



Sustaining Productivity while Reducing Methane Emission in Calcareous Soils: Implications of Combining Inorganic Fertilizer and Biochar

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Abstract

A considerable proportion of applied nutrients are adsorbed by the calcite surface of calcareous soils, making them unavailable to plants. A combination of organic amendments and fertilizers can improve nutrient retention and mineralization, and also reduce greenhouse gas (GHG) emissions. A two-years field experiment was undertaken to investigate the impacts of inorganic fertilizer, biochar and silicon on nutrient uptake, growth, yield and post-harvest soil chemistry in calcareous soil using rice (*Oryza sativa* L.) as a test crop. The implication of each treatment on methane emissions was also investigated. The combination of NPK, biochar and silicon significantly improved rice growth, yield, P and Si uptake; and post-harvest soil nutrition. Biochar increased soil organic carbon content between 4.2 and 108.5% across the years. An increase from 2.4 to 6.1% was observed in the inorganic fertilizer treatments, 11.4–12.0% for the biochar treatments and 2.5–19.0% for $\frac{1}{2}$ NPK+biochar from 2020 to 2021. Maximum grain yield was achieved with the treatment $\frac{1}{2}$ NPK+biochar+100 kg Si ha⁻¹ which was comparable to NPK+100 kg Si ha⁻¹. Also, the combination of $\frac{1}{2}$ NPK+biochar+50 kg Si reduced CH₄ emissions and produced a comparable yield to NPK+50 kg Si in both years. While further research is required to explore the effects of the length of time biochar is applied on reducing CH₄ emissions, this study suggests a basis for predicting the impact of biochar on the management of CH₄ emissions in calcareous soils.

Keywords Calcareous soil · Biochar · Greenhouse gas emission · Inorganic fertilizer · Rice production · Methane

Introduction

The fixation of Phosphorus (P) in calcareous soils poses a significant challenge for the agricultural sector (Zhar Shafi et al., 2020). A significant portion of applied P fertilizer is fixed in Ca-P compounds in calcareous soils and unavailable to plants. Soil and crop productivity depends on bioavailable soil nutrients, soil organic matter and soil microbiota (Adnan et al., 2020), of which P plays a crucial role. Phosphorus is mainly responsible for cell division and enlargement, photosynthesis, respiration and the transfer and storage of energy, which is why its deficiency significantly limits crop yield (Zhar Shafi et al., 2020; Ma

et al., 2023). Due to the lower solubility of P, the deficiency is severe in soils with a high Ca content (Menezes-Blackburn et al., 2018; Zhar Shafi et al., 2020). To achieve the desired crop productivity on such soils, larger quantities of inorganic fertilizers (IF) are required to compensate for the increased P inefficiencies (Ma et al., 2023). In addition to higher expenses and increased production costs, the use of larger amounts of IF has been associated with the degradation of organic matter in the soil within the past few years (Ma et al., 2023) and large emissions of important agricultural greenhouse gases. This often leads to environmental concerns focusing on physical destruction, biological processes and nutrients imbalance (Kakar et al., 2020). In

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Ghana, rice holds the position as the second most significant staple food following maize and contributes about 15% of the country's GDP (Addison et al., 2022). Nevertheless, the country relies on domestic production for only 57.14% of its rice consumption, resulting in a situation where it operates as a net importer of rice, as highlighted by Bissah et al. (2022). Currently, production is around 1.28 million metric tons. The rice industry is challenged by degraded soils, limited access to water, lack of machinery, diseases and pests, and ineffective use of pesticides (Bissah et al., 2022). Several efforts have been made to address these problems, particularly soil degradation but rice yield keeps declining, particularly in areas with calcareous soils. The larger proportion of farms are smallholding which is characterized by poverty which renders farmers incapable of purchasing the required amount of IF to support production. As a result, alternative means to improve poor soils and sustain soil productivity is an essential need (Liu et al., 2021a, b).

Research shows that the potential yield of rice and quality rice can be achieved through the combination of organic and inorganic fertilizer amendments. Organic amendments enhance the transfer of particular organic fractions that exist in both the soil solutions (referred to as dissolved organic matter) and the soil matrix (known as soil organic matter) to the roots of plants. Biochar has been suggested as an amendment to enhance soil productivity. Biochar is a carbon-rich substance that is produced through the incomplete combustion of organic waste materials like crop residues, animal manure, and sewage sludge (Kocsis et al., 2022). It contains a high proportion of potassium (K) and P; and can increase carbon (C) sequestration in the soil as well as the water holding capacity of soil (Li et al., 2020; Kocsis et al., 2022). It forms complexes or chelates with heavy metals in the soil (Zhar Shafi et al., 2020) and reduces the mobility of toxic metals, which in turn improves nutrient availability. A major advantage of biochar in this case is its ability to adsorb nutrients, particularly P, on its large surface area and potentially enhance nutrient retention and recycling. This property of biochar reduces the adsorption of P on the calcite surface in calcareous soils, so the application of biochar in combination with fertilizers could simultaneously improve the efficiency of inorganic fertilizer use and crop yield (Kocsis et al., 2022). However, some studies suggest that the efficiency of biochar to reduce P bonding depends on the soil type (Kocsis et al., 2022). Madiba et al. (2016) demonstrated that the application of biochar enhances P uptake and reduce leaching. However, it is important to note that biochar alone may not be a comprehensive solution for reducing P leaching in sandy soils. Therefore, a better understanding of the effect of biochar in calcareous soils is needed, especially in Ghana where very little attention has been directed to this issue. There is lack of research about

the interplay and processes that influence soil nutrients when biochar is paired with fertilizers. The synergistic impact of biochar and inorganic fertilizer within the rice paddy environment is not yet fully understood (Gu, 2022).

Biochar has also been considered as an amendment to reduce methane (CH₄) emissions in rice fields (Han et al., 2016; Lee et al., 2023). The short-term effects have been reported, however, uncertainties remain regarding the long-term effects (Nan et al., 2021; Lee et al., 2023). Reducing CH₄ emissions from rice fields without compromising yield is urgently needed to curb pollution, especially in emerging rice-growing countries like Ghana. The ability of biochar to reduce CH₄ emissions depends on agroecological conditions (Ayaz et al., 2021), therefore an area-specific assessment is required before a recommendation can be made. This study therefore attempts to fill the above gaps by investigating the effect of a combination of biochar and inorganic fertilizer on P availability and CH₄ emission in calcareous soils, while assessing rice productivity. We hypothesized that the combination of biochar and inorganic fertilizer would improve phosphorus availability and uptake as well as rice grain yield and reduce CH₄ emissions in calcareous soils.

