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Phosphorus retention and availability in three contrasting soils amended with rice husk and corn cob biochar at varying pyrolysis temperatures

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ABSTRACT

The reactive nature of phosphorus (P) leads to the formation of insoluble Fe, Al and Ca phosphates in highly weathered tropical soils, thus reducing P availability for plant uptake. Biochar with its heterogeneous surface properties as influenced by feedstock and pyrolysis temperature can affect P retention and availability in tropical soils. In the present study, incubation studies were conducted for 90 days to investigate the effect of corn cob and rice husk biochar on P sorption and desorption in two acid (Typic Plinthustult-A & Plinthic Acrudox-B) and one neutral soil (Quartzipsamment-C). The biochars were pyrolyzed at varying temperatures (300 °C, 450 °C and 650 °C) and applied at a rate of 1% (w/w) to the soils. Phosphorus sorption data were fitted to Langmuir and Freundlich models. Phosphorus desorption was done on the residual samples that received initial P concentrations of 21.5 $\mathrm{mg\,L^{-1}}$, 43.0 $\mathrm{mg\,L^{-1}}$ and 86.0 $\mathrm{mg\,L^{-1}}$ solution using 10 mM KCl. The P sorption capacity of the two acid soils i.e. A (395 $\mathrm{mg\,kg^{-1}}$) and B (296 $\mathrm{mg\,kg^{-1}}$) were more than two fold that of the neutral soil (C) (105 $\mathrm{mg\,kg^{-1}}$). Addition of the biochar types to soil A raised the equilibrium P concentration in solution at decreasing pyrolysis temperature. Similar trend was observed in soil B with the exception of corn cob and rice husk biochar at 650 °C which increased the soil's (B) P sorption capacity. In soil C, both biochar types increased P sorption capacity with increasing pyrolysis temperatures. Phosphorus desorbability increased with increasing initial P concentrations in the three soils. Generally, P desorbability increased in the acid soils but decreased in the neutral soil upon biochar amendment. Decreases in P adsorption and consequently increases in P desorption were more pronounced when the 300 °C biochar types were amended with the soils. The study thus showed that biochar pyrolyzed at 300–450 °C could be used to reduce P sorption and increase P bioavailability especially in acid soils. The addition of biochar to neutral or alkaline soils might increase P retention possibly in the short-term, reducing P bioavailability.

1. Introduction

The high phosphorus (P) fixing capacity of highly weathered soils of the tropics has restrained the development of economically sustainable crop production (Guzman et al., 1994; Abekoe and Sahrawat, 2001). Biogeochemical processes such as dissolution, complexation, adsorption and precipitation determine the availability of P in soil solution for plant uptake (Gérard, 2016). These chemical processes are dependent on soil properties including Al and Fe oxide type and content, the amount and type of silicate clays, ionic strength, soil solution pH, calcium carbonate content, concentration of P in solution and the presence of competing anions (Eriksson et al., 2015; Gérard, 2016). In acid soils, Fe and Al in solution and their oxides adsorb P through precipitation and ligand exchange reactions, respectively (Schoumans and Chardon, 2015). The formation of calcium-P, magnesium-P compounds as well as P adsorption and precipitation by $CaCO_3$ occurs in alkaline and calcareous soils (Eriksson et al., 2015). The amount of P uptake by plants in acidic and alkaline soils is much restricted due to high P fixation.

The use of biochar has been suggested to provide an integrated approach to rectify the challenge of tropical soils infertility (Lehmann, 2007). Biochar is a stable carbon rich material, which is produced through thermochemical reaction in oxygen limited environment (Lehmann et al., 2006). It is highly resistant to microbial degradation and can therefore stay in soils for hundreds to thousands of years (Lehmann et al., 2006). Feedstocks for biochar production are abundant and are low-cost and mainly obtained from agricultural biomass, industrial and domestic waste (Duku et al., 2011). For instance, Ghana as a country generates about 363 × 10^3 and 1650 × 10^3 t of rice husk and

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corn cob biomass, respectively annually (Duku et al., 2011). These wastes are generally disposed off by aerobic burning to pollute the environment. Converting these biomasses into biochar can improve the biomass management and protect the environment (Dong et al., 2013).

Improvement of P availability in soils upon biochar application has been reported (Lehmann, 2007; Atkinson et al., 2010). Various mechanisms by which biochar may directly or indirectly control the biotic and abiotic components of the P dynamics have been reported (DeLuca et al., 2015). Biochar contains ample amount of P and therefore can directly release soluble P into soil solution to enhance P availability (Atkinson et al., 2010). The addition of biochar reduces soil acidity due to its high alkalinity and consequently reduces P precipitation reactions with Fe^{3+} and Al^{3+} (Wang et al., 2012). Joseph et al. (2010) also indicated that application of biochar to soils culminates into the precipitation of Fe oxide on biochar surface. Other studies have on the other hand reported that biochar decreases P availability in most alkaline soils of the tropics due to substantial release of cations including Ca^{2+} and Mg^{2+} (DeLuca et al., 2015). Biochar produced from the same feedstock at different pyrolysis temperature may have diverse physical and chemical properties such as functional groups, cation exchange capacity, porosity and surface area (Liang et al., 2014), which when applied to soils may invariably alter the surface chemistry of soils and therefore affect P availability and retention in soils. For instance, under the same pyrolysis temperature of 400 °C, the surface area and porosity of poultry litter manure was much higher than wheat straw biochar (Sun et al., 2011). Even though much work has been conducted on P sorption and availability in soils using P sorption characteristics (Abekoe and Tiessen, 1998; McDowell and Condron, 2001), very limited work has been done on P adsorption characteristics of biochar-soil complex at varying pyrolysis temperatures. Studies using different biochar types on soils are required to evaluate the reactivity and sorption characteristics of biochar-soil complex vis-à-vis soil P availability after biochar application.

The objectives of the study were to find out (1) the effect of corn cob biochar and rice husk biochar produced at different pyrolysis temperatures on P sorption on soils, and (2) the effect of the biochar types on P desorption on soils.

