IMPACT OF BIOCHAR, CATTLE MANURE AND MINERAL FERTILIZER ON SOIL PROPERTIES AND GRAIN YIELD OF MAIZE (*ZEA MAYS L.*) IN THE GUINEA SAVANNAH ZONE OF GHANA

KNUST

A THESIS SUBMITTED TO THE DEPARTMENT OF CROP AND SOIL SCIENCES, COLLEGE OF AGRICULTURE AND NATURAL RESOURCES, KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI, GHANA, IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF PHILOSOPHY IN SOIL SCIENCE

BY

EZIKE OGECHUKWU BLESSING
MSc UNILORIN

JULY, 2016

DECLARATION

I do hereby declare that this thesis was written by me and that it is the record of my own research work under supervision. It has neither in part nor in whole been presented for another degree elsewhere. Cited references have been duly acknowledged.

Ezike Ogechukwu Blessing	…….	…….
(Candidate)	Signature	Date

Certified by:

Dr. Andrews Opoku	……..	…….
(Principal Supervisor)	Signature	Date
Dr. Nana Ewusi-Mensah	……	.....
(Co – supervisor)	Signature	Date
Dr. Enoch Osekre	……	……
(Head of Department)	Signature	Date

KNUST

KNUST

ABSTRACT

The use of biochar as a soil amendment is being promoted due to its long term ability to improve soil physical and chemical properties. The aim of this work was to improve maize productivity by using different levels of synthetic fertilizer with farm yard manure and biochar in the Guinea Savannah zone of Ghana. A field experiment and laboratory incubation study were conducted at Kpongu in the Upper West region of Ghana (Guinea Savannah Agro – ecological Zone) and the Soil Science laboratory of KNUST respectively. Eighteen treatments including three levels of biochar (0, 2.5 and 5 t ha^{-1}), three levels of mineral fertilizer(0, 50 and 100 % of the 60-40-40 kg ha^{-1} recommended rate) and two levels of manure (0 and 5 t ha^{-1} recommended rate) were applied in a factorial experiment arranged in split - split plot design with three replications. In the laboratory incubation study treatments were applied at 153.6 g to the field soil on mass basis in a 56 day incubation study period to determine the effect of treatments on soil pH, urease activity, ammonium nitrate (NH_4-N) and nitrate nitrogen (NO_3-N). The use of manure at 5 t ha^{-1} gave the highest plant height at 2 weeks after planting (17.39 cm) and 4 weeks after planting (60.1 cm) while the use of NPK (60: 40: 40: kg ha^{-1})gave the highest plant height at 6 weeks after planting (123.7 cm) and 8 weeks after planting (194.6cm) respectively. The highest grain yield (1347 kg ha^{-1}), biomass dry matter (2865 kg ha^{-1}), nitrogen uptake in both biomass (28.68%) and grain (20.4 %), phosphorus uptake in grain (2.09 %) and nitrogen use efficiency (29) was obtained with the use of 30:20:20 kg ha^{-1} NPK while the highest phosphorus uptake in biomass (3.47 %) was obtained with the use of manure at 5 t ha-1. Laboratory soil

analysisafter harvest showed that none of the soil amendments had significant effect on the examined soil properties. However, biochar amended plots at 5 t ha^{-1} was found to have the highest soil organic matter of 1.722

percent.

Manure application at 5 t ha^{-1} gave the highest soil nitrogen content (0.667 %) while mineral fertilizer at 30:20:20 kg ha^{-1} had the highest soil P of 6.55 %. The applications of 30:20:20 kg ha^{-1} NPK and 5 t ha^{-1} Manure + 30:20:20 kg ha^{-1} NPK was the most economically viable imputs (VCR > 2) among the treatments. 5 t ha^{-1}manure increased the soil pH from 5.4 to 6.22 while urease activity was highest with 2.5 t ha^{-1} biochar + 5 t ha^{-1} manure. NH_4-N was highest at 56 DAI following the application of 2.5 t ha^{-1} biochar + No fertilizer and at 42 DAI, NO_3-N was highest with 5 t ha^{-1} manure + 100 % RR NPK. Extensive research based on agro-ecological zone evaluation of biochar should be carried out to ascertain its effectiveness on maize productivity.

KNUST

DEDICATION

This thesis is dedicated to my dearest parents Mr and Mrs Anthony Ezike.

KNUST

ACKNOWLEDGEMENT

I am most grateful to God Almighty, my Rock on which I stand for the opportunity and grace bestowed on me to go through this programme successfully. Blessed be His name forever. Amen.

I wish to express my profound gratitude to the Alliance for a Green Revolution in Africa (AGRA) for the scholarship offered to me which made this research a reality.

I am especially grateful to my supervisor, Dr. Andrews Opoku of the Department of Crop and Soil Sciences, for his immense contribution and advice during the course of this research. May God through His Son Jesus Christ engulf you and all that is yours with His blessings.I am particularly indebted to Dr. Nana Ewusi-Mensah of the Department of Crop and Soil Sciences my co- supervisor and Dr. Samuel Partey, of Faculty of Natural Resources, for their immense contributions.

I acknowledge with special thanks the assistance in technical support and advice received from Mr. Saliu Mahama of the Ministry of Food and Agriculture (MOFA, Wa), Mr. Anthony Abotiate of Soil Resrarch Institute,Kwadaso and Mr. Samuel Joe Acquah of KNUST Soil Science Laboratory.

To my lovely parents Mr. and Mrs. Anthony Ezike and my husband Mr. Kelechi Nnamdi Chukwueme, you have always expressed the most beautiful thing in my life.

I will not fail to appreciate my friends Rechiatu Asei, Mr.Samuel Mesele, Mavis Badu, Ophelia Osei and Patricia Abbam for their unreserved contribution. Finally, my appreciation goes to all my other colleagues, it was worthwhile today because of you. I am grateful.

TABLE OF CONTENT

KNUST

LIST OF TABLES

LIST OF FIGURES vi

KNUST

CHAPTER ONE

1.0 INTRODUCTION

In sub-Saharan Africa, decline in food production capacity has become a major challenge as a result of increasing human population and poor fertility of available land for agricultural production among other socio-economic and political factors (Partey *et al*., 2013). Crop yield of food security crops in sub-Saharan Africa has declined to less than 1 t ha^{-1} in crops such as maize and beans, attributable to loss of soil fertility in smallholder farming systems (Sanchez, 2010). In these regions, including Ghana, low input agriculture (Partey *et al*., 2013) is mostly practiced, which depends on soil organic matter.

This however, is as a result of high cost of inorganic fertilizers and poor accessibility to local farmers who are the major food producers. Therefore, appropriate land use and soil management practices that emphasize on improving and maintaining soil organic matter are keys to sustaining the productive capacity of the soil in these areas (Partey *et al*., 2013).

Decomposition and mineralization of organic resources by soil micro-organisms remain the principal pathway for N supply in the majority of Africa smallholder farming systems (Bekunda *et al.,* 2007), while P supply has to be sought from external sources such as mineral fertilizers (Mafongoya *et al.,* 2003).

The common strategy for increasing crop productivity is the use of mineral fertilizer. Nonetheless, the continued application of inorganic fertilizer, especially nitrogen, caused soil deterioration and many environmental problems (Liu *et al*., 2010). Recently soil fertility management which includes the application of inorganic fertilizer and organic fertilizer to soil (Fageria and Baligar, 2005) has proven to be highly effective in maintaining high soil fertility. However, it is known that under tropical conditions, organic materials incorporated into the soil will be decomposed at a faster rate and nutrients are easily lost (Partey et *al*., 2013).

Furthermore, organic manure is very low in nutrient content and is therefore applied in large quantities repeatedly.

Excessive application of fertilizer has caused the release of nutrient elements, such as nitrogen and phosphorus, from agricultural fields to aquatic system (Laird *et al.,* 2010). Leaching of nutrients from soils may deplete soil fertility, accelerate soil acidification, increase fertilizer costs for the farmers, reduce crop yields, and most importantly impose a threat to environmental health (Ozacar, 2003; Laird *et al*., 2010). It is therefore very important to develop effective technologies to retain nutrients in soils.

An option to reduce nutrient leaching could be the application of biochar to soils. Biochar, sometimes called agrichar, is a charcoal derived from the thermal decomposition of a wide range of carbonrich biomass materials, such as grasses, hard and soft woods and agricultural and forestry residues. The approach of land application of biochar in agriculture is receiving increased attention as a way to create a carbon sink to mitigate global warming, increased soil water holding capacity, and reduced emissions of NOx and CH_4, as well as to control the mobility of a variety of environmental pollutants, such as heavy metals, pesticides and other organic contaminants (Lehmann *et al.,* 2006; Verheijen *et al.,* 2009; Inyang *et al.,* 2010; Van Zwieten *et al.,* 2010). In addition, it is suggested that application of biochar can increase soil fertility and crop productivity by reducing the leaching of nutrients or even supplying nutrients to plants (Glaser *et al.,* 2002; Lehmann *et al.,* 2003; Major *et al.,* 2010).

This idea arises because of the sustainability of crop production in the Amazon black soil which was then known as Terra Preta soil. Terra Preta soil is defined as a fertile soil in an infertile surrounding containing high concentrations of nutrients and stable organic matter

(SOM) (Lehman *et al.*, 2003). This observation forms the basis of the hypothesis that the application of black carbon as pyrolysed biomass will increase the fertility status agricultural soil.

The chemical and biological stability of biochar, together with the aforementioned properties, have a high potential for agronomic systems in most tropical and subtropical soils since they are generally poor in organic matter. While biochar has proven to have a positive conditioning effect on soils, it may be limited as a sole nutrient supplier because of its relatively low nutrient composition and recalcitrance to biodegradation. It is, therefore, reasonable that the effects of biochar and other available nutrient sources are explored. Currently, numerous studies have confirmed the synergistic effects of biochar and inorganic fertilizers (Xie Z *et al.,* 2011) but the combined effect of biochar, inorganic fertilizers and organic manure have been limitedly studied (Sohi *et al.*, 2010). Furthermore, information regarding the mechanisms by which biochar influences the soil properties are still inadequate.

The main objective of this present study therefore, was to increase maize productivity through the application of biochar, with mineral fertilizer and cattle manure in the Guinea Savanah zone of Ghana.

The specific objectives were to:

i. evaluate the effect of biochar, inorganic fertilizer and cattle manure application on maize growth and yield.
ii. determine the nutrient uptake and nitrogen use efficiency ofmaize in biochar amended soils.
iii. assess the cost effectiveness of investments in combined application.
iv. assess combined effects of biochar with organic and inorganic fertilizers on some selected soil properties and urease activity.

The above specific objectives were formulated to test the hypothesis of this study that, the integrated use of biochar, organic and inorganic fertilizers will improve nutrient availability and maize yield than sole applications.

KNUST

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 The importance of biochar in crop production

Amendment of soils with biochar (a solid material obtained from biomass pyrolyzed under low/no oxygen environment) has been proposed as a potential technique to abate climate change by sequestering carbon and reducing concomitant CH_4 and N_2O emissions (Lehmann,

2007; Woolf *et al*., 2010). Biochar materials, depending on the production conditions, vary in their properties and, as a consequence, have potentially contrasting behaviour and impact on agro-ecosystems and the environment.

Biochar is a charred by product of biomass pyrolysis produced from biological wastes, crop residues, animal poultry manure, or any type of organic waste material. Biochar production through pyrolysis is considered a carbon-negative process because the biochar sequesters carbon while simultaneously enhancing the fertility of the soil (Lehmann, 2007). Biochar has the capability to both mitigate greenhouse gas emissions and other environmental hazards. It can also be used as a soil amendment and source of alternative energy. The major potential benefits of biochar are carbon sequestration, greenhouse gases (GHG) emission reduction, and enhancement in soil fertility.

Studies suggest that biochar sequesters approximately 50 % of the carbon available within the biomass feedstock being pyrolyzed, depending upon the feedstock type (Lehmann*, et al.,* 2006). The remaining percentage of carbon is released during pyrolysis and may be captured for energy production. Glaser *et al.* (2002) reported that large amounts of carbon may be sequestered in the soil for long time periods (hundreds to thousands of years at an estimate), but precise estimates of carbon amounts sequestered as a result of biochar application are scarce. Marris (2006) suggested that a 250-hectare farm could sequester approximately 1,900 tons of CO_2 a year. Primary greenhouse gases associated with the agriculture sector are nitrous oxide (N_2O) and methane (CH_4). Cropland soils and grazing lands are an important agricultural source of N_2O emissions. Whereas, paddy fields, livestock manure and enteric fermentation are the number one leading sources of CH_4 emissions. When applied to the soil, biochar can lower greenhouse gas emissions by substantially reducing N_2O emissions. Emissions of N_2O a greenhouse gas that is approximately 300 times stronger than CO_2 in terms of global warming potential, was reduced by 40 percent (Yanai *et al.,* 2007). Laboratory studies suggest that

reduction in N_2O emissions reduction from biochar-treated soil is dependent on soil moisture and soil aeration (Yanai *et al.,* 2007). Greenhouse gas emission reductions may be 12 to 84% greater if biochar is incorporated into the soil instead of being combusted for energy purposes (Lehmann, 2007). Amending soils with biochar was found to increase soil fertility and enhance crop production, especially on soils with low fertility (Asai*et al.,* 2009; Major *et al.,* 2010). However, no noticeable increase in crop production following biochar amendments has been reported in soils with high fertility, and some studies even reported inhibition of plant growth (Gaskin *et al.,* 2010; van Zwieten *et al*., 2010; Zhang *et al*.,2010; Haefele *et al.,* 2011). The growth stimulating effects are generally attributed to biochar‘s capacity to supply nutrients, improve soil physical structure, increase soil pH (in acidic soils), and enhance fertilizer-use efficiency stemming from its high surface area and high cation-exchange capacity (Glaser *et al.*, 2002; Asai *et al.,* 2009; van Zwieten *et al.*, 2010).The beneficial effects of biochar addition on crop production may be determined by changes in soil characteristics and/or the availability of nutrients (Chan *et al.,* 2007; Sohi *et al.,* 2010).

2.2. Basic properties of biochar

Biochar composition can be crudely divided into relatively recalcitrant C, labile or leachable C and ash. The greatest chemical difference between biochar and other organic matter is the much larger proportion of aromatic C and, specifically, the occurrence of fused aromatic C structures, in contrast to other aromatic structures of soil organic matter such as lignin (Schmidt and Noack, 2000). This fused aromatic structure of biochars in itself can have varying forms, including amorphous C, which is dominant at lower pyrolysis temperatures, and turbostratic C, which forms at higher temperatures (Keiluweit *et al.,* 2010; Nguyen *et al.,* 2010). It is clear that the nature of these C structures is the chief reason for the high stability of biochars (Nguyen *et al.,* 2010). The chemical stability of a large fraction of a given biochar material means that microorganisms will not be able to readily utilize the C as an energy source or the N and

possibly other nutrients contained in the C structure. However, depending on the type of biochar, a fraction may be readily leached and therefore mineralizable (Lehmann *et al.,* 2009) and in some cases has been shown to stimulate microbial activity and increase abundance (Steiner *et al.,* 2008). The third major component is comprised of minerals that are present as ash inclusions in biochar. These minerals include several essential macro- and micro-nutrients for biological uptake and, therefore, represent valuable resources in the soil food web. Additionally, the presence of these elements during pyrolysis plays a role in the biochar chemical structure to the extent that they are into the aromatic structure or that organo-metal reactions are thermodynamically favorable at high temperatures. For instance, N may substitute one or two C atoms in aromatic compounds (Leinweber *et al.,* 2007) with largely unknown effects on biochar behavior in soil.

2.3. Effect of pyrolysis temperature on biochar quality

High-temperature pyrolysis (> 550°C) produces biochars that generally have high surface areas > 400m^2/g, (Downie *et al*., 2009; Keiluweit *et al*., 2010), are highly aromatic and therefore very recalcitrant to decomposition (Singh and Cowie, 2008), and are good adsorbents (Mizuta *et al*., 2004; Lima and Marshall, 2005). Low-temperature pyrolysis (< 550°C), on the other hand, favours greater recovery of C and also of several nutrients (e.g. N,

K, and S) that are increasingly lost at higher temperatures (Keiluweit *et al*., 2010). Lowtemperature biochars, which have a less-condensed C structure, are expected to have a greater reactivity in soils than higher temperature biochars and a better contribution to soil fertility (Steinbeiss *et al*., 2009). In fact, pot and field trials indicate that high mineral-ash biochars produced at temperatures < 500°C have, in some cases, given higher crop yields than more recalcitrant biochars produced at higher temperatures (Chan *et al*., 2008). Based on this greater reactivity, low-temperature biochars have been blended with minerals and sludges to balance the nutrient content of the amendments, and results of pot and field trials are now

entering the scientific literature (Chia *et al*., 2010). However, optimal heating rates and soaking times must be determined when operating kilns at temperatures of 180–350°C, and then adopted during production, to avoid the production of compounds that, in sufficiently high concentration, could be toxic to plants, such as acid aldehydes or phenols (Bridgwater and Boocock, 2006).

KNUST

2.4. Limitations of organic and inorganic fertilizers

Soil fertility can be successfully improved using both inorganic and organic fertilizers. The major drawbacks of inorganic fertilizers are their low accessibility to resource-poor farmers (Garrity, 2004) and their low efficiency in highly weathered soils (Laird *et al.,* 2010). While organic fertilizers are able to improve nutrient use efficiency, under tropical conditions they mineralize rapidly in soil and benefits through increases in organic matter last only for a few growing seasons (Bol *et al.,* 2000; Diels *et al.,* 2004). In contrast, biomass-derived black carbon (C), or biochar, is much more stable. While biochar must eventually mineralize in soil (Schmidt and Noack, 2000), a fraction remains in a very stable form with a ^{14}C age greater than that of the oldest soil organic matter (SOM) fractions (Krull *et al*., 2006; Pessenda *et al.*,2001).

2.5. Soil organic carbon management

After texture, acidity and salinity, organic carbon content is the variable having the greatest impact on soil properties. Long-term experiments show that the content of soil organic carbon (SOC) is the result of a balance between the inputs and outputs of organic C (e.g. Johnston *et al.,* 2009; Lützow *et al.,* 2006).The main C inputs are plant roots and root exudates, aboveground plant residues and manures or other organic by-products. Outputs are the decomposition of organic matter by soil microorganisms and fauna leading to evolution of CO_2 to the atmosphere (or CH_4 under anaerobic conditions), leaching of soluble organic C compounds and particulate losses through erosion. Decomposition is normally the dominant output process and is controlled by clay content, temperature, moisture content and oxygen

availability within the soil. Soils with a higher content of clay-sized particles, or higher cation exchange capacity, normally move towards a higher equilibrium content of organic C than sandy soil due to their greater capacity for stabilizing microbial metabolites. The total SOC content of a soil under specified management practices can often be predicted with some success using several current models (Smith *et al.,* 1997) though further research is required for some situations including peat soils, simulating impacts of reduced tillage and the dynamics of fractions within the total.

2.6. Mechanisms for the soil conditioning effect of biochar

Conceptually three main mechanisms have been proposed to explain the beneficial roles of biochar in crop production: (i.) direct modification of soil chemistry through its intrinsic elemental and compositional make up, (ii.) providing chemically active surfaces that modify the dynamics of soil nutrients or otherwise catalyse useful soil reactions and (iii.) modifying physical character of the soil in a way that benefits root growth and/or nutrient and water retention and acquisition (Nassem *et al*., 2013). The actual effects of application, however, depend on various factors such as the soil fertility and the water balance at a given site and possibly even the cultivated genotype.

2.7. Effect of biochar on soil properties

Biochar application has received a growing interest as a sustainable technology to improve highly weathered or degraded tropical soils (Lehmann and Rondon, 2006). Biochar can enhance plant growth by improving soil chemical characteristics (i.e., nutrient retention, nutrient availability), soil physical characteristics (i.e., bulk density, water holding capacity, permeability), and soil biological properties, all contributing to an increased crop productivity (Glaser *et al.,* 2002; Lehmann and Rondon, 2006; Yamato *et al.,* 2006).

2.7.1 Effect of biochar on soil physical properties

The highly porous biochar is believed to improve the physical properties of soil, such as bulk density, total porosity, pore-size distribution, soil moisture content, water holding capacity, and hydraulic conductivity (Ahmad *et al.,* 2014; Belyaeva and Haynes, 2012; Brewer *et al.,* 2012; Chan *et al.,* 2007, 2010; Ventura *et al.,*2012).

The physical propertiesof the soil affected by biochar include soil aggregation, bulk density, soil water holding capacity, Soil moisture, penetration resistance, pore size distribution and soil strength (Chan *et al.,* 2007). Biochar application can also change soil bulk density (Major *et al.,* 2010); with possible effects on soil water relations, rooting patterns and soil fauna. This occurs both because the density of biochar is lower than that of some minerals, and because biochar contains macro and micropores (Downie *et al.,* 2009), which can hold air or water, greatly reducing the bulk density of the entire biochar particle. Surprisingly little bulk density data have been published for biochar or natural char samples.

2.7.1.1. Bulk density

Application of biochar can decrease the bulk density (BD) of soils. An experiment conducted by Mankasingh *et al.* (2011) showed that soil bulk density decreased from 1.66 to 1.53 g cm^{-3}, and another involving biochar-amended soil columns showed significantly lower bulk density compared to no-biochar controls in a column incubation study (Laird *et al*., 2011). Alburquerque *et al.* (2013) found out that wheat straw biochar addition determined a statistically significant increase in soil field capacity from 14.0 to 15.8 % ($P < 0.05$) and a decrease in soil bulk density from 1.56 to 1.49 g cm^{-3} ($P < 0.001$) at the highest biochar application rate in wheat production. Thus, the decrease in bulk density of biochar amended soil could be one of the indicators of enhancement of soil structure or aggregation, and aeration, and could be soil-specific. The higher the total porosity (micro- and macro-pores) the higher is soil physical quality because micropores are involved in molecular adsorption and transport

while macropores affect aeration and hydrology (Atkinson *et al.,* 2010). Clearly, amending top-soil with biochar can decrease BD. However, there are limited available data to understand if this effect of biochar is significantly relevant in the deeper profile.

2.7.1.2. Aggregate stability and penetration resistance

Data are scarce on aggregate stability and Penetration Resistance (PR) of biochar-amended soil. Furthermore, whatever little information exists is conflicting. Examples of the few studies which investigated the effect of biochar on aggregate stability were all carried out under laboratory or greenhouse settings. A low temperature (220℃) hydrochar made from spent brewer‘s grains, a residue from beer brewing, responded positively on aggregation of AlbicLuvisol when (i) incubated for five months at 20 ℃ in dark, and (ii) used in a pot study with same hydrochar/soil combination (Laird *et al*., 2010). These incubation and greenhouse studies involving plant indicates that hydrochar significantly increased water stable aggregates (WSA) compared to control but the extent of WSA differed because the greenhouse study had 2–5 times higher rate of WSA formation compared to laboratory incubation. Thus, soil compaction would not be alleviated by biochar addition over short time period but may be altered in the long run as aging of biochar changes its properties (Cheng *et al.,* 2008; Cheng *et al.,* 2009). Along with time, soil type is also an important factor because another study reported reduction in Penetration Resistance with application of the same biochar on a different soil type (Busscher *et al*., 2010). Clearly, the effect of biochar amendment on soil aggregation and PR requires additional research by including variations in biochar and soil type.

2.7.1.3. Hydrological properties

Soil hydrological properties (*i.e.*, moisture content, WHC, water retention, hydraulic conductivity and water infiltration rate) are invariably related to surface area, porosity, bulk density and aggregate stability. Several studies have reported alterations in WHC and water retention in biochar amended soils (Uzoma *et al.,* 2011) with as low as 0.5% (g g^{-1}) biochar

application rate sufficient to improve. However, the response is biochar and soil-specific. Application of a laboratory-produced biochar from black locust (*Robiniapseudoacacia*) increased the available water capacity (AWC) by 97 %, and saturated water content by 56 %, but reduced hydraulic conductivity (Uzoma *et al*., 2011). A long-term column study indicated that biochar-amended Clarion soil retained up to 15% more water, and 13% and 10% more water retention at −100 k Pa and −500 k Pa soil matric potential, respectively, compared to unamended controls (Laird *et al*., 2010). Piccolo *et al.* (1996) demonstrated that coal-derived humic acid substances can increase water retention, AWC and aggregate stability of inherently degraded soils. Dugan *et al.* (2010) reported no significant difference between 5, 10 and 15 t $ha^{-1,}$ suggesting that the optimum rate of biochar application to improve soil moisture retention was 5t ha^{-1}. Water repellence might have occurred at higher concentrations of the biochar. Another possible explanation is that addition of more biochar negatively affected the soil structure and hence the soil‘s WHC. However, the effect of biochar on water retention also depends on soil texture. Tryon (1948) reported that application of biochar increased AWC in sandy soil, no effect in a loamy soil, and decreased moisture content in a clayey soil. Such a response may be attributed to the hydrophobic nature of the charcoal and to alterations in pore size distribution. Because the soil moisture retention may only be improved in coarse-textured soils, a careful choice of biochar/soil combination needs to be taken into consideration (Glaser *et al*., 2002).

2.7.2. Effect of biochar on soil chemical properties

The chemicals properties influenced by biochar application include soil pH, and CEC and N transformations (Lehman, 2007). In the long term, biochar application increases plant nutrient availability either due to the improvement of soil properties or addition of some plant nutrient in the biochar (Sohi *et al.,* 2010).

2.7.2.1. Soil pH

There are few studies that have demonstrated a reduction in pH due to biochar addition in alkaline soils, however, the addition of acid biochar to acidic soils has been observed to reduce soil pH (Cheng *et al.,* 2008). Alburquerque *et al.*(2013) reported an increase in soil pH with wheat straw and olive tree biochars, both biochars significantly increased soil pH from 6.5 in the control soil to 8.2 and 7.6 in the soil treated with the highest biochar application rate for olive tree pruning biochar and wheat straw biochar, respectively ($P < 0.001$). Partey *et al.* (2013) observed a significantly higher increase in pH following the combined application of biochar and green manure than the application of biochar and inorganic fertilizers.

2.7.2.2. Effect of biochar on electrical conductivity of the soil

Biochar addition also significantly ($P < 0.001$), increased the electrical conductivity of the 1:5 soil/water extract from 50 μS cm^{-1} in the control soil to 104 and 70 μS cm^{-1} in the soil treated with the highest biochar application rate for olive tree pruning biochar and wheat straw biochar, respectively (Sohi *et al.,* 2010).

2.7.2.3. Cation exchange capacity

The cation exchange capacity (CEC) is an important characteristic of soil which determines nutrients adsorption and desorption and thus their availability in soil.CEC not only helps in fertilizer use efficiency by the crop during the growing season, but also improves the ability of the soil to adsorb and retain nutrients from othersources available at other times.

It has been reported that the biochar, a highly porous with high surface area and variable charge organic material, has the potential to CEC, surface sorption capacity and base saturation when added to the soil. (Glaser *et al.,* 2002; Bélanger *et al.,* 2004; Keech *et al.,* 2005; Liang *et al.,* 2006).The reason for an increase in soil CEC followed by biochar application according to Liang *et al.* (2006) may be due to the presence of oxidized functional groups (such as carboxyl

groups), whose presence is indicated by high oxygen and carbon ratios on the surface of charred materials following microbial degradation (Preston and

Schmidt, 2006) and is further influenced by the high surface area (Gundale and DeLuca, 2006) and high charge density of biochar. Additionally, a high specific surface area was attributable to the presence of biochar, which may contribute to the high CEC found in soils that are rich in biochar. (Liang *et al.,* 2006)

The emphasis that the enhancement in CEC with biochar application is crucial in many areas of the humid and subhumid tropics dominated by soils of low cation exchange capacity, the so-called low-acidity clay soils that may quickly lose their fertility if fallow periods, or some analog to fallow conditions, are not imposed (Jeffery *et al*.,2011). Soil exchange capacities may increase over short time during agingas an increase in the CEC of aged biochars compared to fresh ones due to generation of oxygenated surface functional groups by surface oxidation process has previously been reported (Chan *et al.,* 2008).

2.7.2.4. Effect ofbiochar on nitrogen transformations

Mineralization and immobilisation rates in the soil are a function of the C and N pools available to microorganisms. Typically as C : N ratios increase immobilisation of N occurs. Adding biochar to the soil adds another dimension to both the C and N pools. Addition of biochar to soils has been shown to result in slower mineralisation of the biochar materials than the uncharred biomass (Knoblauch *et al.,* 2012), decrease net N mineralisation (Dempster *et al.,* 2012; Castaldi *et al*., 2012), cause increased net N mineralisation (Castaldi *et al*., 2012), have no effect on mineralization (Streubel *et al.,* 2012; Schomberg *et al.,* 2012), and to have little effect on dissolved nitrogen (Dempster *et al.,* 2012). Furthermore, biochar addition has been shown to have no effect on soil-N immobilisation (Cheng *et al.,* 2012).

