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Implications of Acidified and Non-Acidified Biochars on N and K Availability and their Uptake by Maize Plants

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MAIZE is one of the important crops in Egypt that can be grown successfully on light textured soils. Although amending these soils with biochar may increase the efficiency of nutrient utilization by plants; yet both biochars and Egyptian soils exhibit alkaline nature. The current studyinvestigates to what extent can biochar modified with either sulfuric acid or with elemental sulfur(S)(an acidifying agent)surpass the effect of adding biochar solely to a sandy soil (93% sand), with emphasis onthe increase of N and K availability in soil and their uptake and distribution within maize plants. A greenhouse experiment was conducted in a complete randomized design comprising (1) no biochar application (control), (2) biochar applied at a rate of 10g kg^{-1}, (3) biochar (10g kg^{-1}) + elemental sulfur (2 g kg^{-1}) and (4) biochar acidified with H_2SO_4 (10g kg^{-1}). These treatments were added 2 weeks prior to maize sowing. Thereafter, all pots were planted for 60 days and soil moisture was kept at 80% of the water holding capacity throughout the period of this investigation. Results indicate that only “acidified bioachar” and “biochar+S” treatments raised significantly SO_4^{2-} content in soil; thus they both decreased soil pH. On the other hand, application of non-acidified biochar solely raised soil pH.All treatmentsdecreased soil bulk density and improved soil moisture characteristics (field capacity, permanent welting point and available water content). This, in turn, significantly raisedN- and K- available contents in soil and consequently increasedtheir uptake by maize plants. In particular, the non-acidified biochar recorded the highest increases in N-uptake by plants while acidified biochar recorded the highest K uptake followed by biochar+S. Overall, all biochars significantly boosted root and shoot biomass, especially the acidified one, followed by the combined biochar+S treatment. Furthermore, these treatments recorded the highest N and K utilization efficiencies by maize plants. In conclusion, using elemental sulfur with biochar may effectively increase the efficiency of applied biochar via increasing nutrient use efficiencies; yet this dual application might not be as efficient as acidified biochar for enhancing plant growth.

Keywords: Biochar; acidified biochar; sandy soils; nitrogen; potassium; plant uptake.

1. Introduction

Maize is one of the most important crops worldwide for food, feed, and industrial uses (Revilla *et al.*, 2022), besides being a bioenergy-producing crop (Omar *et al.*, 2022). In Egypt, it is the third important cereal grain (Sayed *et al.*, 2022; Wu *et al.*, 2022) though this country becomes the second largest maize importer worldwide (Wu *et al.*, 2022). Unlike other grain cereals, maize requires massive amounts of nutrients (Gheith *et al.*, 2022) nonetheless inefficient utilization of these nutrients may lead to considerable decline in plant growth rates and grain yield (Bekele *et al.*, 2022).

The large gap between potential and actual maize yields is associated with plant utilization of nutrients such as N (Xing *et al.*, 2022) and K (Ngosong *et al.*, 2022). About half of the global nitrogen (N) fertilizers are added to rice, wheat and maize, and the majority of these fertilizers are wasted without being utilized by plants (Yu *et al.*, 2022). Overall, improving the efficiency of applied fertilizers is the key for sustaining maize production (Ribeiro *et al.*, 2023).

Maize can be grown successfully in newly reclaimed areas (Ouda *et al.*, 2022) where the majority are sandy ones (El-Hassanin *et al.*, 2022) of low capability to retain nutrients; thus, nutrients are subjected to be lost via leaching (El-sherbeny *et al.*, 2022). In spite of that, cultivating newly reclaimed areas could be the optimal chance to ensure food security in Egypt (Ouda *et al.*, 2022). Improving the

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characteristics of these soils is an obligation to improve their productivity,probably via organic additives (Farid *et al.*, 2014; Abdelhafez *et al.*, 2018; Farid *et al.*, 2021a; Farid *et al.*, 2021b; Rashad *et al.*, 2022). Unlike other organic amendments, biochar is a relatively stable one (not easily biodegradable) (Abdelhafez *et al.*, 2017). This carbon rich amendment is produced from the pyrolysis of organic residues in absence of oxygen or under limited conditions (Bassouny and Abbas, 2019; Tolba *et al.*, 2021; Asaad *et al.*, 2022; Farid *et al.*, 2022; Lalarukh *et al.*, 2022). Moreover, biochar increases sequestered carbon in soil; thus decreases the net global warming threat (Han *et al.*, 2022).

Most biochars and Egyptian soils are alkaline; therefore, amending these alkaline soils with biochar may hinder nutrient availability (Salem *et al.*, 2019). Alternatively, adding acidified biochar could be the optimum solution (Abd El-Mageed *et al.*, 2021; Zang *et al.*, 2022). In this context, acidified biochar increases the porous structure of biochar especially with H_2SO_4 which exhibits higher carbon yield and sequestration capacity (Zhou *et al.*, 2021). It also increases the hydrophilic oxygen functional groups (COOH, OH) (Dornath et al., 2016; Wang et al., 2022). Elemental S can be used to alleviate the dermal effects of alkaline biochar (Salem *et al.*, 2019). A point to note is that S is an important nutrient that is incorporated in formation of essential amino acids and different co-enzymes (Mondal *et a*l., 2022). Further, it plays important roles as electron transport (Capaldi *et al.*, 2015); consequently, it is critical in plant growth and development (Li *et al.*, 2010; Shah *et al.*, 2022)besides being important for disease resistance **(***Kopriva et al.*, 2019).