2. Materials and methods

2.1. Soil and biochar

Three soils of varying pH were sampled at a depth of 20 cm from different agro-ecological zones in Ghana. Soil A (A) which is sandy clay loam (Table 1) was collected from a Moist Semi-Deciduous Forest (06°8.6′N; 0°54.144′W) with a mean annual temperature of about 32 °C and a mean annual rainfall between 800 and 1200 mm (Dickson and Benneh, 1995). In accordance with Soil Taxonomy System (Soil Survey Staff, 2010) and World Reference Base (WRB, 1998), the soil is classified as Typic Plinthustult and Gleyi-Plinthic Acrisol, respectively (Dwomo and Dedzoe, 2010). Soil B (B) also sandy clay loam was collected from the Evergreen High Rain Forest (05°13′N; 02°38′W) with a mean annual temperature and rainfall of 30 °C and 2000 mm, respectively. It is classified as Plinthic Acrudox (Dwomo and Dedzoe, 2010) according to Soil Taxonomy System (Soil Survey Staff, 2010) and as Plinthic Ferralsol (Dwomo and Dedzoe, 2010) based on World Reference Base (WRB, 1998). Soil C (C) was sampled from the Coastal Savannah (05°47′N; 00°53′E) located on sand pit and is of low fertility (Awadzi et al., 2008). According to Soil Taxonomy (Soil Survey Staff, 2010), the soil is classified as a Quartzipsamment (Dwomo and Dedzoe, 2010). It is located in a dry equatorial climatic zone with a mean annual rainfall below 900 mm and a mean annual temperature of 28 °C (Dickson and Benneh, 1995).

Two biochar types at three different pyrolysis temperatures (300 °C, 450 °C and 650 °C) produced using Nabertherm furnace from corn cob (*Zea mays*) (CC) and rice husk feedstock (*Oryza sativa*) (RH) were obtained from Soil Research Institute of the Council for Scientific and Industrial Research (CSIR), Ghana. The CC and RH feedstocks charred at 300 °C, 450 °C and 650 °C are herein after designated as CC3, CC4, CC6, RH3, RH4 and RH6, respectively. The biochars were finely ground to < 1 mm using mortar and pestle, dried at 105 °C and stored in airtight bags for characterization and incubation studies.

Table 1
Properties of studied soil types.

Classification[a]	Typic Plinthustult	Plinthic Acrudox	Quartzipsamment
Acronym	A	B	C
Clay (%)	20.30	18.40	4.00
Silt (%)	11.20	8.00	1.00
Sand (%)	68.70	64.60	95.00
pH	5.03	4.73	6.63
CEC (cmol+ kg^{-1})	15.20	12.78	3.42
Total C (g kg^{-1})	14.00	13.30	4.30
Total N (g kg^{-1})	1.23	1.22	0.19
Total P (mg kg^{-1})	353.58	232.75	190.80
Exc. Ca (cmol+ kg^{-1})	1.27	0.32	0.40
Exc. Mg (cmol+ kg^{-1})	0.42	0.10	0.13
Fe$_o$ (g kg^{-1})	2.10	1.56	0.67
Fe$_d$ (g kg^{-1})	20.00	9.41	1.66
Al$_o$ (g kg^{-1})	1.21	1.39	0.17
Al$_d$ (g kg^{-1})	3.03	2.59	0.74

[a] Soil classification based on Soil Taxonomy System; Exc. Ca: exchangeable Ca; Exc. Mg: exchangeable Mg; Fe$_o$: oxalate extractable Fe oxides; Al$_o$: oxalate extractable Al oxides; Fe$_d$: dithionite citrate bicarbonate extractable Fe oxides; Al$_d$: dithionite citrate bicarbonate extractable Al oxides.

2.2. Soil and biochar analyses

Soil samples were air dried, ground and sieved to < 2 mm for successive analyses. The particle size distribution was done using hydrometer method of Bouyoucos (Day, 1965). The pH of soils and biochar types were measured in deionized water at the ratio of 1:2.5 w/w after shaking for 1 h (Gaskin et al., 2008). Cation exchange capacity (CEC) and exchangeable bases (Ca and Mg) were measured by modified NH$_4$-acetate compulsory displacement method (Gaskin et al., 2008). A LECO TIUMAC CNS analyzer was used to measure total C and N. Total P, base cations (Ca, Mg, Na, K), Al and Fe were determined using inductively coupled plasma optical emission spectrometry (ICP-OES). Briefly, the 0.5 g of crushed biochar and blanks in triplicates were digested in 3.5% HF and H$_2$O$_2$. The ICP-OES elemental quantification was carried out by using a Perkin Elmer Optima 5300DV instrument (Waltham, USA). Reactive crystalline and amorphous Fe and Al oxides were determined by dithionite citrate bicarbonate (DCB) and oxalate extractions as described respectively, by Mehra and Jackson (1960) and Schwertmann (1964). The functional groups on the biochar types were examined using photoacoustic spectroscopy (PAS)-FTIR. Briefly, the spectra were recorded using a Nicolet 6700 (Thermo Scientific, USA) spectrometer equipped with a PA-301 photoacoustic detector (Gasera Ltd., Finland). For each sample, 128 scans in the mid-infrared region between 4000 and 500 cm^{-1} at a resolution of 4 cm^{-1} were recorded and averaged.

2.3. Incubation experiment

An incubation study was done to find out the effect of biochar types at the various pyrolysis temperatures on P sorption and desorption in the three soils. The biochar types were mixed with soil at a rate of 1% (30.4 t ha^{-1}) in small pots of 5 cm diameter and 7 cm height. Soils without (control) and with biochar types were incubated at 70% field capacity at room temperature (28 °C) for 90 days in the dark. Each treatment was replicated thrice. After the 90 days of incubation, the soils (control) and soil-biochar mixtures were air-dried (70 °C) and stored for P sorption studies. The biochar amended soils after the 90-day incubation period were analyzed for pH, organic carbon, CEC, total P, exchangeable Ca, DCB and oxalate extractable Fe and Al according to their respective methods described earlier.

