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Potential of biochar amendment as phosphorus source in tropical paddy soil

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ABSTRACT

Phosphorus (P) is an essential element for crop production but its non-renewable natural sources are on the verge of depletion. The few remaining P sources may be depleted in the next 30–50 years. This calls for P recycling strategies with biochar application being an appealing approach. However, very limited information is available on the use of biochar as a P source and how it affects the various P fractions in tropical paddy soils. Therefore, the aim of this study was to establish whether biochar could potentially be used as a P source. A sample tropical paddy soil was treated with 1% biochar (derived from maize straw) and/or potassium dihydrogen phosphate, waterlogged and then incubated in airtight amber glass containers at 25 °C, to mimic tropical paddy soil conditions. Soil aliquots were sampled periodically, followed by extraction and analysis of P fractions. The generated data was subjected to correlation analysis to explore the relationships among the P fractions. The study established that under anaerobic conditions, biochar amendment and P fertilization had no effect on aluminium bound P, calcium bound P, occluded P, moderately labile P and non-labile P. Additional P increased loosely sorbed P but biochar reduced it, even when combined with supplementary P fertilization. It was established that biochar increased iron bound P and to a greater extent with P fertilization. Additional P increased labile P while it was not affected by biochar. Apart from the effect on loosely sorbed P, biochar performed as well as the P fertilizer—or better in case of Fe-bound P. There is therefore promising potential for utilization of biochar as an alternative renewable P source.

Keywords: maize-straw-derived-biochar; phosphorus pools; anaerobic conditions; River Yala; Lake Victoria basin; soil incubation

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1. Introduction

Phosphorus (P) is an essential element for plant and animal nutrition^[1] and the second most limiting nutrient after nitrogen for crop production in agricultural areas within the tropics^[2]. Even though soils may contain several hundreds to thousands kilograms of phosphates per hectare, much of this may not be available for plant uptake^[3]. This availability is controlled by sorption, desorption and precipitation processes in the soil^[4]. Phosphorus occurs in soil in both organic and inorganic forms, which vary in their rates of P release^[5]. The original sources of soluble P in soil are the primary P minerals, mainly apatite. However, the levels of these minerals decrease in soil with continued weathering^[5]. Natural sources of P (phosphate rock) have decreased and only a few mines are left in the world (in North Africa)—and these may be depleted in the next 30–50 years^[6]. This demands the need for P recycling approaches (from flora and fauna) and biochar use could be a potential P source.

Biochar technology has gained a lot of attention worldwide because of its potential to enhance plant available P, and serve as an alternative source of P when used for soil amendment^[7,8]. The plant available P fractions are mainly the loosely sorbed and those bound on aluminium and calcium^[9]. In acidic soils, biochar is reported to greatly increase available P by releasing its labile fraction of P^[7], forming mineral—organic matter complexes with aluminium and iron thus lowering the soil P sorption capacities^[10] or facilitating the growth and activity of P solubilizing soil microorganisms^[11].

Anaerobic conditions could potentially increase P availability of fixed P forms^[12]. The mechanisms for release of the fixed P forms include microbially mediated reductive dissolution of Fe^{3+} oxides, soil organic matter mineralization, and solubility of iron bound P due to increasing pH^[12]. This, however, depends on soil characteristics such as abundance of iron oxides, soil organic matter content and their availability as electron donors, total P content and the soil pH^[13].

Most field trials of the agricultural benefits of biochar have been carried out in poor soils from tropical regions with lower rates of nitrogen fertilization^[14]. Little information is available on the use of biochar with phosphorus fertilization and most of these studies focus on crop yield and nutrient availability rather than nutrient fractions. Moreover, most of the studies are conducted under aerobic conditions.

