BIOCHAR AS A LIMING AGENT AND PHOSPHORUS SOURCE TO ENHANCE THE GROWTH OF SOYA BEAN IN TWO ACID SOILS.

BY

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DECLARATION

I hereby declare that this thesis has not been submitted for a degree to any other university and it is entirely my own work and all help and references have been duly acknowledged.

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DEDICATION

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ABSTRACT

Unavailability and high cost of conventional liming materials have contributed largely to low food production in acid soils of Ghana. Biochar produced from agricultural waste materials have high concentration of basic cations and available P that could be exploited for use as liming material and/or P source. However, the biochar type that will provide a conducive soil pH vis-à-vis P availability for food crop production in acid soils of Ghana has received little attention. Consequently, two typical acid soils, Ankasa series (Plinthic Acrudox) and Tikobo series (Typic Hapludult) were amended with corn cob and rice husk biochar types charred at 500 and 700 ^{o}C at a rate of 80 tons/ha in a screen house experiment to ascertain the efficacy of the biochar types as substitutes for agricultural lime and sources of P. The Ca equivalent of the biochar types from $CaCO_3$ was amended to the soils to serve as a realistic control. 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 and basic cations monitoring. After pH equilibration, inoculated soya bean seeds were sown at stake. Nitrogen was applied at rates of 0 kg/ha and 10 kg/ha. Phosphorus was applied at zero and the biochar P equivalent from triple super phosphate was applied to the non-biochar-amended soils. Extra 30 kg P/ha from TSP was applied to some of the biochar amended soils to ascertain if any, the combined effect of synthetic P and biochar on growth and nodulation of soya bean. At flower initiation, crops were harvested, nodules counted, root volume, shoot and root dry matter and P uptake were determined. Results showed that corn cob charred at 700 ^{o}C was able to raise pH from 4.2 to 5.2 in Ankasa Series and from 4.9 to 6.2 in Tikobo Series within a six-week incubation and equilibraation period. Rice husk charred at 700 ^{o}C was able to raise pH from 4.2 to 5.0 Ankasa Series and 4.9 to 5.8 in Tikobo Series within the incubation period. All the biochar types reduced Al concentration from 0.4 cmol/kg to undetectable levels in the Tikobo Series with the element being reduced from 1.31 cmol/kg to 0.45 cmol/kg in the rice husk and corn cob at 700 °C biochar amended Ankasa soils within the six-week equilibration period. Soya bean nodulated in the rice husk biochar charred at 700 °C amended Tikobo Series without any form of synthetic fertilization. There was no nodulation in the Ankasa series. Shoot P uptake of soya bean was 1.5 and 1.4 times more in Ankasa and Tikobo Series, respectively when amended with rice husk biochar charred at 700 °C than the same soils amended with conventional lime and equivalent biochar P from triple super phosphate. Apparent nutrient recovery efficiency was higher in biochar amended soils than the $CaCO_3$ amended soils. The biochar amended soils showed an increase in organic carbon contents. The residual total P increased from 101.4 mg/kg to 257.8 mg/kg when rice husk biochar charred at 700 °C was applied to Tikobo Series whilst there was an increase from 164.0 mg/kg to 344.9 mg/kg when corn cob biochar charred at 500 °C was added to Ankasa Series. There was high increase in residual available P after amending the soils with the liming materials. The study concludes that corn cob and rice husk biochar can be used as liming materials and P source in acid soils, particularly Tikobo Series for growth of soya bean.

CHAPTER ONE

1 INTRODUCTION

1.1 Background

Soils of Ghana apart from the notable variants of the Vertisols and the salt affected soils on the eastern coast are generally low in bases. The low base saturation is as a result of intense weathering and high rainfall. The high rainfall has led to leaching of bases culminating in the exchange sites of the soils being dominated by H^+ and Al^{3+} and its species. 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 low 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 has been through the use of inorganic fertilizers, particularly sulphate of ammonia, albeit in low application rates in Ghana (Buri *et.*, *al.*, 2005). An oxidation of a mole of NH_4^+ leads to the production of two moles of H^+ (Tisdale *et al.*, 1993). Consequently, the application of sulphate of ammonia might have contributed to the acidic pH (pH< 6.0) of the majority of soils in Ghana (Buri *et al.*, 2005; Oppong, 2011). Soils with low pH are no longer restricted to the deciduous and semi deciduous forest belts and especially to the Western Region. 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 being grown in soils of pH below 6.

According to Sparks (2003), acid soils are generally found in highly weathered areas where rainfall surpasses evaporation and plant use. These soils are characterized by prolonged leaching of basic cations over long period of time with the exchange sites dominated by acidic ions leading to low pH (Tisdale *et al.*, 1993). These soils are inherently low in fertility with high concentrations of Fe and Mn, high toxic levels of Al^{3+} and low P and Mo (Brady and Weil, 2002).

Marine fish catches in Ghana are decreasing as a result of illegal fishing methods such as pair trawling, use of unapproved nets and use of light (Nunoo *et al.,* 2015). Fresh water fish catches have equally dwindled mainly because of the menace of illegal mining activities referred to as ‘’galamsey’’, which tend to pollute river bodies. Eutrophication has also resulted in the growth of aquatic weeds depleting fish stocks in fresh water bodies (Naylor *et al.,* 2000). There is also low production of ruminants due to high incidence of tsetse flies, poor animal husbandry and the sparse grassland in Ghana. Game could have been an alternative for protein. However, it is not a reliable source in that, their populations have declined over the years. Also, there is contamination due to the use of poisonous baits in trapping these game (Ogada, 2014). Production of plants-based protein could, therefore, be seen as the panacea to Ghana’s self-sufficiency in dietary protein.

There is increased advocacy for production of soya bean by farmers in Ghana as a result of the crop’s multiple uses as a source of livestock and aquaculture feed, and protein and oil for the human diet (Mutegi and Zingore, 2013). Soya bean is an oilseed, which has a significant amount of all the essential amino acids, minerals and vitamins for human nutrition. It has on the average 40% protein, 30% carbohydrate and oil content of 20% (Adu - Dapaah *et al.,* 2004; MoFA and CSIR, 2005). Its high protein content coupled with the fact that it contains all the essential amino acids may, in part, be the reasons behind the recent advocacy for its wide-scale cultivation in Ghana and use as a substitute for animal protein.

According to Ugwu and Ugwu (2010), the benefits of soya bean over other grain legumes such as groundnut and cowpea include lower susceptibility to pests and diseases, better storage quality and larger leaf biomass which translate into soil fertility benefit to subsequent crops. Soya bean has the ability to fix between 60 kg and 168 kg of nitrogen per hectare per year under favourable conditions (Rienke and Joke, 2005). Soya bean is non-host plant to Striga. It however, exudes chemical substances that promote the germination of Striga seeds. The germinated Striga seeds die off within a few days because the parasitic plant is unable to attach itself to the host, soya bean. This attribute of soya bean has, therefore, been exploited by researchers and farmers in northern Ghana for the control of Striga in millet, sorghum and maize production (MoFA and CSIR, 2005).

Growth and nodulation of soya bean is affected by soil acidity, soil P status and presence of efficient Rhizobia strains. Production of soya bean requires among others, sufficient water supply; between 350 – 750 mm per annum, ideal temperature ranges between 20 ^{o}C and 30 ^{o}C, phosphorus requirement of 80 – 120 P_2O_5 kg/ha and pH from 5.5 to 7.0 with an optimum of 6.0 (Assuming-Brempong *et al.*, 2013). However, with the large expanse of soils in Ghana being acidic, it is evident that yields of soya bean would be low. There has to be a conscious effort to manage the soils such that a favourable pH would be created for sustainable and high productivity of the crop.

The use of agricultural lime is a potential option for sustainable soils management among the other options for restoring soil health and fertility. Application of agricultural lime is the conventional way of reducing soil acidity. Agricultural lime is any material that contains Ca^{2+}, and/or Mg^{2+} as cation and OH^-, CO_3^{2-}, O^{2-} or SiO_3^{2-} as anion and is capable of raising the soil pH to a desired level for crop production (Brady and Weil, 2002). In agriculture, lime plays a great role in reducing soil acidity and hence favours plant nutrition. Application of agricultural lime reduces Al and Mn toxicity, increases Ca, Mg, Mo and P uptake and improves on plant rooting system (Brady and Weil, 2002). Calcite, dolomite, quick and slaked lime are common liming materials used.

Although soils in Ghana are becoming acidic, the use of agricultural lime by farmers is low due to a myriad of reasons, chief of which is the high cost involved in acquisition. The material is also not readily available on the market when needed and when available is mostly not of pure grade. There is also the problem of high haulage cost to remote farm lands because it is not normally available, at fertilizer sales and distribution centres. It is imperative that a suitable alternative is provided to farmers in Ghana if the productivity of the soils and crops, particularly soya bean, are to be increased. Any alternative material that would be appealing to farmers for liming acid soils should be relatively cheaper, readily available and preferably found in close proximity to the farm.

The application of biochar to agricultural soils has recently received attention in Ghana as a result of its multiple benefits to soil quality and improved crop yields, as well as the potential of gaining carbon credits by way of carbon sequestration (Berek *et al.*, 2011). Biochar is a carbon rich material produced by pyrolysing biomass such as manure, wood or leaves under limited oxygen (Sohi *et al.*, 2010). Pyrolysis is the thermal decomposition of organic material under restricted supply of oxygen (Lehmann, 2006). This process employed in biochar production is similar to the age old method of charcoal production, which is one of the most ancient industrial technologies developed by mankind (Harris, 1999).

Biochar, due to its molecular structure is chemically and biologically more stable compared to the application of the same un-charred biomass added directly to soil (Lehmann and Joseph, 2009). Consequently, it is more difficult for carbon from biochar to be transformed back to CO_2, implying storage of carbon for several decades (Lehmann, 2007, Berek *et al.* 2011,). Biochar, depending on the types 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 form 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 the soil 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). A 30% to 40% increase in wheat height has been recorded on addition of biochar produced from paper mill sludge applied at a rate of 10 t ha^{-1} to an acidic soil (Van Zwieten *et al.*, 2007).

Addition of biochar also increases organic matter content of the soil which affects ion exchange capacity, plant nutrient retention, increase water holding capacity, reduces bulk density and improve soil structure (Gaskin *et al.*, 2007). Sam (2014) has noted that biochar from rice husk and cocoa pod husk charred at 450 °C has available P concentrations of 531 mg/kg and 3897 mg/kg, respectively. Biochar could therefore be exploited for use as a liming material with an added advantage of being a P source.

1.2 **Problem Statement**

Production of soya bean requires among others; 80 to 120 kg P_2O_5/ha and soil pH between 5.5 and 7.0 with an optimum of 6.0 (Assuming-Brempong, *et al.*, 2013). However, the majority of soils in Ghana have pH below 6.0 (Buri *et al.*, 2005; Oppong 2011;). Phosphorus is an important nutrient for growth and nodulation of soya bean. A majority of the highly weathered soils of Ghana abound in kaolinite and oxides of Fe and Al (Nartey *et al.*, 1998). With the low pH of these soils coupled with their low organic matter contents, P availability is also very low especially in the concretionary soils of northern Ghana on which a bulk of soya bean is currently being cultivated (Nartey *et al.*, ;1998; Abekoe and Sahrawat, 2001). Hence, increasing the productivity of these soils for soya bean cultivation, would require amendment that will not only raise the pH but also provide available P.

Biochar could be the panacea for the low pH and low P availability problem of Ghanaian soils. There is abundance of farm waste such as rice husk, cocoa pod husk and corncob which could be charred anaerobically to produce biochar. However, the feedstock and charring temperature which would produce an ideal biochar for use as a liming material and provide available P for use on acid soils of Ghana has received little attention. Equilibration time or how long a farmer should wait upon amendment of biochar to an acid soil before sowing or planting has not been investigated.

1.3 **Justification**

Soya bean, among other legumes, contains all the essential amino acids and can be used as a substitute for animal protein in human diet and also to feed livestock (Reinke and Joke, 2005).

Presently, Ghana is not self-sufficient in dietary protein as there are inadequate and unreliable sources of protein to meet the ever growing demand of the inhabitants of the country. This is not denying the fact that most of the protein in diets of people living in Ghana are from animal sources which are largely imports from outside the country. Ironically, animal sources of protein are low in fibre content, very high in essential amino acids, and when consumed by humans induce high circulating levels of trimethylamine N-oxide (TMAO), a substance that causes inflammation of the lining of blood vessels and therefore fraught with health hazards such as high cholesterol contents (Tang *et al.*, 2013).

Soya bean has become a major source of high quality and cheap protein source for the poor and rural households in West Africa (IITA, 2009). It is low in cholesterol and has the unique property of being a plant source of protein with the complement of all the essential amino acids ((Lokuruka, 2010)). It is thus used to fortify various traditional foods such as gari, sauces, stews, soups, banku and kenkey to improve their nutritional, particularly protein content in Ghana (MoFA and CSIR, 2005). Soya bean can, therefore be conveniently used as a substitute for animal protein. Consequently, the Ghana's Ministry of Food and Agriculture has for the past two decades been promoting the production and consumption of the crop and this has resulted in rapid expansion in production (Sarkodie-Addo *et al.*, 2006).

Despite its numerous benefits, yield of soya bean in West Africa and in Ghana is very low with an average of 1.1 Mg/ha (IITA, 2009). The low productivity in Ghana among others includes low soil fertility of which low pH and low P are the primary factors. Any intervention that would improve on the soil conditions for cultivation of soya bean in Ghana must include amelioration of the acid soils and/or making P more available.

Corn cob and to a lesser extent rice husk are agricultural waste which abound in virtually all the ten regions of Ghana. There are ‘’mountains’’ of rice husk at the rice milling centres in the country because the resource is of limited use to farmers and the mills. The material is therefore left in the open to breed rodents which in turn attract snakes. Corn cob apart from being used as fuel source is also left in the open or sent to garbage grounds after shelling. These two organic resources are hardly added as organic amendment to soils probably because of their high C: N ratio and therefore slow decomposition rates. These feedstock types are mainly disposed of by aerobic burning which increases the greenhouse gas (CO_2) concentration in the atmosphere.

Thermal decomposition of these feedstocks through pyrolysis would convert the organic C into a recalcitrant form to persist for many years in soils. Thermal decomposition could also hasten the liberation of bases from cell walls which may combine with anions like carbonates to form cheap liming materials (Van Zwieten *et al.*, 2007). The charred feedstock could also produce a cheap source of P (Sam 2014; Tetteh, 2014), an important nutrient needed for nodulation, pod formation and root extension in legumes but which is deficient in Ghanaian soils. The high pH of the charred material could also help in ameliorating the acid problems of the soils and also reduce Al toxicity in extremely acid soils (Van Zwieten *et al.*, 2007).

Pore spaces in biochar have been found to serve as sites for microbial proliferation to help in nodulation (Dias *et al.*, 2010). It is, therefore, being postulated that with its high inherent available P which is an energy source for microbes coupled with the liming effect, addition of biochar to acid soils would provide an enabling environment for the proliferation of rhizobia to help in the growth and nodulation of soya bean. Production of biochar especially from rice husk could help reduce the garbage collection problem that has bedeviled Ghana as a country and reduce CO_2 emission into the atmosphere.

1.4 **Objectives**

It is in the light of the above that this work seeks to;

i. ascertain the liming potential of corn cob and rice husk biochar types on typical acid soils in Ghana

ii. ascertain the influence of rice husk and corn cob biochar as liming materials on the growth and nodulation of soya bean.

iii. determine the suitability or otherwise of biochar as a P source for the growth and nodulation of soya bean on typical acid soils of Ghana

1.5 **Hypothesis**

H_o: Addition of corn cob or rice husk biochar will neither reduce the soil acidity nor improve growth and nodulation of soya bean on acid soils in Ghana.

H_A: Addition of corn cob or rice husk biochar will reduce the soil acidity and consequently improve growth and nodulation of soya bean.

CHAPTER TWO

2 LITERATURE REVIEW

2.1 Definition of pH

The availability of nutrients and therefore the fertility and productivity of agricultural soils chiefly depend on the pH of the soil. Soil pH is the level of hydrogen ion concentration or activity in the soil system. It measures the degree of soil acidity or alkalinity. As H^+ ion concentration increases, pH value decreases and hence soil acidity increases (USDA, 1999). There are descriptive terms associated with soil pH. Unlike the pure system where neutrality is at seven, the range of between 6.1 and 7.3 on the pH scale is considered neutral in soil (USDA, 1999). Table 2.1 gives the descriptive terms of pH ranges in soils according to the USDA system.

2.1.1 Causes of Soil Acidity

About 25% of the earth's croplands are affected by problems associated with soil acidity (Graham *et al.*, 2000). It is therefore, worth knowing the causes of acidity if effective remedial measures are to be taken. Soil acidity is caused by several natural and anthropogenic factors. The natural factors include leaching of bases as a result of excessive rainfall, plant uptake of basic nutrients, decomposition of organic matter whilst the anthropogenic causes include application of inorganic fertilizers mainly the ammonium based ones. Generally, soil acidity increases as rainfall increases.

Table 2. 1: Descriptive Terms Associated with Soil pH

pH ranges	Descriptive Term
< 4.0	extremely acid
4.1 – 5.0	very strongly acid
5.1 – 5.5	strongly acid
5.6 – 6.0	moderately acid
6.1 – 7.3	neutral
7.4 – 8.0	slightly alkaline
8.1 – 9.0	alkaline
> 9.0	strongly alkaline

Source: USDA (1999).

Soil acidity deals with the H^+ ions in soil solution, thus high H^+ ion concentration will result in lower pH value and hence higher acidity. Some sources of H^+ in soils include:

i) Carbon dioxide released from plant roots and microbial respiration which combines with soil water to produce carbonic acid. This acid then dissociates to release H^+.

$$CO_2 + H_2O \longrightarrow H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad [2.1]$$

(ii) Decomposition of organic matter with concomitant releases of H^+.

(iii) Roots of plants also release H^+ and organic acids to lower the pH of soils.

(iv) Nitrification of ammonium

$$NH_4^+ + 2O_2 \leftrightarrows NO_3^- + 2H^+ + H_2O \qquad [2.2]$$

(v) Hydrolysis of Al in soils releases large quantities of H^+ into soil solution as shown in the equations below.

$$Al^{3+} + H_2O \longrightarrow Al(OH)^{2+} + H^+ \qquad [2.3]$$

$$Al(OH)^{2+} + H_2O \longrightarrow Al(OH)^+ + H^+ \qquad [2.4]$$

$$Al(OH)^+ + H_2O \longrightarrow Al(OH)_3 + H^+ \qquad [2.5]$$

A summary of the three reactions is thus

$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+ \qquad [2.6]$$

(vi) Oxidation of sulphur compounds in soils leads to acidification as depicted in equation

$$S^0 + 3/2\ O_2 + H_2O \longrightarrow H_2SO_4 \qquad [2.7]$$

S^0 is elemental sulphur

2.1.2 Types of Soil Acidity

There are three general pools, or types of ac idity: active, exchangeable and residual

2.1.2.1 Active Acidity

Active acidity indicates the H^+ ion concentration in soil solution and it determines the pH of the soil. The active pool of hydrogen ions is in equilibrium with the exchangeable hydrogen ions that are held on the soil's cation exchange complex (CTAHR, 2007). It is a very small part of the total acidity of a soil. However, it is very important to the plant since it determines the solubility and availability of many elements and nutrients in the soil solution. Active acidity can be directly determined using a pH meter (CTAHR, 2007).

2.1.2.2 Exchangeable Acidity

Exchangeable acidity is due to the exchangeable acidic cations Al^{3+} and H^+ on the colloidal surface of soils. When the CEC of a soil is high but has a low base saturation, the soil becomes more resistant to pH changes (CTAHR, 2007). When salt such as KCl or $CaCl_2$ is added to the soil, the cations Al^{3+} and H^+ at the exchange site are released into soil solution by exchanging with K^+ or Ca^{2+}. The Al^{3+} released undergoes hydrolysis to produce more H^+ into soil solution as depicted in equation [2.6]. This then lowers the soil pH. Due to the fact that basic cation, K^+ or Ca^{2+} in the salt displaces the acidic cations into soil solution, the name exchangeable acidity is used. This type of acidity is greater than the active acidity. Application of agricultural lime targets the replacement of the exchangeable acidity with basic cations, usually Ca^{2+} and Mg^{2+} (Brady and Weil, 2002).

2.1.2.3 **Residual Acidity**

This is the acidity due to Al^{3+} and H^{+} bound to clay and organic matter to form complexes that are non-exchangeable and least available (CTAHR, 2007). This form of acidity is greater than either active or exchangeable acidity**.** Combination of the three types of acidity gives the total acidity soils.

2.1.3 Effect of Soil Acidity on Nutrient Availability and Plant Growth

The influence of soil pH on growth of plants is mostly indirect, through its impact on chemical reactions and biological processes. According to Giller and Wilson (1991), ideal nutrient absorption by most crops occurs at a soil pH within the neutrality range. Plant growth and development can also be negatively affected when soil acidity is not properly controlled (Nduwumuremyi, 2013). Generally, availability of nutrients such as nitrogen, molybdenum, phosphorus and potassium are negatively affected as soil acidity increases (Brady and Weil, 2002).

According to Kochian (1995), solubilized rhizotoxic aluminum species in highly acidic soils can inhibit root growth and function in most plants. Pineros *et al.* (2005) showed that Al toxicity limits plant growth primarily through its adverse effects on growth and development of roots. Aluminium toxicity also increases drought susceptibility and restricts plant access to subsoil nutrients inhibiting the total expression of plant genetic potential (Ownby and Popham, 1990). According to Giller *et al.* (1998), Al toxicity reduces the agronomic and recovery efficiencies of nutrients.

Strong soil acidity restricts the growth and multiplication of soil microorganisms which suppresses plant growth. For example, biological nitrogen fixation by bacteria that live in nodules of legumes, such as cowpea, groundnut and soya bean, are negatively affected in soil with pH below 6. According to Brockwell *et al.* (1995), there is reduction of nearly 10^{-3} in number of *S. meliloti* in soils at pH below 6 compared to those with a pH >7.0. A consequence of the inhibition of microbial growth and multiplication under low soil pH conditions is the slow decomposition of organic matter

In highly acidic soils, P is particularly a limiting nutrient. Under extremely to strongly acid conditions such as in Oxisols, there is high concentration of soluble Al^{3+} and Fe^{3+} in the soil. Any added P is then precipitated as depicted in equation [2.8]

$$Al^{3+} + H_2PO_4^- + 2H_2O \quad 2H^+ + Al(OH)_2H_2PO_4 \qquad [2.8]$$

The freshly precipitated hydroxy phosphates are slightly soluble because they have a great deal of surface area exposed to the soil solution. With time, the precipitated hydroxy phosphate ages and becomes less soluble and therefore unavailable to plants (Tisdale *et al.*, 1993). This decreases P fertilizer use efficiency. In the Oxisols, Ultisols and Alfisols which incidentally are the dominant soils in Ghana, the dominant clay minerals are kaolinites and oxides of Al and Fe (Nartey, 1998). These clay minerals have exposed OH groups which have high affinity for P (Tan, 1998). At low pH, the exposed OH groups in the clay minerals become protonated and subsequently retain added P as in equation 2.9.

$$Al \quad OH_2^+ \quad + \quad H_2PO_4^- \quad + \quad Al \quad OH_2\,H_2PO_4 \qquad [2.9]$$

The phosphate anion may also replace structural OH of the clay to form an inner sphere complex. There is ligand exchange between the $H_2PO_4^-$ and the protonated OH. This reaction while reversible binds the anion too tightly to the mineral and availability is very low (Brady and Weil, 2002).

Low soil pH also makes availability of Mo, a key nutrient in nodulation, and B very low in soils (Tisdale *et al.*, 1993). Basic nutrients such as K, Ca, Mg and Na also become deficient in plants because of low solubility in acid soils. However, there are toxicities of Fe, Mn, Zn and Cu in plants under acidic soil conditions because of the high solubility of these micro nutrients in soil solution (Tisdale *et al.*, 1993). High soil acidity especially causes high accumulation of toxic heavy metals such as Hg, As, Pb and Cd in crops especially on soils in mining environments and on soils which agro-chemicals are applied (Sparks, 2003)

2.1.4 Control of Soil Acidity

Breeding and planting of crops that are tolerant to soil acidity have been proposed as an option. It is, however, time consuming and more often than not, certain traits of the crop modified are either lost or suppressed. Breeding and the use of tolerant crops are actually not remedial measures but rather adaptive and or coping strategies (Curtin and Trolove, 2013). This has not been largely effective because of the relatively slow decomposition to release bases and the fact that organic matter acts as a buffer and therefore resists changes in pH (Curtin and Trolove, 2013). Liming to date, therefore, remains the most viable option and has traditionally been used to correct soil acidity and to improve soil productivity (Curtin and Trolove, 2013).

According to Brady and Weil (2002), an agricultural lime is any material that contains Ca and Mg as cations in combination with anions such as carbonates, hydroxides, oxides and silicates which are added to acid soils with the sole aim of raising pH. Commonly used liming materials include calcite, dolomite, slaked lime and quick lime as well as basic slag (Brady and Weil, 2002). Mechanisms by which calcite, the most commonly used agricultural lime increases soil pH when applied to a moist soil are depicted in a series of reaction below;

(1) water dissolves the material in the soil to produce Ca^{2+} and hydroxide (OH^-) according to the equation 2.9:

$$CaCO_3 + H_2O \longrightarrow Ca^{2+} + 2OH^- + CO_2 \qquad [2.9]$$

(2) The released Ca^{2+} substitutes for Al^{3+} and H^+ at the exchange sites of the soil.

(3) The OH^- produced from equation 2.9 reacts with Al^{3+} to form $Al(OH)_3$, and/or H^+ to form H_2O:

$$3OH^- + Al^{3+} \longrightarrow Al(OH)_3 \qquad [2.10]$$

$$OH^- + H^+ \longrightarrow H_2O \qquad [2.11]$$

The $Al(OH)_3$ formed precipitates out of solution raising the soil pH

Thus, liming reduces high levels of Al^{3+} and H^+ through the combination with OH^- (Tisdale *et al.*, 1993). Superfluous OH^- released from lime will raise the soil pH, which is the most noticeable effect of liming. Liming, depending on the material, provides two macro nutrients, calcium and magnesium to the soil. The size of particles and surface area of liming materials control their reactivity rates in soil. The inherent soil pH, the degree of mixing with the soil, and the chemical nature and composition of the material also effect the reaction rate (Brady and Weil, 2002). For example, oxides and hydroxides react faster than carbonates because of the higher solubilities of the former (Brady and Weil, 2002). Adequate soil moisture is required for the reaction to take place (Brady and Weil, 2002).

2.2 **Lime Requirement**

Lime requirement of a soil refers to the amount of agricultural liming material needed to neutralize the undissociated and dissociated acidity in the range from the initial acid condition to a desired neutral or less acid condition (McLean, 1971). Economically, lime requirement is defined as the mass of liming material necessary to produce maximum economic yield of crops grown on soils of low pH (McLean, 1971).

There are different practical methods used to predict the lime application rate required to accomplish an adequate level resulting in elimination of Al toxicity towards plant growth and development. One of the common methods for predicting the lime requirement is to monitor the concentration of exchangeable Al. According to Bell and Bessho (1993), the enrichment of soil with basic ions, especially Ca^{2+} ions in soil neutralizes exchangeable Al thus enhancing root growth. Hakim *et al.* (1989), indicated that the optimal lime rate to improve food crops production on Ultisol is about 6 Mg $CaCO_3$/ ha. Over liming, however can occur at rates exceeding 12 Mg/ha. The KCl extraction method is most commonly used although several extracting solutions have been proposed to estimate the extractable Al (Oates and Kamprath, 1983).

2.2.1 Types of Liming Materials

Limestone is mostly mined and then ground into fine particle sizes to increase the surface area and consequently reactivity. Limestone usually contains $CaCO_3$ and some other impurities. Limestone makes up the majority of lime that is applied to the soil. Ground limestone with less than 6% Mg is known as calcitic limestone and if the limestone has more than 6% Mg it is called dolomitic limestone (Carey *et al.*, 2006).). Burnt lime (quicklime) is ground limestone exposed to high temperatures to eliminate carbon dioxide. Calcium oxide is obtained after the process of heating. Magnesium oxide will only be present if it was a constituent of the ground limestone before heating. Burnt lime reacts quickly with water to produce hydrated lime or slake lime ($Ca(OH)_2$ and release high amount of heat and therefore must be handled with care (Carey *et al.*, 2006). Calcium hydroxide is very reactive because of its high solubility and excessive application to the soil can quickly raise the pH above the desirable point. Its caustic nature causes injury to plants that are already established in the field. Marls comprise sea shell remains and $CaCO_3$. These are used among farmers in the coastal areas. Marls have similar reactivity as ground limestone (Carey *et al.*, 2006).

2.2.2 Advantages of Liming in Acidic Soils

Liming plays vital role in ensuring maximum yields from many food crops established on soils of low pH. Kaitibie *et al.* (2002), reported liming as the most widely used technique for rectifying problems of soil acidity. Addition of lime to the soil at the required rate results in numerous soil chemical and biological changes that are beneficial in ensuring maximum productivity of acid soils. The concentrations of soluble aluminum and manganese decrease to non-toxic levels as a result of liming. Increasing pH decreases the availability of Mn, which becomes a major problem in many plants at pH lower than 5.0 (Nduwumuremyi, 2013). Liming improves Ca and Mg content of acid soils. Acid soils are generally deficient in total and available plant phosphorus and this is as a result of significant portions of applied P fertilizer being biologically fixed to oxides of Fe, Al and clay minerals. Liming improves available P content for plant uptake and utilization. At pH ranges between 5.0 and 6.5, soil available P content increases due to the release of P from Al and Fe oxides (Tan, 1998).

