USING BIOCHAR TO REDUCE LEACHING AND ENHANCE NITROGEN UPTAKE IN TWO GHANAIAN SOILS

BY

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DECLARATION

I hereby declare that this thesis has been written by me and that it is an outcome of my own research. It has neither in whole nor portion been presented for another degree elsewhere. Research work of other researchers has been duly cited by references to the authors and any form of assistance received also acknowledged.

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DEDICATION

I dedicate this piece of work to my children Michaelina and Stephannie.

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I thank the all-knowing God for bringing me this far in education, glory be to his name.

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ABSTRACT

In recent times the use of biochar as soil amendment has been proposed as one of the ways for reducing nitrogen leaching particularly in sandy soils because it has the potential to retain cations and anions. Three different biochar types (sawdust, rice husk and corn cob) pyrolysed at 400°C were tested in the laboratory to investigate their retention capacity for NO_3^- and NH_4^+. One hundred and fifty grams (150 g) of each biochar was packed into acrylic cylinders to create biochar column. The soluble cations in these biochar types were then leached out completely. Three nitrogen fertilizer solutions (ammonium sulphate, potassium nitrate and ammonium nitrate) prepared at 1.36 g N per litre were allowed to pass through the column and leachate collected to determine NO_3^-N and NH_4^+N. Results from the column leaching experiment showed that the sawdust biochar had superior retention capacity for NO_3^- and NH_4^+. This could be due to its relatively higher surface area when compared to the other biochar types. In another experiment in the screen house, the sawdust and rice husk biochar types were applied at 0, 20 and 40 t/ha and treated with different N sources (cow dung and ammonium sulphate; 265 N kg/ha) in two soils, Keta series (Quartzi Psamment) and Nyankpala series (Plinthic Acrisol) and maize was grown for five weeks. During the growth period the treated soils were leached at 14 and 28 days after planting to determine the quantity of available nitrogen (N) leached out. Biochar amendment of the soils reduced leaching of NO_3-N and NH_4-N, indicative of their ability to retain N in the soils. The amendment also enhanced dry matter production and N uptake by maize, therefore biochar amendment is recommended for reducing leaching. It was also recommended that the experiment should be conducted under field condition.

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CHAPTER ONE

INTRODUCTION

Nitrogen (N) is one of the nutrients that limit crop growth, especially in sandy soils and soils with low organic matter (OM) content. It is needed for the sustenance of the global agricultural production and it also has high essence on crop yield (Fan and Li, 2009; Leip *et al*., 2011). Most soils in Africa are low in N due to intensive weathering. When N fertilizers are applied, about 50% to 70% is lost through combination of factors like leaching, erosion, denitrification and microbial incorporation of the N into their biomass (McAllister *et al.,* 2012). Therefore application of inorganic N fertilizers does not always translate into yield (Jaynes *et al.,* 2001).

Leaching of nitrogen is one of the most common ways through which nitrogen especially NO_3^- is lost from the soil system, with the situation being severe in light textured soils and under heavy rainfall (Razzaque and Hannafi, 2005). When fertilizers are applied in excess in agricultural fields, it causes the release of nutrients like N and phosphorus (P) from the agricultural fields into water bodies (Laid *et al.*, 2010). Applying N fertilizers in soluble form to sandy soils cause leaching of N which may pollute underground water (Paramasivan and Alva, 2008). This has subsequent effect on nutrients availability in the soil for plant uptake.

Leaching of plant nutrients occurs when dissolved N in applied fertilizers moves downwards with percolating water within the soil profile. This is a crucial aspect of nutrients recycling in agriculture (Brady and Weil, 2008) and accounts for up to 80% loss of N in fertilizer applied to the soil.

According to Lehman and Schroth (2003), leaching of N may significantly contribute to negative N balances in agricultural systems. Sandy soils and ferrallitic soils with low activity clays are particularly most prone to nutrients leaching. These soils have high infiltration rates, low nutrient

retention capacity, low OM and high water conductivity which affect nutrients uptake by plants, fertilizer use efficiency and yield (Sitthaphanit *et al*., 2009; Zotarelli *et al*., 2007). This makes such soils inherently infertile and relatively unproductive (Yao *et al*., 2012).

In Ghana cultivation of maize is mostly done in the transitional, coastal and guinea savanna zones because it is a staple for the people within these zones. In an attempt to sustain the fertility in the soils, farmers in these agro ecological zones apply large quantities of fertilizers especially N containing fertilizers. The applied N fertilizers leach under heavy rainfall resulting in environmental pollution and increase cost of production for the farmer. The use of organic fertilizers such as manure and planting of leguminous cover crops has been used in an attempt to limit the leaching of N in sandy soils in Ghana but the effect of these measures are short lived. The use of nitrification inhibitors and other control-released fertilizers had also been tried elsewhere (Baligar *et al.*, 2001: Di and Cameron, 2002).

In recent times the use of biochar has been proposed as one of the ways for reducing leaching in agriculture, because it has the capacity to improve the retention of cations and anions in soils (Major *et al*., 2009). According to Lehman and Joseph (2009), Maesek *et al.* (2011) and Kuppusamy *et al*. (2016), biochar addition to the soil is an evolving technology which has the potential to enhance food security whiles sequestering carbon to combat climate change. Biochar is a carbon rich material produced when biomass is heated under relatively low temperature < 700°C in the absence of oxygen (Lehman and Joseph, 2006).

Biochar has increased negative - charged functional groups like carboxylates, positive charge sites and high surface area (Lehman *et al*., 2003; Laing *et al.*, 2006). Therefore when applied to

the soil it improves the adsorption of NH_4^+ and NO_3^- and hence prevents their leaching in the soil profile (Chintala *et al*., 2013).

Economic considerations on how to manage NO_3^- in agricultural system concentrate on efforts to enhance N utilization and reduce cost of N inputs. Nitrogen management aims to balance N uptake with crop requirements and minimize leaching of N during rainfall (Zhaohui *et al*., 2012). Biochar has shown the ability to minimize loss of inorganic N from inorganic and organic sources in sandy soil (Lehman *et al.*, 2009). However, little work has been done on biochar reducing leaching of nitrogen in Ghanaian soils. Therefore, this research seeks to investigate the influence of biochar amendment in sandy soils on leaching of N as the main objectives.

The specific objectives of this research are to;

(1) Identify biochar type from different feedstocks with better retention for NO_3^- and NH_4^+.

(2) Investigate the ability of biochar to reduce leaching and enhance N uptake by maize.

(3) Investigate the residual effects of biochar amendment on N leaching, growth of maize and N uptake.

CHAPTER TWO

LITERATURE REVIEW

2.1 The role of nitrogen in crop production

Nitrogen is essential to life because all living things possess considerable amount of nitrogen. Nitrogen is an integral part of the DNA molecule. Among plant nutrients, nitrogen has the most complex behavior in soil. Nitrogen (N) is an essential input in crop production, but is inadequate in soils of the world, making it one of the nutrients that limit crop growth and yield, especially in sandy soils and soils with low organic matter content. It is required in increasing crop yield needed to feed the world's population (Fan and Li, 2009; Leip *et al*., 2011). The nitrogen content of most soils in Africa and the tropics is low, because about 50% to 75% of N applied to the soil in the form of fertilizer is lost through combination of factors like leaching, erosion, denitrification and microbial incorporation of the N into their biomass, sorption and volatilization which renders the applied N inaccessible to the plants roots (McAllister *et al*., 2012). Therefore application of inorganic N in fertilizers does not always translate into yield (Jaynes *et al*., 2001).

2.2 Leaching of nutrients in sandy soil

Leaching of nutrients is one of the common ways through which applied N is lost from the soil systems (Lehmann and Schroth, 2003) and is an essential component of nutrients cycling in agriculture (Brady and Weil, 2008). Nutrient loss through leaching is unavoidable in high rainfall areas (Widowati and Asnah, 2014). Leaching occurs when dissolved nutrients move downwards with percolating water within the soil profile. Nutrients held onto particles and colloidal surfaces can also be moved away from the reach of plant roots through facilitated transport (Lehmann *et*

al., 2004). Subsoil acidity restricts the rooting depth of sensitive plants (Lehmann and Schroth, 2003) and together with poor water quality causes leaching of nutrients (Jalali and Merrikhpour, 2006), which can hasten nutrients depletion, soil acidity and increase fertilizer cost to farmers (Yao *et al*., 2012).

Leaching of dissolved anions in soil solution must be accompanied by leaching of cations in order to maintain electro-neutrality. As such the loss of anion like nitrate from applied N fertilizer must occur with leaching of cations like calcium (Ca), magnesium (Mg) and potassium (K) (Lehmann *et al*., 2004).

2.3 Effect of Nitrogen leaching in the environment

Excessive application of fertilizers on agricultural fields can release nitrogen (N) and phosphorus (P) into aquatic systems (Attiq-ur-Rehman, 2011; Irshad *et al.*, 2012) which may result in contamination of underground water, eutrophication and overproduction of photosynthetic aquatic microbes in fresh water and marine ecosystems (Havlin *et al.*, 1999, Karaca *et al.*, 2004). This phenomenon significantly contributes to negative nitrogen imbalances in agricultural systems (Lehman and Schroth, 2003). Species community structure, diversity, changes and functioning of terrestrial, freshwater and marine ecosystems are also directly affected by reactive nitrogen (Matson *et al*., 1997; Vitousek *et al*., 1997; Ribaudo *et al.*, 2011).

In an experiment by Irshad *et al*. (2014), they observed that maximizing nitrogen use efficiency on sandy soil is crucial in reducing ground water contamination and increasing economic yield. According to Knox and Moody (1991), actual leaching of nitrogen depends on the nitrogen source and its application rate. Leaching risk of nutrient increases with its mobility in the soil,

nitrate is very mobile in the soil and it is therefore easily leached under heavy precipitation and high application rate because of its low interaction with the negatively charge soil matrix. NH_4^+ is readily immobilized by soil microorganisms and easily adsorbed by the negative charges on the soil (Schroth *et al*., 1999; Havlin *et al*., 1999).

According to Burgo et al. (2006), leaching of nitrate from soils amended with organic materials depends on the application rate, time of application, amount of water applied, soil type and plant uptake. Nitrate leaching results from excessive irrigation and fertilizer use therefore nitrate leaching from fertilizers into ground water can be minimized by applying nitrogen fertilizers during active growth phase of crops (Hu *et al*., 2007) and also by improving fertilizer use efficiency through proper irrigation management techniques (Shresda *et al.,* 2010; Zotarelli *etal*., 2006). It is difficult to coordinate the control of NO_3^- leaching and economic benefit of NO_3^- during the active growth period of crops. Therefore, it is imperative to nutrients managers to devise reliable techniques to minimize nitrate leaching (Zhang *et al*., 2012).

Ribando *et al*. (2011) prescribed several measures such as improved management of nitrogen fertilizers and application of animal manure as means of enhancing overall nitrogen use efficiency (NUE) in order to decrease the loss of reactive nitrogen to the environment while sustaining crops yields.

In an experiment by Nakamura et al. (2004) to assess root zone nitrogen leaching as affected by irrigation and nutrient practices, they observed that splitting the application of N fertilizer into two was able to reduce the amount of N leached by one-third compared to the lump application of the N fertilizer. They therefore, suggested that N fertilizer application should be done in split form during single cropping period in order to minimize leaching of NO_3- N into groundwater.

Nyanmangara *et al*. (2003) reported that leaching of nitrate from sole manure application is relatively low compared to combination of manure and inorganic fertilizer. The use of strategies such as nitrification inhibitors, slow and controlled-release fertilizers can be employed to reduce leaching of N in soil (Baligar *et al*., 2001; Di and Cameron, 2002).

In recent times one of the proposed ways for reducing leaching in agriculture is by use of biochar, which has shown to improve the retention of cations and anions in leached soils (Major *et al*., 2009).

2.4 Origin of biochar

Amazonian Indians started using biochar about 1000 years ago to produce terra preta soils which remained more fertile than the surrounding soil (Lehman *et al*., 2006). They developed the terra preta by adding large quantities of charcoal to the poor soils of the rainforest to enhance their fertility (Yu *et al.*, 2013). According to Gul *et al.* (2015) the enhanced productivity of terra preta soils amended with biochar compared to unamended oxisols has created world-wide interest in applying biochar to agricultural soils. The terra preta soils that regularly receive biochar and other organic amendment have higher pH, high nutrients content, larger and diverse microbial population than unamended oxisols (Germano *et al*., 2012; Taketani *et al.*, 2013; Gul *et al.*, 2015). Biochar is a carbon rich material produced when biomass is heated under relatively low temperature < 700°C in the absence of oxygen. According to Hale *et al.* (2013), one unexplored avenue to increase nutrients availability in impoverished soils is the addition of biochar, but biochar did not receive the deserved attention until the publication in Nature article″ Putting the carbon back; Black is the new green″ (Marris, 2006).

2.5 Biochar as a material for soil amendment

Although in recent times biochar production has received much attention, the mechanism of its formation is still unclear and structure of biochar still remains uncertain (Ye *et al.,* 2015). Biochar is usually considered as highly efficient and cheaper adsorbent material which is environmentally friendly (Chen *et al*., 2008) which has now provided a new means of sequestering carbon and enhancing soil fertility (Beesley *et al*., 2011). It is an evolving technology which has the potential to enhance food security whiles sequestering carbon (C) to combat climate change (Lehman and Joseph, 2009; Masek *et al*., 2011; Kuppusamy *et al*., 2016).

Any form of organic material such as crop residues, forest by-product, urban yard waste, industrial by-product, manure and sewage sludge can be charred into biochar. Notwithstanding this it is not every organic waste that is suitable for producing biochar good for agricultural purposes. Because the physico-chemical properties of biochar are significantly influenced by the raw material and pyrolysis temperature (Ronsse *et al*., 2013) which subsequently affects sorption ability of the biochar produced (Ogbonnaya and Semple, 2013). According to Gwenzi *et al.* (2015) biochar can be applied as soil amendment together with inorganic fertilizer without any negative effect on plant growth.

