter Vine (*Mikania micrantha* Kunth). The three invasive plants are among the top noxious species that invade economic crops and orchards, leading to biological suppression and great economic losses (Hui et al. 2019, Mtenga and

Ripanda 2022, Qiao et al. 2020). The massive extension in agriculture and industry sectors due to the accelerated increment in global population has resulted in great emissions of nitrogen oxides and sulfur dioxide (SO_2), which are the main causes of acid rain (Liu et al. 2022). Globally, acid rain is one of the most serious environmental hazards influencing the biosphere, hydrosphere, and atmosphere (Li et al. 2021b; Taylor et al. 2021). China is one of the largest affected areas by acid rain, following the USA and Europe (Wang et al. 2021a). Acid rain affected 37.6% of the 494 monitored nationwide counties and cities in China in 2018 (Li et al. 2021b). Soil acidification is a direct result of acid rain, which affects soil physical, chemical, and biological properties such as soil organic carbon content (SOC) (Chen et al. 2015), microbial community and enzyme activities (Chen et al. 2020; Liu et al. 2020), and availability of macronutrients (Mosharraf et al. 2021). Therefore, intensive work has been done to ameliorate these effects of acid rain using natural and cost-effective materials such as lime and biochar.

Liming is the common and most effective method to control the acidification of agricultural soils under acid rain through incorporating with soil in the tillage system or broadcasting on the soil surface in a no-tillage system without altering soil quality (Cho et al. 2019; Ryan 2018; Shoghi Kalkhoran et al. 2019). Lime increases soil content of base cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) (Kunhikrishnan et al. 2016), which raises soil pH and improves soil microbial and enzymatic activities and nutrients' availability (Dawid 2017). However, the chemical reaction can be triggered when applying lime to a strong acid soil, which degrades lime and increases CO_2 emissions (Cho et al. 2019). Liming rate increased with increasing soil acidity, which could exceed 0.8% for soils with pH less than 4.5 (Holland et al. 2018; Wang et al. 2021b). Our study investigated the effect of severe acid rain (pH=2.5) on acidic soil (pH=5.8); therefore, lime was applied at a rate of 1%, agreeing with Mkhonza et al. (2020) and Das and Saha (2014).

On the other hand, biochar has been investigated as an environmentally risk-free soil conditioner (Gonzaga et al. 2018). It is produced through the pyrolysis of feedstock (such as agricultural residues) at 300–1000 °C under limited or no oxygen conditions (Tomczyk et al. 2020). Biochar, a carbon-rich material raises soil organic carbon and carbon sequestration (Schofield et al. 2019). Biochar addition to the soil increases its pH and improves nutrient availability and uptake by plants (Hossain et al. 2020; Rabileh et al. 2014). For example, biochar increases the availability of fixed phosphorous with high contents of aluminum (Al^{3+}) and iron (Fe^{2+}) under acidic conditions (Chng et al. 2019) and improves the bioavailability

of nitrogen (N), phosphorous (P), potassium (K), Ca^{2+} , and Mg^{2+} (Syuhada et al. 2016). Various feedstocks have been investigated for producing biochar to improve soil properties, such as wood, agricultural crop residues (rice husk and straw, wheat straw, etc.) and grasses (Ippolito et al. 2020). The physio-chemical properties of the produced biochar differ completely based on the used feedstock, which can influence soil properties differently (Uslu et al. 2020). Accordingly, this study hypothesized that the biochar produced from invasive plants may have different effects on the availability of macronutrients in soils. Also, the present study hypothesized that the biochar produced from invasive plants can be used to ameliorate the negative effects of acid rain on soil better than liming by neutralizing soil pH, increasing microbial and enzyme activity, and augmenting the exchangeable Ca^{2+} not as high as lime. This study aimed at investigating the effects of biochar produced from invasive plants on the availability of macronutrients in soil as compared with lime under acid rain conditions. Additionally, this study aimed to follow the relation between the availability of macronutrients and other soil properties in response to the applied biochar as compared with liming under acid rain. The findings of this study may contribute to evaluating the possibility of using biochar produced from new feedstocks to ameliorate the adverse effects of acid rain on soil properties.

2 Materials and methods

2.1 Soil sampling and applied amendments

Soil was collected at a depth of 0–30 cm from subtropical agricultural soil (113°38' E, 23°14' N) in Zengcheng Experimental Base of South China Agricultural University, Guangzhou, Guangdong Province, China. A rice-maize planting pattern is the common cropping system in this area. Ten individual soil samples covering an area of one hectare were collected following the S sampling pattern and then mixed gently to form the composite sample. The mean annual temperature and precipitation are 22° C and 1977 mm, respectively. The soil texture was sandy loam (647 g sand kg^{-1} soil, 309 g silt kg^{-1} soil and 44 g clay kg^{-1} soil) and was classified as lateritic red soil based on the Chinese taxonomy and located in the Ultisols group according to the USDA taxonomy. The soil available N, P, and K contents were 32.8 ± 1.3 , 31.8 ± 0.9 and 114.4 ± 1.58 mg kg^{-1} , respectively. Soil pH (1:2.5 water) was 5.8 ± 0.04 , cation exchange capacity (CEC) was 5.8 ± 0.4 cmol kg^{-1} and EC (1:5 water) was 68.2 ± 0.21 . The total N content was 1.6 ± 0.04 g kg^{-1} and SOC content was 9.1 ± 0.3 g kg^{-1} .

The invasive plants (Blackjack, Wedelia, and Bitter Vine) were collected from the Garden of the South China

Agricultural University. Biochar was prepared through the thermal pyrolysis of the invasive plants' straw slowly (2 h) at a moderate temperature (300 °C) without oxygen to attain the complete pyrolysis of the biomass. The biochar produced from the invasive plants (BJ, WT, and BV, respectively) was then cooled, milled, and passed through a 0.25-mm mesh sieve (Yang et al. 2022). The properties of the produced biochar are presented in Fig. 1. For

liming, calcium oxide (quicklime) with 3.34 g cm^{-3} density and 90% purity was utilized. The simulated acid rain was prepared at two pH levels 4.5 ($\text{pH}_{4.5}$) and 2.5 ($\text{pH}_{2.5}$) based on the current acidity of the rain in the experimental area and expected future acidity using H_2SO_4 (98%) and HNO_3 (68%) at a 1:1 mol ratio (Liu et al. 2020). The acidity of the prepared acid rain was adjusted by a pH meter using tap water.