Materials and Methods

Study Location and Weather Characteristics

The study was conducted in the Savelugu community (9.6165° N, 0.8246° W) in the Guinea Savannah agroecological zone of Ghana in 2020 and 2021. The community experiences unimodal rainfall patterns mostly ranging from May to October. The community experiences an annual precipitation ranging from 600 to 1000 mm, coupled with peak and trough temperatures of 42 °C and 16 °C respectively. The weather characteristics for 2020 and 2021 are presented in Table 1.

Soil, Biochar and Fertilizers

The initial attributes of the paddy soil and biochar are delineated in Table 2. The land was level and had adequate irrigation and drainage infrastructure. The soil had a silty loam texture with a pH of 7.6. The biochar utilized in this study was manufactured at the CSIR-Crops Research Institute (5.05491° N, -2.48821° W) from groundnut straw and pods. The production was carried out using the Slow Pyrolysis Technology (C₄H₄) process at 550 °C. Nitrogen and carbon concentrations were quantified through dry combustion employing an elemental analyzer (vario MACRO CNS; Elementar, Germany). The pH level and electrical conductivity (EC) were assessed in a solution with a 1:5 ratio of

Table 1 Mean weather conditions of Savelugu in 2020 and 2021 cropping seasons. Source: Ghana Meteorological Agency, Tamale

	Rainfall (mm)	Air temperature (°C)		Relative humidity (%)		Sunshine (hr)
		Min	Max	Min	Max	
2020						
July	19.57	23.97	34.65	67.00	91.70	6.66
August	39.65	24.71	32.43	71.16	94.12	5.13
September	29.89	24.68	31.90	74.48	93.91	5.23
October	20.14	22.28	33.45	72.97	94.90	4.84
November	14.02	21.48	30.66	70.48	92.47	6.97
2021						
June	20.41	23.88	33.24	58.79	76.31	7.18
July	8.52	23.79	30.26	72.81	89.68	5.93
August	16.02	23.92	29.79	73.97	92.39	4.78
September	12.35	23.67	30.30	73.00	92.50	5.33
October	8.47	24.33	32.37	64.48	92.29	8.21

Table 2 Initial paddy soil and biochar properties

Properties	Concentration	
	Soil	Biochar
Sand (%)	25.0	-
Silt (%)	67.4	-
Clay (%)	7.5	-
Textural class	Silt loam	-
Total C (%)	1.13	56.4
Total N (%)	0.02	0.54
Ex. P ₂ O ₅ (mg kg ⁻¹)	5.4	34,000
Ex. K ₂ O (mg kg ⁻¹)	98	174,000
Av. SiO ₂ (mg kg ⁻¹)	59	123.8
pH _(1:5)	7.8	9.0
EC _(1:5) ds m ⁻¹	0.25	7.9
CEC (cmol kg ⁻¹)	2.36	33.6
Pore volume (m ² /g)	-	187.9

NB: EC- electrical conductivity; CEC-cation exchange capacity; pH-potential hydrogen

weight to volume. Other soil characteristics such as total carbon, CEC, EC-, P%, K%, and SiO₂ were analyzed following established protocols (AOAC, 2006). The inorganic fertilizer was procured from OCP Africa Limited.

Experimental Design and Treatments

Nine different interventions were administered following a randomized complete block design, with each intervention being replicated thrice. Treatments were a combination of NPK (90:60:60), biochar and silicon (Si) as NPK, NPK+50 kg Si, NPK+100 kg Si, Biochar (10 tons/ha), Biochar+50 kg Si, Biochar+100 kg Si, ½NPK+Biochar, ½NPK+Biochar+50 kg Si, ½NPK+Biochar+100 kg Si ha⁻¹. Each plot was 6×5 m² in size and an alley of 1.5 m was left between the plots and 2 m between the replicates. A cleared band or strip of 3 m was left around the entire experimental field.

Field Establishment and Treatments Application

The rice variety NERICA 1 was sourced from the CSIR - Savanna Agricultural Research Institute for the experiment. The seedlings were raised and transplanted after 14 days in a row and inter-row spacing of 25 cm × 25 cm, respectively. Two seedlings were transplanted per hill. Biochar was broadcast and mixed into the soil with a rake at a depth not beyond 5 cm 10 days before transplanting. The sources of the NPK included urea, triple superphosphate, and muriate of potash. Urea was split-applied in three equal parts in the recovery, maximum tillering, and heading phases, while superphosphate and potash were supplied in two equal recovery and maximum tillering phases. Si was added via calcium silicate as a base fertilizer one day before transplanting. Pests, diseases and weeds were treated according to the guidelines of the Louisiana State and University (2021). The biomass produced after season one in each treatment plot was ploughed back into the soil during land preparation for the second season planting.

Water Management

The International Rice Research Institute method of alternate wetting and drying water management was adapted in this study (Li, 2001; Adhya et al., 2014). Water was maintained at a level of 5 cm above the soil surface until 20 days after transplanting (DAT). After the 20 DAT (formation of tillers), the field was allowed to dry down to 15 cm soil depth (Nasir et al., 2014). The water level in the soil was checked with a dipstick on a PVC pipe. This process was repeated until the beginning of booting. Subsequently, the water level was upheld at a height of 5 cm above the surface of the soil until the process of grain formation reached completion to prevent any decrease in crop yield (Bouman et al., 2007). Before harvesting, the water level was allowed to dry to a depth of 15 cm (Fig. 1).

