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Gilles Pouangam Ngalani, Frank Dzemze Kagho, Nanseu Njiki Charles Peguy, Pascale Prudent, Jean Aubin Ondo, et al.. Effects of coffee husk and cocoa pods biochar on the chemical properties of an acid soil from West Cameroon. Archives of Agronomy and Soil Science, 2023, 69 (5), pp.1-15. 10.1080/03650340.2022.2033733 . hal-03591905

HAL Id: hal-03591905
https://hal.science/hal-03591905

Submitted on 28 Feb 2022

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Effects of coffee husk and cocoa pods biochar on the chemical properties of an acid soil from West Cameroon

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ABSTRACT

Evaluation of liming and fertility properties of biochar on acid soil was studied in this work. Selected soil properties such as pH, electrical con- ductivity (EC), exchangeable acidity (Ex Ac), exchangeable Al (Ex Al), exchangeable Fe (Ex Fe), available P and, soil organic carbon (SOC) were examined under the effect of biochar amendments. The acid soil was treated with biochar issued from coffee husk (CH) and cocoa pods (CP) pyrolyzed at 350°C and 550°C for 4 hours at amendment rate of 0, 20, 40 and 80 g kg^{-1} and an incubation time of 7, 14, 30, 40 and 60 d. Biochar amendments significantly increased soil pH, soil EC with respect to control and decrease in exchangeable acidity was observed. Results show that biochar improved available P in acid soil, though re-adsorption occurred with increasing incubation time. A significant increase in SOC is observed as compared to control. The impact of biochar on these acid soil chemical properties is due to the properties which are dependent on the biochar type and pyrolysis temperature. Thus, biochar can play the dual role of a liming agent and a source of P fertilizer nutrients.

KEYWORDS

Exchangeable acidity; biochar amendment; liming potential; available P

1. Introduction

Soils in Central Africa and especially in Cameroon are acidic (Takow et al. 1991; Takoutsing et al. 2016) and are manifested with dominance in hydrogen (H^+) and Aluminium (Al^{3+}) ions in the soil solution (Ondo 2011). The presence of soluble Al causes toxicity which inhibits both cell elongations, cell division and also interferes with the uptake, transport and use of several essential elements (Kochian et al. 2005) resulting in a great reduction in crop yield. Phosphorus in the form of phosphate availability in acid soils is extremely low due to the large amounts of Al and Iron (Fe) oxides which retain phosphorus (P) (Balemi and Negisho 2012). Coupled with the acidity of soils in the tropics, sustainable agriculture faces the constraint of low soil organic matter content due to accelerated mineralization (Tiessen et al. 1994), erosion, leaching (Roose and Barthes 2001) and also inappropriate cultivation practices.

To remediate these multiple limitations, amendments are the best ways to: (1) alleviate soil acidity by using lime (Pagani and Mallarino 2012), composted waste (Haynes and Mokolobate 2001), and wood ash (Nkana et al. 2002). The rise of soil pH and alleviation of Al^{3+} from solution are mainly due to (a) the consumption of H^+ and precipitation of soluble and exchangeable Al and Fe by OH^- (Fageria et al. 2014), (b) flow of protons from the soil to the organic matter sites and complexation of Al by soluble humic materials, by soluble organic acids, and by newly-formed organic matter (Haynes

and Mokolobate 2001); (2) improvement of available P by (a) direct P fertilizer (Ondo et al. 2017), application of rock phosphate (Basak and Biswas 2016), which is due to the saturation of the adsorption sites of P on Al and Fe oxides (Fischer et al. 2018); (3) organic carbon can be added in soil using organic waste such as crop residues, animal manures, municipal solid waste, bio-solids, etc. (Park et al. 2011).

The above approach has its limitations such as economical, over liming which may precipitate phosphate with Ca, excess use of P fertilizer which may lead to eutrophication and direct application of manure which may pose a risk of surface – and groundwater impairment (Parvage et al. 2013). Also, the poor stability of organic matter due to much labile C in crop residue or compost (Tiessen et al. 1994). An alternative to these different limitations is the use of biochar which gives the possibility to solve several problems at the same time creating a lot of hopes.

Biochar is a product derived from the pyrolysis of biomass in an atmosphere containing little or no oxygen (Joseph and Lehmann 2009). One of the major reasons in which biochar is applied is its effect on soil quality and plant growth (Wu et al. 2019). Generally, biochar has a higher pH, higher CEC, higher porosity than the uncharred organic amendments (Joseph and Lehmann 2009). Many researchers have shown that biochar itself is a potential source of P (Angst and Sohi 2013; Manolikaki et al. 2016). Also, biochar consists of condensed aromatic forms of organic carbon which are recalcitrant and do not decompose easily in soil (Atkinson et al. 2010), preventing carbon from returning to the atmosphere as carbon dioxide (CO_2) within a short period.

Biochar prepared from different feedstock under a range of pyrolysis conditions exhibits major differences in their physical, chemical, and adsorption properties (Rehrah et al. 2014). The study of changes in soil chemical properties due to the application of biochar is still current research in view to better understand the mechanisms sustaining these changes. The hypothesis for this research is based on the fact that, biochar obtained from different feedstock and produced at different temperatures will have an effect on soil physicochemical properties. The objective of this study is to evaluate the effects of biochar rate and incubation time on soil chemical properties (soil pH, electrical conductivity, soil acidity, exchangeable Al, available P and soil organic carbon).

2. Materials and methods

Soil sampling and feedstock collection

Topsoil samples (ten) were collected randomly (depth of 0–15 cm) on a 2-hectare mixed cocoa and coffee farm in Bafang, in the Upper-Nkam Division the West region of Cameroon. The soil samples were air-dried, crushed, sieved through a 2 mm sieve and stored in plastic bags for physicochemical analyses and incubation studies. Coffee husks and cocoa pods were collected from coffee processing factories and cocoa farms respectively, located in Bafang. These feedstocks were dried and grind to pass through a 2 mm sieve to ensure uniformity of samples during pyrolysis and then dried at 105°C.