Microbial properties of soil can be used to ascertain soil quality (Brady and Weil, 2002). Activities of beneficial microbes, excluding fungi which can flourish over a wide range of soil pH, is restricted by soil acidity. Liming enhances multiplication and activities of most microorganisms which then accelerates rate of soil processes such as decomposition of organic matter to release nutrients (Brady and Weil, 2002). Liming also improves nitrogen fixation in by legumes in acid soils. It helps in the production of phytohormones and increases root surface area and enhance absorption of nutrients that are less mobile, for example P and micronutrients such as Mo and B (Brady and Weil, 2002).

According to McBride (1994), increasing soil pH improves the complexation of heavy metals in soils. Soil properties such as nature and kind of clay, organic matter status, redox potential, and soil pH are the main determinants of heavy metals bioavailability in soil and hence liming positively assists in reducing heavy metals availability to crop.

Calcium released from lime added to the soil was reported by Haynes (1983) to boost plant resistance to many plant pathogens such as *Erwiniaphytophthora*, *R. solani*, *Sclerotiumrolfsii*, and *Fusariumoxysporum*. Haynes (1984), also stated that calcium combines with pectic chains to form rigid bonds that facilitate the resistance of plant cell walls to enzymatic destruction by pathogens.

Soil N_2O emissions has been reported to be reduced by liming if soil moisture content is retained at field capacity and has been recommended as option for mitigation (Stevens *et al.*, 1998). Soil pH has a prospective influence on N_2O emission pathways, and the transformation of N_2O to N_2, and it is recommended that liming may serve as an alternative for the mitigation of N_2O production from farm lands (Stevens *et al.*, 1998).

2.3 **Biochar**

Biochar is progressively receiving attention in agriculture as an environmentally-friendly amendment to principally mitigate climate change (Lehmann *et al.*, 2003). Biochar is defined as a very porous material that is high in carbon and which is obtained by thermal combustion of biomass under restricted oxygen conditions and at comparatively high temperatures mostly between 300 ^{0}C and 1000 ^{0}C (Lehmann *et al.*, 2003). Biochar or black carbon is rich in carbon has a large specific surface area and has been shown to have the ability to increase water and nutrient retention of soils (Lehmann and Joseph, 2009). Biochar as a soil amendment traps carbon from the atmosphere to mitigate climate change. It also enhances productivity of soil by improving water holding capacity, nutrients adsorption and activity of microbes and therefore increasing yield of crops. Charring of feed stocks such as sawdust, animal manure and crop residues to produce biochar helps in recycling of forestry and agricultural wastes (Lehmann *et al.*, 2003).

2.3.1 Biochar Production

Biochar is obtained by burning biomass with little or no oxygen. This makes it different from actual burning of biomass which involves naked flame and oxygen to oxidize the carbon in the biomass completely to carbon dioxide leading to the production of ashes and small amounts of carbon. Limiting oxygen accessibility leads to high carbon retention in the biomass. Yield of carbon in biochar is usually 50% or less due to the fact that the pyrolysis process also produces combustible gases and volatile compounds from the pyrolyzed biomass (Lehmann, 2007).

Heating of biomass under ambient temperatures results in dehydration. Moisture in the biomass is first driven off and this involves the provision of great energy due to high heat capacity of water and large quantity of energy needed to vapourize the water content (Taylor and Mason, 2010). Thus, fresh feed stocks are not ideal for biochar production. The moisture content of biomass should be between 10 and 15% prior to pyrolysis. The torre faction phase in the thermal decomposition process starts when the biomass is dry the biomass is “roasted”, turning dark in colour due to chemical changes. Gases and other volatile compounds are released from the biomass. True pyrolysis starts when the temperature reaches 300^0 C, resulting in exothermic reactions. The feedstock fully readjusts itself to form solid biochar releasing volatile compounds and combustible gases (Taylor and Mason, 2010).

Pyrolysis process can be fast or slow. The rate of pyrolysis process has a significant impact on the characteristics of the end products. The quality of the product is also dependent on the feed stock type (Taylor and Mason, 2010).

2.3.2 Biochar Stability in the Soil

Stability determines how long it can support quality of soil and water system (Lehmann, 2007). Biochar can exist in the soil environment for many years more than any other kind of organic amendment containing carbon. Traces of biochar have been found in the soils of the humid tropical climate such as the amazon, many years after application in spite of the speedy rates of mineralization common to organic matter in those environments (Sombroek, *et al.*, 2003).

2.3.3 Structural Composition of Biochar

Thermal decomposition of cellulose in organic biomass between 250 ^{o}C and 350 ^{o}C leads to considerable loss of volatile compounds with a concomitant increase in aromatic C concentration. According to Demirbas (2004), water evaporates first, followed by hydrocarbons, tarry vapour, hydrogen gas, carbon monoxide and then carbon dioxide. Thereafter, there is the transformation of alkyl and O-alkyl aryl carbon (Baldock and Smernik, 2002). Consequently, a large mass of amorphous carbon matrix is formed. At a temperature of about 330 ^{o}C, there is lateral growth of graphene sheet, at the expense of the amorphous carbon phase and finally coalesce. At temperature above 600 ^{o}C, there is the elimination of most of the remaining non-carbon atoms and carbonization becomes the dominant process; a consequence of which is relative increase in carbon content. Carbonization can reach 90% by weight in biochar produced from woody feed stocks (Demirbas, 2004).

2.3.4 Chemical Composition of Biochar and Surface Chemistry

Carbon, moisture, mineral matter, and volatile compounds are the main components of biochar (Antal and Gronli, 2003). The physical and chemical behaviour of biochar and its function (Brown, 2009) and hence its suitability and fate for a particular application in the environment (Downie, 2009) is determined by its composition.

Biochar surfaces show hydrophobic, hydrophilic, acidic and basic properties and these surface properties are governed by the feed stock and pyrolysis temperature. Brennan *et al.* (2001) stated that the presence of heteroatoms in biochar causes surface chemical heterogeneity mainly as a result of differences in their electronegativity compared to those of carbon atoms. Functional groups such as OH, NH_2, O(C=O)R act as electron donors whilst (C=O)OH, (C=O)H and NO_2 groups are electron acceptors. Carboxylic functional groups are strong Bronsted acids whereas phenols and carbonyl groups are weak acids with chromenes and pyrones being basic functional groups Brennan *et al.* (2001). There are vast variations in mineral matter content and their composition on the surfaces of biochars (Tetteh, 2014). Acidic and basic sites may coexist within micrometres of each other on the outer surfaces and pores of the biochar particles (Brenman *et al.*, 2001).

According to Chan and Xu (2009), carbon content of biochar irrespective of type is between 172 and 905 g/kg, although organic carbon usually accounts for less than 500 g/kg for different materials. Total nitrogen content of biochar ranges from 1.8 to 56.4 g/kg depending on the type of biomass. The high total nitrogen content may not be available to crops as a result of complexation reactions with mineral nitrogen content less than 2 mg/kg. Studies have shown that carbon-nitrogen ratio vary widely from 7 to 500. Total phosphorus and potassium content of biochar fall between the ranges of 2.7 to 480 and 1.0 to 58.0 g/kg, respectively (Chan and Xu, 2009).

Properties of biochar change as it ages in the soil, particularly due to its oxidization and accretion of H^+ from the soil solution in the early weeks on amendment to the soil. The extent to which biochar properties change with age depends on the feed stock used to produce it (Heitkotter and Marschner, 2015), soil and prevailing climatic conditions (Cheng *et al.*, 2008).

2.3.4.1 **Functional Groups**

High-mineral ash biochars contain metals in some of the functional groups. Schnitzer *et al.* (2007) and Koutcheiko *et al*. (2007) reported a range of different N- and S-based functional groups in biochar produced from chicken manure. Data produced by Elizalde-Gonzalez *et al.* (2007) indicate that the relative concentration of each of the functional groups depends upon initial composition of the biomass, final surroundings of the charring particle, rate of heating and post-treatment. Biochar interacts readily with atmospheric oxygen to produce oxygen containing functional groups on the surface (Bourke *et al.*, 2007). Swiatkowski *et al.* (2004) reported that pyrone surfaces may be as a result of the adsorption of molecular oxygen in the form of superoxide ions O^{2-} and the adsorbed O, such as O^{-} or O^{2-}.

Biochar obtained from farm manures and sewage sludge contains nitrogen and sulphur functional groups compared to lignocellulosic biochars. Areas of high nitrogen concentration are mostly basic (Bourke *et al.*, 2007). Koutcheiko *et al.* (2007), prepared chicken manure biochar by heating to 360 °C in a fast pyrolysis unit with no reaction time reported. The biochar was then heated to 800 °C and activated with carbon dioxide. Their results showed that core functional groups containing nitrogen for the low-temperature biochar were pyridinic amines, whereas the high-temperature biochars contained almost equal quantities of pyridinic and quaternary groups. Bagreev *et al.* (2001) reported a similar pattern when they investigated changes in sewage sludge biochars produced between 450 °C and 900 °C in a fixed bed reactor. Their results at lower temperatures showed that amine functionalities were present while at higher temperatures organic nitrogen was incorporated within the biochar as pyridine-like compounds. Koutcheiko *et al.* (2007) identified S functional groups in chicken manure biochar with low-temperatures which produced sulphonates and sulphates whilst thiophene and sulphide groups dominated at high temperatures. Knudsen *et al.* (2004), reported that up to 500 ^{o}C, wheat straw biochar had sulphate but at higher temperatures, sulphur was transformed to an insoluble sulphide such as CaS and K_2S.

Functional groups on biochar may be amphoteric and hence surface charges may change with the pH of the solution. Thus, in acidic conditions, the surfaces are protonated, whilst in alkaline conditions, the surfaces are deprotonated.

2.3.5 Biochar as Liming Material

Many research reports on pH of biochar have shown that they are mostly neutral to basic in soil reaction. Thus, their applications have been found to increase soil pH (Joseph *et al.*, 2010). According to Verheijen *et al. (*2010), the liming property of biochar is one of the most likely mechanisms behind increases in crop yield when it is used as soil amendment. The amendment of biochar on tropical soils has resulted in reduced aluminium toxicity by decreasing the acidity (Verheijen *et al.*, 2010). Noble *et al.* (1996), reported the liming effect of agricultural wastes and other biomass when charred and applied to the soil. Farrell *et al.* (2013) and Masto *et al.* (2013) reported an increase in soil pH after application of biochar on different types of soils, which is attributed to the temperature during pyrolysis and type of feedstock.

According to Yuan *et al. (*2011) decarboxylation of organic anions as exhibited by excess cations contained in biochar consumes H^+ and therefore increases the soil pH. Alternatively, the presence of negatively charged functional groups such as phenol, carboxyl and hydroxyl on biochar surfaces adsorb H^+ from soil solution thereby lowering its concentration with a consequential rise in soil pH (Brewer and Brown, 2012; Chintala *et al.*, 2014).

Silicates, carbonates and bicarbonates emanating from biochar also form complexes with H^+ ions and making the proton unavailable to the soil solution (Brewer and Brown, 2012; Chintala *et al.*, 2014). The influence of biochar in increasing soil pH is more pronounced in acidic soils and in soils with low organic matter status (Stewart *et al.*, 2013). Soils with high organic matter content resist change in pH on application of biochar due to the buffering capacity of organic matter (Curtin and Trolove, 2013). Increases in the variable charges of soils by biochar improve their cation exchange capacity (Chan *et al.*, 2007; Nelissen *et al.*, 2012; Taketani *et al.*, 2013) this is due to the fact that leaching of base cations is reduced as adsorption of H^+ ions to negatively charged functional groups of biochar, organic matter, and organo-mineral complexes is enhanced.

However, the intensity of this impact may be governed by the soil organic matter content, which is the principal determinant of soil cation exchange capacity (Brady and Weil, 2008).

2.4 **Mode of Biochar Application**

The behaviour and fate of biochar materials in the soil and the environment as a whole is influenced by the method of its application to soils (Verheijen *et al.*, 2010). There are three main methods of biochar application viz;

i) topsoil application,

ii) depth application, and

iii) top-dressing.

2.4.1 Topsoil Application

Topsoil application of biochar can be done by either applying it alone or mixing with composts or manures at the surface of soil. The light mass and powdery nature of biochar makes its surface application prone to erosion by both water and wind (Verheijen *et al.*, 2010). It is for this reason that top soil application of biochar is normally done in conjunction with compost (Verheijen *et al.*, 2010).

2.4.2 Depth Application

Under conventional farming practice, biochar and compost are commonly mixed more or less uniformly in the entire topsoil to about 30 cm depth. Application of biochar mixed with compost or manure helps to reduce erosion of biochar by wind and water (Verheijen *et al.*, 2010). In conservation farming systems, the deep incorporation reduces the risk of erosion which results in higher biochar concentrations at equal rate of application (Verheijen *et al.*, 2010). Deep mouldboard ploughing helps in depth application with additional topsoil homogenization occurring during subsequent ploughing and or harrowing (Blackwell *et al.*, 2007). The placement of the biochar directly into the rhizosphere seem to be more advantageous for crop growth and less prone to erosion (Verheijen *et al.*, 2010). The application can be either by pneumatic systems, which can function at high rates, or by adding the biochar in trenches and levelling the soil surface afterwards (Verheijen *et al.*, 2010). Successive mouldboard ploughing and tilling further homogenizes the biochar distribution throughout the topsoil (Blackwell *et al.*, 2007).

2.4.3 Top Dressing

Top-dressing of biochar is the spreading of biochar which is mostly dust at the soil surface and hoping that natural processes would incorporate the it into the topsoil ((Blackwell *et al.*, 2007; Verheijen *et al.*, 2010). Top dressing is considered chiefly under circumstances where mechanical incorporation is not possible, as in no-till systems, and pastures (Blackwell *et al.*, 2007). A major setback of this mode of application is the possibility of the material being eroded by water and wind, as well as human inhalation. There are also no ideal rates of application for different soil-climate-land use systems. The dust fraction of biochar is an issue during storage, handling, and at the applying stages regardless of the method used (Verheijen *et al.*, 2010)

2.5 Agronomic Importance of Biochar

Addition of biochar enhances plant growth and development, crop yields and increases production of food and sustainability in marginal soils with low organic matter, inadequate water and poor nutrient status (Lehman *et al.*, 2006). Due to the fact different soils react differently to the application of the biochar, it takes some time to compare responses of soils (Lehman *et al.*, 2006). The ideal biochar application rate depends on the soil type and the crop management system (Verheijen *et al.*, 2010). Application of biochar is considered a novel approach to establish sink for atmospheric carbon dioxide in terrestrial ecosystem (Lehman *et al.*, 2006). In addition to the positive influence in reducing emissions and increasing the sequestration of greenhouse gases, biochar production and application to the soil provides immediate benefits through enhanced soil fertility and increased crop production (Lehman *et al.*, 2006). Southavong *et al.* (2012), indicated that biochar may be an immediate answer for managing agricultural waste.

The positive plant responses to the application of biochar has been attributed mainly to direct supply of nutrients with very little consideration given to other biochemical factors that may affect nutrient availability (Lehmann *et al.*, 2003; Chan *et al.*, 2007 and Van Zwieten *et al.*, 2007). The positive responses as a result of application of biochar were attributed to either nutrient retention as in fertilizers or enhanced fertilizer-use efficiency and therefore can be viewed as an indirect nutrient value of biochars. Rondon *et al.* (2007), and Van Zwieten *et al.* (2007) reported the plant responses to increased or stable pH as a result of biochar application. Hoshi (2001) concluded that 20% increase in height and 40% increase in volume of tea trees were partly due to the ability of biochar to maintain the pH of the soil. The ability of biochar to maintain pH is related to its liming value. Van Zwieten *et al.* (2007) recorded almost 30% to 40% increase in wheat height when biochar produced from paper mill sludge was applied at a rate of 10 t ha^{-1} to an acidic soil. They concluded that the carbonates in the biochar promoted wheat growth by overcoming toxic effects of exchangeable aluminium contained in the acidic soils.

Other explanations given for positive responses to biochar application that are not connected with plant nutrition included toxin neutralization (Wardle *et al.*, 1998), enhanced soil physical properties such as increase in water-holding capacity (Eswaran *et al*, 1980), and reduced soil strength (Chan *et al.*, 2007). Also, dry matter yield increased by 26% when N fertilizer was also applied at 100 kg N/ha in addition to biochar compared to a control that received the same amount of N without biochar. Biochar application increased N fertilizer-use efficiency of radish and this was attributed to the improved soil physical properties which included, reduced soil strength and higher water holding capacity. Furthermore, Lehmann *et al.* (2003), also reported the ability of biochar to hold applied fertilizer and reduced leaching resulting in increased fertilizer-use efficiency. This ability is due to the high charge density and high surface area of biochar. Lehmann (2007), reported the significant improvement in plant productivity and soil quality and also environmental benefits such as reduced pollution due to reduced fertilizer losses through leaching when biochar was applied.

2.6 **Importance of Biochar in the Environment**

2.6.1 Sequestration of Carbon

Carbon sequestration is defined as the capture and subsequent storage of carbon that would otherwise be emitted to or remain in the atmosphere into plants and soils (FAO, 2008). Large quantities of carbon in biochar can be sequestered in the soil for thousands of years (Lehmann *et al.*, 2006). According to Marris (2006), about 250 ha farm could sequester approximately 1900 tons of carbon dioxide per annum. Carbon sequestration in plant and soil systems suggests greater opportunity for mitigating the greenhouse effect (Lal, 2004). Biochar has recalcitrant carbon which can resist degradation (Schmidt and Noack, 2000). This property of biochar makes it essential for major carbon sink. With respect to other terrestrial sequestration techniques, biochar has a higher potential to increase carbon storage time more than afforestation (Ogawa *et al.*, 2006). Biochar application resulted in decreased emission of nitrous oxide and methane (Duku *et al.*, 2011).

2.6.2 Impact on Soil Performance and Resource Implications

Interactions among soils, biochar, microorganisms and root of plants start occurring within a short time after biochar application (Lehmann and Joseph, 2009). Glaser *et al.* (2002) indicated that water retention in biochar amended soil is 18% higher than in adjacent soils with little or no biochar amendment. The stable macro pore structure of biochar is in part responsible for improving on a soil's water holding capacity (Brodowski *et al.*, 2007).

The large specific surface area and high cation exchange capacity of biochar has accounted for its very high sorption capacity for cations (Gaskin *et al.*, 2007). The specific surface area of biochar increases as temperature increases due to creation of more micropores (Bird *et al.*, 2008), and great quantities of carboxyl groups on the surfaces. Cheng *et al.* (2006) suggested that increases of carboxyl groups on char surfaces with time, is in part due to either partial oxidation of open surfaces by biological and non-biological processes and/or chemisorption. The inherent stability of biochar creates a difference between the cation exchange capacity that it provides, and that from soil organic matter. There is no apparent restriction on the quantum of benefit that could be achieved with repeated addition as there is incremental enhancement of cation exchange capacity.

Biochar has the capacity to remove nitrate and phosphate from water (Mizuta *et al*.,2004; Eduah, 2009). Biochar may loosely hold nutrient elements in a bio-available form which is of importance to crop growth and also has instituted affinity for organic compounds and may sorb toxic substances in the soil (Yu *et al.*, 2006).

Indirect influence of biochar on the chemistry of the soil seem to arise from amendment of soil pH. Studies show that terra preta sites have higher pH and phosphorus than surrounding soils. The ash component of biochar has more available forms of nutrients than the uncharred biomass. The indirect effect of biochar on phosphorus availability in the soil and the mineral ash of its matrix containing phosphorus, potassium and other potentially important micronutrients are essential in explaining its short-term influence on crop growth (Lehmann and Joseph, 2009).

According to Steiner *et al.* (2008) microbial activity in soil is enhanced on addition of biochar. Sam (2014), also found out that degradative abilities of heterotrophs were enhanced when cocoa pod husk biochar was amended to atrazine and paraquat contaminated soils. There is comparatively extensive literature supporting stimulation of indigenous arbuscular mycorrhizal fungi by biochar, and this has been associated with enhanced plant growth (Rondon *et al.*, 2007). Microbial structure in soil that contains aged biochar is distinctively different from those in which fresh biochar has been amended (Kim *et al.*, 2007). Microbial populations react initially with labile components of biochar on its amendment to soil and pyrolysis condensates seem to promote microbial activity in the soil (Steiner *et al.*, 2008).

2.6.3 Biochar and Nitrogen Fertilizer Interactions

Integrated crop management which includes the application of organic manure and some other organic materials is the technology used for increasing fertilizer use efficiency (Fageria and Baligar, 2005). Organic matter added to soil decomposed at faster rate under wet tropical environment compared to the charred biomass.

Biochar is more recalcitrant when applied to the soil but enhances utilization of nitrogen from applied inorganic fertilizers (Steiner *et al.*, 2007 and Widowati *et al.*, 2011). This is due to the reduction in nitrogen loss as a result of increased cation exchange capacity of soil with biochar application (Chan *et al.*, 2008) and also its capacity to inhibit ammonium transformation to nitrate released from fertilizer (Widowati *et al.*, 2011).

2.6.4 Negative Effect of Biochar Applied to the Soil

McClellan *et al.* (2007) reported several instances of reduced plant growth as a result of biochar application due to the temporary high levels of pH and volatile nutrient imbalances associated with it when applied fresh. Mostly, biochar has an initial alkaline pH which is favoured for application to soils with low pH. When applied to alkaline soils, however, plants experience nutrient deficiency particularly basic cations and P. High pH of soils due to biochar addition may also cause NH_3 volatilization when ammonium-based fertilizers or organic manures are applied. Tars, resins, and other short-lived substances that remain on the biochar surface immediately after production can hinder growth of plants (McClellan *et al.*, 2007)

Biochar adsorbs chemicals such as pesticides and also organic matter making these compounds inaccessible to microbial and enzymatic degradation (Kookana *et al.*, 2011; Zimmerman *et al.*, 2011). Kookana *et al.* (2011) also revealed that some biochar products may be toxic to plants and soil micro fauna.

2.7 **Origin and History of Soya bean**

Soya bean, *Glycine max* is a legume from the family Leguminaceae. The plant is thought to have originated from the far East i.e. China, Korea and Japan, from where it spread to other regions of the world (Ngeze, 1993). There is evidence to show that it was used as food and as constituent of medicine in China over 500 decades ago (Norman *et al.*, 1995). Other investigators have suggested Australia and Eastern Africa as possible centres of origin of soya bean (Addo-Quaye *et al.*, 1993).

There is commercial production of soya bean in both the temperate and tropical environments such as China, Thailand, Indonesia, Brazil, USA and Japan; where it has become a major agricultural crop and an essential export commodity (Evans, 1996). According to Ngeze (1993), soya bean was introduced to Africa via Southern Africa in the early 19th century. It was brought to Ghana by the Portuguese missionaries in 1909. According to Mercer-Quarshie and Nsowah (1975), early introduction of the crop failed because it originates from the temperate zone. Collaborative efforts between Ministry of food and Agriculture, Ghana and the International Institute of Tropical Agriculture (IITA) culminated in successful production of the crop in Ghana in the early 1970s (Tweneboah, 2000).

2.7.1 Importance of Soya bean

Soya bean has several benefits. It serves as source of food for both human beings and livestock (Borget, 1992). Soya bean has several nutritional and medicinal qualities and also industrial and commercial uses, and agricultural benefits (Osman, 2011). As reported by Dugje *et al*., (2009), soya bean is more protein-rich than any other legume food sources in Ghana with average protein content of about 40%. Oil content of Soya bean seeds is about 20% on dry matter basis, and it is 85% unsaturated and cholesterol-free. Soya bean can be eaten in various forms such as a vegetable and can also be processed into soy oil, soy milk, soy yogurt, soy flour, 'tofu' and 'tempeh' (MoFA and CSIR, 2005).

Rienke and Joke (2005), reported that soya bean contains all the essential amino acids and is an essential source of carbohydrates, oil, vitamins and minerals. It is cheaper on per mass basis than an equal amount of meat or eggs (Ngeze, 1993). It can, therefore, be a perfect substitute for meat in developing countries, where animal protein food sources such as meat, fish, eggs and milk are mostly scarce and expensive especially for the poor (MoFA and CSIR, 2005). Because of its low cholesterol but high fibre content and high quality of protein, it is seen as a healthy food to prevent diabetes and high blood pressure. There is evidence that consumption of soya bean reduces the risk and incidence of cancer and diabetes. Its high Ca content is exploited for the treatment of ostersporosis (Lokuruka, 2010).

The cake obtained as bye-product from soya bean oil extraction is also an important source of protein feed for poultry, pig and fish. The extension of soya bean production has led to significant growth of the poultry, pig and fish farming (Ngeze, 1993; MoFA and CSIR, 2005). Dugje *et al*., (2009) showed that haulms after extraction of the seeds can also provide good feed for sheep and goats. Soya bean can fix between 60 kg and 168 kg of nitrogen per hectare per year under favourable conditions (Rienke and Joke, 2005). It is thus a good source of N for subsequent plants in a rotation. The matured green parts are used for compost preparation.

2.8 Factors that Affect Growth and Yield of Soya bean

The growth and development of the soya bean plant is largely influenced by both biotic and abiotic factors. These factors include soil microbes, soil water characteristics and availability of plant nutrients, climate, pest and disease infestation, cultivation and management practices. Optimum climatic growing conditions include average temperatures ranging from 20 °C to 30 °C. The crop does not perform well at temperatures below 20 °C and over 40 °C. The ideal rainfall is between 350 and 750 mm, which is well distributed over the entire growth season (Ngeze, 1993)

Soya bean can withstand a wide range of soil conditions but performs best on warm, moist, and fertile loamy soils of good drainage and adequate nutrients (Hans *et al.*, 1997). According to Ngeze (1993), soya bean does well in fertile soils with pH of between 5.5 and 7.0. It is comparatively a better acid tolerant crop than any other legumes. It however, does not flourish in alkaline, saline and reduced soils. Soya beans can only withstand a little water logging conditions (Norman *et al*., 1995). Ensuring soil pH between 5.5 and 7.0 improves the availability of nutrients such as nitrogen and phosphorus, microbial degradation of crop residues and symbiotic nitrogen fixation (Ferguson *et al.*, 2006). Soya bean requires adequate moisture for seeds to germinate and develop.

2.8.1 Nodulation

Several leguminous plants have established symbiosis with nitrogen-fixing soil-bacteria collectively identified as rhizobia such as those in the genera *Mesorhizobium*, *Azorhizobium*, *Rhizobium*, *Allorhizobium*, *Bradyrhizobium*, and *Sinorhizobium* (Ferguson *et al.*, 2013). Root infection usually involves the development of infection threads. Rhizobia enter the roots of compatible legume plants resulting in the formation and the development of specialized root structures known as nodules (Oldroyd *et al.*, 2011). Nitrogenase enzyme complex of rhizobia in the nodules reduces atmospheric nitrogen, which is an unusable form into plant available ammonium for growth and development (Cullimore and Bennet, 1992).

According to Ferguson *et al*. (2013), formation of nodules and fixation of nitrogen require great amount of energy (ATP) and are therefore strongly regulated to ensure a balance between nitrogen acquisition and energy spending. Phosphorus is thus a major nutrient required for growth and nodulation of legumes in general. Thus its deficiency markedly suppresses nodulation

Many nitrogenous compounds are strong inhibitors of nodule formation. Legume plants have evolved a mechanism to detect nitrogenous compounds in the soil, particularly, the plant available forms, nitrate and ammonium. The higher the levels of these compounds in the soils, the lower the nodulation. Several factors control the nodulation of legumes and these include availability of nutrients such as P, N and Mo. Other soil factors such as temperature, moisture content and pH also affect nodulation (Ferguson *et al*.., 2013).

2.8.1.1 **Soil Temperature**

Temperature has noticeable effect on the survival and proliferation of rhizobial strains in soils. The influence of temperature on rhizobia seems to depend on soil type and strain. For example, *R. leguminosarum* bv. *trifolii* performed better than *Bradyrhizobium* sp. at high soil temperatures (Mohammadi *et al*., 2012). According to Triplett and Sadowsky (1992), high soil temperature - induces delay in nodulation or restricts nodulation to the sub-surface soils. Aranjuelo *et al*. (2007) revealed that plant and nodule dry mass are affected by temperature. Hungria and Franco (1993) also reported that high-root temperatures reduced infection, N_2- fixation ability, and legume growth but this is also dependent on rhizobia strain type and strain and cultivar interactions (Arayankoon *et al.,* 1990). Various legumes and *Rhizobia* combinations have their optimum temperature relationships between 35 to 40 °C for soya bean, peanut and cowpea.

2.8.1.2 **Soil pH Stress**

Soil pH governs most chemical and biological processes that occur in the soil system. The impact of soil pH on nodulation has been investigated extensively due the large expanse of acid soils in the world. Low soil pH creates conditions that hinders plant growth and development that directly causing poor growth. Growth of legumes may be adversely affected by soil acidity through reduction of nodule formation and nitrogen fixation. Generally, different rhizobia strains differ in their tolerance to soil acidity than host plant (Mohammadi *et al*., 2011)

Nodules formed by the rhizobia under low pH conditions may be ineffective or fix insufficient nitrogen (Graham *et al*., 2000). Rhizobia have pH ranges within which they can function, only few can thrive in pH between 4.5 and 5.0. Micro-symbiont seems to be more pH sensitive than the host

(Hungria and Vargas, 2000). According to Hungria and Vargas (2000), nodulated legumes are less tolerant to Mn and Al toxicity which are in turn controlled by soil solution pH.

2.8.1.3 **Soil Water Availability**

Soil water affects almost all the activities of soil microbes including their growth and metabolic processes in the soil. Soils with smaller pore spaces provide conducive environments for the growth of soil microbes including rhizobia (Turco and Sadowsky, 1995).

Poor nodulation of legumes in arid soils is as a result of decreases in number of rhizobia during the dry season. Rhizobia adapt to osmotic stress by the intracellular accumulation of inorganic and organic solutes (Boscari, 2002).