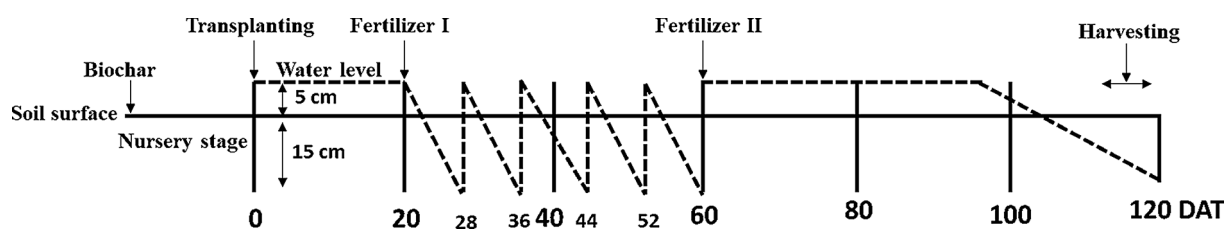


Fig. 1 Water management system deployed for the experiment

Data Collection

Soil and Plant Nutrients Uptake Measurement

After the experiment, soil samples were extracted from a depth of 30 cm using a soil auger to analyze the nutrients. Soil organic carbon content was estimated following the wet oxidation method (Walkey Black, 1934). The value was multiplied by the Van Bemmelen factor (1.73) to obtain the concentration of organic matter. Soil nitrogen concentration was determined using the Micro-Kjeldahl method (Page et al., 1982), P content using the Olsen method (Olsen et al., 1954), K content using the flame photometer method (Black, 1965) and Si content using the ammonium acetate saturation method (AOAC, 2006). Properties such as texture, pH (1:1 w/v), organic matter (OM), organic carbon (OC), total N, available P, available K, exchangeable Si, cation exchange capacity, and bulk density were determined using the AOAC (2006) method. Rice stover and grains oven-dried for dry weight measurement were finely ground and digested with $\text{HNO}_3/\text{HClO}_4$. The total content of P and Si in the digestion were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The individual total dry weight and nutrient concentrations were multiplied to get nutrient uptake. The Si use efficiency was calculated according to Eq. 1 (Dobermann & Fairhurst, 2000).

$$\text{Si use efficiency} = \frac{\text{Yield from Si application} \left(\frac{\text{Kg}}{\text{ha}} \right) - \text{Yield from without Si} \left(\frac{\text{Kg}}{\text{ha}} \right)}{\text{Amount of Si applied} \left(\frac{\text{Kg}}{\text{ha}} \right)} \quad (1)$$

Plant Growth and Yield Measurement

A 4 m² quadrant was established in the center of each plot for data collection. Ten plants were sampled and tagged in the quadrants for the collection of growth data. Rice height was quantified by determining the distance from the base (the soil surface) to the apex of the plant using a meter rule. Leaf chlorophyll content was measured on the 4th and 5th leaf at weeks 2, 4, 6 and 8 after planting. The weekly recordings

were averaged, and recorded. At harvest, the number of tillers and spikes were counted. Both effective and ineffective tillers were counted. The above-ground plant samples were oven-dried at 64 °C for 72 h to measure dry matter. Grain yield was estimated from plants within the quadrant. The measurements were carried out at a grain water content of 14%. The grain yield was recorded per plot and converted to hectares according to Eq. 2.

$$\begin{aligned} \text{Grain yield (kg ha}_{-1}\text{)} &= \text{Grain weight (kg plot}^{-1}\text{)} \\ &\times \frac{(100 - mc)}{86} \\ &\times \frac{10000\text{m}^2}{0.25 \times 0.25\text{m}^2} \end{aligned} \quad (2)$$

Where mc is the grain moisture content, 86 is adjusted moisture content and $\frac{10000\text{m}^2}{0.25 \times 0.25\text{m}^2}$ is the estimated plant stand per hectare.

Methane (CH₄) Measurement

Three acrylic chambers were installed per plot for gas collection using the static chamber method. A syringe was used to collect 10 mL gas samples at 0, 5, 10, 15, and 20 min at 3 days intervals over 3 months (1.5 months during the wet and dry periods, respectively). Sample collection started at 9 am on each collection day. Gas chromatography (Flame ionization detector, CP-3800 Varian, USA) measured CH₄ concentrations in the collected gas samples. The collected methane flux was summed and averaged each month. The mg CH₄ m⁻² month⁻¹ was quantified as in Eq. 3.

$$\begin{aligned} \text{CH}_4 \text{ flux (mg m}^{-2} \text{ month}^{-1}\text{)} &= \frac{d\text{CH}_4}{dt} \times \frac{v}{a} \\ &\times \frac{p \times 100 \times \text{MW}}{R} \\ &\times \frac{273.15}{273.15 + T} \end{aligned} \quad (3)$$

where $\frac{d\text{CH}_4}{dt}$ represents CH₄ concentration gradient over time, a is the horizontal area of the static chamber, v is the volume of the static chamber, p equals atmospheric pressure, R is the ideal gas constant (8.314 L mol⁻¹ K⁻¹), MW

is the molecular weight of CH_4 (16 g mol^{-1}), and T is the temperature ($^{\circ}\text{C}$).

The total CH_4 released over the production period (in mg m^{-2}) was calculated with the averages recorded at a certain time interval by Eq. 4.

$$\begin{aligned} & \text{Cumulative } \text{CH}_4 \text{ emitted} \\ &= \sum_{i=1}^{n-1} \left(\frac{(\text{CH}_4 \text{ Flux}_i) + (\text{CH}_4 \text{ Flux}_{i+1})}{2} \right) \Delta \text{day}_i \end{aligned} \quad (4)$$

note n represents the number days on which gas was measured while Δday_i is the interval between the i^{th} and $(i+1)^{\text{th}}$ measuring days.

Data Analysis

The two-way analysis of variance (ANOVA) was conducted to analyze the data using version 21 of the Statistical Package for Social Sciences (SPSS). Prior to the ANOVA, the dataset underwent assessments for normality and variance heterogeneity through the Shapiro-Wilk and Levenes tests, respectively. In cases where significant differences among means were identified, the Duncan Multiple Range Test (DMRT) was applied for mean separation. Fischer's least significant difference (Lsd) at a confidence level of 95% was utilized to distinguish significant treatment means. The results are tabulated as means \pm standard deviation.