Biochar preparation

Feedstocks were placed in a covered ceramic crucible and put in a muffle furnace. The pyrolysis processes were done at two different temperatures (350 °C and 550 °C) at pyrolysis rate of 10 °C min^{-1} and held constant for 4 h. After the 4 h duration, the biochar samples were left to cool in the muffle furnace to room temperature, and then it was grinded to very fine particles (< 2 mm sized fraction). The biochars were labelled as CH350 and CP350, CH550 and CP550 for coffee husk and cocoa pods produced at 350 °C and 550 °C respectively. Biochar samples were kept in polythene bags in a warm environment for characterization and incubation studies.

Laboratory incubation design for soil-biochar

To examine the effects of biochar on cited parameters in the objectives, incubation experiment was established in the laboratory. 100 g of dry soil was mixed with biochar at application doses of 0, 20, 40 and 80 g kg^{-1} in transparent plastic pots and mixed thoroughly. Then, the potted samples were wetted with deionized water to 70% of field water holding capacity of the soil and left for 7, 14, 30, 45 and 60 d of incubation with lids having small holes on them to prevent the rapid evaporation of soil moisture and permit the passage of air. All treatments were done in quadruples and left at room temperature. Every three days, water was added to maintain constant moisture content throughout the experiment. At the end of incubation periods, the samples were ground and sieve to < 2 mm and then store back in their incubation plastic cups.

Analyses of biochar, soil and soil-biochar mixture

Biochar, soil and soil-mixture analysis

Biochar ash content was determined by calculating the percentage of remaining solid ash to biochar mass after dry combustion of biochar samples in a muffle furnace at 750 °C for 6 h (Rehrah et al. 2014). Construction of the acid-base titration curve to evaluate biochar alkalinity was determined by the acid-base titration method (Yuan et al. 2011). The acid-neutralizing capacity of biochar was determined by mixing biochar in a solution of HCl and back titrating with NaOH (Martinsen et al. 2015). $CaCO_3$ equivalence from biochar samples was determine by the method proposed by Rayment and Lyons (2011). Fourier transform infrared spectroscopy (FTIR) was recorded on an Alpha spectrometer from Bruker Optics. The scans were obtained in the range from 400 to 4000 cm^{-1}. The XRD patterns of the prepared biochars were registered with CuKα radiation between 5 and 80° (2θ) for 7 h in steps of 0.03° using Bruker D4. Biochar pH and EC were determined were measured using 1:5 solid: solution ratio after shaking for 30 min in deionised water (Singh et al. 2010) while soil and soil-biochar mixture pH and EC were determined by shaking water and deionised water in the ratio 1:2.5 and 1:5 respectively (Pansu and Gautheyrou 2007). Available P from biochar, soil and soil-biochar was determined using the Olsen P solution (0.5 M $NaHCO_3$ at pH 8.5) and the aliquot taken for P spectrocolorimetry determination (Olsen et al. 1954; Murphy and Riley 1962). Quantification of organic carbon from biochar, soil and soil-biochar mixture was determined by the Walkley and Black method (Walkley and Black 1934). Exchangeable acidity, exchangeable Al (Ex Al) and exchangeable Fe (Ex Fe) were based on the principle of sample washing with a saline solution of 1 M KCl solution (Pansu and Gautheyrou 2007), then titrating an aliquot for exchangeable acidity and exchangeable Al determination. Ex Fe was determined by Fe-ortho-phenanthroline complexation and absorbance read with visible-spectroscopy.

Statistical analyses

Statistical analyses were done using Excel 2013 and graphics using Origin 6.0. A one-way analysis of variance was performed for each incubation time interval, amendment rate, biochar type and a Two-way analysis of variance was performed by crossing the following dependent factors: incubation time interval, amendment rate and biochar type. The significant difference between the factors means for parameters under analysis were determined at a 5% level of significance ($\alpha = 0.05$). A Pearson correlation and t-test was performed to measure the strength of correlation and significance of the factors on the parameters under study.

3. Results and discussion

Biochar characterisation

From Table 1, biochar yield varied with biochar type and pyrolysis temperature. The biochar yield of CH and CP reduced significantly ($p < 0.05$) from 38.7% to 30.3% and 38.4% to 32.0% for pyrolysis temperature of 350 °C and 550 °C respectively. The decrease in yield is due to the volatilization of C, O and H compounds (Waqas et al. 2018). The percentage yield is interesting and can be economically feasible for small-scale farmers. All biochars were basic due to the presence of ash, alkali salts, carbonates and biocarbonates (XRD spectra, Figure 2). High pH values of CP and CH biochar have been reported in previous work (Martinsen et al. 2015; Domingues et al. 2017). Electrical conductivity significantly ($p < 0.05$) varied with biochar type and significantly ($p < 0.05$) increased with pyrolysis temperature (Table 1). Cocoa pods biochar had greater EC values as compared to CH biochar for the same pyrolysis temperature due to increasing amount of soluble salts in the ash thus biochar produced cocoa pods generally has higher EC values (Cantrell et al. 2012; Rehrah et al. 2014). Ash content varied with biochar type and pyrolysis temperature. From Table 1 CH and CP biochars, ash content increased significantly ($p < 0.05$) due to the condensation of mineral elements/compounds (Kloss et al. 2012; Waqas et al. 2018) which confirms with the increase in peaks of minerals observed on the XRD spectrum and the degradation of the organic part of the biomass as can be seen on the FTIR spectra. It was observed that liming potential increased significantly ($p < 0.05$) with pyrolysis temperature for both biochars with lime greater in CP than CH. Increasing liming potential is due to high level of carbonates and bicarbonates (XRD spectra; Figure 2). High liming value has previously been reported, indicating the presence of calcite and other carbonate minerals. The acid-neutralising capacity of CP biochar was significantly ($p < 0.05$) higher than those of CH biochar irrespective of pyrolysis temperature. This was attributed to an increase in alkaline component such as calcite, kalicinite (XRD spectrum; Figure 2) and the presence of $-O^-$ and/or $-COO^-$ groups which can fix H^+. So we can hypothesize a greater H^+ consumption by CP biochar in acid soils as compare to CH biochar for the same temperature of pyrolysis. Biochar produced in this study can be considered as a source of available P. It is higher in biochar produced from CP than those produced from CH. Results from past research have proven biochar as a source of P (Mukherjee and Zimmerman 2013; Manolikaki et al. 2016). From Table 1, the data obtained indicated that all four biochars were alkaline, with alkalinity varying with pyrolysis temperature and biomass type. Data gives the biochar alkalinity when titrated to pH 7.0 and 2.0 and calculated from Figure 1. Biochar produced from CP has alkalinity almost twice that of biochar produced from CH. The plateau region observed in Figure 1 for CH550 and CP550, suggests a relatively higher buffer capacity for acids in the pH range at which the titration curve plateau occurred (Yuan et al. 2011).

