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Sustainability of biochar amendment in a tropical paddy soil

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ABSTRACT

Biochar use as a soil amendment has attracted increased attention from researchers worldwide but its effects on soil properties, nutrients and greenhouse gas emissions remain scanty especially for tropical paddy soils. Biochar amendment increased initial total P from 500.11 in soil (S) to 978.90 μg/g of soil in soil amended with biochar (SB) but significantly reduced mean DOC. Biochar, however, had no effect on total nitrogen, total organic carbon, TON, organic–N and ammoniacal N. The initial soil pH was raised from 3.96 in S to 4.84 in SB by biochar amendment. It reduced CO_2 emission, had no significant effect ($P \leq 0.05$) on N_2O emissions but increased CH_4 emissions, although the levels of CH_4 were very low compared to the other greenhouse gases hence the high CO_2/CH_4 ratios. In addition, when co-applied with P, it suppressed the stimulating effect of P on production of greenhouse gases. Significant positive correlations were observed between CO_2 and N_2O as well as N_2O and CO_2 in SP. pH showed significant positive correlations with CH_4 in S and SP, organic–N in S, SP and SPB but negatively correlated to CO_2 in SPB as well as TON in SB. S and SP registered a significant negative correlation between ammoniacal–N and CH_4. DOC positively correlated to TON and ammoniacal N but negatively correlated to organic-N in SP and SB. Total P positively correlated to DOC in SB, ammoniacal N in SP and SPB and TON in S. It however, negatively correlated to CH_4 in SP and N_2O in SPB. It is therefore a suitable additive for sustainable agriculture since it enhances soil fertility and minimizes greenhouse gas emissions, especially when combined with P fertilizer.

1. Introduction

Biochar is a carbon rich biomass [1] that has attracted a lot of attention from researchers due to its potential benefits like organic pollutant immobilization [2,3], carbon sequestration [4], and as a stable source of soil nutrients [5]. Although these benefits have been reported, the exploration of biochar effect on soil properties has not been exhaustively done for tropical soils. In particular, researchers have not interrogated the sustainability of amending soil with biochar. It is therefore not known whether biochar amendment of soil has a potential negative downside.

Carbon (C), nitrogen (N) and phosphorous (P) are the major soil nutrients needed for plant growth [6]. C and N are renewable but P, that enters soil naturally via weathering of mineral rocks, is a limiting nutrient since it is non-renewable [6-8]. Furthermore, world deposits of phosphate rock – from which P fertilizers are obtained – are rapidly diminishing and might be exhausted in the next 30 – 50 years [9]. It is for this reason that potential alternative sources of P, such as biochar, are being investigated.

Biochar acts as a source of soil nutrients to plants and microorganisms, as well as a nutrient sink thus impacting mobility, bioavailability and fate of soil nutrients, in addition to altering the environment and properties of soil thus influencing reactions and cycling of nutrients [10] . Other than impacting soil nutrients, biochar may also mitigate climate change by reducing emission of greenhouse gases from soil by serving as carbon sink, in addition to influencing microbial composition and activity in soil [11].

Biochar's high labile carbon content and carbon sequestering capacity has been shown to improve both total organic carbon (TOC) and dissolved organic carbon (DOC) content of temperate soils [12], which results into increased storage of carbon in soil [13]. However, reports on biochar effects on soil nitrogen are conflicting: decreased ammoniacal nitrogen (NH_4^+-N) and nitrate-N [14,15], no effect [16], and reduction in organic-N [17]. Soil pH is a major factor in determining nutrient

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availability in soil because it impacts various processes (physical, chemical and biological) in soil [18]. However, studies on the impact of biochar on soil pH report contradicting findings: increased pH [18-20], and no significant effect [21,22]. Majority of these studies were conducted on temperate soils under aerobic conditions. It is therefore imperative to explore the impact of biochar on nutrients, pH and other properties of tropical paddy soils under anaerobic conditions. Wetlands and paddy farms have been identified as major methane emitters, with paddy rice farms covering approximately 154 million hectares worldwide [23]. Biochar could potentially reduce emission of greenhouse gases from these soils, but published reports give contradicting results on biochar amended soil. For methane, there are reports of reduced emissions [24-26], almost complete suppression of CH_4 emissions [27], increased CH_4 emissions in high water content soil [28,21,29] and no significant change in CH_4 emissions [30]. Studies on flooded soils amended with biochar have reported reduced N_2O emissions [31-33,28,34-36]. Similarly, conflicting results have been reported on CO_2 emissions from soils amended with biochar: No significant effect [37,38], variable emissions [39], and reduced emissions from paddy soils [33,34]. Given the conflicting reports on CH_4, CO_2 and N_2O, it is important to ascertain how biochar affects GHGs emissions from soil. This study therefore aimed at assessing the sustainability of biochar utilization in a tropical paddy soil by establishing how it affects soil nutrients (P, N, TOC, DOC), pH and greenhouse gas emissions.

2. Materials and methods

2.1. Soil material

2.1.1. Sampling area for soil material

The soil samples were collected from Dominion farm (longitudes $34^0$1E'7 S and latitudes $00^0$02'N, $00^0$02'S) in Siaya County between 00.00931^{0}S and 034.15915^{0}E at an elevation of 1134 m.

2.1.2. Soil collection and characterization

A soil auger was used to collect ten 1 Kg soil samples to a depth of 30 cm from different randomly selected sites within Dominion Farm [40]. The samples were air dried for one week under a shade, crushed, pulverized, and then sieved using a 2 mm diameter stainless steel sieve. A composite sample was prepared by pooling 200 g of each of the ten collected samples, and thoroughly mixing the pooled sample for 10 minutes at 200 rpm. The soil consisted of 68.04 % sand, 7.40 % silt, 24.56 % clay, 1694.2 ppm calcium, 406.2 ppm iron and 823.9 sodium. The textural class was sandy clay loam and it had a pH of 4.2.

2.2. Biochar

The biochar was obtained by pyrolysis of maize straw under limited supply of oxygen (For details on preparation and characterization of the biochar see [3]). Briefly, the maize straw was washed with deionized-distilled water and then oven-dried for 12 h at 80 °C. The maize straw was heated in a biochar reactor at increasing temperatures from 200 °C, to 250 °C and ended at 300 °C, with a hold time of 1.5 h at each temperature. At 300 °C, heating was stopped when there was no further emission of smoke from the gas exit pipe. The biochar was allowed to cool to room temperature in a dessicator, after which it was crushed and sieved using a 60 mesh sieve. Some measured parameters of the biochar that are of relevance to this study include a pH of 6.98, phosphorous content of 0.09 %, iron content of 0.09 % carbon at 60 %, nitrogen at 2.49 % and aluminum content of 0.08 %.