Several mechanisms have been proposed to explain the apparent retention of N in biocharamended soils and the reduction of N leaching. These include adsorption of NH_3 or

organicN onto biochar, cation or anion exchange reactions, and enhanced immobilisation of N as a consequence of labile C addition in the biochar. Addition of biochar resulted in marked changes in the N (NH_4^+ - N and NO_3 - N) content of soil (Shenbagavalli *et al.,* 2012). Both NH_4^+ - N and NO_3 - N content were found decreased due to biochar application material. Lehmann *et al.* (2006) have suggested that biochar can adsorb both NH_4^+ and NH_3^- from the soil solution thus reducing solution inorganic N at least temporarily, but perhaps concentrating it for microbial use.

Recent research has clarified the potential role of biochars with respect to NO_3^- adsorption. Yao *et al.* (2012) evaluated biochar materials that had been slowly pyrolysed at 300, 450 or 600 ℃, and a hydrochar) to determine their potential to remove NO_3^- from solution. It was found that four high temperature (600 ℃) biochars (bagasse, bamboo, peanut hull, and Brazilian pepperwood) were able to remove between 0.12 to 3.7% of NO_3^- (0.02 – 0.64 mg NO_3^- per g of biochar) from a solution (0.1 g: 50 mL of 34.4 mg L^{-1} NO_3^-) with variation in removal due to species of feedstock used.

Yao *et al.* (2012) found that 9 of the 13 biochars tested in their sorption experiment could remove NH_4^+ from solution (0.1 g biochar in 50 mL of 10 mg NH_4^+ L^{-1}), with removal rates ranging from 1.8 –15.7 % (0.05 to 0.79 mg NH_4^+ per g biochar), varying widely with feedstock and pyrolysis temperature, but with no pyrolysis temperature trend. The *Eucalypt* sp. biochar (600 °C) used by Dempster *et al.* (2012) adsorbed 75% of the NH_4^+ in solution (10 g biochar in 100 mL) at 2.5 and 5 mg NH_4^+-N L^{-1} (0.02–0.04 mg NH_4^+-N per g biochar) but this was reduced to 54% at 50 mg NH_4^+-N L^{-1}, although the adsorbtion rate had increased to 0.25 mg NH_4^+-N per g biochar.

It is also possible that some amount of decomposition might have occurred when fresh biochar is added to soil (Liang *et al*, 2006), which could induce net immobilization of inorganic N already present in the soil solution. Gundale and DeLuca (2006) reported that the biochar addition to soil caused reduction in ammonification compared to the control due to adsorption and reduce the potential for NH_3 volatilization. The reduction could be due to high C/N ratio of biochar and greater potential for N immobilization (Lehmann *et al.,* 2006).

2.7.2.5. Effect of biochar on soil microbial biomass carbon

Research has shown that microbial biomass under different organic inputs may have implications for nutrient availability to crops (Tu *et al*., 2006). It is known that high microbial biomass often leads to high nutrient availability to crops through enhancing both the microbial biomass turnover and the degradation of nonmicrobial organic materials (Wang*et al*., 2004).

Shenbagavalli *et al*. (2012) reported that the soil microbial biomass carbon (SMBC) contents were more with the higher rates of biochar application than the lower rates at all times. Partey *et al.* (2013) also observed a significant increase in soil microbial biomass C (SMBC) after treatment application with a significant positive correlation ($r^2 = 0.67$, $p < 0.001$) observed between SMBC and extractable C.

2.7.2.7. Effect of biochar on soil organic carbon

Shenbagavalli *et al.* (2012) observed the SOC increased markedly during a 90 days Incubation study, due to biochar application, whereas the SOC was found decreased in control soil (without biochar) after 30 days. At the end of the incubation the control soil had only 4.5 g SOC kg^{-1}, whereas the soils with biochar had SOC ranged between 6.9 and 18.1 g kg^{-1}.The highest SOC was recorded in soil amended with 5 % biochar.

2.8. Effect of biochar on greenhouse gases

Agriculture is a major contributor of greenhouse gases (GHG) to the environment, and these agricultural emissions (60 % of N_2O and 50 % of CH_4) are 10–12 % of the total global anthropogenic emissions in 2005 (Smith *et al.,* 2007). Therefore, it is urgent to establish effective agricultural management practices that can mitigate GHG emissions while increasing crop production. The application of biochar to agriculture has been proposed as an appealing approach for mitigating GHG emissions and improving crop productivity (Lehmann *et al*., 2011). Woolf *et al*. (2010) have estimated that annual net emissions of CO_2, N_2O and CH_4 could be reduced by 12 % of current anthropogenic CO_2–C equivalent emissions with biochar application. The use of biochar significantly reduced the N_2O emissions from various studied soils (Singh *et al.*, 2010; Taghizadeh-Toosi *et al*., 2011; Wang *et al.,* 2011; Zhang *et al.,* 2010). For example, the incorporation of biochar into pasture soil that contained ruminant urine reduced N_2O emissions by up to 70 % (Taghizadeh-Toosi *et al*., 2011). Zhang *et al*. (2010) also reported that biochar additions significantly lowered the N_2O emissions from both paddy and upland soils. However, Singh *et al.* (2010) observed that N_2O emissions following the addition of biochar were dependent on the nitrogen (N) content of the biochar feedstock (poultry manure versus wood). Similarly, Spokas and Reicosky (2009) and Clough *et al*. (2010) observed these specific effects of biochar. Biochar amendment affects carbon cycling and CO_2 emissions by changing the characteristics of the soil and of the microbial community.

In many studies where biochar has been shown to reduce N_2O fluxes, a number of mechanisms have been proposed based mainly on prior knowledge of the requirements of nitrifiers and denitrifiers. These include: (i) enhanced soil aeration (reduced soil moisture) inhibiting denitrification due to more oxygen being present; (ii) labile C in the biochar promoting complete denitrification *i.e* dinitrogen (N_2) formation; (iii) the elevated pH of the biochar creating an environment where N_2O reductase activity is enhanced thus promoting N_2

formation and higher N_2:N_2O ratios; and (iv) a reduction in the inorganic-N pool available for the nitrifiers and/or denitrifiers that produce N_2O, as a result of NH_4^+ and/or NO_3^- adsorption, greater plant growth, NH_3 volatilisation loss, or immobilisation of N. Increases in N_2O fluxes have been attributed to: (i) the release of biochar embodied-N or priming effects on SOM following biochar addition; (ii) biochar increasing soil water content and improving conditions for denitrification; and (iii) biochar providing inorganic-N and/or carbon substrate for microbes.

2.9. Influence of biochar on carbon sequestration

Studies suggest that biochar sequesters approximately 50 % of the carbon available within the biomass feedstock being pyrolyzed, depending upon the feedstock type (Lehmann*, et al.,* 2006). The remaining percentage of carbon is released during pyrolysis and may be captured for energy production.Lehmann*, et al.* (2006) reported that large amounts of carbon may be sequestered in the soil for long time periods (hundreds to thousands of years at an estimate), but precise estimates of carbon amounts sequestered as a result of biochar application are scarce. Marris (2006) suggests that a 250-hectare farm could sequester approximately 1,900 tons of CO_2 a year.

In a basic cycle eventually the plants decay, and this dead biomass begins to release captured carbon dioxide into the atmosphere yielding an ineffective natural cycle (Steiner, 2008). Organic biomass from decaying plant species or remnants of agriculture can be converted into a charcoal or biochar that can prevent global climate change by displacing fossil fuel use by sequestering carbon into soil carbon pools and by dramatically reducing emissions of nitrous oxides, a more potent greenhouse gas than carbon dioxide‖ (IBI, 2010). Biochar slows down the decaying and mineralization of the biological carbon cycle to establish a carbon sink and a net carbon withdrawal from the atmosphere of 20 %. Additionally, calculations have shown that putting this biochar back into the soil can reduce emissions by 12 to 84 % of current values;

a positive form of sequestration that offers the chance to turn bioenergy into a carbon negative industry‖ (Lehmann, 2007).

Energy from biochar production displaces fossil fuel energy, and if CCS (carbon capture and storage) is used, sequestering ‗biochar' in soil, which makes soil darker in colour, is a robust way to store carbon.

KNUST

2.10. Effect of biochar on plant growth

Crop response to biochar amendment depends on the chemical and physical properties of the biochar, climatic conditions, soil conditions and crop type (Zwieten *et al*., 2010; Yamato *et al*., 2006; Gaskin *et al.,* 2010; Haefele *et al*., 2011). Improvements in plant growth and yield following biochar application also have been reported for a variety of crops, such as radish (*Raphanus sativus L.* Chan *et al.,* 2008), common beans (*Phasealus vugaris* L.: Rondon *et al.,* 2007) and maize (Yamato *et al.,* 2006).

Studies in both tropical and temperate climates have demonstrated biochar's ability to increase plant growth, reduce leaching of nutrients, increase water retention, and increase microbial activity. In a study done on a Colombian Oxisol, total above-ground plant biomass increased by 189 percent when biochar was applied at a rate of 23.2 tons per hectare (Major *et al.,* 2005).

2.11. Effect of biochar on grain yield

Scientists have reported that application of biochar on soil has significant effect on net primary crop production, grain yield and dry matter production (Chan *et al.,* 2008; Chan and Xu, 2009; Major *et al*., 2009; Spokas *et al.,* 2009). Biochar addition to soils does not always result in consistent yield increases (Yao *et al.,* 2010) and plant responses to biochar addition have been reported to vary considerably.

Alburqueque *et al*. (2013) reported that at the highest mineral fertilizer rate, addition of biochar led to about 20–30 % increase in grain yield compared with the use of the mineral fertilizer

alone. The application of wheat straw biochar decreased total dry plant biomass, but in the case of olive tree pruning biochar it had no effect on total plant biomass. Biochar addition to soil generally increased wheat grain production in the absence of the mineral fertilization, ranging from 3 to 42 % compared to the control soil. Partey *et al.* (2013) reported a 27 % increase in maize grain yield when fertilizer was combined with biochar as compared to sole treatment.

Biochar effects on yield were reviewed by Spokas *et al.* (2012) and occur as a result of changes in soil nutrition, water holding capacity and microbial activity, with results varying due to soil type. Positive yield increases were generally associated with hardwood biochars and chars possessing plant nutrients, such as high N content poultry manure biochars (Spokes *et al.,* 2012).

One of the reasons for increasing crop yield with biochar application is the increasing of nitrogen utilization from the applied fertilizer (Steiner *et al.*, 2007; Widowati *et al.*, 2011). This is as the result from the decrease of nitrogen lost due the increase of soil CEC with biochar application (Chan *et al.*, 2008; Masulili *et al.*, 2010) or because of the biochar's ability to inhibit $N\text{-}NO_3$ transformation from $N\text{-}NH_4$ released by fertilizer (Widowati *et al.*, 2011).

2.12. Biochar and mineral fertilizer application

Most of the studies have shown that the beneficial effects of the addition of biochar on crop production are most evident when biochar is combined with mineral fertilizers (Asai *et al.,* 2009; Chan *et al.,* 2007; Lehmann *et al.*, 2003; Schulz and Glaser, 2012; Van Zwieten *et al.,* 2010).Studies have confirmed the positive synergy in combining biochar and inorganic fertilizer in relation to soil productivity and crop yields (Sohi *et al.,* 2010).

Thus, the highest wheat grain productions were obtained by combining both the highest biochar and mineral fertilization application rates ($P < 0.001$). These represented an increase of 407

and 328 % with respect to the control soiland of 33 and 22 % with respect to the control soil plus the highest mineral fertilization for the olive tree pruning biochar and the wheat straw biochar (Alburquerque *et al*., 2013). Purakayastha (2010) clearly explained that application of biochar prepared from wheat straw (1.9 t ha^{-1}) along with recommended doses of NPK at 180:80:80 kg ha^{-1} significantly increased the yield of maize in Inceptisol of IARI farm and this treatment was superior to either crop residue incorporation or 30 crop residue burning.

2.13. Effect of biochar on nutrient use efficiency

The detected increases in nutrient efficiency after biochar amending have been mainly related to a greater nutrient retention, minimizing nutrient losses; improvements in soil properties like increase in water-holding capacity, decrease in soil compaction, and liming effect leading to immobilization of contaminants or nutrient mobilizations; and enhancement in soil biological properties such as more favorable root environment, microbial activities favoring nutrient availability, etc.

2.14. Effect of biochar on plant nutrient uptake

Soil nutrient availability in highly weathered tropical soils has repeatedly been increased by those biochar materials studied in prior experiments (Glaser *et al.,* 2002; Lehmann *et al.*, 2002, 2003; Rondon *et al*., 2007; Steiner *et al*., 2008). Nutrients applied with certain biochar materials can be responsible for short-term increases in crop growth (Lehmann *et al*., 2003).

Alburqueque *et al*. (2013) reported that biochar affected plant nutrient uptake by increasing P and Mg (olive tree pruning biochar) or Zn and Cu (wheat straw biochar) and decreasing Cu (olive tree pruning biochar) or K, Ca, and Mg (wheat straw biochar). Both biochars decreased plant uptake of N, Na, Fe, and Mn. As for the aboveground plant nutrient concentration, wheat straw biochar addition to soil increased P, K, Zn, and Cu. Both biochars decreased N, Fe, and Mn aboveground plant concentrations.

Kammann *et al.* (2011) also observed reductions in foliar N concentrations in a pot trial with a relatively nutrient-rich peanut hull biochar, but in this case the reduction likely resulted from increased N use efficiency since the authors reported biomass increases of up to 60 %.

Uzoma *et al.* (2011) conducted a glasshouse experiment where a biochar manufactured from cow manure (500 °C) was applied at increasing rates to a sandy soil, subsequently planted with maize. Both maize yield and N uptake increased with increasing biochar rate, indicating N release from the biochar. Thus, the latter study further supports the conclusion of Spokas *et al.* (2011).

2.15. Factors affecting biochar impacts on soil quality

Not all biochars are similar in physical and chemical properties (Zimmerman *et al.,* 2010; Cheng *et al.,* 2004) and soil properties also vary widely. Thus, response of soils to biochar amendment also varies widely depending on a range of factors: (i) rate of biocharapplication, (ii) biochar type, and (iii) time of application. Factors during biochar production (feedstock type, temperature, charring time) are important controls which affect GHG fluxes. Soil response to biochar also depends on several soil factors (i.e., WHC, SA, porosity, etc.) as the temporal change of soil‘s WHC as a parabolic response was observed in Norfolk loamy sand and Warden silt loam soils, but not in Declo silt loam (Novak *et al.,* 2012). Biochar ages in soil environment after application because of various chemical and biological reactions on biochar/soil interface which alter soil quality over time. While surface oxidation and higher acidity are presumably the main changes during aging (Cheng *et al.,* 2008), recent data also indicate (i) possible transformations or conversions of surface functional groups such as increase in phenols and conversion of carboxylic acids to cyclic acid anhydride derivatives and (ii) oxidation and subsequent solubilization or microbial uptake of surface functional groups with increase in carboxyl and carbonyl groups in the bulk structure (Mukherjee *et al.,* 2013).

2.16. Soil biochar interaction

The soil response to biochar involves complex physical, chemical, and biological interactions. Whereas the physical and chemical interaction of biochar with soil are interrelated and create a faster response, the biological interaction is slower at the onset because of other factors such as moisture content, organic matter or nutrient source, surface area and porosity which are important controls to biological functions.

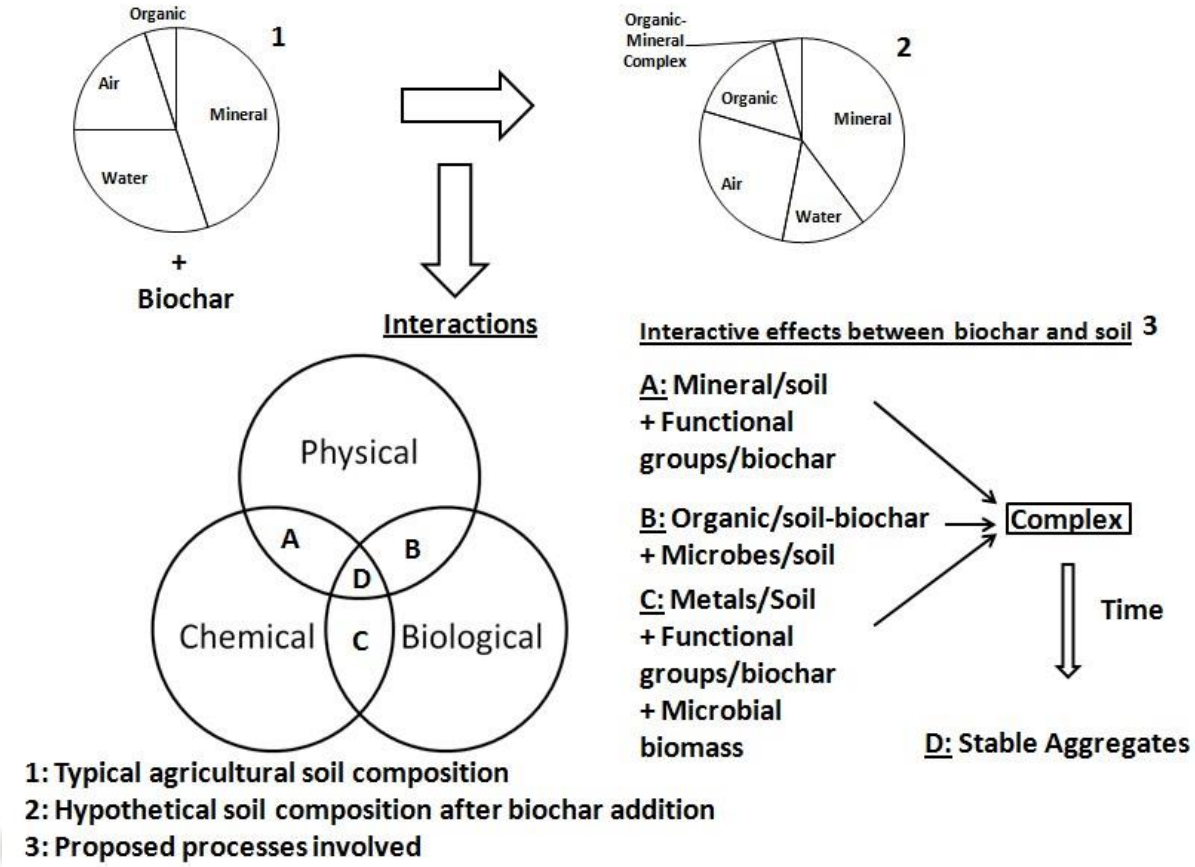
The interaction between biochar and soil is based on the biochar properties. The properties are viz., large surface area (SA) and presence of micropores (Mukherjee *et al.,* 2011; Braida *et al.,* 2003; Nguyen *et al.,* 2004; Rutherford *et al.,* 2004). Key properties are those which contribute to the adsorptive properties of biochars and potentially alter soil‘s SA, pore size distribution (PSD), bulk density (BD), water holding capacity (WHC) and penetration resistance (PR).

Recent studies (Steiner *et al*., 2007; Bruun *et al*., 2008; Singh and Cowie, 2008; Kuzyakov *et al*., 2009) suggest that the types and rates of interactions (e.g. adsorption–desorption, precipitation–dissolution, redox reactions) that take place in the soil depend on the following factors: (i) feedstock composition, in particular the total percentage and specific composition of the mineral fraction; (ii) pyrolysis process conditions; (iii) biochar particle size and delivery system; and (iv) soil properties and local environmental conditions.

Addition of biochar triggers the physical contact of biochar/soil surface and sets-in-motion the physical-chemical interaction. The complex formed between biochar surface and soil organic and mineral phases may stabilize aggregates (Lin *et al.,* 2012) and form the basis of biological interaction. Most parts of the biochar are microbially stable as C from biochar is protected due to presence of thermodynamically stable (i.e., refractory) cyclic organic compounds (Ruherford *et al.,* 2004). The surface area of biochar comprises of aromatic and aliphatic organic surface functional groups (Mukherjee *et al.,* 2011) which create direct and indirect bonds with soil

mineral and organic phases. The complex formed between biochar surface and soil organic and mineral phases may stabilize aggregates (Lin *et al.,* 2012) and form the basis of biological interaction. The high amount of Surface Area and distinct pore volumes of biochar surface (Mukherjee *et al.,* 2011) are potential microbial habitat and accentuate nutrient release upon microbial decomposition and degradation of soil/biochar initial complex. Complex formation within the inner core of biochar material consisting of stable cyclic aromatic compounds begins simultaneously through interactions of biochar aromatic organic-C, soil mineral and microbial biomass. This stable complexation may take place either through specific bonding by biochar surface functional groups and mineral phase of soil, metal-organic cation bridge formation or for some biochar by sorption of SOM on biochar-mineral phase over time as evident by recent study (Mukherjee *et al.,* 2011). Thus, stable soil aggregates may be formed through interaction with soil minerals on the higher Surface Area of biochar. The specific bonding of SOM and minerals can retard microbial decomposition of SOM (Six *et al.,* 2002), and SOM is physically and chemically protected from microbial attack through formation of stable aggregates (Kyung-Hwa*et al.,* 2010).

KNUST



Source: Mukherjee and Lal, 2013

Figure 2.1. Schematic presentation of interactions between biochar and soil

2.17. Effect of biochar on soil microorganisms

The current knowledge about soil microbes is based on the experimental evidence with which biochar has symbiotic relationship with the mycorrhizal system. The four mechanisms by which biochar could improve mycorrhizal abundance and functioning are given by Warnock *et al.* (2007). The mechanisms are:

i. alteration of soil physic-chemical properties, ii. indirect effects on mycorrhizae through effects on other soil microbes, iii. plant-fungus signaling interference, and iv. detoxification of allelochemicals on biochar.

There are 50 to 72 % increases of soil biological nitrogen fixation (BNF) through biochar application (Lehman and Rondon, 2006). Biochar has positive effects on soil biology. It

provides microbial habitat and refugia for microbes where they are protected from grazing. Both bacteria and fungi are hypothesized to be better protected from grazers or competitors by exploring pore habitats in biochars (Ezawa *et al.,* 2002; Saito and Marumoto, 2002; Thies and Rillig, 2009). Earthworms have been shown to prefer some soils amended with biochar to those soils alone. However, this is not true of all biochars, particularly at high application rates (Verheijen *et al.,* 2010).

KNUST

2.18. Biochar–soil mineral–soil organic matter interactions

Interactions between organic matter and clay mineral surfaces in soil are complex and depend on the type of clay (2: 1 or 1: 1), the distribution of different functional groups on the clay (siloxane, OH) and the organic matter (COOH, C=O, C–O, CN), the polarity of these compounds, and the composition and concentration of cations and anions in solution (Kleber *et al*., 2007). Similar complex reactions are likely to take place on biochar surfaces, especially for those biochars that have high mineral content. Based on the literature related to organic matter and mineral interactions, and on the mechanisms described in previous sections, several mechanisms for interactions between biochar and organic matter and/or minerals in soil can be hypothesised as follows:

(i) Surface hydrophobic and hydrophilic interactions of biochar, organic compounds, and clay minerals, following the conceptual model of organo-mineral interactions proposed by Kleber *et al*. (2007). This occurs through direct electrostatic interactions, H bonding, cation bridging, and ligand exchange reactions in the hydrophilic zone (Yariv and Cross, 2002), whereas the bilayer formed in the hydrophobic zone is entropically driven (Kleber *et al*., 2007);

Interactions can occur between aromatic compounds (including biochar) and mineral surfaces, as well as between two aromatic compounds, as described in detail by Keiluweit and Kleber (2009), Soluble organic compounds released from the biochar particles and/or from other organic matter in soil can become intercalated within 2:1 and 1:1 clay minerals. Replacement

of interlayer water in smectites by neutral organic molecules and binding of organic compounds in tubular kaolinites through strong hydrogen bonds and/or strong dipole interaction to silicate layers have been reported (Matusik *et al*., 2009). Deprotonated multidentate organic acids are known to form complexes with transition metals (Violante and Gianfreda, 2000) and also silicic acid (Marley *et al*., 1989).

KNUST

2.19. Possible negative effects of biochar addition

Little is known about the potential toxic effects of biochar in soil, and specifically of those related to the presence of heavy metals and plant-available organic compounds that have condensed on the surfaces of biochar during their manufacture. A discussion of possible effects is given in Lehmann and Joseph (2009). The following is a brief summary.

Condensates on the surface of biochars may contain compounds such as polycyclic aromatic hydrocarbons, cresols, xylenols, formaldehyde, acrolein, and other toxic carbonyl compounds that can have bactericidal or fungicidal activity (Painter 2001). However, Ogawa (1994) has shown that these substances can, and do, serve as C and energy sources for selected microbes. McClellan *et al*. (2007) found that residual volatiles on biochar made using a flash carboniser proved toxic to plants, when the biochar soaking time was increased these toxic effects were removed.

2.20. Summary of literature review

Low soil fertility due as a result of poor agricultural imput has been a major challenge in food production with an increasing human population in sub-SaharanAfrica. Maize production has declined to less than 1 t ha^{-1} in these regions which is attributable to loss of soil fertility in smallholder farming systems.

The common strategy has been the use of mineral fertilizer which is quiet expensive for small holder farmers and organic manure which is highly mineralized under the tropic and sub tropic areas.

Biochar has the potentials for carbon sequestration, green house gases emission reduction and enhancement in soil fertility. Biochar has the capacity to influence soil physicochemical properties such as water holding capacity, bulk density, penetration resistance, pH, lectrical conductivity, cation exchange capacity e.t.c as well as nitrogen and carbon dynamics there by affecting soil fertility positively.

KNUST

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1. Location of the study area

The experiment was carried out on a farmer‘s field at Kpongu in the Upper West region of Ghana. The site is situated in the Guinea Savanna agro-ecological zone of Ghana (longitude 09º57‘48.6“ N and latitude 002º30‘31.4“ W at an elevation of 286 m above sea level).

3.1.1 Climate of the study area

This zone has a unimodal pattern of rainfall which starts from July to October. The mean rainfall is 1000 mm (800 - 1200 mm) with an average annual temperature of 28.1 ºC relative humidity of 61 %, wind speed of 138 km day^{-1}, sunshine hours of 7.3 hours and solar radiation of 19.6 MJ $m^{-2}day^{-1}$ respectively. The vegetation is mainly Guinea Savannah consisting of ground cover of grasses of various heights interspersed with short drought and fire resistant trees.

3.1.2 Soil of the study area

The soil of the siteis mainly savannah ochrosols and groundwater laterites.The same soil was sampled for the incubation study.

3.1.3 Soil sampling and preparation

In order to characterize the soil of the experimental field, 10 samples were taken across the field with plot at 72 m x 54 m at a depth of 15 cm and bulked for laboratory analysis. In the laboratory, the soil samples were air-dried, crushed using a wooden mortar and pestle and then sieved through a 2 mm mesh. The sieved samples were stored in polythene bags for laboratory chemical and physical analyses at the Soil Science Laboratory of the Department of Crop and Soil Sciences, KNUST.

Table 3. 1: Initial soil properties at the experimental site

Properties	**Value**
Soil Texture	Sandy
Clay ⟶ (%)	4.06
Silt (%) ⟶	6.04
Sand ⟶ (%)	89.00
Bulk density (g cm^{-3})	1.50
Soil pH (1:1 H_2O)	5.40
Organic carbon (%)	0.77
Total nitrogen (%)	0.07
Available phosphorus (mg kg^{-1})	5.70
Available potassium (mg kg^{-1})	98.65
Exchangeable Ca (cmol kg^{-1})	1.70
Exchangeable Mg (cmol kg^{-1})	0.61
Exchangeable acidity (Al + H) (cmol kg^{-1})	0.84

3.2. Soil chemical properties

3.2.1. Soil pH

Soil pH was measured in a 1:1 soil-water ratio using a glass electrode (H19017 Microprocessor) pH meter. Approximately 25 g of soil was weighed into a 50 mL polythene beaker and 25 mL

of distilled water was added to the soil. The soil-water solution was stirred thoroughly and allowed to stand for 30 minutes. After calibrating the pH meter with buffers of pH 4.01 and 7.00, the pH was read by immersing the electrode into the upper part of the soil solution and the pH value recorded.

