# Use of Corn Cob and Rice Husk Biochar as Liming Materials in Acid Soils

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## Abstract

Most soils in Ghana are acid with those of the Evergreen Rain Forest belt having Al toxicities. Unavailability, high cost and poor grade of conventional liming materials have led to poor yields of food crops grown on these acid soils. Preliminary works on biochar produced from agricultural waste in Ghana have shown that some types have high concentration of basic cations and contain $CaCO_3$, an active ingredient in conventional lime. Biochar could, therefore, be exploited for use as liming material. However, the biochar type that would be ideal for use as liming material in acid soils of Ghana has received little attention. Two typical acid soils viz., Typic Hapludox and Typic Hapludult were thus amended with corn cob and rice husk charred at 500 and 700 °C at a rate of 80 Mg/ha in a screen house experiment to evaluate their respective efficacies as substitutes for conventional agricultural lime. The Ca equivalent of the biochar types from $CaCO_3$, the conventional lime, was amended to the soils to serve as realistic controls. The amended soils, in addition to their un-amended counterparts were all kept at 80% field capacity in a completely randomized design in the screen house to allow for pH equilibration amidst weekly pH and bi-weekly exchangeable Al, Ca and Mg monitoring. Results showed that corn cob charred at 500 °C was able to raise pH from 4.2 to 5.2 in Hapludox and from 4.9 to 6.2 (an optimum pH for most food crops) in Hapludult within a six-week incubation period. All the biochar types reduced Al concentration from 0.4 $cmol_c$ /kg to undetectable levels in the Hapludult. The element was reduced from 1.3 $cmol_c$ /kg to 0.45 $cmol_c$ /kg in the rice husk and corn cob charred at 700 °C amended Hapludox.

## Introduction

Soils of Ghana, apart from the notable variants of the Vertisols and the salt affected ones on the eastern coast are generally low in bases. The low base saturation is as a result of intense weathering and high rainfall. High rainfall has led to leaching of bases culminating in the exchange sites of the soils being dominated by $Al^{3+}$ and its species and $H^+$. The soils in Ghana are consequently, mainly Alfisols, Ultisols and Oxisols (Effland *et al*., 2009). These soils are generally low in primary minerals and consequently in Ca and Mg (Buri *et al*., 2005). High temperatures in Ghana have led to fast mineralization rates and coupled with the use of fire as a land clearing method, gains from organic matter additions are short lived. Maintenance of soil fertility in the past three decades in Ghana has been through the use of inorganic fertilizers, chief of which is sulphate of ammonia, albeit low application rates (Buri *et. al*., 2005). An oxidation of a mole of $NH_4^+$ applied to soil leads to the production of two moles of $H^+$. Thus, the application of sulphate of ammonia may have in part contributed to the acidic pH (pH < 6.0) of the majority of soils in Ghana (Buri *et al*., 2005; Oppong, 2011).

Acid soils now occur extensively in lowlands occupying over a million hectares in Ghana (Buri *et al*., 2005). A majority of crops in Ghana are presently therefore being grown in soils of pH below 6. Acid soils are inherently poor in fertility with low P and Mo in soil solution (Brady and Weil, 2002). They have toxic levels of $Al^{3+}$ which lead to root deformation (Brady and Weil, 2002). Consequently, crop yields are generally below the optimum. Although soils in Ghana are increasingly becoming acidic, the use of agricultural lime by farmers is low due to a myriad of reasons, chief of which is the high acquisition cost. The material is also not readily available on the West African market when needed and when available, is mostly of low purity. There is also the problem of high haulage cost to remote farm lands as the product is not usually stocked by agrochemical and input dealers. It is imperative that a suitable alternative is provided to farmers in Ghana and West Africa, if productivity of the soils and crops are to be increased. Any alternative material that would be appealing to farmers for liming acid soils should be relatively cheap, readily available and preferably found in close proximity to the farms.

The application of biochar to agricultural soils has recently received attention in Ghana as a result of its obvious benefits to soil quality and improved crop yields, as well as the potential for carbon sequestration. Biochar is a carbon rich material produced by pyrolysing biomass such as manure, wood or leaves under limited oxygen conditions (Sohi *et al*., 2010).

Biochar, due to its molecular structure is chemically and biologically more stable in soil compared to the same carbon equivalent of un-charred biomass added directly to soil (Lehmann and Joseph, 2009). Consequently, it is more difficult for biochar carbon to be transformed back to $CO_2$, implying storage of carbon for several decades (Lehmann, 2007; Berek *et al*., 2011). Biochar, depending on the type can have numerous chemically reactive functional groups, such as carboxylic, hydroxyl and carbonyl compounds that impart on the material's high adsorptive properties for toxic substances, such as aluminium, and manganese in acid soils. Thus, biochar could be used to remediate the effects of soil acidity (Berek *et al*., 2011). The persistence of biochar carbon in soil would give the material an added advantage should it be exploited for use as a liming material.

Lehmann and Joseph (2009), have indicated that the kind and rate of reactions such as adsorption, desorption, precipitation, dissolution and redox reactions that occur in soils amended with biochar are governed by factors such as pyrolysis temperature, type of feedstock, surface area of biochar, soil properties and local environmental conditions. Rondon *et al.* (2007) and Van Zwieten *et al.* (2007) noted positive plant responses due to increased soil pH as a result of biochar addition. The ability of biochar to maintain pH is related to its liming value (Van Zwieten *et al*., 2007). X-ray analyses have revealed the presence of $CaCO_3$ in rice straw biochar, $MgCO_3$, $Mg(OH)_2$ in rice husk biochar and MgO in cocoa husk biochar (Sam *et al*., 2017; Tetteh, 2014). Biochar could therefore be exploited for use as a liming material. Rice husk and corn cob are agricultural wastes which abound in almost every region of Ghana. These wastes are hardly exploited for use as soil amendment. Preliminary studies by these authors have shown that pyrolysing corn cob and rice husk at 500°C and 700 °C have produced biochar types with high levels of basic cations such as $Ca^{2+}$ and $Mg^{2+}$. Rice husk and corn cob charred at 500 and 700°C could serve as Ca and Mg sources to replace $Al^{3+}$ and $H^+$ at the exchange sites of acid soils to ameliorate soil acidity.

There is to date very little information on the use of corn cob and rice husk biochar types as liming materials on acid soils in Ghana in particular and West Africa and the mechanisms thereof by which these biochar types could act as liming agents in acid soils. It has become necessary therefore to fill this gap in knowledge. This work therefore seeks to ascertain the suitability or otherwise of use of rice husk and corn cob biochar as liming materials on two typical acid soils in Ghana.

## Materials and Methods

Two acid soils were sampled from the rain forest zone in the Western Region of Ghana. The soils sampled are Typic Hapludox and Typic Hapludult (Dwomo and Dedzoe, 2010). The Typic Hapludox was sampled from a forest conservation area with no known history of farming whilst the Typic Hapludult was sampled from a fallowed land at the Council for Scientific and Industrial Research Crop Research Satellite Station at Tikobo, Ghana. The Typic Hapludox was located at $5^0$ 14. 599’ N and $2^0$ 38.453’ W and the Typic Hapludult at $5^o$ 03.558’ N and $2^0$ 28.2825’ W. Random disturbed samples of the plough layer (0 – 20 cm) of the soils were taken, bulked, homogenized and sub sampled for routine characterization and pot experiment. Undisturbed samples were also taken for bulk density determination. The disturbed samples were air-dried and a portion ground and passed through a 2 mm sieve to obtain the fine earth fraction. The remainder which was not processed (whole soil) was saved for an incubation pot experiment in a screen house.

### *Soil Characterization*

Bulk density was determined by the core method of Blake and Hartge (1986). Soil texture was determined using the Bouyoucos hydrometer method modified by Day (1965). Moisture content at field capacity was determined by covering water saturated sample of the disturbed soil with plastic sheet and determining the water content after allowing water drainage for 48 hours in open air.