2.3. Chemicals and reagents

Ascorbic acid (98.0 % purity), potassium persulfate (99.0 % purity), potassium nitrate (99.5 % purity) and potassium chloride (99.5 % purity) were obtained from Unichem, India. Potassium antimony tartarate (99.5 % purity), ammonium molybdate (98.0 % purity), ammonium chloride (99.0 % purity), sodium hydroxide pellets (98.0 % purity), N-1-napthylethylene diamine dihydrochloride (99.5 % purity), phenol (99.47 % purity) and cadmium turnings were obtained from Loba chemie PVT, India. Cupric sulfate (99.5 % purity) was obtained from Starchem, India. Tri-sodium citrate dehydrate (99.0 % purity), p-nitrophenol indicator, calcium chloride (99.5 % purity) and copper turnings were obtained from Rankem, India. Potassium dihydrogen phosphate (99.6 % purity) was obtained from Central Drug House Limited, India. Sodium nitroprusside(99.5 % purity) was obtained from Riedel-de Haen, India. Sodium hypochlorite was purchased from Di avin enterprises limited, Kenya. All other chemicals and reagents were of analytical grade, and were obtained from Kobian Chemical Limited, Kenya.

2.4. Experimental set-up

Four treatments consisting of unamended soil (S), soil amended with 1% phosphorous (SP), soil amended with 1 % biochar (SB) and soil amended with 1% phosphorous plus 1% biochar (SPB) were made from the composite soil sample. The combined mass of each treatment was 1000 g SP, SPB and SB. The different treatments were shaken at 200 rpm for ten minutes in a mixer. Aliquots of 250 g of each treatment (in triplicates) were transferred into 500 ml amber glass containers. Deionized water was added, the soil mixed and compacted to a density of 1.3 g/cm^3, then topped up with more water to 2 mm above the soil surface. The glass containers were then sealed using airtight lids (with septum) to induce anaerobic conditions [41]. The air tight amber containers were incubated at 25 ^{0}C in a Panasonic cooled incubator MIR-154-PE (Japan).

2.5. Determination of total phosphorus

Alkaline persulfate oxidation and ascorbic acid reduction as described in APHA [42] were used to determine the phosphorous levels in the soil samples. The method is based on the formation of a molybdate complex and its subsequent reduction to a highly colored complex, which was quantified using a UV-Vis spectrophotometer (Jasco V-630 UV/VIS – Tokyo, Japan) at 885 nm.

2.6. Determination of nitrogen

Total nitrogen and total oxidized nitrogen were extracted and determined as described in APHA [42].

2.6.1. Total nitrogen

An aliquot of 0.2 g wet soil sample was digested at 121 ^{o}C for 15 min in an autoclave steam sterilizer after addition of 1 g potassium persulphate, 1 ml of 3.75 M sodium hydroxide and 40 ml deionised water. After cooling, the mixture was filtered and the filtrate eluted through a copper cadmium column to reduce nitrates to nitrites. The column was prepared by reacting 100 g of cadmium turnings with 10 g in 500 ml copper (II) sulfate solution, followed by packing them in a glass tube plugged at the bottom with copper turnings and cotton wool. The column was filled with copper-cadmium mixture and ammonium chloride solution to a 30 cm height.

A volume of 1 ml sulfanilamide was added to each eluate and the mixture vigorously shaken and allowed to rest for 5 minutes. To this mixture, 1 ml of N-1-Naphthylethylene diamine dihydrochloride was added followed by vigorous shaking to ensure proper mixing, and the resultant solution was also shaken thoroughly. The samples were rested for 1 h for the pink color to form before spectrophotometric analysis at 543 nm. Standard solutions were made from anhydrous potassium nitrate, and treated in a similar manner to the samples.

2.6.2. Total oxidized nitrogen

An aliquot of 2 g wet soil sample was mixed with 30 ml of 2 M

potassium chloride. The mixture was then shaken for 30 minutes, centrifuged at 5000 rpm for 15 minutes and then filtered. The filtrate was then passed through the copper-cadmium column and total oxidized nitrogen determined as earlier described.

2.6.3. Ammoniacal nitrogen

The indophenol blue photometric determination of ammonium as described by APHA [42] was used. Indophenol blue complex was formed after conversion of ammonium to monochloroamine under alkaline conditions. This process is very slow and takes 24 hours. Sodium citrate was used to prevent precipitation of hydroxides as nitroprusside served as a catalyst. The absorbance was measured at 630 nm using different concentrations of anhydrous ammonium chloride for calibration.

2.6.4. Organic nitrogen

Organic nitrogen was calculated as;

Organic N = Total N – (TON + ammoniacal N)

2.7. Determination of organic carbon

2.7.1. Determination of total organic carbon

Total organic carbon (TOC) was determined as described by Bojko and Kabala [43]. The soil was oven-dried to constant mass at 105 ^{o}C. A 5 g aliquot of the dried soil was heated for 5 h in a furnace at 550 ^{o}C, and the post ignition mass weighed. The total organic matter (TOM) was calculated by substracting post-ignition mass from the pre-ignition mass. TOC was then obtained from the expression y = 0.52x – 0.55, where y is the TOC and x is the TOM.

2.7.2. Determination of dissolved organic carbon

Dissolved organic carbon (DOC) was determined by extracting 0.5 g soil sample aliquots with 50 ml of 0.01 M calcium chloride solution (soil: solution ratio of 1:2, m/V). The mixture was equilibrated by gentle shaking for 24 hours on an orbital shaker, followed by centrifugation for 10 minutes at 2000 rpm. The resultant supernatant was passed through 0.45 μm filters, and the filtrate subjected to UV-Vis spectrophotometric analysis (Jasco V-630 UV/VIS – Tokyo, Japan) at 340 nm and 355 nm [44]. DOC was calculated by using the absorbance measurements obtained at the two wavelengths (For details of the calculations, see [45]).

2.8. Determination of soil pH

A 5 g soil aliquot was mixed with 0.01 M calcium chloride in the ratio of 1:2 (m/V) in a 50 ml centrifuge tube and shaken for 1 hour. The mixture was allowed to settle for 1 hour, then vigorously shaken for 1 minute and the pH instantly determined by a pH meter.

2.9. Determination of greenhouse gas emissions

A gas chromatographic method described by Wang et al. [46] was used for determining the greenhouse gases (GHGs). Sampling was done after 1, 2, 4, 8, 12, 14, 18, 21, 25, 40, 46, 50, 54, 60, 65, 67, 70, 73, 76, 81, 83, 87, 90, 95 and 100 days. A syringe was inserted into the head space of the flask through the septum on the lid, and a volume of 5 ml was sampled. Analysis of GHGs was done using a Gas Chromatograph (SRI 8610 C, USA).