FTIR and XRD analyses

From FTIR in Figure 2, all four biochar presented a dome centered at 3418 cm^{-1}, which was attributed to the O–H stretching vibration of hydrogen-bonded hydroxyl groups from phenolic, carboxylic or alcohol hydroxyl group (Keiluweit et al. 2010). The peak at 2925 cm^{-1} and 2966 cm^{-1} on the spectrum of CH350 and CP350 respectively corresponded to the asymmetric C–H stretching vibration in aliphatic compounds suggesting the presence of cellulose and hemicellulose (Usman et al. 2015). The peaks appearing at wavenumber 1594 cm^{-1}, 1577 cm^{-1} very intense on CH350 and CP350 and 1559 cm^{-1}; 1576 cm^{-1} less pronounce on CH550 and CP550 corresponded to the C = C aromatic stretching and C = O stretching of conjugating ketones and quinones (Behazin et al. 2016). The absorption bands at 1410, 874, and 702 cm^{-1} for CH550 1406, 872, and 694.1 cm^{-1} for CP550 corresponded to the in-, out plane bending and asymmetric stretching vibrations respectively of C–O–C which indicate the presence of calcite and other mineral carbonates mineral in the biochar (Cao and Harris 2010). These peaks were not observed in CH350 and CP350 due to very low carbonate content as observed with the $CaCO_{3(eq)}$ equivalence (Table 1). The band around 1376 cm^{-1} and 618 cm^{-1} on CH350 and CP350 spectrum indicates the presence of O–H bending mode and the

Table 1. The yield and properties of biochar from coffee husk and cocoa pods produced at different temperatures.

									Alkalinity	
	Yield	Ash	pH	EC	$CaCO_{3eq}$	Acid-neutralizing capacity	Available P	Organic carbon	pH = 7	pH = 2
Biochars	(%)	(%)		(mS cm^{-1})	(%)	(cmol + kg^{-1})	(mg kg^{-1})	(g kg^{-1})	(cmol + kg^{-1})	
CH350	38.7 ± 0.7	16.7 ± 0.2	9.33 ± 0.01	9.66 ± 0.60	4.0 ± 0.0	151.9 ± 2.3	866.02 ± 2.4	67.10 ± 1.10	15.2	70.4
CH550	30.3 ± 0.7	24.1 ± 0.4	9.69 ± 0.01	20.65 ± 0.21	12.2 ± 0.1	252.5 ± 2.3	954.54 ± 23.18	6.67 ± 0.30	42.7	140.5
CP350	38.4 ± 0.6	21.9 ± 0.1	9.53 ± 0.02	18.06 ± 0.20	10.1 ± 0.0	198.1 ± 3.7	1232.45 ± 16.34	76.10 ± 1.40	22.7	120.3
CP550	32.0 ± 2.0	29.0 ± 0.3	9.63 ± 0.01	30.50 ± 0.28	14.2 ± 0.1	340.7 ± 5.4	1076.90 ± 42.25	11.01 ± 0.10	71.7	219.7

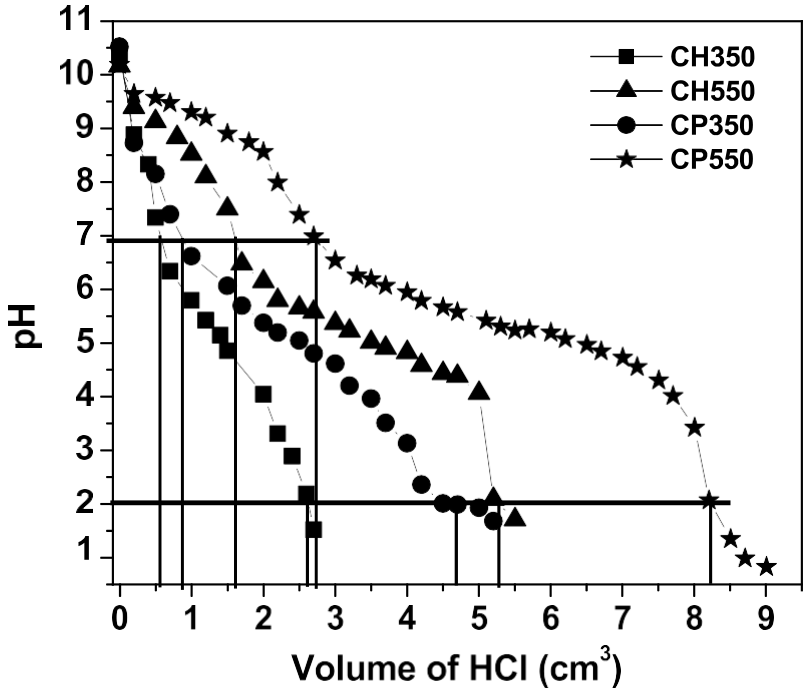


Figure 1. Acid-base titration curves of biochars produced from coffee husk and cocoa pods at different pyrolysis temperatures.

deformation out-of-plane of the C-O-H bond of phenol (Cantrell et al. 2012; Waqas et al. 2018). Additionally, with the presence of high level of quartz observed in the XRD spectra for CH550 and CP550, the bands at 1007 cm^{-1} and 832 cm^{-1} were attributed to silica (Keiluweit et al. 2010). Biochar production temperature affected the existing functional groups due to the dehydration of the ligneous and cellulosic contents and reduction in the aliphatic group with an increase in temperature of production. Furthermore, increase in temperature resulted in the presence of inorganic functional groups (carbonates) which is consistent with the increase in ash content and the presence of more crystalline minerals as seen on the XRD spectra.