3.2.2. Soil organic carbon

Soil organic carbon was determined by the modified Walkley-Black method as described by Nelson and Sommers (1982). The procedure involves a wet combustion of the organic matter with a mixture of potassium dichromate and sulphuric acid. After the reaction, the excess dichromate is titrated against ferrous sulphate. Approximately 1.0 g of air-dried soil was weighed into a clean and dry 250 mL Erlenmeyer flask. A reference sample and a blank were included. Ten mL of 0.1667*M* potassium dichromate ($K_2Cr_2O_7$) solution was accurately dispensed into the flask using the custom laboratory dispenser. The flask was swirled gently so that the sample was made wet. Then using an automatic pipette, 20 mL of concentrated sulphuric acid (H_2SO_4) was dispensed rapidly into the soil suspension and swirled vigorously for 1 minute and allowed to stand on a porcelain sheet for about 30 minutes, after which 100 mL of distilled water was added and mixed well. Ten mL of orthophosphoric acid and 1 mL of diphenylamine indicator was added and titrated by adding 1.0 *M* ferrous sulphate from a burette until the solution turned dark green at end-point from an initial purple colour. About 0.5 mL 0.1667 *M* $K_2Cr_2O_7$ was added to restore excess $K_2Cr_2O_7$ and the titration completed by adding $FeSO_4$ drop-wise to attain a stable end-point. The volume of $FeSO_4$ solution used was recorded and % C calculated.

Calculation:

The organic carbon content of soil was calculated as:

$$\% \text{ O. C} = \frac{0.39 \text{ mcf } (V_1 - V_2)}{S} \quad \text{.....eqn (1)}$$

where;

M = molarity of Ferrous sulphate solution

V_1= mL of ferrous sulphate solution required for blank
V_2= mL of ferrous sulphate solution required for sample

S = weight of air – dry sample in grams

Mcf = moisture correction factor $\frac{100 \times \% \, moisture}{100}$

0.39 = 3 x 0.001 x 100% x 1.3 (3= eqivalent weight of carbon)

1.3 = a compensation factor for incomplete combustion of organic carbon.

3.2.3. Total nitrogen

Total nitrogen was determined by the Kjeldahl digestion and distillation procedure as described in Soil Laboratory Staff (1984). Approximately 0.2 g of soil was weighed into a Kjeldahl digestion flask and 5 mL distilled water added. After 30 minutes, a tablet of selenium and 5 mL of concentrated H SO were added to the soil and the flask placed on a

2 4

Kjeldahl digestion apparatus and heated initially gently and later vigorously for at least 3 hours. The flask was removed after a clear mixture was obtained and then allowed to cool. About 40 mL of distilled water was added to the digested material and transferred into 100 mL distillation tube. Twenty mL of 40 % NaOH was also added to the solution and then distilled using the Tecator Kjeltec distiller. The digested material was distilled for 4 minutes and the distillate received into a flask containing twenty mL of 4 % boric acid (H BO)

3 3

prepared with PT5 (bromocresol green) indicator producing approximately 75 mL of the distillate. The colour change was from pink to green after distillation, after which the content of the flask was titrated with 0.02 *M* HCl from a burette. At the end-point when the solution changed from weak green to pink the volume of 0.02 *M* HCl used was recorded and % N calculated. A blank distillation and titration were also carried out to take care of traces of nitrogen in the reagents as well as the water used.

Calculation:

The percentage nitrogen in the sample was expressed as:

$$\% N = \frac{M \times (a - b) \times 1.4 \times mcf}{S} \quad \text{.....eqn (2)}$$

Where

M = concentration of Hydrochloric acid used in titration

a = volume of hydrochloric acid used in sample b =

volume of hydrochloric acid used in blank S = weight

of air – dry samples in grams

mcf = moisture correction factor $\frac{100 \times \% \, moisture}{100}$ .....eqn (3)

3.2.4. Available phosphorus

The readily acid-soluble forms of phosphorus were extracted with a HCl:NH_4F mixture called the Bray's no.1 extract as described by Bray and Kurtz (1945) and Olsen and Sommers (1982). Phosphorus in the extract was determined on a spectrophotometer by the blue ammonium molybdate method with ascorbic acid as reducing agent. Approximately 5 g of soil was weighed into 100 mL extraction bottle and 35 mL of extracting solution of Bray's no. 1 (0.03*M)* NH_4F in filtered through Whatman no.42 filter paper. The resulting clear solution was collected into a 100 mL volumetric flask.

An aliquot of about 5 mL of the clear supernatant solution was pipetted into 25 mL test tube and 10 mL colouring reagent (ammonium paramolybdate) was added as well as a pinch of ascorbic acid and then mixed very well. The mixture was allowed to stand for 15 minutes to develop a blue colour to its maximum. The colour was measured photometrically using a spectronic 21D spectrophotometer at 660 nm wavelengths. Available phosphorus was extrapolated from the absorbance read.

A standard series of 0, 1.2, 2.4, 3.6, 4.8 and 6 mg P L^{-1} was prepared from a 12 mg L^{-1} stock solution by diluting 0, 10, 20, 30, 40 and 50 mL of 12 mg P L^{-1} in 100 mL volumetric flask and made to volume with distilled water. Aliquots of 0, 1, 2, 4, 5 and 6 mL of the 100 mg P L^{-1} of the standard solution were put in 100 mL volumetric flasks and made to the 100 mL mark with distilled water.

Calculation:

P (mg kg^{-1}) = $\frac{(a - b) \times 35 \times 15 \times mcf}{S}$ .....eqn (4)

where; a = mgl^{-1} P in sample

extract b = mgl^{-1} P in blank

S = weight of air – dry samples in grams

mcf = moisture correction factor $\frac{100 \times \% \, moisture}{100}$ .....eqn (5)

35 = volume of extracting solution

15 = final volume of sample solution

3.2.5. Determination of available potassium

Available potassium extracted using the Bray‘s no. 1 solution was determined directly using the Gallenkamp flame analyzer. Available potassium concentration was determined from the standard curve. Potassium standard solutions were prepared with the following concentrations: 0, 10, 20, 30, and 50 µg K mL^{-1} of solution. The emission values were read on the flame

analyser. A standard curve was obtained by plotting emission values against their respective concentrations.

Calculation:

P (mg kg^{-1}) = $\frac{(a - b) \times 35 \times mcf}{S}$ .....eqn (6)

Where; a = µg K mL^{-1} in sample extract b = µg K mL^{-1} in blank

S = weight of air – dry samples in grams

mcf = moisture correction factor $\frac{100 \times \% \text{ moisture}}{100}$

35 = volume of extracting solution

3.2.6. Exchangeable cations

Exchangeable bases (calcium, magnesium, potassium and sodium) in the soil were determined in 1.0 *N* ammonium acetate (NH OAc) extract.

4

3.2.6.1. Extraction of the exchangeable bases

A 5 g soil sample was transferred into a leaching tube and leached with 100 mL of buffered 1.0 *N* ammonium acetate (NH OAc) solution at pH 7.

4

3.2.6.1.1. Determination of calcium

A 25 mL portion of the extract was transferred to an Erlenmeyer flask. Hydroxylamine hydrochloride (1.0 mL), potassium cyanide (1.0 mL of 2 % solution) and potassium ferrocyanide (1.0 mL of 2 %) were added. After a few minutes, 4 mL of 8 *M* potassium hydroxide and a spatula of murexide indicator were added. The solution obtained was titrated with 0.01 *N* EDTA solutions to a pure blue colour. The titre value was again recorded.

3.2.6.1.2. Determination of calcium and magnesium

For the determination of the calcium plus magnesium, a 25 mL of the extract was transferred into an Erlenmeyer flask. A 1.0 mL portion of hydroxylamine hydrochloride, 1.0 mL of 2.0 percent potassium cyanide buffer (from a burette), 1.0 mL of 2.0 per cent potassium ferrocyanide, 10.0 mL ethanolamine buffer and 0.2 mL Eriochrome Black T solution were added. The solution was titrated with 0.01 N EDTA (ethylene diaminetetraacetic acid) to a pure turquoise blue colour. The titre value was recorded.

The titre value for calcium was subtracted from this value to get the titre value for magnesium.

Calculation:

$$\text{Exchangeable calcium (cmol of ca }_{(+)}\text{ kg}^{-1}\text{ soil)} = \left[\frac{V_1\text{-}V_2 \text{ X } V_4 \text{ X N X100 X mcf}}{V_3 \text{ x W}}\right] \text{.....eqn (7)}$$

Where;

V_1 = volume of EDTA required for aliquot sample titration, mL

V_2 = volume of EDTA required for blank titration, mL

V_3 = volume of aliquot taken, mL

V_4 = total volume of original NH_4OA_C extract, mL

N = Normality

W = weight of sample taken in g

mcf = moisture correction factor $\frac{100 \times \%\, moisture}{100}$

1 mL 0.01N EDTA = 0.2004 mg Ca^{2+} = 0.1216 Mg^{2+}

3.2.6.1.3. Exchangeable potassium and sodium determination

Potassium and sodium in the percolate were determined by flame photometry. A standard series of potassium and sodium were prepared by diluting both 1000 mg L^{-1}potassium and sodium solutions to 100 mg L^{-1}. This was done by taking a 25 mL portion of each into one 250 mL volumetric flask and made to volume with water. Portions of 0, 5, 10, 15 and 20 mL of the 100

mg L^{-1}, standard solution were put into 200 mL volumetric flasks respectively. One hundredmilliliters of 1.0 *N* NH_4OAc solution was added to each flask and made to volume with distilled water. The standard series obtained was 0, 2.5, 5.0, 7.5, 10.0 mg L^{-1} for potassium and sodium. Potassium and sodium were measured directly in the percolate by flame photometry at wavelengths of 766.5 and 589.0 nm respectively.

Calculations:

Exchangeable K (cmolkg^{-1}soil) = $\frac{(a-b)x\ 250\ x\ mcf}{10\ x\ 39.1\ x\ s}$ ……..eqn (8)

Exchangeable Na (cmolkg^{-1}soil) = $\frac{(a-b)x\ 250\ x\ mcf}{10\ x\ 23.1\ x\ s}$ ……eqn (9)

Where; a = mg L^{-1} K or Na in the diluted sample

percolate b = mg L^{-1} K or Na in the diluted blank

percolate S = weight of air – dry samples in

grams

mcf = moisture correction factor $(\frac{100 \times \%\ moisture}{100})$

3.2.6.1.4. Exchangeable acidity

Exchangeable acidity is defined as the sum of Al + H and this was determined in 1.0 *M* KCl extract as described by Page *et al*. (1982). The soil sample was extracted with unbuffered 1.0*M* KCl, and the sum of Al + H was determined by titration. Ten grams of soil sample was put in a 100 mL bottle and 50 mL of 1.0 M KCl solution added. The bottle was capped and shaken for 1.0 hour and the filtered. Twenty five milliliters portion of the filtrate was taken with a pipette into a 250 mL Erlenmeyer flask and 2 – 3 drops of phenolphthalein indicator solution added. The solution was titrated with 0.1*M* NaOH until the colour just turned permanently pink. A blank was included in the titration.

Calculation:

Exchangeable acidity (cmol kg^{-1} soil) $= \frac{(a-b)\ x\ M\ x\ 2\ x\ 100\ x\ mcf}{s}$ ……..eqn (10)

Where; a = mL NaOH used to

titrate sample b = mL NaOH used

to titrate blank M = molarity of

NaOH solution

2 = 50/25 (filtrate pipetted volume)

S = weight of air – dry samples in grams

Moisture correction factor (mcf) = $\frac{100 \times \%\, moisture}{100}$

3.3. Soil physical analysis

3.3.1. Soil texture

The soil texture was determined by the Hydrometer method. Approximately 40 g of soil was weighed into 250 mL beaker and oven dried at 105 ℃ overnight. The sample was removed from the oven and then placed in a desiccator to cool, after, which it was weighed and the oven dry weight taken. A 100 mL of dispersing agent commonly known as calgon (sodium bicarbonate and sodium hexa-metaphosphate) was measured and added to the soil. It was then placed on a hot plate and heated until the first sign of boiling was observed. The content in the beaker was washed completely into a shaking cup and then fitted to a shaking machine and shaken for 5 minutes. The sample was sieved through a 50 microns sieve mesh into a 1.0 litres cylinder. The sand portion was separated by this method while the silt and clay went through the sieve into the cylinder. The sand portion was dried and further separated using graded sieves of varying sizes into coarse, medium and fine sand. These were weighed and their weights taken.

The 1.0 litre cylinder containing the dispersed sample was placed on a vibrationless bench and then filled to the mark. It was covered with a watch glass and allowed to stand overnight. The hydrometer method was used to determine the silt and the clay contents. The cylinder with its content was agitated to allow the particles to be in suspension, it was then placed on the bench

and hydrometer readings taken at 30 seconds, 4 minutes, 1 hour, 4 hours and 24 hours intervals. At each hydrometer reading, the temperature was also taken. Coarse silt, medium silt, fine silt and clay portions were then calculated graphically. The various portions were expressed in percentage and using the textural triangle the texture was determined.

3.3.2. Bulk density

Bulk density in the field at 0 – 15 cm and 15 – 30 cm depth was determined by the core method described by Blake and Hartge (1986). A cylindrical metal sampler of 5 cm diameter and 15 cm long was used to sample undisturbed soil. The core was driven to the desired depth (0 – 15 cm and 15 – 30 cm) and the soil sample was carefully removed to preserve the known soil volume as existed in situ. The soil was then weighed, dried at 105 °C for two days and reweighed. Bulk density was computed as:

$$p_b = \frac{Mg}{Vt} \quad \text{.....eqn (11)}$$

Where;

P_b = soil density (g cm^{-3})

Mg = mass of oven dry soil (g)

Vt = total volume of soil (cm^3)

3.4. Characterization of cattle manure used in the experiments

3.4.1 Manure collection, sampling and analysis

Decomposing cattle manure heaped at different Fulani cattle ranches at Kpongu, Wa, were collected in sacks. Samples from each sack were taken and they were mixed to form a composite. Part of the composite sample was taken for laboratory analysis.

Table 3.2. Cattle manure characterization

PROPERTY	VALUE
Total Nitrogen (%)	2.53

Total Phosphorus (%)	0.33
Total Potassium (%)	2.02
Total Calcium (%)	0.30
C:N Ratio	15.22

From the laboratoryanalysis, the manure contained 2.53, 16.5 and 101 kg ha^{-1} N, P and K, respectively for each full recommended rate (5 t ha^{-1}) applied (losses inclusive). The manure as an organic resource was of a good quality due to its high N content (> 2.5) (Palm *et al.,* 2001) and low C:N ratio (8.58) (Bationo *et al*., 2007)

3.4.2. Chemical analysis

The cattle manure used in the experiment was characterized for pH, organic carbon, and N, P, K following thelaboratory procedures described in section 3.4.

3.4.2.1. Dry matter content

Five hunded grams of fresh manure samples were taken in triplicates, oven-dried at 70 °C for 24 hours and the dry weight taken. The dry matter content was calculated as the ratio of the average dried weight and the average fresh weight expressed as a percentage.

$$\% \text{ dry matter} = \frac{\text{average dried weight}}{\text{average fresh weight}} \text{x } 100\ \%$$

3.4.2.2 Manure application

Thirty six out of the fifty- four plots received manure treatments, eighteen of which had a 5 t ha^{-1} recommendedrate each and the other eighteen a 2.5 t $ha^{-1}$of recommended rate each. Manure was weighed with a Camry dialspring scale and broadcasted at their required quantities based on the treatment (randomization). It was then thoroughly mixed with the soil using a hoe to about 10 cm depth and allowed for seven days before planting.

3.5Characterization of biochar used in the experiments

3.5.1 Biochar, collection and characterization

Biochar made from rice husk was used for this experiment, rice husk was obtained from a local commercial rice mill producer in Kumasi and slow pyrolysis used to produce biochar at a temperature of 350 to 500 ℃. Pryolysis time was 48 hours. The process of pyrolysis was carried out at the Soil Research Institute, Kwadaso. Biochar was milled into a coarse powder and dry-sieved over a 0.5 mm mesh sieve before laboratory analysis while the biochar for field trial was used without any further treatment. Samples of the biochar were characterized for pH, total N, P, C, K, CEC, ash content and water content. The biochar contained 28.60 % carbon and 0.89 % N (analyzed with an elemental analysis apparatus, Flash EA 2000, Thermo Electron Corporation, Italy). Available phosphorus content was 0.11 % (extracted with 0.5 M $NaHCO_3$ at a pH of 7.5, and analysed using the colorimetric method), and available potassium content was 1.12 % (extracted with 2.0 *M* HNO_3, and analyzed with a flame photometer, FP640, Cany, China). Ash content of the biochar was 42.80 % (determined by dry combustion in a muffle furnace at 550 °C for 2 h). The biochar was applied to each crop at either the rate of 0, 2.5 or 5 t ha^{-1}. Inorganic basal N fertilizer (urea) of 60 kg N ha^{-1} (165 kg N ha^{-1} yr^{-1}, P as triple superphosphate of 40 kg P_2O_5 ha^{-1}), and K as muriate of potash of 40 kg K_2O $ha^{-1}$was applied to all treatments.

Table 3. 3: Biochar characterization

NUTRIENT	VALUE
Carbon (%)	28.60
Total sodium (%)	0.09
Total nitrogen (%)	0.89
Total phosphorus (%)	0.11
Total potassium (%)	1.12
Total calcium (%)	0.32
Ash content (%)	42.80
Total magnesium (%)	0.11

CEC	8.32
pH	7.5

From the analysis biochar had low carbon content (28.60 %) and very low nitrogen content (0.89 %) due to dehydration during the carbonization process.The ash content of the biochar was 42.80 % which isconsidered relatively low.

KNUST

3.6. Field experiment

3.6.1. Land preparation

The field experiment wassited on farmer's field in Kpongu, Upper West Region of Ghana. The site was slashed and later ploughed and harrowed to a fine tilt. There were three blocks with nine plots each across the slope. Plot sizes measured 4 x 3 ($12\ m^2$). Plots were pegged and separated from each other by 0.50 alleys. In all, 54 plots consisting of 18 treatments and 3 replications were laid out in randomised complete block design (RCBD).

3.6.2. Experimental design and treatments

The trial was a factorial experiment laid in randomized complete block design (RCBD). Eighteen treatments (three levels of biochar by three levels of mineral fertiliser by two levels of manure) were allocated randomly to each plot according to their recommended application rates.

The fertiliser recommended rate (RR) for N: P_2O_5: K_2O for maize in the Guinea Savannah agro-ecological zone of Ghana is 60-60-40 kg ha^{-1} which corresponds to 2 bags NPK (15-1515) plus 1 bag $(NH_4)_2SO_4$ per hectare recommended to be applied by farmers (ANTIKA Agro inputs Company) while recommended rate (RR) for manure is 5 t ha^{-1} (Williams *et al*., 1995), biochar was applied at 0, 2.5 t ha^{-1} and 5 t ha^{-1}.

Table 3. 4: Treatment applied in the study

Code No	**Description**

T1	0 % Biochar + 0 % Manure + 0% NPK
T2	0 % Biochar + 100 % Manure + 50 % NPK
T3	0 % Biochar + 100 % Manure + 0 % NPK
T4	0 % Biochar + 100 % Manure +100 % NPK
T5	0 % Biochar + 0 % Manure + 50 % NPK
T6	0 % Biochar + 0 % Manure + 100 % NPK
T7	50 % Biochar + 100 % Manure + 0 % NPK
T8	50 % Biochar + 100 % Manure + 100 % NPK
T9	50 % Biochar + 50 % Manure + 50 % NPK
T10	50 % Biochar + 0 % Manure + 50 % NPK
T11	50 % Biochar + 0% Manure + 0 % NPK
T12	50 % Biochar + 0 % Manure + 100 % NPK
T13	100 % Biochar + 100 % Manure +50 % NPK
T14	100 % Biochar + 100 % Manure + 100 % NPK
T15	100 % Biochar + 100 % Manure + 0 % NPK
T16	100 % Biochar + 0 % Manure + 0 % NPK
T17	100 % Biochar + 0 % Manure + 50 % NPK
T18	100 % Biochar + 0 % Manure +100 % NPK

Biochar 0, 2.5 and 5 t ha^{-1}, manure 0, 5 t ha^{-1} and mineral fertilizer 0, 30-30-20, 60-60-40 kg ha^{-1} NPK

KNUST

6.3. Seed acquisition and germination test

The test crop used for this experiment was a maize variety called Abontem which is an extra early maturing maize (75 days) with yield potential of 13.6 t ha^{-1}. It was obtained from the Crop Research Institute, Fumesua. A germination test was done using a germination tray filled with top soil. Fifty maize seeds were put on this tray and monitored for germination and emergence. Forty eight out of the fifty seeds germinated and emerged after seven days representing a germination percentage 96 %.

3.6.4. Planting and fertilization

The planting was done on 24th July, 2014 at a planting spacing of 40 cm within rows and 80 cm between rows using 3 seeds per hole. Filling was done on 7thAugust, 2014. The plants were thinned to two per hole to give a plant population of about 58,331 per hectare and the various treatments imposed.

The mode of biocher application was broadcast. Nitrogen in the form of urea was split applied. Half of the dosage was applied at two weeks after planting and the other half applied 5 weeks later.

3.7. Other agronomic practices

3.7.1. Weed control

Weeding was done as and when the need arose. The first weeding was done chemically (using glyphosate) a day after seeds were sown to control the weeds before seedling emergence. The second weeding was done with a hoe, 3 weeks after planting, thus a week after mineral fertiliser application.

3.7.2. Fertiliser application

Fertiliser application was done 2 Weeks After Planting (WAP) using the dibbling method (58 cm away from the plant) at a recommended rate of 60-60-40 kg ha^{-1} of N- P_2O_5 - K_2O. The

fertilisers used were urea, triple superphosphate and muriate of potash which supplied 46 % N, 46 % P_2O_5 and 60 % K_2O respectively. The necessary conversions (based on the required recommended rate of the experiment) were made to evaluate the amount of the Fertilisers needed for each 12 m^2 plot. The urea was applied in split while the triple superphosphate and murate of potash were applied inusing the full recommended rates.

KNUST

3.8 Data collection

3.8.1. Growth parameters

Data was collected on plant height at 2, 4, 6 and 8 weeks after planting. Five plants were randomly tagged on each plot. Three leaves of each plant were also randomly labelled, before the measurements were taken.

Plant height was measured using a measuring tape. The plant height was taken from the soil surface to the apical tip of the plant. Five measurements of each plant height was taken and then averaged. Data were collected fortnightly for a period of eight weeks after planting.

3.8.2. Yield parameters

3.8.2.1. Grain yield

Harvesting was done on 28th October, 2014. The entire plants on the plots were harvested except for the border rows by cutting at the ground level and weighed to represent the total fresh weight. A subsample of 6 plants were randomly selected andalso weighed. The plants were then separated into ears (cob + grains). The various plant parts were put in brown paper envelopes and then oven dried at 60 °Cfor 48 hours to estimate their dry matter.

Dry matter of the various plant parts were calculated as follows:

TDM (stover) in 12 $m^2 = \frac{DMS \times TFW}{FWS}$ ……..eqn (12)

TDM (grain) in 12 $m^2 = \frac{DMS \times TFW}{FWS}$ ……..eqn (13)

Where;

TDM= Total dry matter weight

DMS= Sub-sample dry matter weight

TFW= Total fresh weight

FWS= Sub-sample fresh weight

Maize stover and grains were milled and sievedseparately through a 20 mm mesh sieve for plant nutrient analysis. All nutrients estimated were reported on elemental percentage basis. Grain and stover yields were also estimated per hectare.

Stover yield (kg ha^{-1}) = TDM Stover x harvested area

Grain yield (kg ha^{-1}) = TDM Grain x harvested area

3.8.3 Plant analysis

3.8.3.1. Plant sampling, preparation and laboratory analysis

Maize grain and Stover parts sampled at harvest were kept in paper envelopes and oven-dried at 60 ℃ for 48 hours after which they were milled to pass through 20 mm mesh sieve. The leaf samples of the plants were milled in a miller, after which nitrogen and phosphorus contents were determined. Total nitrogen was determined according to the procedure described for the determination of total nitrogen in soil. Total phosphorus was determined using the spectrophotometric vanadium phosphomolybdate method. One gram of plant sample was weighed into the digestion tube. One millilitre of digestion mixture ($HCLO_4$ and HNO_3) was added. It was digested and made up to 500 mL in a volumetric flask. Ten millilitres of the digest was measured into a 50 mL volumetric flask and 10 mL of vanadomolybdate added. Distilled water was then added to make the required volume. The mixture was then shaken vigorously

and kept for 30 minutes. This was then read on a 430 nm spectrophotometer after a yellow colour had developed to record the percentage absorbance.

The absorbance and the P content were determined from a standard curve.

3.8.3.3. Nutrient uptake

Nutrient uptake was determined separately for maize stover and grain. This was calculated from the nutrient concentrations obtained from the tissue analysis and oven-dry matter weight and expressed in kg ha^{-1}.

3.8.3.4 Nutrient use efficiency

This is the total biomass or grain yield produced per unit of fertilizer applied. Nitrogenuse efficiency of maize for nitrogen was calculated as:

$$NUE = \frac{\text{Total grain or biomass yield}}{\text{rate applied}} \quad \text{.....eqn (14)}$$

3.8.3.5 Nitrogen and phosphorus uptake

Nutrient uptake was calculated by multiplying the nitrogen and phosphorus content of soybean shoot biomass and grain with their respective yield.

Calculation:

$$\text{N or P uptake (kg ha}^{-1}) = \frac{\text{N or P conc in biomass (\%)} \times \text{biomass Yield}}{100} \quad \text{.....eqn (15)}$$

3.9. Economic analysis

The information regarding the value cost ratio analysis in this study was collected at the specific time of each activity in the course of the season. The data mainly from farmers and agro-input retailers and market women using the farm gate prices of the various inputs. Labour for collection, transport and application of manure and fertilizer were also taken into account.

3.9.1 Value cost ratio

Value cost ratio was calculated using the formula:

VCR = $\frac{(Y-Yc)}{x}$ (adopted from Nziguheba *et al.,* 2010)

Where Y = Monetary value of crop in intvention (treated) plots,

Yc = monetary value of the crop harvested in control plots and X is the monetary cost of inputs (seeds and fertilizers).

3.10. Statistical Analysis

All data were subjected to ANOVA. The statistical package used was GenStat 2012 version. Least significance differencemethod was used for the mean separationat 5 % level of probability.

3.11. Combined effects of biochar, mineral fertilizer and manure on soil pH, NH_4-N, NO_3-N and urease activity

3.11.1 Soil laboratory incubation studies

The incubation study was done to determine the effect of treatments on soil pH, ammonium nitrogen (NH_4-N), nitrate nitrogen (NO_3-N) and urease activity.

3.11.1.1. Study site

The set-up for the incubation study was done at the Soil Science Laboratory of KNUST. The laboratory has an average temperature of 30.33 ^oC which ranges from 28 to 33^oC. The analyses were done at the Soil Science laboratory of KNUST and Soil Research Institute, Kwadaso. Soils used for this study were collected at different locations randomly selected from the field before planting.

3.11.1.2. Determination of moisture content field capacity

A 1 mm wire mesh was folded twice and used to cover one end of an open polyvinylchloride tube of diameter, 10.7 cm and length of 29.8 cm. The tube was filled half way with soil collected from the field, weighed and placed in a basin of water. Water was allowed to flood the soil by capillarity until some settled on top of the soil. The tube was removed and raised over a water

sink to drain the soil. The setup was left to drain over 48 hours when free drainage had ceased. Weight of the soil was taken again and the difference calculated as themoisture at field capacity.