2.6 Effect of pyrolysis temperature on biochar

According to Demirbas *et al*. (2004) pyrolysis of biochar involves three stages; first step involves loss of volatiles; formation of primary biochar occurs during the second step and the third step involves decomposition of primary biochar at very slow rate and chemical rearrangement to form carbon-rich residual solid (biochar). In an experiment by Sun *et al*. (2014)

to assess the effect of type of feedstock, production method and pyrolysis temperature on biochar and hydrochar, they observed that biochar yield decreased as the pyrolysis temperature increased. They attributed it to the decomposition of organic matter as temperature increases. Higher pyrolysis temperature increases stability, aromaticity and strengthens bonds of biochar material (Zimmerman, 2009). Pyrolysis temperature higher than 400°C can cause loss of aliphatic-C moieties and a centralization of C compound to poly-condensed aromatic-C type which significantly affects the stability of biochar C in soil (Novak *et al.*, 2010).

According to Uchimiya *et al*. (2011) the charring temperature of biochar can influence the type of functional groups on its surface and its heavy metal sequestration capacity in soil. Sun *et al.* (2014) also observed that the pyrolysis temperature of biochar affects its elemental compositon. Biochar charred at lower temperatures may have better adsorption ability (Liang *et al*., 2006) due to increased negatively-charged functional groups like carboxylates on their surfaces.

Chemical composition of biochar pyrolysed at lower temperature is closer to the chemical composition of the original feed stock whiles those biochar charred at higher temperature has its chemical composition closer to that of graphite (Masiello, 2004). According to Parakayastha *et al*. (2016) biochar from crop residues pyrolysed at higher temperature is more stable than those pyrolysed at lower temperature. Biochar charred at lower temperature has higher content of volatile matter such as bound carboxylic acid, phenol, ketone and aldehyde functional groups but has lower fixed carbon and ash compared to biochar charred at higher temperature (Bourke *et al*., 2007). Yuan *et al.* (2011) observed that nitrogen (N) content of sewage sludge biochar decreases as the pyrolysis temperature is increased. Nutrients such as P, K and Ca, surface area, pH, carbon: nitrogen (C: N) ratio and carbon: oxygen (C: O) ratio of biochar increases as pyrolysis temperature increases (Novak *et al.*, 2013; Gul *et al.*, 2015). Higher pyrolysis temperature

generally reduces H: C and O: C ratios but increases the alkalinity, ash content, pH and C: N of the biochar (Yuan *et al*., 2011). Therefore, biochar charred under different temperatures need to be characterized in order to determine its agronomic usefulness (Wang *et al*., 2015).

2.7 Chemical composition and surface chemistry of biochar

Biochar is heterogeneous in nature and has both stable and labile constituents (*Sohi et al., 2009*). Biochar feedstock influences its physical and chemical properties which determine its behavior and uses (Brown, 2009; Demiebas, 2004). It is stable and recalcitrant when applied in the soil due to its high carbon content and aromaticity (Sohi *et al*., 2010). The chemical composition of biochar dictates its surface chemistry and reaction with organic and inorganic compounds within the environment. The outer surface and pore surface of biochar is occupied by aldehyde – (C=O) H, carboxyl–(C=O) and OH (Zwieten *et al*., 2009). The characteristics of biochar ranges from basic to acidic, hydrophobic to hydrophilic, because the functional groups on the material can accept electrons or donate electrons (Amonette and Joseph, 2009).

Biochar materials are porous with high surface area and CEC (Demirbas 2004; McElligot, 2011;Kongthod *et al*., 2015) and when it stays longer in the soil, its surface undergoes oxidation which helps in improving the cation exchange capacity of the soil (Liang *et al*., 2006; Chintala *et al*., 2015). There are also positive charge sites on biochar which gives anion exchange capacity to the material which can attract nitrate and phosphate ions (Chintala *et al*., 2015).

According to Borchard *et al*. (2012), only biochar with hydrophilic surfaces can enhance nutrients retention, aggregation of particles and cation exchange capacity. Biochar can affect the

nitrogen dynamics in soil by changing the rate of transformation processes (Clough and Condron 2010; Clough *et al*., 2013).

2.8 Biochar as source of plant nutrients

Biochar is recalcitrant in nature and this increases its potential as soil amendment for longer term compared to most soil organic materials which easily degrade when added to the soil (Chanet *al.*, 2007). The recalcitrant nature of biochar in soil and its resistance to loss through degradation, leaching and chemical oxidation is due to its aromatic structure, surface functionality and sorption properties of other minerals and organic compounds (Shrestha *et al*., 2010). According to Wang *et al.* (2007) biochar with high H: C and O: C ratio has higher number of functional groups which provide more chemical bonding with polar compounds. It is comparatively stable in most environments as charred materials and has residence time between 1000-1500 years (Glaser *et al*., 2010).

According to Spoka (2010), the stability of biochar is based on its half – life and is determined by the O: C ratio. The half-life of biochar could be > 1000 years when the O: C ratio is < 0.2 with the half-life decreasing to < 100 years when O: C ratio > 0.6. Despite its recalcitrant nature biochar can be degraded biotically (microbial incorporation or oxidative respiration of C) and abiotically (chemical oxidation, photo oxidation or solubilization) (Major *et al*., 2010) to release the nutrients in it.

Biochar characteristics alter with time in the soil, as a result of its oxidation and accumulation of H^+ from the soil solution during the first weeks of its addition. The level of changes in the biochar properties with time depends on the biochar source and climatic conditions (Heitkotter and Marschner, 2015, Chan *et al*.; 2008).

According to Lehman *et al*. (2002) biochar can act as soil fertilizer when applied to the soil. The uses of biochar as soil amendment to enhance soil fertility and plant growth had received much research focus in recent time (Ibrahim *et al*., 2013). Biochar addition to soil can increase soil fertility and crop production; therefore it is beneficial to agricultural ecosystem just like any other organic material.

Although the nutrients in biochar material originate from the feedstock, the amount of nutrients in the feedstock cannot be used as reliable assessment for the nutritive value of the biochar in crop production. Because during the charring process the proportion of individual elements mineralized, co-stabilized with C and volatilized are not equal (Angst and Sohi, 2013). The improvement in soil fertility when amended with biochar is due to increase in cation exchange capacity of the soil caused by biochar addition to the soil (Laing et al., 2006). Basso et al. (2012) reported that amending sandy soils with biochar increase availability of some nutrients and therefore should be considered as management alternative.

Biochar material contains nutrients therefore when added to the soil can release basic cations such as K, Ca and Mg (Glaser *et al*., 2002). According to Wadowati and Asnah (2014) when biochar is applied at rate of 30 t ha^{-1}it can act as K fertilizer which is sufficient for meeting crop K requirement. There is great potential for enhancing the environmental and economic benefits of biochar by fortifying it with nitrogen (N) from both inorganic and organic sources (Clough *et al*., 2013). According to Zimmerman *et al.* (2011) biochar serves as source of easily mineralized C, N, P and micronutrients which helps in stimulating the mineralization of more refractory soil organic matter components.

Biochar can act as reservoir of P for soils, large portion of the P in biochar exists in plant available form but the amount of P in the biochar material is determined by the feedstock and the

pyrolysis conditions (Zhang *et al*., 2016). Charring of agricultural residue into biochar helps stabilize and retain the P contained in it and this helps to reduce the P mobility in the soil. Unlike other agricultural residues, the amount of P recycled by the biochar is relatively slow and reduces the amount of labile P applied to the soil. This provides lasting P source to the soil and help minimize potential loss of P from the soil system (Dai *et al*., 2016). Cui *et al*. (2011) reported that biochar amendment may enhance P availability to plants by reducing P adsorption on ferrihydrite in Oxisol. Accoring to Ma and Matsunaka (2013) biochar can be used as P source in soil with low P content.

According to Gaskin *et al*. (2008), nitrogen from biochar might not be available for plant. Although the biochar material contains plant bioavailable nutrients, these constitute just small fraction of the total nutrients in biochar (Yuan *et al*., 2016). An improvement in plant growth when biochar is added to soil is suggested to be caused by biochar ability to influence changes in available nitrogen and phosphorus (Yao *et al.*, 2012; Kongthod *et al*., 2015).

Some biochars are also enriched with cationic elements like K, Ca and Mg due to high quantities of ash contained in them (Yuan *et al*., 2011; Butnan *et al*., 2016). Prendergast-Miller *et al.* (2014) reported that in biochar amended soil, plant root growth is stimulated when the roots absorb biochar constituents. According to Ren *et al.* (2015), plant root produce exudates which may affect sorption ability of biochar. Wu *et al*. (2011) noted that mallee wood biochar contain 15% - 20% calcium (Ca), 10% - 60% phosphorus (P) and 2% nitrogen (N) which can easily be leached with distilled water. According to Clough *et al.* (2013) recent studies has shown varied indirect effects of biochar on soil nitrogen (N) with potential effects for nitrogen cycling and plant nutrition. Yao et al. (2012) reported that adding biochar to the soil releases biochar associated P and transforms soil P into more available form for plant uptake. In microcosm study

by Molner *et al.* (2016) in assessing biochar improvement on acidic sandy soil, they observed that application of grain husk biochar and paper fibre sludge biochar beneficially influenced available phosphorus and potassium. Biochar addition to the soil can also influence biogeochemical processes in the soil such as carbon (C) and Nitrogen cycling (Nelissen *et al*., 2012) which can induce immobilization of nitrogen (Zavalloni *et al.*, 2011).

The high surface charge density on biochar enables it to retain cations by cation exchange. The high surface area, internal porosity and existence of both polar and non-polar surface sites on biochar allow biochar to adsorb nutrients (Laid *et al*., 2010). Studies have shown that biochar may sorb and retain nutrients thereby enhancing soil nutrients availability to plants (Lehmann *et al*., 2011; Ventura *et al*., 2013). This can subsequently enhance fertilizer use efficiency (Zhao *et al*., 2014).

2.9 Effects of biochar on physical properties of the soil

According to Mukherjee *et al.* (2014) the effects of biochar on field soil conditions is poorly understood. The effects of biochar on physical properties of the soil have not received much attention compared to its effect on chemical properties of the soil, despite the importance of enhanced soil physical properties in increasing crop production in sandy soil (Atkinson *et al.*, 2010; Cornelissen *et al.*, 2013).

Studies on biochar have reported that its addition to the soil influences physical, chemical and biological properties of the soil (Laid *et al.*, 2010; Lone *et al*., 2015) which hinges on the soil and erimental conditions (Liu *et al*., 2016). The texture of the soil determines the effect of biochar on its physical properties such as water retention, hydraulic conductivity and aggregate stability

(Malnar *et al*., 2016). Soil porosity is an important soil characteristic influencing plant growth. Biochar application to the soil increases the overall porosity of the soil, but the extent of increase is determined by the biochar and soil types and where the biochar is applied (Herath *et al*., 2013). Biochar ability to enhance soil porosity could be attributed to its high porous nature (Mukherjee *et al*., 2013).

When biochar is added to the soil it helps in decreasing the bulk density of the amended soil (Mukherjee *et al*., 2013) and bulk density decreases with high biochar application rate (Githinji, 2013). Decreased bulk density enhances plant roots extension and spreading of the plant roots within the soil medium (Laid *et al*., 2010). Application of biochar also indirectly enhances soil aggregation by providing refuge for soil microbes which secrete polysaccharides which glue soil colloidal particles together (Dorioz *et al., 1993;* Aslam *et al*., 2014).

According to Yu *et al*. (2013) addition of biochar to the soil, has been suggested as a technique for enhancing soil water holding capacity but there are few quantitative studies on the efficiency of the biochar material in improving water retention. Biochar has high porosity which improves water retention in biochar amended soils. Singh *et al.* (2010) documented that this retains dissolved nutrients in water making them available for plants uptake. The enhancement in water retention is influenced by type of feed stock, soil type and biochar mixture rates (Singh *et al.*, 2010).

Zhan and You (2013) reported that biochar capacity to improve soil water holding capacity is influenced by the surface functional groups, total pore volume, porosity structure and specific surface area of the biochar material. According to Hardie *et al*. (2014) biochar possess higher proportion of hydrophilic micropores which can retain water, therefore when biochar is added to

sandy soil it may enhance water holding capacity of the sandy soil. Addition of biochar to soil enhances plant available water which is one of the factors that hinders crop production (Basso *et al*., 2013). Biochar can increase both soil water holding capacity and available water content (Mukherjee and Lal, 2013; Obia *et al*., 2016). According to Amonette and Joseph (2009) addition of biochar to the soil can influence the soil structure, texture, porosity, particle size and density, oxygen content, water holding capacity, microbial and nutritional status of the soil within the rhizosphere.

2.9.1 Biochar effect on cation exchange capacity of the soil

When biochar is added to the soil, its surface undergoes oxidation (Cheng *et al*., 2008) leading to higher CEC and charge density on the biochar material (Liang *et al*., 2006). The cation exchange capacity of biochar material increases as the biochar material ages in the soil (Laing *et al.* 2006). Biochar material has high surface area and porosity (Nigussie *et al*., 2012) therefore when added to soils with low CEC it can enhance the CEC of the soil (Van Zwieten *et al.*, 2010). According to Mohamed *et al*. (2016), the high CEC of biochar material is caused by the presence of significant quantity of hydrophilic oxygen-containing groups like carboxylic and phenolic compounds with higher cation exchange capacity on biochar surface. Dume *et al.* (2016) also observed an increase in soil CEC following addition of biochar to the soil, and attributed the increase to inherent characteristics of the biochar feedstock.