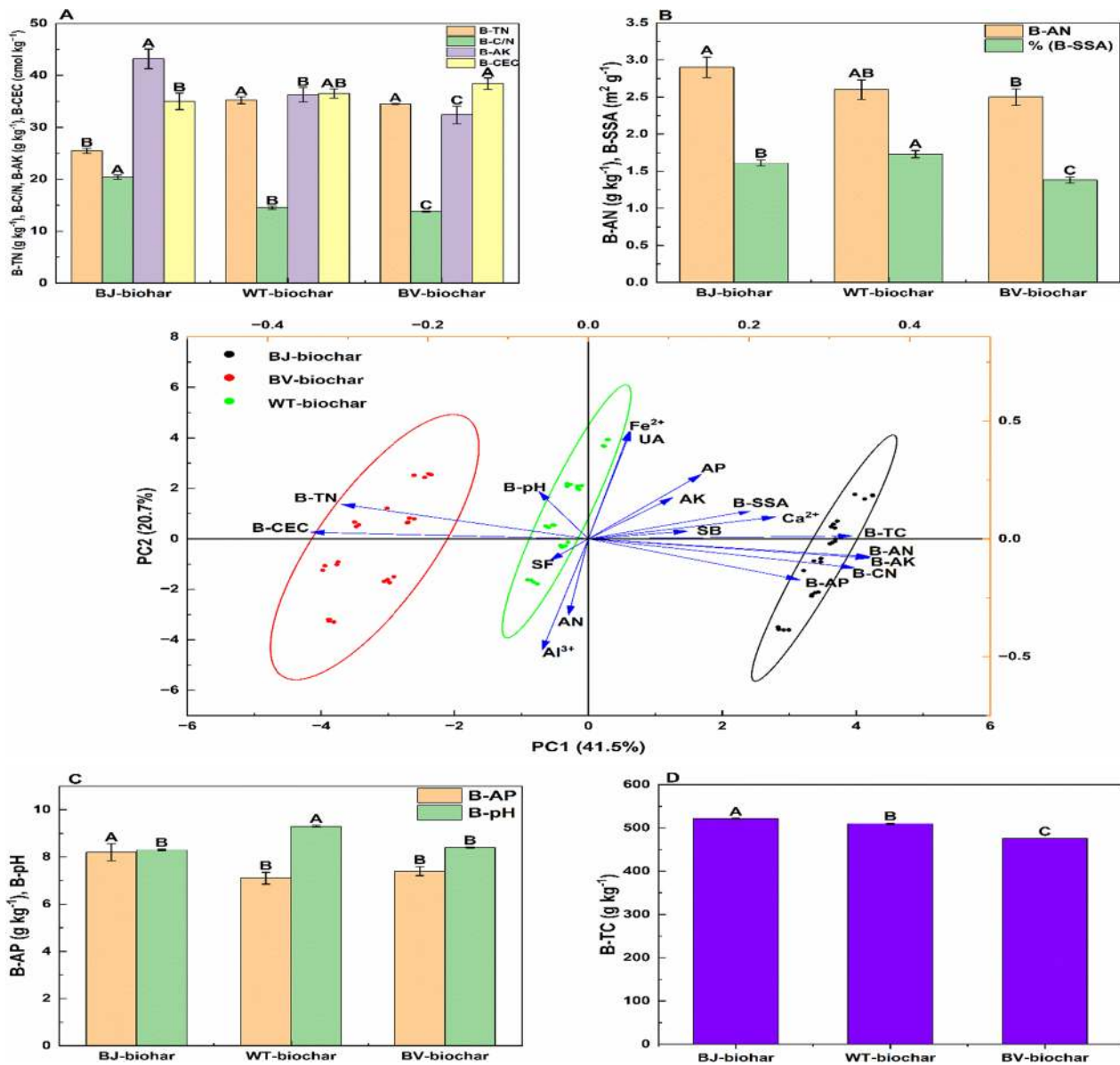


Fig. 1 The properties of biochar produced from the three invasive plants presented by the column figures and the relations between these properties and the soil properties as presented by the PCA. The three invasive plants used in biochar production included Blackjack (BJ-biochar), Wedelia (WT-biochar) and Bitter vine (BV-biochar). The soil properties included available N (AN), P (AP) and K (AK), urease activity (UA), exchangeable calcium (Ca^{2+}), aluminum (Al^{3+}) and iron (Fe^{2+}), and alpha diversity of bacteria (SB) and fungi (SF). The biochar properties included B-TN: total N content, B-TC: total carbon content, B-C/N: C/N ratio, pH, B-AN: available N, B-AP: available P, B-AK: available K, B-CEC: cation exchange capacity and B-SSA: specific surface area

2.2 Trial setup

A pot trial was carried out from May 4 to August 5, 2022, and protected from precipitation effects using coverage. This study was implemented using polypropylene pots with dimensions of 9.5 cm bottom diameter, 12.2 cm upper diameter, and 11.2 cm height. The pot bottom had 24 small holes for drainage and was covered with 0.150 mm mesh to avoid leaching soil with the drained water. Before placing the soil into pots, biochar and lime treatments were added at rates of 1 and 3% and well mixed with the soil samples according to a completely randomized split-plot design. The treatments were applied at four replicates. Three water types [tap water ($\text{pH}_{7.1}$), $\text{pH}_{4.5}$ and $\text{pH}_{2.5}$] were applied each two days at a rate of 100 ml based on the mean annual precipitation during 2015–2021 (GMB 2022). The total number of pots used in this experiment was 108, including lime and three biochar types at rates of 1% and 3% under three water pH levels ($\text{pH}_{7.1}$, $\text{pH}_{4.5}$ and $\text{pH}_{2.5}$) and control treatments (tap and simulated waters without amendments) at 4 replicates.

2.3 Investigated parameters

The fresh soil samples were collected as composite samples of the whole pot, air dried, and sieved through a 2-mm mesh. The soil pH was measured using a pH meter (Mettler-Toledo Instruments Co., Ltd., Shanghai, China) in a soil/water suspension (1:2.5). The total N and carbon (C) contents in soil samples were investigated using the elemental analyzer (VarioEL III, Germany). Following the potassium dichromate titration method, SOC was determined in the soil samples (Pansu and Gautheyrou 2006). Available N (NH_4^+ and NO_3^-) was extracted from the soil samples using 2 M KCl and determined by AA3 Continuous Flow Analyzer (Seal Analytical, Germany). Available P was extracted using 0.5 M sodium bicarbonate and tested according to the molybdenum-antimony anti-spectrophotometric method (Olsen and Dean 1965). The exchangeable cations, including Ca^{2+} , were extracted at pH 7 using a 1 M ammonium acetate solution and determined by flame photometer method, and then the CEC was calculated as the summation of cations (Chapman 1965). Similarly, soil K availability was tested. The contents of Fe^{2+} and Al^{3+} were determined using an inductively coupled plasma-optical emission spectrometer after extraction of 1 g of soil and 1 ml of 0.1 M sodium polyphosphate decahydrate solution (Quan et al. 2020).

The activity of the urease enzyme was measured calorimetrically using a spectrophotometer at a wavelength of 578 nm (Tabatabai 1994). Briefly, 5 g of fresh soil were incubated at 37 °C for 24 h with 20 mL of citrate buffer (with pH adjusted at 6.7), 10 mL of urea solution (with a

concentration of 10%), and 1 mL of toluene. After incubation, the suspension was filtrated, and 3 mL of the filtrate was moved into a 50 mL volumetric flask. Then, 4 mL of sodium phenolate and 3 mL of sodium hypochlorite (0.9%) were added to produce the color. The alpha diversity of bacteria and fungi was determined using a high-throughput sequencing method. Briefly, following the manufacturer's protocols, the total DNA was extracted from soil samples using the FastDNA® SPIN Kit for Soil (MP Biomedicals LLC, Solon, OH, USA) (Caporaso et al. 2011). The concentration and quality of the extracted DNA were determined using Nanodrop™ (Nanodrop, Wilmington, DE, USA). To produce the amplicons, the V4 region of the bacterial 16S rRNA gene was amplified using 515F/806R primer pairs, and the internal transcribed spacer 1 (ITS1) gene was amplified by the primer pairs ITS1/ITS2F. An Illumina MiSeq platform (Illumina, USA) was used to perform the sequencing. The quality of raw sequences was screened and trimmed through the QIIME pipeline as described by Caporaso et al. (2010).

The C and N contents of the produced biochar were determined using an Elementar Vario EL Cube elemental analyzer. The pH of the produced biochar was tested with a pH meter in the biochar/water solution at a ratio of 1:20 (w/v) (Yang et al. 2016). Similar to soil analysis, biochar CEC, organic C, and available N, P, and K were determined (Yang et al. 2018).