The following calculations were used to determine the concentration of the GHGs in μg/ g soil. The total mole (N_{tot}) of all the gases in the flask was determined as:

$$N_{tot} = PV/RT \quad (I)$$

where V is volume of headspace (0.00035) in m^3, P is atmospheric pressure (101325 Pa), R is a proportionality constant (8.314 J/mol.K) and T is the incubation temperature of 298 K.

$$\text{Moles of greenhouse gas (GHG), A} = (\text{ppm value}/1000000) \times N_{tot} \quad (II)$$

The concentration of a GHG in μg/g of soil was then given as:

$$(\text{GHG})\ \mu g/g \text{ of soil} = \{(\text{GHG})A \times RFM \times 106)\}/\text{Mass of soil used (100 g)} \quad (III)$$

Addition of all the measured gas concentrations of a treatment gave the cumulative GHG emission.

2.10. Quality assurance

Standards were run before analysis of real samples to check for degradation and sample analysis only done once the system was stable, and a standard was also injected after every 3 samples. External standard calibration was done for both UV-Visible and GC analysis. For UV–visible spectroscopy, and the absorbance of all analyzed samples and standards was between 0.1 and 1.0 to ensure adherence to Beer Lambert's law. The integrity of the calibration curve was confirmed after every ten samples by running the maximum and minimum concentration standard mixtures. All samples were prepared and analysed in triplicates.

2.11. Statistical analysis

The significance of analytical results was determined at confidence limits of 5%. Analysis of variance (ANOVA) was done and T- test ($P \leq 0.05$) was used to check for significant variations in phosphorus, nitrogen and greenhouse gases in the various treatments. Correlation studies were also conducted to ascertain relationships between the various parameters.

3. Results and discussion

3.1. Phosphorous

3.1.1. Initial total P levels

Fig. 1(a) shows the total P levels in the four treatments. The total P values were 500.11 ± 34.38, 1001.98 ± 30.34, 1709.51 ± 101.40, and 978.90 ± 47.2 μg/g of soil, for S (soil), SP (soil + phosphorus), SPB (soil + phosphous + biochar) and SB (soil + biochar), respectively. These results established that biochar increased total phosphorus. This is attributed to the 0.09 % P in the biochar used. Increased total P with biochar amendment is also reported by Kahura et al. [47], Chen et al. [48] and Lehmann and Joseph [5], who further claimed that the main source of P found in biochar is the charring of woody tissues during biochar manufacture.

3.2. Effect of biochar amendment on initial total N levels

Fig. 1(b) shows variations in the initial total nitrogen of the four treatments. The mean total nitrogen, in decreasing order, for the treatments was S, SB, SPB and lastly SP. The decrease in total N with P amendment, as evident in the significant difference between S and SP, could mean that P enhances N mineralization in soil. This P reduction of total N is, however, minimized by co-application of P and biochar (SPB). This result contradicts the increased total N result reported by Naiz et al. [49]. There was no significant difference between S and SB. This implies that biochar had no effect on total N. A similar result was reported by Knicker [50], who attributed this to the formation of heterocyclic compounds like pyrrole, imidazoles, and pyridines, by nitrogen inherent in plant biomass during pyrolysis. This makes them unavailable in the short term [51].

3.3. Effect of biochar amendment on initial total organic carbon (TOC) levels

Fig. 1(c) shows the initial total organic carbon (TOC) levels in the

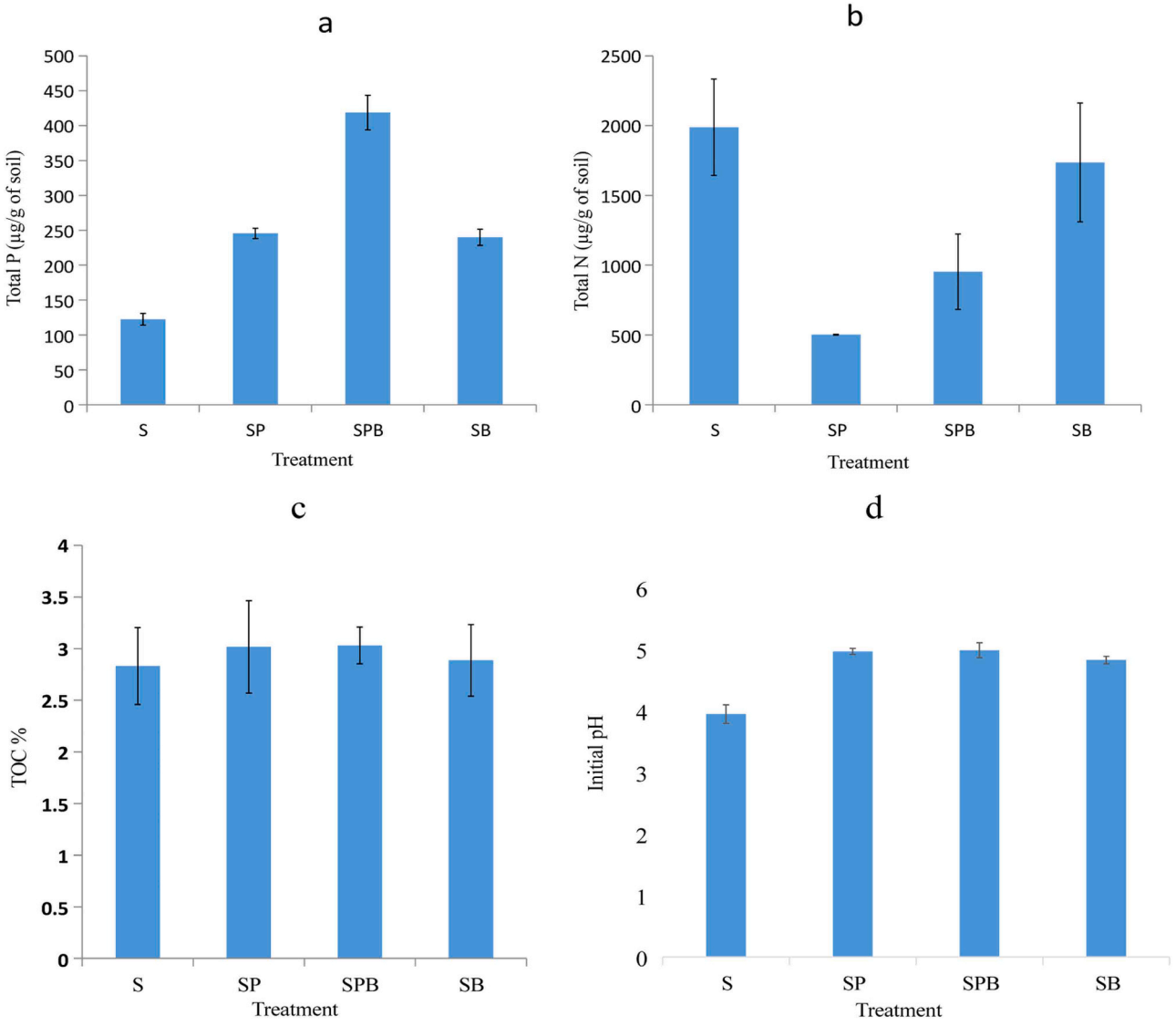

Fig. 1. Initial total P (a), total N (b), total C (c) and pH levels in the different treatments.

four treatments. The mean TOC values, expressed as percentages (W/W) for S, SP, SPB and SB, were 2.83 ± 0.37, 3.02 ± 0.45, 3.03 ± 0.18, and 2.89 ± 0.35, respectively. The lack of significant differences between the treatments implies that biochar had no impact on soil TOC content. This contradicts the findings of decreased TOC [52] and increased TOC [53,54] with biochar amendment. These two studies were, however, conducted under aerobic conditions.