In high P fixing soils, such as the case of western Kenya^[15], the application of large amounts of inorganic fertilizers can quench the soil P need^[16,17]. However, this is impractical for the impoverished small holder farmers in Kenya^[18]. It has been established that soils in Siaya County are weakly acidic and contain Al^{3+} and Fe^{3+} ions which are responsible for P fixation^[19]. However, they do not explain how and why the soils are deficient of available P. Furthermore, they did not explore the effect of ecological conditions and organic amendments on soil nutrient levels. Moreover, how this high P fixation can be overcome still remains unknown.

Biochar researches conducted in Kenya by Camilla^[20], Aslund^[21] and Andrew and Abigail^[22] report increase in crop yields with application of biochar. The same is reported by Kätterer et al.^[23], and Ernsting^[24]. Whereas the effect of biochar on plant growth is reported, limited information is available on its effect on soil chemistry and nutrient availability. Moreover, the effect on soil fertility parameters with respect to nutrients was not investigated. Soil P dynamics is controlled by pH, Fe³⁺and Al³⁺oxides^[25] as well as soil moisture through redox processes^[26,27]. Many researchers have reported increase in soil available P for soils amended with biochar^[3,28–31]. However, these results are only available for temperate soils with limited reports on tropical soils. Moreover, these studies focus only on plant available P and not on the effect on the various P fractions in the soil, especially under anaerobic conditions.

P availability is a mandatory requirement for sustainable agriculture^[32], although it is deficient in most tropical soils. This has resulted into intense use of mineral fertilizers which are very expensive and the sources are on the decline hence the need for alternative sources. The aim of this study was to investigate the effect of anaerobic conditions and biochar amendment on phosphorus fractions.

2. Methodology

2.1. Sampling area for soil material

The soil material was collected from Dominion farm in the lower Yala River basin area of Siaya County. The area is located between longitudes 34°1E'7S' and latitudes 00°02'N, 00°02'S covering an area of 17,050 acres. The sample was collected between 00.00931°S and 034.15915°E with an elevation of 1134 m. Yala swamp was reclaimed for agricultural activities to produce cereals and horticultural crops by Lake Basin development authority. They leased the land to Dominion group of companies (USA) for the main purpose of producing rice which is an important crop for global food security^[33].

2.2. Sample collection and characterization

2.2.1. Collection and characterization of soil material

A mass of 1 kg soil samples were collected from ten randomly selected sites within the Dominion farm using a soil auger to a depth of 30 cm^[34]. The samples were packed in labelled cellulose bags then transported to the laboratory. The samples were air dried for one week then ground and sieved through a 2 mm diameter stainless steel sieve. A composite sample was then prepared by mixing 200 g of each sample in a mixer operating at 200 rpm. The soil was characterized at Kenya Forestry Research Institute (KEFRI) in Maseno and Kenya Agricultural and Livestock Research Organization (KALRO) in Kisumu Kenya. The soil consisted of 68.04% sand, 7.4% silt and 24.56% clay. It had a pH of 4.2, cation exchange capacity of 9.3 meq/100 g of soil and contained 1694.2 ppm, 406.2 ppm and 823.9 ppm of calcium, iron and sodium respectively.

2.2.2. Preparation of biochar

The maize-derived biochar was prepared and characterized as reported by Jia et al.^[35]. Maize straw was used to produce biochar under oxygen-limited conditions by a patented biochar reactor (NO. ZL2009 20232191.9). The maize straw was first washed with deionized water and oven-dried for 12 h at 80 °C, then transferred to the biochar reactor and subjected to a step-wise heating program. The starting temperature was 200 °C, followed by elevation to 250 °C and finally 300 °C—with the temperature held constant for 1.5 h at each point. The heating was stopped, at the final temperature, when no further smoke was emitted from the gas exit pipe. After cooling to room temperature, the biochar sample was crushed and passed through a 60 mesh sieve. It had a pH of 6.98, phosphorus content of 0.09%, iron content of 0.09% and aluminium content of 0.08%.