Results and Discussion

Effect of Biochar and Fertilizer on Soil Chemistry

Soil chemistry was significantly ($p < 0.05$) affected by the amendments after two years of experiment (Table 3). The combination of NPK + biochar + Si improved the soil organic carbon content between 1.66 and 1.75% compared to their separate application. The sole application of biochar did not improve the soil organic carbon content as much as the sole application of NPK, but when Si was added, the combination of biochar and Si improved the organic carbon concentration to $1.63 \pm 0.18\%$ and $1.66 \pm 0.21\%$ compared to $1.43 \pm 0.04\%$ and $1.41 \pm 0.05\%$ obtained with NPK + Si for 50 kg and 100 kg Si ha^{-1} , respectively. Soil N concentration was also significantly affected by NPK fertilizer and its combination with biochar and Si. Biochar alone and its combination with Si affected the least N and were only comparable to $\frac{1}{2}$ NPK + biochar. The P content in the soil was higher in plots fertilized with NPK + Si, and $\frac{1}{2}$ NPK + biochar + Si, while the lowest values were found in the plots with biochar alone and biochar + Si plots. However, P levels in biochar alone and biochar + Si plots were higher than the initial soil concentration. In contrast, the K concentration was mostly influenced by biochar and its combination with the other amendments. The plots that received only NPK or NPK + Si contain the lowest amount. The highest extractable Si content in the soil of $56.24 \pm 21.16 \text{ mg kg}^{-1}$ was retained by $\frac{1}{2}$ NPK + biochar + 100 kg Si, while the lowest content of $24.27 \pm 13.20 \text{ mg kg}^{-1}$ was achieved by sole biochar. The concentration of Si in the soil exhibited an upward trend as the rate of Si application increased but this was not the case for the other chemical properties measured.

Table 3 Effect of biochar and fertilizer on soil chemistry

	Organic carbon (%)	Total nitrogen	Available phosphorus (mg/kg)	Available potassium	Extractable Silicon
Season					
2020	1.57 ± 0.24^a	0.03 ± 0.01^a	16.10 ± 3.55^b	21.65 ± 7.22^b	30.55 ± 15.09^b
2021	1.62 ± 0.38^a	0.06 ± 0.02^a	25.61 ± 6.28^a	25.46 ± 6.21^a	49.46 ± 21.12^a
Lsd (0.05)	0.13	0.01	1.48	1.55	3.06
Amendments					
NPK	1.36 ± 0.06^b	0.05 ± 0.01^{ab}	21.50 ± 8.65^a	17.54 ± 1.70^c	24.85 ± 11.57^c
NPK + 50Kg Si	1.43 ± 0.04^b	0.06 ± 0.02^a	22.17 ± 7.19^a	18.53 ± 2.96^c	42.45 ± 25.26^{bc}
NPK + 100Kg Si	1.41 ± 0.05^b	0.06 ± 0.02^a	22.99 ± 11.05^a	19.35 ± 5.05^c	50.26 ± 24.04^{ab}
Biochar (10 tons/ha)	1.18 ± 0.15^c	0.04 ± 0.02^b	16.71 ± 5.67^b	26.54 ± 5.64^{ab}	24.27 ± 13.20^c
Biochar + 50Kg Si	1.63 ± 0.18^a	0.04 ± 0.02^b	16.86 ± 6.59^b	26.91 ± 5.46^a	36.68 ± 8.95^{cd}
Biochar + 100Kg Si	1.66 ± 0.21^a	0.04 ± 0.02^b	18.12 ± 6.44^b	28.25 ± 6.08^a	43.64 ± 12.38^{bc}
$\frac{1}{2}$ NPK + Biochar	1.66 ± 0.29^a	0.05 ± 0.03^{ab}	21.54 ± 7.25^a	23.67 ± 6.18^b	30.43 ± 15.86^{de}
$\frac{1}{2}$ NPK + Biochar + 50Kg Si	1.75 ± 0.46^a	0.06 ± 0.03^a	23.91 ± 10.07^a	26.26 ± 4.41^{ab}	51.25 ± 18.70^{ab}
$\frac{1}{2}$ NPK + Biochar + 100Kg Si	1.75 ± 0.48^a	0.06 ± 0.04^a	23.91 ± 8.96^a	24.99 ± 6.57^{ab}	56.24 ± 21.16^a
Lsd (0.05)	0.17	0.01	2.79	3.14	9.17
Season \times Amendment	ns	0.01	ns	ns	0.008

Note Column means carrying dissimilar alphabets are significant at $p < 0.05$; ns represent non-significant; Lsd represents least significant difference

The amount of Si retained increased with increasing Si rate but there was no statistically notable distinction observed between 50 kg and 100 kg Si ha⁻¹. The measured properties were higher and more significant in 2021 compared to 2020, except for soil organic carbon and nitrogen concentrations, which were statistically similar. Total N and extractable Si were influenced by the amendments and the interaction with the season. The increases observed in soil chemistry could be attributed to the slight improvement in the concentration of organic carbon in the soil. A higher turnover of biomass (stover and roots) in 2020 after the addition of NPK, biochar and Si could increase soil organic carbon, as there is a close relationship between plant biomass and soil organic carbon content (Agostinho et al., 2017; Lee et al., 2023). In the present study, the application of biochar increased soil organic carbon content by about 4.2 to 108.5%, which is consistent with previous studies (Agostinho et al., 2017). An increase in organic carbon content could improve soil structure and porosity to retain more moisture (Lee et al., 2023). Increasing the water-holding capacity of the soil could enhance the dissolution and uptake of nutrients and reduce the loss of nutrients, especially in calcareous soils (Agostinho et al., 2017). Kocsis et al. (2022) reported that the addition of biochar can reduce the leaching of N (NO₃⁻-N) from soil by 49.2%. Several mechanisms, including enhanced nitrification, nitrate adsorption capacity of biochar, improved microbial respiration, mineralization of organic N, and increased water-holding capacity of soil by biochar, could be responsible for the enhanced soil fertility. Therefore, the use of biochar could affect the N cycle in calcareous soils and influence N distribution (Kocsis et al., 2022). In other studies, similar results have been reported on improved N retention of fertilizers by biochar (Ennis et al., 2012; Brtnicky et al., 2019). Increased K and P values indicate a net release

of K and P by biochar due to the high content in Table 2, which is supported by Agostinho et al. (2017). Similarly, Agegnehu et al. (2016) found an increase in soil available K content after biochar application and attributed this to improved CEC and intrinsic elemental nutrients of biochar. The increase in available P is related to the P supplied to the soil by NPK fertilizers and biochar, as well as the ability of biochar to reduce P fixation and provide more water-soluble P in calcareous soils. Agostinho et al. (2017) have substantiated this assertion, demonstrating that the incorporation of P from various sources, such as biochar, led to an augmentation in the P levels within the soil solution. The application of biochar was shown to diminish the formation of insoluble P compounds induced by the elevated pH levels and liming of calcareous soils. Similar to other organic substances, biochar has the capacity to create soluble compounds with P, consequently enhancing its abundance in the soil solution (Zhar Shafi et al., 2020). These findings imply that the utilization of biochar alone or in conjunction with fertilizers in calcareous soils could potentially enhance the soil's nutrient retention capabilities, thereby ameliorating nutrient utilization efficiency. Furthermore, the incorporation of inorganic Si fertilizer might alleviate Si deficiency in calcareous soils. The enduring impacts of biochar and fertilizers on amended soils warrant further investigation.