3.4. Effect of biochar amendment on initial pH levels

Fig. 1(d) shows the initial pH levels in the four treatments. A significant difference ($P \leq 0.05$) was registered between S and SP, SPB and SB. Addition of both biochar and P increased the initial pH but their co-application had no effect on initial soil pH. The reduced initial pH with biochar amendment could be attributed to its liming effect caused by its ash content, base cations as well as intrinsic alkaline functional groups found within the biochar [3,55]. This shows that both biochar and P could neutralize some of the acids in the soil. This result agrees with other findings of increased soil pH with biochar amendment [18-20,56].

3.5. Variation of total P during the incubation of biochar-amended soil

Fig. 2(a) shows the variation in total P over the incubation period in the four treatments. Using S as the control, a significant difference in total P was noted with SP, SPB and SB, and also between SP and SB. However, between SP and SPB, and S and SB, no significant difference was registered. P addition therefore increased total P throughout the incubation period, as evident in SP and SPB, while biochar had no effect. The initial total P was high but reduced during the incubation period for all the treatments. This could be due to P loss as it dissolves in the water used to flood the soil [57-59].

3.6. Variation of pH during the anaerobic incubation of biochar-amended soil

Fig. 2(b) shows the variation in pH over the incubation period in the four treatments. The mean pH values were 5.22 ± 0.1, 5.73 ± 0.1, 5.94 ± 0.07 and 5.56 ± 0.08 for S, SP, SPB and SB respectively. S was significantly different ($p \leq 0.05$) from SP and SPB. There was also a significant difference between SB and SPB. All the treatments had their pH rising in the first 21 days. S, SP and SPB attained relatively stable pH values after the 21st day while that of SB dropped. The reduction in the pH of SB could be due to acidic intermediates during the mineralization of biochar [60]. The no significant difference between S and SB implies that biochar never impacted on soil pH. This no effect result was also reported by other researchers [21,22]. However, this result differs with

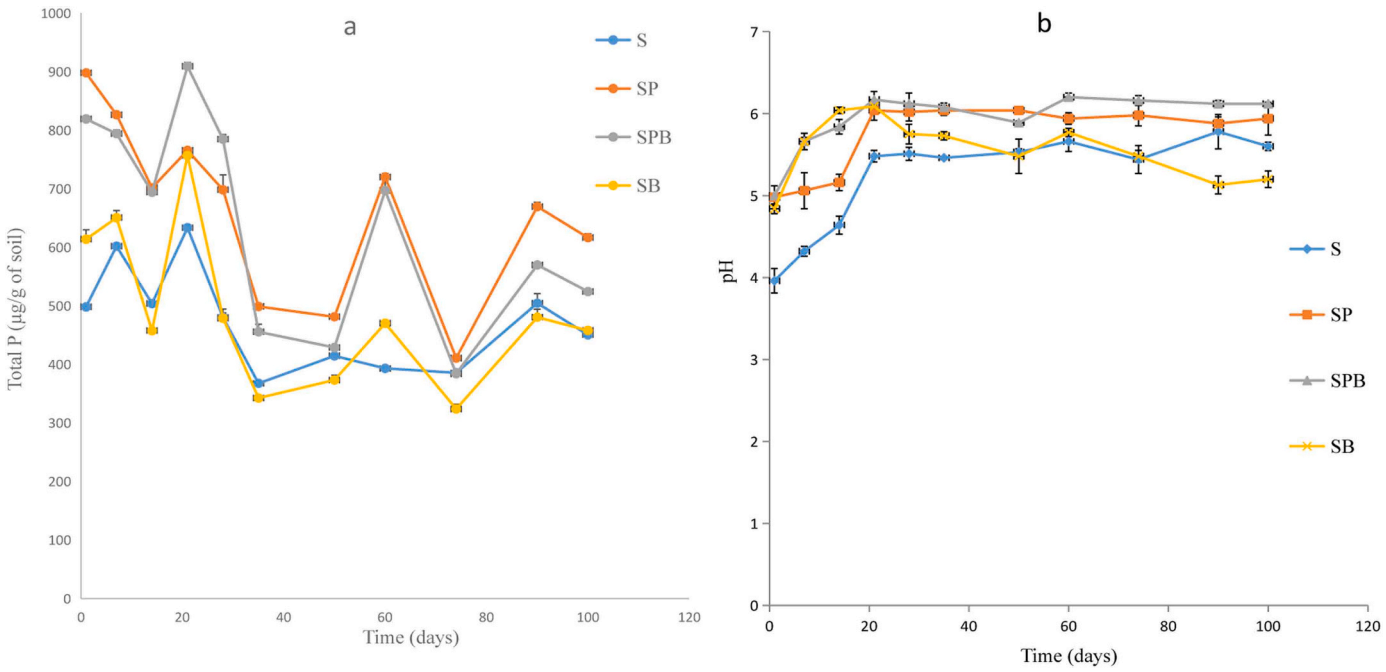

Fig. 2. (a): Variation of total P (a) and pH (b) with time during the anaerobic incubation of biochar-amended soil.

reports of increased soil pH with biochar amendment [18-20].

3.7. Variation of pH during the anaerobic incubation of biochar-amended soil

Fig. 2(b) shows the variation in pH over the incubation period in the four treatments. The mean pH values were 5.22 ± 0.1, 5.73 ± 0.1, 5.94 ± 0.07 and 5.56 ± 0.08 for S, SP, SPB and SB respectively. S was significantly different ($p \leq 0.05$) from SP and SPB. There was also a significant difference between SB and SPB. All the treatments had their pH rising in the first 21 days. S, SP and SPB attained relatively stable pH values after the 21st day while that of SB dropped. The reduction in the pH of SB could be due to acidic intermediates during the mineralization of biochar [60]. The no significant difference between S and SB implies that biochar never impacted on soil pH. This no effect result was also reported by other researchers [21,22]. However, this result differs with reports of increased soil pH with biochar amendment [18-20].

