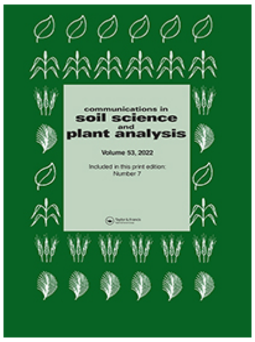

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Acidity and Aluminum Speciation in Biochar Amended Tropical Soils

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ABSTRACT
Soil acidification in the tropics has become a more pressing issue due to its associated aluminum (Al) phytotoxicity. The chemical reactive nature of biochar can alter Al speciation in soils. The study assessed the chemical properties and Al speciation in a Ultisol and an Oxisol amended with corn cob (CC) and rice husk (RH) biochars charred at 300, 450 and 650°C in an incubation study for 120 d. pH was determined periodically while organic carbon (OC), cation exchange capacity (CEC), exchangeable base cations, exchangeable acidity, and exchangeable Al^{3+} were measured at the end of the incubation period. Dissolved organic carbon (DOC) and pH were also determined in soil solution from each treatment. Throughout the incubation period CC and RH biochars significantly increased soil pH, with CC biochar showing a greater effect. Similar effects were also observed for OC, CEC, and exchangeable base cations (Ca^{2+}, Mg^{2+} and K^+). Soil exchangeable Al^{3+} and exchangeable acidity, soluble Al and Al^{3+} activity in soil solution decreased significantly upon biochar application; it was more significant at the 650°C. Biochars at 300–450°C exhibited a more notable increase in soil DOC. At $pH \leq 5.8$, Al-DOC and free Al^{3+} dominated in soil solution while at $pH > 5.8$, Al species was mainly Al-OH ions (i.e. $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, and $Al(OH)_4^-$). Biochars at 300–450°C promoted the large formation of Al-DOC while Al-OH ions dominated in 650°C-biochar treatments. Biochar can be used to ameliorate Al phytotoxicity in tropical acid soils, particularly at 300–450°C.

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KEYWORDS
Biochar; acidity; dissolved organic carbon; aluminum

Introduction

There are large areas of crop production on acidic Oxisol and Ultisol in Ghana. Soil acidity is considered a major precursor of low soil fertility in the tropics. Under natural condition, the rate of soil acidification is slow. However, in recent times it has increased due to the leaching of base cations, namely calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) via intense precipitation (Meng et al. 2019), the over usage of ammonium (NH_4^+)-based chemical fertilizers releasing proton via biochemical oxidation of ammonia to nitrate (Cai et al. 2019) and acid deposition (Driscoll et al. 2016)

In acidic soils, aluminum (Al) toxicity is a pressing challenge since root elongation and growth is repressed by soluble octahedral hexahydrate (Al^{3+}) speciation of Al, even at a low concentration ($< 50 \times 10^{-6}$ M) (Hagvall, Persson, and Karlsson 2015). The inactive Al in soils makes it nontoxic in the soil environment. However, upon soil acidification, the inactive Al forms diverse toxic species, such

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as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, and $Al(OH)_4^-$ via solubility reaction (Pavlů et al. 2019). The solubility of Al is predominant at pHs < 5.5 and >7.5 and is largely dependent on the soil pH, Al in soil solution, ionic strength, temperature, and concentration of organic and inorganic ligands (e.g., dissolved organic carbon). The solubility of Al in acidic soils increases exponentially with the decrease of the soil pH. However, even among the soluble Al species, phytotoxicity depends on their chemical forms with the Al monomeric ions less phytotoxic than AI^{3+} (Hagvall, Persson, and Karlsson 2015). The presence of dissolved organic carbon (DOC) in acidic soil solution is critical for the complexation of Al and such complex (Al-DOC) is supposed to be nontoxic (Kopittke et al. 2016).

A number of studies have reported the use of agricultural lime (e.g. calcite and dolomite) and organic residues for ameliorating Al toxicity in the tropics through neutralization reactions (Kapembwa et al. 2019; Shitumbanuma 2006). Conversely, for developing countries such as Ghana, liming materials are in limited supply and relatively expensive for smallholder farmers. Again, organic residue-reclamation effects do not last long due to the rapid mineralization (Gaskin et al. 2008).

Converting organic residue to biochar via pyrolysis is envisaged to be a better option due to it highly carbonized structure (Lehmann et al. 2011). Aside the recalcitrant nature of biochar, it tends to have high pH, calcium carbonate ($CaCO_3$) content, large surface area, base saturation, DOC and acidic functional groups, i.e., carboxylic (-COOH) and phenolic (-OH) groups (Sun et al. 2016). Applying biochar at 1–3% increases the pH, cation exchange capacity (CEC), base saturation, and water-holding capacity of soils, and also reduces exchangeable acidity and exchangeable Al (Lehmann et al. 2011; Masuda et al. 2020).

Al undergoes a number of speciations (i.e., free Al, hydroxyl Al and organic and inorganic Al complexes) in response to biochar application in tropical acid soils due to changes in soil pH (Alleoni et al. 2010; Nolla and Anghinoni 2006; Zhang et al. 2019). Zhang et al. (2019) observed high dissolution of Al in soil solution forming soluble Al-DOC complexes as a result of biochar amendment. In an Oxisol, Alleoni et al. (2010) concluded that Al–DOC represented 30% to 40% of the total Al in soil solution at pH >5.0 and at pH >5.5, hydroxyl fractions were dominant in soil solution. Hydroxyl Al species were found to be dominant of the total Al in soil solution at pH 6.4 in acidic Oxisol from Brazil while at pH 4, it was mainly free-form (Al^{3+}) and Al-DOC complex (Nolla and Anghinoni 2006).

Biochar has been posited to ameliorate Al phytotoxicity and improve crop production in acidic soils due to its liming and adsorptive properties (Cai et al. 2019; Qian, Chen, and Chen 2016). Upon biochar amendments, the alkaline contents (e.g., $CaCO_{3,}$ $_{-}$ COO^-) are discharged into soil solution to neutralize soil acidity thereby increasing soil pH (DeLuca et al. 2015).

More so, Al in soil solution forms complexes with the abundant – COOH on biochar surface and also surface adsorption and coprecipitation reactions with silicate minerals, minifying Al phytotoxicity (Qian, Chen, and Chen 2016). The use of biochar to ameliorate Al phytotoxicity can therefore be considered a low input approach for acid soil management in the tropics.