The XRD spectra analysis depicts the structure and chemical composition of biochar. The biochar produced presented a variety of mineral crystals, with more in biochar produced at 550°C than those at 350°C. The XRD spectrum of all four biochar showed a broadband hump (2θ = 15–30°) which confirms the presence of a largely poorly crystalline carbon-rich phase, due to increase in the aromatic carbon (Cao and Harris 2010; Singh et al. 2010). The intensity of the dome between 2θ = 15–30° decreases with increase in temperature indicating the increase in the crystallinity of the carbon-rich phase. In Figure 3(c,d), peaks of quartz (Q) minerals in all four biochar, Calcite (C) and kalicinite in CH550, CP350 and CP550. The XRD spectrum for CH350 did not indicate any peaks for calcite and kalicinite minerals. Sylvite (S) minerals occurred at 2.22 Å for CP350, 3.15, 2.22 and 1.84 Å for CP550. From the spectra, peaks are sharp and intense at higher temperatures indicating the presence of more alkaline crystalline minerals. This observation was consistent with the acid-base titration curve for evaluation of biochar alkalinity (Figure 1) with a plateau for CH550 and CP550 due to buffering action of carbonates and also higher $CaCO_3$eq(%) (Table 1). Results obtained are consistent with the previous work done (Yuan et al. 2011; Domingues et al. 2017).

In conclusion, biochar characteristic depends on the feedstock type and pyrolysis temperature. We can hypothesize that amending acid soils with these biochars will have a distinctive effect on the chemical properties of the soil.

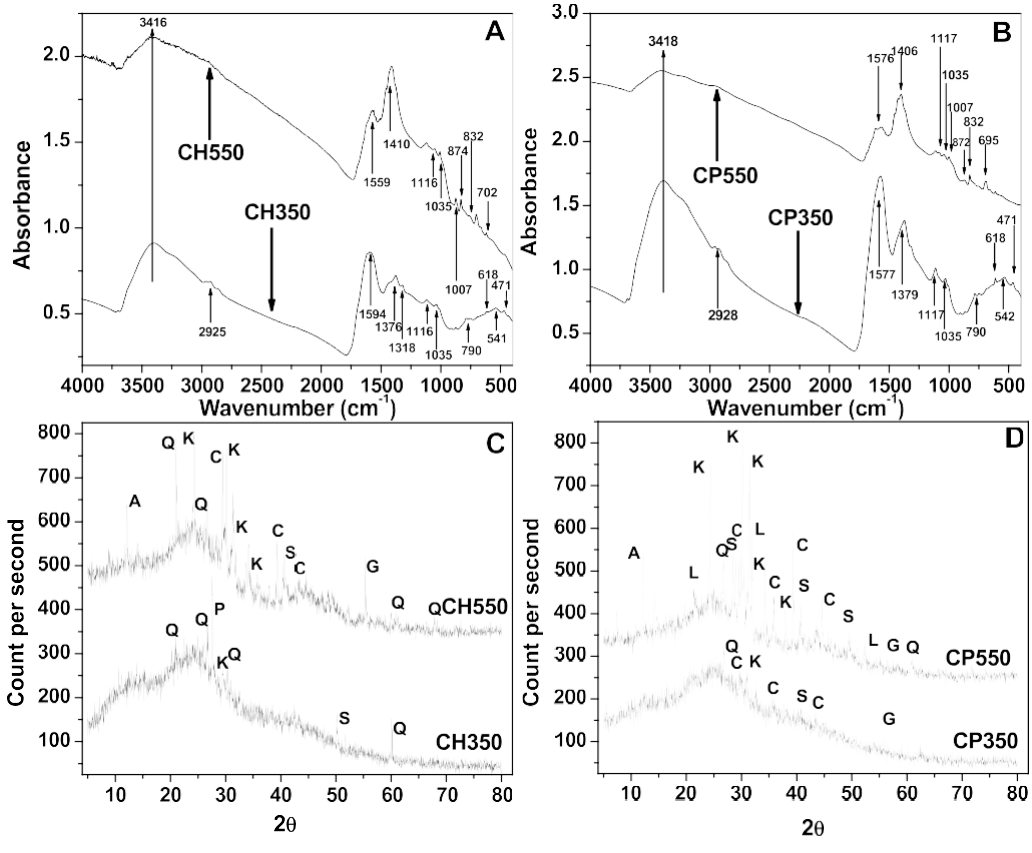


Figure 2. FTIR analysis of (A) CH350 and CH550, (B) CP350 and CP550, XRD spectrum of (C) CH350 and CH550 and (D) CP350 and CP550.

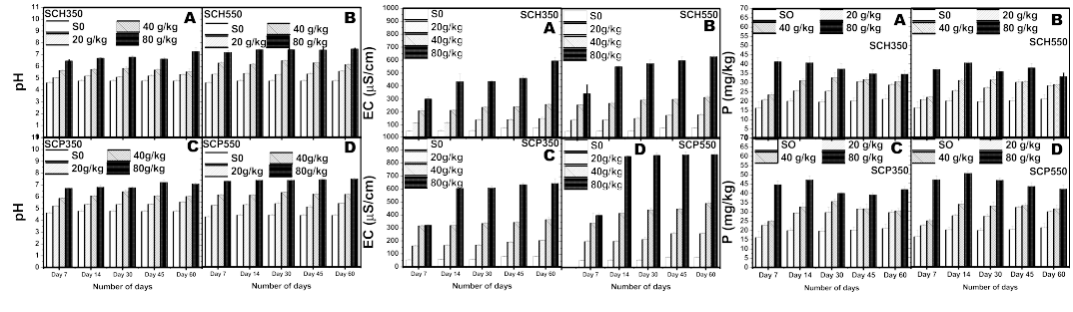


Figure 3. Effect of biochar application rate and incubation time on acidic soil with respond on soil pH (left), electrical conductivity (middle) and available P (right).