Due to high CEC of biochar it can exchange cations such as NH_4^+ with soil solution (Lehman et *al*., 2007). Mukhejee *et al*. (2014) documented that amending sandy and loamy soils with hardwood-derived biochar can effectively increase CEC by 1.5 times.

2.9.2 Biochar effect on soil pH

The pH of biochar material is determined by the feedstock, pyrolysis temperature and duration of the pyrolysis process (Yuan *et al*., 2011). According to Molner *et al*. (2016), pH value of acidic sandy soil significantly increased with increased biochar application rate. Hass *et al.* (2012) reported that when biochar is added to the soil, the resultant increase or decrease in the soil pH depends on the soil and biochar properties.

Liu and Zhang (2012) observed a decrease in pH value of alkaline soil when amended with biochar. They attributed the decrease to the combined effect of the basic cations in biochar and the soil carbonates to form partially soluble carbonates which affected the hydrolyzation of the carbonates leading to reduction in hydroxyl content of the soil. According to Cheng *et al*. (2008) biochar is reactive in nature therefore when added to an alkaline soil its surface undergoes oxidation through chemical and microbial activity to form acidic functional groups like carboxylic acid. The acidic functional groups can neutralize the alkalinity of the soil and decrease the pH of the alkaline soil (Brodowski *et al*., 2005).

In quantitative review by Jeffrey *et al*. (2011) to assess the effects of biochar application to soil on crop productivity using meta-analysis, they observed positive effect of biochar on acidic, neutral pH soils, coarse and medium textured soils and attributed it to the liming effect of biochar on soil. Biochar can act as liming agent due to its alkaline nature, therefore when added to the soil it can reduce exchangeable acidity (Chan *et al*., 2008; Major *et al*., 2010).

When biochar is incorporated in soil, it mineralized to release cations into solution (Keith *et al.*, 2011; Zimmerman *et al*., 2011) which displaced exchangeable acidity and increased soil pH (Wang *et al*., 2013). According to Major *et al*. (2010) biochar can release great amount of

exchangeable Ca^{2+} and Mg^{2+} in acid soil which neutralized the pH and improved yield of maize in oxisols. During the charring process of biochar, basic cations like Ca, K, Mg and silicon are formed from oxides and carbon, and when biochar is added to the soil, these oxides are released and they react with exchangeable Al^{+} and H^{+} and help in elevating soil pH (Novak *et al.*, 2009).

2.9.3 Effect of biochar on nitrogen leaching in soil

Nitrogen is one of the commonest elements occurring in nature and is the main nutrient involving in plant nutrition but excess of it poses threat to the environment (Adomaitis *et al.*, 2008). Leaching of nitrogen (N) is the common way through which N contained in applied fertilizer is lost (Goulding, 2000). Nitrate leaching is one of the main problems associated with intensive agriculture (Beaudoin *et al*., 2005; Kanthle *et al*., 2016). Nitrogen (N) and Phosphorus (P) are plant nutrients that usually influence the quality of surface and underground water (Sparks, 2003). According to Lehman *et al*. (2004) about 80% of applied nitrogen (N) is lost from the root zone through leaching. Over reliance on chemical fertilizers and low supplementation with organic inputs has worsened the situation. Reducing nitrate leaching from agriculture fields can reduce nitrate economic loss to farmers and limit the effect of high loading of nitrate on ecological balance in water bodies (Kanthle *et al*., 2016).

According to Yao *et al*. (2012) an alternate technology to reduce leaching in soil could be the application of biochar to the soil. Amending soil with biochar has been suggested as a reliable long-term measure for safeguarding surface and underground water quality against negative impact of nutrient leaching particularly nitrogen (Steiner *et al*., 2008).

Studies have shown that, biochar due to its high surface area and surface charge, it can be used as environmental absorbent (Ahmad *et al*., 2014). It has been suggested that biochar ability to reduce N leaching is due to its high absorption potential because of elevated surface area and porosity of biochar materials (Liang *et al*., 2006; Van Zwieten *et al*., 2009; Zhao *et al.*, 2015). Karanthanasis (1999) reported that the size of biochar particles can also determine its leaching reduction potential. The nitrogen retention in soil following biochar amendment can positively influence N uptake in crops and productivity (Steiner *et al*., 2008).

Biochar addition to soil influences nutrient leaching through several mechanisms; increasing water retention in the rooting zone through direct binding or sorbing nutrients or by interacting with other soil constituents (Lehman *et al*., 2004). Emperical evidence confirms that biochar improves water and nutrients retention by enhancing electrostatic adsorption sites (Lehman *et al.*, 2003). When biochar is added to the soil it increases soil aggregation which results in high water holding capacity which helps in enhancing nitrogen retention in the amended soil. Biochar ability to reduce leaching of nitrogen in the soil could also be attributed to its ability to increase the cation and anion exchange capacities of the soil (Yoo *et al.*, 2014; Xu *et al.*, 2016).

According to Laing *et al. (*2006), the high surface charge of biochar enables biochar to hold cations such NH_4^+ by cation exchange. In an experiment by Lehmann *et al.* (2003) to measure nutrients leaching in soil biochar mixture using pot lysimeter in greenhouse, they noticed that biochar prepared from Manaus when mixed with typic Hapludox can reduce leaching of ammonium more than 60% over 40 days of cropping rice compared to the control soil without biochar amendment. According to Bai *et al.* (2015) biochar effect on nitrogen retention in field settings is mainly abiotic processes.

2.9.4 Biochar effect on nutrients uptake and dry matter yield of maize

According to Taghizadel *et al.* (2012) recent evidence has indicated that nitrogen adsorbed by biochar is eventually made available for plants uptake. Nigussie *et al.* (2012) in assessing the effect of biochar application on soil properties and nutrients uptake of lettuce in chromium polluted soils, observed that N uptake in lettuce increased with increasing biochar rate and attributed the increase to biochar ability to enhance fertilizer use efficiency in soils especially soils with high leaching tendency.

Applying biochar alone or in combination with organic material (vermicompost) to acidic sandy soil positively affect soil fertility, maize growth and yield and nutrient retention (Doran *et al*., 2015). Uzoma *et al. (*2011) reported an increase of 150% in maize dry matter yield in soils amended with biochar compared to unamended soil.

In an experiment by Ma and Matsunaka (2013) to assess the impact of different size biochar derived from dairy cattle carcasses as an alternate P source and amendment in an acid soil. They observed that when biochar was applied as sole amendment or together with N fertilizer, it could significantly improve dry matter weight of shoot and roots of crops. They therefore concluded that irrespective of the size of biochar applied, dry matter of crops increased with elevated P rate.

Applying biochar alone as soil amendment without fertilization will not increase dry matter yield (Chan, 2007) due to its low bio-availability (Zavalloni *et al*., 2011). Borchard *et al.* (2014) also noted that increasing the rate of biochar charred under slow pyrolysis conditions can decrease dry matter yield of plants. Nguyen (2008) also observed that the elevation in soil pH following biochar addition may result in decline in maize dry matter yield and attributed it to nutrients like phosphorus becoming unavailable as the soil pH is increased beyond 8.0

2.9.5 Maize

Teosinte (Z. Mexicana) is generally accepted to be the ancestor of maize but there are varied opinions as to whether maize is the domesticated form of teosinite (Galinate, 1988). According to Gibson and Benson (2002) evidence suggested that cultivated maize resulted from natural crossings, first with gamagrass to yield teosinte followed by back crossing of teosinte with primitive maize to produce the modern races and is the most completely domesticated of all field crops. Maize scientifically known as *Zea mays* belongs to the family Graminae (poaceae). It is cultivated throughout the world and is a staple for larger proportion of the world's population (Canadian Food Inspection Agency, 1994). According to Chaudhry (1983) maize contains about 72% starch, 10% protein, 4.8% oil, 8.5% fibre, 3.0% sugar and 1.7% ash and forms an important component of animal feed (Khan *et al*., 2014).

Currently about 594 million tons of maize is produced from 139 million hectares in the world FAOSTAT (2000). Maize is one of the most important cereal crops produced in Ghana but production levels are low because its cultivation is mostly done by peasant farmer in soils with low fertility status under rain fed condition (Adu, 1995; SARI, 1996; FAO, 2005).

Maize is grown in both tropical and temperate climates but different varieties have adapted to different climatic zones, the mean daily temperature for maize cultivation should exceed 15°C (FAO, 2015). It survives best in well drained sandy loam soil with pH of 5.7 - 7.5 and average annual rainfall of 500 mm – 800 mm (FAO, 2005). According to Baloyi *et al.* (2014) maize has high demand for nutrients especially nitrogen.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Soils used

The soils used in the present study are Keta and Nyankpala series. The Keta series was sampled from Anloga, a town located in the Keta Municipality of the Volta Region of Ghana. The area is within the coastal savannah zone of Ghana and has mean temperature of 28°C mean annual rainfall of about 900 mm which is evenly spread over the year (Dickson and Benneh, 1995). The Keta series is classified as Quartzi Psamment according to Soil Taxonomy by Awadzi *et al.* (2008). According to Obeng (2000) the soil is developed on costal dunes and consists of yellowish, loose, coarse sand with fragments of shell, droughty in nature and inherently infertile. Although the Keta series has little agricultural prospect due its low fertility status, with heavy fertilization the soil has been used for intensive maize and vegetable production over the years (Obeng, 2000). The soil was sampled at the depth of 0-20 cm, transported to the laboratory, air dried, sieved through 2 mm sieve, analysed and used for the study.

The Nyankpala series was sampled from Nyanpkala in Tolon- Kumbumgu District of Northern Region. Nyanpkala is in the guinea savannah zone of Ghana with unimodal rainfall pattern of 1000-1300 mm per annum and mean temperature of 32°C. The soil is classified as Plinthic acrisol according to USDA, soil taxonomy Ziblim *et al*. (2012). It is moderately shallow to deep concretionary, gravelly with medium texture overlying shale (Obeng, 2000). The soil was sampled at depth of 0-20 cm, transported to the laboratory, air dried and analysed. The two soils were sampled from cultivated fields.

3.2 Characterization of soil

3.2.1 Particle size analysis

Forty grams (40 g) soil was weighed into plastic bottle and 100 mL of sodium hexametaphosphate or calgon solution added. The suspension was put on a mechanical shaker and shaken for 2 hrs after which it was transferred into sedimentation cylinder and distilled water added to 1000 mL mark. A plunger was inserted into the suspension, moved in upward and downward strokes to mix the suspension thoroughly. The suspension was left to stand on the bench for 5 mins, after which a hydrometer was lowered into it and the scale read at the top of the meniscus as the hydrometer reading for clay and silt. The suspension was left on the bench undisturbed for 5 hrs after which the hydrometer reading for only clay was taken. After the second reading had been taken, the suspension was poured out directly into a 47µm sieve from the sedimentation cylinder and the affluent collected into a container. The particles were obtained from the residues by agitating the residues by running tap water through it. The particles were transferred into a moisture can using a wash bottle and dried in an oven at a temperature of 105°C for 24 hrs. Based on the oven dry weight of the soil sample taken, the percentage sand, silt and clay fraction in the soil were calculated as follows:

$$\text{Clay (\%)} = \frac{\text{Hydrometer reading at 5 hours}}{\text{weight of soil (g)}} \times 100$$

$$\text{Silt (\%)} = \text{\% (Clay + Silt)} - \text{Clay (\%)}$$

$$\text{Sand (\%)} = \frac{\text{Weight of oven dry sand retained on the 47 µm sieve}}{\text{weight of soil}} \times 100$$

The textural classes were then determined by using textural triangle.

3.2.2 Bulk density (ρb) determination

Bulk densities of the soils were determined by using the core method. A cylindrical metal core of known height and diameter was used to sample the soil by driving it into the soil by hitting it with mallet. The samples were taken out and the ends of the metal core were trimmed and covered. The soil samples were taken to the laboratory and dried in the oven at a temperature of 105°C for 24 hrs, after which the dry weights were determined. The weight of the empty metal core was also measured.

Bulk density was calculated using the formula (Blake and Hartege, 1986).

$\rho b = M_s/V_t$

Where M_s= mass of oven dry soil

V_t = volume of soil in core sampler.

3.2.3 Determination of soil pH water (1:1)

Ten grams (10 g) of soil were weighed into a beaker and 10 mL of distilled water was added to give a 1:1 (soil to water) ratio. The mixture was stirred several times for 30 mins and left to stand for 1hr to allow most of the clay particles in suspension to settle. Two different solutions of pH 4 and 7 were used to standardize the glass electrode pH meter-CG818, Schott Great. The electrode was then rinsed with distilled water, immersed into the partly settled suspension and the pH reading on the meter recorded.

3.2.4 Determination of pH $CaCl_2$ (1:2)

Ten grams (10 g) of soil were weighed into a beaker and 20 mL of $CaCl_2$ solution was added to give it a 1:2 (soil to salt) ratio. The mixture was stirred several times for 30 mins and left to stand for 1hr to allow most of the clay particles in suspension to settle. Two different solutions of pH 4 and 7 were used to standardize the glass electrode pH meter-CG818, Schott Great. The electrode was then rinsed with distilled water and then immersed into the partly settled suspension and the pH reading on the meter recorded.

3.2.5 Determination of organic carbon

The wet oxidation method of Walkley and Black (1934) modified by Allison (1965) was used to determine organic carbon in the soil. The method involves the reduction of $Cr_2O_7^{2-}$ ions by organic matter and the unreduced $Cr_2O_7^{2-}$ measured by titration with Ammonium Ferrous Sulphate. The quantity of organic matter oxidized is calculated from the amount of $Cr_2O_7^{2-}$ reduced.