Due to the changes in biochar properties as a result of the pyrolysis temperature and feedstock, there is a possible high variation in the ameliorating effect of biochar on soils. For instance, pH, $CaCO_3$ and base cations contents of biochar tend to increase with increasing pyrolysis temperature while organic carbon (OC), CEC, acidic functional groups decrease with increasing temperature (Liang et al. 2014).

However, limited studies have been done on the effect of biochar at different pyrolysis temperature on ameliorating Al toxicity, especially on Ghanaian acid soils. Therefore, this study tends to fill this lacuna by conducting a 120-day incubation study using rice husk and corn cob biochars charred at 300°C, 450°C and 650°C as amendments in two tropical acid soils.

The objectives of the study were to investigate the effects of corn cob and rice husk biochars at different pyrolysis temperatures on pH, OC, exchangeable base cations, CEC, DOC, Al speciation and the degree of Al toxicity in two acid soils in an incubation study. The study will give an insight to soil scientists and the resource-poor local farmers as to how best locally available and low-cost agricultural inputs, such as corn cob biochar and rice husk biochar, can be used to optimize yields of crops in tropical acid soils.

Materials and methods

Experimental setup

Two widely used soils for agronomic activities in Ghana, Typic Plinthustult (Ultisol) and Typic Acrudox (Oxisol) were sampled from the moist semi-deciduous forest (06°8.6′N; 0°54.144′W) and evergreen high rain forest (05°13′N; 02°38′W), respectively. Ultisol with sandy clay loam texture (20.30% clay, 11.20% silt, and 68.70% sand) has a mean annual temperature of about 32°C and a mean annual rainfall between 800 and 1200 mm (Dwomo and Dedzoe 2010). The texture of the Oxisol is also sandy clay loam (18.40% clay, 8.00% silt, and 64.60% sand) having a mean annual temperature and rainfall of 30°C and 2000 mm, respectively (Dwomo and Dedzoe 2010). Briefly, the Ultisol is acidic (pH 5.0) with low OC (14.0 g kg^{-1}) and CEC (15.2 $cmol_c$ kg^{-1}) contents. The exchangeable base cations content of Ultisol are 1.27, 0.42, 0.14, and 0.07 $cmol_c$ kg^{-1} for Ca^{2+}, Mg^{2+}, K^+, and Na^+, respectively. The Oxisol has a pH of 4.7 (very acidic) with low OC (13.30 g kg^{-1}) and low CEC of 12.78 $cmol_c$ kg^{-1}. It exchangeable base cations content are 0.32, 0.10, 0.04, and 0.06 $cmol_c$ kg^{-1} for Ca^{2+}, Mg^{2+}, K^+, and Na^+, respectively.

Two biochars prepared from corn cob (*Zea mays*) (CC) and rice husk (Oryza sativa) (RH) biomass at three pyrolysis temperatures (300°C, 450°C and 650°C) were used for the study. The biochars were acquired from Soil Research Institute of the Council for Scientific and Industrial Research (CSIR), Ghana. The CC and RH biomass produced 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 incubation study. Detailed description of the soils and biochars are shown in previous studies (Eduah et al. 2020a, 2019, 2020b).

Incubation experiment

CC3, CC4, CC6, RH3, RH4 and RH6 were amended to each of the control soils (Ultisol and Oxisol) making fourteen (14) treatments in the incubation study. Each treatment was replicated three times. Soils were thoroughly mixed with amendments (biochars) at a rate of 1% w/w in plastic beakers (7 × 5 cm) and distilled water was added to 70% of field capacity at a temperature of 28°C in the laboratory incubator for 120 d. Soils were sub-sampled at 7, 15, 25, 35, 50, 75, 100, and 120 days. The sub-sampled soils were analyzed for pH as described by Gaskin et al. (2008). At the end of the incubation period, soils were sampled, air-dried, ground, and passed through 2 mm sieve for further analysis. Soil pH was measured in deionized water at a ratio of 1:2.5 w/w after shaking for 1 h (Gaskin et al. 2008). A LECO TIUMAC CNS analyzer was used to measure OC. CEC and exchangeable base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) were measured by modified NH_4-acetate compulsory displacement method (pH 7.0) (Gaskin et al. 2008). Exchangeable acidity and Al^{3+} were determined using 1 M KCl solution titrated by 0.01 M NaOH (pH 7.0) (Pansu and Gautheyrou 2006).

Soil solution from each of the treatments used for the determination of pH, Al, and DOC was obtained according to Wolt (1994) as described by Alleoni et al. (2010). Briefly, subsample of 20 g from the incubation study was weighed into a centrifuge bottle, 20 mL of deionized water was added and shaken at 150 rpm for 20 min. Subsequently, the centrifuge bottles were shaken for 10 min at 220 rpm and 30 min at 1500 rpm after a lag period of 1 h. The extract was passed through 0.45 cellulose membrane filters and 0.7-µm glass microfiber, respectively, for Al and DOC determination. pH of the extracts was also determined. Al concentration was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) as described in a previous study (Eduah et al. 2019) while DOC by LECO TIUMAC CNS analyzer. Visual MINTEQ geochemical software was used to calculate

Al speciation in the solution by inputting temperature, pH values, Al and DOC concentrations in the solution (Gustafsson 2007). Al complexation with DOC was determined using the Gaussian Dissolve Organic Matter (GDOM) model (Alleoni et al. 2010).

Statistical analysis

Data obtained were tested for normality using Shapiro–Wilk test before subjecting to the analysis of variance (ANOVA). The effect of biochars on soil chemical properties was done using one-way ANOVA at a significance level of 0.05. The variations among the mean values were done using Tukey test. The extent of effects among the chemical properties were assessed using regression analysis. All analyses were done using R-studio and are presented as the average of three replicates with standard error.

Results and discussion

Biochar effects on soil pH

The effect of biochar types on soil pH at the various pyrolysis temperatures is shown in Figure 1. Generally, at the earlier stage of the incubation, there was a significant ($p < .05$) upsurge in soil pH after the addition of CC and RH biochars, and altered slightly afterward. This was contrary to the findings of Zhao, Wang, and Xing (2014), observing an initial decreased in soil pH in a biochar (*Pinus massoniana* bark) amended Plinthudults. However, the finding of the present study was consistent with those of Jha et al. (2016), reporting an initial drastic increase in soil pH after application of Leuceana (*Leuceaena leucocephala*) biochar.