Effects of biochar on different soil properties

Soil pH, electrical conductivity and available P

The effect of the number of incubation days and biochar type on soil pH upon amendment of acid soil with biochar is presented in Figure 3. The application of biochar from CH and CP on acid soil had a significant effect ($p < 0.05$) on the increase in soil pH as compared with control. At higher doses (80 g kg^{-1}) CH350 and CP350 had a significant effect on soil pH ($p < 0.05$) while CH550 and

CP550 had no significant effect ($p > 0.05$) on soil pH over incubation time. From Figure 3, an increase in biochar amendment rate for all four biochar, increased the soil pH significantly ($p < 0.05$), with CP550 having the greatest effect. Furthermore, the combined effect of amend- ment rate and incubation time had a significant effect on the increase in soil pH ($p < 0.05$) for each number of incubation days. The greater sensitivity of soil pH upon addition of CP550 at the start of incubation and then maintaining higher soil pH was previously observed (Martinsen et al. 2015). Thus, CP biochar can be said to be a better liming potential agent as compared to CH biochar due to its greater alkalinity, higher $CaCO_3$eq(%) and a greater acid-neutralizing capacity. Moreover, it should be noted that, after 60 days of incubation, the increase in soil pH with amendment rate (20, 40 and 80 g kg^{-1}) for each biochar were: for CH350; 0.46, 0.81, 2.51 units, for CH550; 0.75, 1.41, 2.71 units, for CP350; 0.68, 1.27, 2.32 units and for CP550; 1.02, 1.95, and 3.3 units as compared with the control. Therefore, the liming effect was in the order CP550 > CH550 > CP350 > CH350. In the same way, studies on the impact of biochar on soil pH have previously been reported (Yuan and Xu 2012; Chintala et al. 2014). The increased soil pH by these biochars can be due to the biochar alkalinity, $CaCO_3$(eq)% content, the presence of silicate, carbonate, and bicarbonate minerals, the presence of negatively charged phenolic, carboxyl and hydroxyl groups on biochar surfaces and acid-neutralizing capacity of the biochar. From biochar analysis, CP biochar had higher biochar alkalinity than coffee husk biochar at the same temperature (Table 1) which reacts with H^+ from the solution, reducing the H^+ ions concentration (Dai et al. 2014). The presence of more silicates, carbonates, and bicarbonates in CP550 than in CH550 makes CP550 a better liming potential material. The lower temperature produced biochars cause an increase in soil pH due to functional groups on the biochar such as $-COO^-$ and $-O^-$ which combines with H^+ and thereby removing it from soil solution (Yuan et al. 2011). In this work, we observed a continuous increase in soil pH until 60 d unlike other work who reported a decline in soil pH during the first 20 d of incubation due to nitrification of NH_4^+-N (Zhao et al. 2015). The continuous increase in pH may be due to a slow release of basic ions from the carbonates and bicarbonates (Yuan et al. 2011) and also due to the buffering capacity of the biochar (Alkalinity of biochar in Figure 1) which can reabsorb the H^+ released during nitrification of NH_4^+-N. From the study, analysis of variance showed that amendment type and incubation time had significant effects ($p < 0.05$) on soil pH only at higher incubation rate for all four biochars. Amendment rate and incubation time had a significant effect ($p < 0.05$) for amendments with CH350, CH550 and CP350 only. The increase in soil pH of acidic soils when incorporated with biochar limit metal toxicity and can also lead to negative effect associated with excessively high pH on crop produc- tion (Alburquerque et al. 2014).

Incorporation of all four biochars in soil significantly increased the soil EC ($p < 0.05$) at different incubation days as compared to control (Figure 3). After 7 d of incubation and amendment rate of 20, 40 and 80 g kg^{-1}, the overall increase in soil EC for biochar was in the order CP550 > CH550 > CP350 > CH350 as compared to the control. From 7 d to 14 d, the EC increased drastically for all four biochars before forming a plateau and the increase in soil EC for amendment rate of 80 g kg^{-1} for CP550 was more remarkable. The sharp increase in EC from the 14 d of incubation may be due to the dissolution of low solubility calcite in the biochar due to its reaction with H^+ in the acid soil to release calcium ions and the plateau form the later may be due to the complete dissolution of the calcite. Furthermore, we can note that biochar produced from cocoa pods at 550°C increased EC more remarkably which can be attributed to the presence of sylvite, bicarbonate of potassium on XRD spectra of CP550. After 60 d of incubation, the amended soils at 80 g kg^{-1} presented the highest EC. Besides, previous work had indicated that an increase in soil EC is attributed to alkalinity, $CaCO_3$ equivalence, ash content, and the amount of soluble salts in the incorporated biochar (Cantrell et al. 2012; Singh et al. 2017). Analysis of variance showed that amendment type and amendment rate had a significant effect ($p < 0.05$) on soil EC from 14 d of incubation to 60 d. Also, amendment rate × incubation time, amendment type × incubation time had a significant effect ($p < 0.05$) on soil EC.

The quantity of available P in acidic soil significantly ($p < 0.05$) increased when amended with biochar (Figure 3). During the whole incubation period, a slight increase of available P was observed in the control acidic soil from 16.27 mg kg^{-1} after 7 days to 21.10 mg kg^{-1} after 60 d which can be attributed to P mineralization which occurs when dried soils are rewet (Laboski and Lamb 2003). After 7 d of incubation, the amount of available P increased significantly ($p < 0.05$) into 20, 40 and 80 g kg^{-1} amendments to 23.9%, 40.6%, and 147.5% for CH350, 24.0%, 36.0%, 32.0% for CH550, 37.0%, 49.7% and 167.2% for CP350, and 33.3%, 48.9% and 181.2% for CP550. The increase was in the order CP550 > CP350 > CH350 > CH550. A rise and fall in the amount of available P were observed with increasing incubation time with all four biochar. This rise and fall were dependent on the biochar type and amendment rate. Generally, soil incubated at 20 g kg^{-1} had a longer rising period for available P (averagely 45 d for all four biochars), then followed by an amendment rate of 40 g kg^{-1} whose available P with time up to 30 d (except for CP550 at 14 d of incubation time) and the shortest risen time was for amendment rate of 80 g kg^{-1}, which corresponded for 14 d (except for CH350 at 7 d of incubation time). From the above, we can conclude that increasing the rate of biochar, release rapidly available P. On the other hand, the percentage decrease after 60 d of incubation compared to the maximum amount of available P release was for 20, 40 and 60 d was relatively little.