2.4 Statistical analysis

The effects of acid rain, lime, and biochar on the available N, P, K, and other soil biogeochemical properties were evaluated using factorial analysis of variance (ANOVA). The comparisons among the properties of the three biochar types were performed using a one-way ANOVA. Comparisons of means at the significance level of $p < 0.05$ were carried out by Duncan's multiple range test. The interaction effects of exchangeable Ca^{2+} , Al^{3+} , and Fe^{2+} , pH, CEC, urease activity, and bacterial and fungal alpha diversity on the available N, P, and K in response to acid rain and the applied amendments were tested in IBM SPSS AMOS 16 software using the structural equation model (Abdo et al. 2022). The path analysis had excellent fit ($\chi^2 = 4.92$, $P = 0.71$, $\text{IFI} = 0.98$, $\text{AIC} = 51.15$ and $\text{RMSEA} = 0.0003$). Principal component analysis (PCA) and Pearson correlation were implemented to summarize the changes in the available N, P, and K and the related soil variables in response to the amendments. The statistics were carried out by SPSS Statistics 22 software (IBM, USA), and Origin 2022b software (Originlab, USA) was used to draw the figures.

Table 1 Effect of the amendments' type and rate on the availability of soil N, P and K

Factors	Available N (mg kg ⁻¹)			Available P (mg kg ⁻¹)			Available K (mg kg ⁻¹)		
	pH _{7.1}	pH _{4.5}	pH _{2.5}	pH _{7.1}	pH _{4.5}	pH _{2.5}	pH _{7.1}	pH _{4.5}	pH _{2.5}
Amendment type									
Control	39.1D	56.9D	96.6D	37.0D	34.5D	31.9D	108.7D	107.0D	105.0D
Lime	26.8E	39.5E	71.7E	25.3E	21.6E	20.9E	58.6E	58.5E	58.8E
Blackjack (BJ)	66.3A	81.5B	124.7B	214.6A	170.8A	155.9A	528.9A	521.6A	512.2A
Wedelia (WT)	54.1C	71.4C	120.5C	181.8B	161.5B	144.5B	475.2B	466.7B	464.5B
Bitter vine (BV)	63.7B	87.6A	134.8A	164.4C	146.7C	127.8C	452.9C	448.5C	445.6C
Amendment rate									
1%	46.4B	62.9B	104.1B	102.6B	86.5B	78.4B	231.1B	228.2B	227.0B
3%	53.6A	71.9A	115.3A	146.7A	127.5A	114.0A	418.6A	412.7A	407.4A

The amendment rate refers to the application rates of lime

BJ Blackjack, WT Wedelia and BV Bitter vine that were applied at two rates (1% and 3%)

3 Results

3.1 Overall effect of the amendments' type and rate on the available N, P, and K of the soil

BJ-biochar had the highest carbon content, C/N ratio, and availability of macronutrients, while BV-biochar recorded the lowest values of these properties (Fig. 1). On the other hand, the properties of WT-biochar distributed in the middle of the PCA between the other two types. The available N related negatively with the PCA coordinates and was affected dominantly by the WT and BV-biochar, whereas the available P and K correlated positively with the PCA coordinates in response to the BJ-biochar (Fig. 1). The BJ-biochar resulted in the highest N availability (66.3 mg kg⁻¹) of the soil under pH_{7.1} (Table 1). Similarly, soil available P and K had their highest values under pH_{7.1} (214.6 and 528.9 mg kg⁻¹), pH_{4.5} (170.8 and 521.6 mg kg⁻¹) and pH_{2.5} (155.9 and 512.2 mg kg⁻¹) when applying BJ-biochar, followed by WT-biochar (Table 1). However, the highest values of soil available N (87.6 and 134.8 mg kg⁻¹) under pH_{4.5} and pH_{2.5} were recorded when applying BV-biochar followed by BJ-biochar. Liming resulted in the lowest availability of soil N, P and K and caused a reduction in their availability by an average of 36.3% as compared with the control under different pH levels of rain. The maximum rate of amendments (3%) had the highest effect on soil N, P, and K availability, which increased by an average of 30% as compared with their availability under the 1% rate (Table 1).

3.2 Response of soil available N, P, and K to the applied amendments

Increasing the acidity level of simulated acid rain increased soil available N, while decreasing the availability of P and K (Figs. 2–4). This decline was altered by biochar application. The addition of 3% BV-biochar

maximized the N availability (80.2, 108.4, and 161 mg kg⁻¹) (Fig. 2) and available P (241.7, 216.7, and 187.8 mg kg⁻¹) (Fig. 3) under pH_{7.1}, pH_{4.5} and pH_{2.5}, respectively. On the other hand, the maximum available K (703, 693, and 681 mg kg⁻¹) was obtained by the application of 3% BJ-biochar with a sixfold increment over the control (Fig. 4). The addition of 1% BV-biochar had the lowest effect on soil available N, P, and K as compared with other biochar types and rates. The addition of 1% BJ-biochar and 3% WT-biochar had the same effect on N availability under pH_{7.1} and pH_{4.5}, while 3% BJ-biochar and 3% WT-biochar had the same effect on available N under pH_{2.5}. Interestingly, P availability reduced with the application of 3% BJ-biochar as compared with 1% at different pH levels (Fig. 3).

The soil N availability decreased by 37.4–61.6% under 3% liming and by 1.3–14.1% under 1% liming as compared with the control (Fig. 2). Liming at rates of 1% and 3% had the lowest P availability, which decreased by 20–25% and 44–50%, respectively, as compared with the control. Liming at a rate of 3% resulted in the lowest K availability (49.5, 48.9 and 48.8 mg kg⁻¹), with a decline of 54% as compared with the control.

3.3 Impact of the amendments on soil biogeochemical properties under acid rain

The simulated acid rain resulted in notable reductions in soil exchangeable Fe²⁺, urease activity, pH, and CEC, while causing a significant increment in exchangeable Al³⁺ (Fig. 5). Alpha diversity of soil bacteria and fungi increased by an average of 4.5% under pH_{4.5}, while decreasing by 3.6% and 9.4%, respectively, under pH_{2.5} as compared with pH_{7.1} (Fig. 5G and H). The addition of lime at both rates (1% and 3%) caused sharp increments