At the end of the incubation period, the amendments increased soil pH by 0.54–1.30 and 0.66–0.98 units in the Ultisol and Oxisol, correspondingly, and followed the order of CC6 > CC4 > RH6 > CC3 > RH4 > RH3 for Ultisol and for Oxisol, CC6 > CC4 > RH6 > RH4 > CC3 > RH3 (Table 1). The increased in pH after the 120 d was more significant ($p < .05$) in soils amended with biochars charred at 650°C; CC biochar types had a greater ameliorating effect as compared to its RH counterparts (Table 1).

The pH of the soils from the different biochar treatments was significant and positively related to OC ($R^2 = 0.49$, $p < .05$), CEC ($R^2 = 0.56$, $p < .05$) and exchangeable bases (Ca^{2+}, Mg^{2+}, K^+; $R^2 = 0.66$–0.87, $p < .05$) (Figure 2a-e). This suggests that the changes in soil pH may in part controlled by these

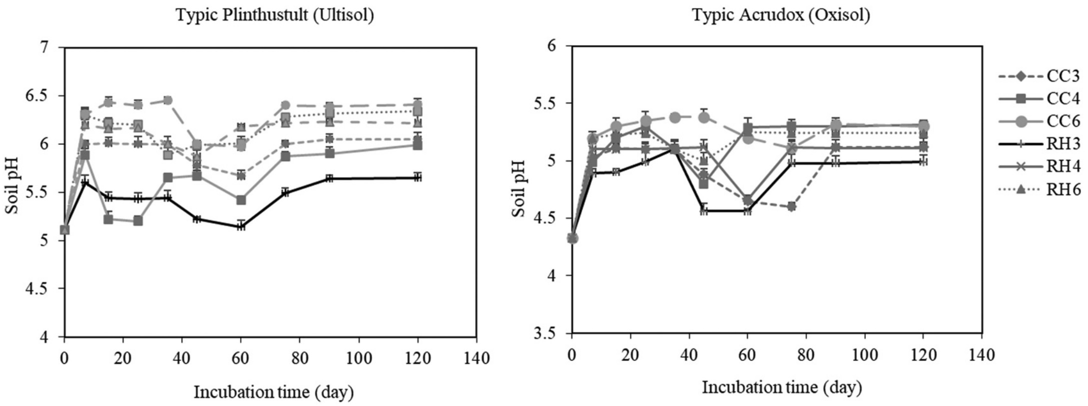

Figure 1. Soil pH changes during the 120 days incubation period for the soils, typic plinthustult (Ultisol) and typic acrudox (Oxisol) amended with corn cob biochar (CC3, CC4, CC6) and rice husk biochar (RH3, RH4, RH6). Bars represent mean ± standard errors, n = 3.

Table 1. Chemical properties of soil and biochar (corn cob and rice husk at 300°C, 450°C and 650°C) amended soils after 120 days incubation. Standard errors are in parenthesis, n = 3, $^{+}$values of the same letter within a column are significantly the same at 0.05 level of significance based on Tukey's test.

			g kg^{-1}	$cmol_c$ kg^{-1}						
			OC	CEC	Exchangeable base cations					
Soil	Treatments	pH			Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Exchangeable Al^{3+}	Exchangeable acidity
Ultisol	Control	5.11	14.23 f^{+}	16.68d	1.21b	0.24 c	0.14b	0.07 c	3.21a	3.71a
		(0.03)	(0.22)	(0.41)	(0.02)	(0.01)	(0.00)	(0.00)	(0.11)	(0.07)
	CC3	6.05	24.04a	25.71a	1.59a	0.46bc	0.23b	0.11b	2.08b	2.80bc
		(0.01)	(0.12)	(0.39)	(0.02)	(0.00)	(0.01)	(0.00)	(0.09)	(0.03)
	CC4	6.34	18.39d	21.67bc	1.68a	0.79ab	0.43b	0.14ab	1.97b	2.73 c
		(0.01)	(0.01)	(0.44)	(0.01)	(0.01)	(0.01)	(0.01)	(0.07)	(0.03)
	CC6	6.41	17.98d	20.60bc	1.73a	1.10a	0.55a	0.14ab	1.56d	1.87d
		(0.01)	(0.27)	(0.22)	(0.02)	(0.04)	(0.03)	(0.01)	(0.01)	(0.01)
	RH3	5.65	21.67b	23.41ab	1.53ab	0.45bc	0.20b	0.13ab	2.01b	3.00b
		(0.00)	(0.42)	(0.18)	(0.03)	(0.03)	(0.02)	(0.04)	(0.06)	(0.01)
	RH4	5.99	19.78 c	20.74bc	1.62a	0.68abc	0.26a	0.13ab	1.77 c	2.11d
		(0.00)	(0.45)	(0.26)	(0.01)	(0.03)	(0.02)	(0.00)	(0.04)	(0.02)
	RH6	6.22	16.40d	19.31 cd	1.70a	1.00a	0.42a	0.15a	1.72 cd	1.96d
		(0.02)	(0.33)	(0.26)	(0.00)	(0.05)	(0.04)	(0.02)	(0.07)	(0.00)
Oxisol	Control	4.33	12.79 c	14.11d	0.37b	0.10 g	0.04e	0.06d	3.89a	4.47a
		(0.02)	(0.21)	(0.56)	(0.01)	(0.03)	(0.00)	(0.00)	(0.07)	(0.00)
	CC3	5.12	19.22a	18.23a	0.51a	0.35e	0.10d	0.14b	2.69b	3.02 cd
		(0.01)	(0.28)	(0.43)	(0.00)	(0.03)	(0.00)	(0.00)	(0.06)	(0.03)
	CC4	5.31	15.01bc	16.40bc	0.54a	0.45	0.27b	0.17a	2.42 c	2.79de
		(0.03)	(0.19)	(0.44)	(0.01)	(0.02)	(0.00)	(0.00)	(0.02)	(0.01)
	CC6	5.30	15.11bc	16.20bc	0.54a	0.72a	0.32a	0.17a	1.86d	2.04 f
		(0.00)	(0.11)	(0.55)	(0.01)	(0.02)	(0.05)	(0.00)	(0.01)	(0.00)
	RH3	4.99	17.27ab	17.64ab	0.46ab	0.21 f	0.11d	0.12 c	2.80b	3.31b
		(0.03)	(0.46)	(0.34)	(0.00)	(0.02)	(0.02)	(0.01)	(0.01)	(0.01)
	RH4	5.11	15.22bc	15.89 c	0.54a	0.38 c	0.20 c	0.15ab	2.42 c	3.14bc
		(0.05)	(0.18)	(0.23)	(0.00)	(0.03)	(0.02)	(0.03)	(0.02)	(0.02)
	RH6	5.24	14.02 c	15.01 cd	0.54a	0.66b	0.31ab	0.16ab	2.01d	2.56e
		(0.05)	(0.27)	(0.12)	(0.01)	(0.01)	(0.05)	(0.00)	(0.02)	(0.02)

CC3, corn cob biochar at 300°C; CC4, corn cob biochar at 450°C; CC6, corn cob biochar at 650°C; RH3, rice husk biochar at 300°C; RH4, rice husk biochar at 450°C; RH6, rice husk biochar at 650°C; OC, organic carbon; CEC; cation exchange capacity; DOC, dissolved organic carbon.