2.3. Chemicals and reagents

The chemicals and reagents used in the extraction and analysis of phosphorus, nitrogen, carbon, and pH were all of analytical grade. Ascorbic acid (98.0% purity), potassium persulfate (99.0% purity) and sodium chloride (99.5% purity) were obtained from Unichem, India; potassium antimony tartarate (99.5% purity), ammonium molybdate (98.0% purity), sodium hydroxide pellets (99.9% purity), sulphuric acid (98.07% purity), hydrochloric acid (38.0% purity) were obtained from Loba chemie PVT, India; sodium hydrogencarbonate (99.9% purity) was obtained from Rankem, India; potassium dihydrogen phosphate (99.6% purity) was obtained from Central Drug House Limited, India; sodium carbonate (99.9% purity) and ammonium fluoride (99.0% purity) were obtained from Finar Limited, India.

2.4. Experimental set-up

The composite sample was subdivided into four portions and then subjected to the treatments as shown in **Table 1**.

Treatment	Soil (g)	P fertilizer KH ₂ PO ₄ (g)	Biochar (g)	Total mass (g)				
S	100.0	0.0	0.0	100.0				
SP	99.0	1.0	0.0	100.0				
SPB	98.0	1.0	1.0	100.0				
SB	99.0	0.0	1.0	100.0				

Table 1. Composition of the various treatments.

The samples were prepared in triplicate with the samples consisting of SP, SPB and SB thoroughly mixed in a mixer at 200 rpm before being transferred into airtight glass flasks (**Figure 1**). Deionized water was then added to each flask up to 2 mm above the compacted soil surface to induce anaerobic conditions. Each flask was then incubated at 25 °C in a Panasonic cooled incubator MIR-154-PE.



Figure 1. Incubation flasks.

2.5. Analysis of phosphorus

2.5.1. Determination of total phosphorus

The soil samples were digested using the alkaline persulphate oxidation and total P determined by ascorbic acid reduction method as described by APHA^[36]. The coloured complex was quantified using a Jasco V-630 UV/V is Spectrophotometer (Tokyo-Japan) at 885 nm. Calibration standard solutions of KH₂PO₄ were made in the range of 0, 5, 10, 20, 40, and 60 μ g/L. The standards and samples were then allowed to stand for 1 h for the blue colour to form prior to spectroscopic analysis.

2.5.2. Inorganic phosphorus fractions

The extraction was based on differences in solubility of various phosphorus fractions in different extracting solvents as outlined by Pierzynski^[37]. A 40 mL volume of ammonium chloride solution was added to each 2 g wet soil sample and then shaken in an orbital shaker (Stuart orbital shaker SO1) at 200 rpm for one hour followed by centrifugation at 3000 rpm for 5 minutes using a Beckman Coulter Allegra X-30R centrifuge (U.S.A). The supernatant was filtered into 100 mL volumetric flask and made up to the mark with deionised water to get loosely bound phosphorus. To the residue was added 40 mL of ammonium fluoride, followed by shaking for 30 min, centrifugation for 15 min and filtration. The residue was rinsed twice with 25 mL aliquots of saturated sodium chloride, and the supernatants were then pooled and analyzed to get aluminium bound phosphorus. The residue was mixed with 40 mL sodium hydroxide, shaken for 17 h, centrifuged at 5000 rpm and vacuum filtered (to avoid re-oxidation of Fe^{2+} to Fe^{3+} due to long exposure to air). The residue was rinsed twice with 25 mL portions of sodium chloride and the supernatant added to the sodium hydroxide extract to give iron bound phosphorus. The residue was added to 40 mL of 0.25 M sulphuric acid, shaken for 1 h, centrifuged and the filtrate was analyzed for calcium bound phosphorus. The pH of the extract was adjusted using 3.75 M sodium hydroxide before addition of the mixed reagent. The residue was then mixed with 40 mL of sodium EDTA, shaken for 1 h, centrifuged and then filtered to obtain occluded phosphorus. The phosphorus level in each of the extracts was determined as described in APHA^[36].