3.8. Variation of nitrogen forms during the anaerobic incubation of biochar-amended soil

3.8.1. Variation of total oxidized nitrogen (TON)

The trend of TON with time for the four treatments is shown in Fig. 3 (a). The mean TON for S, SP, SPB, and SB was 41.31 ± 1.25 µg/g of soil, 42.44± 1.74 µg/g of soil, 43.60± 5.11 µg/g of soil and 45.55 ± 3.97 µg/g of soil, respectively. A significant difference was noted between S and SP, but not between the other treatments. This result differs with other reports of increased TON [16,17] and decreased TON [14,15] in soil amended with biochar.

3.8.2. Variation of ammoniacal nitrogen

Fig. 3(b) displays the trend of ammoniacal N over time for the various treatments. The average levels of ammoniacal N were 250.56 ± 9.13 µg/g of soil, 255.78 ± 8.81 µg/g of soil, 271.56 ± 20.31 µg/g of soil and 192.55± 38.95 µg/g of soil for S, SP, SPB and SB respectively. No significant difference was registered between the treatments using both S and SP as the control. High levels of ammoniacal N was registered in the first week for S, SP and SPB, although it drastically reduced in week two of incubation. The initial increase in ammoniacal N could be due to dissolution of soluble organic and mineral compounds on biochar outer and inner surfaces via dissolution of salts, ion exchange, sub-micrometer particle detachment, and preferential dissolution at crystal imperfections [11,61,62]. Long et al. [11] further reports that release of nutrients from biochar is rapid over the first week and much slower over the subsequent weeks, except for acidic soils that are low in nutrients. Biochar amendment therefore had no effect on ammoniacal N, a result that is similar to other findings [16,17]. However, it contradicts other reports of reduced ammoniacal N with biochar amendment [14,15].

3.8.3. Variation of organic nitrogen

The trend of variations in organic N for the various treatments is shown in Fig. 3(c). The average organic nitrogen levels were 1695.90 ± 118.56 µg/g of soil, 340.38 ± 4.30 µg/g of soil, 637.67 ± 98.43 µg/g of soil and 1498.05 ± 156.12 µg/g of soil, for S, SP, SPB, and SB respectively. S was significantly different from SP and SPB but not SB. The result showed that biochar had no effect on organic N but P amendment reduced it. When biochar was co-applied with P, it reduced the organic N (SPB and SP). Zhu et al. [17] also reported no effect of biochar on organic N. The reduced organic N in SPB could be due to introduction of more N sorption sites by biochar.

3.9. Variation of dissolved organic carbon (DOC) levels during the anaerobic incubation of biochar-amended soil

Fig. 3(d) shows the variation in DOC over the incubation period in the four treatments. The mean DOC levels were 0.802 ± 0.016 mg/L, 0.769 ± 0.036 mg/L, 0.769 ± 0.013 mg/L and 0.776 ± 0.025 mg/L for S, SP, SPB and SB, respectively. S had high initial DOC levels. which reduced then rose steadily to a high of 0.8686 ± 0.033 mg/L. SP, SPB and SB registered the highest DOC levels on the 35th day, followed by a drop and then a slight increase between 74th -100th day. There was no significant difference between the treatments. However, a comparison of the means with S as control showed significant differences with the other treatments. The study established that P and biochar decreased mean soil DOC levels under anaerobic conditions. This finding on biochar use agree with a report by Johnson and Couto (2015). Biochar provides high DOC levels at the initial stages [63], that it further stabilizes by raising the cation exchange capacity of the soil.

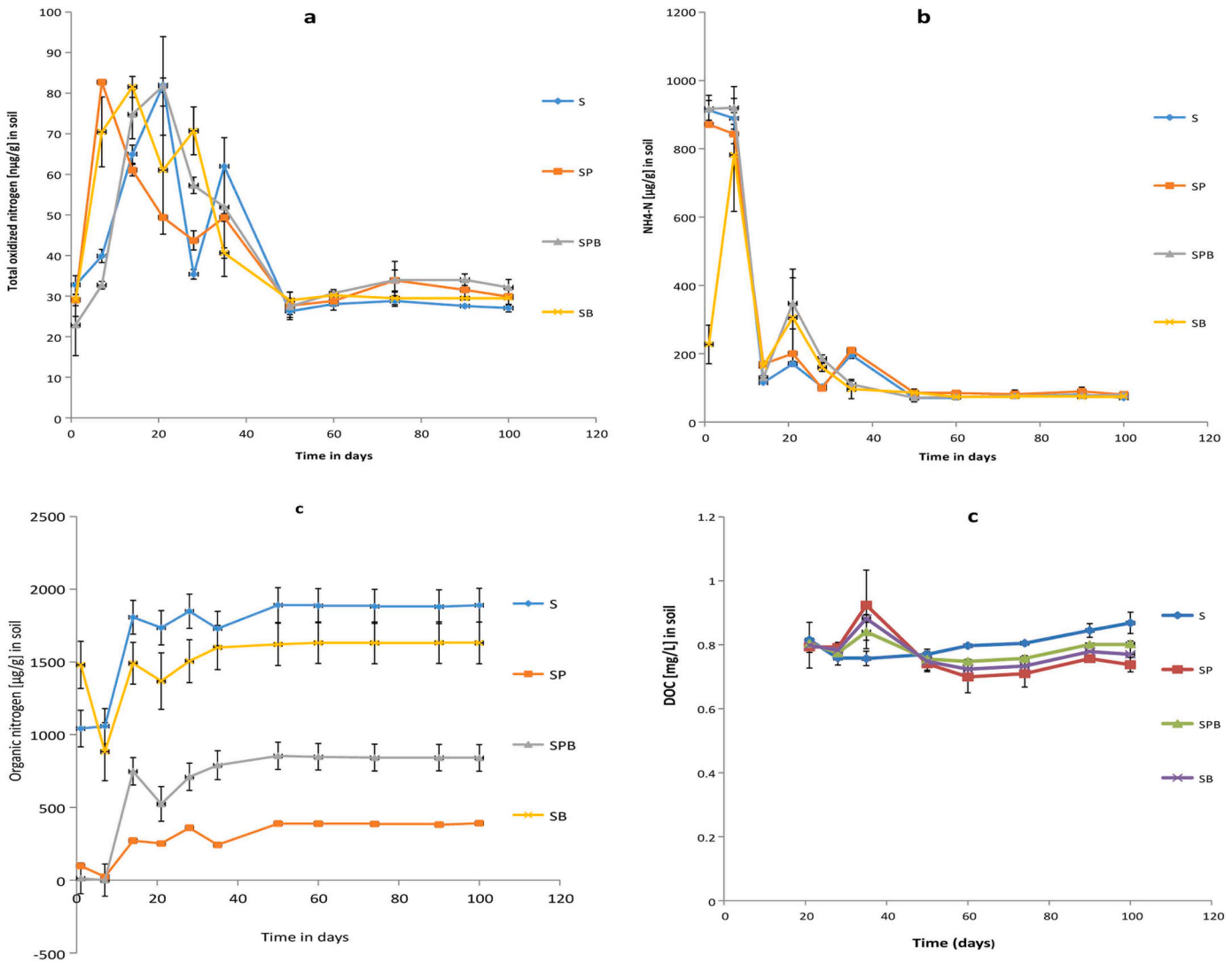

Fig. 3. : Variations in TON (a), $NH4^{+}$-N (b), organic-N (c) and DOC (d) during the anaerobic incubation of biochar amended soil.