3.11.1.3 Soil moisture

Ten grams of soil each were weighed into three metal containers with the weight of the containers already taken and labelled. The samples were placed in an oven at 105 ^{0}C and weighed at regular intervals until a constant weight was attained. The soil moisture was determined as:

$$\text{Soil moisture} = \frac{W_1 - W_2}{W_1} x100\ \% \quad \text{.....eqn (16)}$$

Where

W_1- weight of wet soil

W_2 - weight of dried soil

Table 3. 5: Treatment Description

Treatment	Description	Code
1	0 % Biochar + 0 % Manure + 0 % NPK	TR_1
2	0 % Biochar + 100 % Manure + 50 % NPK	TR_2
3	0 % Biochar + 100 % Manure + 0 % NPK	TR_3
4	0 % Biochar + 100 % Manure + 100 % NPK	TR_4
5	0 % Biochar + 0 % Manure + 50 % NPK	TR_5
6	0 % Biochar + 0 % Manure + 100 % NPK	TR_6
7	50 % Biochar + 100 % Manure + 0 % NPK	TR_7
8	50 % Biochar + 100 % Manure + 100 % NPK	TR_8
9	50 % Biochar + 50 % Manure + 50 % NPK	TR_9
10	50 % Biochar + 0 % Manure + 50 % NPK	TR_{10}
11	50 % Biochar + 0 % Manure + 0 % NPK	TR_{11}
12	50 % Biochar + 0 % Manure + 100 % NPK	TR_{12}
13	100 % Biochar + 100 % Manure + 50 % NPK	TR_{13}
14	100 % Biochar + 100% Manure+ 100% NPK	TR_{14}
15	100 % Biochar + 100 % Manure + 0 % NPK	TR_{15}
16	100 % Biochar + 0 % Manure + 0 % NPK	TR_{16}
17	100 % Biochar + 0 % Manure + 50 % NPK	TR_{17}
18	100 % Biochar + 0 % Manure + 100 % NPK	TR_{18}

Biochar 0, 2.5 and 5 t ha^{-1}, manure 0, 5 t ha^{-1} and mineral fertilizer 0, 30-30-20, 60-60-40 kg ha^{-1} NPK

3.11.1.4. Setup Installation

The eighteen treatments used on the field were repeated four times in a completely randomized design (RCBD) with three replications to make 216 containers which were raised on a platform in the soil science laboratory of KNUST. Destructive sampling was done on the four sampling

dates which were 14, 28, 42 and 56 days after incubation. A 153.6 g of soil each was weighed into each of the cups. The initial water content of the soil was 2.8 % and the moisture content at field capacity was 14.6 %. The soil amendments were weighed and added according to the treatment description. 14 mL of deionized water was added to each soil to top up the 3.2 % moisture already in the soil to make afield capacity moisture content of 7.7 %. The soil was mixed thoroughly with the 15 mL water and the amendment and then covered with a gas permeable transparent polythene bag and held with a rubber band, the polythene was perforated all round with the aid of a needle to add microbial respiration. The set up was kept in an unused oven under dark at a temperature rangeof from 28 ℃ to 33 ℃ to minimize evaporation.

3.12. Soil laboratory incubation set-up

3.12.1. Soil analysis

A series of soil analysis were done after 14, 28, 42 and 56 days after incubation (DAI) on the following parameters: pH, nitrate nitrogen (NO_3^--N), ammonium nitrogen (NH_4^+-N) and soil urease activity.

3.12.2. Soil pH

Soil pH was measured in a 1:1 soil-water ratio using a glass electrode (H19017 Microprocessor) pH meter. Approximately 10 g of soil were weighed into a 50 mL glass beaker and 10 mL of distilled water was added to the soil. The soil-water solution was stirred thoroughly and allowed to stand for 30 minutes. After calibrating the pH meter with buffers of pH 4.00 and 7.00, the pH was read by immersing the electrode into the upper part of the soil solution and the pH value recorded.

3.12.3. Nitrate Nitrogen, NO_3^--N (Salicylic acid method)

Twenty millilitres of 0.5 *M* K_2SO_4 was added to 5 g of wet soil sample and shaken for 1 hour and the solution filtered. 1 mL aliquot of the filtrate and standards were pipetted into suitably marked test tubes. One millilitre of 5 % salicylic acid solution was added, mixed thoroughly

and left for 30 minutes. Ten millilitre of 4 *M* sodium hydroxide solution was added, mixed well and left for 1 hour for full colour development. Each of the standard and sample absorbance was read with a spectrophotometer at 410 nm.

The NO_3-N was calculated as: NO_3-N (mg kg^{-1} of soil) = $\frac{\text{absorbance (y)} * \text{dilution factor}}{0.0343}$

Dilution factor = $\frac{\text{volume of K2SO4}}{\text{dry weight of soil}}$

3.12.4. Ammonium nitrogen, NH_4^+ (Indolephenol-blue method)

Twenty millilitre of 0.5 *M* K_2SO_4 was added to 5 g of wet soil sample and shaken for one hour and the solution filtered. One millilitre aliquot of the filtrate and standards were pipetted into suitably marked test tubes. One millilitre of phenol solution, 1 mL sodium nitroprusside solution and 2.5 mL oxidising solution were added in sequence with thorough mixing after each addition. The samples were covered with parafilm and kept in the dark at room temperature for 1 hour. The absorbance was measured with a spectrophotometer at 636 nm.

The results were expressed as follows:

NH_4-N (mg kg^{-1}) = $\frac{\text{absorbance(y) X dilution factor}}{0.0199}$

3.12.5. Soil urease activity

Ten millilitres of 0.2 *M* urea solution was added to 2 g soil and incubated for 6 hours. NH_4-N was determined as follows:

Twenty millilitre of 0.5*M* K_2SO_4 was added to 5 g of wet soil sample and shaken for one hour and the solution filtered. One millilitre aliquot of the filtrate and standards were pipetted into suitably marked test tubes. One millilitre of phenol solution, 1 mL sodium nitroprusside solution and 2.5 mL oxidising solution were added in sequence with thorough mixing after each addition. The samples were covered with parafilm as outlined above to express urease

activity and kept in the dark at room temperature for 1 hour. The absorbance was measured with a spectrophotometer at 636 nm. The results were expressed as follows:

Urease activity (mg kg^{-1}) = $\frac{\text{absorbance(y) X 10}}{0.0199}$

KNUST

CHAPTER FOUR

4.0RESULTS

4.1. On farm evaluation of the effect biochar, mineral fertilizer and manure on maize growth and yield

4.1.1. Effects of biochar, mineral fertilizer and manure on maize growth

The effect of soil amendments on maize plant heights are presented in Table 4.1. The amounts of biochar applied had no significant ($P > 0.05$) effect on height of maize throughout the study (Table 4.1.). No significant variation was also observed among the manure rates from 2 WAP to 4 WAP. However, from 6 WAP onwards, the use of manure significantly ($P < 0.001$) increased the height of the plant with 13 % over the control (Table 4.1.). Similarly, fertilizer application rate had no significant ($P > 0.05$) effect on maize height during 2 and 4 WAP, nevertheless the use of 50 % and 100 % RR produced significantly ($P < 0.001$) higher heights at 6 and 8 WAP relative to the control (Table 4.1.). However, no significant ($P > 0.05$) effect was observed for the combined effect of the treatment on plant height. No significant differences were observed in the combined effect of the treatments.

Table 4.1. Effect of biochar, manure and mineral fertilizer on plant heightat 2, 4, 6 and 8 weeks after planting

Treatment	Plant height (cm)			
Biochar(B) application rate(t ha^{-1})	2WAP	4WAP	6WAP	8WAP
0	18.68	65.01	121.8	179.1
2.5	16.38	54.4	108.4	178.1
5	16.12	56.1	115.5	174.5
F.Pr	0.76	0.122	0.658	0.971
Lsd (0.05)	3.319	11.62	38.55	55.72
Manure(M) application rate (t ha^{-1})				
0 Manure	16.73	56.9	108.3	166.1
5 Manure	17.39	60.1	122.1	188.4
F.Pr	0.241	0.154	0.006**	0.009**

Lsd (0.05)	1.255	4.84	8.21	14.7
Mineral fertilizer (MF) application rate (% RR)				
0	16.9	59.4	99.6	155.6
50	17.4	57.3	122.4	181.5
100	17.13	58.9	123.7	194.6
F.Pr	0.911	0.685	< 0.001***	< 0.001***
Lsd (0.05)	1.316	5.08	10.24	12.78
CV (%)	8.6	8.8	14.8	13.9
F .Pr (B x M)	0.901	0.210	0.130	0.821
F. Pr (B x M F)	0.815	0.808	0.394	0.366
F. Pr (M x M F)	0.353	0.961	0.879	0.883
F. Pr (B x M x M F)	0.137	0.351	0.253	0.614

KNUST

Values are means of three replicates.*, **, ***, means significant at 5%, 1% and 0.1% probability level, respectively.RR= Recommended Rate. WAP= Weeks after planting.

4.1.2. Effect of biochar, mineral fertilizer and manure on shoot biomass, grain yield and

nitrogen use efficiency

Maize shoot biomass, grain yield and nutrient use efficiency as affected by application of the various treatments are illustrated in Table 4.2. The rates of biochar and manure applied had no significant ($P > 0.05$) effect on maize shoot dry matter relative to the control at harvest. There was however, significant difference ($P < 0.001$) in shoot dry matter due to the mineral fertilizer application which significantly ($P < 0.001$) increased shoot DM yield by 105 % and 91 % for 50 % RR and 100 % RR respectively relative to the control (Table 4.2).

No significant ($P > 0.05$) variations existed between biochar and manure rates on maize grain yield. Grain yield from the 50 and 100 % RR treatment plots significantly ($P < 0.005$) were higher by 109 and 105 %, respectively relative to the control (Table 4.1.2). No significant differences were observed in the combined effect of the treatments.

Table 4. 2. Effect of biochar, manure and mineral fertilizer on shoot biomass, grain yield and nitrogen use efficiency

Treatments	Dry Shoot Biomass (kg ha^{-1})	Grain yield (kg ha^{-1})	NUE
Biochar (B) application rate (t ha^{-1}) 0			
	2540	884	20.3
2.5	2289	1306	17.7
5	2109	1119	14.7
Fr. P	0.377	0.206	0.465
Lsd (0.05)	758.3	536.6	11.2
Manure (M) application rate (t ha^{-1}) 0			
	1966	928	18.6
5	2660	1278	16.5
Fr. P	0.028	0.085	0.573
Lsd (0.05)	587.5	416	8.7
Mineral fertilizer (MF) application rate (% RR)			
0	1399	644	6.7
50	2865	1318	29
100	2675	1347	19.1
Fr.P	< 0.001***	<0.001***	0.003**
Lsd (0.05)	505.5	346.6	10.74
CV (%)	14.5	21.5	22.1
F .Pr (B x M)	0.541	0.395	0.932
F. Pr (B x MF)	0.003**	0.094	0.170
F. Pr (M x MF)	0.147	0.557	0.218
F. Pr (B x M x MF)	0.867	0.397	0.420

Values are means of three replicates.*, **, ***, means significant at 5%, 1% and 0.1% probability level, respectively. RR= Recommended Rate. WAP= Weeks after planting.

4.1.3. Nitrogen andPhosphorus uptake as affected by biochar, manure and mineral fertilizer

Biomass and grain N and P contents of maize under the various treatments in the study are as shown in Table 4.3. The amount of N in the biomassand grain ranged from 22.36 - 25.84 mg $kg^{-1}$and 13.3–20.40 mg kg^{-1}, respectively for biochar rates. Biomass and grain N uptake were not significantly ($P > 0.05$) affected by the soil amendments (Table 4.1.3).

Manure application did enhance N uptake of maize (19.80 mg kg^{-1}) biomass significantly ($P > 0.001$). The amounts of N in maize grain (7.70 mg kg^{-1}) was also not significantly ($P < 0.05$) enhanced by the manure application.

Conversely, 50 % RR fertilizer (28.68 mg kg^{-1}) and 100 % RR fertilizer (28.33 mg kg^{-1}) resulted in significantly ($P < 0.05$) higher biomass N uptake than the control which recorded the least uptake (14.39 mg kg^{-1}). The 50 fertilizer and 100 % RR fertilizer treatments increased grain N uptake over the control by 103 % and 88 % respectively (Table 4.3).

The application of biochar significantly improve P uptake in maize ($P < 0.05$) and no significant uptake was observed in the grain ($P > 0.001$).The application of manure at 5 t ha^{-1} significantly ($P < 0.05$) increased biomass P uptake relative to the control by (88 %) but did not translate into significantly ($P > 0.05$) different grain P uptake (Table 4.3). The fertilizer application rate 50 and 100 % RR led to significant increase in biomass P uptake over the control and translated to 82 % and 103 % increase respectively over the control. Grain P uptake also recorded significant ($P < 0.05$) percentage increases of 70 % and 99 % for 50 % and 100 % RR of fertilizer over the control.

The combined effect of biochar and mineral fertilizer had significant effect on biomass N uptake. The application of mineral fertilizer at 50 % RR without biochar or with 2.5 t ha^{-1} biochar led to the highest N uptake while the application of 2.5 t ha^{-1} biochar without mineral fertilizer led to the lowest biomass N uptake.

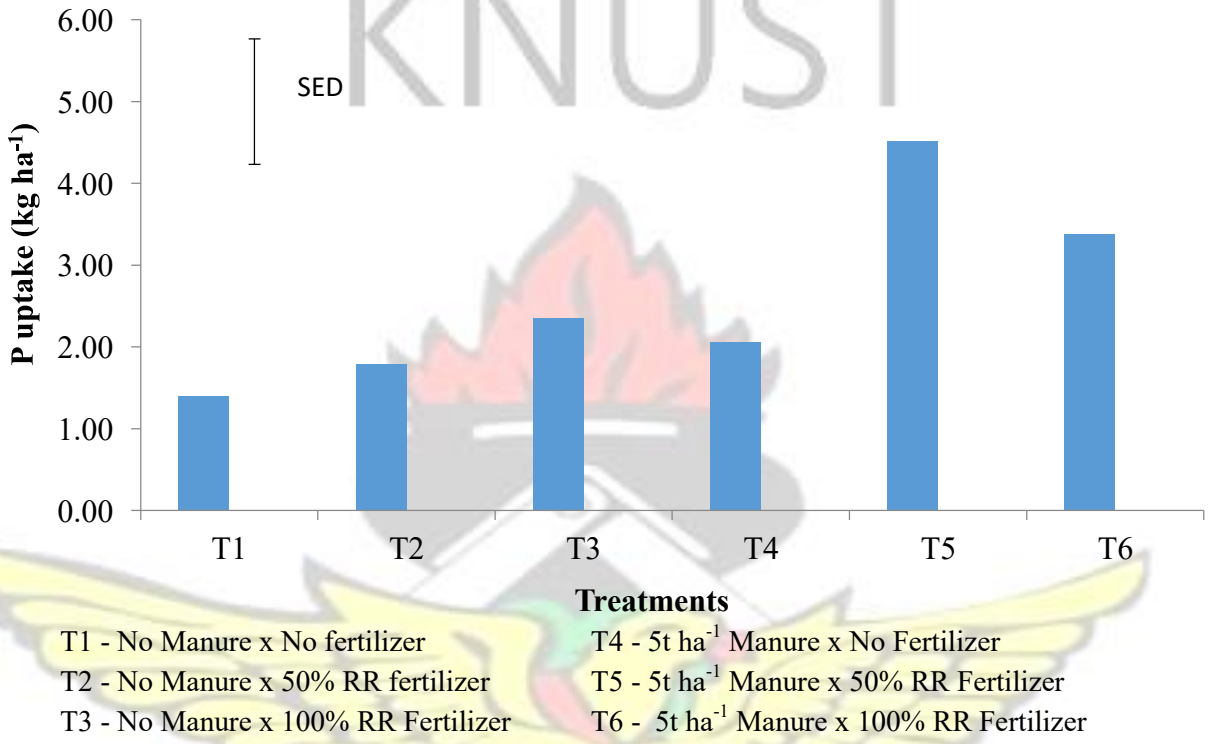


Figure 4. 1. Combined effect of biochar, manure and mineral fertilizer as affecting P uptake

4.1.4. Combined effect of manure and mineral fertilizer on biomass P uptake

The application of manure and mineral fertilizer had significant effect on biomass P uptake. The application of 50 % RR mineral fertilizer without biochar gave the highest P uptake in plant biomass while the application of 2.5 t ha^{-1} biochar without mineral fertilizer gave the lowest P uptake on biomass basis.

Table 4.3. Main Effect of biochar, manure and mineral fertilizer on P and N uptake in both grain and plant biomass after harvesting

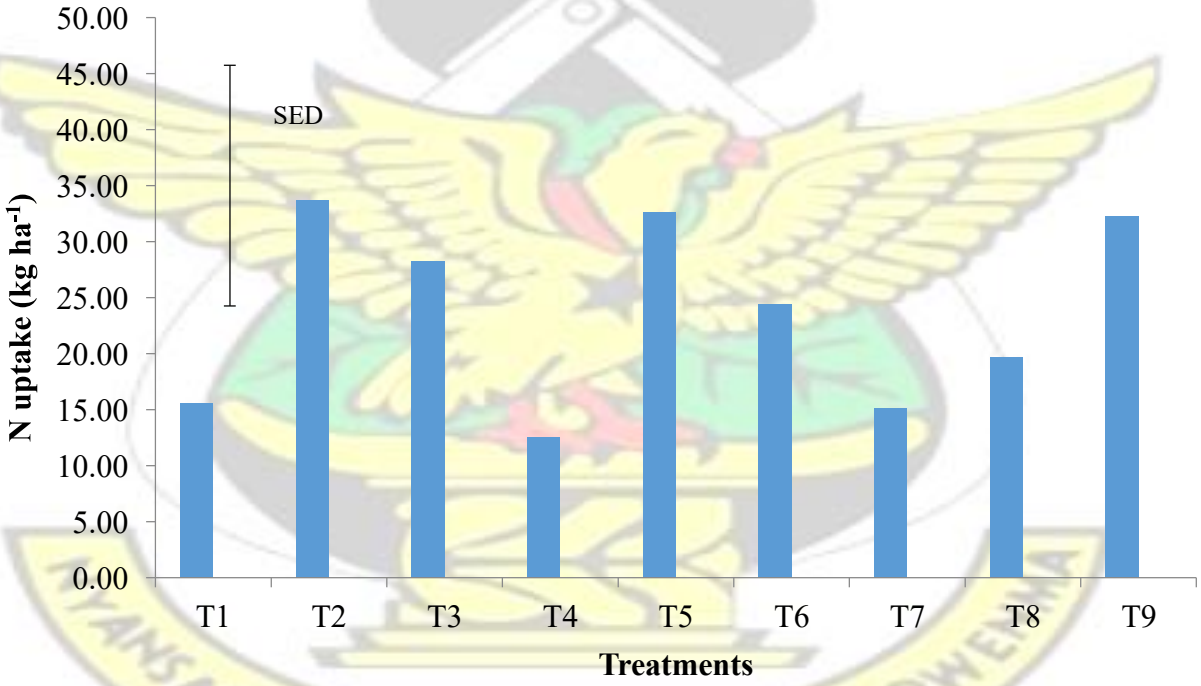
Treatments	Biomass N uptake	Grain N uptake	Biomass P uptake	Grain P uptake
		(kgha^{-1})		
Biochar (B) t ha^{-1}				
0	25.84	20.40	3.07	1.81
2.5	23.20	17.20	2.67	1.73
5.0	22.36	13.30	2.30	1.38
F.Pr	0.585	0.19	0.022**	0.671
Lsd (0.05)	9.11	8.48	0.49	1.35
Manure (M) t ha^{-1}				
0	20.30	14.00	1.85	1.47
5	27.30	19.80	3.47	1.81
F.Pr	0.027*	0.086	< 0.001***	0.303
Lsd (0.05)	5.89	6.93	0.42	0.79
Mineral fertilizer (MF) (% RR)				
O	14.39	10.30	1.73	1.05
50	28.68	20.90	3.15	1.78
100	28.33	19.40	3.09	2.09
F.Pr	< 0.001***	< 0.001***	< 0.001***	0.006**
Lsd (0.05)	5.04	5.63	0.72	0.62
CV (%)	16.9	22.20	8.1	36.20
F.Pr (B X M)	0.414	0.490	0.189	0.030
F.Pr (B X MF)	0.015*	0.184	0.054	0.477
F.Pr (M X MF)	0.312	0.589	0.022**	0.356
F.Pr (B X M X MF)	0.873	0.513	0.512	0.123

Values are means of three replicates. *, **, ***, means significant at 5%, 1% and 0.1% probability level, respectively. RR= Recommended Rate.

4.1.5. Combined effect of biochar and mineral fertilizer applications on biomass N uptake

The results of the combined effects of biochar, manure and mineral fertilizer on biomass and grain N and P are presented in Figure 4.1. The combined application of the different levels of biochar and manure had no significant influence on the biomass and grain N and P uptakes.

The combined application of biochar and the recommended fertilizer rates equally had significant effect on biomass and grain N and P uptakes.The application of sole biochar and manure likewise did not have significant ($P < 0.05$) effect on the biomass and grain N and P uptake.



T1 - No Biochar x No Fertilizer
T2 - No Biochar x 50 % RR Fertilizer
T3 - No Biochar x 100 % RR Fertilizer
T4 - 2.5t ha^{-1} Biochar x No Fertilizer
T5 - 2. 5t ha^{-1} Biochar x 50 % RR Fertilizer
T6 - 2. 5t ha^{-1} Biochar x 100 % RR Fertilizer
T7 - 5t ha^{-1} Biochar x No Fertilizer
T8 - 5t ha^{-1} Biochar x 50 % RR Fertilizer
T9 - 5t ha^{-1} Biochar x 100 % RR Fertilizer

Figure 4. 2. Combined effect of biochar and mineral fertilizer on N uptake

4.2. Effect of soil amendments on soil chemical properties

The effect of soil amendments on the chemical properties of the soil after harvest is summarized in Table 4.4. Percentage soil organic carbon (OC), nitrogen (N) and phosphorus (P) levels analysed after harvest were not significantly ($P > 0.01$) improved by the application levels of biochar, manure and fertilizer. Neither the application of biochar, manure nor mineral fertilizer significantly affected the total N, available P and organic content of the soil.

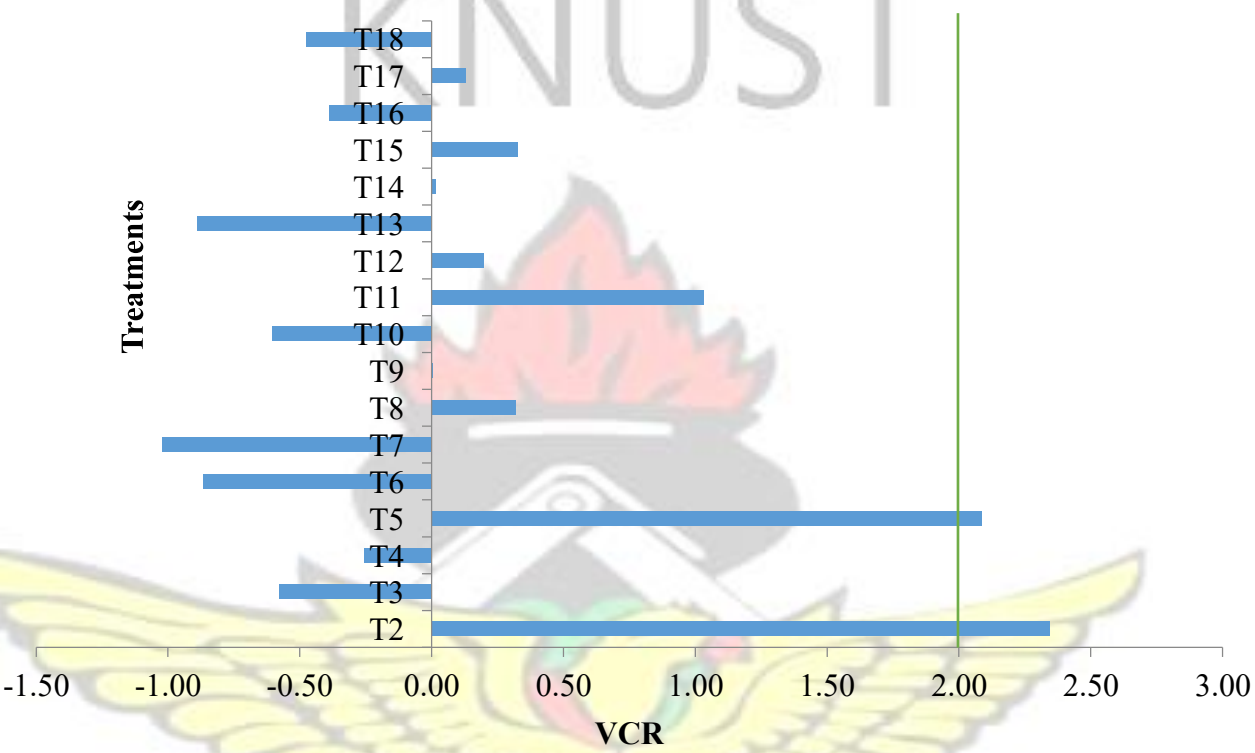
Table 4.4. Effect of biochar, manure and mineral fertilizer on soil chemical properties after harvest

Treatments	% OC	Total N (%)	Available P (mg kg^{-1})
Biochar (B) application rate (t ha^{-1})			
0	0.717	0.061	6.25
2.5	0.835	0.073	5.02
5.0	0.648	0.05	6.39
F.Pr	0.41	0.352	0.486
Lsd (0.05)	0.3545	0.032	3.307
Manure (M) application rate (t ha^{-1})			
0	0.708	0.061	5.24
5	0.759	0.064	6.53
F.Pr	0.514	0.667	0.124
Lsd (0.05)	0.179	0.016	2.227
Mineral fertilizer (MF) application (% RR)			
0	0.687	0.059	6.17
50	0.786	0.067	6.55
100	0.727	0.062	4.94
P value	0.141	0.24	1.07
Lsd (0.05)	0.099	0.009	4.123
CV (%)	21.3	23	23.8
F .Pr (B xM) 0.451 0.398 0.808 F. Pr (B x MF) 0.268 0.205 0.377 F. Pr (M x MF) 0.195 0.240 0.084			
F. Pr (B x M x MF)	0.886	0.887	0.792

Values are means of three replicates. *, **, *** means significant at 5%, 1% and 0.1% probability level, respectively. RR= Recommended Rate

4.2.1. Returns on investment from biochar, manure and mineral fertilizer application

The application of 30:20:20 kg ha^{-1} NPK and 5 t ha^{-1}Manure + 30:20:20 kg ha^{-1} NPK (Figure 4.3) were the most economically viable imputs (VCR = 2) among all treatments while 5 t ha^{-1} biochar + 60:40:40 kg ha^{-1} NPK was the least economical (VCR<2)



T2-No Biocharx No Manure x 50% RR Fertilizer, T3-No Biochar x No Manure x 100% RR Fertilizer, T4-No Biochar x 5 t ha^{-1} Manure x No Fertilizer, T5-No Biochar x 5t/ha Manure x 50% RR Fertilizer,T6-No Biochar x 5 t ha^{-1} Manure x 100% RR Fertilizer,T7-2.5 t ha^{-1} Biochar x No Manure x No Fertilizer,T8-2.5 t ha^{-1} Biochar x No Manure x 50% RR Fertilizer,T9-2.5 t ha^{-1} Biochar x No Manure x 100% RR Fertilizer,T10-2.5 t ha^{-1} Biochar x 5

t ha^{-1} Manure x No Fertilizer, T11-2.5 t ha^{-1} Biochar x 5 t ha^{-1} Manure X 50% RR Fertilizer, T12-2.5 t ha^{-1} Biochar x 5 t ha^{-1} Manure x 100% RR Fertilizer, T13-5t/ha Biochar x No Manure x No Fertilizer, T14-5 t ha^{-1} Biochar x No Manure x 50% RR Fertilizer, T15-5 t ha^{-1} Biochar x No Manure x 100% RR Fertilizer, T16-5 t ha^{-1} Biochar x 5 t ha^{-1} Manure x No Fertilizer, T17-5 t ha^{-1} Biochar x 5 t ha^{-1} Manure x 50% RR Fertilizer, T18-5 t ha^{-1} Biochar x 5 t ha^{-1} Manure x 100% RR Fertilizer

Figure 4.3. Value cost ratio of the applied treatments

4.3. Study 2: Combined effect of biochar, manure and mineral fertilizer on soil properties

4.3.1. Effect of biochar, manure and mineral fertilizer on soil pH

The effect of either biochar or manure or mineral fertilizer on soil pH is presented in Table 4.5. The application of biochar to the soil did not significantly ($P > 0.05$) affect the soil pH until 42 DAI. Manure applied at 5 t ha^{-1} significantly increased the soil pH ($P < 0.001$) at 14, 28 and 56 DAI compared to the control. In contrast to the above results, mineral fertilizer treatments at 50 % RR and 100 % RR significantly ($P < 0.001$) decreased the pH of the soil throughout the incubation period. A significant combined effect was observed ($P < 0.001$) at all interaction level at 28 DAI a significant combined effect of biochar and manure, manure and mineral fertilizer were observed. (Figures 4.4 to 4.6) However, a significant combined effect between biochar and manure on soil pH observed consistent at 14, 28 and 42 DAI. The combined application of biochar and mineral fertilizer had no significant variation ($P > 0.05$) of pH during the incubation period. Manure and mineral fertilizer application recorded a significant effect ($P < 0.001$) on the pH at 42 DAI. The combined effect of biochar, manure and mineral fertilizer influenced pH significantly ($P < 0.05$). At 42 DAI, 0 t ha^{-1} biochar + 5 t ha^{-1} manure gave the highest pH (6.14) while 5 t ha^{-1} biochar + No fertilizer (6.22) and 5 t ha^{1} manure + No mineral fertilizer (6.34) had the highest pH and increased the soil pH at 28

DAI.