Several works have asserted the inconsistency on the effect of biochar on soil P availability due to the manner in which biochar application affect the P cycle either directly or indirectly through various mechanisms. Manolikaki et al. (2016) reported that biochar from agricultural waste have a potential to be a source of P, and biochar as a modifier of soil pH and ameliorator of P complexing metals (Al^{3+}, Fe^{3+}, Fe^{2+}), and biochar as a promoter of microbial activity (DeLuca et al. 2015). In this work, an increase in the availability of P from soil-biochar mixture could be as a result of direct supply of P from biochar and dissolution of inorganic P in the acid soil. The second phase of incubation time shows a retention of available P after the increase as observed in past research work (Zwetsloot et al. 2016). The reduction in available P may be due to ash minerals and the presence of high $CaCO_3$ equivalent in biochar produced at higher temperature which causes the retention of P through the formation of Ca-P precipitates (Hollister et al. 2013; Wang et al. 2015).

Exchangeable acidity, Al and Fe

Results showing the effect of all four biochars in Ex Ac can be depicted on Figure 4. Compared to control, treatment application of all four biochars decreases drastically exchangeable acidity ($p < 0.05$). After 45 d of incubation time, the amendments 20, 40, and 80 g kg^{-1} led to a significant decrease which was higher for CP550 (89.2%, 95.5% and 98.7% respectively), followed by CH550 (75.6%, 90% and 97.3% respectively), then CP350 (81%, 89.4% and 96.1% respectively) and finally CH350 treatment (60.8%, 87.2% and 95% respectively). Thus, the effect of the different biochars on Ex Ac decreased in the order CP550 > CH550 > CP350 > CH350. There was a significant difference

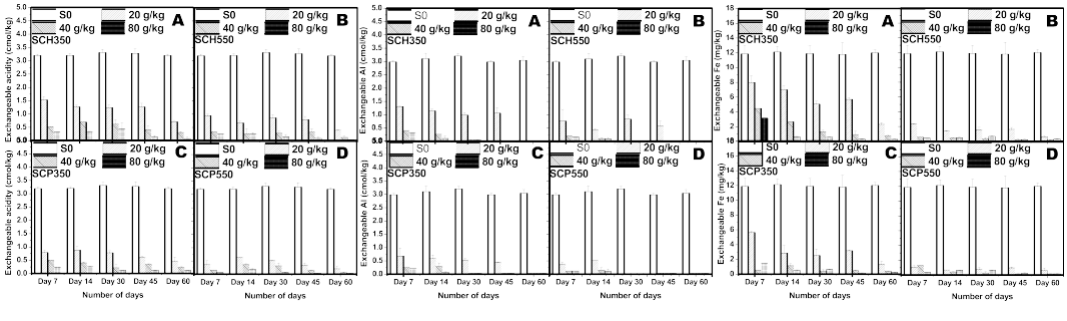


Figure 4. Effect of biochar application rate and incubation time on acidic soil with respond on Exchangeable acidity (left), Exchangeable Aluminium (middle) and Exchangeable Iron (right).

($p < 0.05$) on the effect of soil acidity with application rate of the four biochars, but on the 60th day, application rate had no significant difference ($p > 0.05$) on Ex Ac. Analysis of variance showed the effect of amendment type and incubation time significantly varied ($p < 0.05$). The soil Ex Ac at all biochar dosage for all four biochar and the effect of amendment rate and incubation time on soil Ex Ac had a significant effect on it variation ($p < 0.05$) for CH350, CH550, and CP350 while for CP550 there was no significant difference during treatment ($p > 0.05$).

Acid soil treated with all four biochars decreased significantly Ex Al and Fe significantly ($p < 0.05$). The decrease was very rapid after 7 d of incubation then decreased slowly to its minimum value. As can be depicted from the Figure 4, the order of alleviation of Al and Fe by the different biochar treatment is in the order CP550 > CH550 > CP350 > CH350. Incubation time had a significant effect ($p < 0.05$) on the amount of Ex Al and Fe with biochar type and amendment rate from the study, analysis of variance showed the effect of amendment type and incubation time had a significant effect ($p < 0.05$) on soil Ex Al and Fe at all biochar dosage. For all the four biochars, amendment rate and incubation time had a significant effect ($p < 0.05$) on soil Ex Al and Ex Fe for CH350, CH550, and CP350 and was not influence significantly ($p > 0.05$) with CP550. The major ions concern in this exchangeable medium are the H^{+}, Al^{3+}, Fe^{2+}, and Fe^{3+}. The mechanism in their reduction in soil solution involves precipitation of the metallic ions by alkaline oxides, carbonates, and silicates in the biochar, complexation with organic functional groups (e.g. – O, – OH, – COOH) (Qian et al. 2013). CP550 had the highest liming potential, acid-neutralizing capacity, biochar alkalinity and contain many basic minerals which can relate to its ability to have a greater reduction in Ex Ac, Al and Fe. Recent works of the application of biochar into soils and its effect on soil acidity and Ex Al and Fe asserted the same observation (Chintala et al. 2014; Dume et al. 2017).