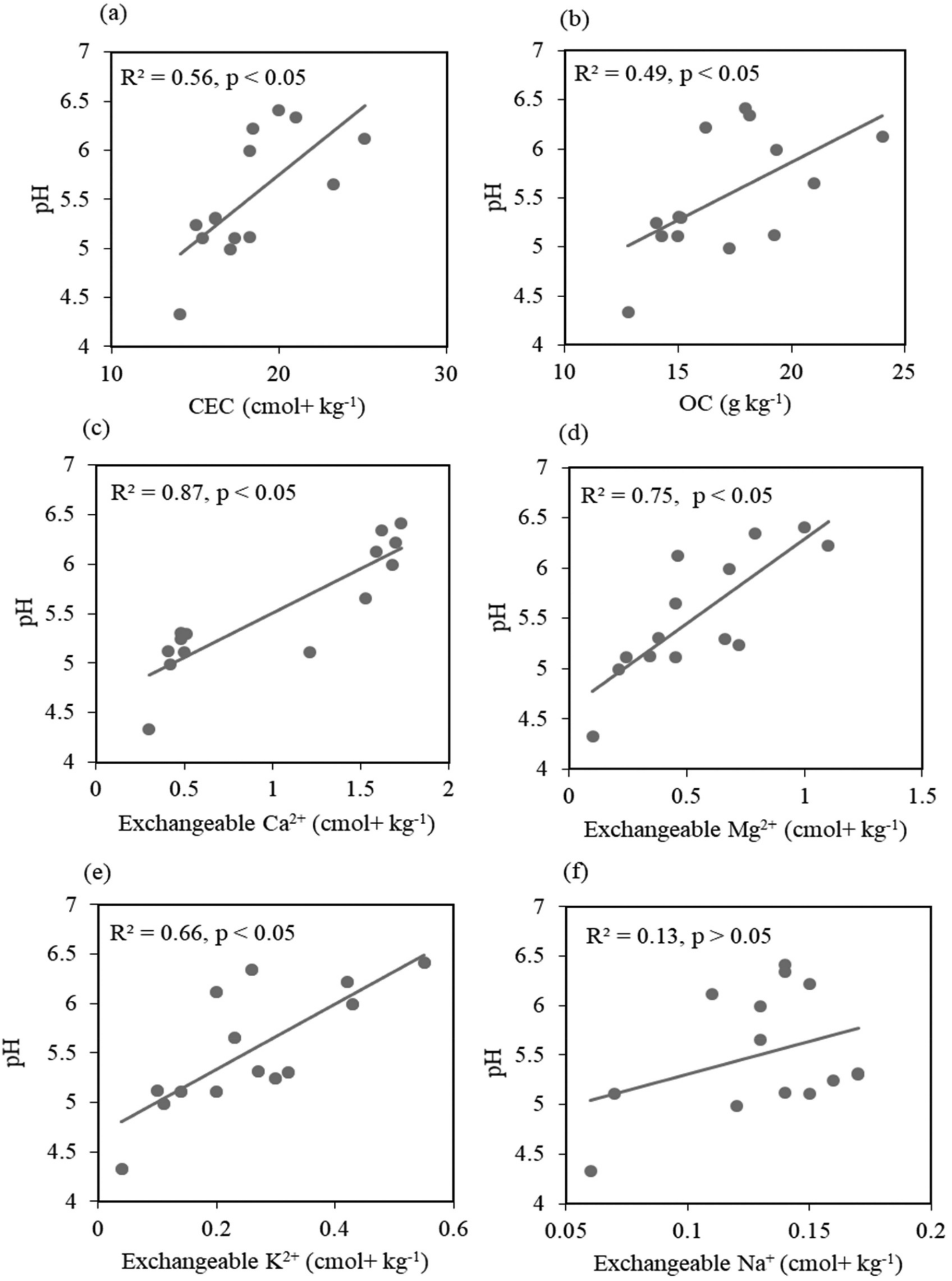

Figure 2. Linear fitting of soil pH vs soil chemical properties (a) cation exchange capacity (CEC), (b) organic carbon (OC), (c) exchangeable Ca^{2+}, (d) exchangeable Mg^{2+}, (e) exchangeable K^+ and (f) exchangeable Na^+ after amending soils with corn cob biochar (CC3, CC4, CC6) and rice husk biochar (RH3, RH4, RH6) at the end of 120 days incubation. Each point is the mean of 3 replicates (n = 3).

chemical properties. This finding is consistent with the results of prior studies (Shi et al. 2019; Xu et al. 2012). Even though exchangeable Na^+ is reported to control soil pH (Jha et al. 2016), the present study showed no significant ($R^2 = 0.13$, $p > .05$) effect of exchangeable Na^+ on soil pH (Figure 2f).

The released of OC following manure amendment in an Oxisol has been reported to increase soil pH (Shi et al. 2019). In the present study, the OC content of the soils was improved, decreasing with increasing pyrolysis temperature (Table 1). The more significant ($p < .05$) effect on OC of the CC3 and RH3 treatments is due to the high labile C content of CC3 and RH3 biochars as reported in a previous study (Eduah et al. 2020b). The protonation reaction of dissociated acidic functional groups, i.e., $-O^-$ and $-COO^-$ of the OC in the presence of H^+, thereby the consumption of protons by the acidic functional groups may have resulted in the increased soil pH.

CEC, which expresses the negative surface charge of the soils increased after adding the biochars. It increased from 16.68 $cmol_c\ kg^{-1}$ (Ultisol) to a range of 20.60 to 25.71 $cmol_c\ kg^{-1}$ in the CC treatments while 19.31 to 23.41 $cmol_c\ kg^{-1}$ in the RH treatments. In Oxisol, CC and RH raised CEC significantly ($p < .05$) from 14.11 $cmol_c\ kg^{-1}$ to between 16.20 and 18.23 $cmol_c\ kg^{-1}$ and 15.01 to 17.64 $cmol_c\ kg^{-1}$, respectively (Table 1). This change can be attributed to the abundance of $-COOH$ and $-OH$ functional groups on the CC and RH biochars (Lehmann et al. 2011), eventually allowing for exchange reactions of the negatively charged surface soils with protons, thereby increasing soil pH. The released of hydroxyl ion (OH^-) via chemisorption involving ligand exchange reaction between orthophosphate and clay minerals (i.e., Al-OH and Fe-OH) could have also culminated into the increase in soil pH (Shepherd et al. 2017).