Soil pH was determined in water and 0.01 M $CaCl_2$. The total carbon and nitrogen contents of the soils were determined using a Leco Trumac Carbon Nitrogen Sulphur version 1.3 Analyzer. Available phosphorus was determined using the method of Bray and Kurtz (1945). Exchangeable bases were determined by the ammonium acetate method after which the concentration of the bases were read on a Perkin Elmer Analyst 800 Atomic Absorption Spectrometer. Exchangeable acidity ($Al^{3+}$ and $H^+$) was determined by the KCl extraction method. The cation exchange capacity (CEC) of the soil was determined by the ammonium acetate method and the effective cation exchange capacities (ECEC) determined by summation of the respective exchangeable bases and exchangeable acidities.

### *Biochar preparation*

Air dried rice husk and corn cob obtained from farmers’ fields were carbonized in a furnace at pyrolysis temperatures of 500 ºC and 700 ºC. The charred rice husk (RH) and the corn cob (CC) were washed with deionized water, air dried, and then ground. The ground biochar types were then passed through a 2 mm sieve and saved for chemical characterization. The four biochar types produced were RH and CC charred at 500 ºC and 700 ºC herein after referred to as RH 500, RH 700, CC 500 and CC700, respectively

*Characterization of corn cob and rice husk feedstock and biochar derivatives*

The pH of ground air dried corn cob and rice husk feed stocks and their biochar derivatives in both water and 0.01M $CaCl_2$ was determined in a biochar to liquid ratio of 1:10. Carbon and N contents were determined on a Leco Trumac Carbon Nitrogen Sulphur version 1.3 Analyzer. Water soluble and subsequently ammonium extractable bases i.e. Ca, Mg, K and Na in the biochar types were extracted sequentially with de-ionized water and 1M ammonium acetate, respectively and the various concentrations read on a Perkin Elmer Analyst 800 Atomic Absorption Spectrometer.

*Incubation Study*

Preliminary studies using the rice husk and corn cob biochar types prepared at both 500 $^0$C and 700 $^0$C had revealed that application rates between 60 and 80 tonnes/ha to a typical acid soil could raise soil pH by 2 pH units. The unprocessed bulk soils of the Typic Hapludox and Typic Hapludult were thus each mixed with each of the four biochar types i.e. RH 500, RH 700, CC 500 and CC 700 at the rate of 80 tonnes/ha to attain the soils' respective field bulk densities in cylindrical PVC pots of internal diameter and height of 20 cm. Equivalent amounts of Ca in the biochar types from $CaCO_3$ (Analar) of 99% purity was added to the soils as conventional agricultural lime. In estimating the amount of $CaCO_3$ to be added, the Ca equivalent in the biochar with the highest exchangeable and soluble Ca was used. The $CaCO_3$ amended treatments served as realistic control or standards to which the biochar treatments would be judged. Treatments with no amendment were also included to simulate farmers' practice. The moisture contents of the soils in the pots were kept at 80% field capacity in the screen house. All the treatments were replicated four times and arranged in completely randomized design. Thus with two soils, five amendments, no amendment and four replications, there were 48 treatment units. Average temperature during the period of incubation was between 27 $^o$C and 32 $^o$C. The pH of the soils was read at 7 days' interval till there was no apparent change in soil pH (equilibration). Exchangeable bases, exchangeable $H^+$ and $Al^{3+}$ were read once every 14 days during the equilibration period.

## Results

*Physico-chemical properties of the soils*

The determined physico-chemical properties of the plough layer (0 -20 cm) of the two soils used for the study are presented in Table 1. The Hapludox has a sand content of 61.5% which is 20.4% lower than that of the Hapludult. The Hapludox again has a lower silt content of 7.8% compared to the 12.5% of the Hapludult. Clay concentration was, however, almost six times higher in the Hapludox (30.7%) than in the Hapludult (5.6%). The 1.1 Mg/m$^3$ bulk density of the Hapludox was lower than the 1.3 Mg/m$^3$ of the Hapludult.

Hapludox is extremely acid with pH in salt and water being 3.7 and 4.2, respectively. Hapludult on the other hand is very strongly acid with a pH of 4.9 in water and 4.0 in salt at the depth of 0-20 cm. The Hapludox which is from a forest reserve has an organic carbon content of 15.3 g/kg and that of Hapludult sampled from a fifteen a year fallow area is 5.4 g/kg. Despite the almost 2.8 times more C in the Hapludox than the Hapludult, total N in the former (1.6 g/kg) was similar to that of

TABLE 1
Some physical and chemical properties of the soils used for the study

| PARAMETER | HAPLUDOX | HAPLUDULT |
|---|---|---|
| Sand (%) | 61.5 | 81.9 |
| Clay (%) | 30.7 | 5.6 |
| Silt (%) | 7.8 | 12.5 |
| Textural class | Sandy clay loam | Sandy loam |
| Soil pH($H_2O/_{1:1}$) | 4.2 | 4.9 |
| Soil pH($CaCl_2/_{2:1}$) | 3.7 | 4.0 |
| OC (g/kg) | 15.3 | 5.4 |
| Total N (g/kg) | 1.60 | 1.2 |
| Available P (mg/kg) | 1.54 | 2.71 |
| Ca ($cmol_c$/kg) | 0.64 | 0.70 |
| Mg ($cmol_c$/kg) | 0.05 | 0.07 |
| K ($cmol_c$/kg) | 0.08 | 0.06 |
| Na ($cmol_c$/kg) | 0.06 | 0.06 |
| Al ($cmol_c$/kg) | 1.31 | 0.40 |
| H ($cmol_c$/kg) | 0.29 | 0.34 |
| Exchangeable acidity ($cmol_c$/kg) | 1.60 | 0.74 |
| CEC ($cmol_c$/kg) | 17.8 | 8.9 |
| ECEC ($cmol_c$/kg) | 2.63 | 1.63 |
| Al Saturation (%) | 53.90 | 24.54 |

OC = Organic Carbon, CEC = Cation Exchange Capacity, ECEC= Effective Cation Exchange Capacity

Hapludult (1.2 g/kg). The two soils have very low available P concentrations of 1.54 mg/kg (Hapludox) and 2.71 mg/kg (Hapludult).

The Hapludox being an Oxisol has a higher exchangeable acidity (exchangeable $Al^{3+}$ + $H^+$) of 1.60 $cmol_c$ /kg which is more than twice the value, (0.74 $cmol_c$ /kg) for the Ultisol. It is worthy of note that even though the two soils have similar exchangeable $H^+$ values i.e. 0.29 and 0.34 $cmol_c$ /kg, the exchangeable $Al^{3+}$ in the Hapludox (1.31 $cmol_c$ /kg) is thrice more than that of the Hapludult (0.40 $cmol_c$ / kg). Relatively, the exchangeable bases of the two soils are very low between 0.83 and 0.9 $cmol_c$ /kg. It is also worthy of note that the CEC of the two soils are far higher than their respective ECECs and the CEC of Hapludox is twice more than that of the Hapludult. The CEC and ECEC are 17.8 $cmol_c$ /kg and 2.43 $cmol_c$ /kg, respectively for the Hapludox and 8.9 $cmol_c$ /kg and 1.63 $cmol_c$ /kg for Hapludult. Aluminium saturation which was calculated as a percentage of the ECEC was 53.9% for Hapludox and 24.5% for Hapludult.