3.10. Effect of biochar amendment on greenhouse gases emissions in tropical soil under anaerobic conditions

3.10.1. Nitrous oxide emissions

Fig. 4(a) shows the variations in cumulative N_2O emission with time for the four treatments. The average N_2O levels emitted from S, SP, SPB, and SB were 20.91±2.45 µg/g of soil, 19.97±2.94 µg/g of soil, 18.59 ±2.10 µg/g of soil and 16.47±1.09 µg/g of soil respectively. Initially, in all the treatments, the levels of N_2O were low while ammoniacal N levels were high. This implies that denitrification was dominated over by dissimilatory reduction of nitrates, although it later surpassed it [64]. A sudden rise was noted in the concentration of N_2O emitted in all the treatments from the 40th day. Significant differences were registered between S and SP, and also between SP and SB, from the 40th day onwards. SP had a sharp rise but it was eventually overtaken by S. Relatively low mean N_2O emissions were witnessed in SPB and SB. SP had higher cumulative emission than the other treatments showing that P increases N_2O emission. Increased N_2O emission with P addition was also reported by Liimatainen et al. [65], who attributed the increase to P stimulating the mineralization of organic N and providing substrates for microbial activity. A co-application of P and biochar, in this work, results into lower N_2O emissions indicating that biochar suppresses the enhancing effect of P on N_2O emissions. The lack of difference between S and SB shows that biochar had no effect on N_2O emissions. A similar finding was reported for acidic ultisols amended with maize stalk biochar [66]. This finding, however, differs from other studies that reported increased N_2O emissions with biochar amendment [67,68] and reduced N_2O emissions with biochar amendment [24,31,34,35,69,70,36].

3.10.2. Carbon dioxide emissions

Fig. 4(b) shows the variations in cumulative CO_2 emission against time, for the various treatments. The average CO_2 emitted were 9.55± 5.06 µg/g of soil, 6.97± 2.97 µg/g of soil, 7.11± 3.68 µg/g of soil and 5.96± 2.89 µg/g of soil, for treatments S, SP, SPB and SB respectively. There was a reduction in mean CO_2 emissions from biochar treated soils (SPB and SB) with respect to S. A reduction of 26.99 %, 25.53 % and 37.58 % in mean CO_2 emissions for SP, SPB and SB with respect to S was registered. From Fig. 4(b), the cumulative CO2 emission was higher in S than in the other treatments (SP, SPB and SB), hence both P and biochar suppress CO_2 emissions. This reduced CO_2 emission could be because of inhibition of microbial activity as a result of soil environment alterations, and the strong adsorption of organic matter by biochar making them unavailable for mineralization [71]. Furthermore, the rise in cation exchange capacity of soils due to biochar amendment stabilizes DOC resulting into low mineralization hence less emission of CO_2 [63, 72]. This reduced CO_2 emission due to biochar amendment is also reported in other studies [28,73,26].

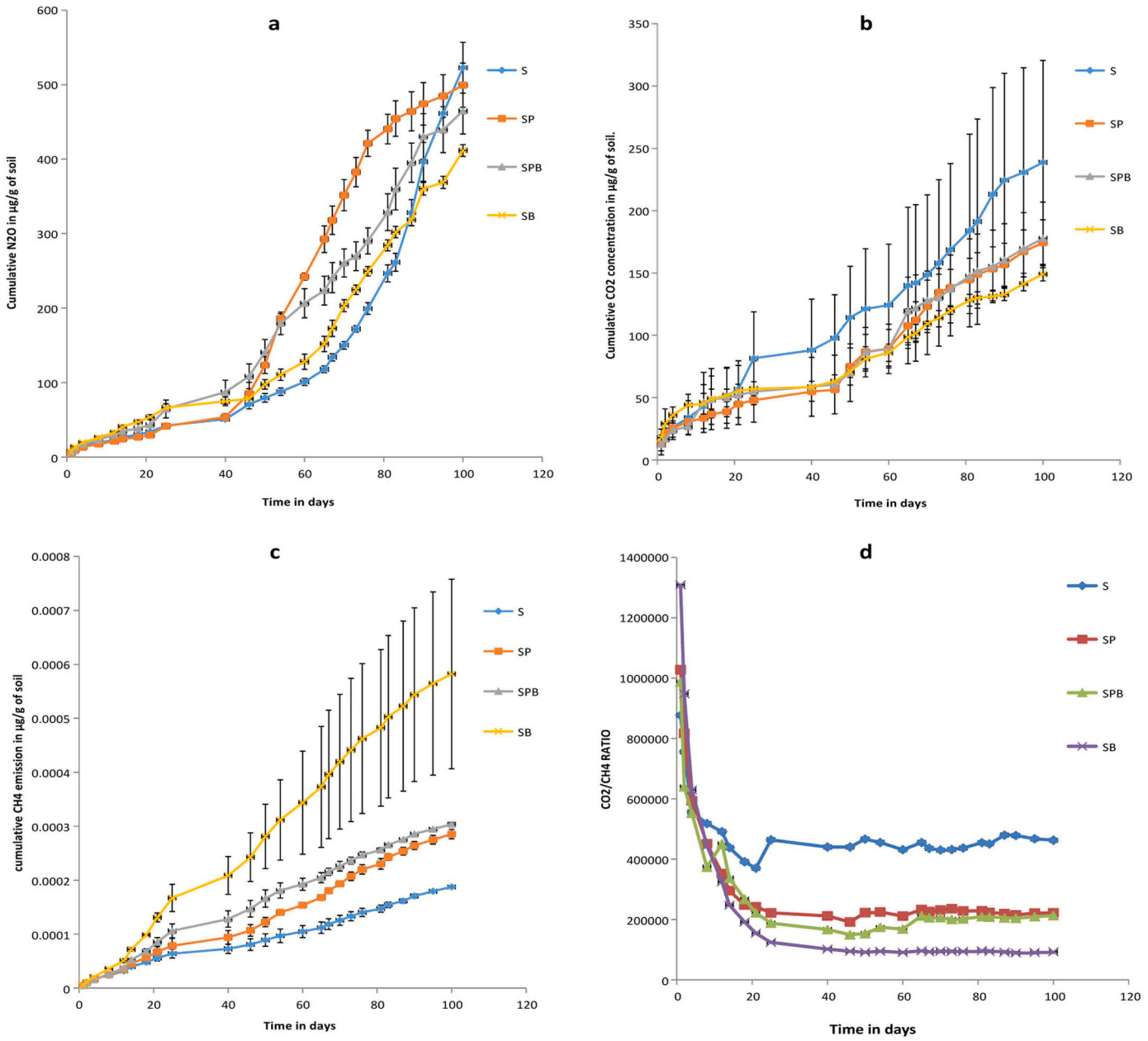

Fig. 4. : Cumulative N_2O emissions (a), CO_2 emissions (b), CH_4 emissions (c) and CO_2:CH_4 ratio (d) in the four treatments over the incubation period.