The high linear dependency of soil pH on exchangeable Ca^{2+}, Mg^{2+}, and K^+ (Figure 2c-e) goes to suggest that there was a discharge of base cations into soil solution after biochar amendments. This phenomenon has been reported to be the dominant mechanism of biochar-amelioration effect on soil acidity in tropical soils because of the greater consumption of protons of exchangeable bases once released into soil solution (Shi et al. 2019). The exchangeable base cations of the amended soils increased with pyrolysis temperature (Table 1). This obviously explains the greater ameliorating effect of biochars charred at high temperature (650°C) as compared to low temperature (300°C). It also confirmed the greater effect of CC biochar on soil pH than RH biochar due to the higher base cations in the former biochar (Table 1).

The subsequent decrease in soil pH in the course of the incubation period could be due to nitrification of NH_4^+; while N mineralization of biochar results in the neutralization of soil acidity, nitrification of NH_4^+ counteracts the amelioration effects of these biochar amendments. Yan and Schubert (2000) reported a significant negative correlation between soil pH and NO_3^- formation in organic amended soils. Jha et al. (2016) also observed fluctuating changes over a 90-day incubation period in a biochar amended soil and attributed the decline in pH to nitrification reaction. Again, the subsequent decline in soil pH can also be attributed to the oxidized non-aromatic C component of the biochar during aging in soil (Nguyen et al. 2010).

Biochar effect on exchangeable Al, exchangeable acidity, soluble Al, and Al activity

Exchangeable Al^{3+} is the major determinant of soil acidity since the content of exchangeable H^+ is generally low in acid mineral soils (Yu 1997). Again, the exchange reaction between the soil exchangeable sites and soil solution controls the activity of Al^{3+} in soil solution. Therefore, exchangeable Al^{3+} is an essential factor for soil exchangeable acidity, the transformation of diverse Al species as well as the toxicity potential of Al in soil solution (Collignon, Boudot, and Turpault 2012). In comparison with the control soils (Ultisol and Oxisol), the addition of biochar significantly ($p < .05$) decreased soil soluble Al (Al^{3+} activity), exchangeable Al^{3+} and exchangeable acidity (Table 1). For instance, at the end of the incubation period, CC and RH biochars at 650°C significantly ($p < .05$) reduced exchangeable Al^{3+} of the Ultisol from 3.21 $cmol_c\ kg^{-1}$ to 1.56 $cmol_c\ kg^{-1}$ and 1.72 $cmol_c\ kg^{-1}$, respectively (Table 1). In the Oxisol, exchangeable Al^{3+} significantly ($p < .05$) decreased from 3.98 $cmol_c\ kg^{-1}$ to 1.86 $cmol_c\ kg^{-1}$and 2.01 $cmol_c\ kg^{-1}$, respectively, in CC and RH treatments at 650°C (Table 1). In a study by Masuda et al. (2020), it was observed that poultry litter biochar can decrease exchangeable Al^{3+} in acid soils which was consistent with the findings of the present study. Applying 1% of paper mill biochar to a Ferrasol was reported to increase soil pH from 4.2 to between 5.4 and 5.9, thereby decreased exchangeable Al^{3+} (Van Zwieten et al. 2010).

CC and RH biochars drastically decreased Al^{3+} activity in the Oxisol from 17.6×10^{-6} mol L^{-1} (17.6 μM) to between 2.59×10^{-7} to 5.17×10^{-7} mol L^{-1} (0.259–0.517 μM) and 7.97×10^{-7} to 9.33×10^{-7} mol L^{-1} (0.797–0.933 μM), respectively (Table 2). The 1.04×10^{-6} mol L^{-1} (1.04 μM) Al activity in the Ultisol was reduced to between 3.83×10^{-9} to 1.72×10^{-8} mol L^{-1} (0.004–0.017 μM) in the CC treatments whiles 7.38×10^{-9} to 2.76×10^{-7} mol L^{-1} (0.007–0.276 μM) in the RH treatments (Table 2). In consonance with the present study, Vieira et al. (2009) reported a significant decrease in Al activity from 2.98×10^{-6} mol L^{-1} to between 2.39×10^{-8} and 2.70×10^{-15} mol L^{-1} after amending a Spodosol with organic materials. Again, in an Inceptisol the addition of green manure and peat + green manure reduced Al activity from 47.94 μM to 0.10 μM and 1.04 μM, respectively (Muhrizal et al. 2003).

Studies have indicated a number of critical thresholds for Al activity toxicity to root elongation of some crops including 3.5 μM Al^{3+} activity for mungbean (*Vigna radiata*) (Muhrizal et al. 2003), 4 μM Al^{3+} activity for soybean (*Glycine max*) (Bruce et al. 1988), 9 μM Al^{3+} activity for coffee seedlings (Pavan, Bingham, and Pratt 1982) and 1.5 μM Al^{3+} activity for gramineous species (Brenes and Pearson 1973). Considering the critical levels earlier reported and relating it to the level of Al activity in both the Oxisol (17.6 μM) and the Ultisol (1.04 μM), these soils have the tendency of causing Al toxicity to root development of Al-sensitive crops. Obviously, amending the soils with the CC and RH biochars culminated into about 10 to 1000-fold less in Al activity, far below the critical levels mentioned in earlier studies. This implies that the addition of biochar to tropical acid soils will potentially alleviate Al phytotoxicity.