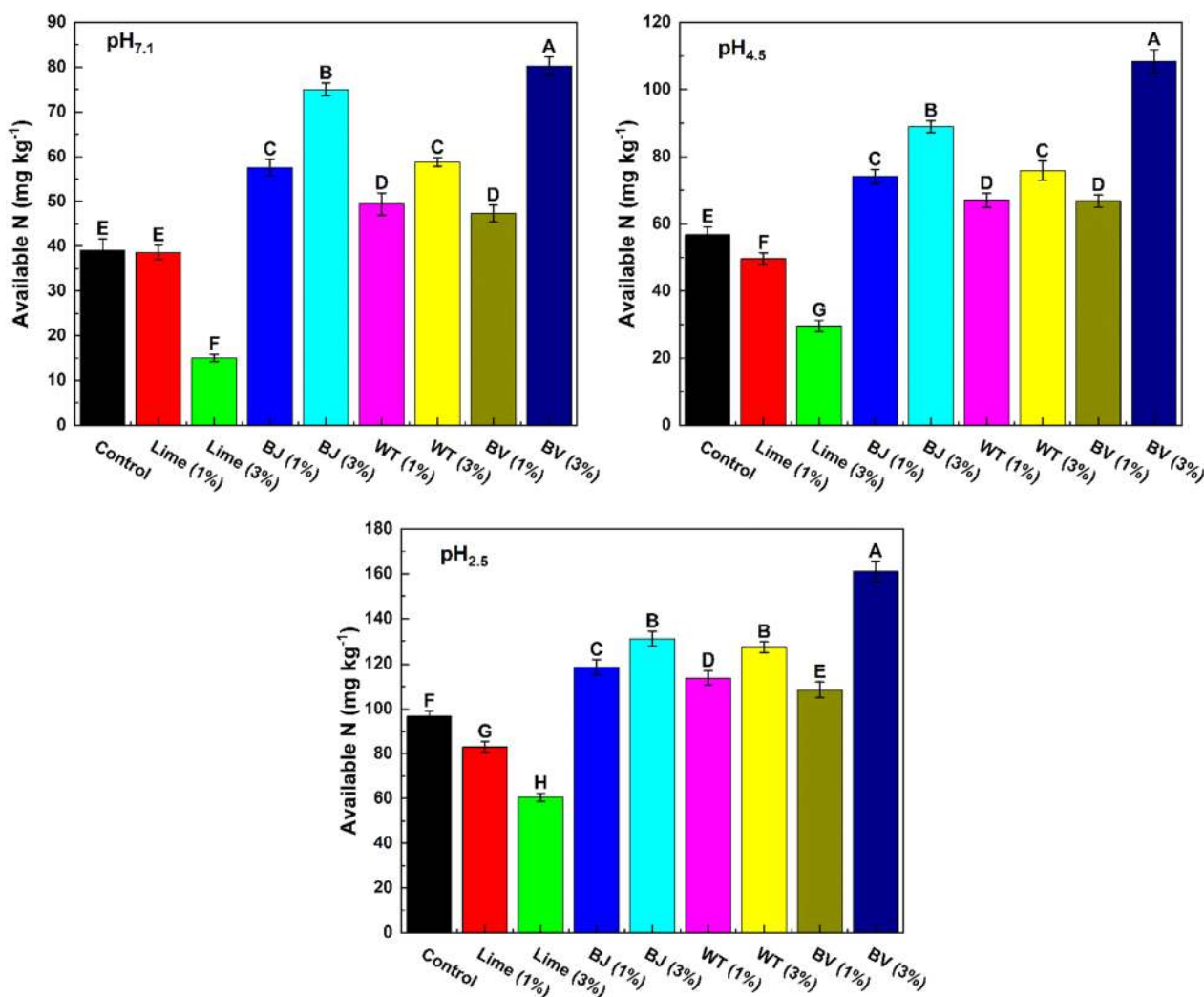


Fig. 2 Effect of the amendments on the soil available N under simulated acid rain. pH_{7.1}, pH_{4.5} and pH_{2.5} indicate the levels of pH of tap water and two simulated acid rain. BJ, WT and BV refer to the three biochar types produced using different feedstocks (Blackjack, Wedelia and Bitter vine, respectively). Uppercase letters refer to the significance at $p \leq 0.05$

in soil exchangeable Ca^{2+} by 11–23 times (Fig. 5A) and pH by 44–73% (Fig. 5E) as compared with the control under different acidity levels of simulated rain. On the other hand, biochar resulted in increments in soil exchangeable Ca^{2+} by three folds and pH by an average of 22.5% as compared with the control. The highest rate of lime and BJ-, WT- and BV-biochar had the same impact on soil exchangeable Al^{3+} , which decreased by an average of 44%, while Al^{3+} declined by 35% when adding 1% lime and 25–30% under the application of 1% of BJ-, WT- and BV-biochar (Fig. 5B). Liming decreased the soil exchangeable Fe^{2+} by 8–13%, while biochar increased Fe^{2+} by an average of 3.3% as compared with

the control (Fig. 5C). Liming increased soil urease activity by 3–11%, while biochar augmented urease activity by 14–20% (Fig. 5D). The addition of 1% lime reduced the CEC by 6%, while 3% lime increased the CEC by 11%. Biochar addition augmented the soil CEC by 34–57% (Fig. 5F). Liming sharply decreased the alpha diversity of soil bacteria by 21–33%, while biochar reduced the alpha diversity by 1–8%. Moreover, the BV-biochar caused the highest reduction (8%) in the bacterial diversity as compared with the other biochar types (Fig. 5G). Liming reduced the alpha diversity of soil fungi by 7–13%, while biochar increased the alpha diversity by 9–13% (Fig. 5H).

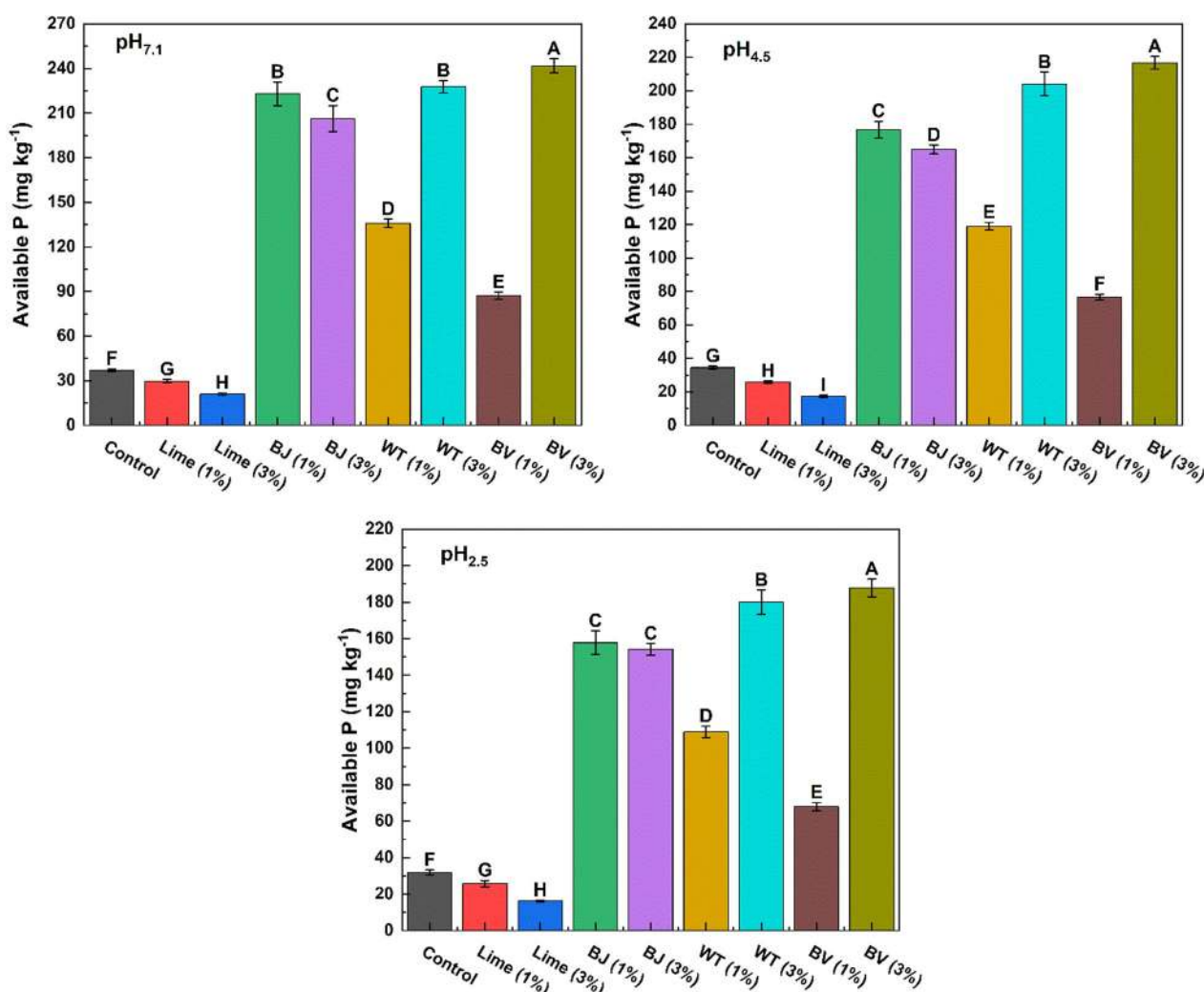


Fig. 3 Effect of the amendments on the soil available P under simulated acid rain. pH_{7.1}, pH_{4.5} and pH_{2.5} indicate the levels of pH of tap water and two simulated acid rain. BJ, WT and BV refer to the three biochar types produced using different feedstocks (Blackjack, Wedelia and Bitter vine, respectively). Uppercase letters refer to the significance at $p \leq 0.05$