Soil pH might not exhibit direct impacts on the availability of nitrogen and potassium (Tabak *et al.*, 2020); yet sulfur(S) addition may indirectly influence their uptake by plants. Being a structural component of many amino acids (cysteine and methionine), vitamins, and coenzyme A (Kathpalia and Bhatla, 2018); thus, S addition to soil can modulate several metabolic processes within plants (Shah *et al.*, 2022);and increase their capabilities to mobilize and utilize soil nutrients (Narayan *et al.*, 2022).

This study investigates to what extent can biochar modified with either sulfuric acid or elemental S (an acidifying agent) surpass the effect of adding biochar solely to a sandy soil (93% sand), especially on increasing the availability of both N and K in soil hence uprising their uptake and distribution within maize plants. Specifically, we assume that: application of biochar can enrich the soil with N and P thus improve their uptake by plants and consequently enhance plant growth (hypothesis 1). The effect of acidifying biochar or biochar+sulfur(S) might be superior to the effect of non-acidified biochar (hypothesis 2), and finally the application of elemental sulfur might not be efficient enough as acidified biochar for enhancing plant growth because the oxidation of elemental S temporarily influences nutrient availability and uptake (hypothesis 3).

2. Materials and Methods

2.1. Materials of study

A surface soil sample (0-30 cm) was collected from Arab Agadeer area, Qualubia Governorate, Egypt (31° 16′ 42″ E and 30° 21′ N) prior to the experimental study. This sample was air dried, crashed and sieved via a 2 mm sieve then analysed for its chemical and physical analyses as outlined by Sparks *et al.*(1996) and Klute(1986). The obtained results are presented in Table 1.

Table 1. Chemical and physical characteristics of the soil under study.

Parameter	pH*	EC* (dS m^{-1})	Soil organic carbon (g kg^{-1})	$CaCO_3$ (g kg^{-1})	**Available-N** (mg kg^{-1})**	**Available-K ** (mg kg^{-1})**
Value	7.20	3.33	6.03	29.90	14.7	3.64
Parameter	Coarse sand (%)	Fine sand (%)	Silt (%)	Clay (%)	Textural class	WHC (%)
Value	86.00	17.00	6.51	5.79	Loamy sand	26.6

*EC was determined in soil paste extract while pH was determined in 1:2.5 soil: water suspension; WHC: water holding capacity, **Available Nwas extracted by potassiumsulfate whileavailable Kwas extracted by ammonium acetate.

Maize seeds (cultivar SC-P3444) were obtained from Pioneer International Company in Egypt. Potato straw was obtained from the experimental farm at the Faculty of Agriculture, Benha University. These residues underwent pyrolysis at 450° C in a muffle furnace (VULCAN D-550) for 5 h to produce biochar. Half of the obtained amount of biochar was acidified by H_2SO_4 as outlined by **Vithanage *et al.*, (2015)** while the other half was left non-acidified; afterwards these biochars were ground and sieved to pass through a 0.18 mm sieve. Compost was obtained from the Compost Production Unit, Faculty of Agriculture, **Benha University**. Characteristics of the used biochars and compost are presented in Table 2.

Table 2. Chemical characteristics of the investigated organic additives

Property	EC*	pH *	Organic carbon (g kg^{-1})	Total N (g kg^{-1})	Total P (g kg^{-1})	Total K (g kg^{-1})	C:N ratio
Non-acidified biochar	7.9	8.4	288.4	3.5	0.4	2.3	82.4:1
Acidified biochar	3.4	3.08	242.0	4.9	0.4	9.2	49.4:1
Compost	4.9	7.6	197.3	7.0	0.38	2.1	28.2:1

*The pH and EC of organic amendments were determined in 1:10 suspension.

2.2. The greenhouse investigation

A pot experiment was conducted at the greenhouse of the Faculty of Agriculture, Benha University, Egypt, in whichplastic pots (20cm diameter ×17.5cm depth) were uniformly packed with soil portions (equivalent to 5 kg) and mixed with 80 g of compost as a source of beneficial biota and nutrients in addition to one of the following four treatments i.e. (1) no biochar application, (2) biochar applied at a rate of 10g kg^{-1}, (3) biochar (10g kg^{-1}) + elemental sulfur(S) (2 g kg^{-1}) and (4) biochar acidified with H_2SO_4 (10g kg^{-1}). The experimental design was a randomized complete one with three replicates for each treatment. Soils,that received the abovementioned treatments, wereleft without planting for 2 weeks to equilibrate while being moistened continuously with deionized water to bring soil moisture to 80% of the water holding capacity (WHC on weight bases).Thereafter, 5 seeds of maize cultivar (SC-P3444) were planted in each pot and thinned to 3 after germination. Soils were kept at 80% of WHC for 60 days (experimental period), thensoil samples were collected from the rhizosphere of each pot. Also, whole plants were removed gently from these pots to avoid root damage then placed on plastic sieves and washed several times with tap then deionized water to remove stunt dirt. Afterwards, plant material was separated into roots and shoots then oven dried for 72h at 60-70° C and the dried weights were determined.