2.8.1.4 **Availability of Phosphorus**

Availability of P in the soil during seedling development is essential for determining growth, N_2 fixation and grain formation of legumes and its shortage can hinder nodulation (Giller, 2001). Nodule formation and function are important sinks for P and nodules generally have the highest P content in the plant (Sinclair and Vadez, 2002). Deficiency of P leads to reduction in nodule formation and application of P fertilizers mostly leads to increased nodule number and dry mass, as well as higher N fixation (Sinclair and Vadez, 2002). According to Yakubu *et al.* (2010), low soil phosphorus levels suppress rhizobia number and root development in legumes which in turn decreas N_2 fixing potential. An increase in whole plant growth and plant nitrogen concentration corresponding to increased soil P supply from 20 to 40 kg P_2O_5 ha^{-1} has been observed (Sinclair and Vadez, 2002; Magani and Kuchinda, 2009).

Productivity of legumes in Africa is low because farmers do not have access to P fertilizers (Sinclair and Vadez, 2002). Various experiments have shown that recommended rate for P fertilizer in production of legumes should be location specific. Singh *et al.* (2011) reported significant response to applied P up to 60 kg P_2O_5/ha with all the varieties of cowpea used in the Sudan Savanna zone of Nigeria. Higher grain yield in cowpea has been credited to higher availability of P that is responsible for effective nodulation and nitrogen fixation (Singh *et al.*, 2011). Study by Asuming-Brempong *et al.* (2013) have revealed that growing legumes at the coastal savanna zone of Ghana requires phosphorus between 90 and 120 kg P_2O_5/ha. Vesterager *et al.* (2008) reported that even though grain yield was not affected, the quantity of N fixed in a cowpea monocrop increased from 58 to 77 kg N/ha and from 30 to 43 kg N/ha in a cowpea intercrop due to P application in the semi-arid zone of Tanzania. Nodulation has been found to decrease with increasing P and N application suggesting an antagonistic effect of readily available N on the functions of P Vesterager *et al.* (2008). This observation shows that application of P may not optimize biological nitrogen fixation in the presence of readily available N in the soil.

2.8.1.5 **Population of Rhizobia Strain in the Soil**

Rhizobia form symbiotic relationship with legume roots to fix atmospheric nitrogen. As the population of rhizobia increase, the more likely it would be for nodule infection. Soil rhizobia population can be extremely variable in composition and symbiotic characteristics of species (Martins *et al.*, 2003). Native and inefficient rhizobia strains may compete with inoculated efficient species for place of infection on the host plant roots. Nodules made by different strains and different species can occur on the root of the same plant (Moreira and Siqueira, 2006). Legume-Rhizobia symbiosis can sustain agriculture in the tropics at moderate levels of output, provided all environmental constraints to the proper functioning of the symbiosis have been lessened (TSB-CIAT, 2004).

Work done by Singleton *et al*. (1992) showed that less than 60% of tropical soils sampled from Africa had less than 1,000 rhizobia/g soil and 47% with 100 rhizobia/g soil that belong to the cowpea cross-inoculation. Fening and Danso (2002), reported that 68% of rhizobia sampled from 20 Ghanaian soils were moderately effective in nodulating cowpea.

2.8.1.6 **Soil Nutrient**

Soil nutrient status generally has a remarkable influence on the symbiosis and also independent growth and survival of legumes. Nitrogen fixation decreases with increasing legume age, mainly because of the related increase in soil N content. A negative exponential relationship has been observed between N fertilizer rate and N_2 fixation (Ledgard and Steele, 1992).

Calcium deficiency, with or without the confounding influence of low pH, also affects attachment of rhizobia to root hairs, and nodulation and nodule development (Alva *et al.*, 1990). Calcium plays a pivotal role in symbiotic interactions at the molecular level. Poor nodulation of soya beans in acid soil has been attributed to an Al induced Ca deficiency (Biswas *et al.*, 2003).

In addition to macro nutrients, the growth and persistence of rhizobia in soils is also influenced by several other nutritional factors (Brockwell *et al.*, 1995). Supplementation of soil and inoculants with glutamate, glycerol, and organic matter has been shown to enhance the survival and numbers of rhizobia in soils and increase both early nodulation and N_2 fixation (Rynne *et al.*, 1994). This result indicates that, although, rhizobia can surely persist in soils, their efficacy can be enhanced by carbon addition, which suggests that they are C limited in the natural state.

CHAPTER THREE

3 MATERIALS AND METHODS

3.1 Soils and Sampling

Two Oxisols were sampled from the rain forest zone in the Western Region of Ghana. The area has an average annual rainfall of about 2200 mm, mean temperature of 27 ^{0}C and relative humidity of about 90% (MoFA, 2012). The soils sampled are Ankasa and Tikobo Series. These soils have been classified by Dwomo and Dedzoe (2010), according to the USDA system as Plinthic Acrudox and Typic Hapludult, respectively. The Ankasa series was sampled from a forest conservation area with no farming record whilst the Tikobo series was sampled from a fallowed land with no known history of legume production at the Council for Scientific and Industrial Research, Crop Research Satellite Station, Ghana. The sampling point of Ankasa Series was located at 5^{0} 14. 599' N and 2^{0} 38.453' W and Tikobo Series at 5^{o} 03.558' N and 2^{0} 28.2825' W. Disturbed soil samples were randomly taken from the plough layer (0 – 20 cm), bulked, homogenized and sub samples taken for routine characterization and pot experiment. Undisturbed samples were also taken for bulk density determination. The disturbed samples were air-dried and portions were ground to pass through a 2 mm sieve to obtain the fine earth fraction. The remaining soil was not processed (whole soil) and was used for incubation studies and pot experiment in a screen house.

3.2 Soil Characterisation

Physico-chemical analyses of the undisturbed soil samples were undertaken.

3.2.1 Total Phosphorus

Total phosphorous was determined by digesting 0.2 g of biochar with 25 mL of a mixture of concentrated HNO_3 and 60% $HClO_4$ in the ratio of 1:1.5 (HNO_3: 60% $HClO_4$). Distilled water was added to the digest, filtered and made up to volume in a 100 mL volumetric flask with distilled water. Phosphorus in the digest was determined as described by the Murphy and Riley (1962) method as outlined earlier in section 3.2.2.4. The P content of the samples in triplicates was then read with the spectrophotometer, and the calculations were done as follows:

$$\text{P (mg/kg)} = \frac{\text{SP reading x Volume of Extract}}{\text{Volume of Aliquot x Weight of Biochar}} \text{ x } \frac{10^6}{1000} \qquad [3.14]$$

3.2.2 Physical Properties

The physical properties of the soils measured included bulk density, particle size distribution and moisture content at field capacity.

3.2.2.1 **Bulk Density (Core Method)**

Bulk density was determined using the core method of Blake and Hartge (1986). Core samples were randomly taken from the sampling sites to avoid root disturbance and at the same time representative of the whole area. The soil surface was cleared and a cylindrical metal core sampler of known diameter and height was gently driven into the soil with the aid of a plank of wood and a mallet. To avoid compaction, another core sampler of similar size was placed on the one driven into the soil and hammered gently until one in the soil was completely buried. The first core sampler was dug out from the soil using an earth chisel making sure there was minimal disturbance to the sampler and its contents. Both ends of the sampler were trimmed with a knife and all extraneous materials were removed. Thereafter, the samplers were capped at both ends placed into labelled polythene bags and transported to the laboratory for bulk density determination in the laboratory.

In the laboratory, the content of the sampler was emptied into a clean moisture can with known weight (W_1). The moisture can together with its contents were oven dried at 105˚C until a constant weight (W_2) was attained. Bulk density was calculated using the formula by Blake (1965).

$$\rho_{b\,(\mathrm{Mg/m^3})} = \frac{\mathrm{M}}{(\pi \mathrm{d}^2/4)\mathrm{h}} \qquad [3.1]$$

Where

P_b= Bulk density of soil

M= mass of soil = W_2-W_1

W_2 = Weight in grams taken after oven drying the moisture can and its contents.

W_1 = Weight in grams of empty moisture can.

d = internal diameter of core

h = height of core sampler

(Π $d^2/4$) h = volume of core = volume of soil

3.2.2.2 **Particle Size Analysis**

Bouyoucos hydrometer method modified by Day (1965) was used to determine the particles size distribution of the soil samples. Forty grammes (40 g) of the fine earth was weighed into a dispersing bottle. The soil was treated with H_2O_2 (1:1 soil: solution) to destroy the organic matter after which 100 mL of 5% calgon (sodium hexametaphosphate) solution was added to form a suspension. The suspension was shaken on a reciprocating mechanical shaker for 2 hours to help disperse the soil into the various separates (sand, silt and clay). The soil suspension was then transferred into a 1 L graduated sedimentation cylinder and topped up to the 1 L mark with distilled water.

The suspension was thereafter agitated vigorously with a plunger and left to stand. After five minutes, a hydrometer was immersed and the first hydrometer reading taken. The first density reading was for both silt and clay in suspension. The second hydrometer reading (density of clay only in suspension) was recorded after 5 hours. The sand content was determined by pouring the suspension directly onto a 47 µm sieve. The contents on the sieve was washed thoroughly with tap water to get rid of any clay and silt particles and then transferred into a moisture can of known weight for oven drying at 105 ^{0}C for 24 hours. The hydrometer readings at five minutes and five hours were also taken in the blank which contains 5% calgon only.

Temperatures of the suspensions at both hydrometer readings were recorded with the aid of a thermometer. Temperature effects on density of the soil particles were accounted for using the relation provided by Day (1965). For every 1°C increase in temperature, above 19.5 °C, there is an increase of 0.3 in the density of the particles in suspension.

Correction for temperature = blank hydrometer reading – increase in weight of particles

The concentration of the three separates were calculated as follows:

$$\%\ \text{Clay and Silt} = \frac{(\text{5 minute reading} - \text{correction for temperature})}{\text{oven dry mass of sample}}\ \text{X}\ 100 \qquad (3.2)$$

$$\%\ \text{Clay} = \frac{(\text{8 hour reading} - \text{correction for temperature})}{\text{oven dry mass of sample}}\ \text{X}\ 100 \qquad (3.3)$$

% Silt = % (Clay and Silt) - % Clay (3.4)

$$\%\ \text{Sand} = \frac{(\text{oven dry weight of particles retained on the 47 }\mu\text{m sieve})}{\text{oven dry mass of sample}}\ \text{X}\ 100 \qquad (3.5)$$

The values for the soil separates were used to determine the textural class of the soils using the USDA textural triangle presented in Appendix.

3.2.2.3 **Moisture Content at Field Capacity**

One kilogramme of the bulk (un-sieved) soil was weighed into a pot with drainage holes which had been plugged with glass wool saturated with water. The saturated soil was covered with polythene to avoid evaporation and then allowed to drain for 48 hours in open air. Thereafter, sub samples of the soil were taken into moisture cans, weighed and oven dried at a temperature of 105 ^{0}C until constant weights were attained. The percentage water content at field capacity was then calculated as follows:

$$\%\ \text{water content} = \frac{\text{weight of wet soil} - \text{weight of oven dried soil}}{\text{Weight of the oven dried soil}} \times 100 \qquad [3.6]$$

3.2.3 Soil Chemical Properties

The sieved soil samples were subjected to various chemical analyses to determine properties including pH (in water and in salt), total and available phosphorus, total and available nitrogen, cation exchange capacity, and percent organic carbon.

3.2.3.1 Soil pH

Twenty grams of the fine earth fraction was weighed into a 50 mL beaker and 20 mL of deionized water added to give a 1:1 soil: water ratio. The suspension was stirred many times within 30 minutes and left to stand for about one hour. The glass pH meter was standardized using two buffer solutions of pH 4 and 7 and then the pH of the supernatant read. A pH was again determined in 0.01 M $CaCl_2$ at a soil: salt ratio of 1:2. All the pH readings on the two soils were done in triplicates

3.2.3.2 Total Carbon and Nitrogen

Both soils were not likely to contain carbonates because they are highly weathered. The total carbon in the soils are, therefore, likely to be mainly of organic source. The total carbon and nitrogen content of the soils were determined using a Leco Trumac Carbon Nitrogen Sulphur version 1.3 Analyzer. Two hundred milligramme of the fine earth fraction of each soil was weighed into platinum crucibles mixed with 500 mg of comcat and placed in the furnace of the analyzer. The C and N concentrations in the samples were read after 6 minutes of combustion.

3.2.3.3 Available Nitrogen

Ten grammess of the fine earth of each of the soil was weighed into a 100 mL extraction bottle and 50 mL of 2 M KCl added. The soil suspension was shaken for 20 minutes in a reciprocating shaker. The suspension was then filtered through a No 42 Whatman filter paper into a clean empty plastic bottle. Ten millilitres aliquot of the filtrate was transferred into a 250 mL Kjeldahl flask and 0.2 g MgO powder was added to oxidise the NH_4^+ present to NH_3 after which 100 mL of distilled water was added and distilled on a Markham distillation unit. Ammonia (NH_3) was liberated into 5 mL of 2% boric acid (containing a methylene blue and methyl red indicator mixture) in a 150 mL conical flask. The solution left in the 250 mL Kjeldahl flask was allowed to cool and 0.2 g of Devarda's alloy was added to reduce the NO_3-N to NH_4^+-N. Nitrite in the sample was destroyed by the addition of 1 mL of sulphamic acid. Fifty millilitres of the distillate was collected into 5 mL of 2% boric acid indicator mixture in a separate conical flask. The distillates were then titrated against 0.01M HCl. The concentration of NO_3^- / NH_4^+ mg L^{-1} soil was calculated as follows:

$$NH^+_{4g_{(kg^{-1}soil)}} = \frac{M_{HCl} \times V_{HCl} \times 10^{-3} \times 18 \times V_{KCl} \times 1000\ mg}{\text{Volume of Aliquot} \times \text{Weight of soil (g)}} \qquad [3.7]$$

Where:

M_{HCl} = Molarity of the HCl

V_{HCl} = Titre of the HCl

V_{KCl} = Volume of KCl extractant

18 = Molecular weight of NH_4^+

3.2.3.4 **Available Phosphorus**

Available phosphorus was determined using the method of Bray and Kurtz (1945). Five grammes of the fine earth of each soil sample was weighed into an extraction bottle. Fifty millilitres of Bray 1 solution (0.03M NH_4F in 0.025M HCl) was added. The suspension was shaken for 3 minutes on a mechanical shaker after which it was allowed to settle. It was then filtered through a No. 42 Whatman filter paper into a 100 mL volumetric flask and made up to the volume. Phosphorus in the filtrate was determined using the molybdate-ascorbic acid colour development method of Murphy and Riley (1962) as follows:

A five millilitre aliquot (in triplicates) of the supernatant was pipetted into a 100 mL volumetric flask and the pH adjusted with para-nitrophenol indicator. The solution was neutralized with a few drops of ammonium hydroxide (4M NH_4OH) until the colour changed to yellow. This was followed by addition of distilled water till a colourless solution was observed. Reagent A was prepared by dissolving 12 g of ammonium molybdate and 0.2998 g of antimony potassium tartrate in 250 mL of distilled water. Reagent B was prepared by dissolving 1.056 g of ascorbic acid in 200 mL of Reagent A. The dissolved reagents were added to 1000 mL of 2.5 M H_2SO_4, mixed thoroughly and made to volume in a 2000 mL volumetric flask. Eight millilitres of Reagent B was then added to the sample solution and made to volume in a 100 mL volumetric flask. A blank was also prepared using 5 mL of distilled water and 8 mL of reagent B.

A Philips PU 8620 spectrophotometer was calibrated using six P standard solutions including a blank which was the Bray background solution and the reagents A and B. Phosphorus in the solution was determined by reading the resultant colour intensity on the Philips PU 8620 spectrophotometer, at a wavelength of 712 nm. The available P concentration in the soil sample was read and calculated using the spectrophotometer reading as follows

$$\text{P (mg/kg)} = \frac{\text{spectrophotometer reading } (mgL^{-1}) \times \text{total volume of extract}}{\text{volume of aliquot} \times \text{weight of soil sample} \times 10^6} \times 100 \qquad [3.8]$$

3.2.3.5 **Total Phosphorus**

Total phosphorus was determined by digesting 2 g of 0.5 mm sieved soil with 25 mL of a mixture of concentrated HNO_3 and 60% $HClO_4$ in a ratio of 2:3 (HNO_3 : $HClO_4$). The digestion was continued until white fumes of $HClO_4^-$ ceased. The digest was cooled, diluted with distilled water and then filtered into a 100 mL volumetric flask using a No. 42 Whatman filter paper. The volume was brought to the 100 mL mark with distilled water. Phosphorus in the filtrate was measured by colour development and read on Philips PU 8620 spectrophotometer as described in section 3.2.2.4 and the calculation for percent P in soil sample was calculated using equation [3.8].

3.2.3.6 **Exchangeable Bases and Cation Exchange Capacity (CEC)**

3.2.3.6.1 Extraction of Exchangeable Bases.

Five grammes (5 g) of the fine earth fraction was weighed into a 200 mL extraction bottles. Fifty (50) mL of 1 M ammonium acetate (NH_4OAc) solution buffered at pH 7.0 was added. The bottles were covered and shaken on a reciprocating shaker for 1 hr. The soil suspension was then filtered through a No. 42 Whatman filter paper. The filtrates were used for the determination of Ca, Mg, K and Na. The concentrations of the basic cations in the filtrate were read on an atomic absorption spectrometer (AAS) (A Analyst 800). The AAS was calibrated with the appropriate standards for Ca, Mg, K and Na, respectively and the absorbance for each element determined. Exchangeable bases were calculated as follows:

$$X\ (\mathrm{cmol_c kg^{-1}}) = \frac{\mathrm{R} \times \mathrm{Vol.of\ extract} \times 10^{3}\ (\mathrm{g}) \times 10^{2}(\mathrm{cmol}) \times \mathrm{E}}{\mathrm{Weight\ of\ soil} \times 10^{6}\ (\mu\mathrm{g}) \times \mathrm{M}} \qquad [3.9]$$

Where X = Basic cation

R = AAS (Atomic absorption spectroscopy) reading in mg L^{-1}

E = Charge of basic cation

M = Atomic mass of basic cation

3.2.3.6.2 Cation Exchange Capacity (CEC)

The residue after filtration in section 3.2.2.6.1 was immediately leached with four portions of 50 mL methanol (to get rid of excess ammonium) into empty plastic bottles. The soil was leached again with four 50 mL portions of acidified 1 M KCl. Each portion was added at a time and allowed to pass through, before adding the next portion. Five millilitres of the leachate was transferred into a Kjeldahl flask and 5 mL of 40% NaOH added and then distilled into 5 mL of 2% boric acid. This was then back titrated against 0.01M HCl. The ammonium ion concentration in the filtrate in $\mathrm{cmol_c kg^{-1}}$ soil was determined as the CEC of the soil.

3.2.3.7 **Exchangeable Acidity (H^+ and Al^{3+}).**

Five (5) grammes of soil was weighed into a 100 mL extraction bottle and 50 mL of 1 M KCl solution was added. The bottle and its content were placed on a mechanical shaker and shaken for 1 hour. The soil suspension was then centrifuged and the supernatant decanted into an empty clean bottle. Twenty millilitres aliquot was pipetted into a 100 mL conical flask, heated to near boiling point to drive out CO_2, allowed to cool down and 2-3 drops of phenolphthalein indicator added for titration to a permanent pink end point against 0.01 M NaOH. The titre value was recorded as titre for both H^+ and Al^{3+}. Five millilitres of 4% NaF was added to the solution at the endpoint and back titrated against 0.01M HCl until a colourless end point was reached. The titre was recorded as that for Al^{3+}.

$$\text{cmol}_c\text{/kg KCl acidity} = \frac{(mL\ NaOH\ sample - mL\ NaOH\ blank) \times N \times 100}{sample, g} \qquad [3.10]$$

$$\text{cmol}_c\text{/kg KCl exchangeable Al} = \frac{mL\ HCl \times N \times 100}{sample, g} \qquad [3.11]$$

$$\text{cmol}_c\text{/kg H} = \text{KCl exchangeable acidity} - \text{KCl exchangeable Al} \qquad [3.12]$$

3.2.3.8 **Effective Cation Exchange Capacity (ECEC)**

The Effective Cation Exchange Capacity (ECEC) of the two soils were estimated as the sum of the exchangeable Ca^{2+}, Mg^{2+}, Na^+, K^+, H^+, and Al^{3+}. (i.e. $Ca^{2+} + Mg^{2+} + Na^+ + K^+ + H^+ + Al^{3+}$)

3.3 **Preparation of Biochar**

Biochar from the feedstock of corn cob and rice straw were used as liming material in this study. Both the rice straw and the corn cob biochar were carbonized in a furnace at pyrolysis temperatures of 500 ºC and 700 ºC at the Soil Research Institute of the Council for Scientific and Industrial Research, Kwadaso, Kumasi. The charred rice straw and the corn cob were washed with deionized water and air dried, and then ground. The ground biochar was then passed through a 2 mm sieve and saved for chemical characterization which included pH both in water and salt, total and available P, total N, organic carbon, and soluble K, Mg, Ca and Na.

3.3.1 Biochar pH

One gramme of each of the ground biochar types was weighed into a beaker and 10 mL of de-ionised water added to give biochar water ratio of 1:10. This ratio was used to ensure enough volume of supernatant for immersion of electrode. The mixture was then stirred several times for about 30 minutes and left to stand for about an hour to allow most of the suspension to settle and also for the suspension temperature to equilibrate with the temperature in the instrument room. The glass electrode pH meter- CG818, Schott Great was standardized using two solutions of pH 7 and 9. The electrode was then rinsed with distilled water and then immersed into the partly settled suspension and the reading on the pH meter recorded. The determination of pH of the sample was repeated using 0.01 M $CaCl_2$ solution according to the protocol outlined earlier for reading pH of biochar in water.

3.3.2 Biochar Available Phosphorus

Available phosphorus was determined by the Olsen method (1965). One gramme of biochar sample was weighed into an extraction bottle and 50 mL of 0.5 M $NaHCO_3$ solution was added and shaken for 30 minutes on a mechanical shaker. The biochar extractant mixture was filtered through a Whatman No. 42 filter paper. A 10 mL aliquot was taken and 10 mL sulphuric acid (H_2SO_4) added and centrifuged at 3000 rpm for 15 minutes. The concentration of the P in each sample was then determined after colour development using the Murphy and Riley (1962) method as described in section 3.2.2.4 The intensity of the colour developed at a wavelength of 712 nm was read on the UV spectrophotometer and recorded. The P was calculated using the formula in [3.8].

3.3.3 Exchangeable Cations in Biochar

Two grammes of biochar was weighed into an extraction bottle and 50 mL of 1 M ammonium acetate (NH4OAc, pH 7) was added. The bottle was shaken on a mechanical shaker for one hour and the contents filtered through a Whatman No. 42 filter paper into clean empty bottles. Addition of the ammonium acetate extracted the soluble basic cations in the ash of the biochar and the cations at the exchange site of the material. The concentration of both soluble and exchangeable calcium, sodium, potassium and magnesium in the extract were determined using the Atomic Absorption Spectrophotometer (AAS) and calculated as in equation [3.9].

3.3.3.1 **Soluble Cations in Biochar**

Two grammes of biochar was weighed into an extraction bottle and 50 mL of de-ionised water was added. The suspension in the bottle was shaken on a mechanical shaker for an hour and the contents filtered through a Whatman No. 42 filter paper into clean empty bottles. Addition of water extracted the water soluble basic cations in the ash of the biochar. The concentration of water soluble calcium, sodium, potassium and magnesium in the extract were determined using the Atomic Absorption Spectrophotometer (AAS) and calculated as in equation [3.9].

3.4 Incubation Study

Cylindrical PVC pipes of 20 cm internal diameter were cut into of 20 cm lengths. One end of the 20 cm pipes was covered with a wire mesh tired to the pipes and also held in place by metal clips to form pots of height 20 cm and internal diameter 20 cm. Preliminary studies using the rice husk and corn cob biochar types prepared at both 500 ^{o}C and 700 ^{o}C have revealed that application rates between 60 and 80 tonnes/ha to a typical acid soil was able to raise the pH by 2 pH units. An incubation study using samples of the two soils, the four biochar types and a conventional liming material, laboratory grade (Analar) $CaCO_3$ of 99% purity as control was undertaken to establish the efficacy of the biochar types as liming materials, and if efficacious ascertain the equilibration time i.e. how long a farmer has to wait upon amendment of the soils with biochar before sowing or planting.

The unprocessed bulk soils of the Ankasa and Tikobo Series were mixed with each of the four biochar types i.e. rice husk and corn cob biochar types prepared at both 500 ^{o}C and 700 ^{o}C at 80 tonnes/ha to attain their respective bulk densities. Equivalent amounts of Ca in the biochar from $CaCO_3$ was added to the soil 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. A treatment with no amendment was also included. The moisture contents of the soils in pots were kept at 80% field capacity in the screen house. All the treatments were replicated four times and arranged in completely randomized design. 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). Available bases, available phosphorus, exchangeable H^+ and Al^{3+} were read once every 14 days during the equilibration period. The experimental set up for the incubation study is shown in plate 1.

3.5 Evaluation of Effect of Liming on Growth Characteristics of Soya bean

Upon equilibration of the soils amended with the five liming materials viz. rice husk and corn cob biochar at 500 ^{o}C and 700 ^{o}C and the conventional liming material, an agronomy study using the limed soil and soya bean (*Glycine max*) of variety Jankuma as a test crop was carried out in the screen house to investigate the effect of liming on growth characteristics of soya bean. Soya bean was the preferred crop because it is sensitive to pH.

The soya bean seeds of 80% germination were inoculated with Histick Soy, a commercial inoculant from BASF chemical company in Germany and sown at stake at four seeds per pot

Plate 1 Experimental set up of the incubation study in the screen house

and were later thinned to one seedling per pot. The levels of available P in the four biochar types added as lime were similar and were therefore averaged and the equivalent from TSP added as a P source to half the number of pots receiving $CaCO_3$ as a liming material. To ascertain the efficacy of the available P from the biochar, the nutrient from two sources i.e. biochar and TSP were compared on the limed soils. Triple super phosphate (TSP) as synthetic source of P and urea as synthetic source of N were applied at a rate of 30 kg P $ha^{-1}$of P and 10 kg N/ha, respectively to half the number of limed soils to evaluate the effect of synthetic P and N on growth characteristics of soya bean and also on P availability. The inorganic fertilization was done two weeks (2) after germination. Thus, with two soils, five liming amendments, two synthetic P and N rates i.e 0 P and N ha^{-1}, 10kg N ha^{-1} and 30 kg P ha^{-1} and four replicates. There were 2 soil x 5 amendments x 2 P Rates x 2 N rates factorial experiment which were replicated four times in a completely randomized design as explained in the incubation study. In addition to these, there were four un-amended soils each for the two soils. The moisture contents of the soils were maintained at 80% throughout the experiment. The experimental set up showing the plants growing in the screen house is shown in Plate 2.

At flower initiation, six weeks after sowing which is the critical stage for nodulation, the soya bean plants were harvested. The whole plant with soil were gently put into a big basin and soil carefully separated from the roots.

Plate 2 Pot experiment showing soya bean plants in the screen house.

3.5.1 Crop Parameters Determined

The plants in the pots were harvested by cutting off the shoot at the surface of soil in the pots. The shoots were then kept in envelopes and dried to a constant weight at 65 ^{0}C in an oven to determine the shoot dry weight. Part of the oven dried shoot was milled for total P determination. The below soil plant biomass was uprooted making sure the roots and the nodules were intact. The soil adhering to the roots were then carefully washed off in a bowl of water. The nodules were then detached from the roots and counted into envelopes. The nodules were dried to a constant weight at 65 ^{0}C for in oven to determine the nodule dry weight.

The respective volumes of the washed roots from individual pots were measured by using the water displacement method. A known volume of water was poured into measuring cylinder and individual roots per pot were immersed gently into the water with the aid of forceps. The changes in water levels were recorded and used as the volume of the roots. The water in the measuring cylinder was changed after each measurement to enable the roots displace their actual volume and also to ensure accurate reading. The roots were then transferred into separate envelopes and dried to a constant weight at 65 ^{0}C in oven to determine the root dry weight. Part of the oven dried roots was milled for total P determination.

3.5.1.1 **Total P of Plant Material**

Hundred milligrammes of each of the milled shoot and root samples were weighed into 50 mL conical flask and 5 mL of concentrated sulphuric acid (H_2SO_4) was added. The flask was then swirled to ensure that the acid mixed thoroughly with the milled sample and left to stand overnight. This allowed for a thorough dissolution of the samples by the acid. The flask and its content were then heated on a sand bath for 1 min and H_2O_2 was added drop wise with intermittent swirling till the solution was clear. Deionized water was added to the solution and left to cool, after which the solution was filtered through a No. 42 Whatman filter paper into a 100 mL volumetric flask and made to the mark with deionized water.

A 5 mL aliquot of the digest was pipetted into 50 mL volumetric flask in duplicates and colour developed according to the method of Murphy and Riley (1962) as outlined in section 3.2.2.4. The shoot and root total P were determined as P% content as:

$$\text{Total P (mg/pot)} = \text{shoot dry weight (g/pot)} \times \frac{\text{shoot \% P}}{100} \times 1000 \qquad [3.15]$$

3.5.2 Residual Analyses

The soil samples after harvesting were homogenized, subsampled, air dried, sieved through a 2 mm sieve, labelled and used in the determination of residual pH, total and available P.

3.5.2.1 Soil Residual pH

Twenty grammes (20 g) of the soil sample was weighed in triplicates into 50 mL beakers, 20 mL of distilled water was added to the samples and stirred continuously for 30 min. The soil suspension was then left to stand for an hour. The glass electrode pH meter was standardized and the pH measured as described in section 3.2.2.1.