2.4. *P sorption of soils and soil-biochar mixtures*

Phosphorus sorption isotherms were determined on each soil and soil-biochar mixture. Orthophosphate stock solution containing 200 mg L^{-1} was prepared from KH_2PO_4 salt of Analar grade. Thirty (30) mL of 0.01 M KCl solution containing 0 (blank), 10.1, 21.5, 32.3, 43.0, 64.5 and 86.0 mg P L^{-1} were added to centrifuge tubes containing 2 g of sample (soil or soil-biochar mixture). The suspensions in the centrifuge tubes were shaken on an end-to-end shaker at 120 rpm for 24 h at 28 °C. The suspension was then centrifuged (3500 rpm, 15 min) and the resulting supernatant filtered through a 0.45 μm filter paper. The filtrate was analyzed for equilibrium pH and P by the colorimetric molybdenum-blue method (John, 1970). The initial aqueous P concentration Ci (mg L^{-1}) and equilibrium P concentration Ce (mg L^{-1}) were measured and the P adsorbed (qt) was calculated from the mass balance equation as follows (Eq. (1)):

$$qt = \frac{(Ci - Ce)V}{M} \tag{1}$$

where V is the volume of the aqueous solution (L) and M is the dry weight in grams of soils and soil-biochar mixtures (adsorbent).

The sorption data were fitted to Langmuir (Eq. (2)) and Freundlich equations (Eq. (3)):

$$q_t = \frac{bQ_{\max}Ce}{1 + bCe} \tag{2}$$

$$q_t = K_f Ce^{1/n} \tag{3}$$

where b and K_f indicate the Langmuir binding energy (L mg^{-1}) and the Freundlich affinity coefficient (mg$^{(1-n)}$ L^{n} g^{-1}), respectively, $Q_{\max}$ is the Langmuir maximum sorption capacity (mg kg^{-1}), and $1/n$ is the Freundlich linearity constant.

2.5. *P desorption of soils and soil-biochar mixtures*

Desorption studies were done using the residual samples, which received initial P concentration of 21.5 mg L^{-1}, 43.0 mg L^{-1} and 86.0 mg L^{-1}. After filtering the supernatant from the previous sorption experiment, the centrifuge tube plus the wet sample was weighed and a total of 20 mL of 0.01 M KCl solution was added to the sample in the centrifuge tube on a weighing balance. The suspension was then shaken for 3 h and centrifuged at 3500 rpm for 10 min at room temperature. The supernatant was filtered through a 0.45 μm filter paper into a clean plastic bottle and a suitable aliquot taken for P analysis. The P carried over between desorption steps was determined from the weight of the entrapped solution that remained after decanting the supernatant solution. The extraction was repeated for three successive times and P released into the supernatant at each extraction period was then measured (John, 1970). The percentage of P desorbed was calculated as P desorbability (Eq. (4)), where P desorbed is calculated as P adsorbed minus P remaining on the soil surface.

$$P\ desorbability\ (\%) = \frac{P\ desorbed\ (\mathrm{mg\ kg^{-1}})}{P\ adsorbed\ (\mathrm{mg\ kg^{-1}})} \times 100 \tag{4}$$

2.6. *Statistical analysis*

A generalized linear model function in R studio (3.4.0) was used to generate a linear model for Langmuir and Freundlich equations. Selection of the best fit model to sorption data was based on the computed residual mean square error (RMSE) as described in Eq. (5), where Q_c is the calculated values, Q_e is experimental values and n is the number of observations. Shapiro-Wilk test was used to test for the normality of soil-biochar mixture and desorption data before subjecting it to one-way ANOVA test at a significance level of 1%. The variations among the mean values were done using Tukey test.

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n} (Q_c - Q_e)^2} \tag{5}$$

3. Results and discussion

3.1. *Properties of the studied soils, biochar types and the soil-biochar mixtures*

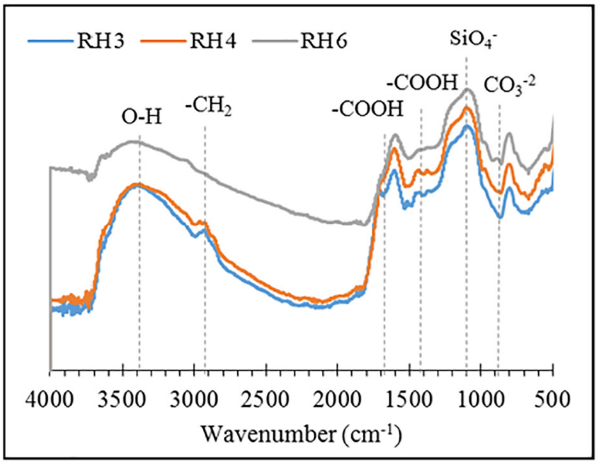
Table 1 shows the physical and chemical properties of the soils used for the study. Soils A, B and C were acidic (pH = 5.03), very acidic (pH = 4.73) and neutral (pH = 6.63), respectively. Soils A and B are highly weathered and contain 1:1 clay minerals (low activity clays). The organic carbon (OC) content of the soils was low (< 15 g kg^{-1}), which is typical of soils of the humid tropics. The low activity clays coupled with the low organic matter content of these soils may have contributed to the low cation exchange capacity (CEC) of the soils. The two acid soils (A and B) had almost the same non-crystalline (oxalate extractable) contents. The crystalline (DCB) Fe contents in soil A was twice more than that of soil B. Comparably, the non-crystalline and crystalline Fe and Al oxides of the acid soils were higher than that of soil C, probably due to the more advanced weathering stage of the former soils. This implies a higher P sorption capacity of the acid soils than the neutral soil. The low to modest content of Fe and Al oxides in soil C coupled with its low clay content of 4% depicts restrained P adsorption capacity (Borggaard et al., 2004).