Table 4.5. Effect ofbiochar, manure and mineral fertilizer on soil pH

Treatment	14	28	42	56
	Days after Incubation			
Biochar (B) application rate (t ha^{-1})				

0	5.74	5.76	6.00	5.76
2.5	5.76	5.73	5.78	5.78
5.0	5.71	5.74	5.79	5.76
F.Pr	0.688	0.746	0.028*	0.937
Lsd (0.05)	0.13	0.098	0.17	0.108
Manure (M) application rate (t ha^{-1})				
0	5.66	5.64	5.80	5.69
5	5.83	5.83	5.91	5.85
F.Pr	0.003**	< 0.001***	0.12	< 0.001***
Lsd (0.05)	0.106	0.08	0.146	0.088
Mineral fertilizer application (MF) (%RR)				
0	5.97	5.94	6.21	6.12
50	5.63	5.58	5.70	5.71
100	5.61	5.71	5.66	5.49
F.Pr	< 0.001***	< 0.001***	< 0.001***	< 0.001***
Lsd (0.05)	0.13	0.098	0.178	0.108
CV (%)	3.4	2.5	4.5	2.8
F. pr (B x M)	0.001**	0.004**	0.030*	0.569
F. pr B x MF 0.061 < 0.001*** 0.05 0.312 f.pr B x MF 0.586 < 0.001*** 0.334 0.704 F. pr				
B x M x MF 0.157 0.016** 0.280 0.203				

Values are means of three replicates. *, **, ***, means significant at 5 %, 1 % and 0.1 % probability level, respectively. RR = Recommended Rate. **Figure 4. 4. Effect of biochar and manure on soil pH**

KNUST

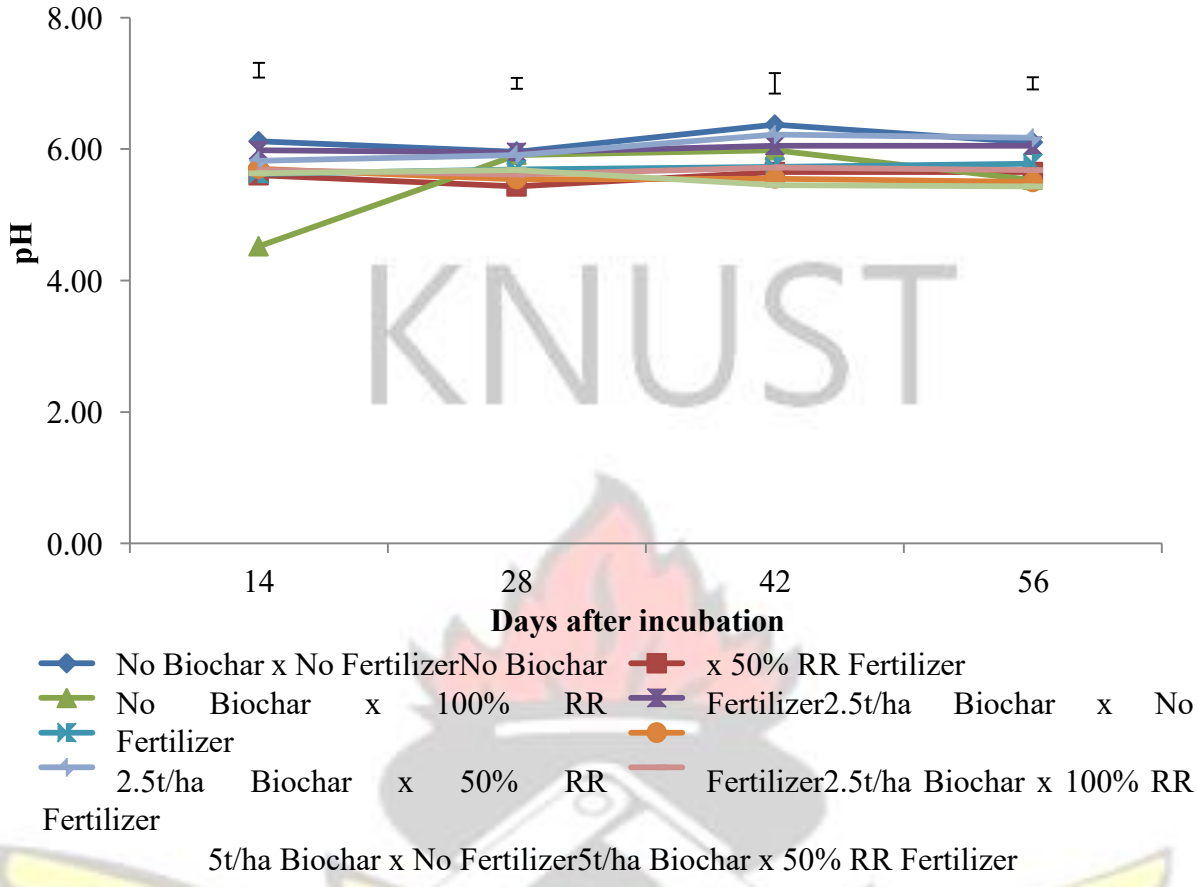
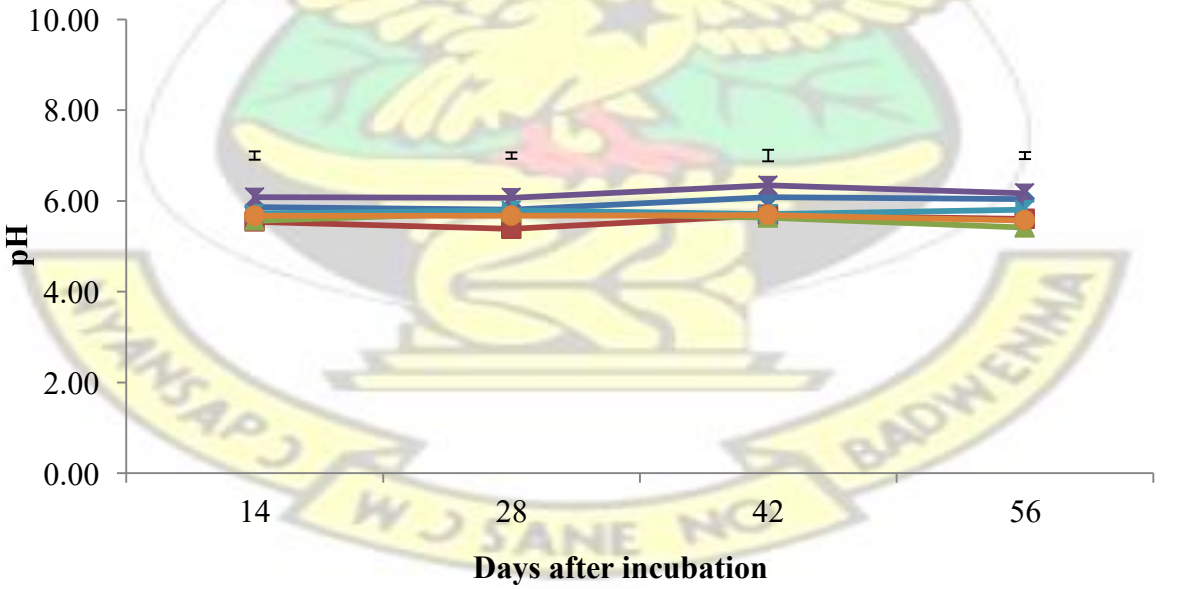


Figure 4. 5. Effect of biochar and mineral fertilizer on soil pH



KNUST

Figure 4.6. Effect of manure and mineral fertilizer on soil pH

4.3.2. Effect of biochar, manure and mineral fertilizer on urease activity under laboratory incubation

Urease activity with biochar application was significantly influenced at 42 ($P < 0.001$) with urease activity being higher at 2.5 t ha^{-1} biochar application than 5 t ha^{-1} and control treatments. Relative percentage increases in urease activity at 42 and 56 DAI were 48 and 76 % respectively over the control. Manure application resulted in significant increases at 14 and 56 DAI. The application of mineral fertilizer did not have any effect ($P < 0.05$) on urease activity at the initial stage of incubation but increased at the 56 DAI. At 42 DAI, application of 2.5 t ha^{-1} biochar + 5 t ha^{-1} manure recorded the highest urease activity (66.4 mg kg^{-1}) while No manure + 100 % RR NPK gave the highest urease activity (50.0 mg kg^{-1}) at 28 DAI. The combined application of biochar, manure and mineral fertilizer increased urease activity significantly ($P > 5$ %) at 42 DAI (Figures 4.7 and 4.8).

KNUST

Table 4.6. Effect of biochar, manure and mineral fertilizer on soil urease activity

Treatments	14DAI	28DAI	42 DAI	56 DAI
			kg ha^{-1}	
Biochar (B) application rate(t ha^{-1})				
0	18.7	53.5	23.9	23.9
2.5	24.1	47.2	25.7	26.9
5.0	23	46.9	22.4	20.9
F.Pr	0.304	0.351	< 0.001***	0.402
Lsd (0.05)	7.45	10.2	9.02	8.96
Manure (M) application rate (t ha^{-1})				
No Manure	22	49.8	21.6	17.5
5t ha-1	21.9	48.6	39.7	30.3
P value	0.978	0.768	< 0.001***	0.001**
Lsd	6.08	8.33	7.36	7.32
Mineral Fertlizer (MF)application rate				
(%RR)	19.2	45.5	22.8	13.9
50 % RR	20.4	46.9	33.9	32.5
100 % RR	26.3	55.2	35.3	25.2
P value	0.131	0.127	0.015	< 0.001***
Lsd	7.45	10.2	9.02	8.96
CV (%)	50.2	30.7	43.5	55.5
F. pr (B x M)	0.912	0.687	< 0.001***	0.009
F. pr(B x MF)	0.664	0.432	0.198	0.414
F. pr(M x MF)	0.318	0.071	0.001**	0.88
F. pr(B x M x MF)	0.978	0.66	0.039*	0.09

Values are means of three replicates. *, **, ***, means significant at 5 %, 1% and 0.1% probability level, respectively.ns= not significant. RR= Recommended Rate. DAI=Days afte r incubation

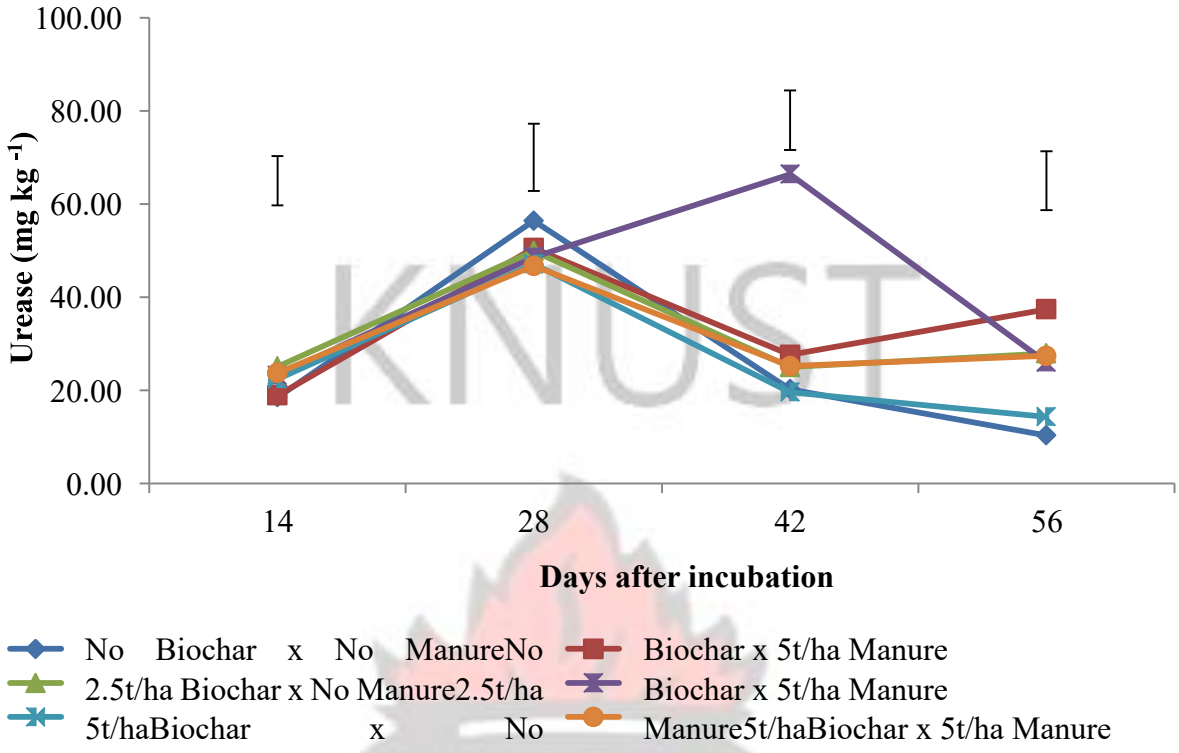


Figure 4. 7. Effect of biochar and manure on soil urease activity

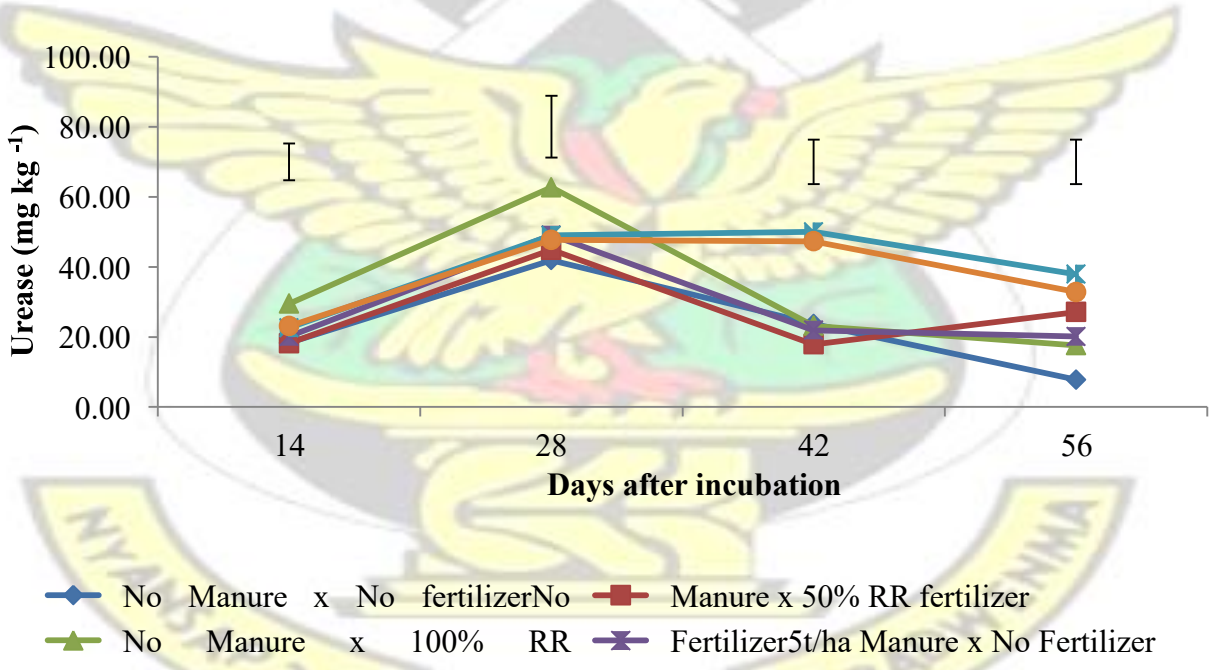


Figure 4. 8. Effect of manure and mineral fertilizer on soil urease activity

4.3.3. Effect of biochar, manure and mineral fertilizer on NH_4-N in the soil

Ammonium nitrogen content of the soil was significantly increased by biochar addition at the initial stage of incubation rather than the later stage (Table 4.9). Application of biohar at 5 t ha^{-}

^{1} significantly ($P < 0.001$) increased NH_4-N by 12 % over that of the control. No significant differences ($P > 0.05$) were observed among the treatments at 28, 42 and 56 DAI. Manure application recorded significance ($P < 0.001$) at 42 DAI with the control increasing NH_4-N by 110 % over 5 t ha^{-1} manure application. Significant variations were observed among the mineral fertilizer treatments during the incubation study (Table 4.7). The recommended rates of mineral fertilizer significantly increased soil NH_4-N over that of the control. The application of 100 % RR gave the highest NH_4-N at 14, 28 and 42 DAI relative to those of other treatments.

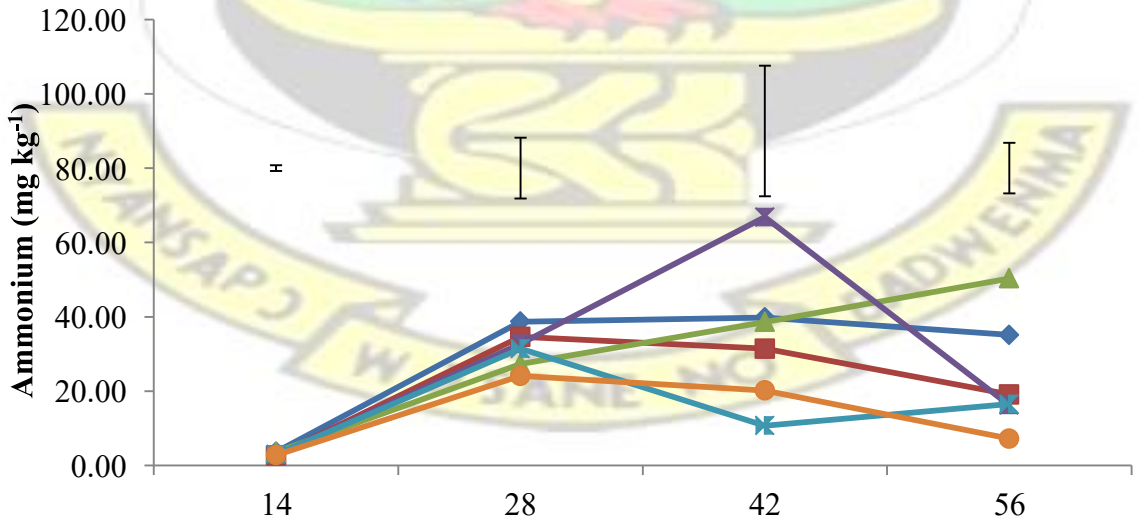
The combined effects of treatments had significant ($P < 0.001$) increase at the 56 DAI of incubation rather than the initial stages (Figures 4.9 and 4.11). The application of 2.5 t ha^{-1} biochar + 5 t ha^{-1} manure and 2.5 t ha^{-1} biochar + 50 % RR NPK increased NH_4-N relatively by 43.3 % and 225.9 % over the control at 56 DAI.

Table 4.7. Effect of Biochar, Manure and Mineral Fertilizer on soil NH_4-N

Treatments	14DAI	28DAI	42 DAI	56 DAI
		NH_4-N (mg kg^{-1})		
Biochar application rate (t ha^{-1})				
0	3.15	36.60	35.60	27.40
2.5 3.20 30.60 52.70 48.20 5.0 2.87 27.80 15.40 11.90 F. pr 0.796 0.282 0.016* 0.001**				
Lsd (0.05)	1.05	11.56	24.84	18.61

Manure application rate (t ha^{-1})				
0	3.42	32.40	29.70	44.20
5	2.73	30.50	39.40	14.20
F. pr	0.012**	0.675	0.335	< 0.001***
Lsd (0.05)	0.857	9.44	20.28	15.2
Mineral fertilizer (MF) application rate (%RR)				
0 2.66 17.70 4.70 60.20 50 2.52 32.40 49.80 9.30				
100	4.04	44.3	49.30	17.90
F. pr	0.01*	< 0.001***	< 0.001***	< 0.001***
Lsd (0.05) 1.05 11.56 44.84 18.61 CV (%) 50.50 54.40 106.30 94.40 F pr (B x M) 0.706 0.516 0.338 0.001**				
F. pr(BxMF)	0.984	0.703	0.05	< 0.001***
F. pr M x MF	0.410	0.342	0.413	< 0.001***
F. pr(B xMxMF)	0.727	0.703	0.170	< 0.001***

Values are means of three replicates. *, **, ***, means significant at 5 %, 1% and 0.1% probability level respectively. RR= Recommended Rate. DAI =Days after incubation



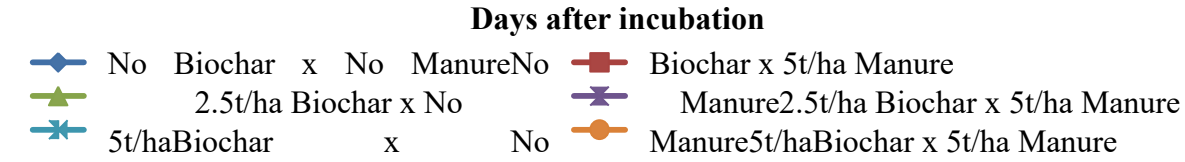


Figure 4. 9. Effect of biochar and manure on soil NH_4-N

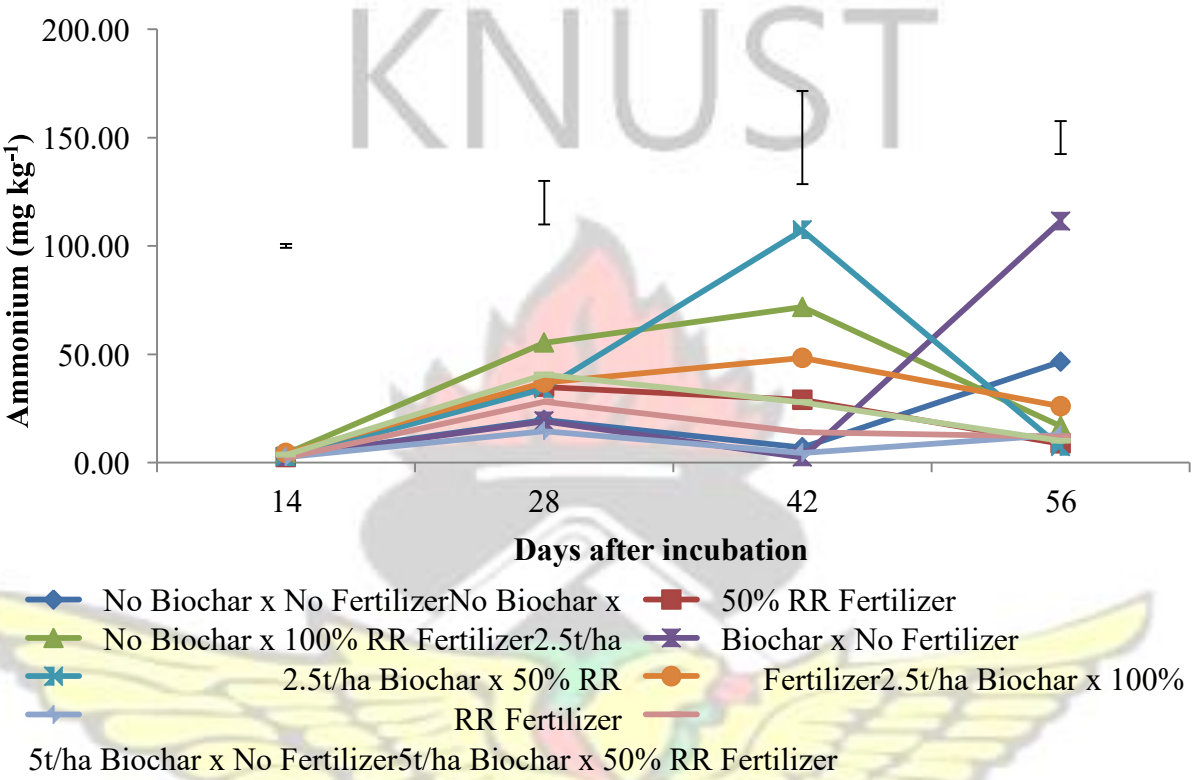


Figure 4. 10. Effect of biochar and mineral fertilizer on soil NH_4-N

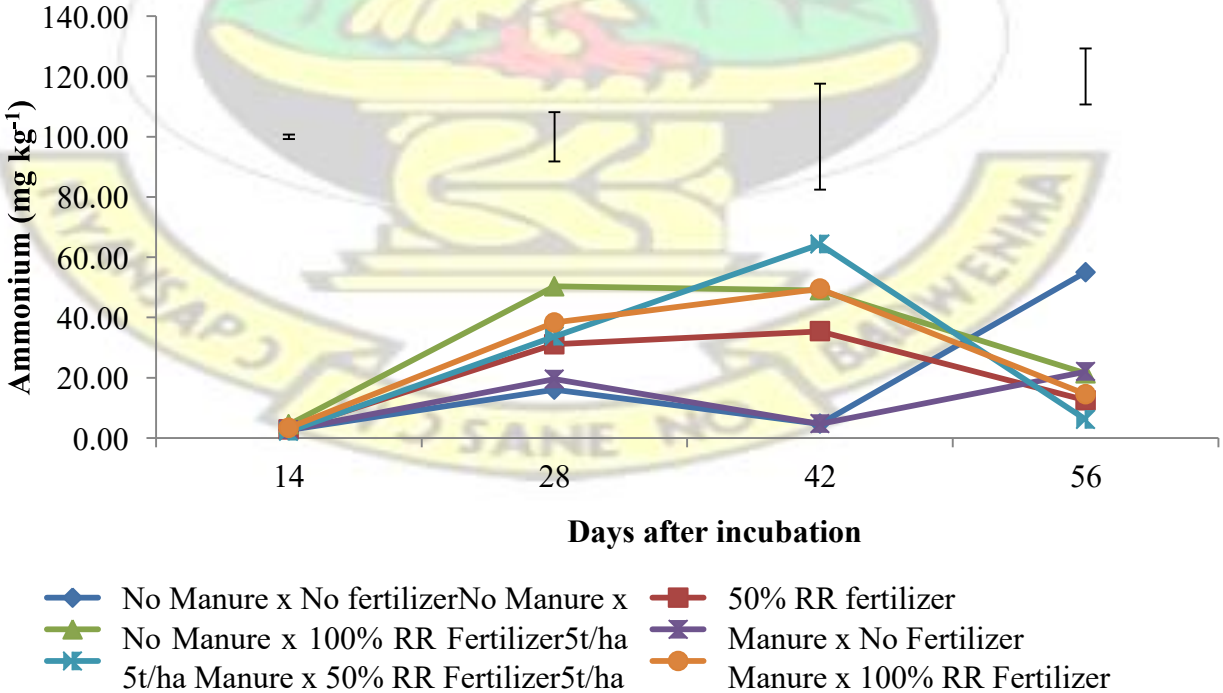


Figure 4. 11. Effect of manure and mineral fertilizer on soil NH_4-N

4.3.4. Effect of biochar, manure and mineral fertilizer on soil NO_3-N

At 14 DAI, 5 t ha^{-1} biochar significantly increased the NO_3-N content of the soil by 12 %. No significant ($P > 0.05$) difference was observed at 28, 42 and 56 days incubation period. There was no significant ($P > 0.05$) increase in the NO_3-N in the soil with manure application but a significant decrease was observed to occur at 42 DAI following manure application (Table 4.8). Mineral fertilizer had a significant ($P < 0.001$) increase on soil NO_3-N content at 14, 42 and 56 DAI. The application of 50 and 100 % RR significantly increased NO_3-N by 36 and 52 % at 14 DAI and 118 and 229 % at 42 DAI, respectively.

No significant variations were observed at 14, 28 and 56 DAI for the combined effect of biochar and manure on NO_3-N (Figure 4.12). Similarly, the combined effect of manure and mineral fertilizer were significant ($P < 0.001$) at 42 DAI. At 42 DAI, 0 t ha^{-1} manure + 100 % RR NPK increased NO_3-N by over 500 % in relation to the control (Figure 4.13).