Half a gram (0.5 g) of finely ground soil that had been sieved through 0.5mm sieve was weighed in triplicate into 500 mL Erlenmeyer flasks. Ten millimeters (10 mL) of 1.0M ($K_2Cr_2O_7$) was added to the soil followed by 200 mL of concentrated H_2SO_4. The flask was swirled to ensure that the solution comes into contact with the soil particles. After swirling it for some time it was allowed to stand for 30 mins. After 30 mins, 200 mL of distilled water was added followed by 5 mL of 85% orthophosphoric (H_2PO_4) acid, 2 mL of Barium diphenyl-4-suphonate indicator before titrating against 0.5 M acidified Ammonium Ferrous Sulphate from an orange colour to

green end point. Organic matter content was calculated by multiplying percent organic carbon by the conventional factor of 1.33 using formula.

$$\%OC = \frac{(0.33\times10-VN)\times1.33}{W} \times 100$$

Where %OC = Percent organic carbon

V = Titre value (mL)

N = Normality of Fe $(NH_4)_2SO_4$

W = Weight of soil sample.

3.2.6 Determination of available nitrogen in the soil

Five grams (5 g) of soil that had been sieved through 2 mm sieve was weighed into a 100 mL centrifuge bottle and 50 mL of 2M KCl solution added. The content of the bottle was placed in mechanical shaker and shaken for 30 mins, after which the suspension was filtered through Whatman No 42 filter paper into another container. Five milliliters (5 mL) of the filtrate was pipetted into micro Kjedahl digestion flask and 0.2 g of MgO was added. The flask was connected to a distillation apparatus and 30 mL of the distillate collected in 5 mL of 2% boric acid containing (methyl red-methylene blue indicator mixture). The distillate collected in the boric acid was titrated against 0.01 M HCl till a purplish end point was reached to determine NH_4^+.

One milliliter (1 mL) of sulphamic and 0.2 g of Devada′s alloy were added to remaining content of the flask and another distillate collected in a separate conical flask containing 5 mL of 2%

boric acid containing methyl red-methylene blue indicator mixture. The distillate collected in the boric acid was back titrated against 0.01M HCl till a purplish end point was obtained to determine NO_3^-. Concentrations of NH_4^+ and NO_3^- in the soil were determined from the number of moles of HCl consumed in the back titrations.

$$NH_4\text{-N mg/kg} = \frac{MHCl \times VHCl \times 10^{-2} \times 18 \times VKCl \times 1000mg}{volume\ of\ aliqout \times weight\ of\ soil(g)}$$

$$NO_3 - N\ mg/kg = \frac{MHCl \times VHCl \times 10^{-2} \times 18 \times VKCl \times 1000mg}{volume\ of\ aliqout \times weight\ of\ soil(g)}$$

Where M = Molarity of HCl

V=Volume of HCl consumed in back titration

V=Extraction volume of KCl

3.2.7 Determination of total nitrogen in the soil

The total nitrogen in the soil was determined using the Kjedahl method. Half a gram (0.5 g) of soil that had been sieved through 2 mm sieve was weighed into 250 mL Kjedahl flask and a tablet of digestion accelerator (selenium catalyst) was added, followed by addition of 5 mL of concentrated H_2SO_4 acid. The mixture was digested till it became clear, after which the flask was allowed to cool. The mixture was transferred into 100 mL volumetric flask and made to volume with distilled water. An aliquot of 5 mL of the digest was taken to a Markham distillation apparatus. The mixture was distilled after adding 5 mL of NaOH. The distillate was collected in 5 mL of 2% boric acid (containing indicator methylene blue and methyl red mixture) in 50 mL

Elenmeyer flask and then titrated against 0.01M HCl acid solution (Bremner, 1965). The percentage (%) total nitrogen was calculated as

$$\% \text{ N} = \frac{0.01 \times \text{titre value} \times 0.014 \times \text{volume of extraction}}{\text{sample weight (g)} \times \text{volume of aliquot (mL)}} \times 100$$

3.2.8 Determination of available phosphorus

Bray and Kurtz (1945) method was used to determine the available phosphorus in the soil. Five grams (5 g) of soil that had been sieved through 2 mm sieve were weighed into an extraction bottle. Fifty milliliters (50 mL) of Bray 1 solution was added. The suspension was shaken for 3min in a reciprocating shaker, after which the suspension was allowed to settle and then filtered through Whatman No 42 filter paper into a 100 mL volumetric flask and made up to volume. The phosphorus content in the filtrate was determined by using the molybdate-ascorbic acid colour development method of Watanabe and Olsen (1965) described below.

An aliquot of 5 mL was pipetted from the supernatant into 50 mL volumetric flask in triplicate and pH adjusted with para-nitrophenol indicator. Few drops of ammonium hydroxide (4 M NH_4OH) were added till the colour changed to yellow, distilled water was added till the colourless solution was observed. Reagent A was prepared by dissolving 12 g of ammonium molybdate and 0.2998 g of antimony potassium tatrate in 250 mL distilled water. Reagent B was prepared by weighing and dissolving 1.056 g of ascorbic acid in 200 mL of Reagent A. The dissolved reagents were added to 1000 mL of 2.5M H_2SO_4 mixed thoroughly and made to volume in 2000 mL volumetric flask. Eight milliliters (8 mL) of Reagent B was added to the solution in the flask and made to 50 mL mark with distilled water. A blank was prepared by

using 5 mL of distilled water and 8 mL of Reagent B. Philips PU8620 spectrophotometer was calibrated using 25 mgL^{-1} standard P solutions. The colour intensity was determined on the Spectrophotometer at wavelength of 712 nm. The available phosphorus concentration in the soil sample was calculated using the spectrophotometer reading as follows.

$$P\ (\%) = \frac{\text{spectrophotometr reading } \left(\frac{mg}{L}\right) \times \text{total volume of extract}}{\text{volume of aliqout} \times \text{weight of sample} \times 1000} \times 100$$

3.2.9 Exchangeable bases and cation exchange capacity.

3.3.0 Exchangeable bases determination

Ten grams (10 g) of soil that had been sieved through 2 mm sieve were weighed into 200 mL extraction bottle, 100 mL of 1N ammonium acetate (NH_4OAC) solution buffered at pH 7.0 was added to the soil in the extraction bottle. The bottle was then placed on a mechanical shaker, shaken for 1hr and centrifuged at 3000 rpm for 20 min. The solution was filtered through Whatman No 42 filter paper into a clean bottle. An aliquot was taken from the filtrate in the bottle and used for determination of Ca, Mg, K and Na. The Atomic Absorption Spectrometer was used for reading the content of Ca, Mg, K and Na in solution calculated as follows:

$$Ca\ (cmol/kg) = \frac{R \times Vol.\ of\ extract \times 10^3\ (g) \times 10^2 \times E}{Weight\ of\ soil \times 10^6\ (ug) \times 40}$$

Where 40 = Atomic mass of Ca

R= AAS reading in mgL^{-1}

E = Charge of Ca

$$\text{Mg (cmol/kg)} = \frac{R \times Vol.\ of\ extract\ 10^3\ (g) \times 10^2 \times E}{Weight\ of soil \times 10^6\ (ug) \times 24}$$

Where 24 = Atomic mass of Mg

R= AAS reading in mgL^{-1}

E = Charge of Mg

$$\text{K (cmol/kg)} = \frac{R \times Vol.\ of\ extract\ 10^3\ (g) \times 10^2 \times E}{Weight\ of\ soil \times 10^6\ (ug) \times 39}$$

Where 39 = Atomic mass of K

R= AAS reading in mgL^{-1}

E = Charge of K

$$\text{Na (cmol/kg)} = \frac{R \times Vol.\ of\ extract\ 10^3\ (g) \times 10^2 \times E}{Weight\ of\ soil \times 10^6\ (ug) \times 22}$$

Where 22 = Atomic mass of K

R= AAS reading in mgL^{-1}

E = Charge of Na

3.3.1 Cation Exchange Capacity

Ten grams (10 g) of soil that had been sieved through 2 mm sieve was weighed into 200 mL extraction bottle, 100 mL of 1N ammonium acetate (NH_4OAC) solution buffered at pH 7.0 was added to the soil in the extraction bottle. The bottle was placed in a mechanical shaker and

shaken for 1 hr, and centrifuged at 3000 rpm for 20 min. The solution was filtered through Whatman No 42 filter paper into a clean bottle. The residual soil obtained after filtration was immediately leached with 25 mL methanol into empty bottles. The soil was again leached with 25 mL portion of acidified 1M KCl into another empty bottle. Ten milliliters (10 mL) of the leachate from leaching with portions of acidified KCl was pipetted into a Kjedahl flask and 10 mL of 40% NaOH was added and then distilled. The distillate was trapped in 2% boric acid and titrated against 0.01M HCl. The cation exchange capacity in cmol kg^{-1} soil was then calculated from the number moles of HCl consumed in the back titration.

3.4 Biochar types used

The feedstocks used for the biochar production are rice husk, sawdust and corn cob. These biochar types were produced by pyrolysis technique described by Lehmann *et al* (2003) at a temperature of 500°C in kiln at Soil Research Institute (SRI) in Kumasi. After the pyrolysis the biochar samples obtained were ground and the particles homogenized by sieving through 2 mm sieve and analysed for pH, total P and total surface area.

3.4.1 Determination of total surface area of biochar

The total surface area of the biochar material was determined using Sears's method for silica-based material, 1.5 g of biochar sample was added to 100 mL dilute hydrochloric acid (pH 3) in 250 mL flask whilst agitating the mixture. Thirty grams (30 g) of sodium chloride was added with stirring to the mixture and the volume made to 150 mL mark using deionised water. The

solution was titrated against 0.1M NaOH and the volume required to raise the pH from 4 to 9 recorded. The total surface area was calculated using the relation

$(m^2/ g) = 32V – 25$

Where

V = the volume of sodium hydroxide required for raising the pH from 4 to 9.

3.5 Cow dung used

Cured cow dung sample was obtained from Livestock and Poultry Research Centre (LIPREC) of University of Ghana for the experiment. The cured cow dung sample was air dried under room temperature, sieved through 0.5 mm sieve and used for the experiment. The concentrations of nitrogen, phosphorus and potassium in the cow dung were determined as described earlier.

3.6 Laboratory experiment

3.6.1 Leaching of water soluble basic cations and phosphorus

Three biochar types sawdust, rice husk and corn cob were packed in columns to determine the concentrations of water soluble cations and phosphorus present in these biochar types. The columns were made of acrylic cylinders with volume of 1000 cm^3. The bottoms of the columns were covered with Whatman No 42 filter paper, followed by nylon mesh of size 25 µm pore size. The filter paper and nylon mesh were secured at the mouth with circular metal clips to prevent biochar particles from falling.

The biochar samples were sieved through 0.5 µm sieve to obtain uniform particle size among the biochar samples. One hundred and fifty (150) g of each biochar sample was weighed into the acrylic cylinder and packed to 200 cm^3 by gently tapping the sides of the cylinders. The set up was replicated three times for each biochar type. The set up is shown in Fig. 1. The columns were completely leached with deionised water and the leachate collected in 1000 mL conical flask placed under the columns and the concentrations of K^+, Ca^{2+}, Mg^{2+}, Na^+ and P were determined.

Figure 1. Set-up for leaching of soluble cations and phosphorus

3.6.2 Retention of nitrogen

Two point one (2.1) g of $(NH_4)_2SO_4$ was dissolved in 500 mL of deionised water and allowed to pass through the leached biochar sample in the column described above. A constant head of 50 cm was maintained and the leachate collected. The concentration of NH_4-N in every 50 mL of leachate collected and the amount of NH_4-N retained by the biochar types was determined and calculated as follows:

$$A = M_1 - M_2 / W$$

Where

A = amount of NH_4-N retained by the biochar

M_1 = Mass of NH_4-N applied

M_2 = Mass of NH_4-N in leachate

W = weight of biochar in the column

For nitrate retention, 3.42 g of KNO_3 was dissolved in 500 mL of deionised water and allowed to pass through the leached biochar sample in the column described above. A contant head of 50 cm was maintained and the leachate collected. The concentration of NO_3-N in every 50 mL of leachate collected determined and the amount of NO_3-N retained by the biochar types was calculated as follows:

$$A = M_1 - M_2 / W$$

Where

A = amount of NO_3-N retained by the biochar

M_1 = Mass of NO_3-N applied

M_2 = Mass of NO_3-N in leachates

W = weight of biochar in the column

For the retention of both NH_4-N and NO_3-N, 1.28 g of NH_4NO_3 was dissolved in 500 mL of deionized water and allowed to pass through the leached biochar sample in the column described above. A contant head of 50 cm was maintained and the leachate collected. The concentration of NH_4-N and NO_3-N in every 50 mL of leachate collected determined and the amount of NH_4-N or NO_3-N retained by the biochar types was calculated as follows:

$A = M_1 - M_2 / W$

Where

A = amount of NH_4-N/ NO_3-N retained by the biochar

M_1 = Mass on NH_4-N/NO_3-N applied

M_2 = Mass of NH_4-N/NO_3-N in leachates

W = weight of biochar in the column

3.7 Plant culture experiments

2.3 kg soil of the Keta and Nyankpala series were weighed into experimental pots of height 15 cm and 8 cm in diameter. Four holes were created at the bottom of the pots and the holes plugged

with cotton wool to prevent soil particles from falling. The moisture content of the soil was maintained at 80% field capacity. Each pot was placed in a bowl to allow collection of leachate and the treatments below (table 1) were imposed.

In all forty treatments were replicated three times and completely randomised. Four seeds of Obaatanpa maize variety were sown per pot and thinned to 2 plants per pot after germination.