Effect of Biochar and Fertilizer on Nutrient Uptake and Nutrient Use Efficiency

The treatments had a significant effect ($p < 0.05$) on P uptake in 2020 and 2021 (Fig. 2). ½NPK + biochar + 100 kg Si supplied the highest P to the plants in 2020 (28.6 kg P ha⁻¹), while NPK + 100 kg Si supplied the highest, 36.7 kg P ha⁻¹ in 2021. The lowest P uptake of 12.0 and 14.7 kg ha⁻¹ was

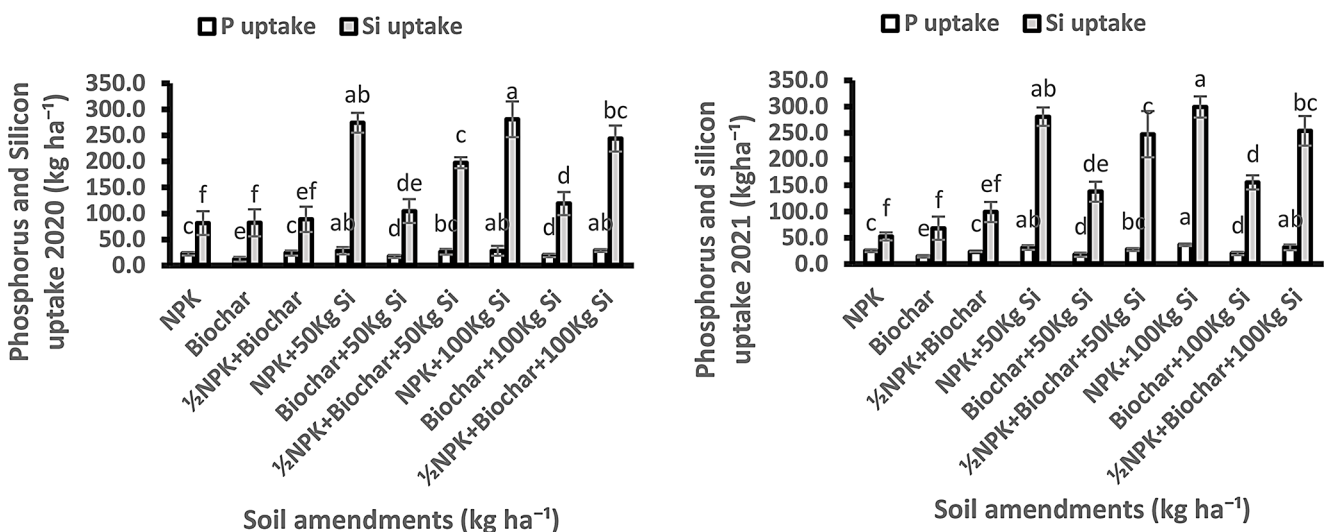


Fig. 2 Effect of inorganic fertilizer and biochar on phosphorus uptake. Means bars carrying dissimilar alphabets are significant at $p < 0.05$

observed within sole biochar in 2020 and 2021, respectively. P uptake increased when the Si rate was increased in all amendments, but no statistical difference ($p > 0.05$) was found between 50 and 100 kg Si ha⁻¹. In contrast, Si uptake was most enhanced by NPK+100 kg Si ha⁻¹, with the uptake of 280.8 and 299.3 kg Si ha⁻¹ recorded, while the lowest values of 81.5 and 52.6 kg Si ha⁻¹ were obtained by sole NPK. Similar to P uptake, no significant difference was observed in Si uptake after increasing the Si rate from 50 to 100 kg Si ha⁻¹, however an increase of 2.4–6.1% was recorded in the NPK treatments, 11.4–12.0% in the biochar treatments and 2.5–19.0% among ½NPK+biochar from 2020 to 2021 (Fig. 2). In 2020, Si use efficiency was highest for NPK+100 kg Si (2088.7) and lowest was found in biochar+50 kg Si (1578.8) (Fig. 3). A change was observed in 2021, where biochar+100 kg Si ha⁻¹ had the highest utilization efficiency (2866), but closely followed by NPK+50 kg Si ha⁻¹ with 2840 (Fig. 3). Plant response to increasing rate of Si from 50 to 100 kg ha⁻¹ was generally higher (percentage increase) in plants nourished with biochar. Although Si uptake was higher in the NPK+Si treatments, the efficiency of Si utilization increased over time in the biochar+Si treatments. The combination of Si with NPK or biochar or both significantly increased the efficiency of Si utilization compared to the application of NPK or biochar alone. Nonetheless, all the treatments that received Si were statistically the same. The response observed in nutrient uptake and utilization is explained by the impacts of the treatments on soil chemistry (Table 3). The mechanisms responsible for the high P uptake after the application of NPK+100 kg Si ha⁻¹ and other Si-amended treatments are explained by the high P concentration in these treatments. There is a strong correlation between Si and P. When both are present in sufficient quantities, they can interact to improve their availability and utilization efficiency. Si competes with P for the adsorption sites on soil minerals, consequently enhancing

the availability of S. This process results in a significant release of P from the soil minerals, as indicated by studies conducted by Schaller et al. (2019) and Mberg et al. (2020). The high P uptake observed in treatments containing Si could also be caused by a plant's internal mechanism in which Si enhances the utilization of P by increasing phosphorylation (Eneji et al., 2008). Biochar can improve the soil biochemical environment by increasing oxygen levels, resulting in a promotion of soil enzymatic activities, microbial activities and population, which ultimately enhances nutrient uptake. Due to its large surface area, biochar is excellent at binding nutrients and moisture. This does not only reduce leaching from the topsoil to deeper layers but also enhances the availability of nutrients to plants. Consequently, it has the potential to enhance soil structure, alleviate soil compaction, and promote the growth of roots.

Zhar Shafi et al. (2020) associated the Si utilization efficiency caused by biochar with improvements in water holding capacity, exchangeable cations and soil pH, which promotes nutrient retention. Biochar has a positive effect on mycorrhizal colonization by increasing the surface area of microorganisms, thereby enhancing N and P uptake (Solaiman et al., 2020). The results support the role of biochar and Si in increasing P uptake.