3.5.2.2 Soil Residual Available Phosphorus

The available and total P levels in the processed soils after harvesting were determined according to their respective methods outlined in sections 3.2.2.4 and 3.2.2.5.

3.5.2.3 Soil Residual Total Nitrogen and Carbon

The soil residual total nitrogen and carbon were determined by using the Nitrogen and Carbon Analyzers, as outlined in section 3.2.2. 2.

3.6 Data Analyses

The measured crop parameters, nutrient uptake and the residual soil analyses after harvest were subjected to analysis of variance (ANOVA) using Genstat 12th edition to establish if there were any significant treatment effects at $p < 0.05$. mean separations were done using Lsd (0.05).

CHAPTER FOUR

4 RESULTS

4.1 Characterization of Soils.

Some physico-chemical properties of the plough layer (0 -20 cm) of the two soils used for the study are presented in Table 4.1. The Acrudox, Ankasa Series has a sand content of 61.5% which is 20.4% lower than that of the Hapludult, Tikobo Series. The Acrudox 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 Acrudox (30.7%) than in the Hapludult (5.6%). The bulk density of the Ankasa Series, 1.1, Mg/m^{3,} was lower than the 1.3 Mg/m^{3} of the Tikobo Series.

Ankasa Series is extremely acid with pH in salt and water being 3.7 and 4.2, respectively. Tikobo Series 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 organic carbon content of Ankasa which is from a forest reserve is 15.3 g/kg and that of Tikobo sampled from a fifteen a year fallow area is 5.4 g/kg. Despite the almost 2.8 times more C in the Ankasa Series than the Tikobo Series, total N in the former (1.6 g/kg) was similar to that for Tikobo Series (1.2 g/kg). Consequently, the available N concentration of Ankasa Series, 0.42 g/kg is close to that of Tikobo, 0.31 g/kg. The Acrudox has a total P concentration of 164 mg/kg which is 63 mg/kg more than the 101.4 mg/kg of Hapludult. The two soils have very low available P concentrations of 1.54 mg/kg and 2.71 mg/kg for the Acrudox and Hapludult, respectively.

Table 4. 1: Some Physical and Chemical Properties of the Soils Used

	---------SOIL TYPE--------------	
PARAMETERS	**ANKASA**	**TIKOBO**
Soil pH_{water}	4.2	4.9
Soil pH_{Salt}	3.7	4.0
Sand (%)	61.5	81.9
Clay (%)	30.7	5.6
Silt (%)	7.8	12.5
Textural class	sandy clay loam	loamy sand
OC (g/kg)	15.3	5.4
Total N (g/kg)	1.60	1.2
Available N (g/kg)	0.42	0.31
Total P (mg/kg)	164.0	101.4
Available P (mg/kg)	1.54	2.71
Ca (cmolc/kg)	0.64	0.70
Mg (cmolc/kg)	0.05	0.07
K (cmolc/kg)	0.08	0.06
Na (cmolc/kg)	0.06	0.06
Al (cmolc/kg)	1.31	0.40
H (cmolc/kg)	0.29	0.34
CEC (cmolc/kg)	17.8	8.9
ECEC (cmolc/kg)	2.63	1.73
Al Saturation (%)	54.80	24.54

The Ankasa Series 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 Ankasa Series is thrice more than that of the Tikobo Series (0.40 $cmol_c/kg$). Relatively, the exchangeable bases of the two soils were very low between 0.83 and 0.9 $cmol_c/kg$. It is also worthy of note that the CEC of the soils are far higher than their respective ECECs and the CEC of Ankasa Series is twice more than that of the Tikobo Series. The CEC and ECEC are 17.8 $cmol_c/kg$ and 2.68, respectively for the Ankasa Series and 8.9 $cmol_c/kg$ and 1.73 $cmol_c/kg$ for Tikobo Series. Aluminium saturation which was calculated as a percentage of the ECEC was 54.8% for Ankasa Series and 24.5% for Tikobo Series.

4.2 Chemical Characterisation of Biochar

The 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 herein after referred to as RH 500, RH 700, are rice husk charred at 500 ^{0}C and 700 ^{0}C and CC 500 and CC700 are corn cob charred at 500 ^{0}C and 700 ^{0}C are presented in Tables 4.2 and 4.3. The pH in water of the un-charred feed stocks are generally neutral in reaction with the pH of rice husk and corn cob in water being 6.1 and 6.8, respectively. Upon charring however, pH in water of RH500 biochar 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 being 10.7 and 11.0 for CC700.

Table 4. 2: Chemical Properties of Feedstock and Biochar Types Used*

Feedstock	Pyrolysis Temp °C	----------pH---------- 1:1(H_2O)	1:1(KCl)	Total C	Total N	C: N	Total P	Av. P
				------------ g/kg----------			---------- mg/kg--------------	
CC	---	6.8	--	402.6	9.7	41.5	1408.1	--
RH	--	6.1	--	353.1	7.6	46.5	1543.9	--
CC	500	10.7	10.8	567.9	0.82	692.6	4950.1	2162.5
CC	700	11.0	11.4	602.9	0.78	772.9	5910.2	2287.5
RH	500	7.6	7.9	387.1	0.55	703.8	5870.0	2378.8
RH	700	8.8	9.1	389.0	0.51	762.7	6020.5	2290.1

*CC = corn cob, RH = rice husk

Table 4. 3: Total, Exchangeable and Soluble Bases of Feedstock and Biochar Types Used*

Feedstock	pyrolysis	Total bases				Exchangeable base				Soluble bases			
	Temp ^oC	Ca	Mg	K	Na	Ca	Mg	K	Na	Ca	Mg	K	Na
		%											
CC	-	0.32	0.05	0.24	0.32	-	-	-	-	-	-	-	-
RH	-	0.36	0.07	0.19	0.28	-	-	-	-	-	-	-	-
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

*CC = corn cob, RH= rice husk,

The slightly alkaline to strongly alkaline pH of the biochar types agrees with Verheijen *et al.* (2010) who reported that anaerobic charring of feedstock leads to biochar with pH between neutral and strongly alkaline. The pH in the salt (KCl) was similar to that of in water as change was not more than 0.5 pH units (Nartey, 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 4.2). 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 ^{o}C and 700 ^{o}C.

Total nitrogen (TN) contents of the CC and RH were 9.7 and 7.6 g/kg (Table 4.2), respectively. On charring, TN decreased from 9.7 to 0.82 and 0.79 in the CC500 and CC700 biochar types respectively. 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

Unlike total C and N which were higher in the CC feedstock than its rice husk counterpart, total P in the two feed stocks was close with concentrations of 1408.2 mg/kg (0.14%) for CC and 1543.9 (0.15%) for RH. Available phosphorus concentrations, just as in the total P was close in the four biochar derivatives with values between 2162.5 mg/kg and 2378.5 mg/kg.

The concentration of total bases in the CC was 0.93% whilst the RH was 0.90% (Table 4.3). 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 feedstocks from which the biochar types were derived, total Na and K was higher in the CC biochar types than RH biochar types whereas total Ca and Mg were higher in the RH biochar typesthan CC 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.

4.3 Effect of Amendments on Soil pH

The changes in soil pH upon amendment of Ankasa Series with the four biochar types and the conventional agricultural lime ($CaCO_3$) are presented in Figure 1. The pH in water of the un-amended Ankasa Series, the Acrudox, increased from its inherent 4.2 to 4.7 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 after one week of incubation in the screen house. Thereafter, there was marginal change in pH with time for the ensuing five weeks. When the four biochar types were applied at the 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 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 changes in pH on amendment of Tikobo Series, is presented in Figure 2. The Tikobo Series, an Ultisol had an initial pH of 4.9 which rose to about 5.3 after one week of incubation when the conventional liming material, $CaCO_3$ was applied at 260 kg/ha. Within that same one week

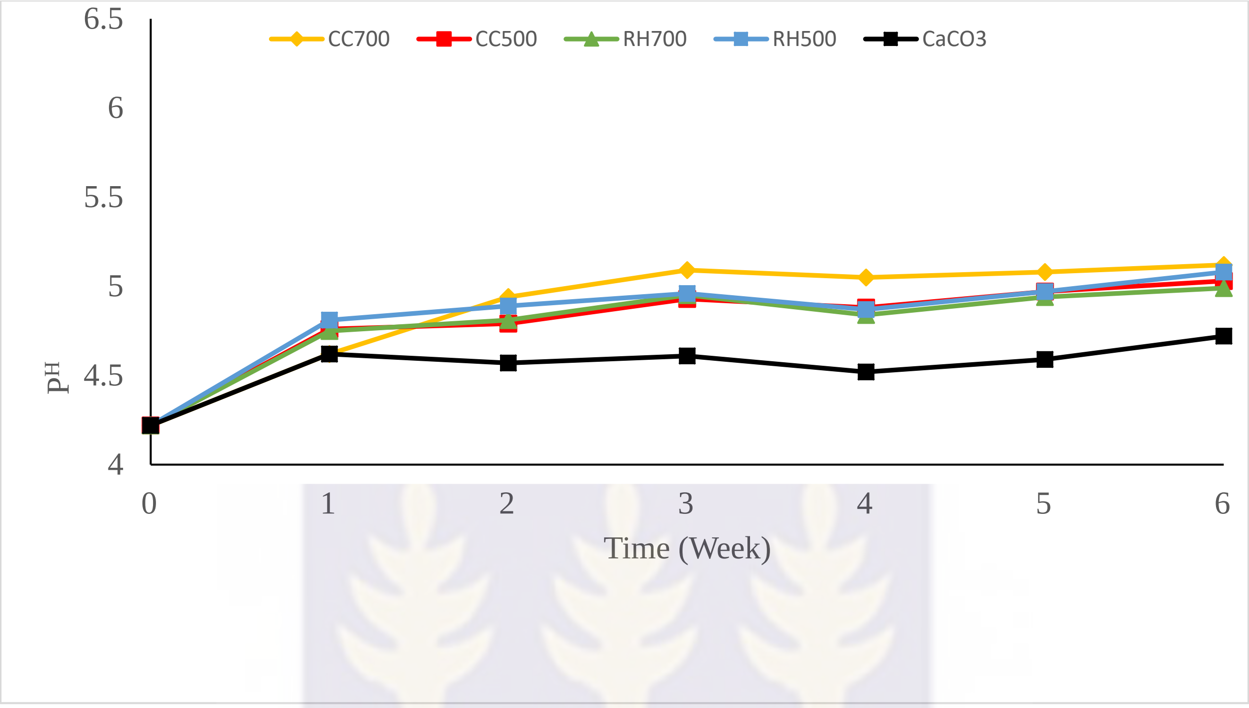


Figure 1. Changes in pH upon addition of amendments in Ankasa Series

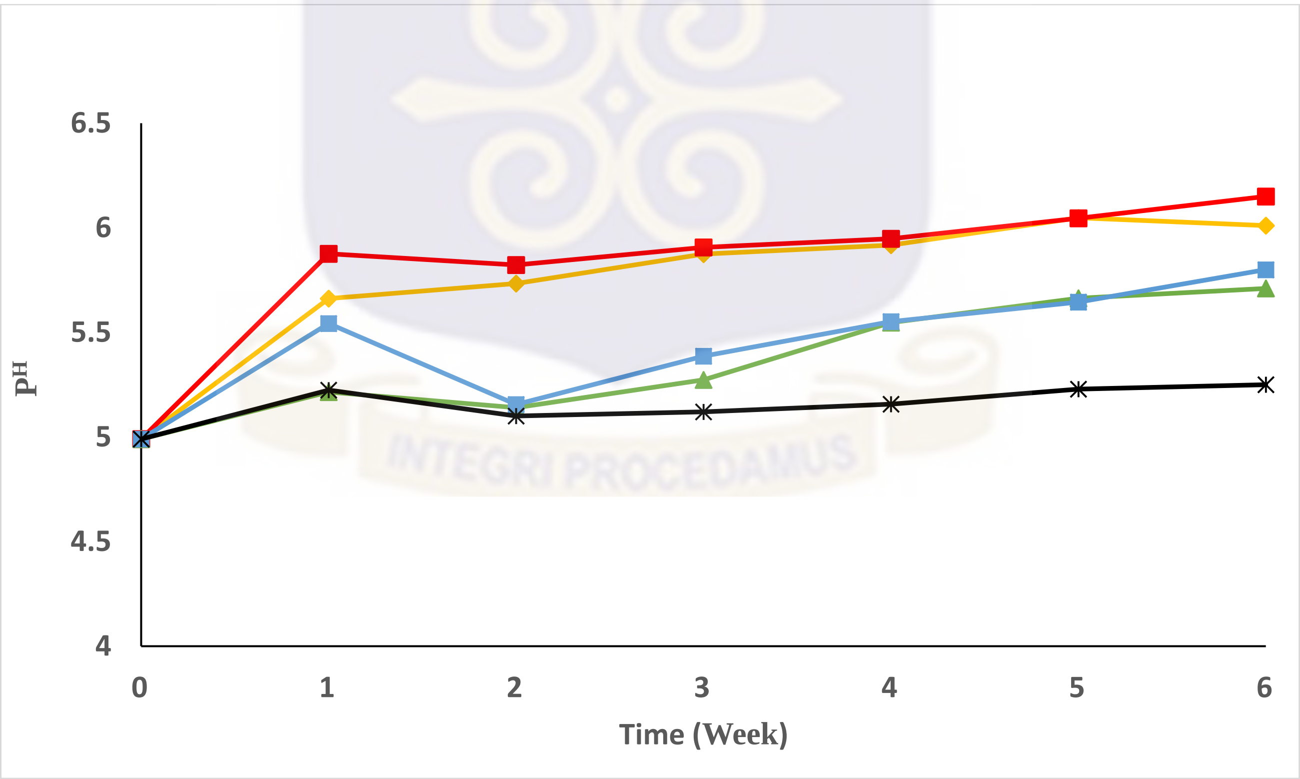


Figure 2. Changes in pH upon addition of amendments in Tikobo Series

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.

4.4 Effect of Amendments on Changes in Concentration of Exchangeable Al and Ca in the Soil

The changes in concentrations of Al and Ca in Ankasa Series are shown in Figure 3. The broken lines represent Al concentrations whilst the full lines represent concentrations of Ca. The concentration of Al in the Ankasa Series 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 soil solution 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 with a corresponding highest value in Al concentration in soil solution. The RH biochar amended soils had the highest Ca concentrations in soil solution with values between 2.0 and 2.5 cmolc/kg. Co-incidentally their Al concentration in the amended soils was among the lowest with values between 0.52 and 0.6 cmolc/kg. From Figure 3, it is clear that Al concentrations after amendment of Ankasa Series with the liming materials Ca application rate of 104 kg/ha did not reduce Al to the barest minimum as concentrations after six weeks were above 0.5 cmolc/kg in soil solution. Corn cob biochar charred at 700 ^{o}C reduced Al concentration to 0.44 cmolc/kg from 1.31 cmolc/kg during incubation whilst it increased Ca concentration from 0.64 cmolc/kg to 1.12 during the six weeks of incubation in Ankasa Series. $CaCO_3$ decreased Al concentration from 1.31 cmolc/kg to 0.70 cmolc/kg and also

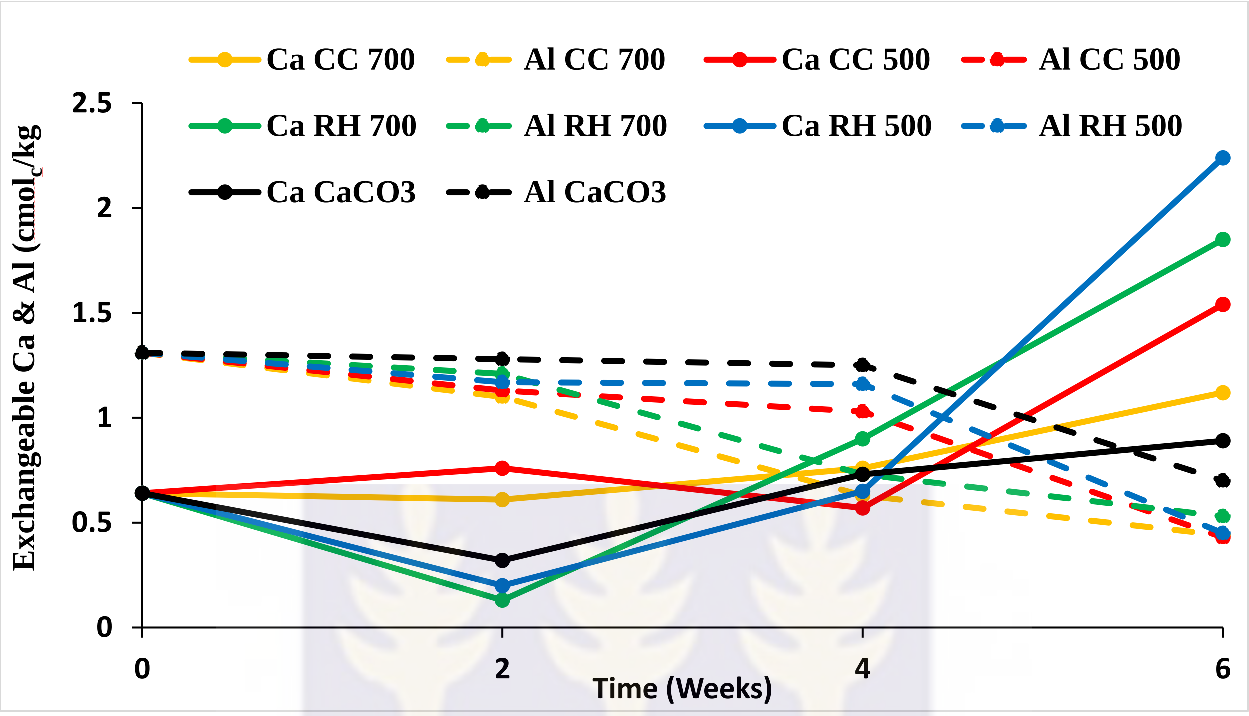


Figure 3. Changes in Exchangeable Al and Ca concentration upon addition of amendments to Ankasa Series.

increased Ca concentration from 0.64 cmolc/kg to 0.89 cmolc/kg in Ankasa Series. Rice husk biochar was able to increase Ca concentration to 2.20 cmolc/kg during the incubation period.

In the Tikobo Series 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 4). It is noteworthy that by the end of the six weeks incubation period, even though the conventional lime amended soil had a very high Ca concentration in solution (1.8 cmolc/kg), it was the only amended soil that still had Al in soil solution albeit low level (0.08 cmolc/kg; all other amended soils had non-detectable levels of Al. The $CaCO_3$ was able to increase Ca concentration from 0.70 cmolc/kg to 1.58 cmolc/kg during the incubation period in Tikobo Series. Corn cob biochar at 700 0C also increased Ca concentration to 1.15 cmolc/kg.

4.5 Effects of Amendment on Mg^{2+}, K^+, Na^+ and H^+ Concentrations in the Soil.

The concentrations of Mg^{2+}, K^+, Na^+ and H^+ in soil solution upon amendment of the two soils with the five liming materials are presented in figures 5 to 12. Generally, Mg, K, and Na increased in both soils whilst concentration of H decreased during the incubation period. It is clear from the figures, that is was only the basic cation Mg that started increasing in solution from the onset of incubation, i.e first week of incubation (Figure 5). The other two basic cations, K and Na generally increased in soil solution from week two. Generally, the concentrations of Mg, K and Na in the biochar amended soils were higher than in $CaCO_3$ amended soil. Though the $CaCO_3$ did not contain Mg and Na as active ingredients, it is clear from Figures 5 and 6 that addition of the conventional liming material to the Ankasa Series increased Mg from 0.05 cmolc/kg in the un-amended Ankasa soil to 0.3 cmolc/kg. Sodium concentration also increased from 0.06 cmolc/kg to 0.82

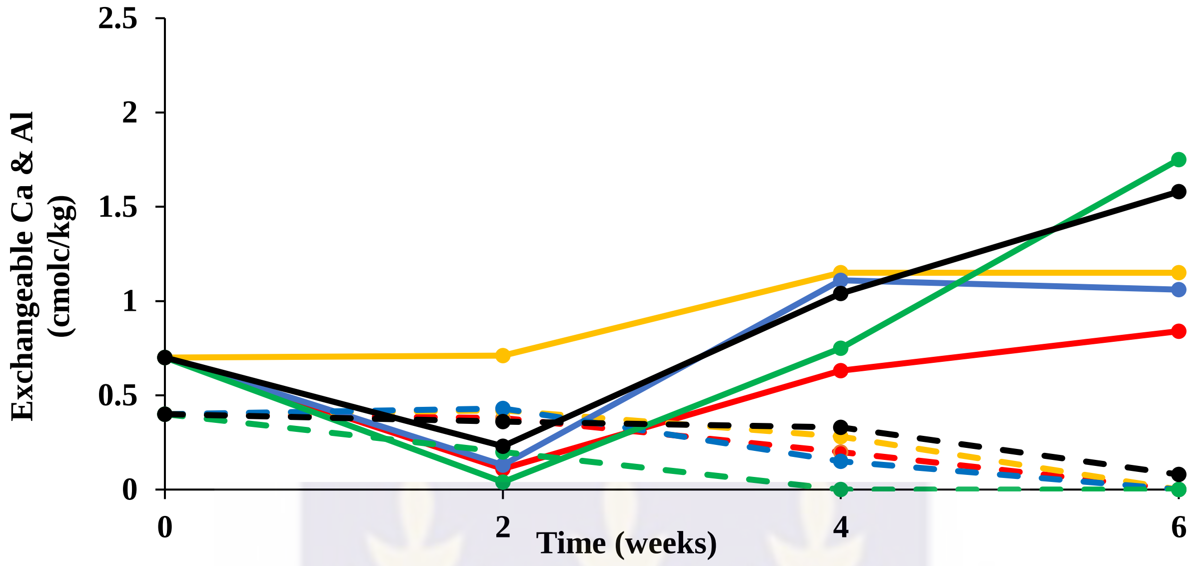


Figure 4. Changes in Exchangeable Al and Ca concentration upon addition of amendments to Tikobo Series.

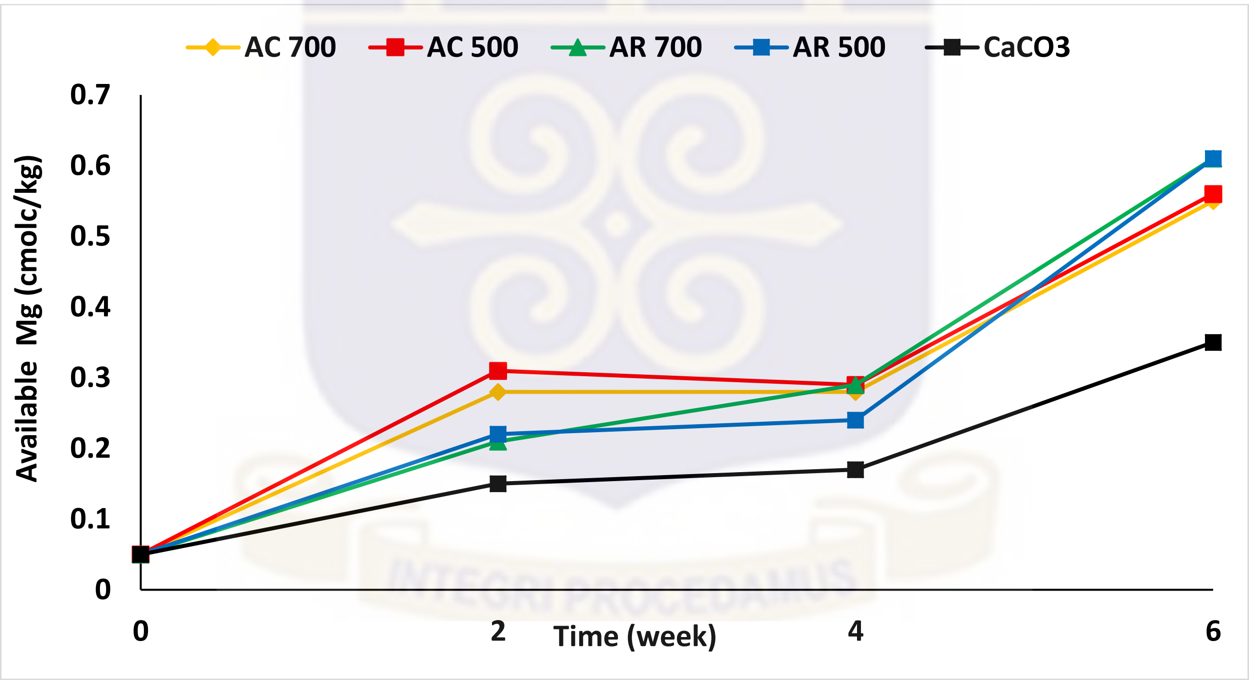


Figure 5. Changes in Mg concentration upon addition of amendments to Ankasa Series

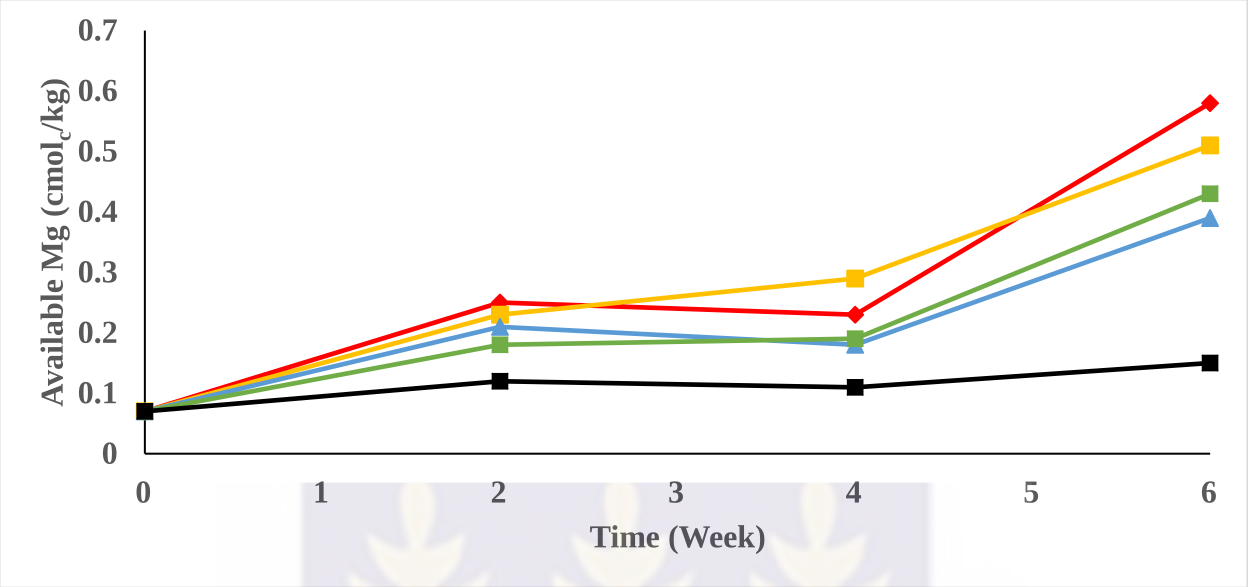


Figure 6. Changes in Mg concentration upon addition of amendments to Tikobo Series

cmolc/kg. Increase of Mg in the Tikobo Series was, however, marginal ranging from 0.07 cmolc/kg to about 0.15 cmolc/kg. Sodium availability in Tikobo increased from 0.06 to 0.73 cmolc/kg at the end of the six weeks incubation period.

Availability of the basic cations, Mg, K and Na increased greatly when the two acid soils were amended with the four biochar types with level of increases being in the order of Na > K > Mg. Available Na in the Ankasa soil amended with the four biochar types was between 1.6 and 1.9 cmolc/kg while available K was between 0.6 and 1.2 cmolc/kg. Magnessium was least with availability being between 0.5 and 0.6 cmolc/kg within the six weeks of incubation. In Tikobo Series, availability of Na was between 0.9 cmolc/kg and 2.5 cmolc/kg; K between 0.7 and 1.2 cmolc/kg and Mg between 0.4 and 0.6 cmolc/kg. Availability of K was especially higher in the CC biochar types after two weeks of amendment than in the RH types when applied to Tikobo Series

The acidic cation, H^+ on the other hand generally decreased in solution from the onset of incubation (Fig. 11 and 12). The concentration of H^+ in solution at the end of the six week incubation period was highest in the $CaCO_3$ amended soils and higher in the Acrudox (0.28 cmolc/kg) compared to the Hapludult (0.21 cmolc/kg)

4.6 Changes in Available P with Liming

The changes in available P concentration with time in Ankasa Series after amendment with the five liming materials are presented in Figure 13. Two weeks of amendment with $CaCO_3$ increased available P concentration from 1.54 mg/kg to about 5 mg/kg and to about 12.65 mg/kg by the sixth week. The biochar amended Ankasa Series increased in available P content to between 12 and 18 mg/kg by the end of the second week. The CC biochar types recorded the highest available P concentration of between 15 and 18 mg/kg. By the end of the sixth week, available P was highest in the RH biochar amended soils with concentration of 30.10 mg/kg. The CC500 biochar amended soil recorded available P concentration of 25 mg/kg with its CC700 amended soil having a concentration of about 15 mg/kg

On amendment of $CaCO_3$ to the Tikobo soil, there was marginal change in P concentration till after four weeks when increase in P availability was steep rising from about 3 mg/kg to about 12 mg/kg (Fig. 14). Amending Tikobo Series with the four biochar types increased P availability steadily with time (Fig. 14). By the end of the sixth week of incubation, availability of P in Tikobo had increased from a paltry 2.71 mg/kg to between 22 mg/kg and 30.10 mg/kg.

Rice husk biochar at 500 ^{o}C improved Tikobo P status from 2.71 to 30.10 mg/kg with the corn cob biochar at the same temperature increasing the P level of Tikobo Series to 27.79 mg/kg at the end of the incubation period. It is worthy of note that in both Ankasa and Tikobo Series amended with $CaCO_3$, sharp increases in P availability coincided with decreases in Al solubility around the fourth week.