3.10.3. Methane emissions

The cumulative methane emission in the four treatments over time is presented in Fig. 4(c). The mean methane emission levels from S, SP, SPB and SB were 7.52 $\times 10^{-6} \pm$ 1.05$\times 10^{-6}$ µg/g of soil, 1.14 $\times 10^{-5} \pm$ 2.97$\times 10^{-6}$ µg/g of soil, 1.21 $\times 10^{-5} \pm$ 2.61$\times 10^{-6}$ µg/g of soil, and 2.33 $\times 10^{-5} \pm$ 3.4$\times 10^{-6}$ µg/g of soil, respectively. Biochar amendment significantly increased cumulative methane emission. S was significantly different from SP, SPB and SB. This increase in methane emission could be because biochar supplies labile carbon to the soil [21,46], and the labile carbon provides increased substrates for methanogenic activity [44]. The chemicals in biochar may also contribute to this increase by inhibiting the activity of methanotrophs [73]. Methane is a by-product of mineralization of organic matter under anaerobic conditions. The main pathways for this process are acetotrophy and reduction of carbon dioxide by hydrogen [74]. Temperatures above 30 ^{o}C and pH levels below 6 attenuate methane production via these pathways [75]. All the treatments in this study had pH values below 6 although the temperature was fixed at 25 ^{o}C.

SP was significantly different from SB but not SPB. The lack of significant difference between SP and SPB implies that P lowers methane emission from biochar amended soils, although how this is achieved remains unclear.

Methane emissions from all the treatments were much lower than those of nitrous oxide and carbon dioxide. This could be because of few methanogens, toxic environment for methanogenesis, or availability of readily degradable organic matter serving as terminal electron acceptors [64]. Furthermore, the high concentration of nitrous oxide could mean the presence of large amounts of toxic denitrification intermediates suppressing the operation of methanogens, hence low methane emission [76]. Increased methane emission by soils amended with biochar has also been reported by other researchers [30,21,46,77,13]. In addition, the methane emission was attenuated by increased rate of biochar [13] and high water content [30,77].

3.11. Variation in the CO_2:CH_4 ratio over the incubation period

To further understand the carbon mineralization dynamics and processes, the cumulative CO_2:CH_4 ratio for the various treatments, over time, was computed and the results are shown in Fig. 4(d). S had the highest CO_2:CH_4 ratio, showing dominance of fermentation over methanogenesis [64]. SP and SPB had relatively lower ratios showing that P reduced the levels of methane and carbon dioxide emitted. Biochar (SB) on the other hand decreased carbon dioxide emission but enhanced methane emission to a greater extent, thus resulting in a much lower ratio. Fermentation predominated over methanogenesis in all the treatments as evidenced by CO_2:CH_4 ratios that are much greater than 2. This very high ratio could be because of predominance of humic substances or thermodynamically favorable dissolved organic matter as terminal electron acceptors, thereby lowering the production of methane [78].

3.12. Interactions among greenhouse gases and soil properties

3.12.1. Interactions among greenhouse gases

Table 1 shows a summary of the results of regression analysis of the greenhouse gases

A significant positive correlation was registered between N_2O and CO_2 as well as between N_2O and CH_4 in SP. This showed that additional P influenced the activity of the anaerobic micro-organisms involved in the production of greenhouse gases. The direct proportionality between N_2O and CO_2 was also reported elsewhere in literature [79-81]. This could be due to shared available substrates like labile carbon and nitrogen [79,82] or shared microbial processes [83]. Ellert and Janzen [80] suggest that soil oxygen consumption during high CO_2 emissions may promote N_2O production. The increase in N_2O production with increased emission of CH_4 was also reported by Kuzyakov [84] in soils with readily available C. These results, however, differ with those of Manono [81] who recorded a negative correlation. Addition of P enhances decomposition of soil organic matter [85,86] thereby releasing carbon, which is a substrate for these reactions. Furthermore, P facilitates desorption of organic C from soil particles by competing with them for sorption sites [41,87]. Table 2

3.13. Correlations among soil properties and GHG emissions

The soil pH negatively correlated with CO_2 emission in SPB but was positively correlated to CH_4 emissions in S and SP (Fig. 2). The negative correlation with CO_2 disagrees with reports of positive correlation with N fertilization published by Wang et al. [88]. The difference could be as a result of the treatments: This study utilizes P and biochar under anaerobic conditions, but in that study N fertilization was utilized under aerobic conditions. The increased CH_4 emission with increase in pH has been reported for acidic soils by other authors [89-91]. Methanogenesis proceeds faster when the pH is maintained between 6.7 and 7.4 [92]. A significant positive correlation was registered between pH and organic N in S, SP, SPB as well as with TON in SB. Similar results were recorded by Sanchez *et. al.* [92] for organic-N. This was attributed to the fact that low pH attenuates hydrolysis of organic matter, thus favoring organic-N and P decomposition [93-95]. Positive correlation with TON has also been reported [96–98]. This could be due to high pH increasing the abundance and diversity of soil bacteria, hence impacting on mineralization of organic-N [96]. Biochar also provides readily available C, which promotes the degradation of organic-N. A significant negative correlation between pH and NH_4-N was recorded in S, SP and SPB, and similar results have been recorded [96,99,100]. N mineralization is limited by low amounts of labile carbon and degradable organic-N Tian et al. [101] and since low pH raises the amount of organic-N, its mineralization results into more NH_4-N.

Methane emission negatively correlated with NH_4-N in S and SP, a finding that is in agreement with other reports in literature [102-104, 89]. This is attributed to the relatively high toxicity of NH_4-N to methanogenic bacteria [76]. It could also be due to NH_4-N stimulating and enhancing the growth and activity of methane consuming bacteria in soils [102,104].

DOC positively correlated with NH_4-N and TON, but negatively correlated with organic-N, in SP and SB. Similar results have been reported by Tian *et al.* [101]. DOC contains readily available C for microorganisms [28] and hence attenuates the mineralization of organic-N to NH_4-N and TON. A significant positive correlation was also recorded between DOC and P in SB, a finding that is similar to other reports [105, 106,86]. This could be because P addition increased the decomposition of organic matter in biochar, thus releasing available carbon [86]. Furthermore, P addition may cause desorption of organic C from mineral surfaces [87] causing an increase in DOC.