2.6. Organic phosphorus fractions

Organic phosphorus separates into labile, moderately labile and non-labile pools^[38]. Labile organic P was extracted using 0.5 M sodium hydrogen carbonate, moderately labile P using 1 M hydrochloric acid and non-labile P using 2.5 M sulphuric acid as outlined by Pierzynski^[37]. A mass of 2 g wet soil sample was placed into a centrifuge tube and 40 mL of 0.5 M sodium hydrogen carbonate added. The mixture was shaken for 16 h, centrifuged at 5000 rpm for 15 min, filtered through Whatman number 41 filter paper into 100 mL volumetric flask and brought to volume. The supernatant was divided into two equal portions of 50 mL. To the first portion,

5 drops of p-nitrophenol indicator was added, and the pH adjusted using 2 M hydrochloric acid, until it turned colourless. The phosphorus content was then determined as in APHA^[36]. To the second portion, 1 g potassium persulphate and 1 mL 3.75 M sodium hydroxide were added and the mixture digested in an autoclave steam sterilizer at 121 °C for 15 min. The sample was then allowed to cool, filtered and phosphorus determined as in APHA^[36]. The difference in phosphorus levels between the two portions gave the labile organic phosphorus. To the residue was added 40 mL of 1 M hydrochloric acid followed by shaking for 3 h, centrifugation and filtration into 100 mL volumetric flask. The supernatant was brought to volume, mixed and divided into two equal portions. The first portion was analyzed directly for phosphorus, while the second portion was first subjected to alkaline persulphate digestion prior to phosphorus analysis. The difference between the two gave part of the moderately labile phosphorus. The residue was rinsed with deionised water and the supernatant discarded. The resultant residue was mixed with 40 mL of 0.5 M sodium hydroxide and shaken for 3 h, centrifuged and vacuum filtered. The pH of the supernatant was adjusted to 2.0 using 2 M hydrochloric acid, followed by centrifugation at 5000 rpm for 15 min, followed by filtration. Phosphorus was determined in 50 mL of this extract and pooled with the hydrochloric acid extracted moderately labile phosphorus to give the total moderately labile organic phosphorus. The residue was rinsed with deionised water and the supernatant discarded. To the resultant residue was added 40 mL of 2.5 M sulphuric acid followed by 1 g potassium persulphate then digested in a steam sterilizer for 15 min at 121 °C. The mixture was allowed to cool, filtered and the pH adjusted using 3.75 M sodium hydroxide. The phosphorus level was then determined to give nonlabile organic phosphorus.

2.7. Statistical analysis

Data analysis was done using Microsoft Excel version 2010. The means and ranges of the data collected were determined at confidence limits of 5%. One way analysis of variance (ANOVA) was used to determine significant differences at 95% confidence interval and *T*-test $P \le 0.05$ used to check phosphorus variations with each treatment and the duration of incubation.

3. Results and discussion

3.1. Total phosphorus

The total phosphorus content of the various treatments is shown in **Figure 2**. The total P levels for S, SP, SPB and SB were 500.11 ± 34.38 , 1001.98 ± 30.34 , 1709.51 ± 101.40 , and $978.90 \pm 47.2 \ \mu g/g$ of soil, respectively. A significant increase in total P ($P \le 0.05$) was recorded between S and the other treatments while between SP and SB there was no significant difference. These results indicate that addition of biochar increased total phosphorus. This is not surprising given that the biochar had a P content of 0.09% that it brings to the soil. Similar results were reported by Lehmann and Joseph^[14], Zhang et al.^[39] and Kim et al.^[40]. This confirms that the charring conditions during manufacture of biochar does not destroy the P content of the biomass but maintains them in various forms within the particles.



Figure 2. Initial total phosphorus content in the different treatments.