Table 4. 8. Effect of biochar, manure and mineral fertilizer on soil NO_3-N

Treatments	14DAI	28DAI	42 DAI	56 DAI
	mg kg^{-1}			
Biochar (B) application rate (t ha^{-1})				
0	34.5	28.5	15.5	24.19
2.5	31.7	30.9	7.5	22.44
5.0	38.7	48	15.2	20.91
F. pr	0.036*	0.313	0.085	0.394
Lsd (0.05)	5.27	27.77	7.99	4.801
Manure (M) application rate (t ha-1)				

0	34.8	33.2	17.3	21.3
5	35.2	38.5	8.2	23.99
F. pr	0.867	0.64	0.007**	0.134
Lsd (0.05)	4.3	22.67	6.53	3.92
Mineral fertilizer (MF) application (%RR)				
0	27	36.1	5.9	3.4
50	36.8	35.3	12.9	23.31
100	41.1	36.1	19.4	3883
F. pr	< 0.001***	0.998	0.006**	< 0.001***
Lsd (0.05)	5.27	27.77	7.99	4.801
CV (%)	22.3	114.7	92.7	31.5
F pr (B x M)	0.495	0.827	0.029*	0.083
F. pr (B x MF)	0.658	0.71	0.601	0.476
F. pr(M x MF)	0.213	0.165	0.029	0.697
F. pr B x M x MF	0.108	0.516	0.337	0.104

Values are means of three replicates. *, **, ***, means significant at 5%, 1% and 0.1% probability level, respectively. RR= Recommended Rate. DAI=Days after incubation

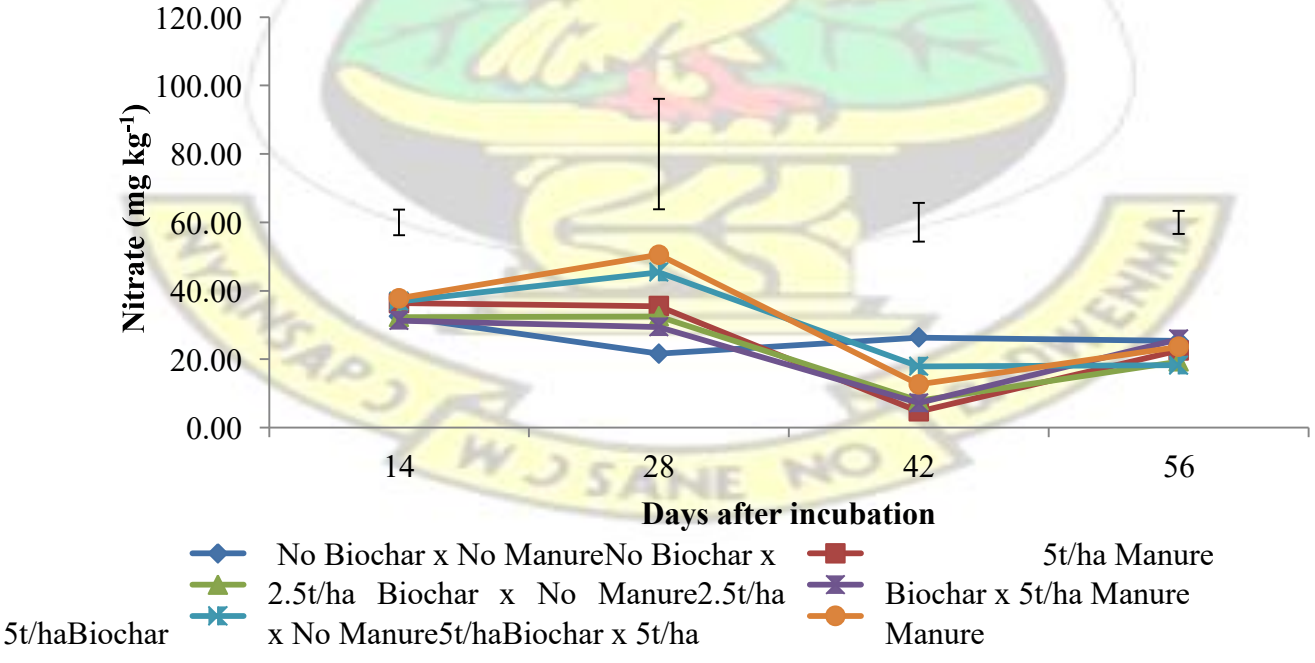


Figure 4. 12. Effect of biochar and manure on soil NO_3-N

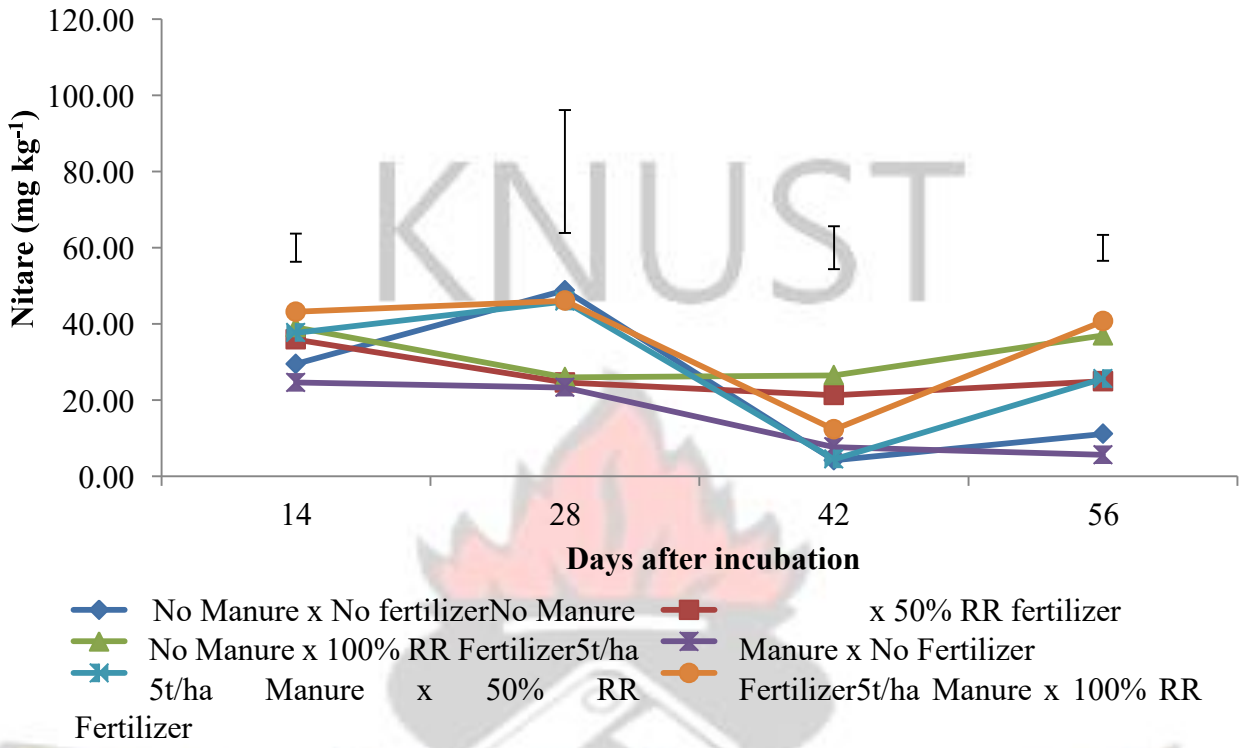


Figure 4. 13. Effect of manure and mineral fertilizer on soil NO_3-N

CHAPTER FIVE

5.0 DISCUSSION 5.1 Study 1: Contribution of biochar, manure and mineral fertilizer to maize growth and yield

5. 1.1 Effect of biochar, manure and mineral fertilizer on plant height

Plant height apart from being a genetic trait, is a reflection of nutrient availability and favourable weather conditions. The observed significant variation in maize plant height could be due to the effect of the amendments. Biochar has previously been shown to increase crop productivity by improving the physical and biochemical properties of the soil (Asai*et al.,* 2009). However, the magnitude of response would depend on the chemical and physical properties of the biochar, soil conditions, climatic conditions and the type of crop (Zwieten*et al.,* 2010; Yamato *et al.,* 2006). The results of this study indicated that the application of biochar

at 2.5 and 5 t ha^{-1} alone did not significantly increase plant height, confirming the findings of Major *et al*. (2010) that plant height was not affected by biochar addition. This phenomenon could be attributed to the low nutrient content of the biochar material as well as the low rate of biochar applied to the soil which is a sandy soil as compared to other studies where the use of biochar affected plant height. Uzoma *et al. (*2011) observed a maximum increase in plant growth with biochar at 15 t ha^{-1}. Other reasons for the non significant effect of biochar on plant growth could be attributed to the direct phytotoxicity of volatile fractions or the negative impacts of metals and N immobilization after biochar (Bruun *et al*., 2011), which could lead to decreased growth.

Manure applied at 5 t ha^{-1} and mineral fertilizer at 50 % RR and 100 % RR improved plant growth by increasing plant height, especially at 6 and 8 weeks after planting (Table 4.1), compared to biochar application only and the control. This was similar to the findings of Akinrinde *et al.* (2004), that both cattle manure and inorganic fertilizers produced taller plant at 25 mg kg^{-1} and 50 mg kg^{-1} soil while working on Nigerian Alfisols. This increase in plant height could be attributed to positive effect of N on vigorous vegetative growth (Khan *et al*., 2008) as well as improved nutrient synchrony. The fact that optimal fertilizer treatment gave the highest height is an indication that nutrient supply is directly correlated to growth.

5.1.2. Effect of biochar, manure and mineral fertilizer on shoot biomass, grain yield and nitrogen use efficiency

Grain yield is the end result of morphological and physiological processes occurring during growth and development of a crop. Biochar often enhances crop growth in poor soils, but exhibits either no effect or a slight negative effect in fertile soils (Asai *et al*., 2009; Haefele *et al.,* 2011; Uzoma *et al*., 2011). However, no significant effect of biochar application was observed on maize biomass and grain yield. This is however, contrary to the findings of Asai

et al. (2009) where biochar enhanced upland rice yield at sites with low P availability. Biochar applied at 2.5 t ha^{-1} produced a higher yield compared to biochar application at 5 t ha^{-1}. This is similar to the findings of Asai *et al.* (2009) who reported a decreased grain yield following application of a biochar amendment without N fertilization in a soil that had poor N availability. Uzoma *et al.* (2011) also observed that the highest corn yield was obtained at a biochar application rate of 15 t ha^{-1}, and the yield increases were attributed to greater P availability. In contrast, findings from this study were similar to that of Blackwell *et al.* (2010) were increasing application rate of biochar had no effect on grain yield of wheat and even led to negative effect when applied at 10 t ha^{-1} rate.

Lower yields from biochar field could have been caused by the very low available P and SOM content of this site (Table 4.2). Asai *et al.* (2009) reported that a single biochar application (4 t ha^{-1}) resulted in a decreased grain yield or no change in yield. This may be due to the biochar induced reduction of plant N uptake through immobilization process.

However, from this study, application of biochar at 5 t ha^{-1} increased the yield of crop compared to the control, one of the reasons for the observed increase in crop yield with biochar application is the increases in N utilization (Steiner *et al.*, 2007; Widowati *et al.*, 2011). Perhaps as a result of the increase in soil CEC with biochar application (Chan *et al.*, 2008; Masulili *et al.*, 2010) and the attendant reduction in N losses.Vaccari *et al.* (2011) found as much as 40 % increase in crop yield of durum wheat (*Triticum durum* L.) after high biochar amendments (30-60-30 t ha^{-1} NPK) was made to Mediterranean soils.

The biochar amended soils did not significantly increase shoot biomass.The result presented in Table 4.3 shows that the soil treated with biocharat 2.5 t ha^{-1} produced shoot biomass of between 2.1 t ha^{-1} and 2.3 t ha^{-1}. Manure application significantly increased biomass yield as compared to the control, this was similar to the findings of Akinrinde *et al.* (2004).

Nitrogen fertilization has been reported to increase grain yield (43 – 68 %) and biomass (25 - 42 %) in maize, it contributes 18-34 % increase in soil residual N (Yang *et al*., 2007). The higher maize grain yields obtained from mineral fertilizer at 30 kg N ha^{-1} and 60 kg N ha^{-1} could be attributed to nutrients being readily available from the mineral fertilizers as compared to nutrients from manure which must undergo mineralization before becoming available for crop uptake. The split application of mineral N could have also resulted to minimal leaching losses and better synchrony between nutrient availability and crop demand.

Kimani *et al*. (2004) suggested that split N application should be implemented so as to increase plant N uptake and decrease potential for N losses. The lower yield obtained from fertilizer at 60 kg ha^{-1} N in comparison to the 30 kg ha^{-1} N was probably due to the cropping history of the site, the site has been used for an experiment in the last cropping season for maize production before the current research, therefore there could be residual effect of nutrients on the field, this could have also affected all the treatment on the field. The increase in grain yield due to cattle manure and optimal fertilizer treatments was mainly due to high number of cobs per plant and improved grain filling due to adequate nutrient supply. Use of poultry manure at 100 kg ha^{-1} N and 100 kg ha^{-1}N as urea gave maximum grain yields (Tasneem*et al*., 2004). Biochar was found to decrease the nitrogen use efficiency of the maize. Possible mechanisms for the biochar induced decreases in NUE include retention of N by biochar, inhibition of plant development by increased pH, volatilization of NH_3, and losses of other N gases as a result ofdenitrification (Liang *et al.,* 2006; Steiner *et al*., 2008; DeLuca *et al.,* 2009). Another reason for a biochar-induced decrease of NUE might be an inhibitory effect of biochar on early plant development as observed by Zhang *et al.* (2010). These findings were similar to the assertion of Deenik *et al.* (2011) that a temporary decrease in plant growth was due to the high contents of volatile matter in one of the biochars they tested. The volatile matter was bioavailable and likely caused N immobilization which would have decreased NUE. However, mineral fertilizer

application increased NUE of maize crop significantly. This is however, contrary to the findings of Partey *et al.* (2013) that a lower NUE in sole inorganic fertilizer or green manure treatments than mixed treatments. The NUE was greater when lower quantities of N fertilizers were applied and decreased with increasing fertilizer N quantities (Table 4.2).

5.1.3. Main influence of biochar, manure and mineral fertilizer on nutrient uptake

Nutrient uptake was not significantly increased with increasing rates of biochar applications. This finding is however contrary to that of Yeboah *et al.* (2009). These results indicated that biochar applied at 5 t ha $^{-1}$ decreased plant N uptake and confirms the results of Lehmann *et al.* (2002) that a decrease in plant N uptake was due to the effect to N immobilization caused by the high C/N ratio of the applied biochar. However, biochar application at 2.5 t ha $^{-1}$ increased phosphorus content of the biomass and soil. A possible explanation is that biochar increased plant available P due the amount of P present in the biochar material. A similar effect of biochar on P availability was reported in previous studies (Lehmann *et al.,* 2002; Glaser *et al.,* 2002; Yamato *et al.,* 2006).

Manure applied at 5 t ha $^{-1}$ increased N and P uptake in biomass, this can be attributed to nutrient availability from the mineralized organi material. Nutrient concentration in shoot and grain of plant supplied with mineral fertilizer amendments showed that increasing doses of mineral fertilizer decreased shoot and grain nutrient concentration due to a dilution effect since the mineral fertilization application led to a greater dry matter plant production and significantly increasing nutrient uptake at at 50 % RR and 100 % RR respectively. Increased P uptake was observed with biochar and mineral fertilizer this is as a result of biochar acting as a P source.

5.1.4. Main effect of biochar, manure and mineral fertilizer on soil organic carbon, organic matter, total N and available P

The results in Table 4.4 show that soil organic-C in biochar, manure and mineral fertilizer treated soils were not significantly different. The application of different rates of biochar had

no significant effect on SOC content (Table.4.4). Although there was a slight increase in the SOC content of the soil following the application of various soil amendments, they were not significantly different. Biochar applied at 2.5 t ha $^{-1}$ did not significantly increase the organic carbon content of the soil.This is however contrary to the observations of Lehmann *et al.* (2003) and Chan *et al*. (2008) who observed a remarkable increase in organic carbon and organic matter content of the soil after the application of biochar and attributed it to the fact that biochar is a recalcitrant organic material. Glaser *et al.* (2002) and Golchin *et al.* (1994) reported that the mechanism for SOM stabilization and higher stability of C in the Terra Preta soils was found due to chemical inertness and the interaction of carbon compounds with clay minerals. Previous studies also confirmed that under the wet conditions of the tropics, organic C from cattle manure decomposed almost completely within one season (Diels *et al.,* 2004). Hence this could be a major factor affecting the organic carbon and matter content with manure application. Although a decrease in soil organic C, could be partly due to downward movement by percolating water, the drop in soil organic C observed is presumably due to decomposition (Cheng *et al.,* 2006). On average, the organic carbon was higher in soils receiving organic amendments or a combination of mineral fertilizers with organic amendments compared to soils receiving mineral fertilizers alone. This was because whereas the organic material had a major impact on mineralization rate by increasing soil C directly, the effect of mineral N fertilizer was less pronounced since it increased C only indirectly by improving plant growth (Jama *et al.,* 2000). Differences in soil organic matter (SOM) between treatments were not significant; value in the control treatment was at par with values in most of the treatments. The effect of biochar, manure and mineral fertilizer on accumulation of SOM was generally inconsistent.

The application of the various soil amendments did not significantly affect the nitrogen and phosphorus concentration in the soil. In this study, biochar amendment had no significant influence on soil available P and disagreed with the findings of Lehmann*et al*. (2003) and

Glaser*et al*. (2002) who found increased plant-available P concentrations after biochar addition. Total N was highest in all treatments that received organic residues in comparison to sole mineral N treatments. This could be attributed to the fact that the organics underwent microbial decomposition to furnish the soil with plant nutrients unlike the mineral N fertilizers which were applied in plant available form with subsequent losses through leaching and denitrification very early in the season. Mineral-fertilizer application also lead to low nitrogen content in the soil partly as a result of leaching of N during the growth period after application. These results suggested that biochar, mineral fertilizer and manure had no considerable influence on accumulation of soil nitrogen.

5.2 Combined effects of biochar, mineral fertilizer and manure on soil pH,NH_4-N, $N0_3$-N and urease activity

The pH of the soils ranged from 4.8 to 6.22 indicating that these soils were slightly acidic**.** The application of the different soil amendment significantly affected the pH of the soil, however no significant difference with biochar until the third week of incubation despite the gradual increase in soil pH. The liming effect of biochar on soils has been largely reported (Sohi *et al.,* 2010) and consistent with the results of this research. The liming effect has been discussed in the literature as one of the most likely mechanisms behind increases in plant productivity after biochar applications (Vanlauwe *et al.,* 2002). This however is in line with the findings of Partey *et al.,* 2013 who also reported a significant increase in soil pH with the application of biochar

The application of biochar at 2.5 t ha^{-1} and 5 t ha^{-1} significantly increased the soil pH at 14 DAI, 28 DAI and 42 DAI, this could be as attributed to the ash carbon accretion as ash are generally dominated by carbonates of alkali and alkaline earth metal, variable amounts of silica, heavy metals, sequioxides, phosphates and small amount of organic and inorganic N (Raison, 1979). Khanna *et al*. (2004) also reported the capacity of ashes to neutralize acidic soils. The high

surface area and porous nature of biochar which increases the cation exchange capacity of soils is another factor responsible for observed initial increase in soil pH.

However, a decrease in soil pH was observed with Biochar application at 2.5 t ha^{-1} at 28 DAI and 5 t ha^{-1} at 56 DAI, the driving force behind a pH decrease is oxidation of Cto form acidic carboxyl groups (Cheng *et al*., 2006), whereas the increase in pH is likely related to the dissolution of alkaline minerals.

The increment of soil pH with additions of manure could be attributed to the reduction of exchangeable aluminium in the acidic soils. This reduction is considered to occur through aluminium precipitation or chelation of organic colloids (Hue *et al.,* 1992). Manure application at 5 t ha^{-1} increased soil pH significantly through the incubation study except at 42 DAI, this could also be attributed to increased levels of exchangeable bases (K, Mg and Ca).

The significant increase in pH with manure application corresponds with the findings by (Mugendi *et al.,* 2010). Increasing the pH of acidic soils improves plant-availability of macro-nutrients while reducing the solubility of elements such as Al and Mn (Mucheru *et al.,* 2007). The magnitude of the rise in soil pH varies depending on the type of manure, its rate of application and the buffering capacity of the soil (Haynes *et al.,* 2001). Nzigubeba *et al.* (1998) noted that manures have the advantage of supplying essential plant elements either directly or indirectly by alleviating aluminium toxicity or producing organic acids thereby increasing nutrient availability. The results show that mineral fertilizer treatments have significant effects on soil properties. During the study, a significant decrease in soil pH was detected due to fertilization (Table 4.5). The mineral fertilizer addition at 50 % RR and 100 % RR led to a consistent decrease in soil pH. The decrease in pH of the surface layer in the fertilizer might be attributed to the nitrification and acidification processes stimulated by application of fertilizers (Liang *et al.,* 2012). Where N fertilizer was applied, the pH slightly decreased with respect to the initial value. Results from the study were in agreement with the findings of

Tsadilas *et al*. (2005), who reported that the application of ammonium fertilizer significantly decreased soil pH more than the nitrate treatments. Results from a pot fertilizer experiment by Liu *et al.* (2007) showed that application of NH_4Cl lowered soil pH from 4.51 to 4.07. The major mechanism of soil acidification by N fertilization is related to hydrogen ion release through nitrification of and subsequent leaching of NO_3. The most important acid forming reaction by fertilizers is microbial oxidation of ammoniacal fertilizers (Barak *et al.,* 1997). However, a significan increase was observed with the combined application of biochar and manure at 5 t ha^{-1} and 5 t ha^{-1} 28 and 42 DAI was attributed to the liming effect of biochar.

One of the objectives of this research was to determine if the effect of soil amendments on soil enzyme activity in such a way that would help explain how they could impact soil functions. It was difficult to understand the inconsistent effects of biochar on soil urease activity, as these responses vary in direction and magnitude. In this study, when biochar was applied at 2.5 t ha^{-1} and 5 t ha^{-1} to the soil of the urease activities increased after 14 days. This could be due to either stimulation of the microbial activity by the biochar or growth of biomass in response to initially labile biochar-C. Decreased activities may be due to sorption or blocking of either enzyme or substrate. Biochars behave differently in soils depending on the biochar source (Kuzyakov *et al.,* 2009), production method (Amonette *et al.,* 2009), and soil (Kolb *et al.,* 2009), one may see different adsorption behavior and biological activity due to widely varying pH, surface area, pore size distribution, and charge properties (Brewer *et al.,* 2009; Gaskin *et al.,* 2009).

Adding manure at 5 t ha^{-1} significantly increased the urease activity of the soil at 42 and 56 DAI. Soil microbial enzymes are mainly driven by metabolic processes and largely reflecting the level of biochemical reactions (Mandal *et al.,* 2007). Hence the increase in urease activity is attributed to ability of manure to increase soil organic matter by providing a rich source of

carbon and nutrients for enzyme production by microorganisms. This observation is however similar to the findings of Zhang *et al.* (2010).

The application of mineral fertilizer had less influence on soil urease activity. In this work significant difference was observed with 100 % RR at 56 DAI. It is possible that the application of mineral fertilizer inhibited enzyme production in soil microorganism (Mandal *et al.,* 2007). Reduction in enzyme activity by mineral fertilizer application could be attributed to the acidifying effect of mineral fertilizers as shown by lower pH in the previous study.

The soil nitrogen mineralization dynamics was affected differently by each amendment (Table 4.9 and 4.10). Mainly, the addition of mineral fertilizer applied alone released the highest amount of NH_4-N in the soil. This might be due to minimum denitrification, volatilization and immobilization of NH_4^-N (Samuel *et al.,* 2003). Urea fertilizer also released the highest amount of NO_3 -N in the soil. This might be as a result of faster nitrification of NH_4^-N to NO_3^-N by nitrifying bacteria. Ayeni and Adeleye (2011) obtained similar result in the experiment conducted on rate of nutrient release as influenced by organic wastes. The increase in ammonium content with manure within the first 14 DAI after incubation could be attributed to the mineralization of organic matter in the manure.

Addition of biochar resulted in marked changes in the N (NH_4^+ - N and NO_3^-N) content of soil. However, NO_3^- N content of the soil was found to be decreased with biochar application. Although there was significant effect of $N0_3$ with biochar at 2.5 t ha^{-1} and 5 t ha^{-1}, this could be attributed to the fact that some amount of decomposition might have occured when fresh biochar was added to soil (Liang *et al.*, 2006), which could induce net immobilization of inorganic N already present in the soil solution. Gundale and DeLuca (2006) reported that the biochar addition to soil caused reduction in ammonification compared to the control due to adsorption and reduce the potential for NH_3 volatilization. The reduction might also be due to adsorption of NH_4^+ onto biochar particles. Lehmann *et al.* (2006) have suggested that biochar

can adsorb both NH_4^+ and NH_3^- from the soil solution thus reducing solution inorganic N at least temporarily, but perhaps concentrating it for microbial use. This result is however similar to the findings of other researches in previous studies who have reported a decrease in N mineralization and increase in N immobilization with the addition of biochar to soil (Novak *et al.*, 2010; Dempster *et al.*, 2012), especially when the biochar contains a large volatile C content (Deenik *et al.*, 2010).

KNUST

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusion

Results from the field experiment showed that integrated use of biochar, cattle manure and mineral fertilizer did not improve the growth and yield of maize.

However, the use of mineral fertilizer at 60:40:40 kg ha^{-1} and 30:20:20 kg ha^{-1} significantly increased the plant height, nutrient uptake and nitrogen use efficiency and yield of maize compared to sole biochar and manure treatment.

The final soil and soil organic carbon analysis after harvest indicated that biochar application at 5 t ha^{-1} and 2.5 t ha^{-1} increased soil organic by 48, carbon and total N by 37 % respectively and also P uptake in plant.

The applications of 30:20:20 $kgha^{-1}$ NPK and 5 t ha^{-1}Manure + 30:20:20 kg ha^{-1} NPK was the most economically viable imputs (VCR = 2) among all treatments while 5 t ha^{-1} biochar + 60:40:40 kg ha^{-1} NPK was the least economical (VCR < 2).

The application of rice husk biochar inhibits soil N mineralization by changing soil physicochemical properties, such as soil pH, and urease activitues. The sole application of manure at 5 t ha^{-1} increased the pH from 5.4 to 6.34 at 42 days after incubation while urease activity was highest with 2.5 t ha^{-1} biochar and 5 t ha^{-1} manure at 42 days after incubation.

For the whole incubation period, NO_3^-N was significantly increased by the sole application of 60:40:40 kg ha^{-1} at 42 days after incubation while the sole application of biochar at 2.5 t ha^{-1} gave the highest NH_4-N at 56 days after incubation.

6.2. Recommendation

There is the need for further study of specific mechanisms by which biochar addition influences the soil physicochemical properties. Extensive research based on agro-ecological zone evaluation of biochar should be carried out to ascertain its effectiveness on maize productivity.

KNUST

REFERENCES

Adeleye, E. O. and Ayeni L. S. (2010). Effect of cocoa pod ash and poultry manure combinations on soil and plant nutrient contents and performance of maize – screenhouse experiment. Researcher 2 (3): 75 - 80

Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D. and Ok, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere, 99*, 19 33.http://dx.doi.org/10.1016/j.chemosphere.2013.10.071

Ahmad, S., Li, C., Dai, G., Zhan, M., Wang, J., Pan, S. and Cao, C. (2009). Greenhouse gas emission from direct seeding paddy field under different rice tillage systems in central China. Soil Till. Res. 106, 54 - 61.

Akinrinde, E. A., Olubakin, O. A., Omotoso, S. O. and Ahmed, A. A. (2006). Influence of zinc fertilizer, poultry manure and application levels on the performance of sweet corn. Agric. J., 1: 96 - 103.

Akinrinde, E. A., Onanuga, O. A., Bello, O. S. and Obigbesan, G. O. (2004). Efficiency of indigenous ground phosphate rocks, organic fertilizers and their mixtures for maize performance in two Nigerian Alfisols. Moor Journal of Agricultural Research, Vol. 4, No. 1.

Alburquerque, J.A, Salazar, P., Barron, V, Torrent, J., delcarmen del campillo, M., Gallardo A. and Villar, R. (2013). Enhanced wheat yield by biochar application under different fertilization levels. Agronomy for sustainabledevelopment. Vol.33. pp. 475 - 484.

Amonette, J. E., Hu, Y., Schlekewey, N., Dai, S., Shaff, Z. W., Russell, C. K., Burton, S. D. and Arey, B. W. (2009). Biochars are Not Created Equal: a Survey of Their Physical, Structural, and Chemical Properties and Implications for Soil Application, North American Biochar Conference, Boulder, CO.

Asai, H, Samson, K. B., Stephan, M. H., Songyikhangsuthor, K., Homma, K. and Kiyono Y. (2009). Biochar amendment techniques for upland rice production in Northern Laos 1. Soil physical properties, leaf SPAD and grain yield. Field Crops Res 111:81 - 84.

Atkinson, C. J., Fitzgerald, J. D., Hipps, N. A. (2010). Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: A review. Plant Soil 337:1 - 18.

Ayeni, L. S. (2012). Combined effect of cattle dung and urea fertilizer on organic carbon, forms of Nitrogen and available Phosphorus in elected Nigerian soils. Journal of Central European Agriculture. 13 (3). Pp. 601- 607.doi 10.5513/JCEA01/13.3 1098.