The chemical composition of corn cob and rice husk biochar types at the three different temperatures are shown in Table 2. The pH, total P, C and Si contents and concentration of the basic cations (Ca, Mg, K and Na) and acidic cations (Fe and Al) increased with increasing pyrolysis temperature. Cation exchange capacity (CEC) and total N, however, decreased with increasing pyrolysis temperature. Biochar produced from corn cob and rice husk at 650 °C had extremely high pH (> 9.0) and could serve as liming agent to ameliorate acid soils of the tropics. The biochar types had a higher CEC as compared to a typical clay mineral (Sohi et al., 2010), such as the studied soil types. Therefore, corn cob and rice husk amendments in the studied soils is likely to increase soil CEC. The high CEC of biochar is a result of oxidative reactions of acid functional groups located on the edges of biochar aromatic C sheet (Agrafioti et al., 2013). The decrease in CEC with increasing pyrolysis temperature can be attributed to the reduction in the —COOH and —OH

Table 2
Properties of corn cob biochar and rice husk biochar produced at 300 °C, 450 °C and 650 °C.

Biochar	Corn cob			Rice husk		
Temperature	300 °C	450 °C	650 °C	300 °C	450 °C	650 °C
Acronym	CC3	CC4	CC6	RH3	RH4	RH6
pH (H_2O)	8.90	9.23	10.30	7.11	7.40	9.50
Total C (g kg^{-1})	729.80	743.10	780.72	415.80	419.80	425.51
Total N (g kg^{-1})	29.31	21.20	19.11	17.72	13.3	12.10
Total P (g kg^{-1})	1.54	1.60	1.94	1.19	1.32	1.52
Ca (g kg^{-1})	3.32	3.88	4.19	2.07	2.56	3.29
Mg (g kg^{-1})	2.43	3.21	3.43	0.91	1.01	1.27
K (g kg^{-1})	1.54	1.56	1.94	0.19	1.12	1.52
Na (g kg^{-1})	24.71	26.31	30.80	5.34	6.36	8.19
CEC (cmol+ kg^{-1})	38.02	37.82	30.10	49.40	42.72	38.00
Si (g kg^{-1})	13.94	14.01	14.44	138.53	169.2	194.49
Al (g kg^{-1})	0.57	0.67	1.10	1.26	1.53	1.88
Fe (g kg^{-1})	0.62	0.70	0.95	1.25	1.50	1.66

(a) Rice husk biochar



(b) Corn cob biochar

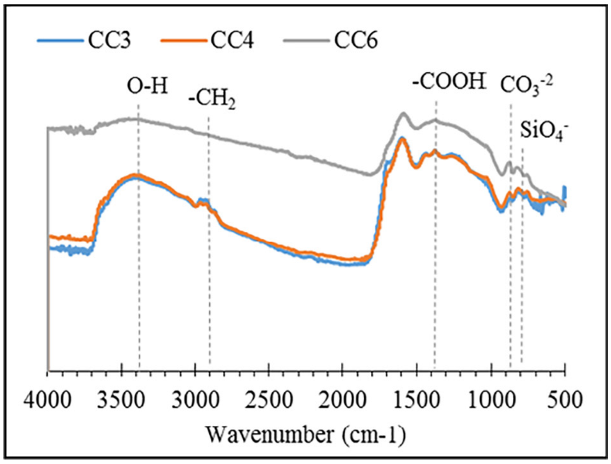


Fig. 1. Photoacoustic spectroscopy-FTIR analysis of (a) rice husk biochar charred at 300 °C (RH3), 450 °C (RH4) and 650 °C (RH6); (b) corn cob biochar charred at 300 °C (CC3), 450 °C (CC4) and 650 °C (CC6).

groups at 650 °C (Fig. 1). Zheng et al. (2013) reported that the enrichment of base cations and P with increasing pyrolysis temperature is due to their high vaporization energy. For instance, K and P are lost at temperatures above 800 °C, whiles Mg and Ca at temperatures above 1200 °C and 1300 °C, respectively (Knicker, 2007). The particularly high level of Si in the rice husk biochar type confirms the element as a nutrient in rice. This is consistent with the high intensity peak of SiO_2 in the PAS-FTIR analysis. Silica is an important constituent of plant phytoliths as it safeguards the plant from biochemical degradation of carbon (Parr, 2006). The high C content at 650 °C can be explained by increased carbonization and probable dehydration and disappearance of volatile H and O— carbon compounds as a result of structural degradation (Antal and Gronli, 2003). This is corroborated by the loss of CH_2 functional groups at higher temperatures as evident in the PAS-FTIR spectra of all the biochar types (Fig. 1). The peak at about 3400 cm^{-1} indicates the presence of O—H stretching and strong hydrogen bonding (Chun et al., 2004). The carboxylic C stretch was around 1720 cm^{-1} and 1396 cm^{-1} (Bourke et al., 2007; Brewer et al., 2009). Adsorption at 2925 cm^{-1} suggested the presence of aliphatic $-CH_2$ groups which disappeared at 650 °C (Chun et al., 2004). The decrease in peaks 2925 cm^{-1}, 3400 cm^{-1}, 1396 cm^{-1} and 1720 cm^{-1} at 650 °C suggests the decrease in polar functional groups at high temperature (Brewer et al., 2009). The peak at 3050 cm^{-1} of rice husk biochar was assigned to the aromatic C—H out of plane bend, indicating the presence of adjacent aromatic hydrogen. The stretching vibration of silicates was at peaks 800 cm^{-1} and 1100 cm^{-1} (Bourke et al., 2007). The peak at 875 cm^{-1} corresponds to the content of carbonate in the biochar types (Brewer et al., 2009).