2.3. Soil and plant analyses

Soil pH was determined in 1:2.5 soil water suspension using a pH meter (Jenco 6173).Soil bulk density was determined on undisturbed soil samples at the end of the experimental period using a steel ring. Soil moisture characteristics were determined at the field capacity and permanent welting point using a pressure plate at 0.33 and 15 bars, respectively. Available N was extracted by K_2SO_4 (1%), then measured by micro Kjeldahel apparatus in presence of MgO and Devarda alloy. Available- K was extracted by the ammonium acetate method as outlined by Sparks *et al.*(1996) then measured by flame photometer (Elico CL 378).

Dried plant materials were acid digested according to Gotteni*et al.*(1982) using a mixture of sulfuric (H_2SO_4) and perchloric ($HClO_4$)acids, at a rate of 4:1. Nitrogen (N) and potassium (K) in plant digests were determined via micro Kjeldahel and flame photometer, respectively.

2.4. Data processing

The obtained data were subjected to analyses of variance (one- way ANOVA) and Dunken’s test via SPSS ver 18 Statistical software and figures were plotted with Sigma plot 10. Nutrient uptake was estimated per pot as following

$$Nutrient\ uptake\ (mg\ pot^{-1}) = \sum dried\ plant\ materials\ (g\ \ pot^{-1}) \times their\ nutrient\ \ contents\ (mg\ pot^{-1}) \qquad Eq\ 1$$

Nutrient Use Efficiency (NUE) was calculated according **to** Hirel*et al.*(2001) considering whole plant dry weight rather than the grain yield as follows

$$\text{Nutrient use efficiency (NUE)} = \frac{\text{Plant dry weight (g pot}^{-1}\text{)}}{\text{Supplied nutrients via soil and fertilizers (g pot}^{-1}\text{)}} \quad \text{Eq. 2}$$

3. Results and Discussion

3.1. Effect on SO_4^{2-} concentrations in soil solution and soil pH

Application of acidified biochar significantly raised SO_4^{2-} content in soil solution (Fig 1A) and this, in turn, reduced soil pH (Fig 1B). The high content of SO_4^{2-} was set free during biochar degradation; thus accounted for significant reductions in soil pH (Sivaranjanee and Kumar, 2021). Likewise, application of elemental sulfur with biochar upraised the concentrations of soluble sulfate ions in water, yet to a lower extent versus acidified biochar. This could be retributed to S oxidation in soil forming sulfuric acid (Yang *et al.*, 2010) that reduces soil pH (Li *et al.*, 2010), especially in soils of low buffering capacity such as sandy soils (El-Naggar *et al*., 2018). On the other hand, biochar provided a suitable environment for stimulating the activity of oxidizing microorganisms (Xiao *et al.*, 2022). A point to note is that application of non-acidified biochar solely raised soil pH exceeding the effect of non-amended control because of its alkaline nature (Abdelhafez *et al.*, 2014; Abdelhafez *et al.*, 2021) while the latter additive (non-acidified biochar) recorded no significant impacts on SO_4^{2-} concentrations in soil solutions versus the control.