*Chemical Characterisation of Biochar*

Some chemical properties of the two un-charred feed stock i.e. rice husk (RH) and corn cob (CC) and their respective biochar derivatives charred at 500 $^0$C and 700 $^0$C are presented in Tables 2 and 3. The pHs in water of the un-charred feed stocks are generally neutral in reaction with the pH of rice husk and corn cob being 6.1 and 6.8, respectively. Upon charring however, pH in water of RH500 increased by 1.5 pH units to 7.6 becoming slightly alkaline whilst its RH700 counterpart became alkaline by increasing to 8.8. The CC biochar types became strongly alkaline after charring with pH of CC500 in water

TABLE 2
Some chemical properties of feed stock and their respective biochar derivatives*

| Feedstock | Pyrolysis Temp (°C) | pH $H_2O$ (1:10) | pH $CaCl_2$ (1:10) | Total C (g/kg) | Total N (g/kg) | C: N | Available P (mg/kg) |
|---|---|---|---|---|---|---|---|
| CC | --- | 6.8 | -- | 402.6 | 9.7 | 41.5 | np |
| RH | -- | 6.1 | -- | 353.1 | 7.6 | 46.5 | np |
| CC | 500 | 10.7 | 10.8 | 567.9 | 0.82 | 692.6 | 2162.5 |
| CC | 700 | 11.0 | 11.4 | 602.9 | 0.78 | 772.9 | 2287.5 |
| RH | 500 | 7.6 | 7.9 | 387.1 | 0.55 | 703.8 | 2378.8 |
| RH | 700 | 8.8 | 9.1 | 389.0 | 0.51 | 762.7 | 2290.1 |

*np = not present

CC = Corn Cob, RH= Rice Husk

TABLE 3
Total exchangeable and soluble bases of feed stock and their respective biochar derivative*

| Feedstock | Pyrolysis Temp. (°C) | Total bases Ca | Mg | K | Na | Exchangeable bases Ca | Mg | K | Na | Soluble bases Ca | Mg | K | Na |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | % | | | | | | | | | | | |
| CC | - | 0.32 | 0.05 | 0.24 | 0.32 | np | np | np | np | np | np | np | np |
| RH | - | 0.36 | 0.07 | 0.19 | 0.28 | np | np | np | np | np | np | np | np |
| CC | 500 | 0.71 | 0.15 | 1.87 | 1.25 | 0.15 | 0.05 | 0.21 | 0.08 | 0.02 | 0.01 | 0.01 | 0.01 |
| CC | 700 | 0.92 | 0.18 | 1.93 | 0.91 | 0.18 | 0.05 | 0.22 | 0.07 | 0.07 | 0.02 | 0.01 | 0.01 |
| RH | 500 | 1.07 | 0.17 | 0.68 | 0.93 | 0.16 | 0.03 | 0.06 | 0.04 | 0.02 | 0.01 | 0.01 | 0.01 |
| RH | 700 | 1.21 | 0.16 | 0.81 | 0.96 | 0.16 | 0.04 | 0.06 | 0.07 | 0.02 | 0.01 | 0.01 | 0.01 |

*np = not present

CC = Corn Cob, RH = Rice Husk

being 10.7 and 11.0 for CC700. The slightly alkaline to strongly alkaline pH of the biochar types agrees with the assertion of Verheijen *et al.* (2010) that anaerobic charring of feedstock leads to the production of biochar with pH between neutral and strongly alkaline. The pH of biochar in the salt was similar to that in water as change was not more than 0.5 pH units (Nartey, *et al.*, 2000).

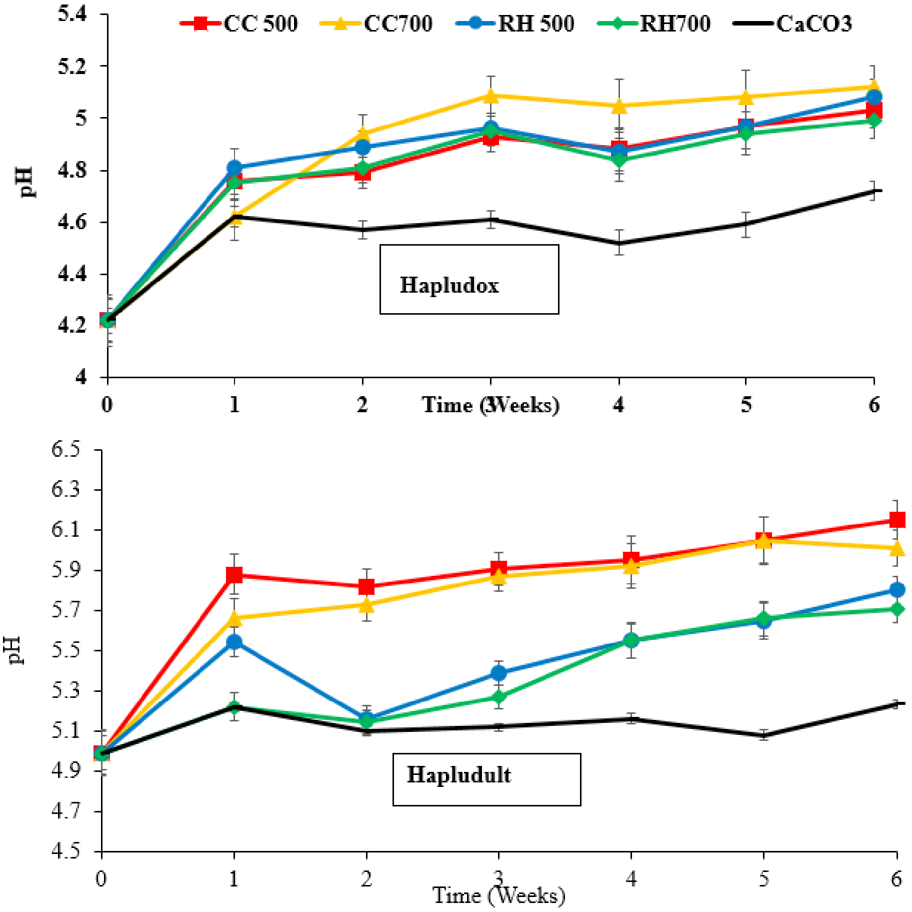
Total organic carbon of the CC feedstock was 402.6 g/kg; 49.5 g/kg more than that in the RH feedstock (Table 2). There were marginal increases in carbon content on charring of the RH feedstock at the two temperatures as carbon concentration in RH500 increased to 387.1 with its RH700 counterpart attaining a value of 389.0 g/kg. There were, however, approximately 41% and 50% respective increases in C concentrations when the CC was charred at 500 °C and 700 °C. Total nitrogen (TN) contents of the CC and RH were respectively 9.7 and 7.6 g/kg (Table 2). On charring, TN decreased from 9.7 to 0.82 and 0.79, respectively in the CC500 and CC700 biochar types. Losses of the volatile element, N, was higher in the rice husk biochar types as TN concentration was 13.8 (RH500) and almost 15 (RH700) times lower than in the original feedstock from which they were derived.

The concentration of total bases in the CC was 0.93% whilst in the RH was 0.90% (Table 3). On charring, the sum of total bases in the four biochar types was in the order of CC 700 (3.94%) ≈ CC500 (3.98%) > RH700 (3.14%) > RH500 (2.85%). Just as was found for the bases in the respective feed stocks from which the biochar types were derived, total Na and K were higher in the CC biochar types whereas total Ca and Mg were higher in the RH biochar types. Order of concentrations of the sum of exchangeable bases in the four biochar types was CC 700 (0.52%) ≈ CC500 (0.49%) > RH700 (0.33%) ≈ RH500 (0.31%). It is worthy of note that exchangeable K is strikingly higher in the two CC biochar types than their RH counterparts.

### *Effect of Amendments on Soil pH*

The changes in soil pH upon amendment of the two soils with the four biochar types and the conventional agricultural lime ($CaCO_3$) are presented in Figure 1. The pH in water of the Hapludox, increased from its inherent 4.2 to 4.7 in one week when the soil was amended with the conventional liming material ($CaCO_3$) at the Ca equivalent in the biochar i.e. 104 kg Ca /ha or 260 kg $CaCO_3$ /ha. Thereafter, there was marginal change in pH with time for the ensuing five weeks.