One percent (1%) corresponding to approximately 30.4 t ha^{-1} amendment of the biochar types to the soils resulted in a > 0.5 unit increases in pH (Table 3) similar to that reported for addition of non-woody biochar types at rates between 15 and 30 t ha^{-1} to soils elsewhere (Soinne et al., 2014). The predominant increase in pH for particularly the RH6 and CC6 amended soils is a reflection of a higher increase in exchangeable Ca in the amended soils (Table 3) which could be due to the inherently high pH and Ca contents of the biochar types (Table 2). Wang et al. (2014) also reported increases in exchangeable Ca and Mg after biochar addition to some tropical soils. The more significant ($p < 0.05$) effect of the CC6 and RH6 on the soils' exchangeable Ca may be attributed to Ca enrichment at high temperatures of 600 °C (Table 2).

Upon addition of the biochar types, there was generally significant increases in OC contents only in the A soil. This increase was from 14.01 g kg^{-1} to between 17.72 and 21.51 g kg^{-1}. The CEC of the three amended soils increased significantly ($p < 0.05$), particularly at low pyrolysis temperatures i.e. CC3 and RH3, obviously due to the increases in solution pH which would facilitate more deprotonation of organic acids and kaolinite present in the soils. Total P of all the three biochar amended soils increased significantly ($p < 0.05$) due to the inherently high P of the biochar types.

It is worthy of note that the acid soil A which had significant ($p < 0.05$) increases in organic carbon contents upon amendment also had increases in the oxalate extractable Fe (Fe_o) with concomitant decreases in DCB extractable Fe (Fe_d) (Table 3). Increases in organic carbon levels may be controlling crystallinity of Fe in soil A within the 90 day incubation period. It is also note-worthy that upon addition of biochar to the acid soils, Fe_d decreased from that of the un-amended soils. This decrease in the Fe_d content of the acid soils may lead to decreases in P adsorption. Apart from Al_o which increased marginally in soil C, there were no changes in oxalate and DCB extractable Fe and Al in the neutral soil C probably due to the soil's low clay content (4%) which reduced its reactivity with biochar.

3.2. Effect of biochar types on P sorption of soils

Table 4 lists the Langmuir and Freundlich adsorption parameters together with the RMSE and equilibrium pH of the solution after the sorption studies. Langmuir and Freundlich models effectively fitted the P adsorption data of the soils and soil-biochar mixtures. Considering the RMSE values of the two models, Langmuir model had a better fit in the three soils without biochar amendment. However, upon biochar application, P adsorption in soils A and B were better fitted to Langmuir model whereas soil C amended with biochar fitted better to Freundlich model. Most of the sorption curves fitted better with the Langmuir model, expressing P adsorption to soil surface with homogenous sorption sites. Similar results were described in Jiang et al. (2015) and Bornø et al. (2018) for P adsorption on soils and biochar amended soils.

Phosphorus adsorption increased with increasing initial P concentration (Fig. 2). This observation is consistent with other studies (Abekoe and Sahrawat, 2001; Bornø et al., 2018). The Langmuir sorption maximum (Qmax) of soil A (395 mg kg^{-1}) and soil B (296 mg kg^{-1}) was relatively higher than that of soil C (106 mg kg^{-1}). The relatively high P sorption capacity of the former is due to the high content of amorphous and crystalline Fe and Al oxides providing more adsorptive sites for P (Jiang et al., 2015). Soil A with relatively higher content of Fe and Al oxides and clay than soils B and C showed much decrease in P availability. The high sand content of soil C may have culminated into its low P sorption capacity.

Incorporating corn cob and rice husk biochar into soil A increased P

Table 3
Chemical properties of soils and soil-biochar mixtures.

Soil	Treatment	pH	Organic C	CEC	Exc. Ca	Total P	Fe_o	Fe_d	Al_o	Al_d
		H_2O	g kg^{-1}	cmol+ kg^{-1}	cmol+ kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
A	Control	5.03	14.01a[a]	15.20a	1.27a	353.60a	2.10a	20.00d	1.21b	3.02ab
	CC3	6.03	21.51d	22.27c	1.50bcd	428.81b	2.77c	14.32a	1.65c	2.55ab
	CC4	6.43	20.10cd	19.20b	1.58de	482.80cd	2.66c	14.95a	1.27b	3.10ab
	CC6	6.43	19.20bc	19.49bc	1.65e	505.82d	2.54b	17.70c	1.12b	3.47b
	RH3	5.73	18.72bc	20.07bc	1.41b	413.60b	2.65bc	16.81b	1.08b	2.55ab
	RH4	6.07	18.91bc	20.27bc	1.44bc	470.50c	2.71c	17.44bc	1.10b	3.44b
	RH6	6.23	17.72b	17.89ab	1.53cd	460.61c	2.55b	17.07bc	0.78a	3.49b
B	Control	4.73	13.30a	13.00a	0.32a	232.71a	1.56ab	9.41c	1.39b	2.59b
	CC3	5.30	17.30c	18.18c	0.46cd	301.00b	1.68ab	5.79a	0.93a	2.71b
	CC4	5.47	15.53abc	18.13c	0.47cd	330.90bc	1.68ab	6.09ab	1.31b	2.31ab
	CC6	5.47	15.11ab	16.09b	0.48d	408.20d	1.51a	6.45ab	1.18ab	2.98b
	RH3	5.17	16.50bc	16.31b	0.35b	304.02b	1.66ab	6.45ab	1.21ab	1.54a
	RH4	5.30	14.91ab	16.14b	0.36b	347.00c	1.72b	6.99b	1.24ab	2.39ab
	RH6	5.23	14.30ab	13.66a	0.45c	325.41bc	1.68ab	7.09b	1.19ab	2.34ab
C	Control	6.63	4.31a	3.50a	0.40a	190.22a	0.67a	1.66ab	0.17a	0.74a
	CC3	7.10	4.50a	7.74d	0.46ab	249.40bc	0.76abc	1.83ab	0.29bc	0.78a
	CC4	7.33	5.30ab	6.83cd	0.64bc	230.81abc	0.78bc	1.72ab	0.26b	0.94ab
	CC6	7.47	5.02ab	6.87cd	0.76c	270.30c	0.80bc	1.87b	0.27bc	0.97ab
	RH3	6.63	6.01b	7.54d	0.49ab	209.80ab	0.86c	1.61a	0.33d	0.95ab
	RH4	6.77	5.20ab	5.11b	0.73c	222.51ab	0.71ab	1.83ab	0.32cd	0.91a
	RH6	7.20	4.62a	5.90bc	0.72c	270.30c	0.72ab	1.90b	0.29bc	1.23b