Table 1: Treatments

CD (30t/ha)	RH20 (F) (132.5 kg N/ha) + CD (15 t/ha)
ASS (265 kg N/ha)	CD (30t/ha) + SD40
ASP (265 kg N/ha)	SD40 (F) (265 kg N/ha)
CD (15t/ha) + ASS (132.5 N/ha)	SD40 + ASP (265 kg N/ha)
CD (30t/ha) + SD20	SD40 (F) (132.5 kg N/ha) + CD (15 t/ha)
SD20 (F) (265 kg N/ha)	CD (30t/ha) + RH40
SD20 + ASP (265 kg N/ha)	RH40 (F) (265 kg N/ha)
SD20 (F) (132.5 kg N/ha) + CD (15 t/ha)	RH40 + ASP (265 kg N/ha)
CD (30t/ha) + RH20	RH40 (F) (132.5 kg N/ha) + CD (15 t/ha)
RH20 (F) (265 kg N/ha)	
RH20 + ASP (265 kg N/ha)	

ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cowdung, CDASS: Cowdung + Ammonium sulphate solution, RH20: 20 t ha^{-1} Rice husk biochar, SD20: 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD40: 40 t ha^{-1} sawdust biochar, RH20 (F): 20 t ha^{-1} rice husk biochar fortify with ammonium sulphate fertilizer, RH40 (F): 40 t ha^{-1} rice husk biochar fortify with ammonium sulphate fertilizer, SD20 (F): 20 t ha^{-1} sawdust biochar fortify with ammonium sulphate fertilizer, SD40 (F): 40 t ha^{-1} sawdust biochar fortify with ammonium sulphate fertilizer.

At 14 and 28 days after planting (DAP) the moisture content of the soils was brought above 100% field capacity in order to leach soils. The leachate collected was analysed for available nitrogen content. Maize plants were grown and harvested 5 weeks after planting. The harvested plants were separated into shoots and roots, and dried in an oven at a temperature of 68°C for 48 hrs to determine dry matter weight and Nitrogen content in the shoots.

In order to investigate the residual effects of the treated soils, maize plants were grown for another five weeks. The soils were also leached on 14 and 28 DAP for analysis of available nitrogen content. The dry weights of the roots and shoots were determined, and nitrogen contents in the shoots were analysed.

3.8 Data Analysis

The data collected were analysed using Genstats (9^{th} edition) and the means separated at Least Significance level of 5%.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Soil characteristics

Some of the physical and chemical characteristics of the soils used are shown in Table 2. Particle size analysis showed that the Keta series had 90% sand, 7% silt and 3% clay, whilst the Nyankpala series had 68% sand, 24% silt and 8% clay. Based on the textural table, the Keta series is classified as sandy and Nyankpala series as sandy loam. These classifications agree with those of Awadzi *et al.* (2008) and Ziblim *et al.* (2012) who classified Keta and Nyankpala soils as sandy and sandy loam, respectively. The bulk densities for the Keta and Nyankpala soils were 1.63 and 1.58 g/ m^3, respectively. These values are within the range ideal for plants growth as documented by Arshad *et al.* (1996). According to Ziblim *et al.* (2012) the critical value is 2.1 g m^{-3} and since the bulk densities for the soils used are below the critical value, bulk density will not be a limiting factor.

The Keta series had pH of 6.6 in water which makes it slightly acidic in nature and this agrees with the findings of Asomaning *et al.* (2012) who reported similar pH value. The Nyanpkala series had pH in water 5.3 and is also classified as slightly acidic and this agrees with the values reported by Ziblim *et al*. (2012) for Nyankpala series. The organic carbon (OC) contents of the Keta and Nyankpala series were 3.6 g kg^{-1} (0.36%) and 9.2 g kg^{-1} (0.92%), respectively. These values are very low and would not maintain sustainable crop yield because Wullschleger and Garten (2004) documented that the critical value is 1%. The low values for the two soils could be attributed to sparse grass vegetation covering the soils as reported by Obeng (2000).

Table 2: Physical and chemical properties of the soils used

Soil properties	Nyankpala	Keta
Sand (%)	68	90
Silt (%)	24	7
Clay (%)	8	3
Texture	SL	S
Bulk Density (Mg/m^{-3})	1.58	1.63
pH H_2O (Soil: Water, 1:1)	5.3	6.6
pH $CaCl_2$ (Soil: $CaCl_2$, 2:1)	5.1	6.3
Organic Carbon ($g\ kg^{-1}$)	9.2	3.6
Total N ($g\ kg^{-1}$)	0.7	0.2
Available N ($g\ kg^{-1}$)	0.16	0.1
Available P ($mg\ kg^{-1}$)	2.23	1.71
Cation Exchange capacity ($cmol_c kg^{-1}$)	8.14	3.03
Exchangeable bases ($cmol_c kg^{-1}$)		
Ca	1.1	1.02
Mg	0.54	0.50
K	0.40	0.30
Na	0.23	0.50

SL: Sandy Loam S: Sand N: Nitrogen P: Phosphorus CEC: Cation Exchange Capacity.

Both soils had very low available and total N content. The low values could be attributed to the low OC content of the soils. The low values could also be attributed to the sandy nature of the soils since there is high leaching of N in such soils. Ziblim *et .al.* (2012) also reported low values for Nyankpala soil and attributed it to low OC content of the soil which could result from low litter accumulation and high decomposition rate of OM in the soils within the savanna zone.

The Keta series had available P content of (1.71 mg/kg) which was relatively lower than that of the Nyankpala series 2.23 mg kg^{-1} (Table 2). Generally the available P contents observed in the two soils were low. The low available P content found in the Keta series might be attributed to high leaching of P in the soil as reported by Asomaning *et al.* (2012). The low available P observed in the Nyankpala series might be due to high P fixation in such a soil making P unavailable for plant uptake (Nartey, 1994).

The cation exchange capacity (CEC) of the Nyankpala series was (8.14 $cmol_c$ kg^{-1}) which was comparatively higher than that of the Keta series (3.03 $cmol_c$ kg^{-1}). These values are low and very low for Nyankpala and Keta series, respectively. Both soils have low clay and OC contents and that might have accounted for the low CEC observed in them. The CEC of the soil is a colloidal property which is influenced by the clay and OM content of the soil (Landon, 1991).

The Keta series had Ca and Mg contents of 1.02 and 0.50 cmol kg^{-1} respectively. The Ca content observed for the Keta series was normal for soils which contains shell fragments and formed on calcareous pan (Obeng, 2000). The relatively low magnesium content of the Keta series was normal for soils with such loose structure, because the higher the magnesium content of the soil the more compact the structure of the soil. The Keta series had K content of 0.3 cmol kg^{-1} and Na

0.5 cmol kg^{-1} contents which were relatively higher than the amounts observed in the Nyankpala series and could be due to the close proximity of the soil sampled site to the sea.

The Nyankpala series had Ca, Mg, K and Na contents of 1.1 cmol kg^{-1}, 0.54 cmol kg^{-1}, 0.4 cmol kg^{-1}, 0.23 cmol kg^{-1} respectively which was in line with the amounts reported by Ziblim *et al.* (2012) for soils found in the agro ecological zones within which the Nyankpala soil was sampled.

4.2 Some physical and chemical properties of the biochar types

All the biochar types used for the study had alkaline pH (Table 3) resulting from the pyrolysis process which is in conformity with the findings of Struebel (2011). Among the biochar types, sawdust biochar had the highest pH (8.06) followed by corn cob biochar (7.47) and then rice husk biochar (7.35) (Table 3). The relatively higher pH observed in the sawdust biochar was in line with the findings of Zolue (2012) who had higher pH for sawdust biochar compared to that of rice husk. The relatively high pH of the sawdust biochar among the biochar types may be attributed to high basic cation content of the sawdust biochar (Table 3).

The rice husk biochar has the highest total P content (1246.15 mg kg^{-1}) followed by corn cob (938 mg kg^{-1}) and then sawdust (896 mg kg^{-1}). The rice husk biochar was obtained from charring rice husk which is a by-product of an agricultural crop therefore the high P content observed in the rice husk biochar might be due to high P fertilization of the crop in the field (Table 3). The sawdust biochar had the highest total surface area (3.62 g m^{-3}) followed by the rice husk (3.02 mg kg^{-1}) biochar and then corn cob biochar (2.69 g m^{-3}). The high value for sawdust biochar

might probably be due to high micropore spaces within the biochar because Rouquerol *et al.* (1999) reported that surface area of biochar is influenced by the micropore within the material.

Table 3: Some physico-chemical properties of the biochar used

Biochar type	SD	RH	CC
pH	8.06	7.35	7.47
Total P (mg/kg)	896.24	1246.15	938.01
Total surface area (g/m^3)	3.62	3.02	2.69
Exchangeable bases (%)			
Ca	1.23	0.58	0.71
Mg	0.68	0.30	0.39
K	1.19	0.80	0.86
Na	1.89	1.43	1.27

SD: Sawdust RH: Rice husk CC: Corn cob

4.3 Laboratory column leaching experiment

4.3.1 Leaching of water soluble ions in the biochar samples

The sawdust biochar contained the highest amounts of water soluble Ca (48.28 mg) and soluble Mg (12.93 mg) followed by the corn cob biochar with Ca and Mg contents of 22.38 mg and 8.86 mg respectively (Table 4). The rice husk biochar had the lowest water soluble Ca and Mg contents of 19.13 mg and 6.93 mg. The comparatively high contents of water soluble Ca and Mg observed in the sawdust biochar might be attributed to the presence of these cations in the cell

wall of woody plants. According to Marschner (1995) Ca forms an integral component of plant cell wall especially woody plants and it occurs as calcium pectate compounds in cell wall, which gives stability to the cell wall and help bind the cell together.

The rice husk biochar contained the highest water soluble P followed by the corn cob biochar with a value of 157.80 mg. The sawdust biochar had the lowest P contents of 59.20 mg. The rice husk biochar was prepared from rice husk biomass which is a residue from agricultural crop. Therefore the high water soluble P content observed in the rice husk biochar might be due to high P content of the crop from which the residue was obtained. According to Angst and Sohi, 2013) nutrient elements in biochar originate from the feedstock; P and K are converted into inorganic forms and retained in biochar in particulate form during the pyrolsis process. The K contents in the three biochar types were relatively close with the range value of 31.26 mg – 48.33 mg.

Table 4: Some water soluble ions in the biochar

Biochar	Mg (mg/kg)	Ca (mg/kg)	K (mg/kg)	P (mg/kg)
SD	12.93	48.26	31.26	59.20
RH	6.93	19.13	39.27	385.26
CC	8.86	22.38	40.33	157.80

CC: Corn cob biochar, RH: Rice husk biochar, SD: Sawdust biochar

4.3.2 Nitrogen retention

When the columns were loaded with $(NH_4)_2SO_4$ fertilizer solution, the sawdust biochar retained the highest amount of NH_4–N (2273.40 mg kg^{-1}) followed by the rice husk biochar (1809.57 mg kg^{-1}) then the corn cob biochar (1756.70 mg kg^{-1}) as shown in Table 5. When the biochar types

were loaded with KNO_3 fertilizer, the highest amount of NO_3-N (2283.93 mg kg^{-1}) was also retained by the sawdust biochar followed by the corn cob biochar (1881.31 mg kg^{-1}) and then the rice husk biochar (1743.33 mg kg^{-1}).

The sawdust biochar retained the highest amount of NH_4^+-N and NO_3-N from the NH_4NO_3 fertilizer followed by the rice husk biochar whilst the corn cob biochar retained the lowest amount of NH_4-N and NO_3-N from the NH_4NO_3. The relatively high amount of NH_4^+-N and NO_3-N retained by the sawdust biochar when the biochar samples were loaded with the fertilizer solutions could be due to relatively high surface area of the sawdust biochar (Table 5) which provided more surfaces for N adsorption.

Table 5: Amount of NH_4 –N and NO_3 –N retained by biochar

		Amount of nitrogen retained (mg/kg biochar)	
Biochar type	Fertilizer	NH_4	NO_3
SD	$(NH_4)_2SO_4$	2273.4	NA
SD	KNO_3	NA	2283.93
SD	NH_4NO_3	2475.1	2241.44
RH	$(NH_4)_2SO_4$	1809.57	NA
RH	KNO_3	NA	1743.33
RH	NH_4NO_3	1703.88	1860.32
CC	$(NH_4)_2SO_4$	1756.70	NA
CC	KNO_3	NA	1881.31
CC	NH_4NO_3	1022.38	1569.08

NA: not applicable

4.4 Amount of ammonium in leachate (First Planting)

The results for amounts of NH_4-N in leachates collected from the various amended soils on 14th and 28th days after planting (DAP) showed similar trend (Table 6). The results showed that the control treatments in Keta series retain less amounts of NH_4-N as compared to the control treatments in Nyankpala series. The differences in the amounts of NH_4-N retained by the two soils could be attributed to differences in clay contents, besides Keta soil was sandy whilst Nyankpala was sandy loam. High infiltration rate of sandy soil makes leaching of N and other nutrients a limiting factor to productivity in sandy soil (White et al., 1997). Addition of biochar to the soils significantly ($p < 0.05$) increased the retention of NH_4-N in the soils. When biochar is added to the soil it increases water and nutrients retention in the amended soil. According Lehman *et al*. (2004) biochar addition to soil influences nutrients leaching through several mechanisms; increasing water retention in the rooting zone through direct binding, sorbing nutrients or by interacting with other soil constituents. Biochar contains negative charge site therefore when added to soil it holds cations and prevents leaching of cations in the soil. According to Laing *et al*. (2006), the high surface charge of biochar enables biochar to hold cations such as NH_4^+ by cation exchange. These could have accounted for the enhancement in N retention noticed in the biochar amended treatment as compared to treatments with no biochar.