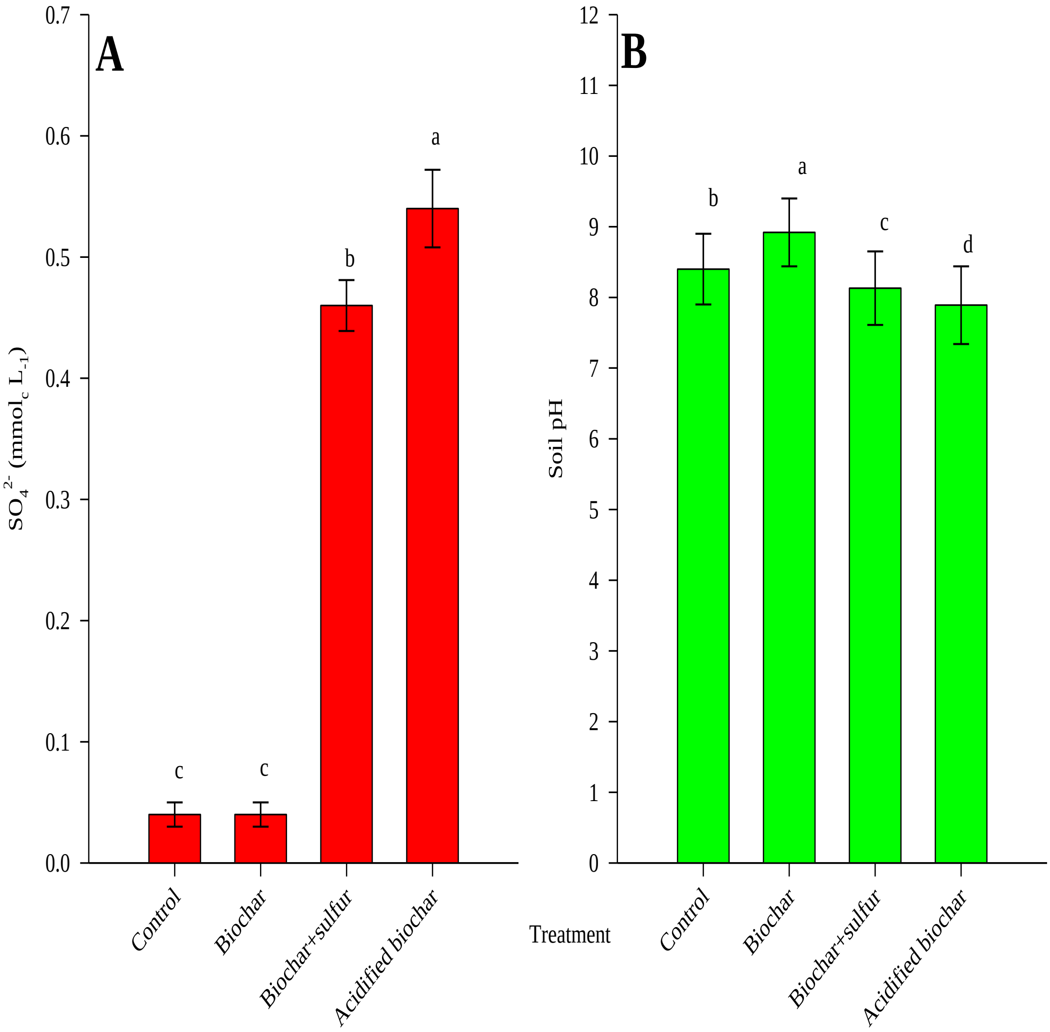

Fig. 1. Soluble SO_4^{2-} ions and soil pH (means± standard deviations) of as affected by biochar applications (-/+ elemental sulfur). Different letters on columns refers to significant variations among treatments.

3.2. Effect on soil bulk density and soil moisture characteristics

Application of acidified and nonacidified biochars decreased significantly soil bulk density (Fig 2A) while improved soil moisture characteristics (moisture content at field capacity (Fig 2B) and the permanent wilting point (Fig 2C) as well as the available moisture content in soil (Fig 2D)). These results are in well agreements with the findings of Bassouny and Abbas (2019) for the effect of biochar on soil characteristics. Also, the application of acidified biochar led to significant reductions in soil bulk density while increased soil available water content, yet to a lower extent versus the application of non-acidified biochar.Acidifiedbiochar exhibited higher soil surface area (Covali*et al.*, 2021) and their functional groups have high hydrophilicity (Duan *et al.*, 2021); though this additive might undergo rapid degradation in soil (Liu *et al.*, 2022). Thus, its capability to retain soil moisture decreased considerably versus non acidified biochar. It can therefore be assumed that the mobility and availability of soil macronutrients could be higher in biochar amended soil than in the non-amended control one (Elshony*et al.*, 2019).