When the four biochar types were applied at similar Ca rate as the conventional liming material, pH increased by 0.5, 0.6, 0.65 and 0.7 pH units to 4.7, 4.8, 4.85 and 4.9, respectively



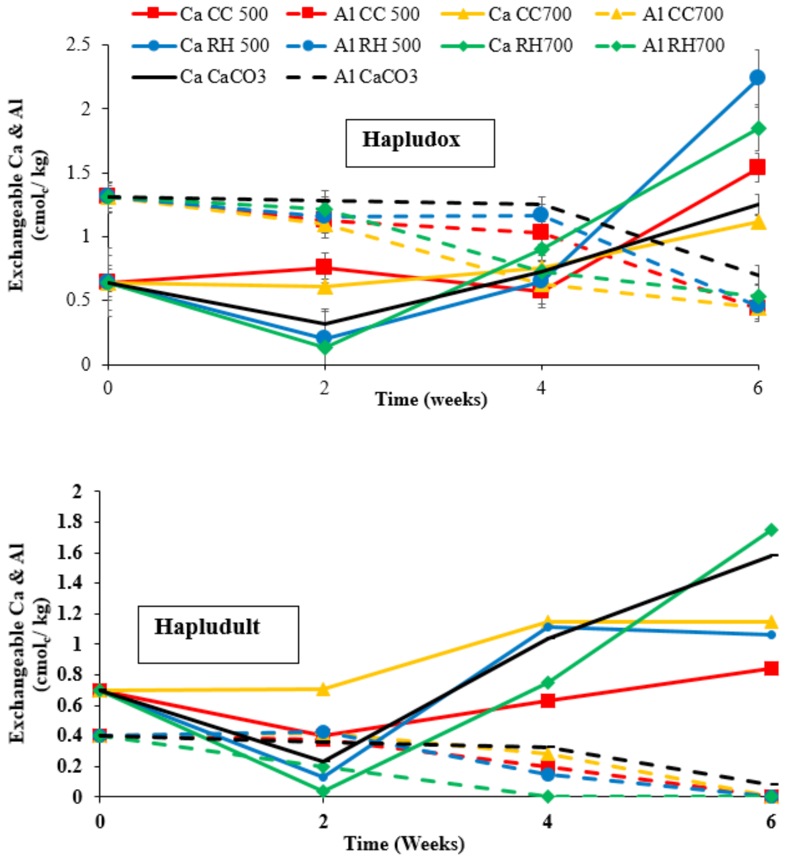
**CC= Corn Cob, RH= Rice Husk, 500 and 700 = Charring temperatures ($^{0}$C) for the biochar types*

Fig. 1 Changes in soil pH with time on addition of amendments for CC700, RH700, CC500 and RH500 after one week of incubation. From the second week of incubation, the CC700 amended soil gave the highest increase in pH rising from 4.9 to about 5.1 at the end of the sixth week. The other biochar amended soils were similar in pH values from the second week with values between 4.7 and 4.8 and rising marginally to between 4.9 and 5.0 at the end of the sixth week.

The Typic Hapludult, had an initial pH of 4.9 which rose to about 5.3 after one week of incubation when the conventional liming material, CaCO3 was applied at 260 kg/ha. Within that same one-week period of incubation, pH in water rose to 5.2, 5.5, 5.6 and 5.9, respectively when the soil was amended with RH700, RH500, CC700 and CC500. Thereafter, the CC500 and CC700 increased the soil pH to 6.2 and 6.0, respectively by the end of the sixth week.

*Effect of Amendments on Changes in Concentration of Al and Ca in the Soils*

The changes in concentrations of Al and Ca in the two soils as a result of amendment with biochar and $CaCO_3$ are shown in Figure 2. The concentration of Al in the Hapludox when amended with the five liming materials generally started decreasing from week four except for the CC700 and RH700 where the decreases started from week two. Generally, Ca concentrations in the soil started increasing from week two rising steadily to a maximum in week six for all the amended soils except the CC500 amended soil where rise in Ca concentration was observed from week four. By the end of the sixth week Ca concentration was least in the $CaCO_3$ amended soils

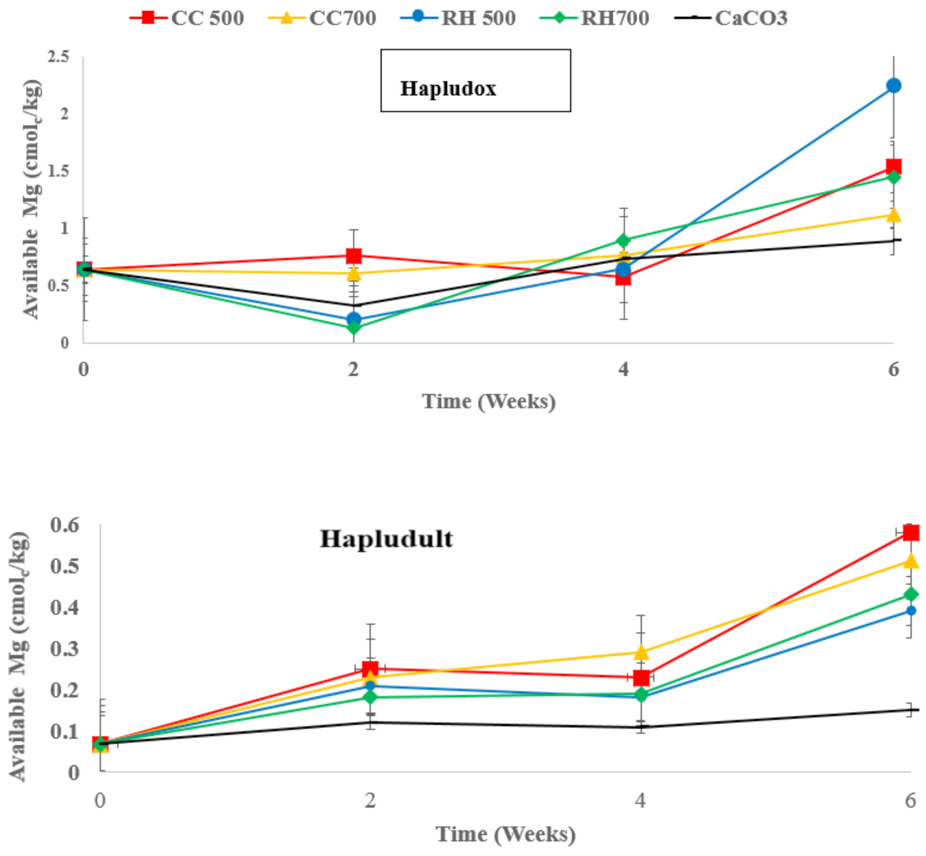


**CC= Corn Cob, RH= Rice Husk, 500 and 700 = Charring temperatures ($^0C$) for the biochar types*

Fig. 2 Changes in Al and Ca concentrations with time on addition of amendments with a corresponding highest value in Al concentration in the Hapludox.