4.7 Effect of Liming Amendments on Growth Parameters of Soya bean

Liming controls pH which in turn controls P availability in soils (Brady and Weil, 2002). Phosphorus is one of the main nutrients that controls root development and expansion in plants and hence nutrient absorption by plants (Marschner, 1998). Root volume, mass and shoot dry weight of the test crop soya bean, were, therefore used as indices for effect of liming in the two soils.

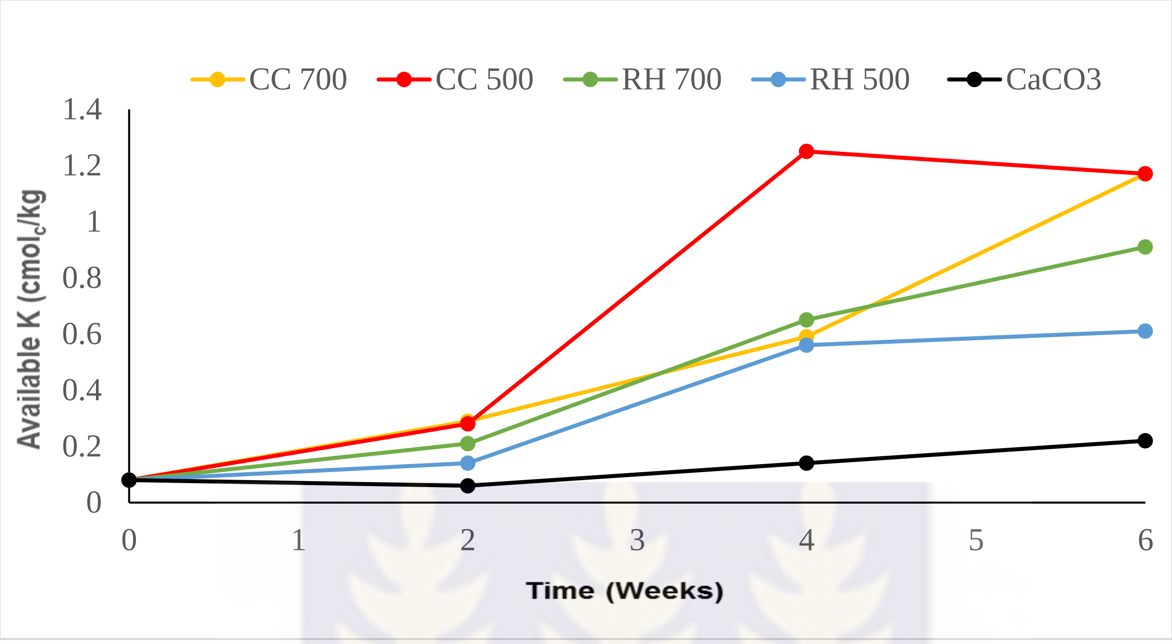


Figure 7. Changes in K concentration upon addition of amendments to Ankasa Series

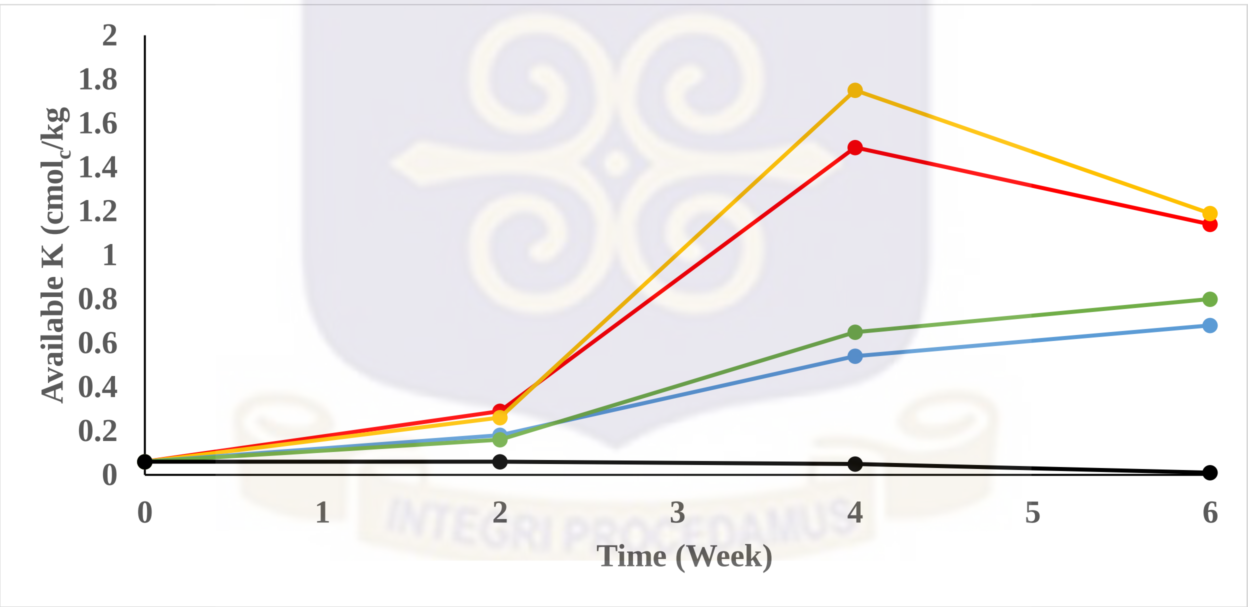


Figure 8. Changes in K concentration upon addition of amendments to Tikobo Series

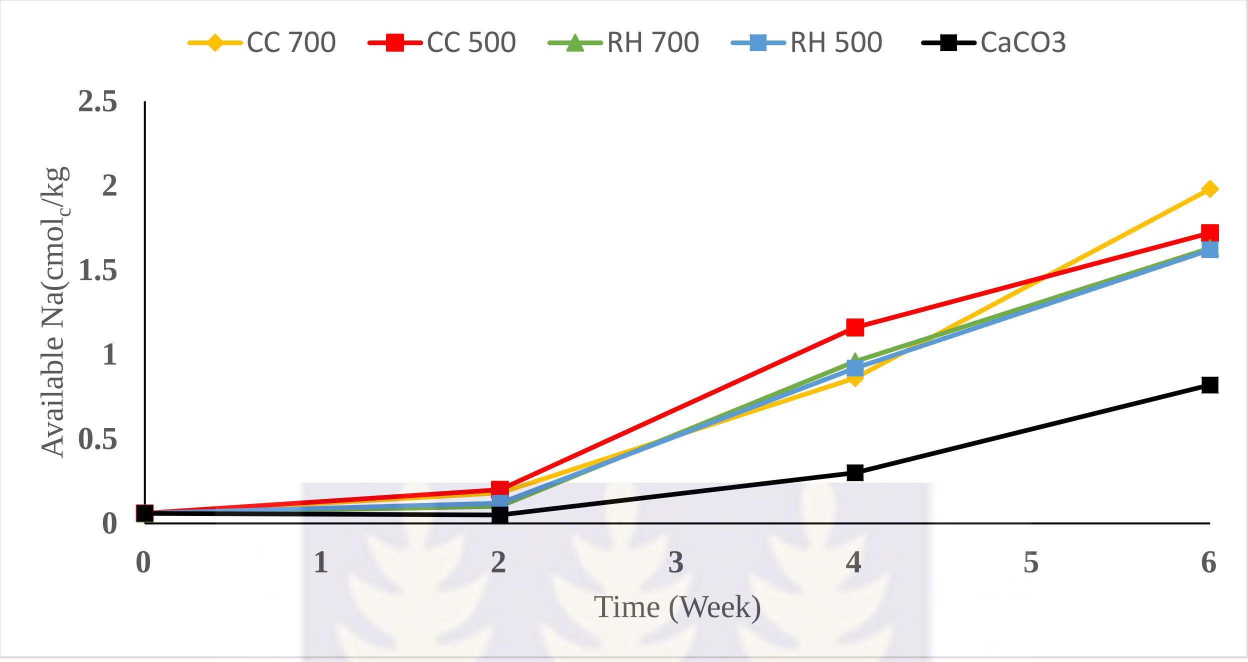


Figure 9. Changes in Na concentration upon addition of amendments to Ankasa Series

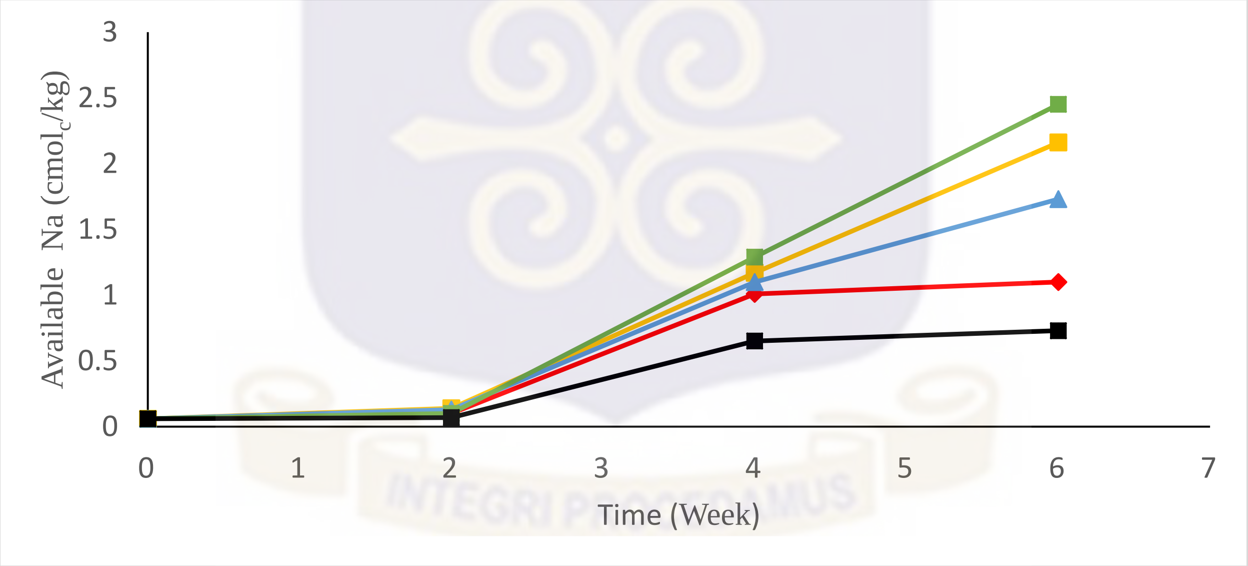


Figure 10. Changes in Na concentration upon addition of amendments to Tikobo Series

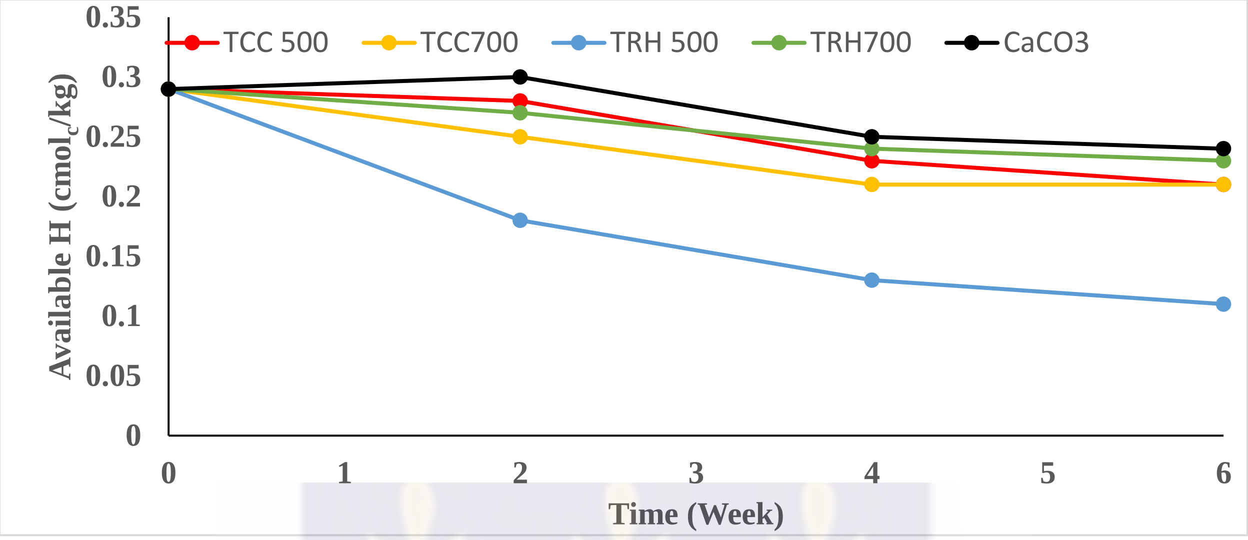


Figure 11 Changes in H concentration upon addition of amendments to Ankasa Series

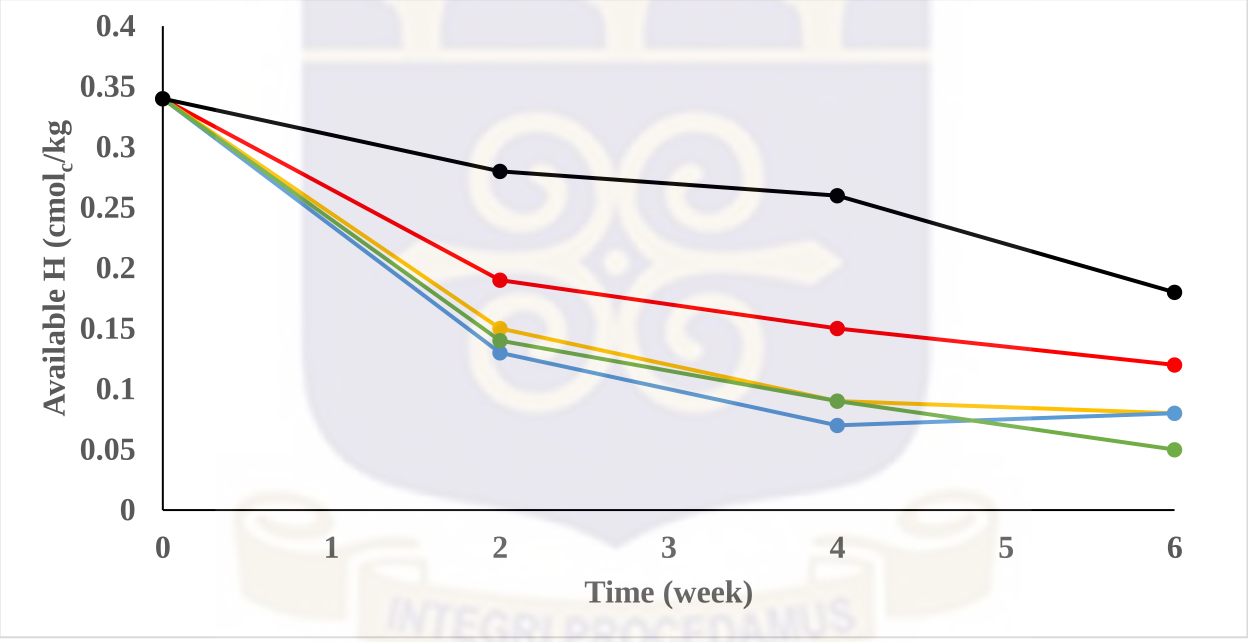


Figure 12. Changes in H concentration upon addition of amendments to Tikobo Series

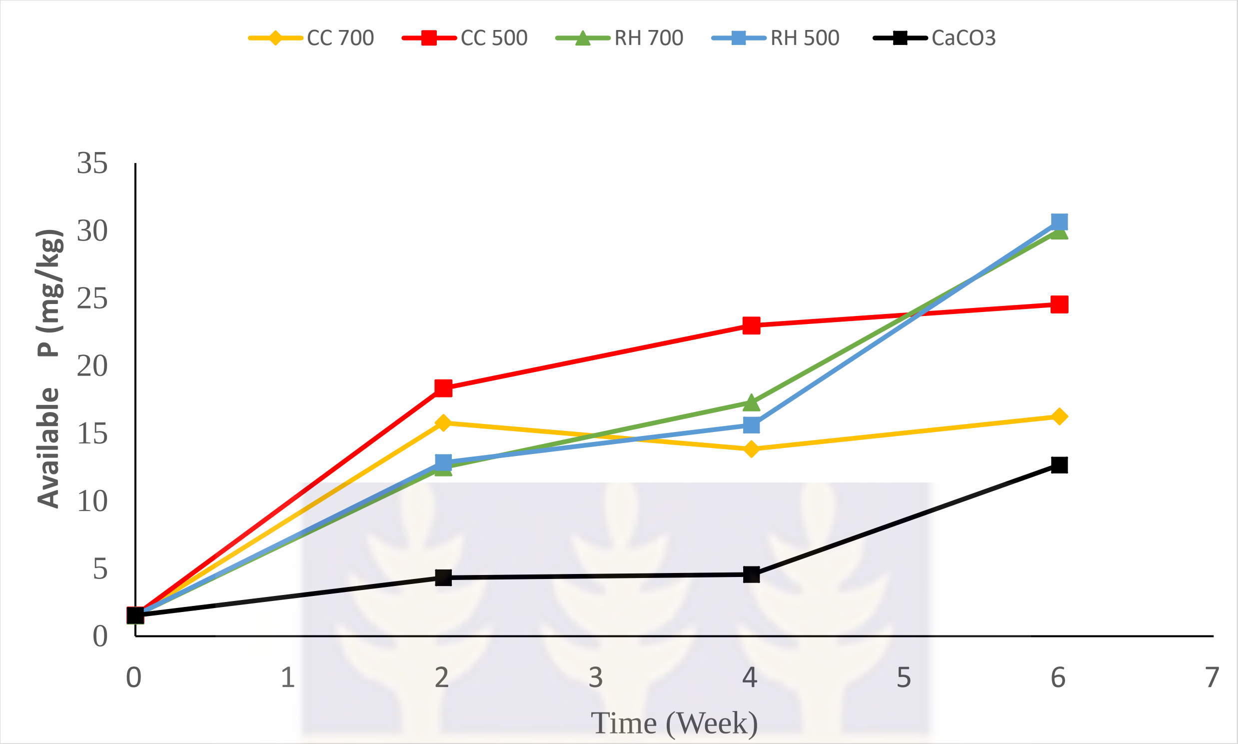


Figure 13. Changes in P concentration after addition of amendments to Ankasa Series

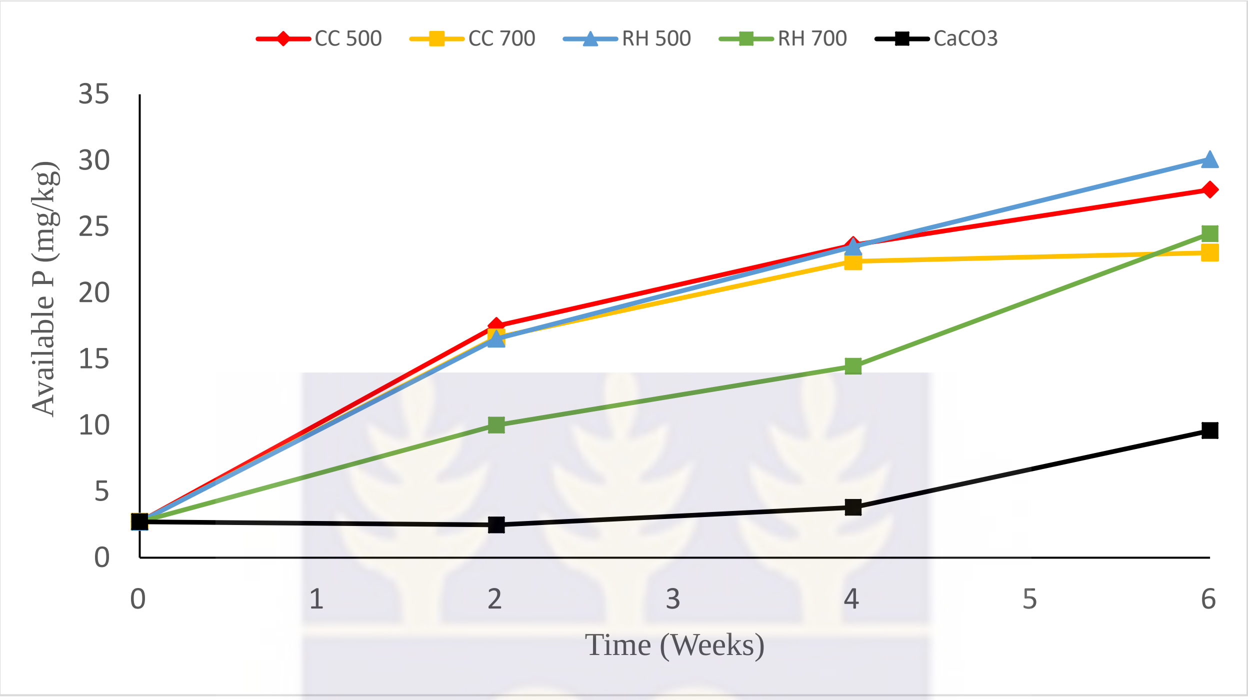


Figure 14. Changes in P concentration after addition of amendments to Tikobo Series

4.7.1 Effect of Liming on Root Volume

The effect of liming on root volume of soya bean plants in the Ankasa Series is presented Table 4.4. From the table, it is seen that root volume of the soya bean plants in the un-amended was very small averaging 1.2 cm^3. On amending the soil with $CaCO_3$, the root volume increased 2.7 times to 3.25. Application of the four biochar types also gave significant ($p < 0.05$) increases in root volumes over that of the un-amended. The CC500 biochar type had the least effect on root expansion with volume increasing by 1.8 times over that of the un-amended soils compared to between 2.6 and 2.8 times when the other three biochar types were applied. The other three biochar types i.e. CC700, RH500 and RH700 did not differ significantly ($p > 0.05$) among themselves with respect to effect on root expansion of soya bean when amended to Ankasa Series.

The root volume in un-amended Tikobo Series was 1.45 cm^3. On liming with the conventional liming material, the root increased significantly ($p < 0.05$) in volume to 3.33 cm^3 (Table 4.4). Liming with the four biochar types also increased root volume significantly ($p < 0.05$) to between 3.89 cm^3 and 5.99 cm^3; The effect of biochar liming on root expansion in the Tikobo Series was in the order RH500 > CC700 > CC500>RH700. All the biochar types except RH700 were superior to the conventional liming material on the effect on root expansion. The roots of soya bean plants after harvesting are shown in plates 3 and 4.

Root in Un-amended soil

Root in $CaCO_3$ amended soil

Root in CC biochar amended soil

Root in RH biochar amended soil

Plate 3. Soya bean Root in Ankasa Series

Root in un-amended soil

Root in $CaCO_3$ amended soil

Root in CC biochar amended soil

Root in RH biochar amended soil

Plate 4. Soya bean Root in Tikobo Series

Table 4. 4: Response of Root Volume to Different Liming Material*

TREATMENT	ROOT VOLUME (cm^3)	
	Ankasa Series	Tikobo Series
Un-amended	1.20a	1.45a
LiN0P0	3.25c	3.33b
CC500	2.15b	3.98bc
CC700	3.38c	4.63c
RH500	3.28c	5.99d
RH700	3.15c	3.89bc
CV%	12.8	

*Li = $CaCO_3$; N0 = zero N application; P0 = zero P application. Means with the same alphabet are not significantly ($p>0.05$) different.

4.7.2 Effect Liming on Root Dry Matter

The root dry mass of soya bean in the un-amended Ankasa Series was 0.21 g (Table 4.5). On amendment with $CaCO_3$, the mass increased significantly ($p<0.05$) to 0.31 g. Amending the soil with RH500, though was superior to the un-amended soil did not increase the root mass (0.28 g) significantly ($p>0.05$) from that of the $CaCO_3$ amendment. The other biochar liming materials, however, increased root mass significantly above that of the $CaCO_3$ even though there were no significant differences among them, (the root masses were between 0.39g and 0.42 g).

In the un-amended Tikobo Series, root mass of the soya bean plant was 0.14 g (Table 4.5). Amending the soil with $CaCO_3$ increased the mass six fold to 0.84 g. Unlike in the Ankasa Series, the roots in the $CaCO_3$ amended Tikobo Series were heavier than in their biochar amended counterparts. The biochar amended Tikobo soil showed only a 2.0 to 4.5 fold increase in root mass with the highest of 0.63 g being harvested from the RH500 amended Tikobo soil.

4.7.3 Effect of Liming on Shoot Dry Matter

Shoot dry matter of soya bean plants harvested from the un-amended Ankasa soil was 0.22 g similar to its root dry mass (0.21 g) (Table 4.6). Liming with $CaCO_3$ significantly ($p<0.05$) gave the highest shoot dry matter of 0.53 g. Amending Ankasa with the four biochar types produced plants with shoot dry matter in the order of CC700 > CC500 = RH500 > RH700. The least shoot dry matter of 0.28 g was from the RH700 pot but significantly ($p<0.05$) heavier than that of the un-amended soil.

Table 4. 5: Response of Root Dry Matter to Different Liming Materials*

TREATMENT	ROOT DRY MATTER (g)	
	Ankasa Series	Tikobo Series
Un-amended	0.21a	0.14a
LiN0P0	0.31b	0.84e
CC500	0.42c	0.21b
CC700	0.39c	0.23b
RH500	0.28b	0.63d
RH700	0.41c	0.35c
CV%	10.3	

*Li = $CaCO_3$; N0 = zero N application; P0 = zero P application. Means with the same alphabet are not significantly (p>0.05) different.

Table 4. 6: Response of Shoot Dry Matter to Different Liming Materials*

TREATMENT	SHOOT DRY MATTER (g)	
	Ankasa Series	Tikobo Series
Un-amended	0.22a	0.26a
LiN0P0	0.53e	0.63d
CC500	0.35c	0.34b
CC700	0.44d	0.53c
RH500	0.34c	1.10f
RH700	0.28b	0.72e
CV%	16.4	

*Li = $CaCO_3$; N0 = zero; N application; P0 = zero P application. Means with the same alphabet are not significantly (p>0.05) different.

Shoot dry matter in the un-amended Tikobo Series was 0.26 g (Table 4.6). This increased to 0.63 g when the soil was amended with $CaCO_3$. Amending the soil with the CC biochar types produced soya bean plant with shoot dry matter (CC500 = 0.34 g; CC 700 = 0.53 g) significantly ($p<0.05$) heavier than the un-amended soil but lower than the conventionally limed soil. The RH biochar types when amended to the Hapludult (Tikobo soils) produced soya bean plants with shoot dry matter significantly ($p<0.05$) heavier than those from the $CaCO_3$ amended soil.

4.8 **Effect of P on Growth Parameters of Soya bean**

4.8.1 Effect of P on Root Volume

The root volumes when the P equivalent from biochar was added from synthetic P source (TSP) to the lime amended Ankasa was 3.05 cm^3, which was not significantly ($p>0.05$) different from when the soil was amended with only $CaCO_3$ (LiN0P0) (Table 4.7). The root volume of the Ankasa Series that had been conventionally limed and to which synthetic P had been applied was, however, significantly ($p<0.05$) higher than the un-amended soil. When synthetic P at the rate of 30 kg P/ha was added to the biochar amended Ankasa Series, root volume did not significantly ($p>0.05$) change from the volumes when only biochar was amended to the soil.

When synthetic P from TSP was added to the $CaCO_3$ limed Tikobo Series at biochar P equivalent rate, root volume increased from 3.33 cm^3 to 4.19 cm^3. An addition of synthetic P at the rate of 30 kg P/ha to the biochar amended Tikobo Series did not show any significant ($p>0.05$) change in root volumes of the soya bean plants from their biochar amended counterpart plants (Table 4.7).

Table 4. 7: Effect of P on Root Volume*

ROOT VOLUME (cm^3)

Treatment	Ankasa Series	Tikobo Series
Un amended	1.20a	1.45a
LiN0P0	3.25c	3.33b
LiN0BEP	3.05c	4.19bc
CC500N0P0	2.15b	3.98bc
CC700N0P0	3.38c	4.63c
RH500N0P0	3.28c	5.99d
RH700N0P0	3.15c	3.89bc
CC500N0P30	2.75bc	4.03bc
CC700N0P30	2.8bc	3.38b
RH500N0P30	2.95bc	4.83c
RH700N0P30	3.18c	5.75d
CV%	15.60	

*Li = $CaCO_3$;N0 = zero N application; P0 = zero P application; P30 = 30 kg P/ha application; BEP = Biochar Equivalent P application from TSP. Means with the same alphabet are not significantly (p>0.05) different.

4.8.2 Effect of P on Root Dry Matter

When synthetic P at the biochar equivalent was applied to the $CaCO_3$ amended Ankasa Series (LiN0BEP), root mass increased significantly ($p<0.05$) 0.21 g to 0.30 g in the un-amended soil (Table 4.8). However, this increase was not significantly ($p>0.0$) different from that of the $CaCO_3$ limed soil with no external P application. On addition of synthetic P at 30 kg /ha to the biochar amended Ankasa Series, an increase in root mass was observed only in the RH amended soil (RH700N0P30) in which root mass increased from 0.41 g to 0.54 g (Table 4.8).

Addition of synthetic P to the limed Tikobo Series produced soya bean plants with lighter roots as root mass decreased from 0.84 g in the unfertilized conventionally limed soil to 0.53 g in the un limed but P fertilized counterpart (LiN0BEP) (Table 4.8). In general, the addition of synthetic P to the biochar amended Tikobo Series produced heavier roots than their counterparts which were not synthetically fertilized.