The increase in pH after the biochar amendment explains the reduction in soluble Al^{3+}, exchangeable Al^{3+} and exchangeable acidity as confirmed by the significant and negative relationship between pH and exchangeable Al^{3+} ($R^2 = 0.73$, $p < .05$), exchangeable acidity ($R^2 = 0.61$, $p < .05$) and soluble Al^{3+} ($R^2 = 0.76$–0.85, $p < .05$) (Figures 3 and 4). The inhibition of soluble Al^{3+}, exchangeable Al^{3+} and exchangeable acidity was more predominant in the 650°C biochar amended soils as a result of the high alkaline content (e.g., carbonates, base cations, silicates) in CC and RH biochars at high pyrolysis

Table 2. Dissolved organic carbon (DOC), soluble Al and Al^{3+} activity (from the Visual MINTEQ geochemical model) of soil and biochar (corn cob and rice husk at 300°C, 450°C and 650°C) amended soils after 120 days incubation. Standard errors are in parenthesis, n = 3, $^+$values of the same letter within a column are significantly the same at 0.05 level of significance based on Tukey's test.

		mg L^{-1}		mol L^{-1}
Soil	Treatment	DOC	Soluble Al	Al^{3+} activity
Ultisol	Control	9.80d (0.03)	1.22a (0.02)	1.04×10^{-06}
	CC3	16.30a (0.10)	0.67bc (0.01)	1.72×10^{-08}
	CC4	15.40ab (0.11)	0.54 c (0.04)	3.83×10^{-09}
	CC6	15.00bc (0.01)	0.54 c (0.01)	7.58×10^{-09}
	RH3	15.90a (0.12)	0.72b (0.01)	2.76×10^{-07}
	RH4	15.00bc (0.15)	0.50 c (0.01)	3.52×10^{-08}
	RH6	13.90 c (0.01)	0.52 c (0.02)	7.38×10^{-09}
Oxisol	Control	7.70e (0.13)	1.70a (0.01)	1.79×10^{-05}
	CC3	15.9a (1.12)	0.80bc (0.03)	3.68×10^{-07}
	CC4	14.51b (0.08)	1.01b (0.00)	5.17×10^{-07}
	CC6	10.32d (0.16)	0.78 c (0.02)	2.59×10^{-07}
	RH3	14.00 c (0.07)	1.00b (0.01)	8.57×10^{-07}
	RH4	14.81bc (0.09)	0.92b (0.01)	7.97×10^{-07}
	RH6	11.20d (0.12)	1.12b (0.04)	9.33×10^{-07}

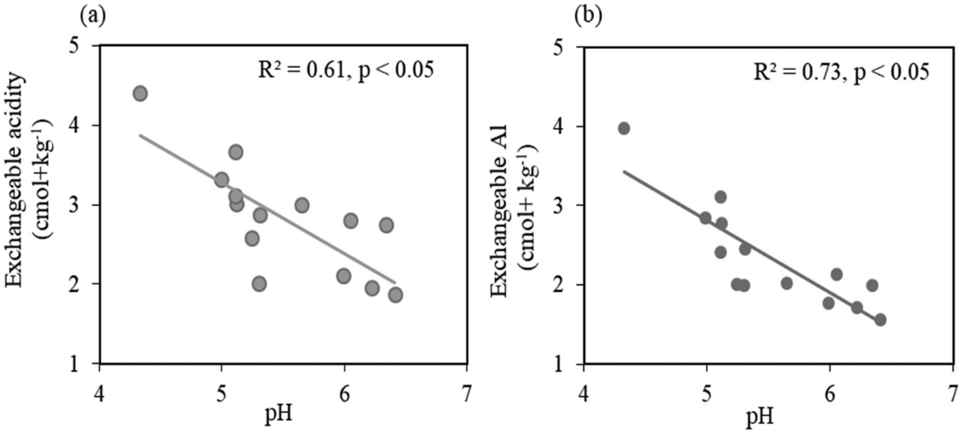

Figure 3. Linear fitting of soil exchangeable acidity (a) and exchangeable Al (b) vs soil pH after amending soils with corn cob biochar (CC3, CC4, CC6) and rice husk biochar (RH3, RH4, RH6) at the end of the 120 days incubation. Each point is the mean of 3 replicates (n = 3).

temperatures (Lehmann et al. 2011). Due to the liming effect of the added CC and RH biochar types, increase in soil pH may have led to the increasing hydrolysis of highly toxic Al^{3+}, converting it to less toxic Al-hydroxyl monomers or precipitates of Al-hydroxides (Figure 4).

Aside the liming effect, the surfaces of CC and RH biochars can act as adsorptive sites for Al binding via their organic groups and mineral content, contributing to the reduction in the exchangeable Al^{3+} thus the decrease in soil exchangeable acidity. The final pH reached 5.12–5.31 and 4.49–5.24 for CC and RH treatments, respectively, in the Oxisol while 6.05–6.41 and 5.65–6.22, respectively, in the Ultisol (Table 1). At these pH values, it is possible that the dissociated oxygen containing functional groups (i.e. carboxyl and hydroxyl) contributing to the negative surface charge of the organic groups of the biochars will form complexation reactions with Al species (i.e., $Al(OH)^{2+}$ and $Al(OH)_2{}^{+}$) via specific adsorption. This was evident in the significant and negative relationship between soluble Al and DOC (R^2 = 0.69, $p < .05$) (Figure 6), suggesting that the increase in DOC coupled with pH caused by biochars played a critical role in reducing Al^{3+} concentration in soil solution.

The presence of Si-O-Si stretching band on RH and CC biochars as reported in a previous study (Eduah et al. 2019), may have also contributed to the adsorption of Al, thereby reducing Al^{3+} in the soil solution. This adsorption mechanism is expected to be prominent in the RH biochar treatments as compared to CC treatments due to the former's high silicon (Si) content. After observing fourier transform infrared spectroscopy (FTIR) spectra of biochar before and after being loaded with Al, Qian and Chen (2014) concluded high adsorption of Al onto the surface of silica. White et al. (2008) also reported the formation of hydroxyl-aluminosilicates in freshwater after adding Si. Despite the relatively lower Si content of CC biochar, it contributed to a relatively higher reduction in Al activity in the soil solution (Table 1). The greater remarkable effect of CC biochar on ameliorating Al toxicity can, therefore, be attributed to the higher surface area, CEC, and abundant acidic organic functional groups on the surface of the CC serving as more adsorption sites for Al (Pan, Jiang, and Xu 2013). It is obvious that through liming effect and complexation reactions, CC and RH amendment to acid soils has the potential of reducing the Al phytotoxicity.