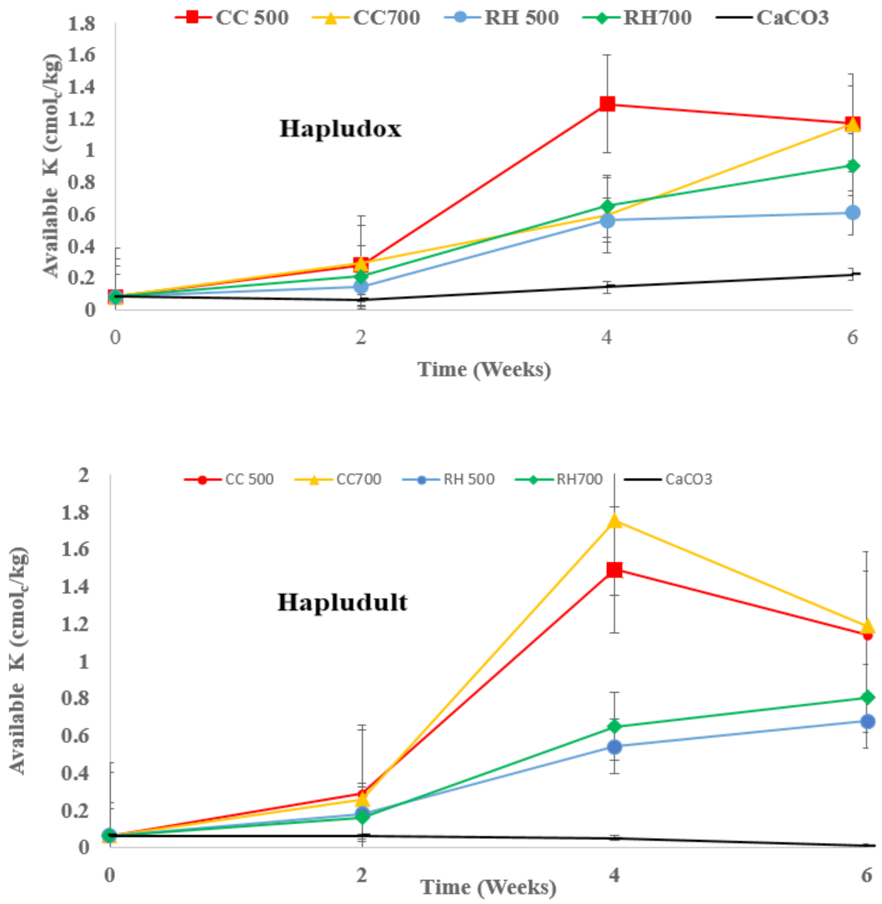
The RH biochar amended Hapludox had the highest Ca concentrations in soil with values between 2.0 and 2.5 cmol$_c$/kg. Co-incidentally their Al concentration in the amended soils was among the lowest with values between 0.52 and 0.6 cmol$_c$/kg. From Figure 2, it is clear that Al concentrations after amendment of the Hapludox with the liming materials did not reduce level of the element to the barest minimum as concentrations after six weeks were more than 0.4 cmol$_c$/kg in the soil. Corn cob biochar charred at 500 $^0$C reduced Al concentration to 0.44 cmol$_c$/kg from 1.31 cmol$_c$/kg whilst increasing Ca concentration from 0.64 cmol$_c$/kg to 1.12 cmol$_c$/kg during the six weeks of incubation in the Typic Hapludox. The $CaCO_3$ decreased Al concentration from 1.31 cmol$_c$/kg to 0.70 cmol$_c$/kg whilst increasing Ca concentration from 0.64 cmol$_c$/kg to 0.89 cmol$_c$/kg in Hapludox. The rice husk biochar types were able to increase Ca concentrations to between 1.7 and 2.20 cmol$_c$/kg whilst decreasing Al to 0.44 cmol$_c$/kg during the incubation period with the RH 500 having the best effect of increasing Ca levels in the soil.

In the Typic Hapludult, decreases in Al concentrations with corresponding increases in Ca concentration were observed from the second week of amending the soil with the five liming materials (Figure 2). It is noteworthy that by the end of the six-week incubation period, even though the conventional lime amended soil had a very high Ca concentration in the soil (1.8 cmol$_c$/kg), it was the only amended soil that still had Al in soil albeit low level (0.08 cmol$_c$/kg), all other amended soils had non-detectable levels of Al. The $CaCO_3$



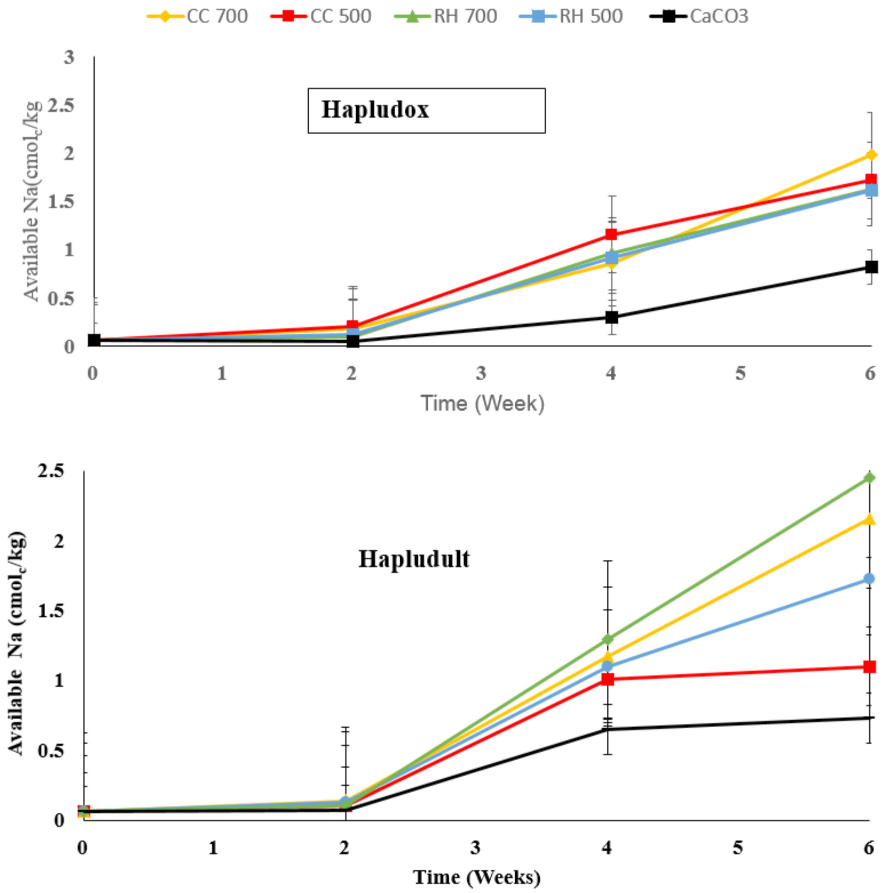
**CC= Corn Cob, RH= Rice Husk, 500 and 700 = Charring temperatures (°C) for the biochar types*

Fig. 3 Changes in Mg concentration with time on addition of amendments



**CC= Corn Cob, RH= Rice Husk, 500 and 700 = Charring temperatures (oC) for the biochar types*

Fig. 4 Changes in K concentration with time on addition of amendments



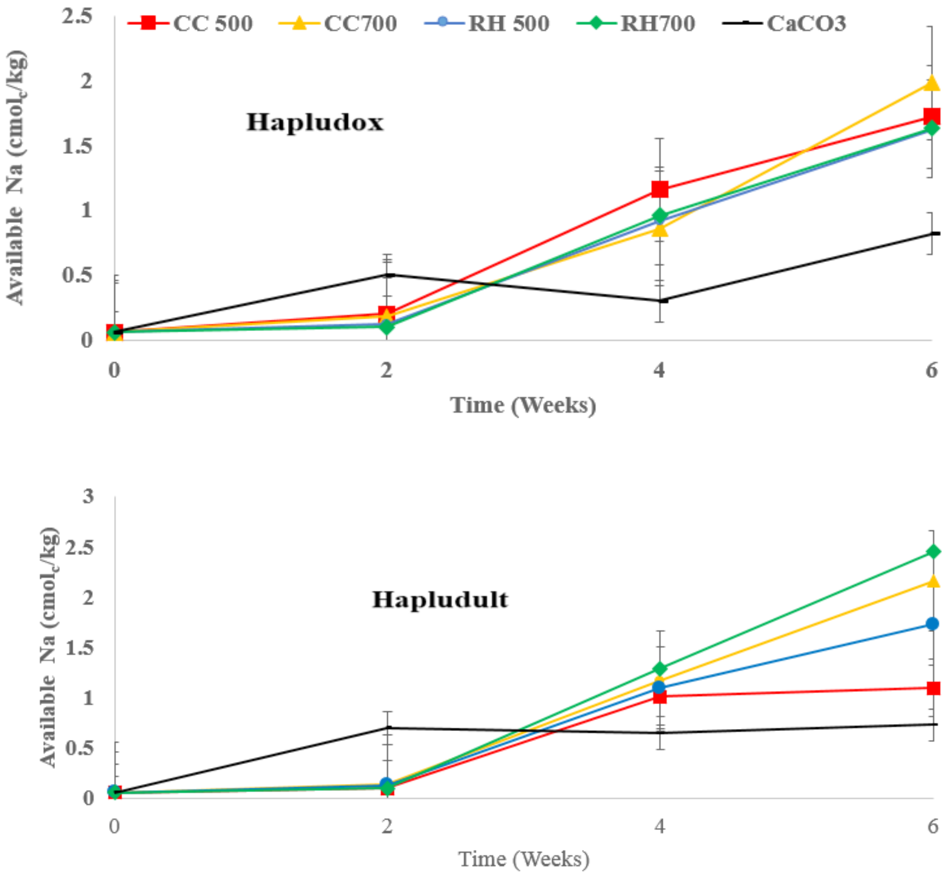
**CC= Corn Cob, RH= Rice Husk, 500 and 700 = Charring temperatures ($^o$C) for the biochar types*

Fig. 5 Changes in Na concentration with time on addition of amendments was able to increase Ca concentration from 0.70 cmol$_c$/kg to 1.58 cmol$_c$/kg during the incubation period in the Typic Hapludult. Rice husk biochar at 700 °C was the biochar type that had the highest influence of Ca accumulation in the soil increasing the concentration of the nutrient to 1.7 cmol$_c$/kg.