3.2. Inorganic phosphorus fractions

3.2.1. Loosely sorbed phosphorus

The results for loosely sorbed P are shown in **Figure 3a**. The mean loosely sorbed phosphorus levels for S, SP, SPB and SB were $66.106 \pm 4.93 \ \mu\text{g/g}$ of soil, $106.652 \pm 5.38 \ \mu\text{g/g}$, $84.924 \pm 5.91 \ \mu\text{g/g}$, and $49.098 \pm 2.30 \ \mu\text{g/g}$, respectively. A significant difference ($P \le 0.05$) was observed with SP, but not with SPB and SB using S as the control. With SP as the control, a significant difference ($P \le 0.05$) was noted with SB but not with SPB. Higher initial loosely sorbed P was recorded in SP, SPB and SB as compared to S. This could be attributed to the soluble P in biochar and the mineral P fertilizer.



Figure 3. Levels of (a) loosely sorbed phosphorus; (b) aluminium bound phosphorus; (c) iron bound phosphorus; and (d) calcium bound phosphorus over time in the different soil treatments.

In S, the level of loosely sorbed phosphorus rose from the 35th day to a high of $145.417 \pm 9.07 \ \mu g/g$ of soil in the 50th day and remained higher (compared to the initial days) for the remaining incubation period. This increase could be due release of iron bound P as reduction of Fe (III) to Fe (II) raises the pH because of decreased ability of Fe (II) for hydrolysis^[41]. In SP, the phosphorus level reduced as more of it got fixed until the 35th day. After that, it increased and remained steadily high. In SPB, the P level was initially high but dropped from the 14th day to the 35th day before rising again. The variation was significant and can be attributed to changes in the soil pH occasioned by the introduced biochar which is almost neutral but more alkaline compared to the soil or the reducing conditions^[41]. In any case, increased pH resulted in decreased phosphorus levels. SB also initially had high phosphorus levels, which dropped during the incubation period.

The results for S and SP agree with those reported by Xu et al.^[42], and Deluca et al.^[43], that showed increased loosely sorbed P in flooded acidic soils. This was attributed to the fact that increased soil pH on flooding enhanced the release of P fixed on iron by facilitated the reduction of Fe (III) to Fe (II)^[41].

Biochar addition in this study resulted in reduction of loosely sorbed phosphorus. The surface of biochar could be carrying organic molecules that chelates and sorbs Al³⁺, Fe³⁺ and Ca²⁺ ions as organo-biochar complexes or organo-mineral-biochar complexes, hence decreasing P solubility in the short term^[10]. This result contradicts reports of increased loosely sorbed P with biochar amendment by Kalyani et al.^[31] and Kim et al.^[40], although they used alkaline soils.

3.2.2. Aluminium bound phosphorus

Figure 3b shows the results for Al-P. The mean Al-P levels recorded for S, SP, SPB and SB were 34.144 \pm 1.94 µg/g of soil, 39.742 \pm 9.38 µg/g, 32.379 \pm 1.39 µg/g, and 33.841 \pm 1.27 µg/g, respectively. No significant difference ($P \le 0.05$) was recorded in Al-P levels over time and among the treatments implying that biochar amendment or phosphorus application had no effect on Al-P. This could be attributed to aluminium reacting with organic molecules from biochar forming organic complexes saturating the space needed for P precipitation^[43].

This differs with the findings of Eduah et al.^[30] who noted a reduction in aluminium bound phosphorus with biochar treatment. The decrease was due to the fact that addition of biochar increased the cation exchange capacity of soil resulting into increased electrostatic anion repulsion between the negative charges in soil-biochar surfaces and phosphorus ions^[30]. Xu et al.^[42], on the other hand, reported an increase in Al-P with biochar amendment for acidic soil, although the study was conducted under aerobic conditions.