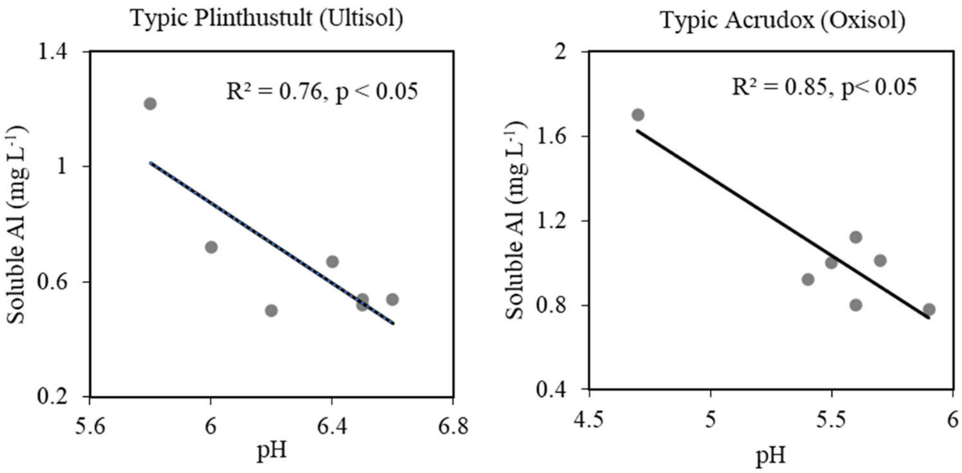

Figure 4. Linear fitting of soluble Al vs soil solution pH for each soil, Typic Plinthustult (Ultisol) and Typic Acrudox (Oxisol) after amending soils with corn cob biochar (CC3, CC4, CC6) and rice husk biochar (RH3, RH4, RH6) at the end of 120 days incubation. Each point is the mean of 3 replicates (n = 3).

Biochar effect on DOC and Al speciation in soil solutions

Compared with the control soils, application of the biochars significantly ($p < .05$) increased DOC. For example, DOC content increased from 9.80 mg L^{-1} in the Ultisol to between 15.00 and 16.30 mg L^{-1} and 13.90 to 15.90 mg L^{-1} in CC and RH biochar amended soil, respectively (Table 1). In a similar study, Zhao et al. (2020) observed a large increase in soil organic matter and DOC in an Ultisol following rice straw, canola straw and peanut straw biochars amendments. The increase in DOC in the soils suggest that CC and RH biochars caused a discharge of DOC and this could be attributed to the increased in pH (Figure 5). Smebye et al. (2016) conducted batch experiments with biochar amended acidic Acrisol and reported that an increase in pH followed the same trend as the discharge of DOC. As pH increases, the deprotonation of acid functional groups in the DOC is enhanced by increasing the charge density and thus the hydrophilicity culminating in DOC solubility (De Wit, Groseth, and Mulder 2001). Again, changes in the soil matrix may have contributed to the increased DOC after biochar application. Biochar induced high negative charge potential of the soil particles via deprotonation reaction as a result of the increase in soil pH. Ultimately, the negative adsorptive sites will result in the desorption of DOC.

The increase in DOC content in soils was more significant ($p < .05$) at low pyrolysis temperature (i.e. 300°C) (Table 1) and could be attributed to the high readily labile C in CC and RH biochars charred at low temperature; 70% and 52% of total C, respectively, in a previous study (Eduah et al. 2020a).

DOC as a mobile phase of soil organic matter is characterized by diverse surface functional groups, thereby has the potential of controlling the bioavailability, fate, mobility, and toxicity of Al in the soil environment (Jansen, Nierop, and Verstraten 2003). The increase in DOC in the soils as induced by the CC and RH biochars can therefore augment the mobilization of Al by forming Al-DOC complexation in the soil solution.

Al phytotoxicity can not only be inferred from the concentration of Al in soil solution since Al can exist as free species, hydroxyl monomers and polymers, and complexes with organic and inorganic ligand, thus informing the potential phytotoxicity of each of the species (Sposito 1995). The phytotoxicity of Al species decreases in the following order: $Al^{3+} > Al(OH)^{2+} > Al(OH)_2{}^{+} > Al(OH)_3 > Al(OH)_4{}^{-}$. Al complexation with DOC and anions such as F^{-} are regarded as nontoxic (Bloom and Erich 1995; Kopittke et al. 2016).

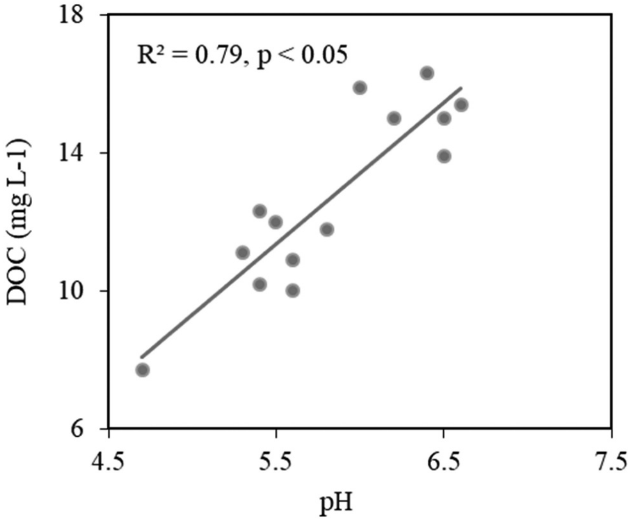

Figure 5. Linear fitting of pH vs dissolved organic carbon (DOC) in soil solution as affected by corn cob biochar (CC3, CC4, CC6) and rice husk biochar (RH3, RH4, RH6) at the end of the 120 days incubation. Each point is the mean of 3 replicates (n = 3).

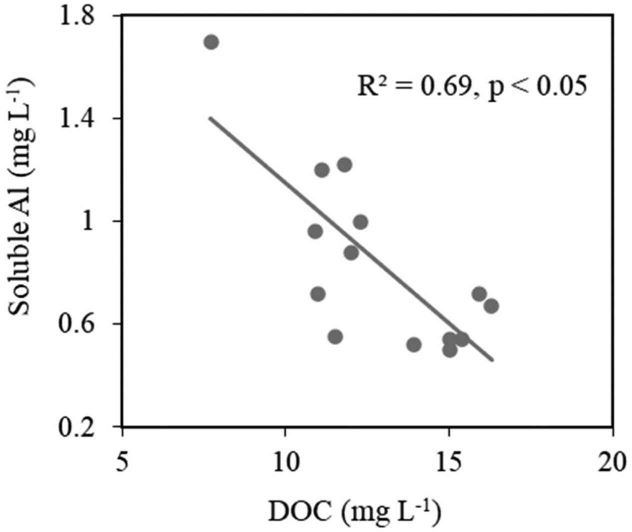

Figure 6. Linear fitting of dissolved organic carbon (DOC) vs soluble Al in soil solution as affected by corn cob biochar (CC3, CC4, CC6) and rice husk biochar (RH3, RH4, RH6) after 120 days incubation. Each point is the mean of 3 replicates (n = 3).