[a] Values of the same letter within a column are significantly the same at 1% level of significance based on Tukey's test.

bioavailability with decreasing pyrolysis temperature. The 395 mg kg^{-1} Qmax of soil A decreased to between 262 mg kg^{-1} and 366 mg kg^{-1} and between 279 mg kg^{-1} and 367 mg kg^{-1} respectively in corn cob and rice husk treatments. Similarly, both biochar amendments to soil B decreased P sorption capacity with the exception of biochar types produced at 650 °C. The result of the present study is consistent with those of Morales et al. (2013) who found that biochar reduces P fixing capacity of degraded acidic tropical soils. Similarly, Cui et al. (2011) also found a decrease in P adsorption onto ferrihydrite when amended with straw biochar. The equilibrium pH value of the P solution is of much importance regarding the process of adsorption, the form of P in solution as well as the surface charge of the soil and or soil-biochar mixture and hence its adsorption capacity for P. Cerozi and Fitzsimmons (2016) proposed that maximum P availability is observed at pH range of 5.5 to 7.2 in an aquatic system. The addition of the two biochar types raised the equilibrium pH of soil A (4.92) to a range of 5.79 to 5.99 and soil B (4.61) to a range of 5.71 to 6.02 (Table 4) which were within the suitable range. Such pH range might have led to the precipitation of polymeric Fe and Al oxides (Gérard, 2016), thereby increasing P availability.

Corn cob and rice husk biochar pyrolyzed at 300 °C were lower in P adsorption when amended to the two acid soils than their counterparts pyrolyzed at 450 °C and 650 °C. Therefore, biochar produced at 300 °C can be considered as better amendment in acid soils for more P bioavailability for plant uptake. The comparatively lower P adsorption onto the 300 °C biochar types could be attributed to the lower Al and Fe

Table 4
Phosphorus adsorption parameters from Langmuir and Freundlich equations, equilibrium pH and root mean square error (RMSE) of soils and biochar amended soils.

Soil	Treatment	Langmuir		Freundlich		Langmuir	Freundlich	Equilibrium pH[c]
		Qmax (mg kg^{-1})[a,b]	b (L mg^{-1})[a,b]	K_f (mg kg^{-1})[a,b]	(1 / n)[a,b]	RMSE	RMSE	
A	Control	395	0.04	42	0.48	20	29	4.92
	CC3	262	0.06	42	0.39	19	27	5.99
	CC4	314	0.08	56	0.38	26	35	5.82
	CC6	366	0.10	79	0.36	31	42	5.83
	RH3	279	0.05	35	0.44	23	29	5.83
	RH4	347	0.06	50	0.43	21	29	5.79
	RH6	367	0.09	71	0.38	19	32	5.80
B	Control	296	0.16	84	0.30	17	24	4.61
	CC3	187	0.19	64	0.25	16	14	6.00
	CC4	249	0.05	36	0.41	28	33	6.02
	CC6	310	0.48	136	0.21	21	28	5.91
	RH3	193	0.29	43	0.42	24	36	5.73
	RH4	286	0.09	56	0.37	18	24	5.71
	RH6	307	0.08	57	0.37	21	30	5.74
C	Control	105	0.09	29	0.28	12	14	6.50
	CC3	122	0.20	47	0.22	14	14	6.53
	CC4	162	0.31	67	0.22	18	15	7.40
	CC6	180	0.39	83	0.20	17	16	7.61
	RH3	148	0.21	54	0.24	17	12	6.58
	RH4	182	0.33	77	0.21	14	12	7.32
	RH6	203	0.43	89	0.16	14	11	7.71

[a] Derived sorption parameters using non-linear least squares function nls in R studio v.3.4.2.

[b] Derived sorption parameters for each models for each treatment for the individual soil types were all significant $p < 0.01$.

[c] Supernatant pH after the sorption experiment.