3.2.3. Iron bound phosphorus

The variations in Fe-P over time in the various treatments are shown in **Figure 3c**. The mean Fe-P were $111.402 \pm 11.80 \ \mu\text{g/g}$, $133.076 \pm 17.51 \ \mu\text{g/g}$, $174.75 \pm 9.78 \ \mu\text{g/g}$ and $130.242 \pm 20.12 \ \mu\text{g/g}$ of soil for S, SP, SPB, and SB, respectively. With S as the control, there was a significant difference ($P \le 0.05$) with SPB but not with SB and SP. No significant difference ($P \le 0.05$) in Fe-P was recorded between SP and the other treatments. The level of Fe-P decreased with time for S. This could be due to it being released to the loosely sorbed fraction because of reduction of iron (III) to iron (II) causing the increase in the soil pH^[41].

From the mean levels, it was noted that biochar amendment increased Fe-P. This could be attributed to organic acids produced by incomplete mineralization of organic matter in water soaked soils facilitating phosphorus fixation on iron^[41]. Moreover, biochar may also be carrying some iron within it particles that it adds to the soil fixing more P^[44]. This result of increased Fe-P with biochar amendment agrees with that of Xu et al.^[42] and Kalyani et al.^[31]. This result however differs with that reported by Eduah et al.^[30], who showed decreased Fe-P with biochar amendment, although the study was conducted under aerobic conditions using alkaline soils.

3.2.4. Calcium bound phosphorus

The variations of levels of calcium bound P with time are presented in **Figure 3d**. The mean calcium bound phosphorus (Ca-P) for S, SP, SPB, and SB were $37.720 \pm 3.44 \ \mu\text{g/g}$, $38.599 \pm 2.15 \ \mu\text{g/g}$, $33.758 \pm 1.18 \ \mu\text{g/g}$ and $35.371 \pm 1.42 \ \mu\text{g/g}$ of soil, respectively. There was no significant difference ($P \le 0.05$) among the treatments. This no biochar effect result agrees with a report by Kalyani et al.^[31]. The soil being acidic (pH of 4.2), addition of biochar raises it to between 5 and 6.2. These pH values do not favour phosphorus precipitation on calcium. The organic anions in biochar also repel phosphate ions from calcium making them available for plant uptake^[44]. However, it differs from the results reported by Eduah et al.^[30] and Xu et al.^[42] where Ca-P increased.

3.2.5. Occluded phosphorus

The levels of occluded P over time are presented in **Figure 4a**. The mean occluded phosphorus levels for S, SP, SPB, and SB were $33.833 \pm 2.59 \ \mu g/g$, $37.447 \pm 2.17 \ \mu g/g$, $31.129 \pm 0.74 \ \mu g/g$ and $39.902 \pm 10.17 \ \mu g/g$ of soil, respectively. No significant difference was recorded among the treatments implying that neither biochar amendment nor P fertilization had an effect on the levels of occluded phosphorus. This could be attributed to biochar providing more sites for phosphorus sorption making them unavailable^[10]. This differs with the results reported by Abolfazli et al.^[45] and Kalyani et al.^[31] of increase in occluded P with biochar amendment.



Figure 4. Levels of (a) occluded phosphorus; (b) labile organic phosphorus; (c) moderately labile organic phosphorus; and (d) nonlabile organic phosphorus over time in the different soil treatments.

3.3. Organic phosphorus fractions

3.3.1. Labile organic phosphorus

Figure 4b presents the variations in labile organic phosphorus with time. The mean labile phosphorus levels were $89.420 \pm 13.15 \ \mu\text{g/g}$, $179.337 \pm 10.69 \ \mu\text{g/g}$, $186.194 \pm 28.94 \ \mu\text{g/g}$ and $97.241 \pm 26.36 \ \mu\text{g/g}$ of soil for S, SP, SPB, and SB, respectively. A significant difference ($P \le 0.05$) was recorded between S (control), SP and SPB, but not with SB. With SP as the control, there was a significant difference ($P \le 0.05$) with SB but not with SPB. The treatments could therefore be divided into two sets: S/SB and SP/SPB. This showed that biochar had no effect on the labile phosphorus content in the soil. This differs with the findings by Eduah et al.^[30] on soils of Ghana, where biochar increased labile organic P.