3.4 Relations among macronutrients' availability and other soil variables

The PCA summarized the response of the soil N, P, and K availability to the changes in soil parameters under the addition of lime and biochar by two main components (PCA1 and PCA2) (Fig. 6). The two components explained more than 82%, 85%, and 78% of these changes under no addition, liming and biochar, respectively. Soil available N and Al^{3+} distributed similarly in relation to the PCA coordinates. Both of them had a strong positive correlation (Fig. 7) and related negatively with PCA1 and positively with PCA2 under biochar or no amendments (Fig. 6A and C), while lime reversed this relation (Fig. 6B). Available N and Al^{3+} distributed differently

from all other variables except fungal diversity under biochar addition (Fig. 6C). On the other hand, available P and K had a positive correlation (Fig. 7) and were distributed similarly in relation to the PCA coordinates under lime and biochar addition (Fig. 6). Liming and biochar changed the distribution of available P across the PCA as compared with no addition, while having no effect on available K. Available P had a positive correlation and similar distribution of pH, urease activity, and Fe^{2+} under no addition, meanwhile under lime treatment, both of available P and K exhibited a negative correlation and opposite distribution with both of pH and Ca^{2+} . Biochar altered these changes and resulted in no negative correlations or opposite distributions among available P and the other soil variables (Figs. 6 and 7).

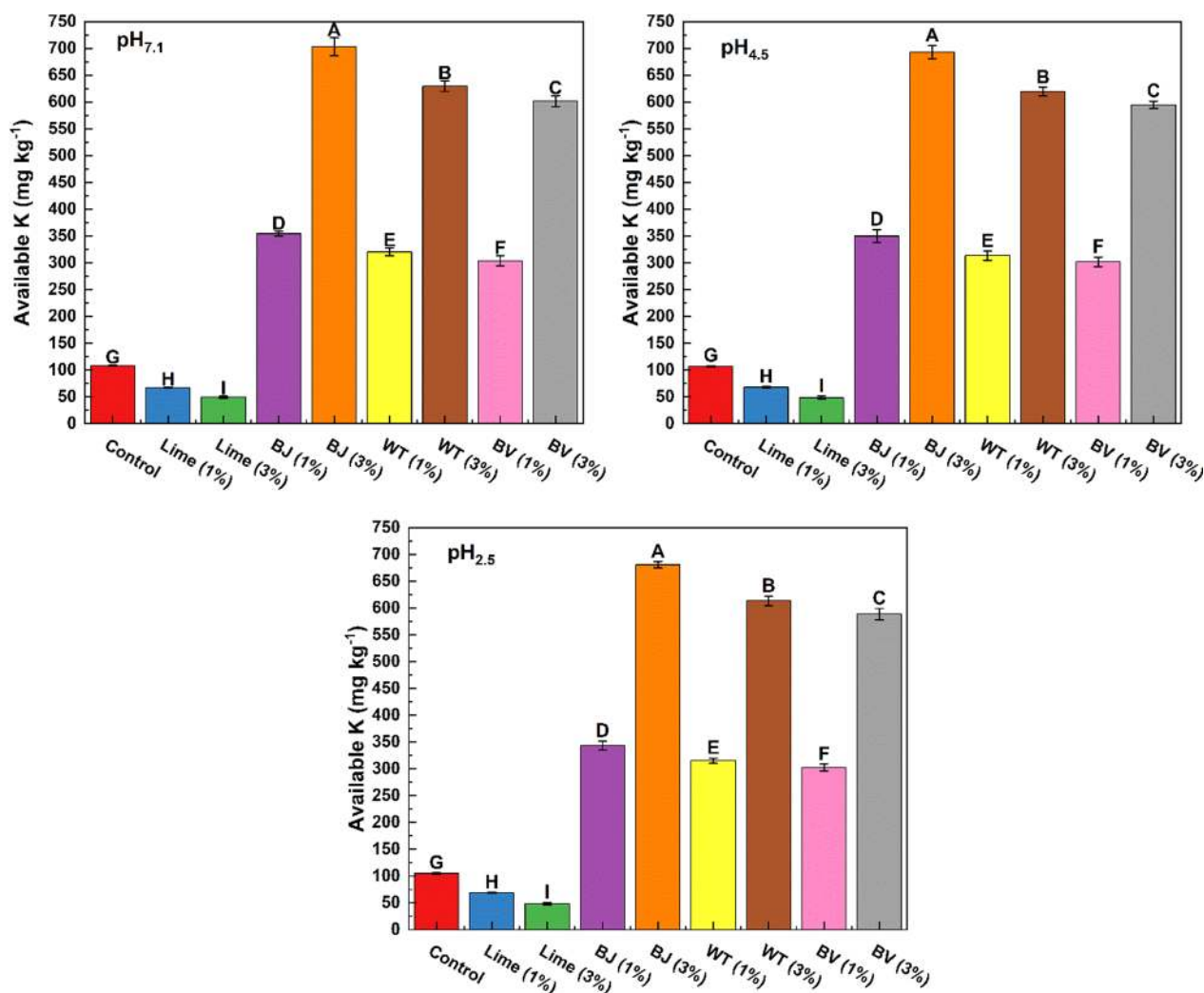


Fig. 4 Effect of the amendments on the soil available K under simulated acid rain. pH_{7.1}, pH_{4.5} and pH_{2.5} indicate the levels of pH of tap water and two simulated acid rain. BJ, WT and BV refer to the three biochar types produced using different feedstocks (Blackjack, Wedelia and Bitter vine, respectively). Uppercase letters refer to the significance at $p \leq 0.05$

4 Discussion

4.1 Effect of acid rain without amendments

Soil nutrients have a direct response to the acidification caused by acid rain and large deposition of active nutrients, such as N and sulfur, which affect soil chemical properties and nutrients status (Hu et al. 2018; Wang et al. 2020). The simulated acid rain increased soil available N (Fig. 2), meanwhile, acid rain reduced the available P and K (Figs. 3 and 4), which is in congruence with the findings by Mosharrof et al. (2021). Acid rain affected soil CEC which contributed positively to the availability of N, P, and K, in addition to changing the soil pH, urease activity, Ca²⁺, Al³⁺, and Fe²⁺, which had a negative contribution to the

availability of N, P, and K (Fig. 8). The notable increment in Al³⁺ resulted from the release of hydrogen ions under acid rain, which increased the leaching of base cations (K, Ca²⁺, and Fe²⁺) and decreased soil CEC (Liu et al. 2014). Considering the distribution of the variables in the PCA (Fig. 6A), the strong positive correlation between available N and exchangeable Al³⁺, and the negative correlation between Al³⁺ and available P and K (Fig. 8A), it can be concluded that the main reason for the decline in available P is the fixation by Al³⁺ hydrous oxides (Haque et al. 2021; Panhwar et al. 2020). The formed aluminum hydroxyl phosphate can form a surface complex on variscite