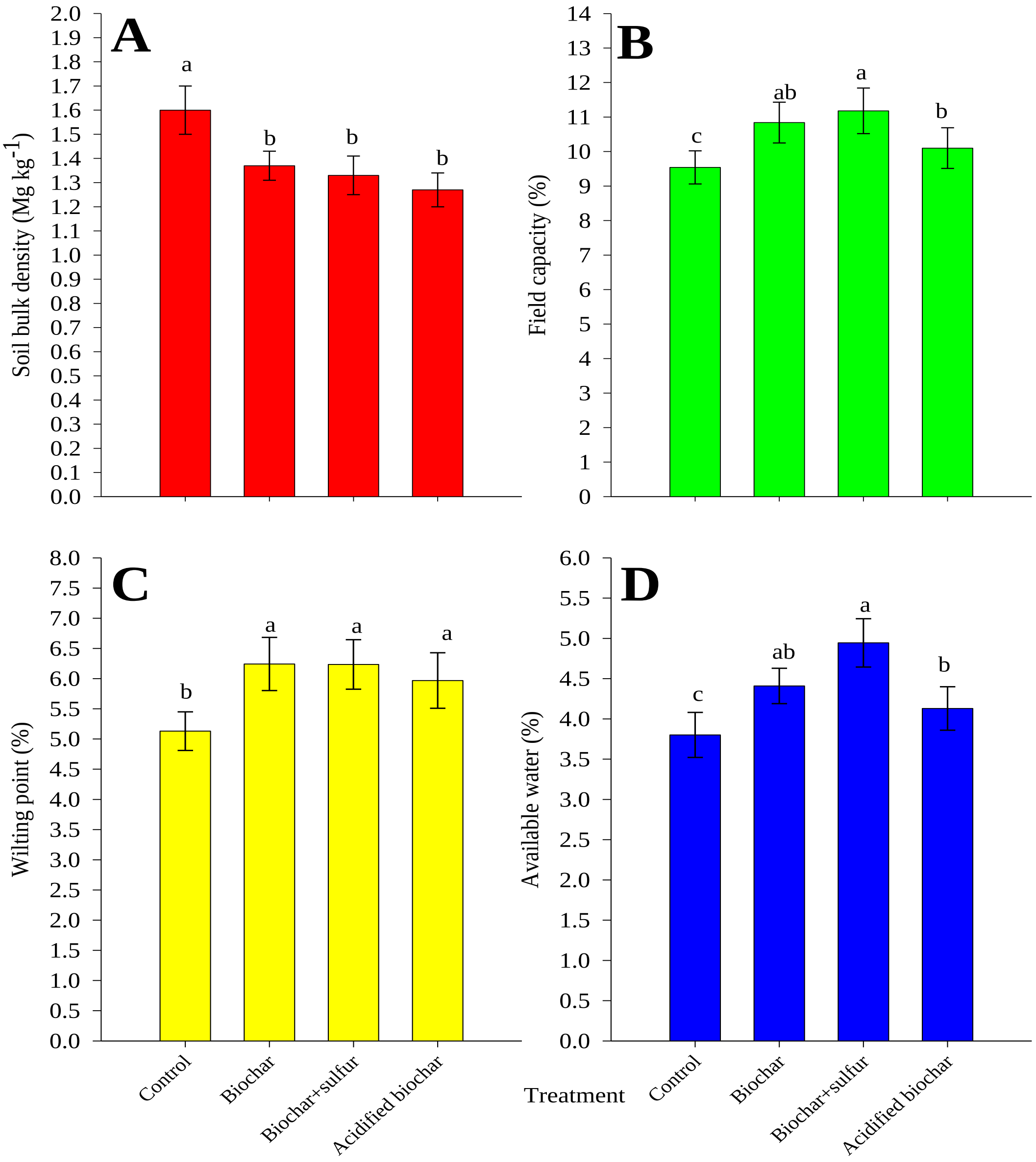

Fig. 2. Soil bulk density and soil moisture characteristics (means± standard deviations) as affected by biochar application (-/+ elemental sulfur). Different letters on columns refers to significant variations among treatments.

3.3. Effect on N availability, uptake by maize and its distribution within different plant parts

Results reveal that available-N content in soil (Fig 3A) and its uptake by maize plants (Fig 3B) increased significantly due to application of all additives. Biochar as a carbon rich product enriched soil with nutrients upon its degradation (Biederman and Harpole, 2013; Elshony *et al.*, 2019). Application of acidified biochar or amending soil with biochar + elemental S recorded significantly lower increases in values of N-uptake versus application of biochar solely. Probably, biochar exhibited more negative functional groups in acidic media (Wang *et al.*, 2020) thus retained temporarily higher concentrations of NH_4^+ ions (Liu *et al.*, 2019) via N–H···O hydrogen bonds with the SO_4^{2-} anion located outside the tripodal cavity (Basu and Das, 2014) thus decreased its uptake by plants on the short run. A point to note is that N content in both roots and shoots did not vary significantly among treatments (Figs 3 C and D). May be this nutrient was utilized continuously in metabolism (Baslam *et al.*, 2021) rather than being accumulated in plant tissues, unless supplied in excess amounts (Saloner and Bernstein, 2020).