Table 6: Amount of NH_4-N leached (first planting)

Soils	Feedstocks/Rates	Treatments (NH_4^+-N mg/kg)							
		ASP		ASS		CD		CDASS	
		Dα	Dγ	Dα	Dγ	Dα	Dγ	Dα	Dγ
Keta	Control	21.58a	16.20a	20.80a	16.31a	20.93a	15.31a	21.60a	15.22a
	RH20	5.79c	4.03c	5.37c	3.87c	5.47c	3.48c	4.91c	4.04c
	RH40	5.41c	3.91c	5.34c	3.60c	4.99c	3.40c	5.47c	3.90c
	SD20	5.01c	3.68c	5.67c	3.97c	6.05c	3.51c	6.10c	3.69c
	SD40	6.17c	3.38c	5.08c	3.36c	5.38c	3.17c	5.90c	3.41c
Nyankpala	Control	10.44b	7.72b	10.55b	8.08b	10.13b	7.82b	9.34b	7.91b
	RH20	1.74d	1.93d	2.08d	1.82d	1.76d	1.74d	1.85d	1.32d
	RH40	1.98d	1.68d	2.01d	1.55d	1.90d	1.83d	1.64d	1.91d
	SD20	2.66d	1.33d	2.20d	2.06d	1.90d	1.53d	1.83d	2.37d
	SD40	2.24d	1.45d	1.74d	1.98d	1.98d	1.56d	1.89d	2.04d

Dα; leahate collected on 14th day after planting, Dγ: leahate collected on 28th day after planting, ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cow dung, CDASS: Cow dung + Ammonium sulphate solution, RH 20: 20 t ha^{-1} Rice husk biochar, SD20: 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD 40: 40 t ha^{-1} sawdust biochar. Values for leachate collected on the same day with same alphabet are not significantly different at p= 0.05

4.5 Amount of ammonium in leachate (Second Planting)

Table 7 shows the results for the quantity of NH_4-N in leachates from the various amended soils. The results showed that, among the controls the quantity of NH_4-N from the Keta series was significantly higher ($p < 0.05$) than that of the Nyankpala series. Therefore the control treatments in Keta series, retained less amount of NH_4-N as compared to that of the Nyankpala series. This could be attributed to the sandy nature of the Keta series which makes it more susceptible to leaching. Sandy soils and ferrallitic soils due to low clay content, poor nutrients and water retention makes them susceptible to leaching (Zotarelli *et al*., 2007, Sitthaphnit *et al*., 2009). Impact of biochar on N retention in Keta series was significantly ($p < 0.05$) higher than in the Nyankapala series. The Keta series is sandy and has larger pore spaces with poor water holding capacity therefore addition of the biochar might have greatly enhanced its water holding capacity and nutrients retention.

Addition of biochar significantly ($p < 0.05$) increased the retention of NH_4-N in the two soils. Amending soil with biochar enhances soil aggregation which helps to improve water and nutrients retention (Yoo *et al.*, 2014; Xu *et al*., 2016). It is therefore observed that the trend of leaching was similar in the first and second planting periods, except the quantities of NH_4-N leached were different.

Table 7: Amount of NH_4-N leached (second planting)

Soils	Feedstocks/Rates	Treatments (NH_4^+-N mg/kg)							
		ASP		ASS		CD		CDASS	
		Dα	Dγ	Dα	Dγ	Dα	Dγ	Dα	Dγ
Keta	Control	8.68a	3.99a	9.24a	4.03a	9.50a	3.97a	9.50a	4.21a
	RH20	1.75c	0.56c	2.00c	0.40c	2.22c	0.55c	1.94c	0.52c
	RH40	2.25c	0.46c	1.93c	0.41c	1.96c	0.43c	2.40c	0.50c
	SD20	2.00c	0.52c	2.06c	0.55c	2.21c	0.51c	2.47c	0.50c
	SD40	2.53c	0.47c	2.14c	0.45c	1.98c	0.46c	2.16c	0.42c
Nyankpala	Control	6.70b	1.98b	6.81b	1.69b	6.05b	1.43b	6.22b	1.52b
	RH20	1.61c	0.53c	1.92c	0.52c	1.74c	0.49c	2.01c	0.48c
	RH40	2.31c	0.48c	1.60c	0.45c	1.75c	0.49c	1.58c	0.52c
	SD20	2.07c	0.54c	1.91c	0.53c	1.93c	0.62c	2.14c	0.38c
	SD40	1.85c	0.56c	1.64c	0.46c	1.59c	0.50c	1.77c	0.47c

Dα: leahate collected on 14th day after planting, Dγ: leahate collected on 28th day after planting, ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cow dung, CDASS: Cow dung + Ammonium sulphate solution, RH 20: 20 t ha^{-1} rice husk biochar, SD20: 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD40: 40 t ha^{-1} sawdust biochar. Values for leachate collected on the same day with same alphabet are not significantly different at p = 0.05

4.6 Amount of nitrate in leachate

The results in Table 8 shows the amounts of NO_3-N in leachates collected on the 14th and 28th DAP during the first planting. The results indicated that among the controls, the Nyankpala series retained significantly ($p < 0.05$) higher amount of NO_3-N as compared to the Keta series. The Keta series is sand whilst the Nyankpala series is sandy loam so this could have made the Keta series more susceptible to leaching than the Nyankpala series. Leaching of nitrogen is one of the most common ways through which nitrogen especially NO_3^- is lost from the soil system, with the situation being severe in sandy soil and under heavy rainfall (Razzaque and Hannafi, 2005). Amending the two soils with biochar significantly ($p < 0.05$) enhanced the amount of NO_3-N retained in the two soils and reduced the amount of NO_3-N leached. Biochar material has positive charge sites therefore when applied to the soil can hold anions like nitrate which helps to prevent leaching of nitrate in the soil. There are also positive charge sites on biochar which gives anion exchange capacity to the material which can attract nitrate and phosphate ions (Chintala *et al*., 2015). Table 9 shows the amounts of NO_3-N in leachates collected on the 14th and 28th days after second planting. Although the amounts of NO_3-N contained in the leachates were lower than that collected during the first planting, the trends were similar in both cases.

Table 8: Amount of NO_3-N leached (first planting)

Soils	Feedstocks/Rates	Treatments (NO_3^- -N mg/kg)							
		ASP		ASS		CD		CDASS	
		Dα	Dγ	Dα	Dγ	Dα	Dγ	Dα	Dγ
Keta	Control	8.56a	6.99a	8.21a	7.44a	9.13a	7.01a	9.15a	7.49a
	RH20	2.01c	0.79c	2.35c	0.77c	2.34c	0.71c	2.08c	0.66c
	RH40	2.35c	0.70c	2.70c	0.65c	1.69c	0.72c	2.64c	0.79c
	SD20	2.03c	0.79c	2.69c	0.73c	2.70c	0.69c	2.63c	0.80c
	SD40	2.68c	0.82c	2.26c	0.73c	2.66c	0.73c	1.99c	0.77c
Nyankpala	Control	6.07b	3.13b	5.10b	3.26b	6.12b	3.33b	5.42b	2.98b
	RH20	1.88c	0.30c	2.20c	0.29c	2.23c	0.32c	1.57c	0.31c
	RH40	1.89c	0.32c	2.21c	0.40c	1.56c	0.35c	2.23c	0.32c
	SD20	2.22c	0.31c	1.55c	0.29c	1.89c	0.33c	1.58c	0.33c
	SD40	1.54c	0.31c	1.91c	0.28c	1.88c	0.30c	2.22c	0.32c

Dα; leahate collected on 14th day after planting, Dγ: leahate collected on 28th day after planting, ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cow dung, CDASS: Cow dung + Ammonium sulphate solution, RH 20: 20 t ha^{-1} Rice husk biochar, SD20: 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD 40: 40 t ha^{-1} sawdust biochar. Values for leachate collected on the same day with same alphabet are not significantly different at p = 0.05

Table 9: Amount of NO_3-N leached (Second planting)

Soils	Feedstocks/Rates	Treatments (NO_3^- -N mg/kg)							
		ASP		ASS		CD		CDASS	
		Dα	Dγ	Dα	Dγ	Dα	Dγ	Dα	Dγ
Keta	Control	3.83a	4.19a	3.94a	4.33a	3.91a	3.95a	3.68a	4.38a
	RH20	0.57c	0.55c	0.47c	0.57c	0.42c	0.54c	0.44c	0.47c
	RH40	0.49c	0.59c	0.47c	0.64c	0.41c	0.58c	0.43c	0.56c
	SD20	0.60c	0.67c	0.45c	0.55c	0.55c	0.51c	0.47c	0.53c
	SD40	0.47c	0.66c	0.46c	0.55c	0.50c	0.60c	0.48c	0.57c
Nyankpala	Control	2.13b	2.02b	2.00b	2.09b	2.03b	2.12b	2.05b	1.95b
	RH20	0.54c	0.57c	0.52c	0.60c	0.47c	0.53c	0.43c	0.39c
	RH40	0.48c	0.49c	0.52c	0.52c	0.50c	0.57c	0.43c	0.38c
	SD20	0.65c	0.50c	0.49c	0.57c	0.47c	0.55c	0.54c	0.43c
	SD40	0.43c	0.48c	0.39c	0.57c	0.43c	0.52c	0.40c	0.56c

Dα; leahate collected on 14th day after planting, Dγ: leahate collected on 28th day after planting, ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cow dung, CDASS: Cow dung + Ammonium sulphate solution, RH 20: 20 t ha^{-1} Rice husk biochar, SD20: 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD 40: 40 t ha^{-1} sawdust biochar. Values for leachate collected on the same day with same alphabet are not significantly different at p = 0.05

4.7 Shoot and root dry weights of maize

The results for dry matter (DM) of maize grown in the various amended soils during the first planting are shown in Figs. 2 and 3, respectively. The shoot and root dry weights produced by the control treatments in both soils were not significantly ($p > 0.05$) different from each other. This could be attributed to the inherent low plant nutrients, especially N of the two soils used (Table 2). Amending the two soils with biochar significantly ($p < 0.05$) increased the DM yield. This increment in DM yield could be due to the N fertilizer adsorbed by the biochar and made available for uptake. According to Taghizadel *et al*. (2012) recent evidence has indicated that N adsorbed by biochar is eventually made available for plant uptake. Ma and Matsunaka (2013) reported that when biochar is applied as sole amendment or together with N fertilizer, it significantly improved DM of shoots and roots of lettuce. Similar trend was also observed during the second planting as shown in Fig. 4 and 5.

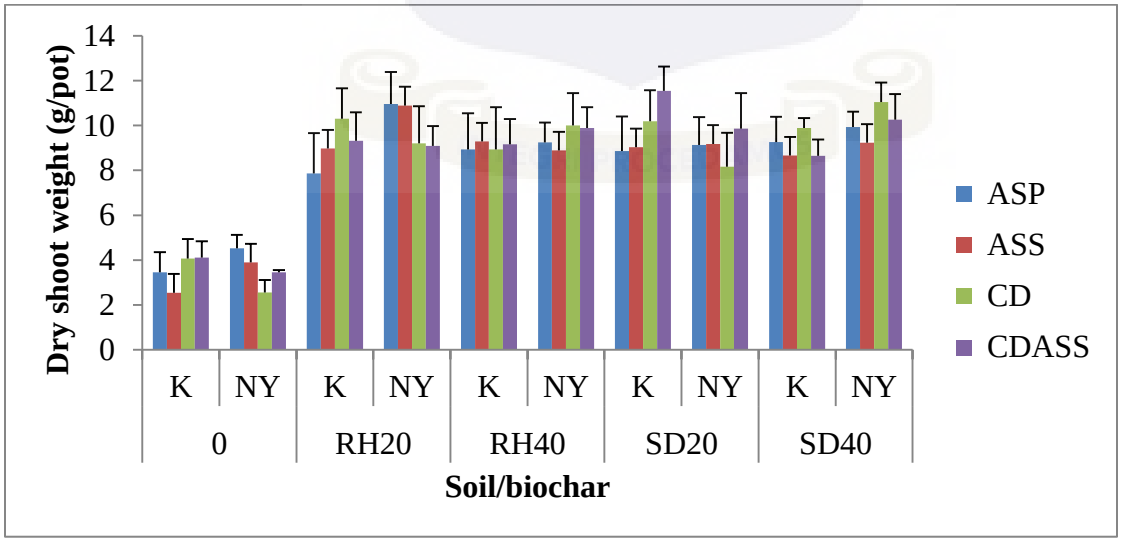

Figure 2: Shoot dry weight of maize (1st planting)

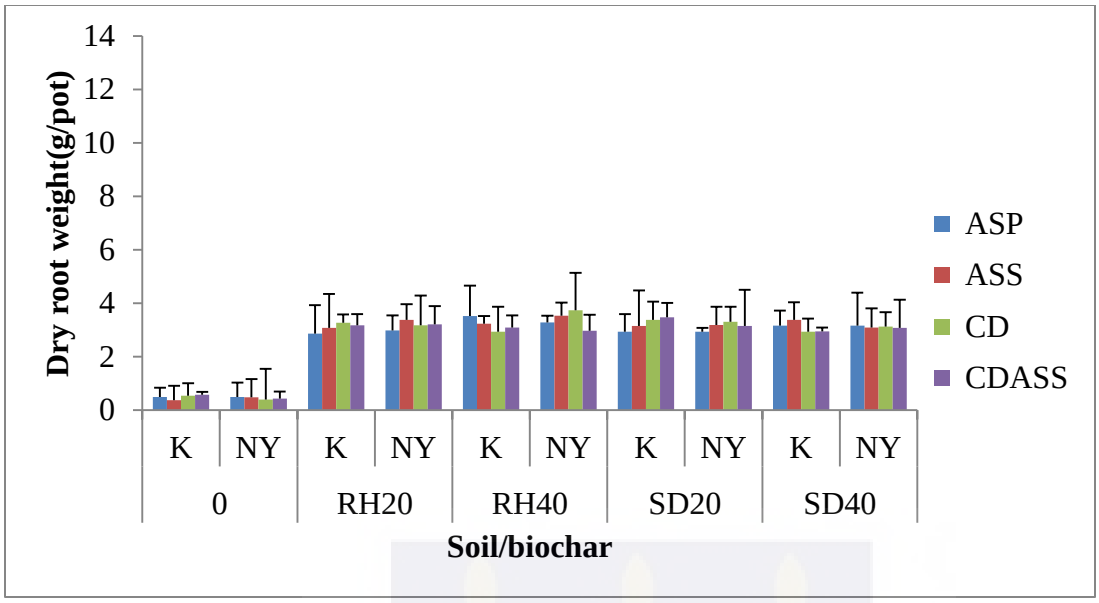

Figure 3: Root dry weight of maize (1st planting).