Ayeni, L. S. (2010). Effect of cocoa pod ash, NPK Fertilizer and their combinations on soil chemical properties and yield of tomato (*lycopersicum lycopersicon*) on two soil types. New York Science Journal 3 (4): 1 - 11.

Ayeni, L. S. (2010). Effect of Combined Cocoa Pod Ash and NPK Fertilizer on Soil Properties, Nutrient Uptake and Yield of Maize (*Zea mays*). *Journal of American Science 6 (3): 79 - 84,* ISSN 1545 - 1003.

Baligar, V. C. and Bennett, O. L. (1986). Outlook on fertilizer use efficiency in the tropics. Fertil Res 10:83 - 96.

Barak, P., Jobe, B. O., Krueger, A. R., Peterson, L. A. and Laird, D. A. (1997). Effects of long-term soil acidification due to nitrogen fertilizer inputs in Wisconsin, Plant Soil, 197, 61 - 69.

Bekunda, M., Gallooway, J., Syers, K and Scholes, M. (2007). Background, Current status and context the African Context of the International Nitrogen Initiative: In; Batiano (Eds). Advances in

integrated soil fertility Management in sub-Sahara Africa: Challenges and opportunities. Pp 115 -119.

Belanger, N. I., Cote, B., Fyles, J. W., Chourchesne, F. and Hendershot, W. H. (2004). Forest regrowth as the controlling factor of soil nutrient availability 75 years after fire in a deciduous forest of southern Quebec, *Plant Soil,* 262, 363 - 372.

Belyaeva, O. N. and Haynes, R. J. (2012). Comparison of the effects of conventional organic amendments and biochar on the chemical, physical and microbial properties of coal fly ash as a plant growth medium.*Environmental Earth Sciences, 66*(7), 1987-1997. http://dx.doi.org/10.1007/s12665-011-1424-y.

Berglund, O. and Berglund, K. (2011). Influence of water table level and soil properties on emissions of greenhouse gases from cultivated peat soil. *Soil Biol. Biochem.*, *43*, 92 - 931.

Blackwell, P., Riethmuller G. and Collins M. (2009). Biochar Application to Soil (Chapter 12), in: J. Lehmann and S. Joseph (Eds.), Biochar for Environmental Management: Science and Technology, Earthscan, London, UK. Pp. 207.

Blackwell, P., Shea, S., Storer, P., Kerkmans, M. And Stanley, I. (2007). Improving wheat production with deep banded oil mallee charcoal in Western Australia. Talk given at the International Agrichar Conference, April 27-May 2, 2007, Terrigal, NSW Australia.

Blake, G. R. and Hartge, K. H. (1986). Bulk density. In: Klute, a (ed.) Methods of soil analysis, Part 1, Physical and Mineralogical methods.Agronomy monograph 9, 2nd edn. Maidson Wiscousin, USA: American Society of Agronomy, Soil scienceof America. Pp. 363 - 375.

Bol, R., Amelung, W., Friedrich, C. and Ostle, N. (2000). Tracing dung-derived carbon in temperate grassland using 13C natural abundance measurements. Soil Biol Biochem 32:1337 - 1343.

Brady, N. C. and Weil, R. R. (1984). *The Nature and Properties of Soils*; Macmillan: New York, NY,USA.

Braida, W. J., Pignatello, J. J., Lu Y., Ravikovitch, P. I., Neimark, A.V. and Xing, B. (2003). Sorption hysteresis of benzene in charcoal particles. Environ. Sci. Technol. 37:409 - 417.

Brewer, C. E., Schmidt-Rohr, K., Satrio, J. A. and Brown, R. C. (2009). Characterization of biochar from fast pyrolysis and gasification systems. Environmental Progress & Sustainable Energy 28, 386 - 396.

Bridgwater, A. and Boocock, D. G. B. (2006). _Science in thermal and chemicalbiomass conversion.‘ (CPL Press: Newbury, UK).

Bruun, E. W., Ambus, P., Egsgaard, H. and Hauggaard-Nielsen, H. (2012). Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. *Soil Biol. Biochem.46*, 73 - 79.

Busscher, W. J, Novak, J. M., Evans, D. E., Watts, D. W., Niandou, M. A. S. and Ahmedna, M. (2010). Influence of pecan biochar on physical properties of a norfolk loamy sand. Soil Sci. 175:10 - 14.

Busscher, W. J., Novak, J. M. and Ahmedna, M. (2011). Physical effects of organic matter amendment of asoutheastern us coastal loamy sand. Soil Sci. 176:661 - 667.

Busscher, W. J., Novak, J. M. And Ahmedna, M. (2011). Physical effects of organic matter amendment of a southeastern us coastal loamy sand. *Soil Sci.*, *176*, 661 - 667.

Busscher, W. J., Novak, J. M., Evans, D. E., Watts, D. W., Niandou, M. A. S. And Ahmedna, M. (2010). Influence of pecan biochar on physical properties of a norfolk loamy sand. *Soil Sci.175*, 10 - 14.

Castaldi, S., Riondino, M., Baronti, S., Esposito, F. R.., Marzaioli, R., Rutigliano, F.A., Vaccari, F. P. and Miglietta, F. (2011). Impact of biochar application to a mediterranean wheat crop on soilmicrobial activity and greenhouse gas fluxes. *Chemosphere* 2011, *85*, 1464 - 1471.

Chan, K. Y, Xu, Z. (2009). Biochar: nutrient properties and their enhancement. In: Biochar for environmental management (J. Lehmann and S. Joseph eds.), Science and Technology, Earthscan, London. Pp. 67 - 84.

Chan, K. Y., Van Zwieten, L., Meszaros, I., Downie, A. and Joseph, S. (2007). Assessing the agronomic values of contrasting char materials on an Australian hard setting soil. Paper presented in International Agrichar Initiative (IAI) 2007 Conference, 27 April–2 May 2007, Terrigal, New South Wales, Australia.

Chan, K. Y., Zwieten, V. L., Meszaros, I., Dowine, A. and Joseph, S. (2008) Using poultry litter biochars as soil amendments. Aust J Soil Res 46:437 - 444.

Chen, H. X., Du, Z. L., Guo, W. And Zhang, Q. Z. (2011). Effects of biochar amendment on cropland soil bulk density, cation exchange capacity, and particulate organic matter content in the North Chinaplain. Yingyong Shengtai Xuebao. 22:2930 - 2934.

Cheng, C. H. And Lehmann, J. (2009). Ageing of black carbon along a temperature gradient. *Chemosphere*, *75*, 1021 - 1027.

Cheng, C. H., Lehmann J. and Engelhard, M. H. (2008). Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence, *Geochimica etCosmochimica Acta*, l72, 1598 - 1610.

Cheng, C. H., Lehmann, J., Engelhard, M. H. (2008). Natural oxidation of black carbon in soils: Changesin molecular form and surface charge along a climosequence. *Geochimica Et Cosmochimica Acta 72*, 1598 - 1610.

Cheng, C. H., Lehmann, J., Thies, J., Burton, S. D., Engelhard, M. H. (2006). Oxidation of black carbonby biotic and abiotic processes. *Org. Geochem.*, *37*, 1477–1488.

Cheng, K., Pan, G., Pete, S., Luo, T., Li, L. Q, Zheng, J.W., Zhang, X. H., Han, X. J., Yan, M. (2011). Carbon footprint of China‘s crop production - An estimation using agro-statistics data over 1993 - 2007. Agric Ecosyst Environ. doi:10.1016/j.agee.2011.05.012.

Chidumayo, E. N. (1994). Effects of wood carbonization on soil and initial development of seedlings inmiombo woodland, zambia. *For. Ecol. Manag.* 1994, *70*, 353 - 357.

Chmidt M. W. I., Skjemstad, J. O. and Jager C. (2002). Carbon isotope geochemistry and nanomorphology of soil black carbon: Black chernozemic soils in central Europe originate from ancient biomass burning, Global Biogeochemical Cycles 16:1123, doi: 10.1029/2002GB001939.

Clough, T. J., Bertram, J. E., Ray, J. L., Condron, L. M., O‘Callaghan, M., Sherlock, R. R., Wells, N. S. (2010). Unweathered wood biochar impact on nitrous oxide emissions from a bovineurine-amended pasture soil. Soil Science Society of America Journal 74, 852e860.

Czimczik, C. I. and Masiello, C. A. (2007). Controls on black carbon storage in soils. Glob Biogeochem Cycl 21:GB3005.

Czimczik, C. I., Preston, C. M., Schmidt, M. W. I., Werner, R. A., Schulze, E. D (2002). Effects of charringon mass, organic carbon, and stable carbon isotope composition of wood. *Org. Geochem. 33*, 1207 - 1223.

Deenik, J. L., McClellan, T., Uehara, G., Antal, N. J. and Campbell, S. (2010). Charcoal volatile matter content influences plant growth and soil nitrogen transformations. Soil Science Society of America Journal 74, 1259e1270.

DeLuca, T. H. and Aplet, G. H. (2007). Charcoal and carbon storage in forest soils of the Rocky Mountain West, *Frontiers in Ecology and the Environment*, 6, 1 – 7.

DeLuca, T. H., MacKenzie, M. D. and Gundale, M. J. (2009). Biochar effects on soil nutrient transformations. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management: Science and Technology. Earthscan, London, pp. 251e270.

DeLuca, T. H., MacKenzie, M. D., Gundale, M. J. and Holben, W. E. (2006). Wildfire-produced charcoal directly influences nitrogen cycling in forest ecosystems. Soil Sci. Soc. Am. J. 70:448 - 453.

Dempster, D. N., Gleeson, D. B., Solaiman, Z. M., Jones, D. L. And Murphy, D. V. (2012). Decreased soil microbial biomass and nitrogen mineralisation with eucalyptus biochar addition to a coarse textured soil. *Plant Soil*, *354*, 311–324.

Di Blasi, C., Signorelli, G., Di Russo, C. and Rea, G. (1999). Product distribution from pyrolysis of woodand agricultural residues. *Ind. Eng. Chem. Res.38*, 2216 - 2224.

Diels, J., Vanlauwe, B., Van der Meersh, M. K., Sanginga, N. and Merck R. J. (2004). Long-term soil organic carbon dynamics in a sub humid tropical climate: 13C data and modeling with ROTHC. Soil Biol. Biochem., 36: 1739 - 1750.

Downie, A., Crosky, A. and Munroe, P. (2009). Physical properties of biochar. In: Biochar for Environmental Management: Science and Technology (Eds. Lehmann, J. & Joseph, S.), Earthscan.

Dugan, E., Verhoef, A., Robinson, S. and Sohi, S. (2010). Bio-char from sawdust, maize stover and charcoal: Impact on water holding capacities (WHC) of three soils from Ghana. In: 19th World Congress of Soil Science, Soil Solutions for a Changing World 11 , Brisbane, Australia, August 1 - 6, 2010 (Published on DVD).

Ezawa, T., Yamamoto, K. and Yoshida, S. (2002). Enhancement of the effectiveness ofindigenous arbuscular mycorrhizal fungi by inorganic soil amendments. Soil Sci. Plant Nutr. 48:897 - 900.

Fageria, N. K. and Baligar, V. C. (2005) Enhancing nitrogen use efficiency in crop plants. Adv Agron 88:97 - 185.

FAO, (2003). Assessment of soil nutrient balance: Approaches and methodologies Fertiliser and Plant Nutrition Bulletin No.14. 101 pp, Rome, Italy.

Gaskin, J. W., Das, K. C., Tassistro, A. S., Sonon, L., Harris, K. and Hawkins, B. (2009). Characterization of char for agricultural use in the soils of the southeastern United States. In: Woods, W.I., Teixeira, W.G., Lehmann, J., Steiner, C., WinklerPrins, A., Rebellato, L. (Eds.), Amazonian Dark Earths: Wim Sombroek‘s Vision. Springer, Netherlands, pp. 433e443.

Gaskin, J. W., Speir, R. A., Harris, K., Das, K. C., Lee, R. D, Morris, L. A. (2010). Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and yield. Agron. J. 102:623 - 633.

Gaskin, J. W., Steiner, C., Harris, K., Das, K.C. and Bibens, B. (2008). Effect of low-temperature pyrolysis conditions on biochar for agricultural use. *Trans. Asabe 51*, 2061 - 2069.

Gerken, A., Suglo J. V. and Braun M. (2001). Pesticide policy in Ghana. MoFA/PPRSD, ICP Project, Pesticide Policy Project/GTZ. Accra, Ghana.

Giller, K. E (2002). Targeting management of organic resources and mineral fertilizers: can we match scientists‘ fantasies with farmers‘ realities? In: Vanlauwe B, Diels K, Sanginga N, Merckx R (eds) Integrared plant nutrient management in Sub-Saharan Africa: from concept to practice. CAB International, Wallingford, pp 155 - 171.

Glaser, B. and Birk, J. J. (2012). State of the scientific knowledge on properties and genesis of Anthropogenic Dark Earths in Central Amazonia (*terra preta de Índio*). *Geochimica et Cosmochimica Acta*, *82*, 39 - 51.

Glaser, B., Haumaier, L., Guggenberge, G. And Zech, W. (2001). The _Terra Preta‘phenomenon: a model for sustainable agriculture in the humid tropics. Naturwissenschaften 88: 37 - 41.

Glaser, B., Haumaier, L., Guggenberger, G. and Zech, W. (2001). The _terra preta‘ phenomenon: A modelfor sustainable agriculture in the humid tropics. *Naturwissenschaften*, *88*, 37 - 41.

Glaser, B., Lehmann, J. and Zech, W. (2002). Ameliorating physical and chemical properties of highlyweathered soils in the tropics with charcoal - A review. *Biol. Fertil. Soils*, *35*, 219 - 230.

Glaser, B., Lehmann, J., Zech, W. (2002) Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - a review. Biol Fertil Soil 35:219 - 230.

Glaser, B., Zech, W. and Woods, W. I. (2004). History, Current Knowledge and Future Perspectives ofGeoecological Research Concerning the Origin of Amazonian Anthropogenic Dark Earths (*terrapreta*). In *Amazonian Dark Earths: Explorations in Space and Time*; Glaser, B., Woods, W. I., Eds.; Springer: New York, NY, USA.

Golchin, A., Oades, J. M., Skjemstad, J. O. and Clarke, P. (1994). Study of free and occluded particulate organic matter in soil by solid state 13C P/MAS NMR spectroscopy and scanning electron microscopy. Aust. J. Soil Res. 32, 285 - 309.

Gundale, M. J. and DeLuca, T. H. (2006).Temperature and substrate influence the chemical properties of charcoal in the ponderosa pine/Douglas-fir ecosystem, *Forest Ecologyand Management, ,* 231, 86 - 93.

Haefele, M. S., Konboon, Y., Wongboon, W., Amarante, S., Maarifat, A. A., Pfeiffer M. E, Knoblauch, C. (2011). Effects and fate of biochar from rice residues in rice-based systems. Field Crops Res. 121:430 - 440.

Haefele, S. M. (2008). Biochar in rice-based systems: characteristics and agronomic effects. Biochar: Sustainability and security in a changing climate. Proceedings of the 2nd International Biochar Initiative Conference, Newcastle 2008.

Haynes, R. J. and Mokolobate, M. S. (2001). Ameriolation of aluminium toxicity and P deficiency in acid soils by Jama, B., Palm, C.A., Buresh, R.J., Niang, A.L., Gach- engo, C., Nziguheba, G. and Amadalo, B. (2000) Tithonia as a green manure for soil fertility improvement in Western Kenya: A review. *Agronomy Journal*, 49, 201 - 221. doi:10.1023/A:1006339025728.

Hilber, I., Wyss, G. S., Mader, P., Bucheli, T. D., Meier, I., Vogt, L. and Schulin, R. (2009). Influence of activated charcoal amendment to contaminated soil on dieldrin and nutrient uptake by cucumbers. Environmental Pollution 157, 2224e2230.

Hue, N. V. (1992). Correcting soil acidity of a highly weathered ultisol with chicken manure and sewage sludge. *Communications in Soil Science and Plant Analysis*, 23, 241-264. doi:10.1080/00103629209368586.

IBI, (2012). Standardized product definition and product testing guidelines for biochar that is used in soil. International Biochar Initiative. In: N. T. Uphoff, (Ed.), Biological Approaches to Sustainable Soil Systems. CRC Press, Boca Raton, pp: 517 - 530.

Inyang, M., Gao, B., Ding, W., Pullammanappallil, P., Zimmerman, A. R. and Cao, X. (2011). Enhanced lead sorption by biochar derived from anaerobically digestedsugarcane bagasse. Separ. Sci. Technol. 46, 1950 - 1956.

Inyang, M., Gao, B., Pullammanappallil, P., Ding, W. and Zimmerman, A. R. (2010). Biochar from anaerobically digested sugarcane bagasse. Bioresour. Technol. 101, 8868 - 8872.

Jama, B., Palm, C. A., Buresh, R. J., Niang, A. L., Gach-engo, C., Nziguheba, G. and Amadalo, B. (2000). Tithonia as a green manure for soil fertility improvement in West-ern Kenya: A review. *Agronomy Journal*, 49, 201 - 221. doi:10.1023/A:1006339025728.

Jeffery, S.,Verheijen, F. G. A. M., van der Velde, and Bastos, A. C. (2011). ―A quantitative review of the effects of biochar application to soils on crop productivity using met-analysis.‖ *Agriculture, Ecosystems and Environment* 144: 175 - 187.

Johnston, A. E., Poulton, P. R. and Coleman, K. (2009). Soil organic matter: its importance in sustainable agriculture and carbon dioxide fluxes. Advances in Agronomy 101, 1 - 57.

Jones, B. E. H., Haynes, R. J. and Phillips, I. R. (2010). Effect of amendment of bauxite processing sand with organic materials on its chemical, physical and microbial properties. J. Environ. Manag. 91:2281 - 2288.

Jones, D. L., Murphy, D. V., Khalid, M., Ahmad, W., Edwards-Jones, G. and DeLuca, T. H. (2011). Short-term biochar-induced increase in soil CO2 release is both biotically and abiotically mediated. *Soil Biol. Biochem.*, *43*, 1723 - 1731.

Joseph, S. D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C. H., Hook, J., van Zwieten, L., Kimber, S., Cowie, A., Singh, B. P., Lehmann, J., Foidl, N., Smernik, R. J., and Amonette, J. E. (2010). Aninvestigation into the reactions of biochar in soil. *Aust. J. Soil Res.*, *48*, 501 - 515.

Kammann, C., Ratering, S., Eckhard, C., Müller, C., 2012. Biochar and hydrochar effects on greenhouse gas (carbon dioxide, nitrous oxide, and methane) fluxesfrom soils. Journal of Environmental Quality 41, 1052e1066.

Keech, O., Carcaillet, C. and Nilsson, M. C. (2005). Adsorption of allelopathic compounds by wood–derived charcoal: The role of wood porosity, *Plant and Soil,* 2005,272,291 - 300.

Keiluweit, M. and Kleber, M. (2009). Molecular level interactions in soil and sediments: the role of aromatic π-systems. Environmental Science and Technology 43: 3421 - 3429.

Khan, A., M. T. Jan, K.B. Marwat and Arif M. (2009). Organic and inorganic nitrogen treatments effects on plant and yield attributes of maize in a different tillage systems. *Pak. J. Bot*., 41(1): 99-108.

Khan, N., Shab, Z., Ahmed, N., Ahmad, S., Mehmood, N., and Junaid, M. (2013). Effect of intergrated use of biochar, FYM and Nitrogen Fertilizer on soil organic fertility. Pure Appl. Bio., 2(2): Pp. 42 - 47.

Khanna, P. K, Raison, R. J. and Falkiner, R. A. (1994). Chemical properties of ash derived from *Eucalyptus* litter and its effects on forest soils. Forest Ecology Management, 66: 107-125.

Kim, I., Yu, Z. Q., Xia, B. H. and Huang, W. L. (2007). Sorption of male hormones by soils and sediments. Environmental Toxicology and Chemistry 26, 264e270.

Kimani, S. K., and Lekasi, J. K. (2004). Managing manures throughout their production cycle enhances their use-fulness as fertilizers: A review. In: Batiano, A., Ed., *Managing Nutrient Cycles to Sustain Soil Fertility in Sub-Saharan Africa*, Academy of Science Publishers, Nairobi. Kenya Agricultural Research Institute (1994) Fertilizer use recommendations. Vol. 1-22. Fertilizer use recommendation project. KARI, Nairobi.

Kleber, M., Sollins, P. and Sutton, R. (2007). A conceptual model of organo-mineral interactions in soils: Self-assembly of organic molecular fragments into zonal structures on mineral surfaces. *Biogeochemistry 85*, 9 - 24.

Knicker, H. ―Black nitrogen‖ (2010). - An important fraction in determining the recalcitrance of charcoal. *Org. Geochem.*, *41*, 947 - 950.

Knoblauch, C., Maarifat, A. A., Pfeiffer, E. M. and Haefele, S. M. (2011). Degradability of black carbon and its impact on trace gas fluxes and carbon turnover in paddy soils. Soil Biology and Biochemistry published online.

Kolb, S. E., Fermanich, K. J. and Dornbush, M. E. (2009). Effect of charcoal quantity on microbial biomass and activity in temperate soils. Soil Science Society ofAmerica Journal 73, 1173e1181.

Krull, E. S., Swanston, C. W., Skjemstad, J. O. and McGowan, J. A. (2006). Importance of charcoal in determining the age and chemistry of organic carbon in surface soils. J. Geophys. Res. P. 111 G04001, doi:10.1029/2006JG000194.

Kudeyarova, A. Y. (2007). Application of basic chemical concepts to understanding the formation andtransformation mechanisms of humic substances: A review of publications and own experimentaldata. *Eurasian Soil Sci.*, *40*, 934–948..

Kuzyakov, Y., Subbotina, I., Chen, H. Q., Bogomolova, I., and Xu, X. L. (2009) Black carbon decompositionand incorporation into soil microbial biomass estimated by C-14 labeling. *Soil Biol. Biochem.*, *41*, 210 - 219.

Kyung-Hwa, H., Sang-Geun, H. and Byoung-Choon, J. (2010). Aggregate Stability and Soil Carbon Storage as Affected by Different Land Use Practices. In Proceedings of the International Workshop onEvaluation and Sustainable Management of Soil Carbon Sequestration in Asian Countries, Bogor,Indonesia, 28 - 29.

Laird, D. A., Fleming, P., Davis, D. D., Horton, R., Wang, B. Q. and Karlen, D. L. (2010). Impact of biochar amendments on the quality of a typical midwestern agricultural soil. Geoderma. 158:443 - 449.

Lal, R. (2004). Soil carbon sequestration impacts on global climate change and food security. Science 304:1623 - 1627.

Lal, R. (2004). Soil carbon sequestration to mitigate climate change. *Geoderma* 2004, *123*, 1–22.Lal, R. Carbon sequestration. *Philos. Trans. R. Soc. B Biol. Sci.* 2008, *363*, 815–830.

Lal, R. (2008). Carbon sequestration. *Philos. Trans. R. Soc. B Biol. Sci.* 2008, *363*, 815–830.

Lehman, J., Da Silva Jr, J. P. Steiner, C., Nehls, T. Zech, W. and B. Glaser, (2003). Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. Plant and Soil, 249: 343 - 357.

Lehmann, C. J., and Rondon, M. (2006). Biochar soil management on highly-weathered soils in the tropics.

Lehmann, C. J., Da Silva Jr., J. P., Rondon, M., Greenwood, J., Nehls, T., Steiner C.and Glaser, B. (2002). Slash-and-char - a feasible alternative for soil fertility management in the central Amazon? In: 17th World Congress of Soil Science. Bangkok.

Lehmann, J. (2007). A handful of carbon. Nature 447:143 - 144.

Lehmann, J. (2007). Bio-energy in the black. Frontiers in Ecology and the Environment 5, doi: 10.1890/060133.

Lehmann, J. and Joseph, S. (2009). Biochar for Environmental Management: Science and Technology. Earthscan, London.

Lehmann, J. and Joseph, S. (2009). *Biochar for Environmental Management: Science and Technology*; Earthscan: London, UK, 2009.

Lehmann, J. and Rondon, M. (2006). Biochar soil management on highly weathered soils in the humid tropics. In: Biological Approaches to Sustainable Soil Systems (N. Uphoff et al.eds), Boca Raton, FL: CRC Press. pp. 517 - 530.

Lehmann, J. and Sohi, S. (2008) Comment on ―fire-derived charcoal causes loss of forest humus‖. Science 321(5894):1295

Lehmann, J., Gaunt, J. and Rondon, M. (2006). Bio-char Sequestration in Terrestrial Ecosystems - A Review, *Mitigation and Adaptation Strategies for Global Change*, 2006, 11, 403 - 427.

Lehmann, J., Gaunt, J., Rondon, M., Bio-char sequestration in terrestrial ecosystems—A review.*Mitig. Adapt. Strateg. Glob. Change* 2006, *11*, 395 - 419. *Agronomy* 2013, *3* 332

Lehmann, J., Kern, D., German, L., McCann, J., Martins, G. and Moreira, A. (2003). Soil fertility and production potential. In: Amazonian Dark Earths: Origin, Properties, Management (eds. Lehmann, J., Kern, D.C., Glaser, B., and Woods W.I) Kluwer Academic Publishers, Netherlands, pp. 105 - 124.

Lehmann, J., Pereia da Silva Jr. J., Steiner, C., Nehls, T., Zech, W. and Glaser, B. (2003). Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. Plan Soil 249:343 - 357.

Lehmann, J., Rillig, M. C., Thies, J., Masiello, C. A., Hockaday, W. C. and Crowley, D. (2011). Biochareffects on soil biota—A review. *Soil Biol. Biochem.*, *43*, 1812 - 1836.

Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., Coleman, K., Woodbury, P. and Krull, E. (2008). Australian climate-carbon cycle feedback reduced by soil black carbon. Nature Geoscience 1, 832e835.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O, Thies, J., Luizao, F. J., Petersen, J. and Neves, E. G. (2006). Black carbon increases cation exchange capacity in soils, *Soil Science Society of America Journal*, 2006, 70, 1719–1730

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O.,Thies, J.; Luizao, F.J.; Petersen, J.; *et al. (*2006)Black carbon increases cation exchange capacity insoils. *Soil Sci. Soc. Am. J.*, *70*, 1719–1730.

Liang, Q., Chen, H., Gong, Y., Fan, M., Yang, H., Lal, R. and Kuzyakov, Y. (2012). Effects of 15 years of manure and inorganic fertilizers on soil organic carbon fractions in a wheat-maize system in the North China Plain, Nutr. Cycl. Agroecosyst., 92, 21 - 33.

Lin, Y., Munroe, P., Joseph, S., Kimber, S. and Van Zwieten, L. (2012). Nanoscale organo-mineral reactions of biochars in ferrosol: An investigation using microscopy. *Plant Soil* 2012, *357*, 369–380.

Liu, E., Changrong, Y., Xurong, M., Wenqing, H., So, H. B., Linping, D., Qin, L., Shuang L. & Tinglu, F. (2010). Long term effect of chemical fertilizer, straw, and manure on soil chemical and biological properties in north-west China. *Geoderma, 150*, 173-180.

Liu, J., Duan, C.-Q., Zhu, Y.-N., Zhang, X.-H., and Wang, C.-X.: Effect of chemical fertilizers on the fractionation of Cu, Cr and Ni in contaminated soil, Environ. Geol., 52, 1601–1606, 2007.

Liu, J., Hardy, S., Susanne B., Herbert, M., Bernd, H., and Bruno G. (2012). ―Short-term effect of biochar and compost on soil fertility and water status of a Dystric Cambisol in NE Germany under fieldconditions.‖ *J. Plant Nutr. Soil Sci.* (2012): 1 - 10.

Liu, Y., Yang, M., Wu, Y., Wang, H., Chen, Y., Wu, W. (2011). Reducing CH4 and CO2 emissions from waterlogged paddy soil with biochar. J Soil Sediment 11:930 - 939.

Lutzowa, M. V., Kogel-Knabnera, I., Ekschmittb, K., Flessac, H., Guggenbergerd, G., Matznere, E. and Marschnerf, B., (2007). SOM fractionation methods: Relevance to functional pools and to stabilization mechanisms. Soil Biology & Biochemistry 39, 2183 - 2207.

KNUST

Mackowiak, C. L., Grossl, P. R., Bugbee, B. G. (2001). Beneficial effects of humic acid on micronutrient availability to wheat. *Soil Sci. Soc. Am. J.*, *65*, 1744 - 1750.