In SPB, addition of P negatively correlated with N_2O emissions, and similar results have been reported [107-110]. This is attributed to P stimulating the immobilization of N thus lowering the denitrification process (Sundareshwar *et al.,* 2013) or P limiting the abundance of denitrifying bacteria in soil [107]. This result, however, contradicts reports of a positive correlation between P and N_2O [65,86]. Addition of P also negatively correlated with CH_4 emissions in SP. This result was also reported by Kumar and Viyol [111] who attributed it to inhibition of methanogens by sulfate impurities in the P fertilizers. Soil NH_4-N was significantly increased by P addition in SP and SPB, a finding that has been reported elsewhere in literature [86,112]. This could have been driven by mineralization of organic-N, stimulated by P [48,113,114]. Arnon [112] stated that rapidly absorbable cations like NH_4^+ favor the absorption of anions like $H_2PO_4^-$. A significant positive correlation was

Table 1
Regression analysis of the greenhouse gases to establish interactions.

Parameters	*Treatment*		*Coefficients*	*Standard Error*	*t Stat*	*P-value*	*R2*	*r*
N_2O vs CO_2	S	*Intercept*	1841.81	1474.93	1.25	0.22	0.08	0.27
		Gradient	1.07	0.78	1.37	0.18		
	SP	*Intercept*	1584.63	1037.9	1.53	0.14	0.17	0.41
		Gradient	1.54	0.72	2.14	0.04		
	SPB	*Intercept*	2999.65	615.25	4.88	6.35E-05	0.008	0.09
		Gradient	0.16	0.37	0.42	0.68		
	SB	*Intercept*	2847.17	710.62	4.01	0.00	6.63E-05	0.008
		Gradient	-0.02	0.57	-0.04	0.97		
N_2O vs CH_4	S	*Intercept*	-5934.85	5891.28	-1.01	0.32	0.10	0.32
		Gradient	2689.17	1651.04	1.63	0.12		
	SP	*Intercept*	-4693.38	1705.99	-2.75	0.01	0.51	0.72
		Gradient	1507.65	306.01	4.93	0.00		
	SPB	*Intercept*	2247.94	1175.17	1.91	0.07	0.03	0.18
		Gradient	164.15	191.94	0.86	0.40		
	SB	*Intercept*	2803.36	1085.52	2.58	0.02	1.87E-05	0.004
		Gradient	1.90	91.82	0.02	0.98		

Table 2
Correlations among soil properties and GHG emissions in (a) S, (b) SP (c) SPB and (d) SB (n = 10, df = 8, critical value for Pearson, Crit. = 0.632, P = 0.05).

(a)

	TON	*NH_4-N*	*ORG-N*	*DOC*	*pH*	*CH_4*	*N_2O*	*CO_2*	*T.P*
TON	1.000								
NH_4-N	0.001	1.000							
ORG-N	-0.057	-0.998**	1.000						
DOC	-0.002	-0.073	0.048	1.000					
pH	-0.181	-0.881**	0.890*	0.464	1.000				
CH_4	0.016	-0.893**	0.891*	0.268	0.859*	1.000			
N_2O	-0.430	-0.418	0.441	0.875*	0.536	0.483	1.000		
CO_2	-0.358	-0.060	0.080	-0.586	0.124	0.088	-0.089	1.000	
T.P	-0.209	-0.383	-0.279	-0.173	0.199	0.712*	0.469	-0.508	1.000

(b)

	TON	*NH4-N*	*ORG-N*	*DOC*	*pH*	*CH4*	*N2O*	*CO2*	*T.P*
TON	1.000								
NH_4-N	0.457	1.000							
ORG-N	-0.667**	-0.955**	1.000						
DOC	0.796*	0.649*	-0.689**	1.000					
pH	-0.539	-0.836**	0.845*	0.413	1.000				
CH_4	-0.225	-0.766**	0.729*	-0.616	0.718*	1.000			
N_2O	-0.530	-0.528	0.643*	-0.536	0.501	0.322	1.000		
CO_2	-0.388	0.136	0.000	-0.216	0.044	0.157	-0.059	1.000	
T.P	-0.821**	-0.642**	-0.547	-0.407	0.511	0.401	0.708*	-0.563	1.000

(c)

	TON	*NH4-N*	*ORG-N*	*DOC*	*pH*	*CH4*	*N2O*	*CO2*	*T.P*
TON	1.000								
NH_4-N	-0.176	1.000							
ORG-N	0.116	-0.998**	1.000						
DOC	0.474	0.465	-0.467	1.000					
pH	0.318	-0.806**	0.794*	0.217	1.000				
CH_4	0.601	-0.440	0.407	-0.134	0.493	1.000			
N_2O	-0.387	-0.589	0.618	0.320	0.516	-0.294	1.000		
CO_2	-0.569	0.289	-0.257	0.103	-0.656**	-0.399	0.083	1.000	
T.P	-0.324	0.08	-0.659**	-0.153	-0.64**	0.605	0.481	0.368	1.000

(d)

	TON	*NH4-N*	*ORG-N*	*DOC*	*pH*	*CH4*	*N2O*	*CO2*	*T.P*
TON	1								
NH_4-N	0.538	1							
ORG-N	-0.604	-0.997**	1						
DOC	0.666*	0.692*	-0.709**	1					
pH	0.716*	0.206	-0.262	0.154	1				
CH_4	0.120	-0.312	0.283	0.013	0.592	1			
N_2O	-0.557	-0.491	0.517	-0.010	-0.428	-0.077	1		
CO_2	-0.341	0.201	-0.158	-0.437	-0.612	-0.651**	-0.285	1	
T.P	0.185	-0.232	-0.437	0.23	0.714*	0.393	0.654*	-0.656**	1

* shows significant positive correlation while ** show significant negative correlation.

recorded between P and TON in S, and this is similar to the results of Ullah et al. [86]. This could be due to activation of microorganisms as a result of addition of P, which caused release of P and N by enhancing mineralization of organic matter.

4. Conclusion

Biochar amendment increased total P, and initial soil pH, decreased mean DOC but had no effect on total nitrogen and DOC over time. Additional P increased total P and soil pH, reduced total N, but had no significant effect on TOC or DOC. Therefore, by not causing suppression of soil nitrogen, biochar outperformed additional P as a fertilizer. Biochar increased methane emission, reduced carbon dioxide emission, but had no effect on N_2O emissions. Fermentation predominated over methanogenesis – with highly suppressed methane production. Therefore, with increased P and limited GHGs emissions, biochar can be sustainably used as a P fertilizer in tropical paddy soil.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

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