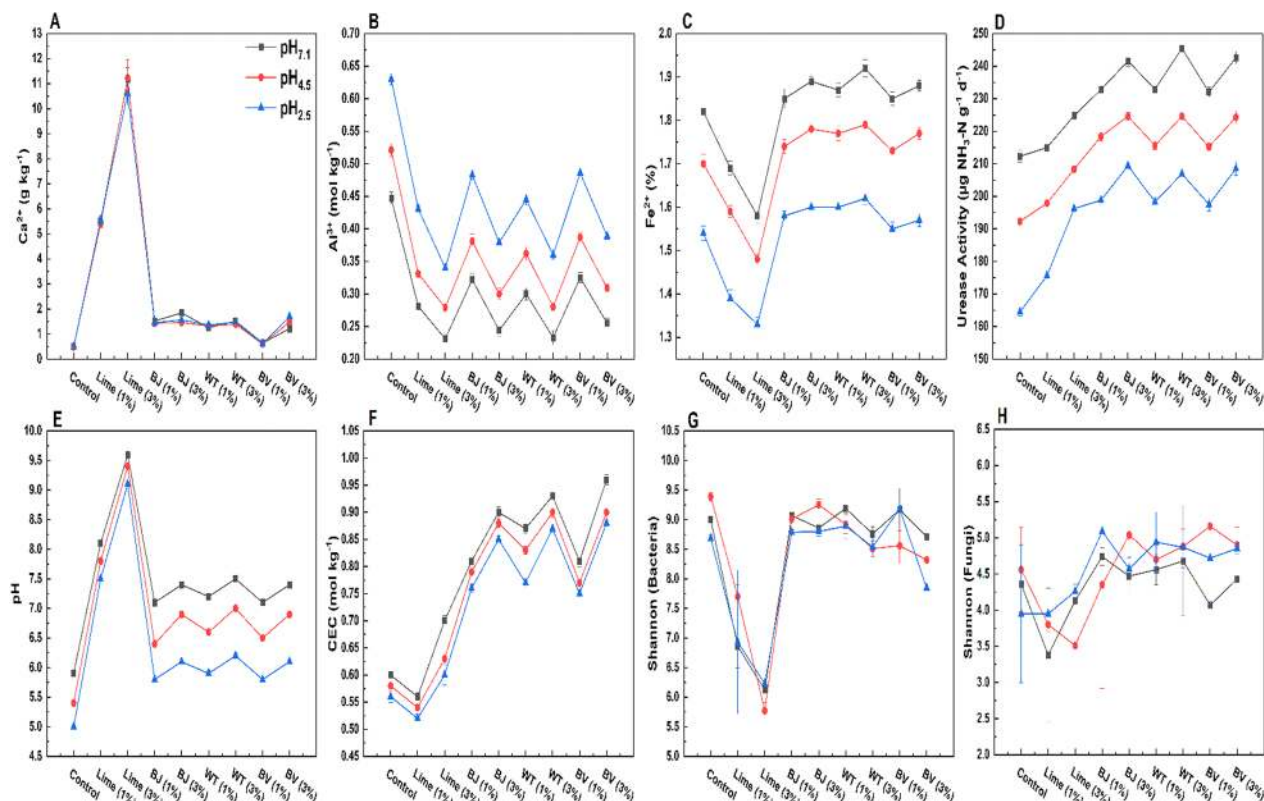


Fig. 5 Effect of the amendments on the soil biogeochemical properties under acid rain. The properties are exchangeable calcium (Ca^{2+}) (A), aluminum (Al^{3+}) (B) and iron (Fe^{2+}) (C), urease activity (D), pH (E), cation exchange capacity (CEC) (F), and alpha diversity of bacteria (G) and fungi (H). $\text{pH}_{7.1}$, $\text{pH}_{4.5}$ and $\text{pH}_{2.5}$ indicate the levels of pH of tap water and two simulated acid rain. BJ, WT and BV refer to the three biochar types produced using different feedstocks (Blackjack, Wedelia and Bitter vine, respectively)

($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), which is the least soluble compound in acidic soils (Muindi 2019; Wang et al. 2023). The N deposition through acid rain increases the Al^{3+} content due to the release of hydrogen ions during the nitrification of ammonium (NH_4^+) to nitrate (NO_3^-), which explains the strong positive correlation between N and Al^{3+} (Che et al. 2015; Zhao and Shen 2018). Additionally, the increment in available N under acid rain was mainly caused by the higher SO_2 contents and nitrogen oxides (Liu et al. 2022). Acid rain decreased the available K directly by reducing CEC and indirectly by increasing the trivalent cation (Al^{3+}), which removes K from the exchangeable sites, agreeing well with the findings by Das and Saha (2014). Acid rain decreased soil pH below 5, which is critical for the growth of almost all microbial lineages, which was accompanied by a significant reduction in the functionality presented by urease activity (Fig. 5). Here, our findings demonstrated a sharp reduction in the alpha diversity of soil bacteria and fungi, which negatively affected the bioavailability of P and K (Wang et al. 2018). We reported no significant relation between available N

and the changes in the microbial community, owing to the abundant existence of N deposited through the acid rain, which agrees with the findings by Liu et al. (2021).

4.2 Liming effect

Liming notably decreased the available N, P, and K as compared with control (Figs. 2, 3, 4) due to the great increment in soil exchangeable Ca^{2+} and pH accompanied by a sharp reduction in exchangeable Al^{3+} , urease activity, CEC, and bacterial and fungal diversity (Fig. 5). The Ca^{2+} sourced from liming replaces the hydrogen ions from exchangeable sites and aluminum compounds, which results in Al^{3+} leaching. The hydrogen ions react with hydroxyl ions under higher pH and form water molecules, which reduces the temporary negative charges and decreases soil CEC (Filipek 2011). The reductions in Al^{3+} and Fe^{2+} under lime application can be linked with the precipitation of these exchangeable ions as insoluble hydroxides, which results in increasing soil pH (Qaswar et al. 2020). We recorded significant declines in the diversity of bacterial and fungal communities due to the sharp