### *Effects of Amendment on Mg$^{2+}$, K$^{+}$, Na$^{+}$ and H$^{+}$ Concentrations in the Soil*

The concentrations of Mg$^{2+}$, K$^{+}$, and Na$^{+}$ in the two soils upon amendment with the five liming materials are presented in Figures 3 to 5. Generally, the concentrations of Mg$^{2+}$, K$^{+}$, and Na$^{+}$ in the biochar amended soils were higher than in their $CaCO_3$ amended counterpart. Though the $CaCO_3$ did not contain Mg and Na as active ingredients, it is clear from Figure 3 that addition of the conventional liming material to the Typic Hapludox increased Mg from 0.05 cmol$_c$/kg to 0.3 cmol$_c$/kg. Increase of Mg in the Typic Hapludult was, however, marginal ranging from 0.07 cmol$_c$/kg to about 0.15 cmol$_c$/kg. Sodium concentration also increased from 0.06 cmol$_c$/kg to 0.82 cmol$_c$/kg in the $CaCO_3$ amended Hapludox after six weeks of incubation. Sodium availability in Hapludult at the end of the six-week incubation period increased from 0.06 to 0.73 cmol$_c$/kg when amended with $CaCO_3$.

Availability of the basic cations, Mg, K and Na increased greatly when the two acid soils were amended with the four biochar types with highest level of increases being from Na. Available Na in the Typic Hapludox amended with the four biochar types was between 1.6 and 1.9 cmol$_c$/kg while available K was between 0.6 and 1.2 cmol$_c$/kg. Magnesium concentration was between 0.7 cmol$_c$/kg and 2.1 cmol$_c$/kg. In the Typic Hapludult, availability of Na was between 0.9 cmol$_c$/kg and 2.5 cmol$_c$/kg; K between 0.7 and 1.2



**CC= Corn Cob, RH= Rice Husk, 500 and 700 = Charring temperatures (oC) for the biochar types*

Fig. 6 Changes in Na concentration with time on addition of amendments

$cmol_c$/kg and Mg between 0.4 and 0.6 $cmol_c$/kg.

The acidic cation, $H^+$ generally decreased in the two soils with increasing incubation time (Fig. 6). The concentration of $H^+$ in the soils at the end of the six-week incubation period was highest in the $CaCO_3$ amended soils and higher in the Hapludox (0.28 $cmol_c$/kg) than the Hapludult (0.21 $cmol_c$/kg).

## Discussion

### *Soil Characterization*

The extremely acid and lower pH in the Hapludox compared to the Hapludult is as a result of the higher exchangeable Al in the former soil. The differences in pH in salt and water (i.e. $\Delta pH = pH_{CaCl2} - pH_{H2O}$) gave negative values which show that, there are negative charges on the surfaces of both soils (Nartey, *et al.*, 1997).

The Hapludult and Hapludox both occur in the Tropical Evergreen Rainforest of Ghana. However, the Hapludox is from a forest reserve where there is continuous litter fall from the vegetative cover. The thick forest cover creates a micro climate with relatively lower temperature compared to the fallow plots from which the Typic Hapludult was sampled. With the associated lower pH, there is likely to be lower microbial activity and therefore slower decomposition rate of organic matter (Giller *et al.* 1998) and this may, in part explain the higher organic carbon content in the Hapludox.

The CEC of the Hapludox which is twice higher than the Hapludult is due to the higher organic carbon and clay contents of the former. The CEC is a measure of negative charges at the colloidal surface of soils and in this study was determined by using ammonium acetate at pH 7; 2.1 and 2.8 pH units above the pH in water of Hapludult and Hapludox, respectively. The ECEC on the other hand is a measure of exchangeable cations at the colloidal surface at the soil's pH (Evangelou, 1998). In this study, the ECEC was determined by the summation of exchangeable cations in the two soils. Thus with CEC being determined at pHs above that of the two soils, it is expected that more negative charges would be created and hence higher CEC. The measured CEC of the two soils at pH 7 is in fact their respective potential CECs. It therefore stands to reason that the two soils all have higher CEC than ECEC.

The high rainfall in the Evergreen Forest belt of Ghana which is above 2000 mm (MoFA, 2012) has led to leaching of bases as evident in the low exchangeable base concentration of the soils. This has culminated in high Al saturation of the soil accounting for the 53.9% and 24.54% for Hapludox and Hapludult, respectively. The Al saturation of the soils is higher than the critical of 15% for optimum production of most legumes (Fageria and Baligar, 2008). Such high levels may cause legumes to have restricted root development, poor nodulation and general poor growth (Ferguson, 2013), especially on soils with similar properties as Hapludox. The high Al saturation, low pH, coupled with the high kaolinite and sesquioxides content that are likely to be the major minerals in Ultisols and Oxisols (Evangelou, 1998) would make the two soils prone to high P sorption (Nartey *et al.*, 1997). Consequently, the two soils are low in available phosphorus contents (1.54 mg/kg for Hapludox and 2.71 mg/kg for Hapludult).

The higher clay and organic carbon contents, higher CEC and Al saturation of the Hapludox than the Hapludult will confer on the former a higher buffering capacity. The Hapludox is therefore expected to be more difficult to lime than the Hapludult.

*Biochar Characterisation*

The slightly higher total bases in the corn cob feedstock (0.93%) than that in the RH feedstock (0.9%) may have accounted for the higher pH of 6.8 in the CC feedstock than the RH feedstock 6.1. Upon charring of the two feed stocks at temperatures of 500 °C and 700 °C, there was liberation of three forms of bases viz. total, exchangeable and soluble. These liberated bases may have accounted for the rise in pH of the four biochar types from neutral in their respective feed stocks to alkalinity in the biochar derivatives. The strong alkalinity (pH between 10.7 and 11) in the CC biochar types is due to their high total and exchangeable bases. The increase in pH as a result of release of bases due to high charring temperature is corroborated by Struebel *et al.* (2011). High pyrolysis temperatures release organic acids and phenolic substances through cracking of hemicellulose and cellulose. These acids react with basic cations in the feed stocks to form alkaline salts which increase the pH of biochar (Streubel *et al.,* 2011. Joseph *et al.* (2010), has reported that most biochars are often alkaline and therefore increase soil pH after application. The RH feedstock had higher Ca and Mg contents and consequently higher contents of these secondary major nutrients in the total fractions upon charring. The higher total Ca and Mg contents of rice husk impart on them good qualities to be exploited for use as liming materials.

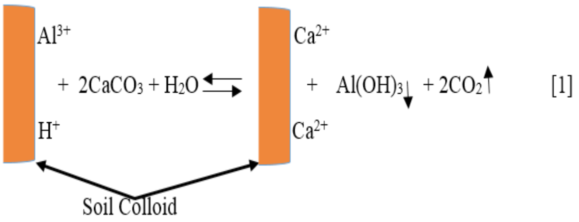
Charring leads to carbonization culminating in high carbon contents per unit mass (Lehman and Joseph, 2007). Thus the carbon contents of the four biochar types being higher than their respective feed stocks. Corn cob is more lignified and has more polyphenol groups than the rice husk (Masulil *et al.*, 2010). Consequently, the CC would have more aromatic C groups (Scott *et. al.*, 2014; Shinogi and Kanri, 2003) and hence more recalcitrant carbon accounting for the higher accumulation of C after charring. In terms of C sequestration, the CC biochar types should be the preferred choice,

Nitrogen is sensitive to heat and is subsequently volatilized leading to low N content of the biochar types. The total N content of the corn cob feedstock was higher than its rice husk counterpart. It is, therefore, not surprising that with its higher polyphenol content, the CC biochar types have more TN than their RH counterparts. The CC biochar types have higher C: N ratios which may reduce microbial decomposition and restrict release of N from the biochar when added to the soil. With the concomitant decrease in their respective N contents, it is expected that the biochar types will have high C: N ratios than their respective feed stocks as reflected in values between 692 and 773 for the four biochar types as opposed to between 42 and 47 for their respective feedstocks. These very high C: N ratios of the biochar imparts stability on the material and thus would persist in soil with the CC 700 and RH 700 being more resistant to degradation than their counterparts charred at 500 °C.