4.8.3 Effect of P on Shoot Dry Matter

The effect of P from biochar and synthetic sources and their respective interactions on shoot dry matter of soya bean plants grown in the two soils are shown in Table 4.9. From the Table, addition of TSP at biochar equivalent P/ha to the $CaCO_3$ limed Ankasa had no significant ($p>0.05$) effect on shoot dry matter just as root volume as the parameter was statistically not different from that in the unfertilized $CaCO_3$ limed soil. It was only the P fertilized RH biochar amended soils that increased in shoot dry matter over their unfertilized P counterparts.

There was about 1.65 times increase in shoot dry matter when the $CaCO_3$ limed Tikobo Series was fertilized with TSP (Table 4.9). On further TSP fertilization of the RH limed Tikobo soils,

Table 4. 8: Response of Root Dry Matter to Different P Source*

ROOT DRY MATTER (g)

Treatment	Ankasa Series	Tikobo Series
Un amended	0.21a	0.14a
LiN0P0	0.31bc	0.84
LiN0BEP	0.30b	0.53e
CC500N0P0	0.42d	0.21b
CC700N0P0	0.39cd	0.23b
RH500N0P0	0.28b	0.63f
RH700N0P0	0.41c	0.35c
CC500N0P30	0.26ab	0.46d
CC700N0P30	0.36c	0.69g
RH500N0P30	0.27b	0.50d
RH700N0P30	0.54e	0.94i
CV%	8.60	

*Li = $CaCO_3$; N0 = zero N application; P0 = zero P application; P30 = 30 kg P/ha application; BEP = Biochar Equivalent P application from TSP. Means with the same alphabet are not significantly (p>0.05) different.

Table 4. 9: Response of Shoot Dry Matter to Synthetic and Biochar P Sources*

SHOOT DRY MATTER (g)

Treatment	Ankasa	Tikobo
Un amended	0.22a	0.26a
LiN0P0	0.53cd	0.63c
LiN0BEP	0.35bc	1.04e
CC500N0P0	0.35bc	0.34a
CC700N0P0	0.44c	0.53b
RH500N0P0	0.34b	1.10e
RH700N0P0	0.28b	0.72cd
CC500N0P30	0.44c	0.54bc
CC700N0P30	0.46cd	0.65c
RH500N0P30	0.55d	0.57bc
RH700N0P30	0.80e	0.78d
CV%	12.70	

*Li = $CaCO_3$; N0 = zero N application; P0 = zero P application; P30 = TSP applied at a rate of 30 kg P/ha; BEP = Biochar Equivalent P application from TSP. Means with the same alphabet are not significantly ($p>0.05$) different.

shoot dry matter increased significantly ($p<0.05$) over the unfertilized counterparts. The converse was observed in the CC amended Tikobo soils.

4.8.4 Effect of P on Nodulation

The effect of P on nodulation is presented in Table 4.10. From the table, it is obvious that apart from RH700, all the biochar types only nodulated in Tikobo Series when they received synthetic P fertilization. On addition of TSP at the rate of 30 kg P/ha, the CC500 and CC700 which could not produce soya bean plants with nodules had plants with four and five nodules, respectively and the nodules weighed 0.004 g. The unfertilized RH500 which hitherto could not produce nodulated soya bean plants, produced plants with five nodules which weighed 0.004 g when fertilized with synthetic P at the rate of 30 kg P/ha. The unfertilized RH700 amended Tikobo Series which produced soya bean plants with 11 nodules had reduction in nodule numbers to 7 on addition of 30 kg P/ha from TSP.

4.9 Effect of N Application on Growth Characteristics of Soya Bean

Nitrogen is one of the main nutrients that control nodulation. It also affects chlorophyll content and hence dry matter production (Marschner, 1998).

4.9.1 Effect of N on Shoot Dry Matter

The sole effect of N on shoot dry matter of soya bean grown on the $CaCO_3$ limed Ankasa and Tikobo Series are presented in Figure 15. Generally, with the exception of the RH700 amended

Table 4. 10: Effect of P on Nodule Number and Nodule Dry Weight*

TIKOBO

Treatment	Nodule Number	Nodule Dry weight(g)
Un amended	0	0
LiN0P0	0	0
LiN0BEP	0	0
CC500N0P0	0	0
CC700N0P0	0	0
RH500N0P0	0	0
RH700N0P0	11	0.011
CC500N0P30	4	0.004
CC700N0P30	5	0.004
RH500N0P30	5	0.004
RH700N0P30	7	0.016

*Li = $CaCO_3$; N0 = zero N application; P0 = zero P application; P30 = TSP applied at a rate of 30 kg P/ha ; BEP = Biochar Equivalent P application from TSP

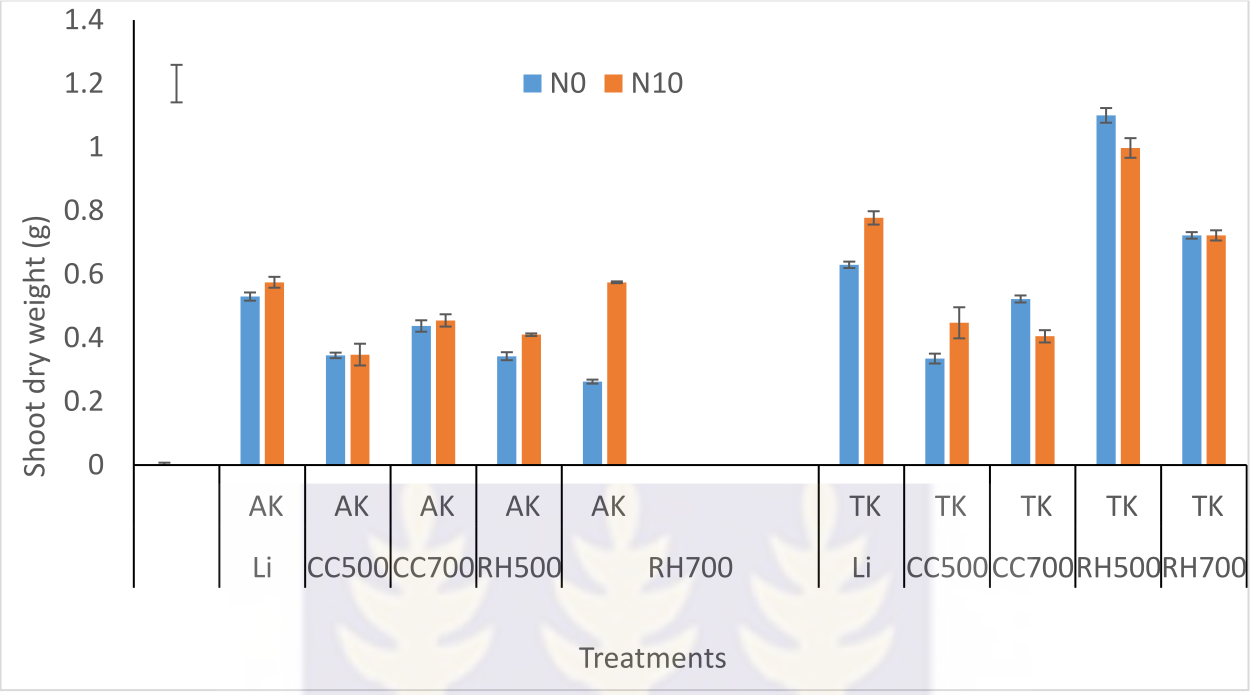


Figure 15. Response of shoot dry mass to N application

Ankasa Series, all the amended soils did not show any response to N application. When N from urea was applied at 10 kg/ha to the RH700 amended Ankasa Series, shoot dry matter increased by almost 2.1 times from 0.28 g to 0.58 g.

4.9.2 Effect of N on root volume and Nodule Number

The effect of N application on root volume of the two soils is presented in Figure 16. It is apparent from the figure that N application at 10 kg N/ha had no effect on root volume as unfertilized limed soils and fertilized limed soils both produced plants with statistically similar root volumes. The effect of synthetic N applied at 10 kg/ha on nodule number is presented in Figure 17. It was only the unfertilized RH700 Tikobo Series that produced nodules upon liming the soils. However, when the soil was fertilized with 10 kg N/ha from urea, nodulation was suppressed to nil. The CC700 amended Tikobo Series which had no nodules on the soya bean plants surprisingly, and inexplicably produced on the average 8 nodules on N fertilization

4.10 Interactive Effects of Biochar Liming, Synthetic P and N Application on Growth Characteristics

The interactive effects of biochar as a liming material, synthetic P and N on some growth characteristics of soya bean are presented in Table 4.11. The RH amended Ankasa Series that had been fertilized with both urea and TSP at respective rates of 10 kg N/ha and 30 kg P/ha produced plants with higher root volumes than their CC amended counterparts. The RH 500 and 700 with both P and N fertilization had respective root volumes of 3.99 and 4.28 cm^3 compared to their CC

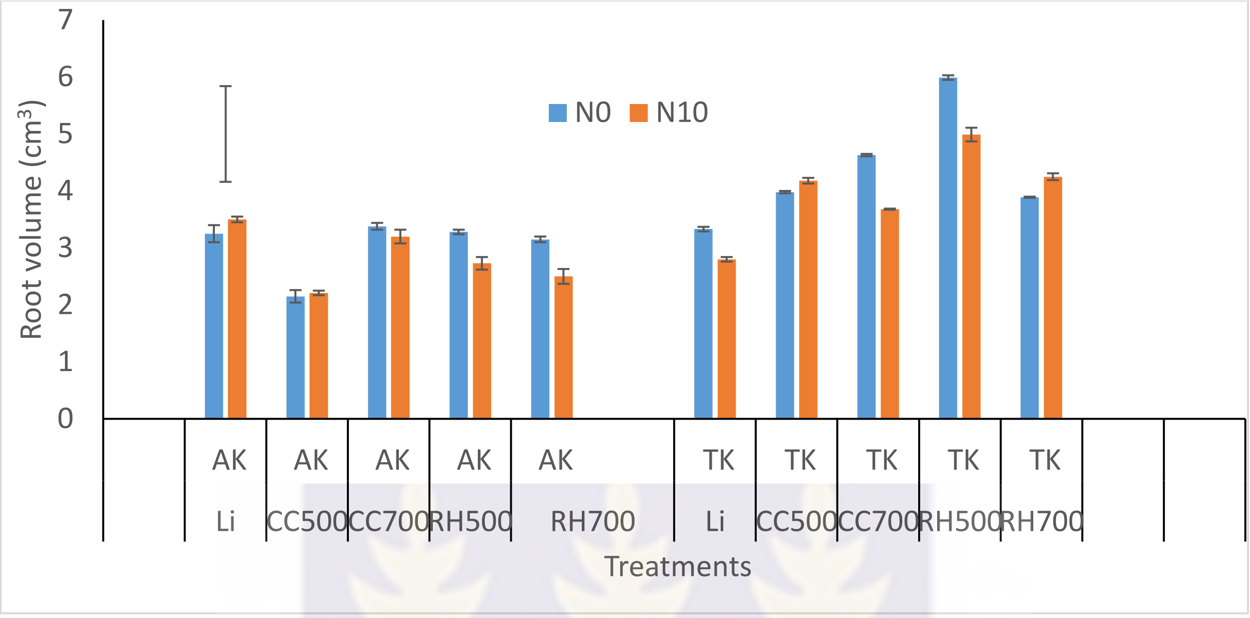


Figure 16. Response of root volume to N applica

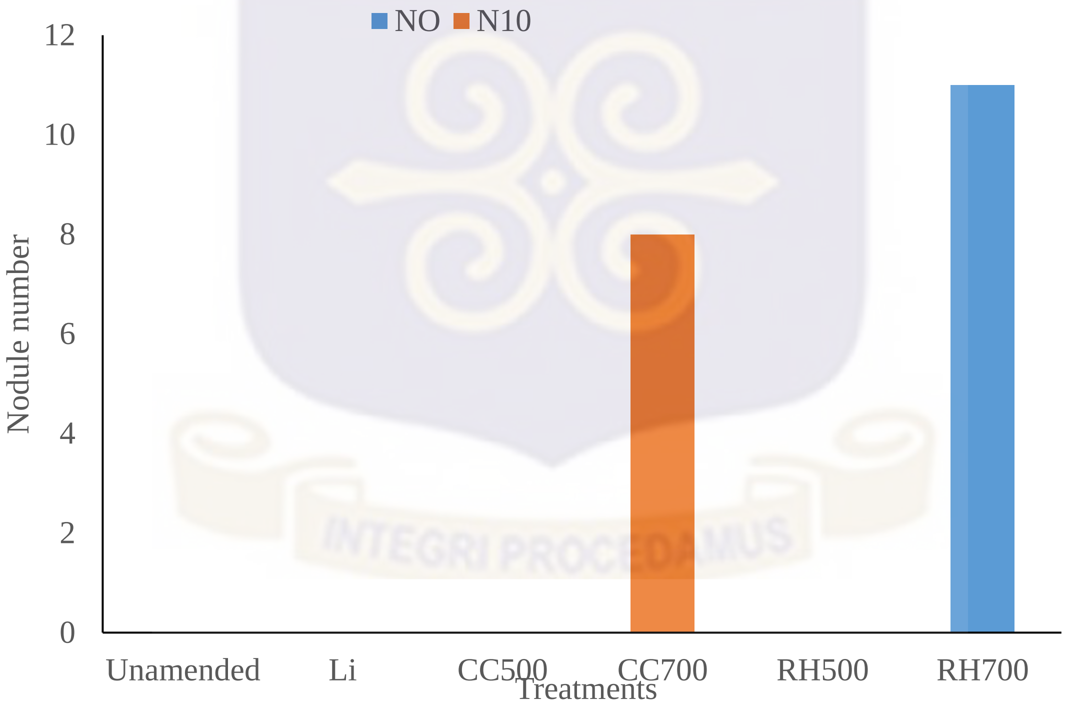


Figure 17. Response of nodulation to N application

Table 4. 11: Interactive Effects of Amendment on Root Volume, Shoot Dry Matter and Nodule Number in Ankasa Series*

TREATMENTS	ROOT VOL. cm^3	SHOOT DRY MAT. (g)	NODULE NUMBER
Un-amended	1.20a	0.22a	0
LiN0P0	3.25cd	0.53fg	0
CC500N0P0	2.15b	0.35c	0
CC700N0P0	3.38cd	0.44de	0
RH500N0P0	3.28c	0.34c	0
RH700N0P0	3.15cd	0.28b	0
LiN0BEP	3.05c	0.35c	0
CC500N0P30	2.75bc	0.44de	0
CC700N0P30	2.80bc	0.46e	0
RH500N0P30	2.95bc	0.55fg	0
RH700N0P30	3.18cd	0.80i	0
LiN10P0	3.50cd	0.58g	0
CC500N10P0	2.21bc	0.35c	0
CC700N10P0	3.20cd	0.46e	0
RH500N10P0	2.73bc	0.41d	0
RH700N10P0	2.50bc	0.58g	0
LiN10BEP	2.23bc	0.33c	0
CC500N10P30	2.25bc	0.44de	0
CC700N10P30	2.23bc	0.56g	0
RH500N10P30	3.99d	0.63h	0
RH700N10P30	4.28d	0.51f	0
CV%	18.10	10.70	

*Li = $CaCO_3$; N0 = zero N application; P0 = zero P application; P30 = TSP applied at a rate of 30 kg P/ha ; BEP = Biochar Equivalent P application from TSP; N10 = 10 kg N/ha from urea. Means with the same alphabet are not significantly (p>0.05) different.

counterparts with root volumes of 2.25 cm^3 and 2.23 cm^3, respectively. The RH amended soils which had been fertilized with both N and P had significantly higher root volumes than those that had been fertilized with only N as soya bean plants grown in RH500N10P0 and RH700N10P0, respectively increased in root volumes from 2.21 cm^3 and 3.2 cm^3 to 3.99 cm^3 and 4.28 cm^3 when the treatments were further fertilized with P at 30 kg/ha. Addition of P from TSP did not however, increase root volume in the CC amended Ankasa Series significantly (Table 4.11)

Generally, with the exception of RH 700, addition of both synthetic N and P increased shoot dry matter more than addition of N to the biochar amended plots. Shoot dry matter in the Ankasa Series was highest (0.63 g) in the P and N fertilized RH500 and least in the fertilized CC500 amended soil (0.44 g)

Just as was observed in the Ankasa Series, the RH amended Tikobo soils produced plants with higher root volumes than their CC counterparts when the soil was fertilized with both urea and TSP (Table 4.12) with a general concomitant increase in shoot dry matter. Shoot dry matter upon N and P fertilization in the biochar amended soils was in the order of RH700N10P30 > RH500N10P30 >= CC700N10P30 > CC500N10P30 (Table 4.12). When both fertilizers were applied to the biochar amended Tikobo Series shoot dry matter, except in the RH500N10P30 amended soil was higher than in the counterparts that had received only N fertilization. Addition of both synthetic fertilizers to the biochar amended soils generally produced plants with nodules except in the RH500N10P30 Tikobo amended soil. It is worthy of note that none of the conventionally limed Tikobo soil produced plants with nodules whilst all the biochar amended soils with additional P at 30kg/ha produced between 4 and 7 nodules per plant (Table 4.12). When

Table 4. 12: Interactive Effect of Amendment on Root Volume, Shoot Dry Matter and Nodule Number in Tikobo Series*

TREATMENTS	ROOT VOL. (cm^3)	SHOOT DRY MAT. (g)	NODULE NUMBER
Un-amended	1.45a	0.26a	0
LiN0P0	3.33bc	0.63e	0
CC500N0P0	3.98cd	0.34b	0
CC700N0P0	4.63d	0.53d	0
RH500N0P0	5.99e	1.10j	0
RH700N0P0	3.89cd	0.72f	11
LiN0BEP	4.19c	1.04i	0
CC500N0P30	4.03c	0.54d	4
CC700N0P30	3.38bc	0.65e	5
RH500N0P30	4.83d	0.57d	5
RH700N0P30	5.75e	0.78g	7
LiN10P0	2.80b	0.78g	0
CC500N10P0	4.18cd	0.45c	0
CC700N10P0	3.68c	0.41c	8
RH500N10P0	4.99de	1.00hi	0
RH700N10P0	4.25c	0.72f	0
LiN10BEP	3.03bc	0.42c	0
CC500N10P30	4.43c	0.78g	6
CC700N10P30	4.93d	0.99h	7
RH500N10P30	5.25de	0.96h	0
RH700N10P30	4.75de	1.08ij	8
CV%	18.10	10.70	

*Li = $CaCO_3$; N0 = zero N application; P0 = zero P application; P30 = TSP applied at a rate of 30 kg P/ha; BEP = Biochar Equivalent P application from TSP; N10 = 10 kg N/ha from urea. Means with the same alphabet are not significantly (p>0.05) different.

N from urea at 10 kg/ha was added to the biochar amended Tikobo Series without synthetic P supplementation, only the CC700 amended soil produced nodules.

4.11 **Nutrient Uptake**

Phosphorus is the most limiting macro nutrient with regards to nodulation in soya bean. The availability of the nutrient is also controlled by pH and hence liming. Thus, this section will focus on uptake of P in the root and shoot.

4.11.1 Root P Uptake

Root P uptake from soya bean plants grown in the Ankasa Series is presented in Table 4.13. Root P uptake in the un-amended Ankasa series was 2.15 mg/pot which increased significantly ($p<0.05$) to 6.79 mg/pot when the soil was limed with $CaCO_3$. Amending the soil with biochar increased root P uptake significantly ($p<0.05$) when compared to $CaCO_3$ limed soil except in the RH500 amended soil where uptake decreased. When the biochar equivalent P from TSP was added to the $CaCO_3$ limed soil, root uptake increased significantly ($p<0.05$) to 7.14 mg/pot. However, this uptake was not statistically ($p>0.05$) different from the uptake levels in the RH700 and CC700. Further addition of synthetic P from TSP at the rate of 30 kg P /ha only gave a significant ($p<0.05$) increase in P uptake (12.75 g) in the RH700 amended soil. It is apparent from the Table that addition of 10 kg N/ha from urea (LiN10P0) increased uptake of P significantly ($p<0.05$) to 12.49g, 1.75 times more than when no N was applied to the $CaCO_3$ limed soil. However, application of both N and P to the $CaCO_3$ limed soil suppressed P uptake to 7.24 g similar to when no synthetic N and P were applied (6.79 g). Root P uptake in unfertilized biochar amended Ankasa series were similar to both the unfertilized and P fertilized

Table 4. 13: Effect of Amendments on Root P Uptake*

TREATMENTS	ROOT P UPTAKE (mg/pot)	
	Ankasa	Tikobo
Un-amended	1.45a	1.55a
LiN0P0	9.93cd	17.13g
CC500N0P0	5.15b	4.56b
CC700N0P0	5.35b	5.49b
RH500N0P0	6.62bc	14.45f
RH700N0P0	5.45b	7.97c
LiN0BEP	5.84b	12.58ef
CC500N0P30	9.17c	11.06d
CC700N0P30	9.22c	13.91f
RH500N0P30	12.44d	12.00e
RH700N0P30	16.24e	22.77h
LiN10P0	9.40cd	8.63cd
CC500N10P0	7.37bc	4.56b
CC700N10P0	9.49cd	8.78cd
RH500N10P0	8.74c	12.01e
RH700N10P0	11.41cd	12.95ef
LiN10BEP	7.88bc	9.77d
CC500N10P30	11.00cd	21.62h
CC700N10P30	12.87d	14.40f
RH500N10P30	12.35d	22.92h
RH700N10P30	12.10d	17.42g
CV%	11.00	

*Li = $CaCO_3$; N0 = zero N application; P0 = zero P application; P30 = TSP applied at a rate of 30 kg P/ha; BEP = Biochar Equivalent P application from TSP; N10 = 10 kg N/ha from urea. Means with the same alphabet are not significantly (p>0.05) different.

a.

$CaCO_3$ limed soil except in the CC500 amended Ankasa Series with a higher P uptake of 9.8 g. Phosphorus fertilization from TSP to the biochar amended soil gave an increase in P uptake (12.75 g) only in the RH700N0P30 Ankasa soil. Addition of both urea and TSP at their respective rates to the biochar amended soils did not generally increase root P uptake.

Root P uptake in the Tikobo Series was generally higher than in the Ankasa Series when either of both of the synthetic fertilizers were added. Liming the soil with $CaCO_3$ increased P uptake from 1.55 g in the un-limed soil to 17.13 g which upon addition of the biochar equivalent P from TSP was suppressed to 12.58 g. Addition of both P and N to the $CaCO_3$ limed soil increased root P uptake to 21.62 g.

The addition of biochar to the Tikobo Series though increased root P uptake above that of the un-amended had values significantly lower than that in the $CaCO_3$ limed soil. When TSP was added to the biochar amended Tikobo Series at 30 kg P/ha, P uptake increased over that when synthetic P was not applied. On addition of synthetic P to the biochar amended Tikobo Series, root uptake was in the order of RH700N0P30 > CC700N0P30 > RH500N0P30 = CC500N0P30. Nitrogen application to the biochar limed and $CaCO_3$ limed soils increased root P uptake over when the soil was not fertilized. However, these uptake P values were expectedly lower than when synthetic P was added. On addition of synthetic P and N to the biochar limed Tikobo Series, P uptake of roots were significantly enhanced with the CC500N10P30 and RH500N10P30 treatments having the highest P root uptake.

4.11.2 Shoot P Uptake

Shoot P uptake recorded after harvest is presented in Table 4.14. In the two soils, the amended soils were significantly ($p<0.05$) higher than the un-amended soil. The un-amended soil recorded shoot P uptake of 2.15 mg/pot. Soil amended with rice husk biochar charred at 700 ^{o}C with the addition of 30 kg P/ha synthetic fertilizer gave the highest shoot P uptake (16.24 mg/pot). Shoot P uptake was generally higher in Ankasa Series amended with the biochar types than the $CaCO_3$ and the un-amended soils.

Tikobo Series on the other hand, recorded shoot P uptake of 3.46 mg/pot to 25.67 mg/pot. The un-amended soil recorded the lowest shoot P uptake of 3.46 mg/pot. Soil amended with rice husk biochar charred at 700 ^{o}C with the addition of 10 kg N/ha and 30 kg P/ha synthetic fertilizer gave the highest P uptake of 25.67 mg/pot. Generally, shoot P uptake was higher in soils amended with the biochar types than in the $CaCO_3$ and the un-amended soils. All the amended soils were significantly ($p<0.05$) different from the un-amended soils.

4.12. Soil Residual Total C, Total N, Total P and Available P.

The residual total C, total N, total P and available P for Ankasa Series are presented in Table 4.15. The initial organic carbon content of the Ankasa Series (Table 1) was 15.3 g/kg and this did not vary much from the residual carbon content of 15.95 g/kg after harvest. The unfertilized $CaCO_3$ amended treatment (LiN0P0), the $CaCO_3$ amended with P equivalent from biochar (LiN0BEP) and the N fertilized $CaCO_3$ amended soil (LiN10P0) also had statistically similar carbon content of 16.23 g/kg, 16.25 g/kg and 17.16 g/kg, respectively after harvest. The LiN10BEP which is the N and P

Table 4. 14: Effect of Amendments on Shoot P Uptake*

TREATMENTS	SHOOT P UPTAKE (mg/pot)	
	Ankasa	Tikobo
Un-amended	2.15a	3.46a
LiN0P0	6.79cd	12.59cd
CC500N0P0	9.80e	6.32b
CC700N0P0	8.72de	12.71cd
RH500N0P0	3.76b	18.49ef
RH700N0P0	8.96de	14.47de
LiN0BEP	7.14cd	11.55cd
CC500N0P30	6.23c	17.34ef
CC700N0P30	8.44de	12.82c
RH500N0P30	6.54cd	16.87e
RH700N0P30	12.75f	14.88de
LiN10P0	12.49f	13.84d
CC500N10P0	4.98bc	11.37cd
CC700N10P0	8.17d	11.55cd
RH500N10P0	7.44c	17.15e
RH700N10P0	15.19g	16.44de
LiN10BEP	7.24cd	10.02c
CC500N10P30	8.33d	20.00f
CC700N10P30	8.32de	19.21ef
RH500N10P30	12.86f	19.26ef
RH700N10P30	7.97d	25.67g
CV%	16.10	

*Li = $CaCO_3$; N0 = zero N application; P0 = zero P application; P30 = TSP applied at a rate of 30 kg P/ha; BEP = Biochar Equivalent P application from TSP; N10 = 10 kg N/ha from urea. Means with the same alphabet are not significantly (p>0.05) different.

fertilized $CaCO_3$ amended Ankasa Series had a higher carbon content (20.24g/kg) than the original soil (15.95). The biochar amended Ankasa soils had significantly ($p<0.05$) higher residual total carbon contents than the $CaCO_3$ limed soils. The residual carbon contents in the Ankasa Series irrespective of synthetic fertilization was generally higher in the RH amended soils than the CC amended soils in the order of RH > CC500 = CC700

Total C recorded on biochar amended soils were significantly ($p<0.05$) different from the un-amended soil. Rice husk biochar charred at 500 ^{0}C without addition of N and P fertilizers gave the highest total C (52.79 g/kg).

As was observed for total carbon contents in the residual soil total N (TN) was generally statistically ($p>0.05$) similar in all the $CaCO_3$ limed and un-amended soils with TN values between 0.76 g/kg and 0.92 g/kg. The residual TN contents in the un-amended and CaCO3 limed soil were lower than the initial TN (1.6 g/kg). The residual TN in the biochar amended soils though lower than the original soil to which the material was amended, was higher than in the $CaCO_3$ limed soils with concentrations between 1.07 g/kg and 1.4 g/kg.

Total P (TP) in the residual un-amended (171.3) Ankasa Series did not vary much from that of the original soil (164 g/kg). The $CaCO_3$ limed soils irrespective of whether they had been fertilized or not had higher TP concentrations ranging between 252.6 and 281 g/kg. The higher TP concentrations in the $CaCO_3$ limed soils than the un-amended soils also reflected in a much higher available P in the $CaCO_3$ limed soils with available P increasing from 1.54 g/kg in the original un-amended Ankasa Series to between 6.65 and 13 g/kg. In fact, the $CaCO_3$ limed soil but

Table 4. 15: Effect of Amendments on TC, TN, TP and AP in Ankasa Series*

TREATMENTS	TC(g/kg)	TN(g/kg)	TP(mg/kg)	AP(mg/kg)
Un-amended	15.95a	0.92b	171.30a	3.25a
LiN0P0	16.23a	0.87ab	281.00b	6.65a
CC500N0P0	33.11cd	1.22d	344.90f	13.55bc
CC700N0P0	31.73c	1.25de	291.70c	15.90c
RH500N0P0	52.79g	1.20cd	307.2c	26.60f
RH700N0P0	45.99f	1.35def	324.6d	22.00de
LiN0BEP	16.25a	0.90ab	264.30b	13.00b
CC500N0P30	35.83cd	1.34def	309.4c	19.70de
CC700N0P30	35.33d	1.29def	302.9c	20.65de
RH500N0P30	37.88de	1.33def	301.1c	27.20fg
RH700N0P30	45.35f	1.32def	314.4d	31.00g
LiN10P0	17.16ab	0.91b	252.60b	10.15b
CC500N10P0	36.16d	1.40f	311.00c	19.45d
CC700N10P0	32.83cd	1.25de	319.6d	16.30cd
RH500N10P0	39.71e	1.07c	322.1d	25.90ef
RH700N10P0	44.25f	1.28def	303.3c	22.95e
LiN10BEP	20.24b	0.76a	254.00b	12.30b
CC500N10P30	39.77e	1.37ef	297.2cd	20.00de
CC700N10P30	34.07c	1.14cd	320.8d	23.6ef
RH500N10P30	44.39f	1.14cd	304.5c	30.45g
RH700N10P30	42.53ef	1.25de	327.7df	23.05e
CV%	10.00	13.17	5.60	13.70

*Li = $CaCO_3$; N0 = zero N application; P0 = zero P application; P30 = TSP applied at a rate of 30 kg P/ha; BEP = Biochar Equivalent P application from TSP; N10 = 10 kg N/ha from urea. Means with the same alphabet are not significantly (p>0.05) different.

a.

unfertilized Ankasa Series (LiN0P0) had an almost four-fold increase in available P whereas its counterpart that had received 10 kg/ha N increased more than six fold to 10.15 mg/kg. The biochar amended soils conspicuously had statistically ($p<0.05$) much high TP and available P concentrations in the residual Ankasa Series. Total P concentration in the biochar amended soils almost doubled over that of the initial soils as values ranged between 291.7 mg/kg and 344 mg/kg. Concomitantly, available P concentrations in the biochar amended soils were high. Available P were higher in the RH amended soils than their CC amended counterparts. Expectedly, residual available P in the TSP amended soils were higher than the soils that had not been fertilized with P.