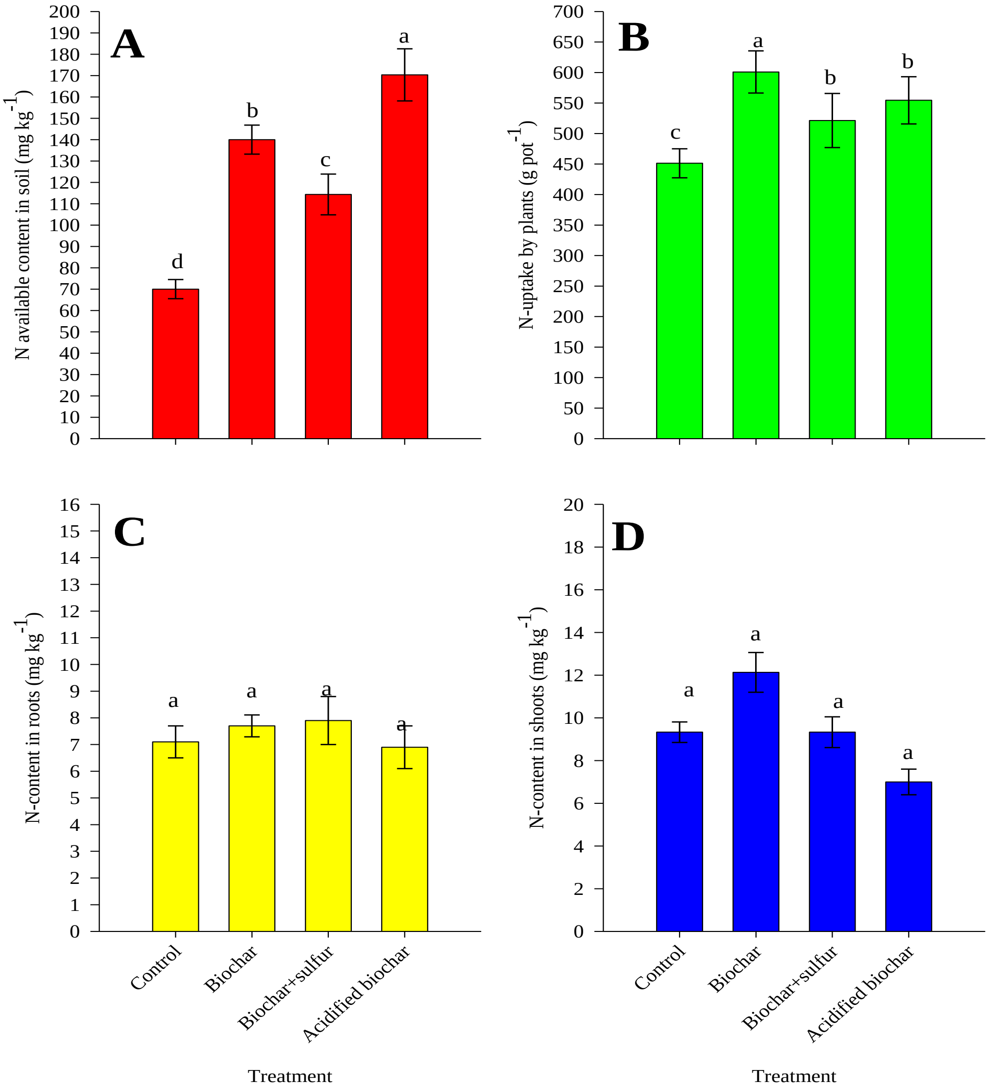

Fig 3. N available content, its uptake by maize plants and distribution within different plant parts (means± standard deviations) as affected by biochar application (-/+ elemental sulfur). Different letters on columns refers to significant variations among treatments.

3.4. Effect on K availability, uptake by maize plants and distribution within different plant parts

Application of all biochars significantly raised K-available concentrations in soil (Fig 4A). Also, these biochars significantly increased K- uptake (Fig 4B) and its content with different plant parts (roots and shoots) (Fig 4 A and D). In particular, acidified biochar recorded the highest increases in K available content, followed by biochar+S. Although, the highest K content in roots was recorded for the non-acidified biochar treatment; yet the highest K-increases in shoots were recorded for each of the acidified biochar and biochar+S with no significant variations between these two treatments. This might indicate that S stimulated K loading to xylem and its translocation to different plant parts (Usmani *et al.*, 2020), besides improving many physiological and molecular processes within plants (Shah *et al.*, 2022) to increase the K-assimilation in plants (Nawaz *et al.*, 2020). In this context, S is mainly absorbed as sulfate ions from soil (Li *et al.*, 2020) and cooperate with K forming ion pairs (Garcia-Araez *et al.*, 2010) that increase the translocation of both nutrients within plants (Moreira *et al.*, 2018).