*Effects of Liming on pH and Availability of Bases*

The increase in pH of the biochar and $CaCO_3$ amended soils during the incubation period in both Hapludox and Hapludult is due to the release of readily available calcium from the five liming materials which replaced the $Al^{3+}$

and $H^+$ at the exchange sites of the respective soil as depicted in equation 1:



The replacement of $Al^{3+}$ and $H^+$ by $Ca^{2+}$ is corroborated by the decreases in $Al^{3+}$ and $H^+$ with concomitant increases of $Ca^{2+}$ in solution of the two soils. This is further supported by significant negative correlation coefficient (r) of -0.78** between exchangeable Al and Ca for Hapludox and -0.57** for Hapludult (Figure 7). The corresponding respective coefficient of determinations ($r^2$) of 0.607 for Hapludox and 0.321 for Hapludult imply that 60.7% and 32.1% respective decreases in Al are attributable to Ca from the amendments. Thus, Typic Hapludox responds more to Ca for Al replacement than the Typic Hapludult. Apart from Ca, the four biochar types had Mg, Na and K. These three other basic cations may have also replaced part of the Al accounting for the much higher rise in pH of the biochar amended soils than the $CaCO_3$ counterpart. These increases in pH of acid soils by biochar is corroborated by several authors (Novak *et al.*, 2009; Joseph *et al.*,2010; Farrell *et al.*,