The various species of Al in soil solution after amending soils with CC and RH biochars is shown in Figure 7. pH was a major controlling factor of Al in solution thereby, Al speciation in the soil solution (Figure 4). Generally, at pH ≤ 5.8, Al species in soil solution were mainly Al-DOC complexes and free Al^{3+} while at pH > 5.8, it was dominated with Al-OH ions (i.e. $Al(OH)^{2+}$, $Al(OH)_2{}^{+}$, $Al(OH)_3$ and $Al(OH)_4{}^{-}$) (Figure 7). Similarly, Nolla and Anghinoni (2006) reported that in acidic Oxisol, majority of Al in solution was complexed with OH at pH 6.4 or complexed with DOC and as free Al^{3+} at pH < 5. Alleoni et al. (2010), also reported that in two Oxisols Al was largely found to complex with organic anions in soil solution (Al-DOC, 70–80%) at pH < 5.

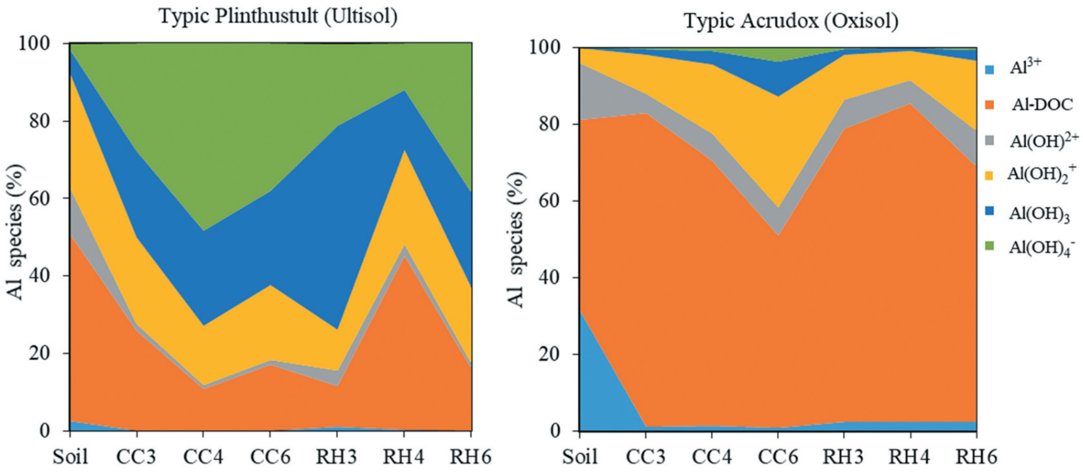

Figure 7. Distribution of Al species, free Al^{3+}, Al complexation with dissolved organic carbon (Al-DOC) and hydroxyl forms of Al ($Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$ and $Al(OH)_4^-$) in soil solution (Typic Plinthustult-Ultisol and Typic Acrudox-Oxisol) as affected by corn cob biochar (CC3, CC4, CC6) and rice husk biochar (RH3, RH4, RH6) after 120 days incubation. Mean of 3 replicates (n = 3).

In the Ultisol, except for the control soil where Al-DOC dominated in the soil solution (53%, pH 5.8), Al-OH ($Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$ and $Al(OH)_4^-$) were predominant in CC treatments (82.04%, pH 6.4–6.6) and RH treatments (75.73%, pH 6.0–6.5) (Figure 7)

Al speciation in the Ultisol was contrary to that in the Oxisol due to the variation in the solution pH. In the Oxisol, at pH 4.7 about 32.20% and 50.00% of the Al in solution existed as free Al^{3+} and Al-DOC complex, respectively (Figure 5). After adding CC and RH biochars, soil solution pH increased to between 5.6 and 5.9 for CC treatments and 5.4–5.6 for RH treatments with a concomitant decreased in free Al^{3+} from 32.2% to 0.9–1.4% and 2.3–2.4% (Figure 7). This was consistent with the findings of Zhao et al. (2020)reporting a decrease in free Al^{3+} from 14% to <1% in biochar amended tropical soil. However, Al-DOC complex increased to an average of 75.52% and 67.02% in the CC and RH treatments, respectively.

Clearly, amending tropical acid soils with biochar resulted in the decreased of highly toxic free Al^{3+} to less toxic Al-OH which was more evident in CC6 and RH6 treatments. However, adding CC3, CC4, RH4 and RH4 increased the nontoxic, Al-DOC complexes especially in the Oxisol due to the increase in DOC in soil solution (Table 2). The deprotonated organic functional groups (i.e., – COO^- and – O^-) on CC and RH biochar charred at low temperatures may have induced complexation reaction with Al. This suggests that increased in DOC as induced by biochar most especially at 300–450°C pyrolysis temperature led to the alleviation of Al toxicity in acidic soils (pH < 4.7) via the formation of Al-DOC complexes. Al as a polyvalent metal is a strong Lewis acid and it can form strong and specific bond with strong Lewis base functional groups (i.e., carboxylic and phenolic OH groups) on DOC molecules (Stevenson 1994). In examining the compositional structures and surface charge density of biochars, Qian and Chen (2014) reported that after exposing biochar to different concentrations of Al^{3+}, there was a chelation reaction between Al^{3+} and carboxyl and hydroxyl groups on the biochar surface.

Conclusion

While increasing soil pH, OC, CEC, and exchangeable base cations, the application of biochar charred from CC and RH reduced exchangeable acidity and exchangeable Al^{3+} in the tropical acid soils. CC and RH biochars lessened Al toxicity, by altering the speciation of Al^{3+} in soil solution via increases in soil solution pH and DOC. CC and RH biochars at 300–450°C exhibited a greater remarkable effect on DOC in the soils. At pH ≤ 5.8, Al-DOC complexes and free Al^{3+} dominated in soil solution while at pH > 5.8, Al species was mainly Al-OH ions (i.e., $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, and $Al(OH)_4^-$). Biochar at low pyrolysis temperatures (CC3, CC4, RH3, and RH4) promoted the large formation of Al-DOC complexes in soils. However, Al^{3+} activity in CC6 and RH6 amended soils were mostly in Al-OH ($Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, and $Al(OH)_4^-$). The results indicated that CC and RH biochars can be considered most especially at 300–450°C to ameliorate Al toxicity in tropical acid soils. In future, there is the need for field studies to assess the alleviating effect of biochar at varying pyrolysis temperatures on soil Al phytotoxicity.

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