The initial total carbon content in the Tikobo Series of 5.4 was not significantly ($p>0.05$) different from the residual un-amended soil and its $CaCO_3$ limed counterparts (Table 4.16). On amendment with biochar which had between 387.1 and 602.9 g/kg C (Table 2), residual C contents of the Tikobo Series increased over that of the un-amended soil to values between 18.88 g/kg to 21.88 g/kg. There were generally no significant ($p>0.05$) differences among biochar amended Tikobo soil Series (Table 4.16). Total N which was 1.2 g/kg in the initial Tikobo Series decreased to 0.35 g/kg in the residual un-amended soil and to lower concentration (0.13 -0.16 g/kg) in the $CaCO_3$ amended Tikobo Series irrespective of whether they were fertilized or not. The TN in the biochar amended soils (0.42 - 0.62 g/kg) was significantly ($p<0.05$) higher than in the un-amended soils though lower than the initial soil.

The residual TP in the un-amended Tikobo Series (127.4 mg/kg) was higher than the initial value (101.4 mg/kg) but significantly ($p<0.05$) lower than the $CaCO_3$ amended soils (152.8 mg/kg – 174.1 mg/kg). The increase in TP in the $CaCO_3$ limed soils also reflected in an increase in their.

Table 4. 16: Effect of Amendments on C, N, TP and AP in Tikobo Series*

TREATMENTS	TC(g/kg)	TN(g/kg)	TP(mg/kg)	AP(mg/kg)
Un-amended	7.42a	0.35b	127.40a	3.15a
LiN0P0	7.31a	0.18a	170.30bc	7.80b
CC500N0P0	20.47b	0.62c	203.00d	13.55c
CC700N0P0	19.32b	0.57c	235.70e	15.90cd
RH500N0P0	20.71b	0.51c	253.40ef	25.65ef
RH700N0P0	18.88b	0.47bc	257.80f	22.55e
LiN0BEP	7.22a	0.16a	174.10c	10.05b
CC500N0P30	19.32b	0.55c	256.90f	21.30de
CC700N0P30	19.49b	0.58c	249.70ef	19.70de
RH500N0P30	20.17b	0.48bc	242.50ef	28.80f
RH700N0P30	20.89b	0.44bc	239.90ef	31.95f
LiN10P0	7.64a	0.14a	158.90bc	5.50a
CC500N10P0	19.64b	0.60c	252.70ef	18.70d
CC700N10P0	21.88b	0.55c	255.30f	15.70cd
RH500N10P0	19.86b	0.47bc	244.80ef	25.90ef
RH700N10P0	20.45b	0.42bc	247.70ef	22.95e
LiN10BEP	7.66a	0.13a	152.80b	9.50b
CC500N10P30	19.55b	0.55c	248.50ef	22.90e
CC700N10P30	19.96b	0.54c	252.80ef	23.90e
RH500N10P30	22.20b	0.46bc	250.10ef	30.45f
RH700N10P30	20.78b	0.45bc	247.90ef	23.05e
CV%	10.00	13.17	5.60	13.70

*Li = $CaCO_3$; N0 = zero N application; P0 = zero P application; P30 = TSP applied at a rate of 30 kg P/ha; BEP = Biochar Equivalent P application from TSP; N10 = 10 kg N/ha from urea. Means with the same alphabet are not significantly (p>0.05) different.

respective available P. Available P increased from 2.71 in the initial soil to between 5.5 mg/kg and 10.05 mg/kg. The residual TP in the biochar amended Tikobo Series was higher than the $CaCO_3$ and the un-amended soils as presented in Table 4.16. Residual TP concentrations in biochar amended soils (203 mg/kg – 257.8 mg/kg) were two times higher than in the initial soil (101.4 mg/kg). As a consequence of the higher TP in the biochar amended Tikobo Series, available P increased in the soil. Increases in available P concentrations five times more than that in the initial soil. In fact, RH500 application without any other form of fertilization increased available P concentrations almost 9.5 times to 25.65. Just as was observed in the Ankasa Series, RH amended soil increased residual available P concentrations more than its CC counterparts.

4.12. Effect of Amendment on Soil Residual Exchangeable Acidity and pH

The soil residual pH and exchangeable Al for both Ankasa and Tikobo Series are summarized in Table 4.17. Concentration of Al in the initial Ankasa Series and Tikobo Series used for the study were 1.31 and 0.4 cmol/kg, respectively. After harvest, the residual exchangeable Al did not change in the un-amended soils. The residual pH of the un-amended soils was 4.1 and 4.6, respectively just as observed in the initial soil prior to crop cultivation. After liming with $CaCO_3$, the residual Al reduced to between 0.47 and 0.59 cmol/kg with a concomitant increase in residual pH of between 4.7 and 5.0 for the Ankasa Series. Amending the Ankasa Series with biochar reduced Al concentration from 1.31 cmol/kg to between 0.15 and 0.59 cmol/kg. The residual Al in the unfertilized amended biochar Ankasa Series were the least ranging between 0.15 and 0.32 cmol/kg. These least residual exchangeable Al were accompanied by corresponding higher pH between 4.9 and 5.2. The fertilized biochar amended Ankasa series generally had higher residual Al contents when compared to the unfertilized biochar amended soils.

Table 4. 17: Effect of Amendment on Residual Al and pH*

TREAMENTS	Al(cmol$_c$/kg)		pH	
	ANKASA	TIKOBO	ANKASA	TIKOBO
Un-amended	1.27g	0.39e	4.1	4.6
LiN0P0	0.47e	0.21cd	4.7	4.8
CC500N0P0	0.24bc	0.00a	5.1	5.4
CC700N0P0	0.32cd	0.00a	4.9	5.5
RH500N0P0	0.29c	0.00a	4.9	5.8
RH700N0P0	0.15a	0.00a	5.2	5.8
LiN0BEP	0.55f	0.24d	4.5	4.7
CC500N0P30	0.31cd	0.00a	4.8	5.7
CC700N0P30	0.35cd	0.00a	5	5.8
RH500N0P30	0.20ab	0.00a	4.8	5.6
RH700N0P30	0.29c	0.00a	4.9	5.5
LiN10P0	0.59f	0.15c	4.6	4.9
CC500N10P0	0.35cd	0.00a	5.1	5.6
CC700N10P0	0.30cd	0.00a	4.8	5.7
RH500N10P0	0.29c	0.00a	5.1	5.7
RH700N10P0	0.22b	0.00a	4.9	5.6
LiN10BEP	0.53e	0.09b	4.8	5
CC500N10P30	0.36d	0.00a	4.7	5.8
CC700N10P30	0.41de	0.00a	5.2	5.8
RH500N10P30	0.25bc	0.00a	4.9	5.8
RH700N10P30	0.37d	0.00a	5.1	5.6
CV%		18.10		

*Li = $CaCO_3$; N0 = zero N application; P0 = zero P application; P30 = TSP applied at a rate of 30 kg P/ha; BEP = Biochar Equivalent P application from TSP; N10 = 10 kg N/ha from urea. Means with the same alphabet are not significantly (p>0.05) different.

Liming the Tikobo series with $CaCO_3$ reduced Al concentrations from 0.40 cmol/kg to levels between 0.09 cmol/kg and 0.24 cmol/kg with a corresponding residual pH between 4.8 and 5. Amending the Tikobo Series with biochar, irrespective of whether the soil had been fertilized or not, reduced exchangeable Al to undetectable levels in the soil after harvest with a concomitant rise in residual pH to between 5.4 and 5.8

CHAPTER FIVE

5 DISCUSSION

5.1 Soil Characterization

The higher sand but lower clay contents in the Tikobo Series than the Ankasa Series is as a result of the different parent materials from which the two soils were developed. Tikobo Series has developed from tertiary sand whilst Ankasa Series has been developed from granite (Dwomo and Dedzoe, 2010). It therefore stands to reason that the Tikobo Series has more sand. Ankasa Series was sampled from a forest reserve and as a result of its high litter fall, organic carbon content was almost 2.8 times more than that in the Tikobo Series. It is, therefore, a matter of consequence that coupled with its higher clay content, the Ankasa Series will have a lower bulk density than the Tikobo series as observed in their characterizations. Hudson (1994) reported decrease in bulk density of soils with different textural classes due to the addition of organic matter.

The extremely acid and lower pH in Ankasa Series compared to the Tikobo Series is as a result of the higher exchangeable Al in the former soil. The differences in pH in salt and water (i.e. $\Delta pH = pH_{CaCl_2} - pH_{H_2O}$) gave negative values which show that, there are negative charges on the surfaces of both soils (Nartey, *et al.*, 1997).

The Tikobo and Ankasa Series both occur in the tropical evergreen rainforest of Ghana. However, the Ankasa Series is from a forest reserve where there is continuous litterization from the vegetative cover. The thick forest cover creates a micro climate with relatively lower temperature compared to the fallow plots from which the Tikobo Series was sampled. With the associated lower pH, there is likely to be lower low microbial activity and therefore slower decomposition rate of organic matter and this may, in part explain the higher organic carbon content in the Ankasa Series (Giller *et al*. 2001). The higher CEC of the Ankasa Series over the Tikobo Series is due to the higher organic carbon and clay contents of the former. The CEC which is a measure of charges at the colloidal surfaces was determined in this study by the ammonium acetate method at pH 7. This pH is 2.8 pH units above that in water for Ankasa and 2.1 pH above that for Tikobo.The ECEC on the other hand, is a measure of the 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 pH 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 This may partly account for the higher CEC than ECEC in the two soils.

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 54.8% and 24.54% for Ankasa and Tikobo Series, respectively. The Al saturation of the soils which is higher than the critical of 15% for optimum soya bean production (Fageria and Baligar, 2008) is likely to cause soya bean grown on especially Ankasa Series to have restricted root development, poor nodulation and general poor growth in the Ankasa Series (Kochian, 1995).

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 status.

5.2 Biochar Characterization

The slightly higher total bases in the corn cob feedstock (0.93%) than that in the RH feedstock (0.9%) might have accounted for the higher pH of 6.8 in the CC feedstock than the RH feedstock value of 6.1. Upon charring of the two feedstocks at temperatures of 500 ^{o}C and 700 ^{o}C, there was liberation of three forms of bases viz. total, exchangeable and soluble. These liberated bases might have accounted for the rise in pH of the four biochar types from neutral to alkalinity. 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 and in effect these acids react with basic cations in the feedstocks to form alkaline salts which increase the pH of biochar (Streubel, 2011; Shinogi and Kanri, 2003).

Total Na and K were higher in the CC feedstock than the RH and consequently on charring the CC biochar types had higher total Na and K. Corn cob is from a fruit which tends to accumulate more sugar and hence K, especially in the pith (Purseglove, 1968) whereas rice husk though also from a grain and hence a fruit contains more Si. It is, therefore, not surprising that the CC feedstock and biochar types contain more K than their RH counterparts. The exchangeable Na and K were also generally higher in the CC biochar types than the RH biochar types implying that for availability of K, the CC biochar materials should be the preferred choice. However, the CC biochar types may impose drainage problems because of their high Na content that may disperse soils. Such CC biochar types should not be applied on salt affected soils. The RH feedstock had higher Ca and Mg contents and consequently higher contents of these secondary major nutrients in the total fractions upon charring. Joseph *et al.* (2010), has reported that most biochars are often alkaline and therefore increase soil pH after application. The high pH of corn cob biochar makes it suitable to lime highly acidic soils whilst rice husk biochar can be used to lime slightly acid soils.

The total carbon contents of the biochar types were higher than their respective un-charred feedstocks. High heating rates have been found to provide a shorter time for the dehydration reactions and the formation of less reactive anhydrocellulose, leading to the production of biochar with a higher carbon yield (Zanzi, 2001). Generally, corn cob biochar types had higher carbon content than rice husk biochar types due to the high carbon content of the corn cob feedstock. 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 (Shinogi and Kanri, 2003) and hence more recalcitrant carbon accounting for the higher accumulation of C after charring.

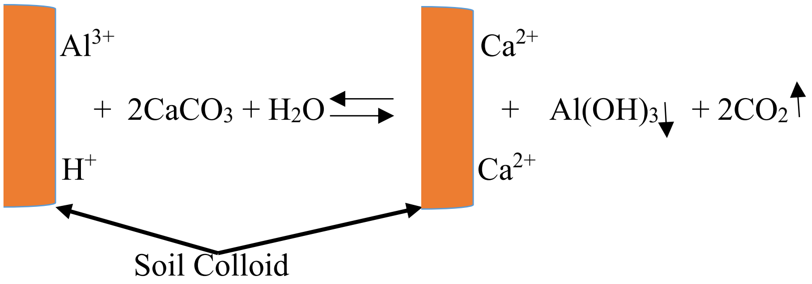
The total nitrogen (TN) content of the biochar types as shown in Table 4.2 was inversely related to pyrolysis temperature. The TN content decreased with increasing pyrolysis temperature. The higher N in the un-charred feedstocks than the biochar can be attributed to volatilization of N on pyrolysis. Nitrogen is sensitive to heat and is subsequently volatilized leading to low N content of the biochar types. Corn cob is more lignified than rice husk and consequently more resistant to charring than RH. It is, therefore, not surprising that CC biochar types have more TN than their RH counterparts. The CC biochar types have high C: N ratio which may reduce microbial decomposition and restrict release of N from the biochar when added to the soil. According to Lehman and Joseph (2007), charring leads to carbonization of the biochar types culminating in high carbon contents per unit mass. With the concomitant decrease in their respective N contents, it is expected that the biochar types will have low 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 for a very long time.

The total P contents in the biochar were far higher than in the feedstocks from which they were charred and this was as a result of conversion of organic P to the inorganic form during pyrolysis. The release of the inorganic orthophosphate ions also combines with the liberated Ca to form Ca-P compounds which are not readily soluble and hence increasing significantly the total P contents of the biochar (Lehman, 2007). Shenbagavalli and Mahimairaja (2012) reported that charring of biomass can greatly enhance P availability from plant tissue by cleaving organic phosphorus bonds, to form soluble P salts in the charred materials. The rice husk biochar types generally had higher total P content than the corn cob biochar due to the higher inherent P content in the former's feedstock. The very high Olsen P of about 2000 mg/kg in the four biochar types coupled with their high pH holds promise for exploitation of the materials for use as P source in tropical acid soils with high P sorption capacity

5.3 Effect 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 Ankasa and Tikobo Series 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 soils as depicted in equation 5.1:



$$\begin{matrix}Al^{3+}\\ \\ H^{+}\end{matrix} + 2CaCO_3 + H_2O \rightleftharpoons \begin{matrix}Ca^{2+}\\ \\ Ca^{2+}\end{matrix} + Al(OH)_3\downarrow + 2CO_2\uparrow \qquad [5.1]$$

The replacement of Al^{3+} and H^{+} by Ca^{2+} is corroborated by decreases in Al^{3+} and H^{+} with concomitant increases of Ca^{2+} in solution of the two soils. This is further supported by significant correlation coefficient (R) of -0.78** between exchangeable Al and Ca for Ankasa Series and -0.57** for Tikobo Series (Figure 18). The corresponding respective coefficient of determinations (R^2) of 0.607 for Ankasa Series and 0.321 for Tikobo Series imply that 60.7% and 32.1% respective decreases in Al are attributable to Ca from the amendments. Thus Ankasa Series responds more to Ca for Al replacement than Tikobo Series.

Apart from Ca, the four biochar types had Mg, Na and K. These three other basic cations might 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 are corroborated by several authors (Novak *et al.*, 2009; Joseph *et al.*, 2010; Farrell *et al.*, 2013; Masto *et al.*, 2013; Masulili *et al.*, 2016). A regression of the sum of Na, K and Mg in soil solution of the biochar amended Ankasa and Tikobo against their respective Al concentrations showed high negative correlation coefficient of -0.91** for Ankasa Series and -0.81** for Tikobo Series (Figure 19). Regressing the sum of the three bases on pH showed a positive correlation coefficient of 0.74** for Ankasa Series and 0.81** for Tikobo Series (Figure 20). Regressing soluble Al on soluble Mg gave R = -0.91**and pH versus Mg giving R = 0.83** for Ankasa Series (Figure 21a and 21b). The R value was 0.84** for Mg against pH and -0.77** for Mg against Al (Figure 22a and 22b). The higher correlation between Mg and Al in the biochar amended soils than Ca between 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 $CaCO_3$.

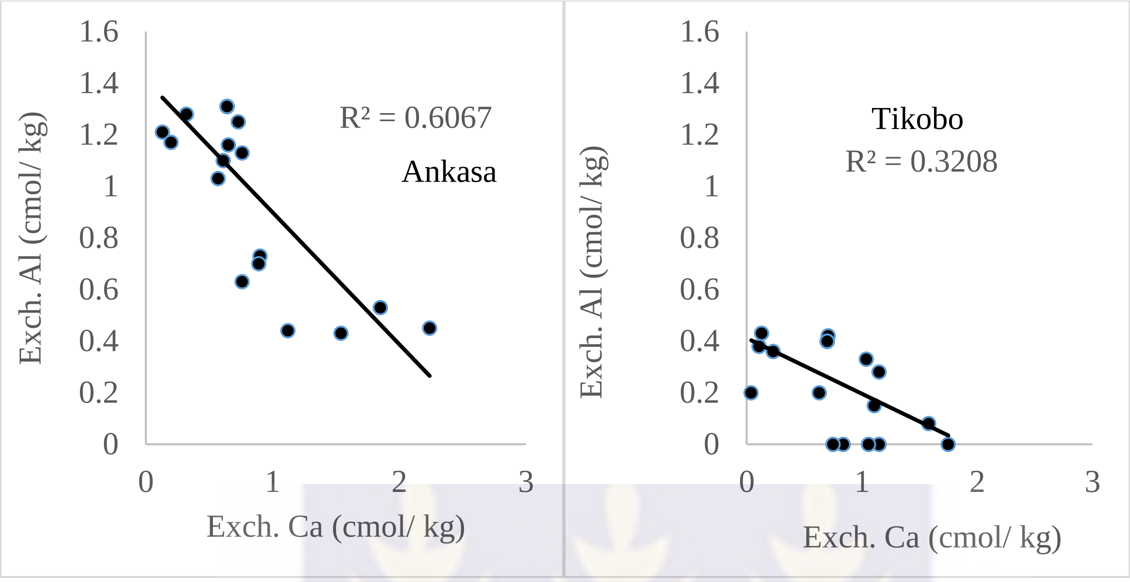


Figure 18. Relationship between exchangeable Ca and exchangeable Al.

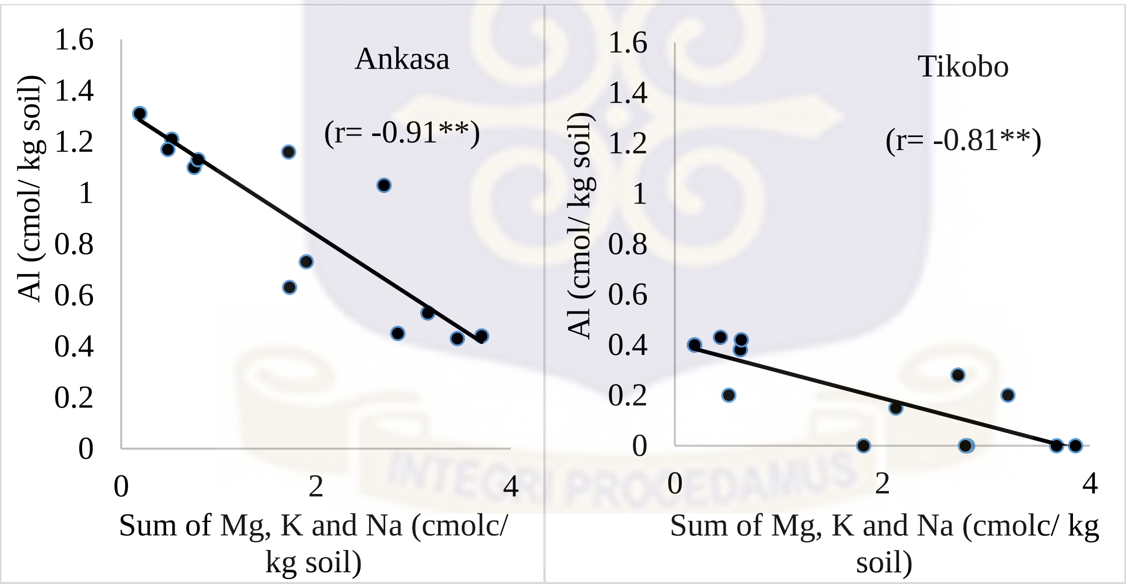


Figure 19. Relationship between sum of bases (Mg, K, Na) and exchangeable Al.

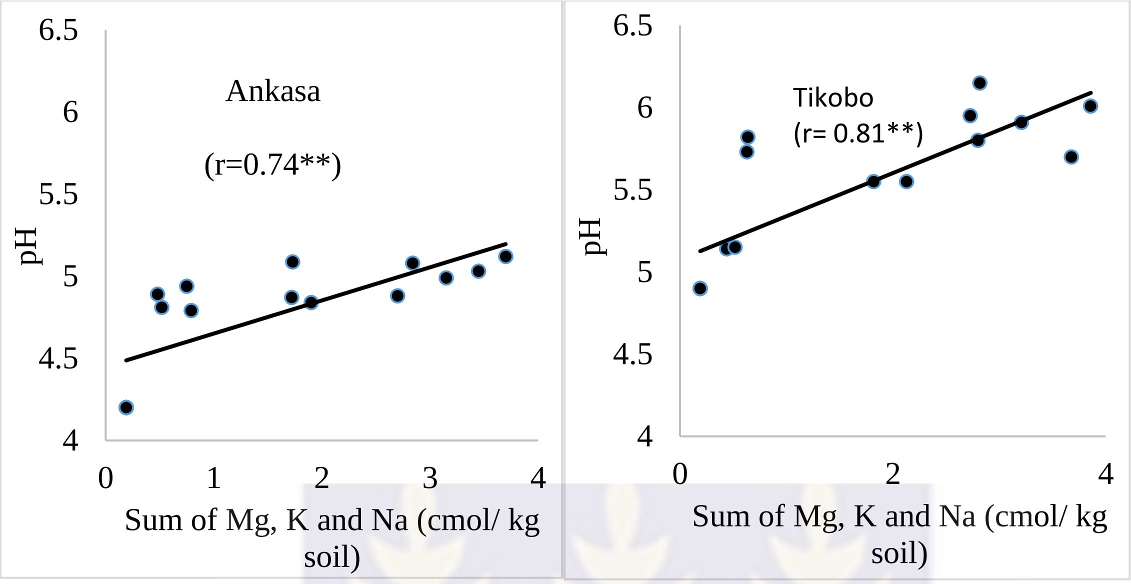
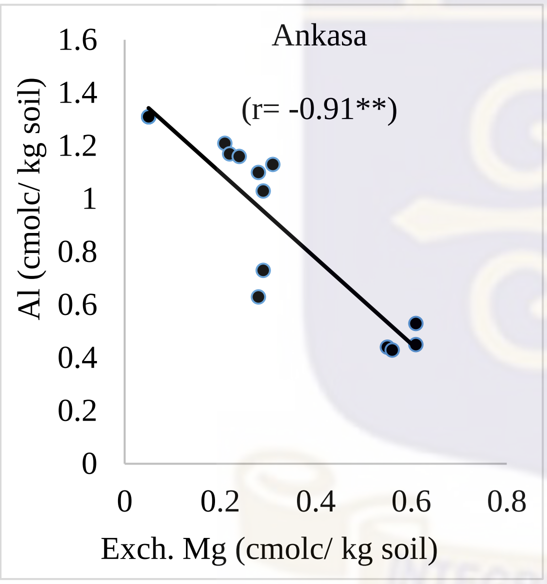


Figure 20 Relationship between sum of bases (Mg, K, Na) and pH.



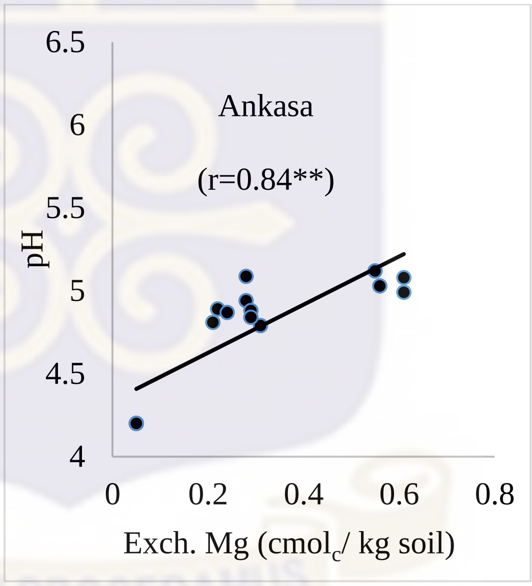


Figure:21a: Relationship between Exchangeable Al and Mg

Figure 21b: Relationship between pH and Mg

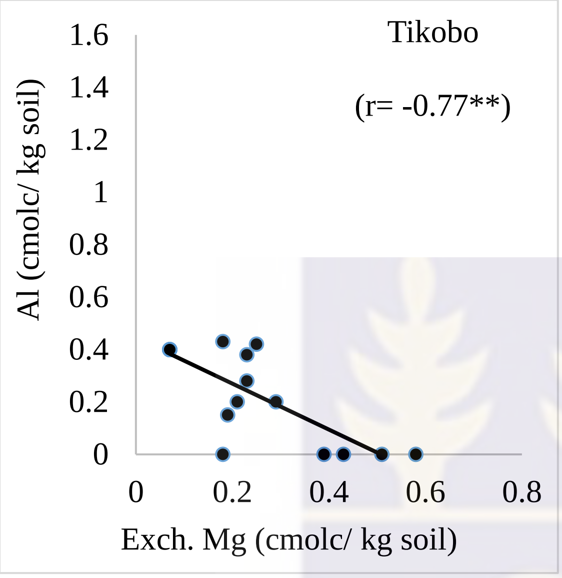


Figure 22a: Relationship between exchangeable Al and Mg

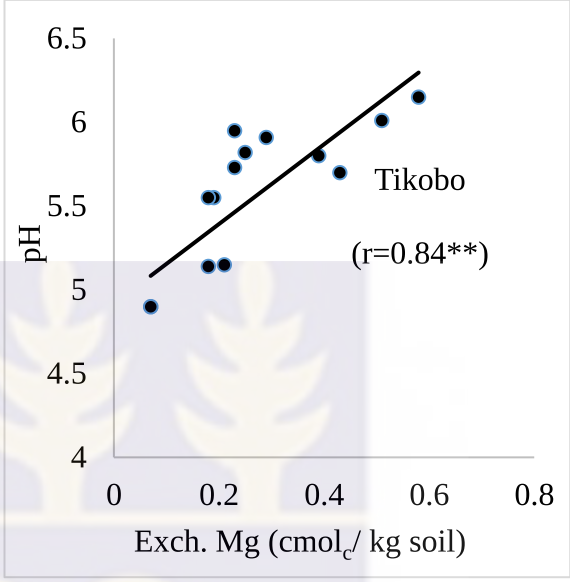


Figure 22b: Relationship between pH and Mg

In the $CaCO_3$ amended soil, Tikobo changed from being very strongly acid to strongly acid whilst Ankasa became strongly acid. The slow response of Ankasa Series to liming was as a result of its high organic matter content which was about 2.8 times higher than that in Tikobo. This moderately high organic carbon content (15.3 g/kg) might have acted as a buffer resisting changes in pH as explained by Stewart *et al.* (2013) and 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 Ankasa and Tikobo Series to the same rate of lime application during the incubation period. The increase in pH on amendment of Ankasa Series and Tikobo Series 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 Ankasa and Tikobo Series might have led to the solubility of hitherto precipitated Mg and Na leading to the increases in the concentration of the two basic cations soil solution of the $CaCO_3$ amended Ankasa Series. 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 actions 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 solution. The highest concentrations of available Na in the two soils upon amendment with the biochar samples is due in part to its relatively higher abundance as a soluble cation in the four biochar types (0.04% - 0.08% as opposed to between 0.01% and 0.02% for Ca, K and Mg). Sodium, among the four bases is the most soluble (Evangelou, 1998) and with increase in pH should be the most abundant cation.

5.4 Effect of Liming on P Availability

The increase in P availability of the $CaCO_3$ limed Ankasa and Tikobo Series is attributed to the decrease in Al concentration with a consequential increase in solution pH. The $CaCO_3$ limed Ankasa Series decreased in Al saturation from 54.8% to 29.3% whilst the Tikobo decreased from 24.54% to 4.91%. These respective decreases led to pH increases from 4.2 to 4.7 and 4.9 to 5.2 respectively. These decreases in Al saturation with concomitant increases in pH might have led to solubilization of some of the total P in the two soils. These increases in available P concentrations as a result of decreases in Al concentration is evident in Figures 23. The significant negative correlation implies that as Al decreases availability of P increases. The respective coefficient of determinations R^2 values were 0.95 and 0.98 respectively for Ankasa Series and Tikobo Series showing that between 95% and 98% of the available P in the $CaCO_3$ limed soils is accounted for by decreases in soluble Al.