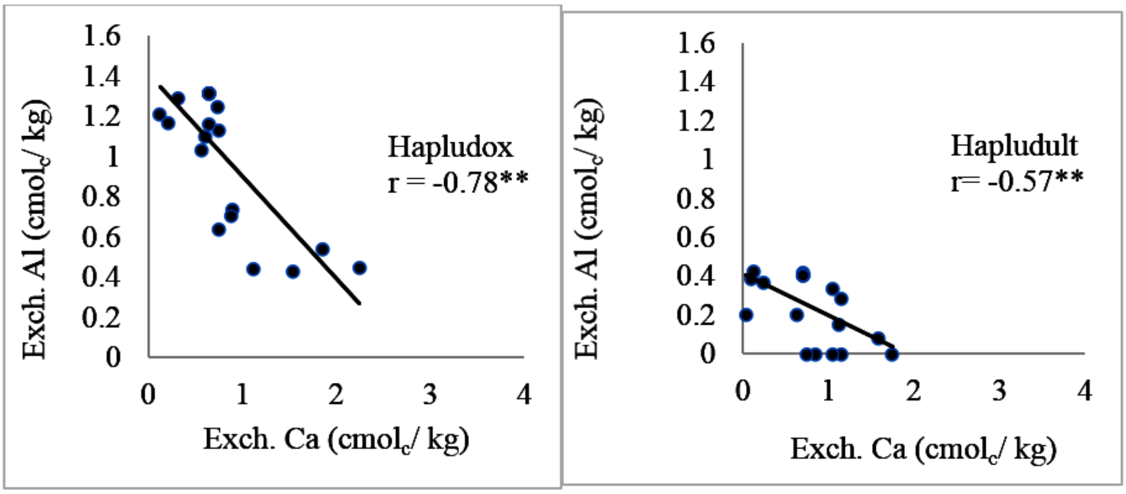


Fig. 7 Relationship between exchangeable Ca and exchangeable Al

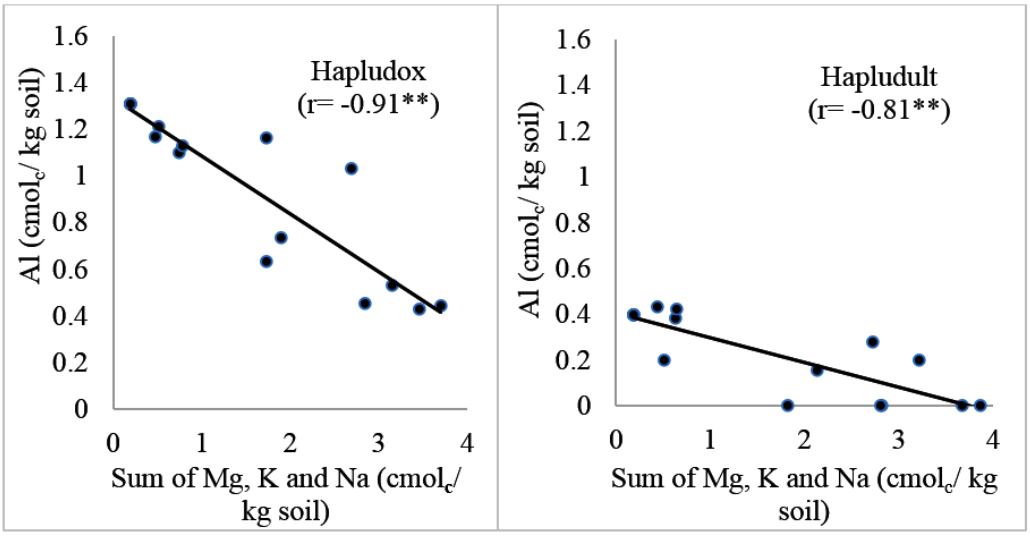


Fig. 8 Relationship between sum of bases (Mg, K, Na) and exchangeable Al

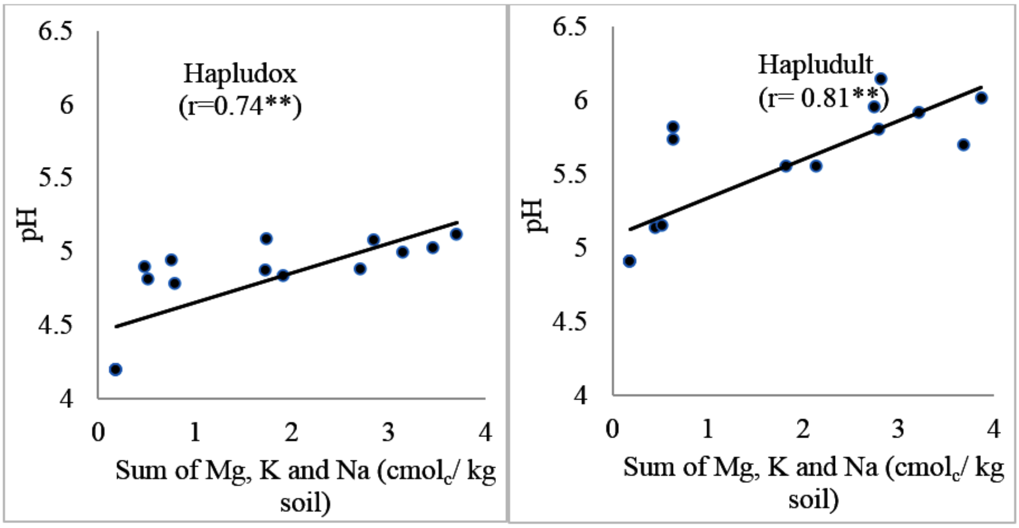


Fig. 9 Relationship between sum of bases (Mg, K, Na) and pH

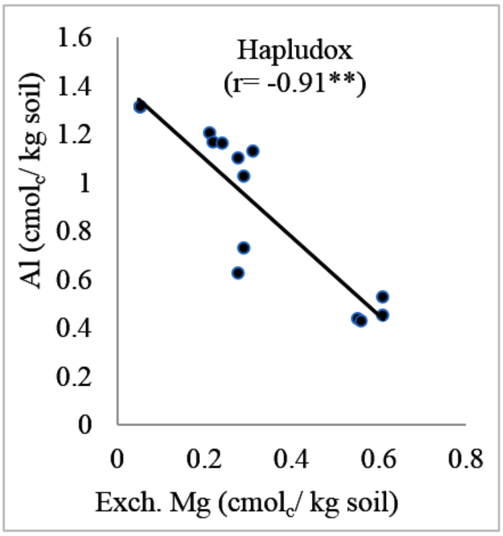


Fig. 10a Relationship between Exchangeable Al and Mg

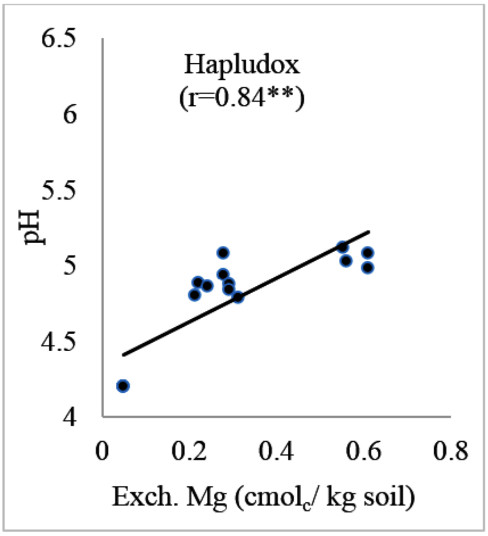


Fig. 10b Relationship between pH and Mg

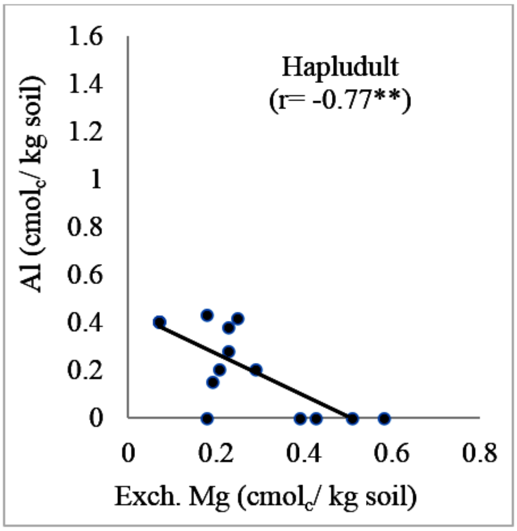


Fig. 11a Relationship between Exchangeable Al and Mg

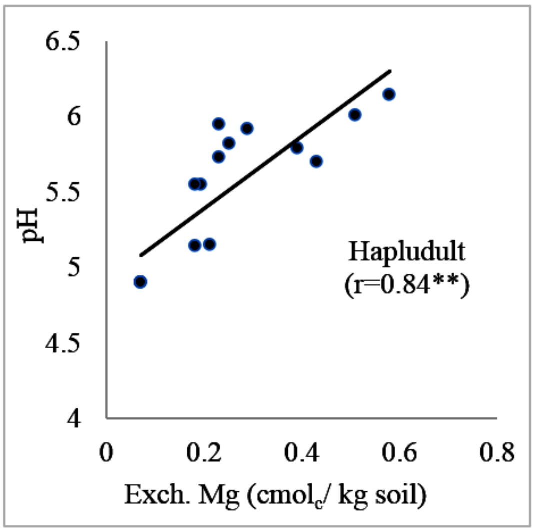


Fig. 11 Relationship between pH and Mg

2013; Masto *et al*., 2013; Masulili *et al*., 2010). A regression of the sum of Na, K and Mg in biochar amended Hapludox and Hapludult against their respective Al concentrations showed high negative correlation coefficient of -0.91** for Hapludox and -0.81** for Hapludult (Figure 8). Regressing the sum of the three bases on pH showed a positive correlation coefficient of 0.74** for Hapludox and 0.81** for Hapludult (Figure 9). Regressing exchangeable Al on Mg gave r = -0.91**and pH versus Mg giving r = 0.83** for Hapludox (Figure 10a and 10b). The r value was 0.84** for Mg against pH and -0.77** for Mg against Al (Figure 11a and 11b) for Hapludult. The higher correlation between Mg and Al in the biochar amended soils than between Ca and Al in the $CaCO_3$ amended soils show that Mg was more effective than Ca in reducing Al concentration in the soils. Dolomite could have, therefore been a better liming material than the $CaCO_3$. However, dolomite as a liming material is also not readily available. The biochar types could therefore be exploited for use as suitable substitutes for the conventional liming material. The fact that CC 500 was able to raise the pH in the Hapludult to about 5.9 after just one week of incubation, increasing to 6.2 after the sixth week coupled with the fact that it reduced Al concentration to undetectable level and did not differ much from the others in improving the pH characteristics of the Hapludox makes it (CC 500) the preferred biochar type for liming among the four on acid soils. The pH of 6.2 in the Hapludult is ideal for most arable crops as P, a major limiting nutrient in tropical soils especially those which are acid will be made more available. The application rate of 80 tonnes per ha may be discouraging to farmers. Considering however, that corn cob and rice husk abound in West Africa and particularly Ghana and can be charred in situ, in addition to the added available basic nutrients and available P that farmers stand to gain from amending acid soils with biochar, not discounting the carbon that will be harnessed to the soil, application of biochar may be the panacea to the liming problem in West Africa.

Soil reaction in the biochar amended Hapludult after the six weeks' incubation was from moderately acid to neutral whilst the Hapludox was from strongly acid to moderately acid. In the $CaCO_3$ amended soil, the Hapludult changed from being very strongly acid to strongly acid whilst the Hapludox became strongly acid. The slow response of Hapludox to liming could have been due to the influence of its high organic matter content which was about 2.8 times higher than that in Hapludult. This moderately high organic carbon content (15.3 g/kg) in addition to the relatively higher clay content may have acted as a buffer resisting changes in pH (Stewart *et al*., 2013; Curtin and Trolove, 2013). According to Campbell (1993), the more humus and clay a soil has, the greater its Al and H content and hence the greater the amount of lime needed to raise the soil pH. This explains the respective responses of Hapludox and Hapludult to the same rate of lime application during the incubation period.

The increase in pH on amendment of Typic Hapludox and Typic Hapludult with $CaCO_3$ is more than 0.5 pH unit which according to Nartey *et al.* (2000) is significant. This significant increase in pH from 4.2 to 4.7 and 4.9 to 5.2, respectively, for Hapludox and Hapludult may have led to the solubility of hitherto precipitated Mg and Na leading to the increases in the concentration of the two basic cations in soil solution of the $CaCO_3$ amended Hapludox. This may explain increases in Na and Mg concentrations in the $CaCO_3$ amended soil even though the amendment did not have Mg and Na as active ingredients.

The four biochar types have readily available basic cations in soluble and exchangeable forms and with the accompanying rise in pH upon amendment to the two acid soils, it stands to reason that the basic cations K, Mg and Na increased in the soils. The highest concentrations of available Na in the two soils upon amendment with the biochar samples may be a reflection of its relatively higher total contents in the biochar types.

## Conclusions

The study has revealed that corn cob charred at 500 °C is a biochar type that would be effective in liming acid soils with initial pH of 4.9 to 6.2. Application of corncob and rice husk charred at 500 °C and 700 °C can also be used to reduce Al toxicities in acid soils and as substitutes for $CaCO_3$, the conventional liming material.

On amendment of biochar to acid soils, a farmer has to wait for at least six weeks for equilibration before planting. Addition of corn cob and rice husk biochar types to extremely acid soils with pH about 4.2 increases pH by about 1 pH unit and increases the Ca, Mg, K and Na contents of the soil.

The relatively higher organic matter and clay contents of the Hapludox had a negative effect on liming compared to the Hapludult. Magnesium seems to have a better correlation with increase in pH and lowering of Al in the Hapludult and Hapludox than Ca.

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