Soil organic carbon (SOC)

All four biochar amended soils had significantly higher SOC ($p < 0.05$) than the control throughout the incubation time (Figure 5). It is observed that application of biochar produced at lower temperature increases SOC proportionally with increase in amendment rate. After 30 d of incubation, the highest SOC was observed. In the soil amended with biochar of 20, 40 and 50 g kg^{-1}, the increase in SOC as compared to the control were 2.7, 2.6, and 3.2 times for CH350, 1.99, 1.97, and 2.1 for CH550, 2.5, 2.6, and 3.6-fold for CP350 and lastly 2.1, 2.4 and 3.04 for CP550 respectively. Also, the increase in SOC was more pronounced when amended with cocoa pods biochar than coffee husk biochar. From 30 d to 60 d of incubation, a decrease in SOC was observed and the decrease was more pronounced in biochar produced at lower temperature as compared to those produced at higher temperature. An increase or a decrease in SOC in soils can be due to negative or positive priming effect of biochar with incubation time. Increase in soil organic carbon is due to the presence of recalcitrant carbon (Nyambo et al. 2018) and decrease in the mineralization of the soil carbon due to sorption of labile soil organic matter onto the biochar particles (Singh and Cowie 2014) and/or a very short-term inhibitory effect of microbial activity of biochar–associated volatile organic compounds (Spokas et al. 2011). The decrease in SOC after 30 d may be due to remains of labile organic material remaining in the pyrolyze biochar (Luo et al. 2011) which in turn activate soil microorganisms.

Analysis of Pearson correlation coefficient between soil properties after amendments

From Table 2, Pearson correlation reveal that, increase in soil pH had a positive significant correlation ($p < 0.05$) when incorporated with CH350, CH550 and CP350 at 20, 40, and 80 g kg^{-1} with incubation time, but for CP550, positive significant correlation ($p < 0.05$) occurred only at high amendment rate ($r = 0.938$). Also, there is a positive significant correlation between soil pH and Soil EC and available P for all four biochars at different amendment rate. Moreover, there is a significant negative correlation of soil pH with Ex Ac, Al and Fe for all four biochars amendment rates. Soil EC had

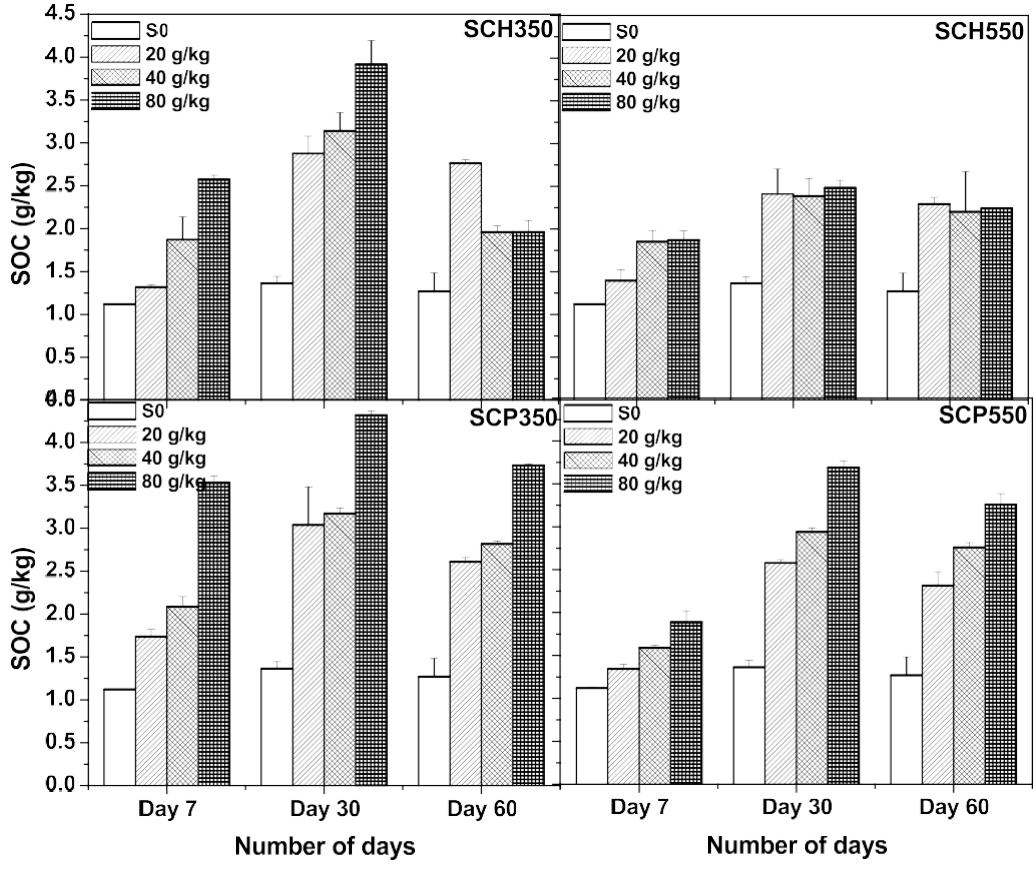


Figure 5. Effect of biochar application rate and incubation time on acidic soil with soil organic carbon.

a positive significant ($p < 0.05$) correlation for all four biochar, irrespective of the amendment rates and incubation days. Furthermore, Soil EC had a positive significant correlation with available P, except at the highest dosage, whereas, negative significant correlations between soil EC and Ex Ac, Al and Fe in all incubation systems were obtained. Available P had a significant positive correlation coefficient with number of incubation days for all four biochars amended at 20 and 40 g kg^{-1}. On the contrary, a negative significant correlation was observed at higher doses. In the same line, available P had a significant negative correlation with Ex Ac, Al, and Fe for all four biochar at 20 and 40 g kg^{-1} dosage was computed. Meanwhile at 80 g kg^{-1}, the correlation is significantly positive. In the case of Ex Al and Fe, all four biochar and their amendment rate had significant ($p < 0.05$) negative correlation with incubation time. A positive correlation of soil pH with incubation time is due to the slow release or dissolution of calcite from the biochar and the buffer properties of the biochar, thus causing a progressive increase in soil pH and a negative correlation with exchangeable acidity, Al, and Fe due to the precipitation of these exchangeable's. Similar to previous studies (Zhao et al. 2015), biochar amendments significantly improve soil pH and decreases exchangeable Al and acidity. A positive correlation in soil ECs with number of days is linked to slow dissolution of the basic compounds in the biochar to release soluble ions responsible for the soil EC. The positive correlation with available P may be due to the addition of P from the biochar, thus enhancing P, whereas the negative correlation at 80 g kg^{-1} may be due to the saturation of the soil solution with soluble basic cations and available P which leads to the precipitation of phosphate as describe by (Hollister et al. 2013). The antagonistic effect of available P with Ex Ac, Al and Fe is well known. It is due to the exchange

Table 2. Pearson's correlation coefficients for the relationships between incubation time (Days), soil pH (pH), soil EC (EC), available P (Avail P), Exchangeable Acidity (Ex Ac), exchangeable Aluminium (Ex Al) and exchangeable Iron (Ex Fe) on the amended soils at different rates.