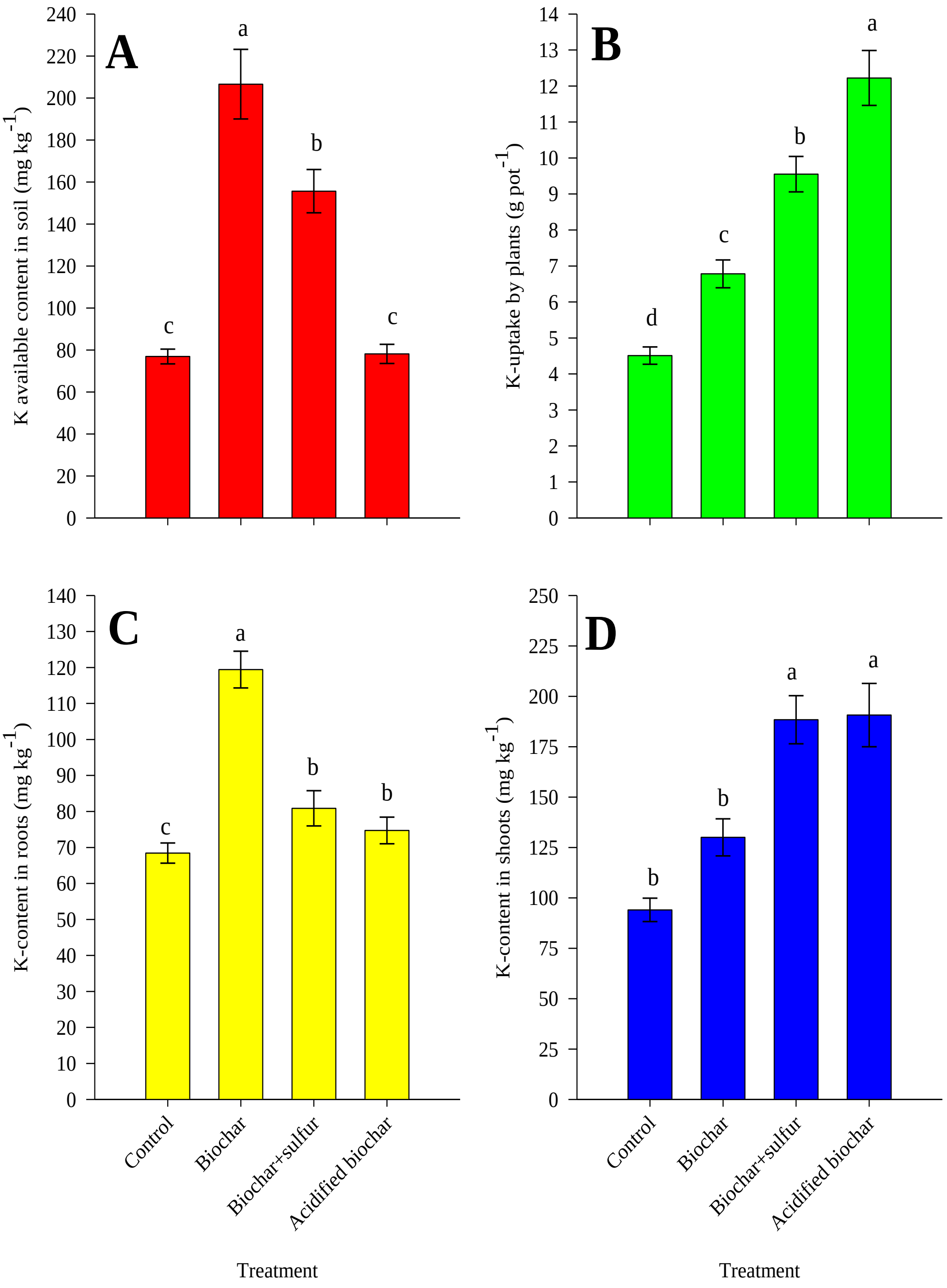

Fig. 4. K available content, its uptake by maize plants and distribution within different plant parts (means± standard deviations) as affected by biochar application (-/+ elemental sulfur). Different letters on columns refers to significant variations among treatments.

3.5. Effect on root and shoot biomasses

All biochars significantly boosted root fresh and dry masses (Fig 5 A and C), especially biochar+S, followed by the acidified biochar treatment. This additive (biochar) is added to poor fertile soils which suffer from low nutrient availability to enrich soils with nutrients and organic matter **(Manirakiza and Şeker, 2020)**. It is also responsible of modulating soil microbial community to increase soil fertility**(Tan *et al.*, 2022)**. In case of plant shoots, there was no significant difference between control treatment and biochar treatment,i.e. biochar treatment had no significant effect on plant shoots, while the acidified biochar exhibited the highest increases in shoot fresh and dry weights (Fig 5 B and D). It can therefore be deduced that the alkaline nature of biochar may lessen the translocation of nutrients within plants **(Maharlouei *et al.*, 2021)** via immobilization in roots.