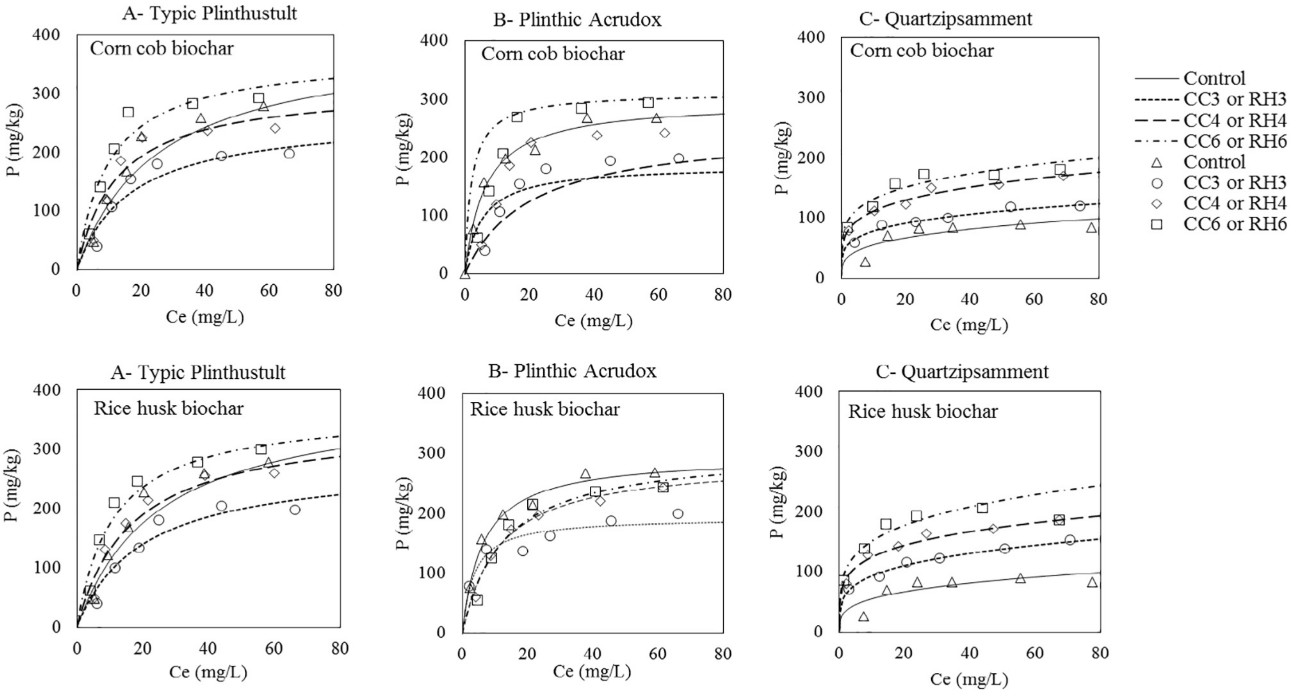


Fig. 2. P sorption curves in three soil types amended with corn cob biochar (CC3, CC4, CC6) or rice husk biochar (RH3, RH4, RH6) in comparison with control soils (soils without biochar amendment). Soil A and B were fitted to Langmuir model and Soil C was fitted to Freundlich model. The sorption curves parameters were obtained from non-linear least squares regression method in R studio 3.4.2.

contents of these materials as depicted in Table 2. At lower temperatures e.g. 300 °C, labile organic C would be more than at 450 °C and 650 °C. This higher labile organic C content would inhibit P adsorption in the soil and thus in part account for the lower P adsorption when the biochar types at 300 °C were amended to the acid soils. This assertion is corroborated by Schneider and Haderlein (2016) who suggested that labile organic C from low temperature pyrolysis biochar inhibit P sorption in Fe and Al oxides dominated soils of the tropics. Such a competitive reaction has been reported between P and several low molecular weight organic acids and anions (Gerke et al., 2000). Comparatively, corn cob biochar was more effective in increasing P availability in soils A and B than rice husk biochar. For instance, CC3 decreased P sorption capacity of soil A and B respectively by 33.7% and 36.8% whereas RH3 did similarly by 29.4% and 34.8%. The relatively lower P adsorption by the soils upon amendment with the corn cob biochar types is as a result of the lower Al and Fe and higher P contents of the biochar type (Table 2).

Unlike the decrease in P sorption in soil A and B amended with biochar, soil C (Quartzipsamment) showed increase in P sorption with increasing pyrolysis temperature (Table 4). The addition of corn cob biochar and rice husk biochar increased the Qmax of soil C from 105 mg kg^{-1} to a range of 112 mg kg^{-1} to 180 mg kg^{-1} and 148 mg kg^{-1} to 203 mg kg^{-1} respectively. This was in agreement with that of Zhai et al. (2014) who reported an increase in P sorption at increasing pyrolysis temperature in a slightly alkaline soil when maize residue biochar produced at different pyrolysis temperature was added. Most of the P are fixed by added alkaline and alkaline earth metals in char (DeLuca et al., 2015; Xu et al., 2014). Corn cob and rice husk biochar have higher inherent Ca and Mg content than Fe and Al (Table 2). The equilibrium pH observed in the Quartzipsamment after adsorption was between 6.50 and 7.71, a range within which most Fe and Al would be precipitating or polymerizing out of solution. The ash in the biochar contains high levels of basic cations as shown in Table 2. There could therefore be biochar surface complexation between the Ca and Mg in the ash and the $H_2PO_4^-$ that will be prevalent in soil solution at these pH ranges. The formation of Ca—P and Mg—P precipitate on the biochar-soil mixture could therefore be the mechanism underlying the increase in P sorption in the neutral soil. It is clear from the study that it is not advisable to add biochar to neutral soils since it could reduce P availability for plant uptake.

3.3. Effect of biochar types on P desorption of soils

Phosphorus desorbability was used to describe the amount of P desorbed from soils and soil-biochar mixtures as shown in Fig. 3. Phosphorus desorbability of all the treatments showed that increasing initial P concentration from 21.5 mg L^{-1} to 86.0 mg L^{-1} resulted in an increase in P desorbability. This was in line with those of Cui et al. (2011) who observed an increase in P released from ferrihydrite when initial P concentration was increased from 1 mg L^{-1} to 200 mg L^{-1}. Phosphorus adsorption mechanism on clay minerals involves basically monodentate and bidentate reactions (Jaisi et al., 2010). At low initial P concentration of < 50 mg L^{-1}, bidentate mechanism of P adsorption dominates whereas monodentate reaction occurs when the initial P concentration is > 50 mg L^{-1} (Antelo et al., 2010). This obviously explains the low amount of P desorbed from the adsorbents at initial P concentrations of 21.5 mg L^{-1} and 43.0 mg L^{-1} as compared to 86.0 mg L^{-1}. The substantial amount of P released from the treatments at all the three P loadings namely 21.5, 43.0 and 86.0 mg L^{-1} implies high P bioavailability for plant uptake. However, the sandy texture of the neutral soil (soil C) could result in high leaching potential of P inducing eutrophication in ground water.