Effect of Biochar and Inorganic Fertilizer Amendment on Rice Growth and Yield

The amendments had a significant effect ($p < 0.05$) on the measured variables for plant growth and yield (Table 4). The cropping seasons also influenced how the measured variables responded to the applied amendments. Plants receiving NPK+Si achieved the highest plant height (121.22±13.74 cm) compared to NPK alone and the other treatments. The addition of Si to NPK had no significant effect on rice height, and increasing the amount of Si from

Fig. 3 Effect of inorganic fertilizer and biochar on silicon use efficiency. Note means bars carrying dissimilar alpha-bets are significant at $p < 0.05$

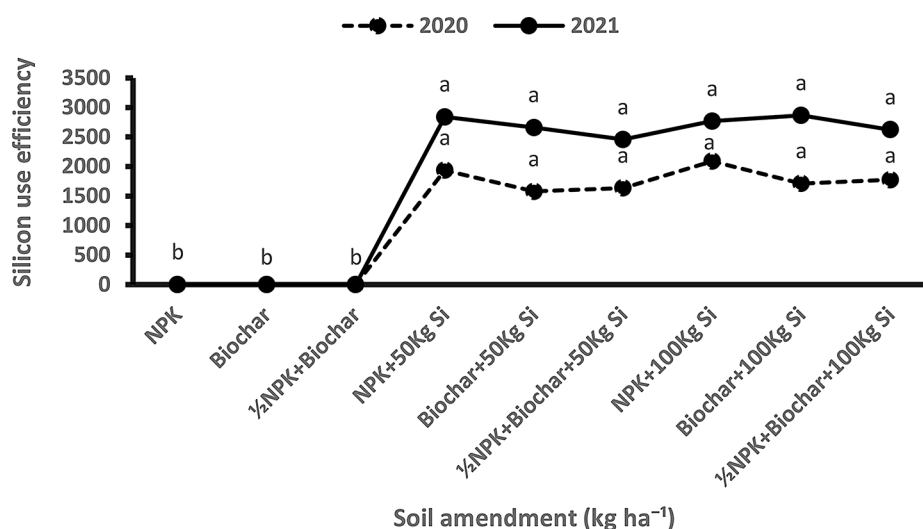


Table 4 Effect of fertilizer and biochar on rice growth

	Plant height (cm)	Dry matter (g)	Total Chlorophyll (mg g ⁻¹)	Number of tillers plant ⁻¹	Number of spikelet plant ⁻¹
Season					
2020	102.12±18.43 ^b	126.20±40.96 ^b	4.41±0.89 ^b	8.89±3.56 ^a	111.73±9.87 ^b
2021	113.21±25.47 ^a	137.24±34.86 ^a	4.78±0.91 ^a	9.41±3.34 ^a	113.86±9.01 ^a
Lsd (0.05)	4.42	3.14	0.17	0.54	2.33
Amendment					
NPK	117.68±17.71 ^{ab}	136.88±11.29 ^d	4.94±0.73 ^a	7.67±2.48 ^{cd}	109.08±5.51 ^{cd}
NPK+50Kg Si	121.22±13.74 ^a	158.22±9.47 ^b	5.12±0.36 ^a	9.42±2.05 ^{bc}	115.87±7.13 ^{abc}
NPK+100Kg Si	121.15±17.23 ^a	173.45±7.97 ^a	5.19±0.61 ^a	10.83±1.24 ^{ab}	120.17±9.89 ^a
Biochar	93.75±28.59 ^e	87.39±9.60 ^e	3.77±0.48 ^c	6.75±0.50 ^d	106.80±5.41 ^d
Biochar+50Kg Si	97.70±19.24 ^{de}	109.06±17.07 ^f	3.98±0.84 ^c	6.42±2.23 ^d	108.08±5.38 ^d
Biochar+100Kg Si	97.92±21.15 ^{de}	113.13±15.02 ^{ef}	4.05±0.82 ^{bc}	7.98±1.20 ^{cd}	109.17±11.52 ^{cd}
½NPK+Biochar	104.08±18.55 ^{cd}	119.55±24.37 ^c	4.71±0.74 ^{ab}	9.58±3.88 ^{bc}	112.73±9.53 ^{bcd}
½NPK+Biochar+50Kg Si	104.05±24.25 ^c	137.57±11.46 ^d	4.73±0.54 ^{ab}	11.58±2.05 ^{ab}	115.27±4.95 ^{abc}
½NPK+Biochar+100Kg Si	111.47±17.06 ^b	150.22±11.06 ^c	4.90±0.68 ^a	12.25±0.32 ^a	118.00±5.59 ^{ab}
Lsd (0.05)	6.34	7.63	0.68	2.40	6.91
Season × Amendment	Ns	0.002	ns	ns	Ns

Note Column means carrying dissimilar alphabets are significant at $p < 0.05$; ns represent non-significant; Lsd represents least significant difference

50 to 100 kg ha⁻¹ did not result in a significant increase in rice height. In contrast, a significant increase in height was observed after the Si rate was increased from 50 to 100 kg ha⁻¹ for ½NPK+biochar. The lowest height was observed with sole biochar (93.75±28.59 cm). Total chlorophyll concentration of leaves was similar for the NPK+Si and ½NPK+biochar+Si treatments, but the highest value, 5.19±0.61 mg g⁻¹, was recorded for NPK+100 kg Si. Biochar alone resulted in plants with the lowest chlorophyll concentration (3.77±0.48 mg g⁻¹). For above-ground dry matter accumulation, NPK+100 kg Si produced the highest value (173.45±7.97 g) and was superior to all other treatments by at least 8.8%. Si affected dry matter accumulation; the application of 50 kg Si increased dry matter accumulation in all treatments. An increase of 13.5%, 19.5% and 13.1% occurred when Si rate was increased from 0 to 50 kg ha⁻¹ for NPK, biochar and ½NPK+biochar, respectively. A further increase from 50 to 100 kg Si ha⁻¹ increased by 8.8% and 8.4% for NPK and ½NPK+biochar, respectively, except for sole biochar where 50 and 100 kg Si were comparable. The highest number of tillers per plant was recorded in the treatment with ½NPK+biochar+100 kg Si (12.25±0.32). The combination of ½NPK+biochar produced more tillers than their respective single application. The application of Si affected the number of tillers but a rate higher than 50 kg ha⁻¹ had no significant effect. NPK alone and its combination with biochar responded effectively to Si and increased the number of spikelets per plant. The highest spikelet number per plant (120.17±9.89) was recorded with NPK+100 kg Si, while the lowest (106.80±5.41) was recorded with sole biochar. The combination of Si with