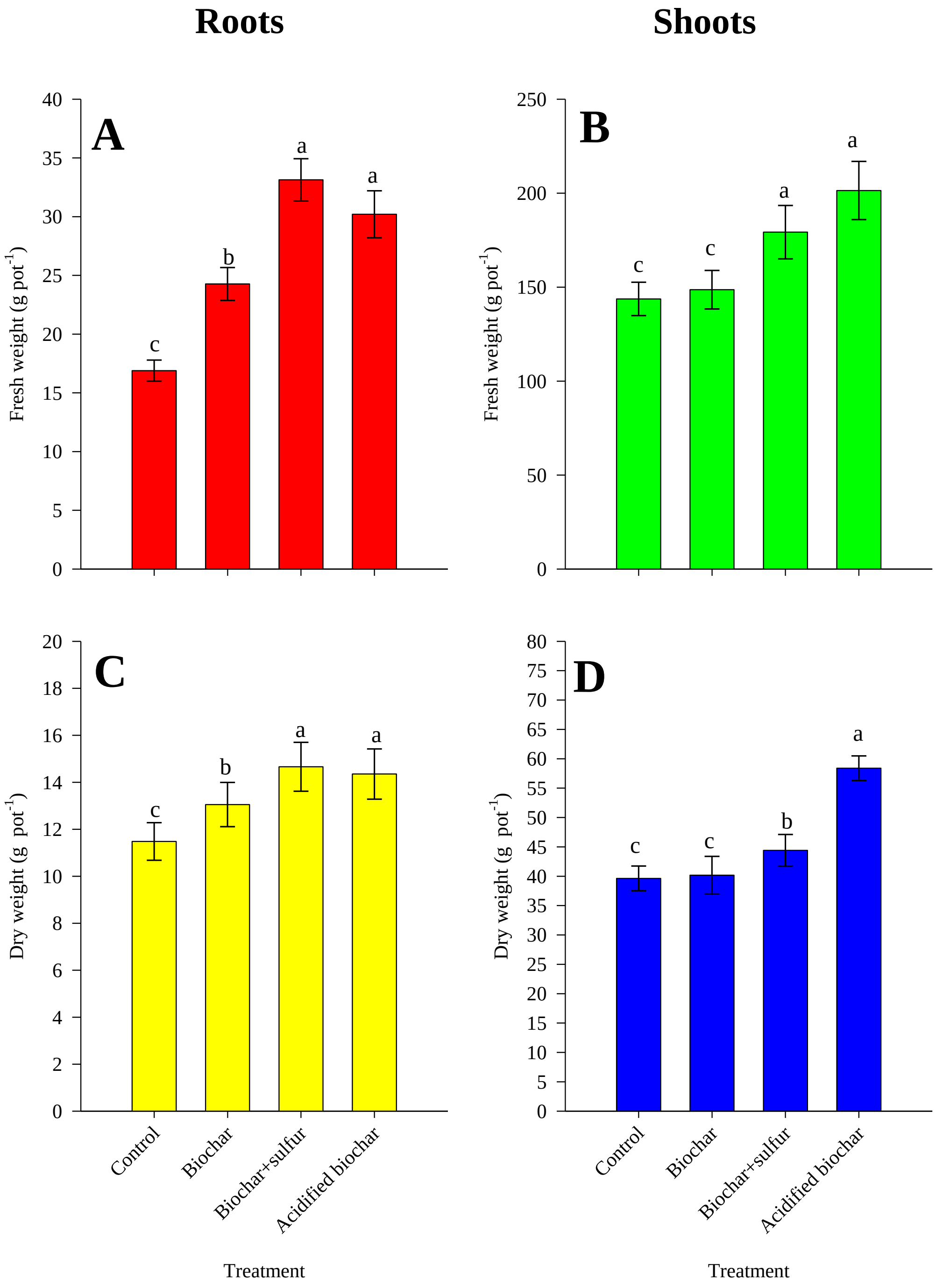

Fig. 5. Root and shoot fresh and dry weights (means± standard deviations) as affected by biochar applications (-/+ elemental sulfur). Different letters on columns refers to significant variations among treatments.

3.6 Effect on N and P use efficiencies by maize plants

Application of acidified biochar, followed by biochar+S recorded the highest increases in values of nutrient (N and K) utilization efficiencies by maize plants (Fig 6 A and B). On the other hand, N and K-use efficiencies did not vary significantly between the control and application of biochar. Such results indicate the positive roles of each of acidified biochar and biochar+S that did not only elevated the uptake of both nutrients i.e.N and K; but also improved considerably their utilization efficiencies by maize plants grown on a poor fertile light textured soil.

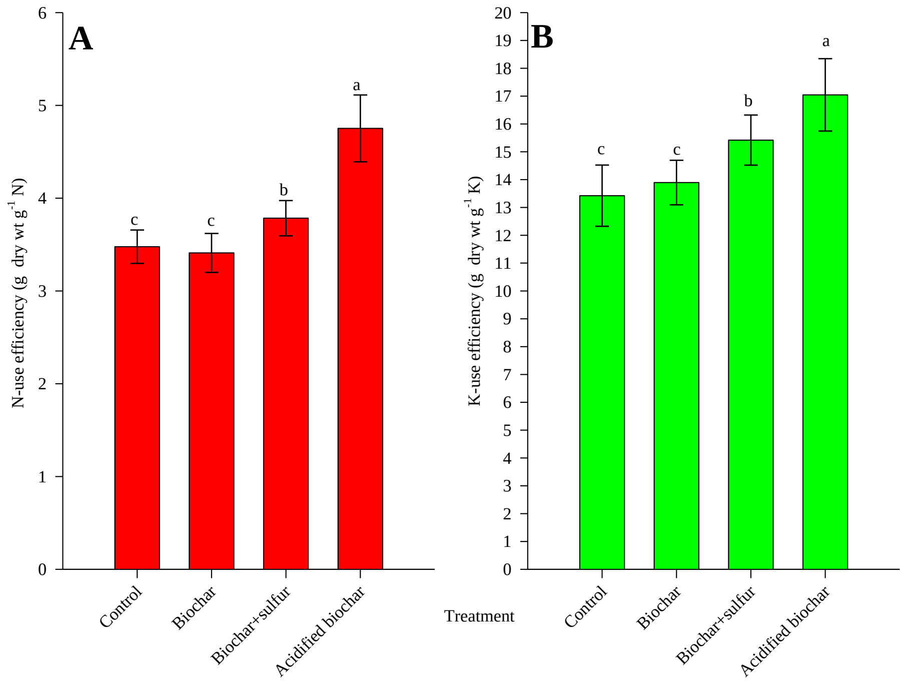

Fig. 6. N and P-use efficiencies (means± standard deviations) by maize plants as affected by biochar applications (-/+ elemental sulfur). Different letters on columns refers to significant variations among treatments.

4. Conclusion

Application of biochar raised significantly soil pH. Nevertheless, it increased the available N and P-contents in soil and their uptake by plants. This boosted plant growth, and therefore the first hypothesis becomes valid. Application of either acidified biochar or biochar+elemental sulfur raised significantly N and K uptake by maize plants. These additives recorded lower increases in N-uptake by plants versus the application of biochar solely, while increased P uptake. Overall, acidified biochar or biochar+elemental sulfur recorded higher increases in shoot and root biomasses versus applying biochar solely and therefore these results endorse partially the second hypothesis. Although, no significant variations were noticed in root biomass between acidified biochar and biochar+elemental sulfur; yet the first treatment exhibited higher increases in N- and P- utilization efficiencies and shoot biomasses than the second one and this result confirms the third hypothesis. Accordingly, using elemental sulfur may effectively increase the efficiency of biochar; yet this dual application might not be as efficient as acidified biochar on enhancing plant growth.

4. Conflicts of interest

There are no conflicts to declare.

5. Formatting of funding sources

No fund

6. Author contributions

All authors have contributed equally

7. Acknowledgments

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