The study showed significant ($p < 0.01$) variation among the treatments for each of the initial P concentration levels. Generally, corn cob and rice husk biochar amendment significantly ($p < 0.01$) increased P released in the acid soils (soil A and B). However, there was a significant ($p < 0.01$) decrease in P desorption in soil C. The increase in P desorbability was more sensitive to biochar type charred at 300 °C and 450 °C in the two acid soils. Similar results for higher P desorption from an Oxisol amended with wheat straw biochar produced at 350 °C than 700 °C was observed by Xu et al. (2014). Acid functional groups such as carboxylic and phenolic groups on organic material can cause P

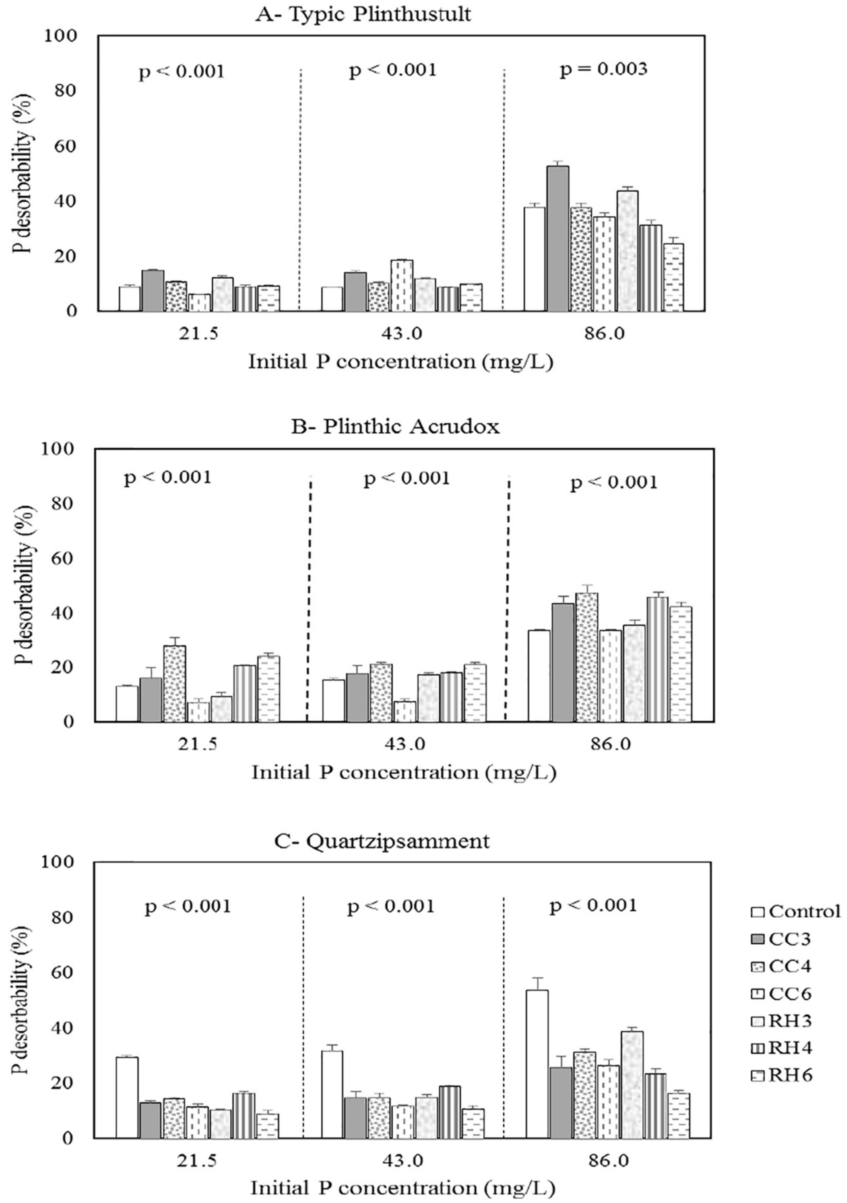


Fig. 3. Effect of initial P concentration (21.5 mg P L^{-1}, 43.0 mg P L^{-1} and 86.0 mg P L^{-1}) on P desorption in the soils types amended with corn cob biochar (CC3, CC4, CC6) or rice husk biochar (RH3, RH4, RH6) as compared to un-amended control soils (A, B or C). Error bars depict standard error. One-way ANOVA was performed on P desorbability for each initial P concentrations with p values showing significant difference at 1%.

removal from clay minerals through ligand exchange and or enhanced ligand dissociation of oxides and hydroxides of Fe and Al (Kirk et al., 1999). Correspondingly, the ample amount of acid functional groups on the low pyrolysis temperature biochar i.e. 300 °C and 450 °C, may explain the high P release. Biochar produced at high temperatures, especially at 650 °C, seems to decrease the amount of P desorbed in acid soils most predominantly at the 86.0 mg L^{-1} loading. The removal of OH groups at high pyrolysis temperature (650 °C) leads to the switch over of Fe—P and Al—P outer sphere complex to an inner sphere complex reaction which eventually affects the amount of P desorbed using neutral salts such as KCl and $CaCl_2$ (Frost et al., 2012). Biochar additions decreased P desorbability in soil C. This was obviously seen in the increase in binding energy (b) of soil C after the two biochar applications, from 0.09 L mg^{-1} to a range of 0.20 to 0.39 L mg^{-1} and 0.21 to 0.43 L mg^{-1} for corn cob biochar and rice husk biochar respectively (Table 4). The small amount of P released in the neutral soil could be ascribed to increasing binding energy as a result of increasing equilibrium pH ($pH > 7$) upon biochar incorporation.

4. Conclusion

The study showed that the properties of corn cob biochar and rice husk biochar were influenced by the pyrolysis temperature and therefore differently affected the P dynamics in the soils. In the acid soils (A and B), both biochar types effectively decreased P sorption capacity with increasing pyrolysis temperature. Contrasting results were observed in biochar amended soil C. It is obvious that the effect of biochar on P sorption was sensitive to the type of feedstock, pyrolysis temperature and equilibrium pH. However, P desorption was less affected by the feedstock type but rather was more dependent on pyrolysis temperature, pH and initial P concentration. Phosphorus desorption in soil A and B increased after the application of all biochar types but decreased in soil C. The study thus suggested that P availability and retention in tropical soils are influenced by biochar addition and that biochar produced at low temperatures (300 °C and 450 °C) can be considered as appropriate amendments in acid soils to make P more available for plant uptake. However, biochar application to neutral or alkaline soils can be considered as inappropriate P management practice since it increases P adsorption and lowers P desorbability.

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