The reasons accounting for the sharp increase in P availability in biochar amended soils is two-fold. Firstly, the liming effects of the biochar on the two soils were far higher than that of the $CaCO_3$ because of the additional bases inherent in the biochar as previously discussed in section 5.3. Thus, Al saturation in the Ankasa Series was reduced from 54.8% to between 18% and 22%

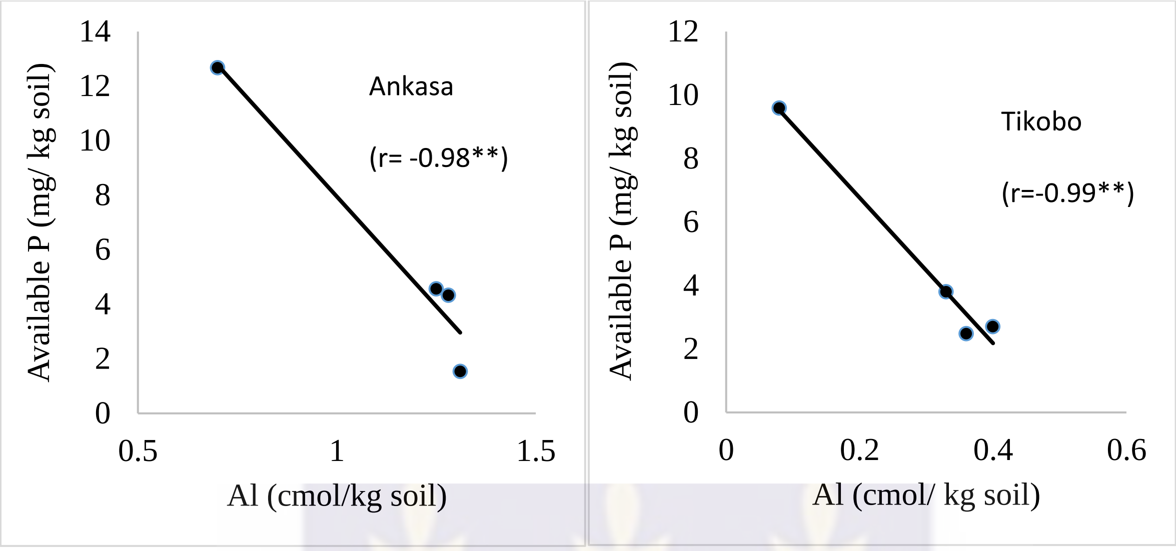


Figure 23 Relationship Between Available P and Al

whilst the Tikobo Series reduced to non-detectable levels. These lower Al saturation in the biochar amended soils with the accompanying increase in pH may have led to higher dissolution of the total P in the soils into available forms. Secondly, the biochar types contain more than 2000 mg/kg available P an equivalent of 120 kg P /ha was from each biochar type. These high levels of available P added may have also led to the high availability of P in the biochar amended soils. The increase in soil available P levels following biochar application has been documented (Özenç and Özenç, 2009; Wang *et al.*, 2012; Darfour, 2016).

5.5. Effect of Soil Amendments on Plant Growth Parameter

The high Al saturation of 54.8% which is above the critical limit of 15% for optimum soya bean cultivation (Fageria and Baligar, 2008) coupled with the low pH in water of 4.2 and low concentration of Bray available P of 1.54 mg/kg contributed to restricted root development and expansion. It is, therefore, not surprising that the root volume in the un-amended Ankasa Series (1.2 cm^3) was the least.

On amending Ankasa Series with $CaCO_3$ for six weeks, pH rose to 4.7 and Al saturation decreased to 29.3% with a concomitant increase in Ca to 0.89 cmol/kg and Mg to 0.35 cmol/kg. Available P then increased from 1.54 to 12.67 mg/kg. These contributed to the 2.7 times increase root volume in the Ankasa to 3.25 cm^3. Amending the Ankasa Series with the biochar types increased pH from 4.2 to about 5.2. This increase in pH reduced Al saturation to between 18 and 22% for the CC and RH biochar types. Correspondingly, Ca concentration increased to about 2 cmol/kg and available P to about 30 mg/kg. These increases led to the 2.6 times increases in root volumes in the biochar amended soils over the un-amended counterpart. The fact that these root volumes are similar to those in the $CaCO_3$ amended soils implies that the biochar types are equally effective as the conventional $CaCO_3$ in promoting root development.

Conventional lime amendment to Tikobo Series increased pH to 5.2 from 4.9 which resulted in reduction in Al saturation to 20%. Consequently, root volume increased from 1.45 cm^3 to 3.33 cm^3. On amendment with the biochar types, however, pH increased from 4.9 to between 5.7 and 6.2 with Al saturation reducing to undetectable levels. These translated into large root development accounting for root volume in the biochar amended Tikobo series increasing from 1.45 cm^3 to between 3.89 and 5.99 cm^3. A significant negative correlation coefficient of 0.747* between root volume and Al in solution of the two soils corroborates the assertion that as Al decreases, root volume increases.

On liming with either $CaCO_3$ or biochar, pH of Ankasa increased to between 4.7 and 5.2 with a corresponding increase in P availability from a paltry 1.54 mg/kg to between 12 mg/kg and 32 mg/kg. It thus appears that other factors such as pH and Al concentration are more important than P availability in root expansion especially in acid soils. The fact that when the synthetic P at the biochar P equivalent applied to the $CaCO_3$ amended Ankasa Series gave statistically similar root volumes as when the soil was amended with biochar show that the P in the biochar was as effective as synthetic P for root development.

The shoot dry matter of soya bean plants harvested from the un-amended Ankasa and Tikobo Series were relatively low i.e. 0.22 and 0.26 g, respectively, mainly because of their lower root volumes which hindered exploitation for nutrients. On amendment with $CaCO_3$, shoot dry matter in Ankasa Series increased to 0.53 g as a result of an increase in root volume from 1.2 cm^3 to 3.25 cm^3. On amendment of biochar to the Ankasa and Tikobo Series, shoot dry matter also increased because of the liming effect which reduced Al saturation and hence increased root volume. A plot of shoot dry matter against root volume showed a positive correlation coefficient. Amending Tikobo with the biochar types also increased shoot dry matter to between 0.34 and 1.10 g.

Table 5.1 shows the shoot to root ratio of soya bean plants harvested from the $CaCO_3$ and biochar limed Ankasa and Tikobo Series. From the Table, it is clear that the plants from the Tikobo Series generally had higher shoot to root ratios than their counterparts from the Ankasa Series. The Ankasa Series having lower shoot to root ratio implies that P as a nutrient is relatively being channeled more into root development whilst the converse holds for the Tikobo Series. This might be a response of the plants to effect of presence of Al in the Ankasa soils. According to Martinez et al (2005) soya bean plants retain more phosphorus in their roots when under stress. This is corroborated by the relatively higher P uptake in roots than shoots of soya bean plants grown in Ankasa Series Tables 4.13. and 4.14. Addition of N to the limed soils irrespective of liming material increased shoot to root ratios indicating the effect of N in leaf production (Marschner, 1998)

Addition of extra 30 kg P/ha from TSP to the biochar amended Tikobo Series did not increase root volume over that in the biochar amended soil implying that the P in the biochar was adequate for root expansion at the pH between 5.7 and 6.2 in the Tikobo Series. The extra P might have been used in producing heavier roots as corroborated by heavier root masses in the TSP fortified biochar amended Tikobo Series. This is also reflected in the higher root P uptake in the plants grown on the TSP-biochar amended Tikobo Series.

The fact that on addition of TSP to the biochar amended Tikobo and Ankasa Series, only the RH700 treatment showed positive response of shoot dry matter to P could be an indication that the RH700 biochar type might be an ideal material for soya bean cultivation should inorganic fertilizer be

Table 5. 1: Shoot to Root Dry Weight Ratio on Ankasa and Tikobo Series*.

TREATMENTS	ANKASA	TIKOBO
Un-amended	1.05d	1.86l
LiN0P0	1.71k	0.75a
LiN10P0	0.92bc	2.17o
LiN0BEP	1.17ef	1.96m
LiN10BEP	1.00d	0.95c
CC500N0P0	0.83b	1.62j
CC500N10P0	1.35h	1.55i
CC700N0P0	1.13e	2.30p
CC700N10P0	1.15e	1.11d
RH500N0P0	1.21f	1.75k
RH500N10P0	1.28g	1.89l
RH700N0P0	0.69a	2.06n
RH700N10P0	0.87b	1.29f
CC500N0P30	1.69k	1.17e
CC500N10P30	1.26fg	0.85b
CC700N0P30	1.28g	0.94c
CC700N10P30	1.56j	1.55i
RH500N0P30	2.04l	1.14de
RH500N10P30	1.13e	0.97c
RH700N0P30	1.48i	0.83b
RH700N10P30	1.50ij	1.42g
CV (%)	2.8	

*CC500= corn cob biochar at 500 ^{o}C, CC700= corn cob biochar at 700 ^{o}C, RH500= rice husk biochar at 500 ^{o}C, rice husk biochar at 500 ^{o}C, P= phosphorus, N= nitrogen, BEP = biochar equivalent phosphorus, Li= agricultural lime. Means with the same alphabet are not significantly (p>0.05) different.

supplemented. This is further supported by the fact that it is only the RH700 that increased in shoot dry matter over its unfertilized counterpart upon addition of both synthetic N and P.

5.6. Liming and P Availability on Nodulation

Nodulation of soya bean occurred only in Tikobo Series. As shown in Figure 1, the pH of Ankasa series rose to 5.2 after the incubation with the liming materials. Ideal pH for soya bean growth and nodulation is near neutral. Therefore, pH of 5.2 will hinder nodulation in Ankasa Series. The fact that no nodules were found in plants grown in the Ankasa Series even though upon liming available P concentration had been increased from 1.54 mg/kg to a minimum of 12 mg/kg and residual available P in the soil was between 13 and 22 mg/kg (Table 4.15) confirms the assertion that pH and Al saturation are more important in nodulation and root development of legumes than P availability (Angle, 1998; Giller *et al.*, 1998).

Nodules formed in Tikobo Series could be attributed to the increase in the soils' pH as reflected at the end of the incubation period with values between 5.7 and 6.2. These increases in pH as already discussed led to reduction in Al concentration to undetectable levels promoting nodulation in the biochar amended Tikobo series. The RH700 proved to be yet a superior amendment for soya bean nodulation as without external P supplementation, it was the only amendment which produced soya bean with nodules.

The four biochar types all had similar available P concentrations of between 2162 mg/kg and 2378 mg/kg. On addition of extra 30 kg P/ha from TSP, there was suppression of nodulation in the RH700 amended Tikobo Series whilst the other three biochar types which hitherto could not produce plants with nodules had soya bean plants nodulating. The residual analyses showed that all the unfertilized biochar pots had available P ranging between 13.5 mg/kg and 26 mg/kg. It thus appears that factors other than pH, Al concentration in solution and available P studied might be involved in nodulation. Factors such as Mo concentration, microbial population and diversity, nitrogenase as an enzyme (Alexander, 1977) which had not been investigated in this study and addition of urea could be playing major roles in nodulation. Nodule numbers in the RH700 reduced to seven upon urea fertilization at 10 kg/ha showing the negative effect of readily available N addition to nodulation (Alexander, 1977). Inexplicably the additional N caused nodulation in the CC700 biochar amended soil when urea was added.

5.7. Residual Nutrients

To assess the effectiveness of the liming materials on P availability, the Apparent P Recovery Efficiency (APRE) was calculated according to the formula by Baligar, *et al.* (2007)

$$\text{APRE} = \frac{Nutrient\ uptake, F\ (mg) - Nutrient\ uptake\ C(mg) \times 100}{Quantity\ of\ nutrient\ applied\ (mg)} \qquad [5.1]$$

Where F = Uptake in soil at specific P application rate and

C = Uptake in un-amended soil

The APRE shows the ability of the plant to obtain P as a nutrient from the soil (Baligar, *et al.* ,2007). In calculating the APRE, the average equivalent available P (BEP) in 80 Mg/ha of biochar applied per pot was used as the amount of P added. This translated to 220 mg P per pot for both biochar and TSP as BEP. The APRE of the various fertilized amendments are shown in Table 5.1. The APRE in the two soils were generally very low and below 12% and this is corroborated by the

Table 5. 2: Apparent Phosphorus Recovery Efficiency in Ankasa and Tikobo Series*

	-------------EFFICIENCY (%)------------	
TREATMENT	ANKASA	TIKOBO
LiN0BEP	2.01	5.25
CC500N0P0	1.68	2.87
CC700N0P0	1.77	5.78
RH500N0P0	2.35	8.4
RH700N0P0	1.81	6.58
CC500N0P30	3.51	7.88
CC700N0P30	3.53	5.83
RH500N0P30	5.00	7.67
RH700N0P30	6.72	6.76
LiN10BEP	2.92	4.55
CC500N10P0	2.69	5.17
CC700N10P0	3.65	5.25
RH500N10P0	3.31	7.8
RH700N10P0	4.55	7.47
CC500N10P30	4.34	9.09
CC700N10P30	5.19	8.73
RH500N10P30	4.95	8.75
RH700N10P30	4.84	11.67

*CC500= corn cob biochar at 500 ^{o}C, CC700= corn cob biochar at 700 ^{o}C, RH500= rice husk biochar at 500 ^{o}C, rice husk biochar at 500 ^{o}C, P= phosphorus, N= nitrogen, BEP = biochar equivalent phosphorus, Li= agricultural lime higher residual total and available P in the soils after harvest. The Ankasa and Tikobo Series had initial total P contents of 164.0 mg/kg and 101.4 mg/kg, respectively. The residual P in the Ankasa Series was between 264.3 and 344.9 mg/kg and the Tikobo to between 170 and 257.8 mg/kg when the two soils were each amended with either biochar or $CaCO_3$ plus biochar equivalent P (BEP) from TSP i.e. LiNoBEP. This high residual P from that of their initial especially from Ankasa shows that most of the added P had been transformed or fixed into non available total P. The Ankasa series being an Oxisol has a very low pH of 4.2 and is high in soluble Al concentration (0.15cmol/kg - 0.55 cmol/kg) coupled with its relatively high sesquioxidic and kaolinite content, it stands to reason that added P recovery is low. Recoveries were slightly higher in the Tikobo Series because of its relatively higher pH and undetectable levels of Al. It is worthy of note that particularly in the biochar amended Tikobo Series with no form of synthetic P input, plants grown from the RH biochar types recovered more P. Recoveries from Tikobo Series were generally higher in the biochar amended than the $CaCO_3$ counterpart whilst the converse is true for the Ankasa Series. The biochar amended soils generally had higher residual available P and this holds promise for subsequent crop cultivation.

The biochar with their inherently high total carbon enhanced the organic carbon contents of the residual soil. The TC in the Ankasa series which was initially 15.3 g/kg had increased to 31.73 to 52.79 g/kg showing between 1.64% and 3.74% addition of organic carbon (Table 4.15) when amended with the four biochar types. The Tikobo series on the other hand, showed between 1.35% and 1.52% addition of organic carbon. The over 1% increase in organic carbon content in the Tikobo Series should improve on the physical properties of the soil considering its inherent high sand content. It also affirms the use of biochar in sequestration of atmospheric C into soil.

CHAPTER SIX

6 CONCLUSIONS AND RECOMMENDATION

6.1 Conclusions

The study has shown that anaerobic charring of rice husk at 500 ^{o}C and 700 ^{o}C produces biochar types with pH in water of 7.6 and 8.8, respectively. Charring of corn cob at the same temperatures produced biochar with pH in water of 10.7 and 11, respectively. Charring the two feedstocks at the two temperatures produced biochar with high concentrations of available P which could be exploited for use as fertilizer in crop cultivation. Corn cob biochar types sequester more carbon than the rice husk biochar types.

The study has revealed that the four biochar types were superior to conventional liming material i.e. $CaCO_3$ in liming Ankasa Series and Tikobo Series and therefore could be used as substitute for conventional agricultural lime.

Amending the soils with corn cob and rice husk biochar as liming materials resulted in significant increase in root volume, root and shoot dry matter in typical acid soils of Ghana. Nitrogen and P uptake can be enhanced by amending acid soils of Ghana with rice husk and corn cob biochar types charred at 500 and 700 ^{o}C. Corn cob and rice husk biochar could be used as P source for growth of soya bean especially in Tikobo Series. Apparent Phosphorus Recovery Efficiencies could be enhanced when soya bean grown on acid soils are fertilized with both biochar and synthetic P

6.2 Recommendation

In order to increase the pH of Ankasa series to 6 for soya bean production, it is recommended that the biochar application rate of corn cob and rice husk be increased above the 80 tonnes per hectare or char the materials at higher temperatures to liberate more basic cations for use. Farmers are advised to give at least a six-week equilibration period upon addition of biochar before planting. Further study on effect of the corn cob and rice husk biochar on growth and nodulation of soya bean in Tikobo Series should be conducted in the field to determine if similar results are attainable.

Subsequent study on growth and nodulation of soya bean upon amendment of biochar to acid soils, should investigate the effect of Mo, microbial population and nitrogenase enzyme on nodulation.

It is also recommended that different feedstocks such as cocoa pods which may have higher levels of Ca and Mg be used as liming materials in a bid to reduce the application rate. Further work should also be carried out to determine how long the liming effect of the biochar types used in the experiment would persist in the soils. It is also recommended for cost benefit analysis to be done for the use of the biochar types in place of the conventional lime and inorganic P fertilizer vis-à-vis yield.

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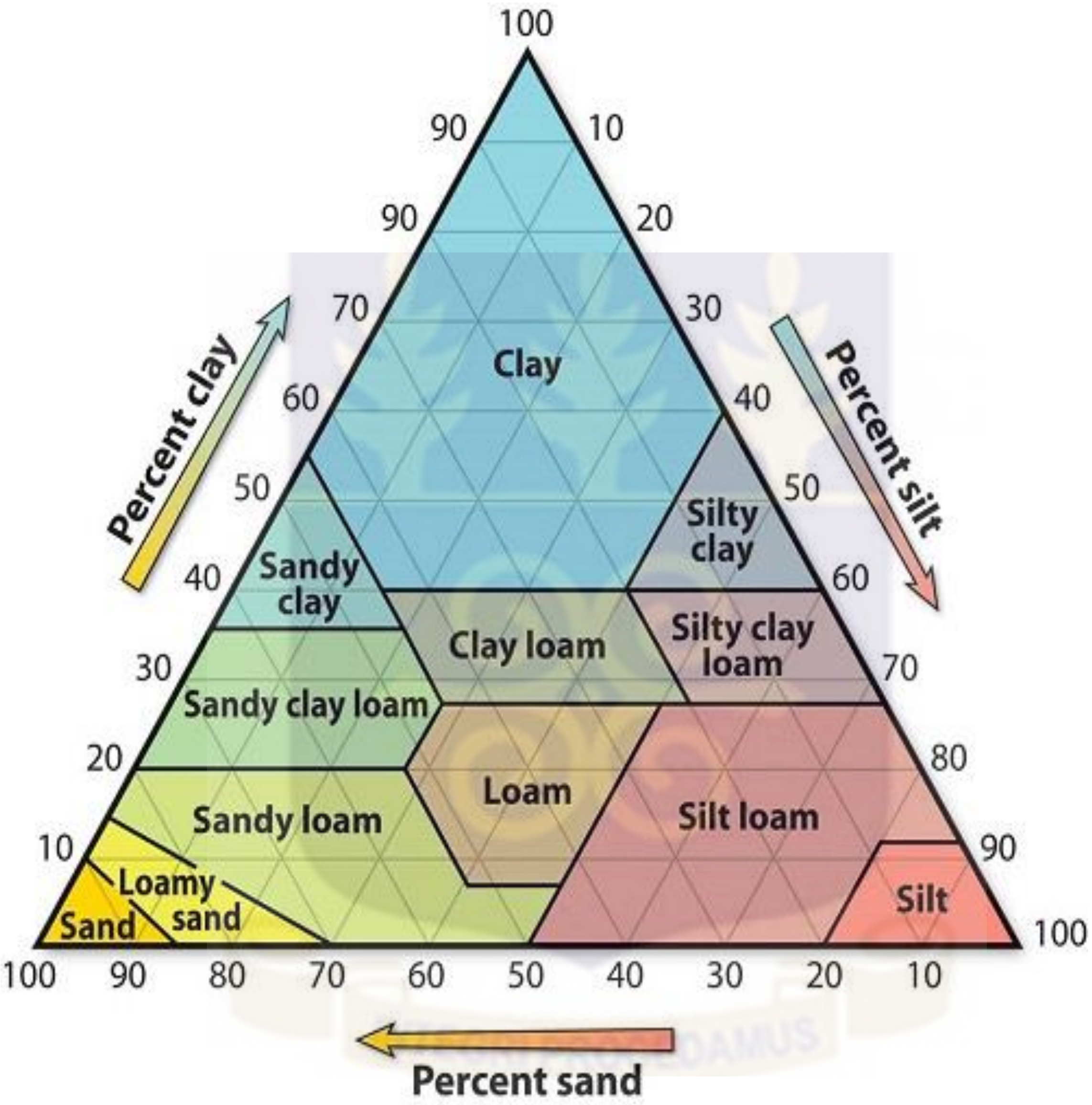
APPENDICES

Appendix A: Textural triangle used in for textural class



Analysis of Variance for Shoot P Uptake (mg/pot_)

Source of Variation	D.F.	(M.V.)	S.S.	M.S.	V.R.	F Pr.
Feedstock	5		354.2105	70.8421	77.98	<.001
Nitrogen	0	(1)	0.0263			
Phosphorus	1		194.5268	194.5268	214.14	<.001
Soil	1		256.2115	256.2115	282.04	<.001
Nitrogen.Phosphorus	0	(1)	0.0355			
Feedstock.Soil	5		215.8260	43.1652	47.52	<.001
Nitrogen.Soil	0	(1)	0.0008			
Phosphorus.Soil	1		6.1865	6.1865	6.81	0.016
Nitrogen.Phosphorus.Soil	0	(1)	0.0012			
Residual	22	(14)	19.9854	0.9084		
Total	35	(18)	863.6172			

Analysis of variance for total N g/kg

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Feedstock	5		4.89818	0.97964	93.85	<.001
Nitrogen	1		0.05733	0.05733	5.49	0.021
Phosphorus	1		0.00220	0.00220	0.21	0.647
Soil	1		24.35210	24.35210	2332.99	<.001
Feedstock.Nitrogen	4	(1)	0.09006	0.02252	2.16	0.078
Feedstock.Phosphorus	4	(1)	0.02643	0.00661	0.63	0.640
Nitrogen.Phosphorus	1		0.02323	0.02323	2.23	0.138
Feedstock.Soil	5		0.33607	0.06721	6.44	<.001
Nitrogen.Soil	1		0.00867	0.00867	0.83	0.364
Phosphorus.Soil	1		0.00470	0.00470	0.45	0.504
Feedstock.Nitrogen.Phosphorus	4	(1)	0.02022	0.00506	0.48	0.747
Feedstock.Nitrogen.Soil	4	(1)	0.06733	0.01683	1.61	0.175
Feedstock.Phosphorus.Soil	4	(1)	0.05438	0.01360	1.30	0.273
Nitrogen.Phosphorus.Soil	1		0.04003	0.04003	3.83	0.052
Feedstock.Nitrogen.Phosphorus.Soil	4	(1)	0.00695	0.00174	0.17	0.955
Residual	125	(19)	1.30477	0.01044		
Total	166	(25)	28.61164			

Analysis of variance for Organic_C_g_kg

```
Source of variation           d.f.  (m.v.)        s.s.        m.s.      v.r.   F pr.
------------------------------------------------------------------------------------------------------------------------
------------
FEEDSTOCK                       5            14507.023    2901.405    513.63   <.001
NITROGEN                        1                5.117       5.117      0.91   0.343
PHOSPHORUS                      1                0.965       0.965      0.17   0.680
SOIL                            1            11866.552   11866.552   2100.73   <.001
FEEDSTOCK.NITROGEN              4     (1)       55.413      13.853      2.45   0.049
FEEDSTOCK.PHOSPHORUS            4     (1)       56.516      14.129      2.50   0.046
NITROGEN.PHOSPHORUS             1               49.987      49.987      8.85   0.004
FEEDSTOCK.SOIL                  5             1881.242     376.248     66.61   <.001
NITROGEN.SOIL                   1                3.337       3.337      0.59   0.444
PHOSPHORUS.SOIL                 1                0.034       0.034      0.01   0.938
FEEDSTOCK.NITROGEN.PHOSPHORUS
                                4     (1)      232.463      58.116     10.29   <.001
FEEDSTOCK.NITROGEN.SOIL4              (1)       88.420      22.105      3.91   0.005
FEEDSTOCK.PHOSPHORUS.SOIL
                                4     (1)      139.405      34.851      6.17   <.001
NITROGEN.PHOSPHORUS.SOIL
                                1               46.766      46.766      8.28   0.005
FEEDSTOCK.NITROGEN.PHOSPHORUS.SOIL
                                4     (1)      104.226      26.057      4.61   0.002
Residual                      123    (21)      694.799       5.649
Total                         164    (27)    24310.923
```

Analysis of variance for root volume

```
Source of variation          d.f.  (m.v.)        s.s.        m.s.      v.r.   F pr.
------------------------------------------------------------------------------------
------------
FEEDSTOCK                      5             110.9448     22.1890     60.99   <.001
NITROGEN                       1               0.0005      0.0005      0.00   0.970
PHOSPHORUS                     1               4.1375      4.1375     11.37   <.001
SOIL                           1              67.4821     67.4821    185.49   <.001
FEEDSTOCK.NITROGEN             4     (1)       5.7466      1.4367      3.95   0.005
FEEDSTOCK.PHOSPHORUS           4     (1)      12.7160      3.1790      8.74   <.001
NITROGEN.PHOSPHORUS            1               2.1984      2.1984      6.04   0.015
FEEDSTOCK.SOIL                 5              23.3974      4.6795     12.86   <.001
NITROGEN.SOIL                  1               0.0887      0.0887      0.24   0.622
PHOSPHORUS.SOIL                1               0.4741      0.4741      1.30   0.256
FEEDSTOCK.NITROGEN.PHOSPHORUS
                               4     (1)       7.4897      1.8724      5.15   <.001
FEEDSTOCK.NITROGEN.SOIL4             (1)       3.2262      0.8065      2.22   0.071
FEEDSTOCK.PHOSPHORUS.SOIL
                               4     (1)       6.1324      1.5331      4.21   0.003
NITROGEN.PHOSPHORUS.SOIL
                               1               0.0670      0.0670      0.18   0.669
FEEDSTOCK.NITROGEN.PHOSPHORUS.SOIL
                               4     (1)       9.3447      2.3362      6.42   <.001
Residual                     126    (18)      45.8394      0.3638
Total                        167    (24)     246.5300
```

Analysis of variance for_root_P_uptake

```
Source of variation          d.f.  (m.v.)        s.s.        m.s.      v.r.    F pr.
-------------------------------------------------------------------------------------
FEEDSTOCK                       5            1614.686     322.937    287.01   <.001
NITROGEN                        1              87.704      87.704     77.95   <.001
PHOSPHORUS                      1             422.781     422.781    375.75   <.001
SOIL                            1             608.400     608.400    540.71   <.001
FEEDSTOCK.NITROGEN              4     (1)     143.825      35.956     31.96   <.001
FEEDSTOCK.PHOSPHORUS            4     (1)     342.349      85.587     76.07   <.001
NITROGEN.PHOSPHORUS             1               7.840       7.840      6.97   0.009
FEEDSTOCK.SOIL                  5             205.441      41.088     36.52   <.001
NITROGEN.SOIL                   1               2.996       2.996      2.66   0.105
PHOSPHORUS.SOIL                 1             488.496     488.496    434.15   <.001
FEEDSTOCK.NITROGEN.PHOSPHORUS
                                4     (1)     505.605     126.401    112.34   <.001
FEEDSTOCK.NITROGEN.SOIL4              (1)     288.652      72.163     64.13   <.001
FEEDSTOCK.PHOSPHORUS.SOIL
                                4     (1)     235.836      58.959     52.40   <.001
NITROGEN.PHOSPHORUS.SOIL
                                1              77.736      77.736     69.09   <.001
FEEDSTOCK.NITROGEN.PHOSPHORUS.SOIL
                                4     (1)      98.243      24.561     21.83   <.001
Residual                      125    (19)     140.647       1.125
Total                         166    (25)    4442.924
```

Analysis of variance for shoot P uptake

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
FEEDSTOCK	5		932.976	186.595	55.96	<.001
NITROGEN	1		244.332	244.332	73.28	<.001
PHOSPHORUS	1		437.104	437.104	131.10	<.001
SOIL	1		886.093	886.093	265.76	<.001
FEEDSTOCK.NITROGEN	4	(1)	101.408	25.352	7.60	<.001
FEEDSTOCK.PHOSPHORUS	4	(1)	351.897	87.974	26.39	<.001
NITROGEN.PHOSPHORUS	1		5.456	5.456	1.64	0.204
FEEDSTOCK.SOIL	5		152.536	30.507	9.15	<.001
NITROGEN.SOIL	1		8.343	8.343	2.50	0.117
PHOSPHORUS.SOIL	1		0.844	0.844	0.25	0.616
FEEDSTOCK.NITROGEN.PHOSPHORUS	4	(1)	26.829	6.707	2.01	0.100
FEEDSTOCK.NITROGEN.SOIL	4	(1)	47.139	11.785	3.53	0.010
FEEDSTOCK.PHOSPHORUS.SOIL	4	(1)	85.470	21.368	6.41	<.001
NITROGEN.PHOSPHORUS.SOIL	1		59.718	59.718	17.91	<.001
FEEDSTOCK.NITROGEN.PHOSPHORUS.SOIL	4	(1)	136.547	34.137	10.24	<.001
Residual	85	(12)	283.404	3.334		
Total	126	(18)	3402.247			