K: Keta series, NY: Nyankpala series, ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cow dung, CDASS: Cow dung + Ammonium sulphate solution, RH 20: 20 t ha^{-1} Rice husk biochar, SD 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD40: 40 t ha^{-1} sawdust biochar.

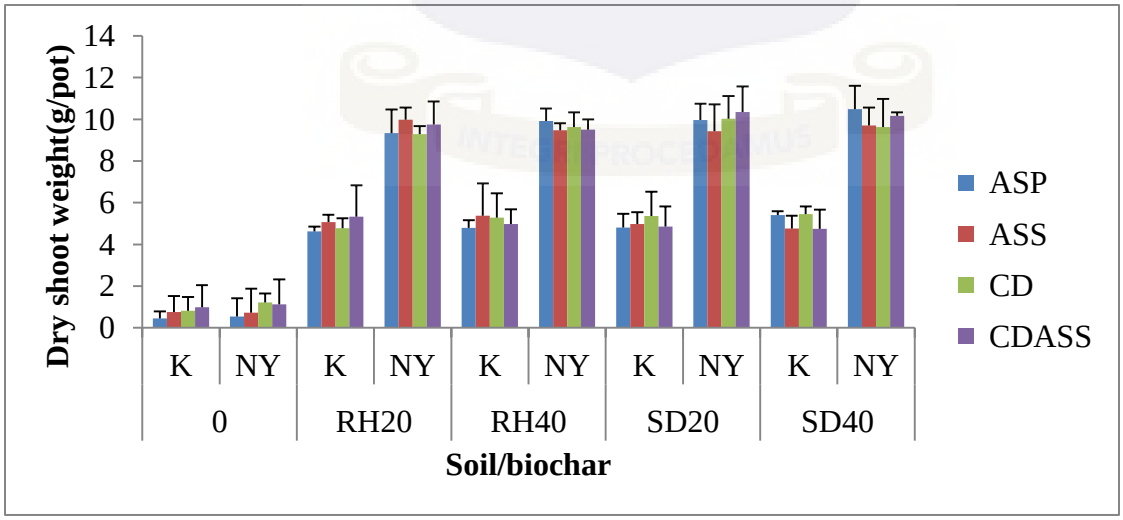

Figure 4: Shoot dry weight of maize (2nd planting)

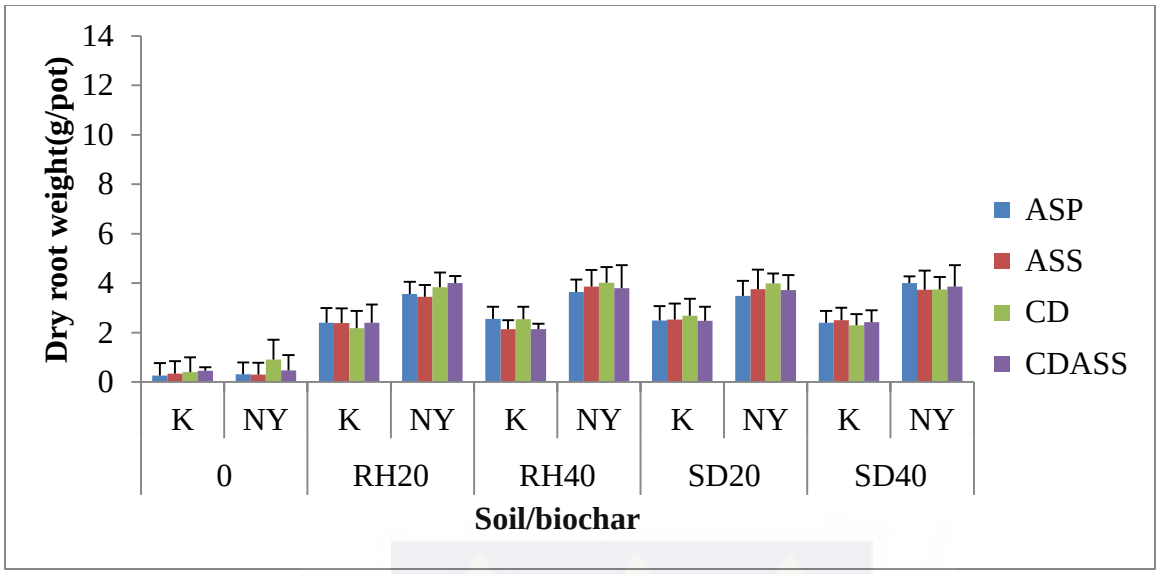

Figure 5: Roots dry weight of maize (2nd planting).

K: Keta series, NY: Nyankpala series, ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cow dung, CDASS: Cow dung + Ammonium sulphate solution, RH 20: 20 t ha^{-1} Rice husk biochar, SD 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD 40: 40 t ha^{-1} sawdust biochar

Table 10: N Concentration in maize after harvest

Soils	Feedstocks/Rates	Treatments (% N in maize)							
		ASP		ASS		CD		CDASS	
		Dϕ	Dϱ	Dϕ	Dϱ	Dϕ	Dϱ	Dϕ	Dϱ
Keta	Control	0.13	0.12	0.11	0.10	0.14	0.12	0.14	0.09
	RH20	0.39	0.41	0.49	0.39	0.38	0.35	0.45	0.33
	RH40	0.35	0.30	0.40	0.37	0.33	0.29	0.38	0.37
	SD20	0.46	0.39	0.42	0.31	0.49	0.32	0.48	0.39
	SD40	0.39	0.32	0.46	0.30	0.48	0.39	0.35	0.30
Nyankpala	Control	0.19	0.16	0.18	0.15	0.17	0.15	0.12	0.17
	RH20	0.54	0.44	0.50	0.39	0.50	0.35	0.49	0.37
	RH40	0.56	0.39	0.48	0.37	0.49	0.38	0.53	0.48
	SD20	0.53	0.46	0.54	0.45	0.53	0.39	0.56	0.38
	SD40	0.57	0.42	0.53	0.40	0.57	0.42	0.58	0.43

Dϕ; %N in maize plants after first planting, Dϱ: %N in maize plants after second planting, ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cow dung, CDASS: Cow dung + Ammonium sulphate solution, RH 20: 20 t ha^{-1} Rice husk biochar, SD20: 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD 40: 40 t ha^{-1} sawdust biochar.

4.8 Nitrogen uptake in maize

The results for N concentration and N uptake in maize are shown in Tables 10 & 11 respectively. The N concentration in maize was used in calculating N uptake in maize. There were no significant ($p > 0.05$) differences between the control treatments of Keta and Nyankpala series in terms of N uptake. This might probably be due to low N contents of the two soils. Amending the soils with biochar significantly ($p < 0.05$) enhanced N uptake. Addition of biochar to the two soils enhanced N retention in the soils, which might helped in making the retained N available for possible uptake by the maize plant. Emperical evidence confirms that biochar improves water and nutrients retention by enhancing electrostatic adsorption sites (Lehman *et al*., 2003). According to Taghizadel *et al*. (2012) it has been suggested that N adsorbed by biochar is eventually released for plants uptake. N uptake in Nyankpala treatments amended with biochar was significantly higher ($p < 0.05$) than N uptake in Keta treatments with biochar. Nyankpala series has relatively higher N content as compare to the Keta series and that might have accounted for the higher N uptake observed in Nyankpala treatments with biochar. Uptake of N in the maize during the second planting follows similar trend.

Table 11: Nitrogen uptake in maize

Soils	Feedstocks/Rates	Treatments (N mg/pot)							
		ASP		ASS		CD		CDASS	
		N∞	N□	N∞	N□	N∞	N□	N∞	N□
Keta	Control	8.97a	9.64e	9.54a	7.94e	8.89a	6.56f	9.02a	7.46e
	RH20	51.47b	43.80f	59.37b	51.38f	52.01b	40.64f	60.10b	48.05f
	RH40	51.60b	50.49f	47.87b	52.71f	56.37b	43.36f	54.12b	50.66f
	SD20	51.29b	47.37f	54.53b	54.64f	50.52b	45.02f	47.85b	50.31f
	SD40	52.36b	44.19f	55.77b	51.71f	53.62b	42.87f	52.70b	50.42f
Nyankpala	Control	9.47a	8.04e	8.29a	6.69e	11.60a	6.68e	13.58a	8.38e
	RH20	84.13c	77.09g	78.70c	66.36g	81.77c	69.89g	73.34c	74.11g
	RH40	78.43c	76.21g	86.91c	67.55g	87.88c	72.57g	86.37c	68.93g
	SD20	81.09c	65.46g	75.99c	73.68g	84.78c	68.93g	83.29c	71.48g
	SD40	79.79c	74.31g	64.66c	67.26g	81.41c	66.50g	71.65c	73.09g

N∞: N uptake in maize (first planting), N□ : N uptake in maize (second planting) ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cow dung, CDASS: Cow dung + Ammonium sulphate solution, RH 20: 20 t ha^{-1} Rice husk biochar, SD 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD 40: 40 t ha^{-1} sawdust biochar. Values under same planting period with same alphabet are not significantly different at p= 0.05

4.9 Available N content of residual soil after planting

The results for NH_4-N and NO_3-N contents in the residual soil after planting are shown in Tables 12 and 13. Results indicated that the amounts of NH_4-N and NO_3- N in the control treatments of Nyankpala series were significantly ($p < 0.05$) higher than that of theKeta series. It is known from this study that Nyankpala series is less susceptible to leaching than the Keta series and this observation could be attributed to its high clay content. The relatively high clay and N contents of the Nyankpala series could have accounted for the high amount of available N found in the residual soil. Amending the two soils with biochar significantly ($p < 0.05$) enhanced the amount of NH_4-N and NO_3- N in the soils. Probably the biochar was able to hold the fertilizer N applied and also increase the water holding capacity of the soil which might have helped to retain the N in the soil and that could account for the high amount of available N found in the residual soils of the amended treatments. Biochar addition to the soil reduced N leaching which helps in making the N available for plant uptake (Lehman*et al*., 2003). There were no significant ($p > 0.05$) differences between the amounts of NH_4-N/NO_3-N retained in the biochar amended treatments in both soils. Although the amounts of available N in the residual soils after second planting were lower than that of the first planting the trend was similar.

Table 12: Residual soil available N (1st planting)

Soils	Feedstocks/Rates	Treatments (NO_3-N/ NH_4^+-N mg/kg)							
		ASP		ASS		CD		CDASS	
		NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3
Keta	Control	18.43a	18.86f	19.77a	17.99f	21.21a	18.8f	22.42a	19.64f
	RH20	39.62c	80.1h	43.35c	81.1h	44.06c	79.42h	41.82c	81.01h
	RH40	40.11c	84.87h	43.44c	76.83h	41.21c	76.57h	43.4c	78.78h
	SD20	39.79c	79.29h	42.85c	78.43h	41.96c	79.61h	44.27c	80.15h
	SD40	45.08c	77.87h	44.47c	81.72h	48.4c	65.93h	45.75c	76.96h
Nyankpala	Control	26.66b	33.32g	27.85b	34.03g	29.84b	38.75g	29.53b	42.45g
	RH20	54.49d	96.73j	53.98d	92.69j	55.22d	102.16j	53.63d	99.82j
	RH40	56.51d	95.53j	55.45d	100.29j	55.54d	97.46j	57.88c	94.2j
	SD20	56.27d	96.09j	52.17d	93.02j	56.13d	104.56j	52.84d	95.61j
	SD40	55.93d	93.94j	54.57d	95.38j	57.51d	100.44j	58.24d	105.19j

ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cow dung, CDASS: Cow dung + Ammonium sulphate solution, RH 20: 20 t ha^{-1} Rice husk biochar, SD 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD 40: 40 t ha^{-1} sawdust biochar. Values under same available N with same alphabet are not significantly different at p = 0.05

Table 13: Residual soil available N (2nd planting)

Soils	Feedstocks/Rates	Treatments (NO_3-N/ NH_4^+-N mg/kg)							
		ASP		ASS		CD		CDASS	
		NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3
Keta	Control	6.14r	12.51u	6.59r	11.12u	9.07r	10.42u	7.44r	9.03u
	RH20	19.71t	39.12w	14.65t	34.83w	15.53t	43.52w	16.05t	34.38w
	RH40	16.83t	39.46w	19.73t	38.13w	20.19t	40.59w	20.99t	43.99w
	SD20	12.80t	42.77w	17.88t	35.17w	19.16t	34.08w	16.37t	42.51w
	SD40	16.42t	33.21w	17.24t	32.35w	19.34t	37.6w	18.66t	37.93w
Nyankpala	Control	11.92rs	18.49v	12.49rs	16.82v	15.86s	17.56v	10.7r	18.5v
	RH20	27.65p	58.47y	29.89p	54.48y	28.64p	56.83y	28.75p	60.49y
	RH40	31.29p	61.68y	31.97p	55.97y	29.29p	5.66y	34.91p	53.62y
	SD20	27.95p	57.95y	35.25p	60.66y	27.12p	55.84y	33.29p	63.04y
	SD40	35.23p	59.84y	28.87p	53.48y	38.92p	52.87y	34.87p	58.95y

ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cow dung, CDASS: Cow dung + Ammonium sulphate solution, RH 20: 20 t ha^{-1} Rice husk biochar, SD 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD 40: 40 t ha^{-1}sawdust biochar. Values under same available N with same alphabet are not significantly different at p = 0.05

4.9.1 Residual soils pH

Residual soils pH

At the end of the experiment the Keta and Nyankpala soils treated with only N fertilizer source showed significant ($p < 0.05$) decrease in soil pH (Tables 14 & 15). The decrease in pH could be due to leaching of the basic cations. However, the amendment of the soils with biochar did not have significant ($p < 0.05$) influence on the pH of the residual soils after planting. Although biochar material has basic cation which gives liming properties, but probably the planting duration was not long enough for the biochar to mineralize to release the basic cations in it. Biochar material contains nutrients therefore when incorporated in soil, it mineralizes to release basic cations such as K, Ca and Mg Glaser et al. (2002) and (Keith et al., 2011; Zimmerman et al., 2011).