3.3.2. Moderately labile organic phosphorus

The variations in levels of moderately labile organic phosphorus are shown in **Figure 4c**. The mean moderately labile phosphorus levels for S, SP, SPB, and SB were $63.629 \pm 3.50 \ \mu g/g$, $78.652 \pm 4.07 \ \mu g/g$, $72.462 \pm 5.58 \ \mu g/g$ and $76.894 \pm 7.37 \ \mu g/g$ of soil respectively. No significant differences were recorded in P levels among the treatments. The moderately labile organic phosphorus levels decreased in the initial days and leveled off after the 28th day until the end of the incubation period. This result agrees with Eduah et al.^[30] who reported no effect of biochar amendment on moderately labile phosphorus.

3.3.3. Non-labile organic phosphorus

The variations in the levels of non-labile organic P for the various treatments over time are presented in **Figure 4d**. The mean non-labile phosphorus levels were $46.939 \pm 2.31 \ \mu g/g$, $48.864 \pm 1.11 \ \mu g/g$, $60.121 \pm 3.84 \ \mu g/g$ and $46.561 \pm 6.49 \ \mu g/g$ of soil for S, SP, SPB, and SB, respectively. No significant differences in levels among the treatments was recorded. The result agrees with Eduah et al.^[30] who reported no significant effect on non-labile organic phosphorus with biochar amendment. However, co-application of biochar with P fertilizer increased non-labile organic P.

3.4. Relationship among the P fractions

Table 2 shows the correlations among the P fractions in the various treatments (n = 11, df = 9, critical value for Pearson, r = 0.60, P = 0.05).

Table 2. Correlation among P fractions.								
Correlation among P fractions		r values						
		S	SP	SPB	SB			
LSP	Al-P	-0.42	-0.51	0.24	-0.24			
	Fe-P	-0.75**	-0.09	-0.71**	-0.55			
	Ca-P	0.15	-0.18	0.96*	0.62*			
	Oc-P	0.61*	-0.06	0.86*	-0.16			
	LP	-0.51	0.05	0.50	0.39			
	MLP	-0.52	0.09	0.33	0.24			
	NLP	-0.38	-0.27	-0.01	-0.13			
Al-P	Fe-P	0.02	0.51	-0.26	-0.05			
	Ca-P	0.17	-0.05	0.16	-0.24			
	Oc-P	-0.15	0.01	0.45	-0.22			
	LP	0.16	-0.01	-0.51	0.17			
	MLP	-0.06	-0.12	0.40	0.08			
	NLP	0.18	-0.07	-0.33	-0.30			
Fe-P	Ca-P	-0.01	-0.43	-0.59	-0.23			
	Oc-P	-0.52	-0.32	-0.57	-0.10			
	LP	0.47	0.12	-0.43	-0.50			
	MLP	0.66*	0.52	0.05	0.14			
	NLP	0.50	0.44	0.20	-0.14			
Ca-P	Oc-P	0.48	0.74*	0.78*	0.03			
	LP	-0.43	0.54	0.55	0.46			
	MLP	-0.14	0.13	0.46	0.62*			
	NLP	0.49	0.09	0.15	0.26			

Correlation among P fractions		r values				
		S	SP	SPB	SB	
Oc-P	LP	-0.60**	0.61*	0.30	-0.50	
	MLP	-0.49	0.06	0.41	-0.17	
	NLP	-0.11	-0.11	-0.27	0.89*	
LP	MLP	0.64*	0.25	0.14	0.45	
	NLP	-0.33	0.16	0.30	-0.23	
MLP	NLP	-0.10	0.77*	0.19	0.09	