biochar had no significant effect on the number of spikelets per plant, although a slight increase was observed. The results obtained for the different growth parameters could be due to the improved soil properties, which supported high nutrient uptake for photosynthesis and carbohydrate production. High P supply can increase the accumulation of photosynthates in plants and facilitate grain maturity, resulting in heavier grains (Mohammed et al., 2021; Dikr & Abayechaw, 2022). The test weight (weight of 1000 grains) and yield per ha were higher in the treatments with a balanced content of P and Si (Fig. 4). Treatments that contain high major nutrients, NPK+100 kg Si, ½NPK+biochar+100 kg Si, NPK+50 kg Si and ½NPK+biochar+50 kg Si produced the highest 1000 seed weights of 29.3 g, 28.8 g, 28.6 g and 28.1 g, respectively. These treatments produced 1000 seeds heavier than the farmer's usual fertilizer (NPK alone), which weighed 26.7 g. In the sole biochar and biochar+Si treatments, the weight of the 1000 seeds was less than NPK alone. The heavier seeds produced by these treatments resulted in a higher rice yield per hectare. The rice yield in 2020 was lower than in 2021 because the soil properties were deficient. In 2020, only NPK+100 kg Si or 50 kg Si produced a grain yield of 2396.2 and 2381.2 kg ha⁻¹, which was comparable to the national average of 2500 kg ha⁻¹ (Fig. 5). As soil properties improved in 2021, yields were above the national average for all treatments except biochar alone, with NPK+50 kg Si ha⁻¹ producing the highest yield of 3464.6 kg ha⁻¹. NPK+100 kg Si ha⁻¹ followed by 3432.8 kg ha⁻¹, and the lowest value (1223.7 kg ha⁻¹) was found for biochar alone. This positive increase can be linked to the balance of plant nutrients created by the increased

Fig. 4 Effect of inorganic fertilizer and biochar on thousand seeds weight. Means bars carrying dissimilar alphabets are significant at $p < 0.05$

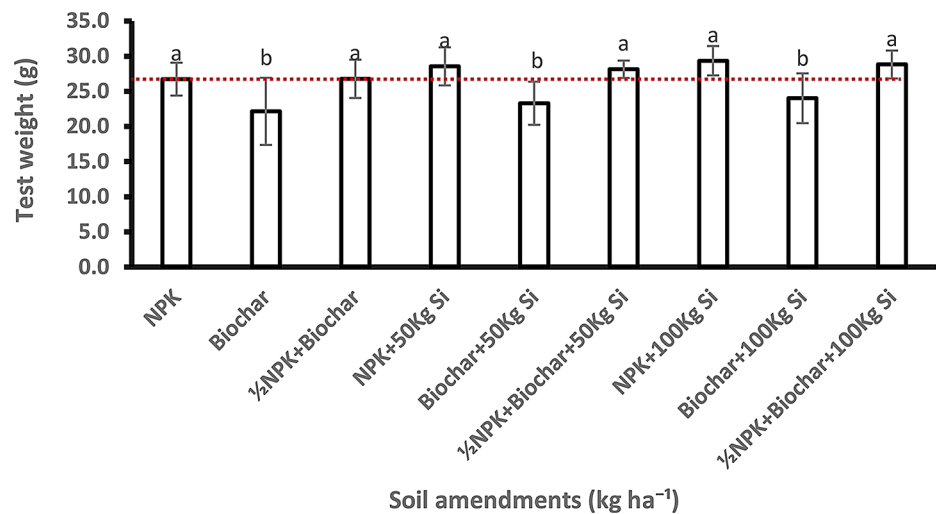
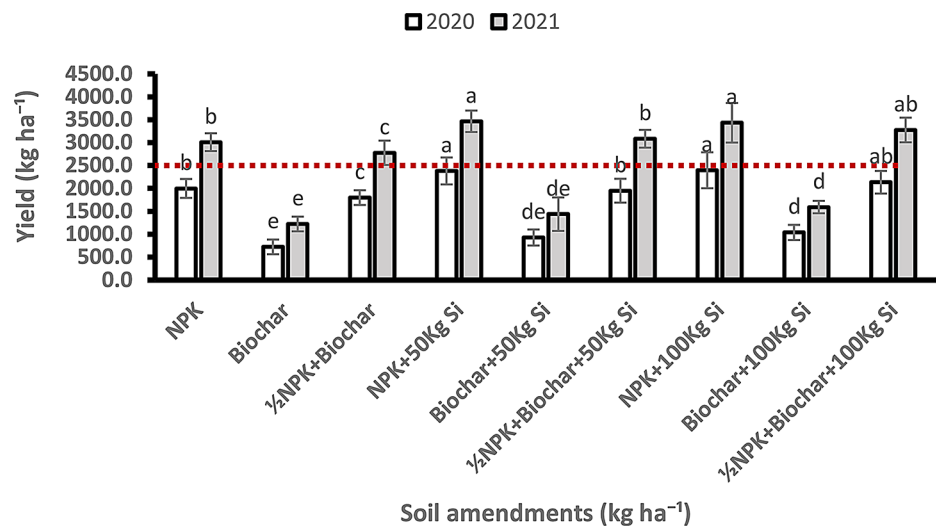


Fig. 5 Effect of inorganic fertilizer and biochar on rice yield. Means bars carrying dissimilar alphabets are significant at $p < 0.05$



availability of nitrogen, phosphorus, potassium and silicon. It is a fact that balanced Si doses can have a positive effect on the uptake of nitrogen, phosphorus and potassium and thus improve crop yields (Pavlovic et al., 2021).