Table 14: pH of residual soils after 1st planting

Soils	Feedstocks/Rates	Treatments			
		ASP	ASS	CD	CDASS
Keta	0	6.5	6.4	6.5	6.6
Nyankpala		4.9	4.8	5.0	5.1
Keta	RH20	6.8	6.9	6.9	6.7
Nyankpala		5.3	5.4	5.5	5.6
Keta	RH40	6.9	6.9	6.8	6.9
Nyankpala		5.5	5.6	5.9	5.8
Keta	SD20	6.7	6.8	6.7	6.9
Nyankpala		5.4	5.6	5.8	5.9
Keta	SD40	6.9	6.8	6.7	6.8
Nyankpala		5.8	5.5	5.9	5.8

ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cow dung, CDASS: Cow dung + Ammonium sulphate solution, RH 20: 20 t ha^{-1} Rice huskbiochar, SD 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD 40: 40 t ha^{-1} sawdust biochar

Table 15: pH of residual soils after 2nd planting

Soils	Feedstocks/Rates	Treatments			
		ASP	ASS	CD	CDASS
Keta	0	6.3	6.2	6.4	6.4
Nyankpala		4.5	4.6	4.8	4.6
Keta	RH20	6.7	6.8	6.7	6.8
Nyankpala		5.0	5.1	5.3	5.1
Keta	RH40	6.8	6.7	6.7	6.8
Nyankpala		5.1	5.4	5.5	5.2
Keta	SD20	6.6	6.7	6.7	6.8
Nyankpala		5.2	5.4	5.5	5.4
Keta	SD40	6.8	6.7	6.7	6.7
Nyankpala		5.3	5.2	5.4	5.3

ASP: Ammonium sulphate fertilizer pellet, ASS: Ammonium sulphate solution, CD: Cow dung, CDASS: Cow dung + Ammonium sulphate solution, RH 20: 20 t ha^{-1} Rice husk biochar, SD 20 t ha^{-1} sawdust biochar, RH40: 40 t ha^{-1} rice husk biochar, SD 40: 40 t ha^{-1} sawdust biochar

CHAPTER SIX

CONCLUSION AND RECOMMENDATION

The present study was carried out in the laboratory and screen house to identify biochar type from different feed stocks (saw dust, rice husk and corn cob) with better retention for NO_3^- and NH_4^+ (using ammonium sulphate, potassium nitrate and ammonium nitrate), ability of biochar to reduce leaching and enhance N uptake. The biochar types were applied at 0, 20 and 40 t/ha and treated with different N sources (cow dung and ammonium sulphate) in two soils (Keta and Nyankpala series) and maize was grown.

Results from the column leaching experiment showed that the sawdust biochar had superior retention capacity for NO_3^- and NH_4^+. This could be due to its relatively higher surface area when compared to the other biochar types.

Biochar amendment of the soils reduced leaching of NO_3-N and NH_4-N which indicated their ability to retain nitrogen in the soils. The amendment also enhanced biomass production (dry matter). Nitrogen uptakes by maize in biochar amended treatments were tremendously enhanced as compared to the control treatments. However, biochar feedstock, N source and rate of biochar application did not influence leaching and retention of N in the soils as well as N uptake. From the present study it is recommended that biochar could be applied at lower rate (e.g. 20 t/ha) to reduce leaching of N, and enhance N uptake and plant biomass in sandy soil. It is also recommended that the experiment should be conducted under field condition.

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APPENDIX

Variate: Amount of NH_4-N in leachate collected on 14th day after planting (first planting)

Source of variation	d.f	s.s	m.s	v.r	F pr.
Fertilizer	3	1.0249	0.3416	0.46	0.709
Soil	1	781.2183	781.2183	1058.49	<.001
Feedstock	4	2694.3569	673.5892	912.66	<.001
Fertilizer.Soil	3	2.2768	0.7589	1.03	0.385
Fertilizer.Feedstock	12	2.8933	0.2411	0.33	0.982
Soil.Feedstock	4	263.3534	65.8384	89.21	<.001
Fertilizer.Soil.Feedstock	12	4.4374	0.3698	0.50	0.908
Residual	80	59.0441	0.7381		
Total	119	3808.6052			

LSD = 1.3959

CV= 14.0%

Variate: Amount of NH_4-N in leachate collected on 28th day after planting (first planting)

Source of variation	d.f	s.s	m.s	v.r	F.pr
Fertilizer	3	1.7235	0.5745	1.24	0.300
Soil	1	286.6284	286.6284	619.52	<.001
Feedstock	4	1597.6606	399.4151	863.29	<.001
Fertilizer.Soil	3	1.3125	0.4375	0.95	0.423
Fertilizer.Feedstock	12	3.0907	0.2576	0.56	0.870
Soil.Feedstock	4	173.0720	43.2680	93.52	<.001
Fertilizer.Soil.Feedstock	12	2.3436	0.1953	0.42	0.950
Residual	80	37.0133	0.4627		
Total	119	2102.8445			

LSD = 1.1052

CV = 15.0%

Variate: Amount of NO_3-N in leachate collected on 14th day after planting (first planting)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Fertilizer	3	0.2073	0.0691	0.12	0.948
Soil	1	32.2196	32.2196	56.02	<.001
Feedstock_rate	4	489.5553	122.3888	212.81	<.001
Fertilizer.Soil	3	0.7876	0.2625	0.46	0.713
Fertilizer.Feedstock_rate	12	6.9331	0.5778	1.00	0.453
Soil.Feedstock_rate	4	32.7644	8.1911	14.24	<.001
Fertilizer.Soil.Feedstock_rate	12	2.6896	0.2241	0.39	0.964
Residual	80	46.0083	0.5751		
Total	119	611.1652			

LSD = 1.23

CV = 23.8%

Variate: Amount of NO_3-N in leachate collected on 28th day after planting (first planting)

Source of variation	d.f	s.s	m.s	v.r	F.pr
Fertilizer	3	0.0590	0.0197	0.12	0.948
Soil	1	40.1016	40.1016	246.07	<.001
Feedstock_rate	4	423.6215	105.9054	649.84	<.001
Fertilizer.Soil	3	0.1518	0.0506	0.31	0.818
Fertilizer.Feedstock_rate	12	0.3026	0.0252	0.15	0.999
Soil.Feedstock_rate	4	61.3805	15.3451	94.16	<.001
Fertilizer.Soil.Feedstock_rate	12	0.2971	0.0248	0.15	1.000
Residual	80	13.0377	0.1630		
Total	119	538.9519			

LSD = 0.65

CV = 27.5%

Variate: Amount of NH_4-N in leachate collected on 14th day after planting (Second planting)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Fertilizer	3	0.5015	0.1672	0.58	0.630
Soil	1	14.2279	14.2279	49.30	<.001
Feedstock	4	486.3668	121.5917	421.28	<.001
Fertilizer.Soil	3	0.6643	0.2214	0.77	0.516
Fertilizer.Feedstock	12	1.5400	0.1283	0.44	0.940
Soil.Feedstock	4	34.6601	8.6650	30.02	<.001
Fertilizer.Soil.Feedstock	12	2.1209	0.1767	0.61	0.826
Residual	80	23.0899	0.2886		
Total 119 563.1713					

LSD = 0.87

CV = 18.34%

Variate: Amount of NH_4-N in leachate collected on 28th day after planting (Second planting)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Fertilizer	3	0.07824	0.02608	0.47	0.702
Soil	1	6.43570	6.43570	116.67	<.001
Feedstock	4	107.09395	26.77349	485.38	<.001
Fertilizer.Soil	3	0.12682	0.04227	0.77	0.516
Fertilizer.Feedstock	12	0.27335	0.02278	0.41	0.954
Soil.Feedstock	4	27.97715	6.99429	126.80	<.001
Fertilizer.Soil.Feedstock	12	0.33975	0.02831	0.51	0.900
Residual	80	4.41280	0.05516		
Total	119	146.73776			

LSD = 0.3816

CV = 24.3%

Variate: Amount of NO_3-N in leachate collected on 14th day after planting (Second planting)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Fertilizer	3	0.11423	0.03808	0.41	0.749
Soil	1	3.75594	3.75594	40.12	<.001
Feedstock	4	116.82377	29.20594	311.94	<.001
Fertilizer.Soil	3	0.00770	0.00257	0.03	0.994
Fertilizer.Feedstock	12	0.10352	0.00863	0.09	1.000
Soil.Feedstock	4	15.52843	3.88211	41.46	<.001
Fertilizer.Soil.Feedstock	12	0.12928	0.01077	0.12	1.000
Residual	80	7.49013	0.09363		
Total	119	143.95300			

LSD = 0.49

CV = 31.4%

Variate: Amount of NO_3-N in leachate collected on 28th day after planting (Second planting)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Fertilizer	3	0.08605	0.02868	0.30	0.828
Soil	1	4.39301	4.39301	45.45	<.001
Feedstock	4	127.73919	31.93480	330.43	<.001
Fertilizer.Soil	3	0.04362	0.01454	0.15	0.929
Fertilizer.Feedstock	12	0.12955	0.01080	0.11	1.000
Soil.Feedstock	4	24.13389	6.03347	62.43	<.001
Fertilizer.Soil.Feedstock	12	0.39061	0.03255	0.34	0.980
Residual	80	7.73167	0.09665		
Total	119	164.64759			

LSD = 0.51

CV = 29.2%

Variate: N uptake in maize (first planting)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Fertilizer_type	3	859.24	286.41	3.23	0.027
Soil	1	394.80	394.80	4.46	0.038
Feedstock	4	96452.49	24113.12	272.22	<.001
Fertilizer_type.Soil	3	387.41	129.14	1.46	0.232
Fertilizer_type.Feedstock	12	487.83	40.65	0.46	0.933
Soil.Feedstock	4	669.40	167.35	1.89	0.120
Fertilizer_type.Soil.Feedstock	12	846.43	70.54	0.80	0.653
Residual	80	7086.35	88.58		
Total	119	107183.96			

LSD = 15.29

CV = 14.9%

Variate: N uptake in maize (Second planting)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Fertilizer_type	3	5602.66	1867.55	19.56	<.001
Soil	1	3285.80	3285.80	34.41	<.001
Feedstock	4	55140.76	13785.19	144.35	<.001
Fertilizer_type.Soil	3	1953.32	651.11	6.82	<.001
Fertilizer_type.Feedstock	12	3560.65	296.72	3.11	0.001
Soil.Feedstock	4	1991.33	497.83	5.21	<.001
Fertilizer_type.Soil.Feedstock	12	3287.98	274.00	2.87	0.002
Residual	80	7640.06	95.50		
Total	119	82462.56			

LSD = 15.87

CV = 21.87

Variate: NH_4-N content in residual soil (first planting)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Fertilizer	3	7.12	2.37	0.10	0.962
Soil	1	36713.61	36713.61	1481.03	<.001
Feedstock	4	47840.28	11960.07	482.47	<.001
Fertilizer.Soil	3	21.78	7.26	0.29	0.830
Fertilizer.Feedstock	12	92.56	7.71	0.31	0.986
Soil.Feedstock	4	2089.67	522.42	21.07	<.001
Fertilizer.Soil.Feedstock	12	71.34	5.94	0.24	0.996
Residual	80	1983.14	24.79		
Total	119	88819.50			

LSD = 8.09

CV = 7.6%

Variate NO_3-N content in residual soil (First planting)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Fertilizer	3	188.509	62.836	7.95	<.001
soil	1	2905.063	2905.063	367.61	<.001
Feedstock	4	12482.262	3120.565	394.88	<.001
Fertilizer.soil	3	71.826	23.942	3.03	0.034
Fertilizer.Feedstock	12	94.170	7.848	0.99	0.463
soil.Feedstock	4	55.871	13.968	1.77	0.144
Fertilizer.soil.Feedstock	12	155.723	12.977	1.64	0.097
Residual	80	632.211	7.903		
Total	119	16585.634			

LSD = 4.56

CV = 6.3%

Variate NH_4-N content in residual soil (Second planting)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Fertilizer	3	49.43	16.48	0.70	0.555
Soil	1	10696.28	10696.28	454.67	<.001
Feedstock	4	21378.69	5344.67	227.19	<.001
Fertilizer.Soil	3	22.99	7.66	0.33	0.807
Fertilizer.Feedstock	12	120.80	10.07	0.43	0.948
Soil.Feedstock	4	416.61	104.15	4.43	0.003
Fertilizer.Soil.Feedstock	12	229.86	19.15	0.81	0.635
Residual	80	1882.01	23.53		
Total	119	34796.67			

LSD = 7.88

CV = 12.7%

Variate NO_3-N content in residual soil (Second planting)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Fertilizer	3	15.351	5.117	2.28	0.086
soil	1	3210.157	3210.157	1431.08	<.001
Feedstock	4	3952.584	988.146	440.51	<.001
Fertilizer.soil	3	26.646	8.882	3.96	0.011
Fertilizer.Feedstock	12	27.002	2.250	1.00	0.454
soil.Feedstock	4	517.919	129.480	57.72	<.001
Fertilizer.soil.Feedstock	12	10.277	0.856	0.38	0.966
Residual	80	179.454	2.243		
Total	119	7939.390			

LSD = 2.42

CV= 7.8%