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

S and SPB had a significant negative correlation between iron bound P and loosely sorbed P implying exchange of P between the two fractions. This could be attributed to the fact that reduction of Fe^{3+} to Fe^{2+} under anaerobic conditions could cause release of iron bound P to the loosely sorbed P fraction. For SPB, the Fe^{3+} could have been saturated by either P from biochar or the mineral fertilizer allowing the excess to move to the loosely sorbed fraction or complexed with organic molecules from biochar leaving no room for P fixation. P fixation on calcium is high in alkaline soils but as the pH reduces, more of it could be released to iron bound $P^{[10]}$. There was a significant negative correlation between labile P and occluded P. This could mean that some of the labile organic P generated during decomposition and mineralization of organic matter were strongly sorbed on the active sites of soil and biochar particles hence occlusion.

There were significant positive correlations between occluded P and loosely sorbed P, MLP and Fe-P, as well as between MLP and LP in S. The correlation between Fe-P and MLP indicates movement of P between the organic and inorganic pools while MLP and LP both originate from decomposition of organic matter, hence the positive correlation. For SP, significant positive correlations were recorded between NLP and MLP, LP and Oc-P as well as between Oc-P and Ca-P. SPB showed significant positive correlations between Ca-P and LSP, Oc-P and LSP as well as between Oc-P and Ca-P. Significant positive correlations were also noted between Ca-P and LSP, Ca-P and MLP as well as between Oc-P and NLP in SB. This could be as a result of biochar providing more sorption sites for both organic and inorganic P^[10] hence the positive correlation between occluded P and NLP.

3.5. Utilization potential and sustainability of biochar as a P source

The results show that biochar performed as well as P fertilizer in terms of total P but did much better in iron bound P compared to the mineral fertilizer. The Fe-P can become available for plant uptake over decades provided the soil conditions are favourable for intensive metabolization of P-mineralizing soil biota^[46]. The high sorption of loosely sorbed P as Fe-P in biochar reduces P loss due to leaching that result into eutrophication of water bodies and is also applied with enormous economic benefits in wastewater treatment plants^[9]. In terms of production costs, it is relatively cheap since the raw materials are locally available except for the initial cost of constructing the furnace and would thus be sustainable in the long run as pointed out by Marousek et al.^[47]. Moreover, the energy cost associated with biomass transformation to biochar can be high, hence raising sustainability concerns. This has to be addressed so as to make the production process inexpensive and sustainable. Considering the high cost of P fertilizers and the fact that the remaining sources are nearing depletion, biochar is a potential alternative P source that would release its P at a slower pace based on activity of soil biota in the mineralization process.

4. Conclusion

The study established that under anaerobic conditions, biochar and P amendments had no effect on

aluminium bound P, calcium bound P, occluded P, moderately labile P and non-labile P. P fertilization increased loosely sorbed P while biochar reduced it and even minimized those added by the P fertilizer. It was also established that biochar increased iron bound P and to a greater extent in the presence of P fertilizer. Addition of P fertilizer increased labile P but biochar had no effect on this fraction. Biochar and P amendment could be used to increase the initial readily available P in agricultural production. Other than the effect on loosely sorbed P, biochar performed as well as P fertilizer in total P and even better in iron bound P hence can be used as an economically viable alternative source of P since its raw materials are locally available. Anaerobic conditions may also be used to mobilise fixed forms of P prior to planting to minimize consumption of fertilizers. However, field trials need to be conducted to ascertain the practicality of these experimental results.

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Author contributions

Conceptualization, FOK; project design, FOK; methodology, ROO, FOK and ES; experimental work, ROO; data analysis, ROO and FOK; data interpretation, FOK and ES; writing—original draft preparation, ROO; writing—review and editing, FOK and ES; supervision, FOK and ES; project administration, FOK; funding acquisition, FOK. All authors have read and agreed to the published version of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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