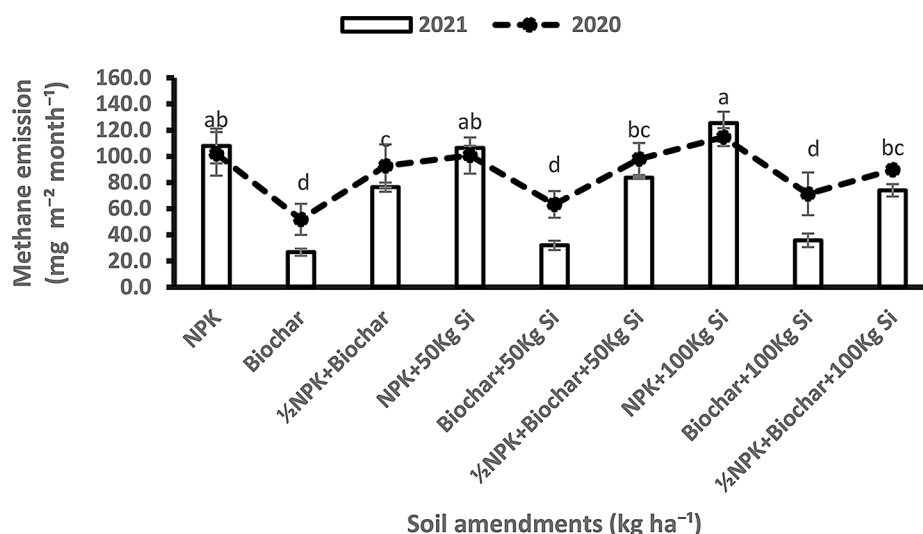
A similar effect was found by Keteku and Intanon (2022) and Brempong et al. (2022), who stated that the combined use of inorganic fertilizers and organic matter can increase the yield of various crops and reduce the fertilizer requirements of plants without affecting yields and quality. The results are also consistent with the study of Azimnejad et al. (2023) who reported that maximum P supply increased the number of grains spike⁻¹, tillers number, 1000-grain weights and grain yield. The combined application of 1/2NPK + biochar + 100 kg Si ha⁻¹ produced rice yield similar to NPK + 50 kg Si ha⁻¹ in both years. This could be related to the improved biochemical environment of the soil, which promoted nutrient uptake, crop growth and seed formation. The high yield resulting from Si application may be associated with the accumulation of sugars and proline (Crusciol et al., 2009). The improvement in dry matter production

ensured that photosynthates were stored in the plants. This accumulation of photosynthates in the plants increases the enzymatic, microbial and catalytic activities in the plants and thus leads to a higher grain yield (Regmi et al., 2020). The comparable grain yields of 1/2NPK + biochar + 100 kg Si ha⁻¹ to NPK + 100–50 kg Si ha⁻¹ indicate a reduction in fertilizer costs and an increase in the efficiency of fertilizer use.

Effect of Biochar and Inorganic Fertilizer on Methane Emission

The effect of the treatments on CH₄ emissions was significant ($p < 0.05$). Significant differences were observed between treatments but not between years, although slight changes were observed (Fig. 6). Inorganic Fertilizers (NPK and Si) increased CH₄ emissions, while biochar alone or in combination with the fertilizers decreased CH₄ emissions. Sole biochar released the lowest CH₄ of 51.8 mg m⁻² month⁻¹ in 2020, which further decreased to 26.8 mg m⁻² month⁻¹ in 2021, while NPK + 100 kg Si released the highest of 114.7

Fig. 6 Effect of inorganic fertilizer and biochar on methane emission. Means bars carrying dissimilar alphabets are significant at $p < 0.05$



mg m⁻² month⁻¹ in 2020, which increased to 125.3 mg m⁻² month⁻¹ in 2021. Biochar with or without Si reduced CH₄ emissions by at least 64.2% in 2020 and decreased to 31.5% in 2021 compared to the application of NPK with or without Si in 2020 and 2021. This result agrees with Lee (2023), who showed that the application of biochar significantly reduced CH₄ emissions in East Asian rice fields by 22.9%. Biochar has shown to have the potential to reduce CH₄ emissions, as the amount of CH₄ released from the sole biochar rice field decreased by an average of 103.7% from 2020 to 2021. Biochar has the potential to decrease CH₄ emissions through enhancing the aeration of paddy fields, leading to a notable rise in the population of methanotrophic Proteobacteria and a decline in the percentage of methanogenic Archaea (Kim et al., 2017). The enhancement of methane-oxidizing bacteria's abundance plays a crucial role in reducing methane emissions facilitated by biochar (Kim et al., 2017). It has been proposed by Ly et al. (2015) that the reduced CH₄ emissions associated with biochar could be attributed to its resistance to microbial degradation. The availability of carbon stands out as a critical constraining factor for methanogenesis (Liu et al., 2021a, b), given that the biochar's highly resistant carbon compounds (Dai et al., 2021) are unsuitable as a viable carbon source for methanogens. Nevertheless, certain investigations indicate that the impact of biochar is temporary and wanes over time due to the gradual consumption of the carbon substrate by microorganisms (Feng et al., 2012; Cayuela et al., 2013; Dai et al., 2021). This scenario underscores the necessity for further exploration into the influence of the duration of biochar application on CH₄ mitigation. Although sole biochar or biochar+Si reduced CH₄ emissions, they resulted in the lowest grain yields, so are not the appropriate option to promote rice cultivation in calcareous soil. The combination of biochar with NPK and Si, which also reduced CH₄ emissions by an average of 64.6%

and resulted in a rice grain yield comparable to that of NPK with or without Si, appears to be the best option for rice production and CH₄ mitigation in calcareous soils. However, NPK + 50–100 kg Si ha⁻¹ remains the best fertilizer option to maximize rice yield in calcareous soils.

Conclusion and Way Forward

The application of NPK, biochar and silicon significantly improved rice growth, yields, P and Si uptake and post-harvest soil nutrition. Biochar increased the organic carbon content of the soil by about 4.2 to 108.5% over two years. The significant superiority of NPK+Si and ½NPK+biochar over sole NPK and biochar at each application rate of Si indicates improvement in P and Si uptake. The grain yield obtained with ½NPK+biochar+100 kg Si ha⁻¹ was statistically comparable to NPK+100 kg Si ha⁻¹. Biochar with or without Si produced the lowest yields but reduced CH₄ emissions by at least 64.2% in 2020, but decreased to 31.5% in 2021. A combination of ½NPK+biochar+50 kg Si reduced CH₄ emissions and resulted in higher rice grain yields. This appears to be the best approach to promote rice cultivation and reduce CH₄ emissions in calcareous soils. Biochar appears to be a valuable soil amendment when its application is supplemented with inorganic fertilizers. This study can serve as a foundation for predicting the impact and management of biochar application on calcareous soils. The effects of the duration of biochar application on CH₄ mitigation still need to be investigated. An economic study of the various amendments is also recommended for future studies.

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Declarations

Conflict of Interest The authors declare no competing financial or personal relationship interest in this work.


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