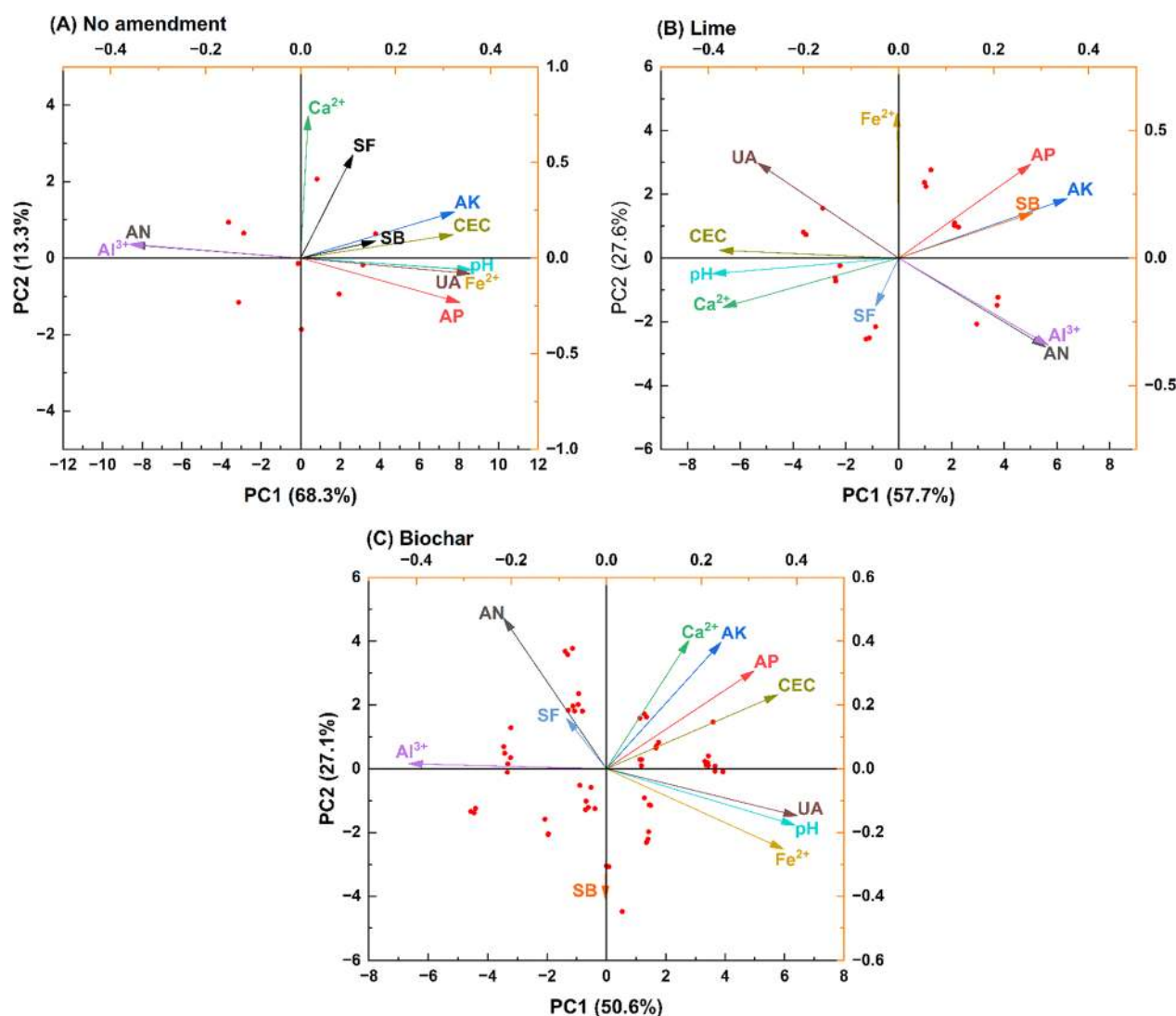


Fig. 6 Principal component analysis (PCA) among available N (AN), P (AP) and K (AK), and other soil parameters. The parameters are urease activity (UA), pH, exchangeable calcium (Ca^{2+}), aluminum (Al^{3+}) and iron (Fe^{2+}), cation exchange capacity (CEC), and alpha diversity of bacteria (SB) and fungi (SF)

increment in soil pH to an unfavorable level for microbial growth, accompanied by significant reductions in the availability of nutrients that are needed for microbial growth (Li et al. 2021a). The exchangeable Ca^{2+} and soil pH had a negative contribution on soil available N, P, and K (Fig. 8). Moreover, liming changed the distribution of availability of macronutrients in relation to soil pH and Ca^{2+} with the PCA coordinates, where pH and Ca^{2+} correlated negatively with both coordinates, while available N, P, and K correlated positively (Fig. 6B). Interestingly, liming turned the insignificant correlation between macronutrients' availability and pH and Ca^{2+} into a negative correlation (Fig. 7B). These relations indicate

that soil pH and exchangeable Ca^{2+} were the moderators of the decline in macronutrients' availability. High pH and exchangeable Ca^{2+} can decrease the available N, P, and K by affecting the microbial diversity as reported by Whittinghill and Hobbie (2012), which agrees with the negative correlation among these variables under liming (Fig. 7). Calcium is a divalent cation with a small hydrated radius, therefore it is adsorbed strongly in soil and removes other cations like $N-NH_4$ and K from the exchange sites. Furthermore, lime decreased CEC, which had a positive contribution with available N, P, and K (Fig. 8), and that may result in more nutrient loss via leaching. Path analysis showed that phosphorous is the

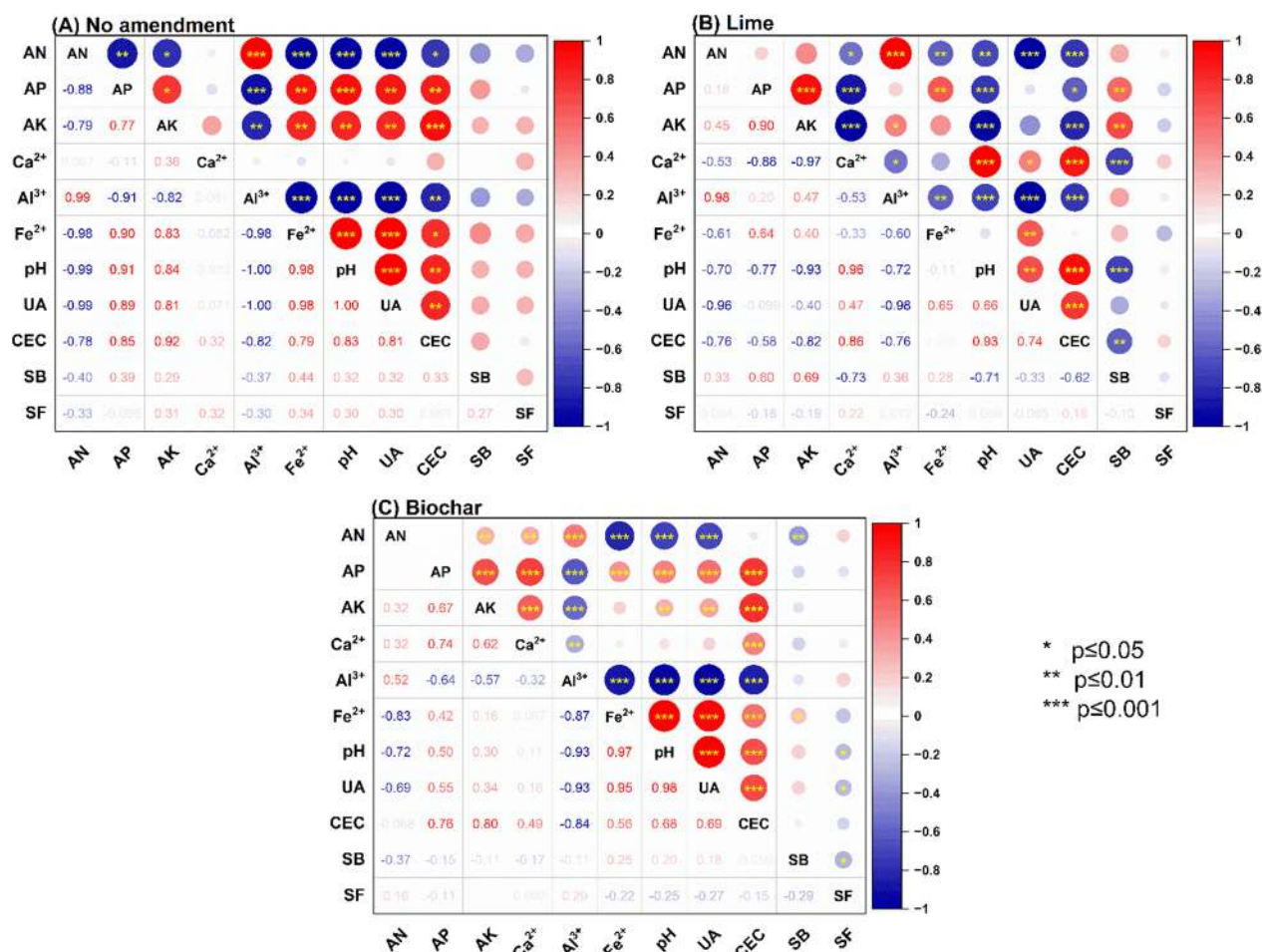


Fig. 7 Pearson correlation among available N (AN), P (AP) and K (AK), and other soil parameters. The parameters are urease activity (UA), pH, exchangeable calcium (Ca²⁺), aluminum (Al³⁺) and iron (Fe²⁺), cation exchange capacity (CEC), and alpha diversity of bacteria (SB) and fungi (SF). *, ** and *** indicate the significance at $p < 0.05$, $p < 0.01$ and $p < 0.001$, respectively. The color scheme refers to the strength of correlation

most sensitive macronutrient to the changes in soil pH and Ca²⁺ content (Fig. 5), and the neutral pH (6.5–7.2) is the best level for its bioavailability; therefore, liming decreased available P significantly (Mosharrof et al. 2021). The addition of lime decreased soil available K as compared with the control, and this decline had a relative relation with the application rate. Similarly, Han et al. (2019) have reported a reduction in soil K by an average of 21–59% under lime application, which can be explained by the large content and influx of divalent cations by the added lime (Kirkman et al. 1994).