SCH350									SCH550							
20 g/kg		Days	pH	EC	Avail P	Ex Ac	Ex Al	Ex Fe	20 g/kg Days	Days	pH	EC	Avail P	Ex Ac	Ex Al	Ex Fe
	Days	1	0.841	0.954	0.847	−0.859	−0.841	−0.923		1	0.702	0.974	0.828	−0.693	−0.649	−0.781
	pH		1	0.670	0.841	−0.571	−0.589	−0.789	pH		1	0.615	0.370	−0.978	−0.981	−0.887
	EC			1	0.773	−0.766	−0.753	−0.907	EC			1	0.831	−0.593	−0.586	−0.658
	Avail P				1	−0.633	−0.519	−0.659	Avail P				1	−0.462	−0.384	−0.650
40 g/kg	Days	1	0.831	0.982	0.547	−0.801	−0.882	−0.893	40 g/kg Days	1	0.737	0.978	0.426	−0.659	−0.833	−0.966
	pH		1	0.803	0.386	−0.748	−0.597	−0.850	pH		1	0.833	0.156	−0.546	−0.780	−0.837
	EC			1	0.555	−0.759	−0.900	−0.894	EC			1	0.554	−0.649	−0.915	−0.989
	Avail P				1	0.048	−0.824	−0.859	Avail P				1	−0.276	−0.818	−0.633
80 g/kg	Days	1	0.802	0.902	−0.973	−0.764	−0.787	−0.705	80 g/kg Days	1	0.738	0.798	−0.676	−0.988	−0.826	−0.522
	pH		1	0.927	−0.661	−0.738	−0.843	−0.603	pH		1	0.976	−0.247	−0.666	−0.896	−0.100
	EC			1	−0.809	−0.646	−0.837	−0.821	EC			1	−0.239	−0.749	−0.956	−0.191
	Avail P				1	0.704	0.809	0.712	Avail P				1	0.713	0.361	0.156
SCP350									SCP550							
20 g/kg	Days	1	0.899	0.958	0.675	−0.921	−0.912	−0.772	20 g/kg Days	1	0.194	0.955	0.794	−0.663	−0.818	−0.448
	pH		1	0.877	0.692	−0.775	−0.951	−0.926	pH		1	−0.010	−0.165	0.010	−0.157	−0.769
	EC			1	0.562	−0.958	−0.925	−0.669	EC			1	0.828	−0.714	−0.770	−0.212
	Avail P				1	−0.354	−0.476	−0.822	Avail P				1	−0.202	−0.563	−0.384
40 g/kg	Days	1	0.852	0.986	0.316	−0.765	−0.848	−0.560	40 g/kg Days	1	0.264	0.910	0.427	−0.611	−0.838	−0.774
	pH		1	0.823	0.378	−0.710	−0.484	−0.885	pH		1	0.829	0.297	−0.593	−0.701	−0.877
	EC			1	0.258	−0.776	−0.817	−0.577	EC			1	0.722	−0.247	−0.722	−0.939
	Avail P				1	−0.736	−0.441	0.080	Avail P				1	0.406	−0.314	−0.901
80 g/kg	Days	1	0.814	0.706	−0.648	−0.877	−0.749	−0.762	80 g/kg Days	1	0.939	0.640	−0.872	−0.670	−0.876	−0.679
	pH		1	0.429	−0.519	−0.594	−0.431	−0.623	pH		1	0.772	−0.677	−0.382	−0.751	−0.545
	EC			1	−0.390	−0.642	−0.983	−0.966	EC			1	−0.207	0.043	−0.705	0.028
	Avail P				1	0.901	0.534	0.419	Avail P				1	0.932	0.735	0.874

* Coefficients that are significant ($p < 0.05$) are shown in bold text.

reaction of Al and Fe with the alkaline from biochar and the functional groups ($-O^-$ and $-COO^-$) with the biochar and liberating phosphate and also the provision of P into the soil solution as biochar plays the role of P provider.

4. Conclusion

The objective of this study was to evaluate the effects of biochar rate and incubation time on soil chemical properties gave the following main findings: (i) increase in biochar rate and incubation time for all four biochar, effectively alleviate the soil acidity by yielding an increase in soil pH, soil EC and a drastic drop in exchangeable acidity, exchangeable Al and Fe. CP550 caused the greatest increase in soil pH; (ii) the fertility aspect of the biochar was demonstrated with the increase in available P upon addition of biochar. Available P increased with biochar rate and incubation time. It was observed a read sorption of P at higher dosage with increasing incubation time; (iv) biochar amendment increased SOC. Increase then a decrease in SOC was more pronounced with biochar produced at lower temperature. The effect of biochar on these soil chemical properties was mainly due to the intrinsic chemical properties of the biochar such as biochar alkalinity, acid-neutralising capacity, $CaCO_3$eq(%), presence of basic inorganic minerals, presence of complexing functional groups and P availability. Thus, clear knowledge liming and fertilizing properties of biochar and its effect on soil properties is useful. Thus, biochar can play the dual role of a liming agent and a source of P fertilizer nutrients. Implementing these types of studies with different biochar obtain from these localities and testing it beneficial agricultural amendments value on their soils, will help to design biochars for farmers in these localities.

Acknowledgements

The authors acknowledge the support of the International Science Programme (ISP) through the grant offered to the African Network of Electroanalytical Chemists (ANEC) and the support of Agence Universitaire de la Francophonie through grant AUF-DRACGL-2017-006.

Funding

This work was supported by the Agence Universitaire de la Francophonie [AUF-DRACGL-2017-006].

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