4.3 Biochar effect

Biochar addition resulted in a significant increment in available N, P, and K as compared with the control and liming treatments, which agrees with the findings by Mosharrof et al. (2021), Gavili et al. (2019) and Wang et al. (2020). This increment can be linked with maintaining neutral pH (7.0) and improving Ca²⁺, Fe²⁺, CEC, and

urease activity, while decreasing Al³⁺ (Fig. 5), which is in consent with the results by Diatta et al. (2020) and Shetty and Prakash (2020). Biochar had a great specific surface area (Fig. 1), which significantly increased soil CEC and base saturation (Jien and Wang 2013, Nepal et al. 2023). That is the main path by which biochar increased the soil functionality and availability of nutrients. Given the great C content in biochar and the significant N depositions under acid rain, biochar maximized the microbial diversity and bioavailability of other nutrients (P and K) under acidic conditions, agreeing well with the findings by Jien and Wang (2013) and Li et al. (2020). Moreover, biochar changed the variables' distribution in the PCA, making them have a positive correlation with the coordinates (Fig. 6C) and reversed the negative correlation among the available macronutrients and pH, CEC, and Ca²⁺ under liming (Fig. 7C). These findings are linked to the neutralization of acidic soil pH under biochar addition, which

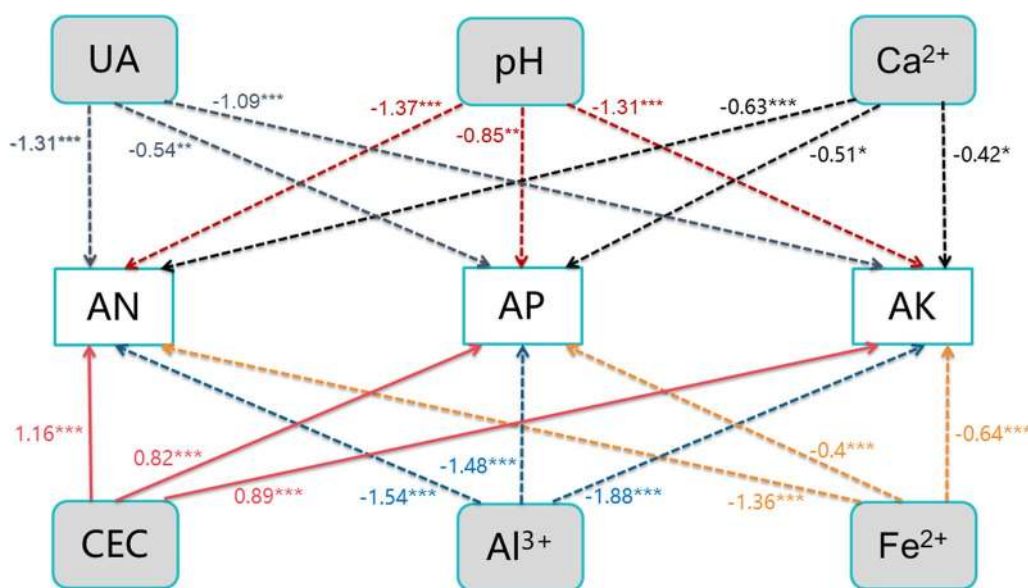


Fig. 8 The structural equation modeling (SEM) of the relation among available N (AN), P (AP) and K (AK), and other soil parameters under all the treatments. The moderators are soil parameters including urease activity (UA), pH, exchangeable calcium (Ca²⁺), aluminum (Al³⁺) and iron (Fe²⁺), and cation exchange capacity (CEC). Estimates of standardized regression weight (β) for each path are kept company with arrow. *, ** and *** indicate the significance at $p < 0.05$, $p < 0.01$ and $p < 0.001$, respectively. Dashed lines refer to negative contributions, while solid lines refer to positive contributions

is favorable for microbial community structure and the bioavailability of macronutrients, especially P (Sheng and Zhu 2018). Moreover, the balanced increments in base saturation (CEC and Ca²⁺) under biochar addition linked positively with the availability of macronutrients, given by less competition on the exchangeable sites. Biochar is a direct source of macronutrients (Fig. 1), as reported by Gautam et al. (2017) and Kloss et al. (2012). Biochar reversed the negative correlation between pH and bacterial diversity as compared with liming (Fig. 8), which refers to more bioavailability of macronutrients in response to the changes in pH (Shetty and Prakash 2020).

The content of soil available N was maximized under the addition of 3% BV-biochar as compared with other biochar types and rates, as it had the highest N content and the lowest carbon content and C/N ratio (Fig. 1), which is suitable for the bioavailability of nutrients. Similarly, Liu et al. (2016) and Zhang et al. (2018) stated a positive correlation between the microbial structure and functionality and the biochar feedstock, which contains more labile carbon and nutrients. BJ-biochar had the highest available P but resulted in the lowest increment in soil available P compared with other biochar types, which can be explained by the higher increment in soil pH under BJ-biochar as compared with BV-biochar. Additionally, the BJ-biochar had the highest C/N ratio, which could affect the bioavailability of phosphorous through different mechanisms such as stimulation

of the organo-mineral complexes' formation, altering the P desorption/adsorption equilibrium, and declining the P solubility (Gao and DeLuca 2018, Gao et al. 2017). A high amount of ash contained in the produced biochar improves the instant mineral nutrients discharged to the soil (Hossain et al. 2020) and decreases the K loss through leaching (Laird et al. 2010; Zhang et al. 2012). Furthermore, biochar addition promotes the exchangeable capacity of Ca²⁺ and K, which activates the proliferation of K solubilizing bacteria (Wang et al. 2018). BJ-biochar caused the highest increment in soil available K compared with other biochar types, as BJ-biochar contained the highest available K (Fig. 1). WT-biochar mediated the distribution of the other two types' properties (Fig. 1); therefore, it had a positive effect on the majority of soil properties and the availability of macronutrients. These findings emphasize the effect of the feedstock utilized in biochar production on controlling the biochar's influence on soil properties.

5 Conclusion

The present study compared the effects of new biochar produced from invasive plants and liming on soil available N, P, and K under simulated acid rain. Liming increased soil pH higher than biochar, but soil pH exceeded 8, which is not suitable for the activities of enzymes and soil microorganisms. On the other hand, biochar addition improved some soil biogeochemical

properties (exchangeable Ca^{2+} , Al^{3+} , and Fe^{2+} , pH, CEC, urease activity, and bacterial and fungal alpha diversity) more than liming. Therefore, biochar was effective in augmenting soil available N, P, and K through improving soil properties and maintaining a neutral pH (6.5–7). In conclusion, biochar can be used effectively instead of lime to alter the adverse effects of acid rain on soil properties. It is recommended to test the utilization of biochar with higher pH values produced from invasive plants under higher temperatures, and also the effect of these biochar types and addition rates on alkaline soils in future studies.

Acknowledgements

Not applicable.

Author contributions

YL and AIA: conceptualization, methodology, investigation, visualization, writing—original draft. ZS and AMAM: data curation, formal analysis, software. AIA and JZ: resources, validation, writing—review and editing. JZ: conceptualization, project administration, funding acquisition, supervision.

Funding

This study was supported by National Natural Science Foundation of China (U1701236), the Laboratory of Lingnan Modern Agriculture Project (NT2021010), Science and Technology Planning Project of Guangdong Province of China (grant number 2019B030301007) and Special Funds for the Cultivation of Guangdong College Students' Scientific and Technological Innovation (grant number pdjh2020b0092).

Availability of data and materials

All data generated or analyzed during this study are included in this published article and its supplementary information files.

Declarations

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Received: 22 April 2023 Revised: 13 August 2023 Accepted: 15 August 2023

Published online: 27 September 2023

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