Mafongoya, P. L., Mugendi, D. N., Jama, B. and Waswa, B. S. (2003). Maize-based cropping systems in the subhumid zones of Easter and southern Africa. In; Gichuru, M. P. (Eds.). Soil fertility Management in Africa: A regional Perspective. TSBF-CIAT, Nairobi, Kenya.

Major, J. (2013). Practical aspects of biochar application to tree crops. IBI Technical Bulletin#102, International Biochar Initiative (Accessed online at http://www.biocharinternational.org/sites/default/files/Technical%20Bulletin%20Biochar%20Tree%20 Planting.pdf).

Major, J., Lehmann, J., Rondon, M. and Goodale, C. (2010). Fate of soil-applied black carbon: Downwardmigration, leaching and soil respiration. *Glob. Change Biol.*, *16*, 1366–1379.

Major, J., Rondon, M., Molina, D., Riha, S. J. and Lehmann, J. (2010). Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant Soil 333:117 - 128.

Major, J., Steiner, C., Downie, A. and Lehmann, J. (2009). Biochar effects on nutrient leaching. In: Biochar for environmental management(J. Lehmann and S. Joseph eds.), Science and Technology, Earthscan, London. pp. 271-287.

Mandal, B., Majumder, B., Bandyopadhyay, P. K., Hazra, G. C., Gangopadhyay, A., Samantaray, R. N., Mishra, A. K., Chaudhury, J., Saha, M. N. and Kundu, S. (2007). The potential of cropping systems and soil amendments for carbon sequestration in soils under long-term experiments in subtropical India. Global Change Biol. 13: 357–369.

Mankasingh, U., Choi, P. C. and Ragnarsdottir, V. (2011). Biochar application in a tropical, agricultural region: A plot scale study in Tamil Nadu, India. Appl. Geochem. 26:S218-S221.

Manya, J. J. (2012). Pyrolysis for biochar purposes: A review to establish current knowledge gaps andresearch needs. *Environ. Sci. Technol.* 2012, *46*, 7939 - 7954.

Marley, N. A., Bennett, P., Janecky D. R. and Gaffney, J. S. (1989). Spectroscopicevidence for organic diacid complexation with dissolved silica in aqueous systems-I. Oxalic acid. *Organic Geochemistry* 14(5), 525–528. doi:10.1016/0146-6380(89)90032-6

Marris, E. (2006). Black is the new green, *Nature*, 2006, 442(10), 624 - 626.

Masulili, A., Utomo, W. H. and Syekhfani. (2010). Rice husk biochar for rice based cropping system in acid soil 1. The characteristics of rice husk biochar and its Influence on the properties of acid sulfate soils and rice growth in West Kalimantan, Indonesia. *Journal of Agriculture Science (Canada), 3*, 25-33.

Matysik, S., Herbarth, O. and Mueller, A. (2009). Determination of microbial volatile organic compounds (MVOCs) by passive sampling onto charcoal sorbents. Chemosphere 76, 114e119.

McClellan, A. T., Deenik, J., Uehara, G. and Antal, M. (2007). Effects of flash carbonized macadamia nutshell charcoal on plant growth and soil chemical properties. In _Proceedings American Society of Agronomy Conference‘. Abstracts. 3–7 November, New Orleans, LA. (ASA: Madison, WI).

McLeod, P. B., van den Heuvel-Greve, M. J., Luoma, S. N. and Luthy, R. G. (20070. Biological uptake of polychlorinated biphenyls by Macoma balthica from sediment amended with activated carbon. Environmental Toxicology and Chemistry 26, 980e987.

Mizuta, K., Matsumoto, T., Hatate, Y., Nishihara, K. and Nakanishi, T. (2004). Removal of nitratenitrogen from drinking water using bamboo powder charcoal. Bioresource Technology 95(3): 255 - 257.

Motojima, H., Yamada, P., Irie, M., Ozaki, M., Shigemori, H. and Isoda, H. (2012). Amelioration effect ofhumic acid extracted from solubilized excess sludge on saline-alkali soil. *J. Mater. Cycles WasteManag. 14*, 169–180.

Mucheru, M., Mugendi D. N., Kung'u, J. B., Mugwe, J. and Bationo, A. (2007) Effects of organic and mineral fertilizer inputs on maize yield and soil chemical proper-ties in a maize cropping system in Meru South District, Kenya. *Agroforestry Systems*, 69, 189-197. doi:10.1007/s10457-006-9027 4.

Mucheru-Muna, M., Mugendi, D., Kung'u J, Mugwe J, Bationo A (2007). Effects of organic and mineral fertilizer inputs on maize yield and soil chemical properties in a maize cropping system in Meru South District, Kenya. Agrofor Syst 69:189–197, pp. 137 - 150.

Mugendi, D. N., Monicah-Munah, Pypers, P., Mugwe, J., Kungu, J., Vanlauwe, B. and Merckx, R. (2010). Maize productivity as influenced by organic inputs and mineral fertilizers in a Nitisol soil in Meru South District. 19*th World Congress of Soil Science*, *Soil Solutions for a Changing World*, 1-6 August 2010, Brisbane.

Mugendi, D. N., Mucheru-Muna, M., Mugwe, J., Kung'u, J. B. and Batiano, A. (2007) Improving food production using ―best bet‖ soil fertility technologies in the central highlands of Kenya. In: Batiano, A., Waswa, B., Kihara, J. and Kimetu, J., Eds., (2007) *Advances in Integrated Soil Fertility Management in Sub-Saharan Africa*, *Challenges and Opportunities*, Springer, Berlin. doi:10.1007/978-1-4020-5760-1_31

Mukherjee, A and Lal, R. (2013). Biochar Impacts on Soil Physical Properties and Greenhouse Gas Emissions Agronomy. 3:313-339.

Mukherjee, A. (2011). Physical and Chemical Properties of a Range of Laboratory-produced Fresh andAged Biochars. Ph.D. Thesis, University of Florida, Gainesville, FL, USA.

Mukherjee, A. and Zimmerman, A. R. (2013). Organic carbon and nutrient release from a range oflaboratory-produced biochars and biochar-soil mixtures. *Geoderma* 2013, *193–194*, 122–130.*Agronomy* 2013, *3* 338

Mukherjee, A., Hamdan, R., Cooper, W. T. and Zimmerman, A. R. (2013). A chemical comparison of freshly-produced and field-aged biochars and biochar-amended soils, *Chemosphere*, submitted.

Mukherjee, A., Zimmerman, A. R., Harris, W. G. (2011). Surface chemistry variations among a series oflaboratory-produced biochars. *Geoderma* 2011, *163*, 247 - 255.

Nelson, D. W. and Sommers, L. E. (1982). Total carbon, organic carbon and organic matter. *In:* Page, A. L., Miller, R. H, and Keeney, D. R. (Eds.) Methods of Soil Analysis, part 2. American Society of Agronomy, Madison, USA, pp. 539 -579.

Nguyen, B. T and Lehmann J. (2009). Black carbon decomposition under varying water regimes. Org Geochem 40:846 – 853.

Nguyen, B. T., Lehmann, J., Hockaday, W. C., Joseph, S. and Masiello, C. A. (2010). Temperature sensitivity of black carbon decomposition and oxidation. Environ Sci Technol 44:3324 - 3331.

Nguyen, T. H., Brown, R. A. and Ball, W. P. (2004). An evaluation of thermal resistance as a measure of black carbon content in diesel soot, wood char, and sediment. Org. Geochem. pp. 217 - 234.

Novak, J. M., Busscher, W. J., Laird, D. L., Ahmedna, M., Watts, D.W. and Niandou, M. A. S. (2009). Impact of biochar amendment on fertility of a southeastern coastal plain soil. *Soil Sci.* 2009, *174*, 105 - 112.

Novak, J. M., Busscher, W. J., Watts, D. W., Amonette, J. E., Ippolito, J. A., Lima, I. M., Gaskin, J., Das, K. C., Steiner, C., Ahmedna, M. (2012). Biochars impact on soil-moisture storage in an ultisoland two aridisols. *Soil Sci.* 2012, *177*, 310 - 320.

Nziguheba, G., Merckx, R., Palm C. A., Mutuo, P. (2002). Combining Tithonia diversifolia and fertilizers for maize production in a phosphorus deficient soil in Kenya. Agrof Syst 55:165 - 174.

Nziguheba, G., Palm, C. A, Buresh, R. J. and Smithson, P. C. (1998). Soil phosphorus fractions and adsorption as affected by organic and inorganic sources. In: The biology and fertility of tropical soils, TSBF report, pp. 22.

Ogawa, M. (1994). Symbiosis of people and nature in the tropics. III. Tropical agricultureusing charcoal. Farming Jpn. 28:21e35.

Ozacar, M. (2003). Adsorption of phosphate from aqueous solution onto alunite.Chemosphere 51, 321 - 327.

Page, A. L., Miller, R. H. and Keeney, D. R. (1982). Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. Agronomy series 9, ASA, SSSA, Madison, Wis. USA.

Painter, T. J. (2001). Carbohydrate polymers in food preservation: An integrated view of the Maillard reaction with special reference to the discoveries of preserved foods in *Sphagnum* dominated peat bogs. Carbohydrate Polymers 36: 335 - 347.

Palm, C. A., Gachengo, C. N., Delve, R. G., Candisch, G. and Giller, K. (2001). Organic inputs for soil fertility management in tropical agroecosystem: application of organic resource database. Agric Ecosyst Environ 83:27 - 42.

Palm, C. A., Giller, K. E., Mafongoya, P. L., Swift, M. J. (2001b) Management of organic matter in the tropics: translating theory into practice. Nutr Cycl Agroecosyst 61:63 - 75.

Partey S. T., Quashie-Sam, S. J, Thevathasan, N. V. and Gordon, A. M. (2011). Decomposition and nutrient release patterns of the leaf biomass of the wild sunflower (Tithonia diversifolia): a comparative study with four leguminous agroforestry species. Agrofor Syst 8:123 - 134.

Partey, S. T, Preziosi, R. F and Robson, G. D. (2012). Effects of organic residue chemistry on soil biogeochemistry: implications for organic matter management inagroecosystems. In: Adewuyi B, Chukwu K (eds) Soil fertility: characteristics, processes and management. Nova Publishers, New York, pp 1 - 28.

Partey, S. T, Thevathasan, N. V. (2013). Agronomic potentials of rarely used agroforestry species for smallholder agriculture in Sub-Saharan Africa: an exploratory study. Commun Soil Sci Plan 44(11):1733 - 1748.

Partey, S. T., Preziosi, R. F., Robson, G. D. (2013). Maize residue interaction with high quality organic materials: effects on decomposition and nutrient release dynamics. Agric Res 2(1):58 - 67.

Pessenda, L. C. R, Gouveia, S. E. M. and Aravena, R. (2001). Radiocarbon dating of total soil organic matter and humin fraction and its comparison with 14C ages of fossil charcoal. Radiocarbon 43:595 - 601.

Petersen, J. B, Neves, E. G. and Heckenberger, M. J. (2001). Gift from the past: Terra preta and prehistoric Amerindian occupation in Amazonia. *In* Unknown Amazonia. Ed. C. McEwan. pp. 86-105. British Museum, London, UK. As referenced in Lehmann *et al.*, 2002.

Piccolo, A. and Mbagwu, J. S. C. (1989). Effects of humic substances and surfactants on the stability of soil aggregates. *Soil Sci.* 1989, *147*, 47 - 54.

Piccolo, A. and Mbagwu, J. S. C. (1997). Exogenous humic substances as conditioners for the rehabilitation of degraded soils. Agro-Foods Industry Hi-Tech: 8(2): 2 - 4.

Piccolo, A., Pietramellara, G. and Mbagwu, J. S. C. (1997). Use of humic substances as soil conditioners to increase aggregate stability. Geoderma, 75(3-4): 267 - 277.

Piccolo, A., Pietramellara, G., Mbagwu, J. S. C. (1996). Effects of coal derived humic substances onwater retention and structural stability of mediterranean soils. *Soil Use Manag.* 1996, *12*,209 - 213.

Preston, C. M. and Schmidt, M.W. I. (2006). Black (pyrogenic) carbon: A synthesis of current knowledge and uncertainties with special consideration of boreal regions‘,*Biogeosciences,* 2006 3, 397 - 420.

Purakayastha, T. J. (2010). Effect of biochar on yield of different crops.IARI. Annual Report201011, Indian Agricultural Research Institute, New Delhi-110012, India. P. 55.

Raison, R. J. (1979). Modification of the soil environment by vegetation fires, with particular reference to nitrogen transformation: A Review. Plant Soil, 51: 73 - 108.

Rogovska, N., Laird, D., Cruse, R., Fleming, P., Parkin, T. and Meek, D. (2011). Impact of biochar on manure carbon stabilization and greenhouse gas emissions. Soil Sci. Soc. Am. J. 75:871 - 879.

Rondon, M. A, Molina, D., Hurtado, M., Ramirez, J, Lehmann, J., Major, J., Amezquita, E. (2006). Enhancing the productivity of crops and grasses while reducing greenhouse gas emissionsthrough bio-char amendments to unfertile tropical soils. In: Presentation at the 18thWorld Congress of Soil Science, July 9–15, Philadelphia, Pennsylvania, USA. 138 - 168.

Rondon, M. A., Lehmann, J., Ramirez, J. and Hurtado, M. (2007). Biological nitrogen fixation by common beans (*Phaseolus vulgaris L.*) increases with bio-char additions. Biology and Fertility of Soils, 43: 699 - 708.

Rondon, M., Lehmann, J., Ramirez, J. and Hurtado, M. (2007). Biological nitrogen fixation by common beans (*Phaseolus vulgaris* L.) increases with biochar additions. Biol. Fertil. Soils 43:688 - 708.

Rondon, M., Molina, D., Hurtado, M., Ramirez, J., Lehmann, J., Major, J. and Amezquita, E. (2006). Enhancing the Productivity of Crops and Grasses While Reducing Greenhouse Gas Emissionsthrough Bio-Char Amendments to Unfertile Tropical Soils. In Proceedings of the 18th WorldCongress of Soil Science, Philadelphia, PA, USA, 9–15 July 2006.

Rondon, M.. Ramirez, J. and Lehmann, J. (2005). Charcoal Additions Reduce Net Emissions of Greenhouse Gases to the Atmosphere. In Proceedings of the 3rd USDA Symposium on Greenhouse Gasesand Carbon Sequestration, Baltimore, MD, USA, 21–24 March 2005; pp. 208.

Rutherford, D. W., Wershaw, R. L. and Cox, L. G. (2004). Changes in Composition and Porosity Occurring during the Thermal Degradation of Wood and Wood Components; 2004-5292; U.S. Department of the Interior, U.S. Geological Survey: Denver, CO, USA, pp. 88.

Rutherford, D. W., Wershaw, R. L., Reeves, J. B. (2008). In *Development of Acid Functional Groups andLactones during the Thermal Degradation of Wood and Wood Components*, 2007-5013, U.S.Department of the Interior, U.S.; Geological Survey: Denver, CO, USA, 2008; pp. 52.

Saito, M. and Marumoto, T. (2002). Inoculation with arbuscular mycorrhizal fungi: thestatus quo in Japan and the future prospects. Plant Soil 244:273-e279.

Samuel, T. P., Richard F. P. and Geoffery, D. R. (2013). Short term combined effect of biochar, Green manure and inorganic fertilizer on soil properties and Agronomic characteristics of maize.Agricultural Research Journal. ISSN: 2249-720X. DOI: 10.1002/s40003-oi4-902-1.

Sanchez, M. E., Lindao, E., Margaleff, D., Martinez, O. and Moran, A. (2009). Pyrolysis of agricultural residues from rape and sunflowers: production and characterization of bio-fuels and biochar soil management. Journal of Analytical and Applied Pyrolysis 85, 142e144.

Sanchez, P. (2010). Tripling crop yields in Tropical Africa. Nature Geoscience 3: 299 - 300.

Schmidt, M. W. I and Noack, A. G. (2013). Black carbon in soils and sediments: Analysis, distribution,implications, and current challenges. *Glob. Biogeochem. Cycles* 2000, *14*, 777–793.*Agronomy* 2013, *3* 331

Schmidt, M. W. I, Skjemstad, J. O., Gehrt, E. and Kögel-Knabner, I. (1999). Charred organic carbon in German chernozemic soils. Eur. J. Soil Sci. 50(2):351 - 365.

Schmidt, M. W. I. and Noack, A. G. (2000). Black carbon in soils and sediments: analysis, distribution, implications, and current challenges. Global Biogeochemical Cycles 14, 777e793.

Schulz, H., Glaser, B. (2012). Effects of biochar compared to organic andinorganic fertilizers on soil quality and plant growth in a greenhouseexperiment. J Plant Nutr Soil Sci 175:410–422. doi:10.1002/jpln.20110014

Shenbagavalli, S. and Mahimairaja, S. (2012). Characterization and effect of biochar on Nitrogen and Carbon dynamics in soil. International Journal of Advancd biological Research.Vol 2 (2) p 249-255. ISSN: 2250-3579

Singh, B. P, Hatton, B. J., Singh B, Cowie, A. L. and Kathuria, A. (2010) Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. J Environ Qual 39:1224–1235

Singh, B. P. and Cowie, A. L. (2008). A Novel Approach, Using 13C Natural Abundance, for Measuring Decomposition of Biochars in Soil. In Proceedings of the Carbon and Nutrient Management inAgriculture, Fertilizer and Lime Research Centre Workshop, Massey University, Palmerston North, New Zealand, 13–14 February 2008; Currie, L.D., Yates, L., Eds.; pp. 549.

Singh, B. P., Hatton, B. J., Singh, B., Cowie, A. L., Kathuria, A. (2010). Influence of biochars on nitrousoxide emission and nitrogen leaching from two contrasting soils. *J. Environ. Qual.* 2010, *39*, 1224 - 1235.

Singh, R. B., Kumar, P. and Woodhead, T. (2002). Smallholder Farmers in India: Food Security and Agricultural Policy. RAP Publication 2002/2003. Bangkok, Thailand, FAO.

Six, J. and Jastrow, J. D. (2002). Organic Matter Turnover. In *Encyclopedia of Soil Science*; Lal, R., Ed.; Marcel Dekker: New York, NY, USA, 2002; pp. 936–942.

Skjemstad, J. O., Clarke, P., Taylor, J. A., Oades, J. M. and McClure, S. G. (1996). The chemistry and nature of protected carbon in soil. *Aust. J. Soil Res.* 1996, *34*, 251–271.

Smith, J. L., Collins, H. P. and Bailey, V. L. (2010). The effect of young biochar on soil respiration. *Soil Biol.Biochem.* 2010, *42*, 2345 - 2347.

Smith, N. J. H. (1999). *The Amazon River Forest: A Natural History of Plants, Animals, and People*; Oxford University Press: New York, NY, USA, 1999.

Smith, P., Martino, D. and Cai, Z. (2007) Agriculture. In: Metz B, Davidson O.R, Bosch PR et al (eds) Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, pp 497 - 540.

Sohi, S. P., Krull, E., Lopez-Capel, E., Bol, R. (2010). A review of biochar and its use and function in soil. *Adv. Agron.* 2010, *105*, 47 - 82.

Sohi, S., Krull, E., Lopez-Capel E., Bol, R. (2010). A review of biochar and its use and function in soil. Adv. Agron. 105:47-82.

Solaiman, Zakaria M., Paul Blackwell, Lynette K. Abbott, and Paul Storer. "Direct and Residual Effect of Biochar Application on Mycorrhizal Root Colonisation, Growth and Nutrition of Wheat." *Australian Journal of SoilResearch* 48.7 (2010): 546-54. Print.

Spokas, K. A, Koskinen W. C., Baker, J. M., Reicosk, D. C. (2009). Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. Chemosphere 77:574 - 581.

Spokas, K. A. (2013). Impact of biochar field aging on laboratory greenhouse gas production potentials, Glob. Change Biol., 5, 165 - 176.

Spokas, K., Baker, J., Reicosky, D. (2004). Ethylene: Potential key for biochar amendment impacts.Chun, Y.; Sheng, G.Y.; Chiou, C.T.; Xing, B.S. Compositions and sorptive properties of cropresidue-derived chars. *Environ. Sci. Technol.* 2004, *38*, 4649 - 4655.

Steinbeiss, S., Gleixner, G. and Antonietti, M. (2009). Effect of biochar amendment on soil carbon balance and soil microbial activity. Soil Biology and Biochemistry 41(6): 1301 - 1310.

Steiner, C. (2008). Biochar Carbon Sequestration. University of Georgia, Biorefining and Carbon Cycling Program, Athens, GA 30602, USA.

Steiner, C., Teixeira, W., Lehmann, J., Nehls, T., de Macêdo, J., Blum, W. and Zech, W. (2007). Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. Plant Soil 291:275 - 290.

Streubel, J. D., Collins, H. P., Garcia-Perez, M., Tarara, J., Granatstein, D. and Kruger, C. E. (2011). Influence of Contrasting Biochar Types on Five Soils at Increasing Rates of Application. *Soil Science Society ofAmerica Journal, 75*(4), 1402 - 1413.

Taghizadeh-Toosi, A., Clough, T. J., Condron, L. M., Sherlock, R. R., Anderson, C. R., Craigie, R. A. (2011). Biochar incorporation into pasture soil suppresses in situ nitrous oxide emissions from ruminant urine patches. J Environ Qual 40:468–476 U.N. Population Division (2008) World Population Prospects: The 2008 Revision Population Database, at esa.un.org/unpp, updated 11 March 2009.

Tagoe, S. O., Horiuchi, T. & Matsui, T. (2008). Effects of carbonized and dried chicken manures on the growth, yield, and N content of soybean. *Plant Soil*, *306*, 211- 220.

Tasneem, K., Tariq, M., Kamal, J., and Masood, A. 2004. Effectiveness of farmyard manure, poultry manure and nitrogen for corn productivity. International Journal of Agriculture and Biology. 1560-8530/2004/06-2-260-263.

Thies, J. E, Rillig, M. (2009). Characteristics of biochar: biological properties. In: Lehmann J, Joseph S (Eds.), Biochar for Environmental Management: Science and Technology. Earthscan, London, pp. 85-e105.

Tryon, E. H. (2013). Effect of charcoal on certain physical, chemical, and biological properties of forestsoils. *Ecol. Monogr.* 1948, *18*, 81–115. *Agronomy* 2013, *3* 336x

Tsadilas, C. D., Karaivazoglou, N. A., Tsotsolis, N. C., Stamatiadis, S., and Samaras, V. (2005). Cadmium uptake by tobacco as affected by liming, N form, and year of cultivation, Environ. Pollut., 134, 239 - 246.

Tu, C., Ristaino, J. B. and Hu, S. (2006). Soil microbial biomass and activity in organic tomato farming systems: Effects of organic inputs and straw mulching Soil Biology & Biochemistry 38: 247 - 255.

Uzoma, K. C., Inoue, M., Andry, H., Fujimaki, H., Zahoor, A. and Ni izar, E. (2011). Effect of cow manure biochar on maize productivity under sandy soil condition. Soil Use and Management, 27: 205 - 212.

Uzoma, K.C., Inoue, M., Andry, H., Zahoor, A and Nishihara, E. (2011). Influence of biochar applicationon sandy soil hydraulic properties and nutrient retention. *J. Food Agric. Environ.* 2011, *9*,1137 - 1143.

Vaccari, .F. P, Baronti, S., Lugata. E., Genesio., L, Castaldi., S, Fornasier. F and Miglietta. F. (2011). Biochar as a strategy to sequester carbon and increase yield in durum wheat. European Journal of Agronomy 34, 231-238.

Van Zwieten, L., Kimber, S,, Morris, S., Chan, K., Downie, A., Rust, J., Joseph, S., Cowie, A. (2010). Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant Soil 327:235–246

Vanlauwe, B., Diels, J., Aihou, K., Iwuafor, E.N., Lyasse, O., Sanginga, N. and Merckx, R. (2002). Direct interactions between N fertilizer and organic matter: Evidence from trials with 15Nlabeled fertilizer. In: Vanlauwe, B., Diels, J., Sanginga, N. and Merckx, R. Eds., *Integrated Plant Nutrient Management in Sub-Saharan Africa*: *From Concepts to Practice*, CAB International, Wallingford.

Venterea, R. T., Maharjan, B., Dolan, M. S. (2011). Fertilizer source and tillage effects on yieldscaled nitrous oxide emissions in a corn cropping system. J. Environ. Qual. 40, 1521–1531.

Ventura, F., Salvatorelli, F., Piana, S., Pieri, L. and Pisa, P. R. (2012). The effects of biochar on the physical properties of bare soil. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh, 103*(1), 5 - 11. http://dx.doi.org/10.1017/S1755691012000059

Verheijen, F. G. A., S., Jeffery, A. C., Bastos, M., Van Der Velde and Diafas, I. (2009). Biochar Application to Soils - A Critical Scientific Review of Effects on Soil Properties, Processes and Functions. EUR 24099 EN, Office for the Official Publications of the European Communities, Luxembourg, pp: 149.

Verheijen, F., Jeffery, S., Bastos, A. C., Van der Velde, M. and Diafas, I. (2010). Biochar Application to Soils: A Critical Scientific Review of Effects on Soil Properties, Processes and Functions. JRC Scient. Technical reports. pp. 1-166.

Violante, A. and Gianfreda, L. (2000). The role of biomolecules in the formationand reactivity towards nutrient and organics of variable charge mineralsand organominerals. In _Soil biochemistry‘. (Eds J Bollag, G Stotzky)(Marcel Dekker: New York)

Walkley, A. and Black, C. A. (1934). An estimation of methods for determining organic carbon and nitrogen in the soils. J Agric. Sci., 1934,25, 598-609 Wenzl, H. F. J., Brauns, F. E. and Brauns. D. A., *Thechemical technology of wood.* New York: Academic Press.1970.

Wang, J. Y., Jia, J. X., Xiong, Z. Q, Khalil, M. A. K. and Xing, G. X. (2011b). Water regime– nitrogen fertilizer–straw incorporation interaction: field study on nitrous oxide emissions from a rice agroecosystem in Nanjing, China. Agric Ecosyst Environ 141:437 - 446.

Wang, J. Y., Zhang, M., Xiong., Z. Q., Liu, P. L. and Pan, G. X. (2011a). Effects of biochar addition on N_2O and CO_2 emissions from two paddy soils. Biol Fertil Soils 47:887 - 896.

Wang, W. J., Smith, C .J. and Chen, D. (2004). Predicting soil nitrogen mineralization dynamics with a modified double exponential model. Soil Sci Soc Am J 68:1256 -1265.

Warnock, D. D., Lehmann, J., Kuyper, T. W. and Rillig, M. C. (2007). Mycorrhizal responses to biochar in soil e concepts and mechanisms. Plant and Soil 300, 9 - 20.

Warnock, D. D., Mummey, D. L., McBride, B., Major, J., Lehmann, J. and Rillig, M. C. (2010). Influences of non-herbaceous biochar on arbuscular mycorrhizal fungal abundances in roots and soils: results from growth-chamber and field experiments. Applied Soil Ecology 46, 450 - 456.

Widowati, Utomo., W. H., Soehono, L. A. and Guritno, B. (2011). Effect of biochar on the release and loss of nitrogen from urea fertilization. *Journal of Agriculture and Food Technology, 1*, 127 - 132.

Winsley, P. (2007). Biochar and bioenergy production for climate change mitigation. New Zealand Sci. Rev. 64:5-10.

Woolf, D. (2008). Biochar as a soil amendment: A review of the environmental implications. http://orgprints.org/13268/01/Biochar as a soil amendment a review.pdf. Retrieved via Internet Explorer Ver. 6, 2 October 2008.

Woolf, D., Amonette., J. E., Stree-Perrott F. A., Lehmann, J. and Joseph, S. (2010) Sustainable biochar to mitigate global climatechange. Nat Comm 1:56

Xie, W. J., Wang, H. Y., Xia, J. B., and Yao, Z. G. (2011). Influence of N, P, and K application on *Zea mays* L. growth and Cu and Pb accumulation, Plant Soil Environ., 57, 128 - 134.

Yamato, M., Okimori, Y., Wibowo, I. F., Anshori, S. and Ogawa, M. (2008). Effects of the application of charred bark of Acacia mangium on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. Soil Science and Plant Nutrition, *52*, 489 - 495.

Yamato, M., Okimori, Y., Wibowo, I. F., Anshori, S. and Ogawa, M. (2006). Effects of the application of charred bark of *Acacia mangium* on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. Soil Sci. Plant Nutr. 52:489 - 495.

Yanai, Y., Toyota, K. and Okazaki, M. (2007). Effects of charcoal addition on N2O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. Soil Sci Plant Nutr 53:181 - 188.

Yang, J. Y., Huffman, E. C., Jong, R. D., Kirkwood, V., MacDonald, K. B. and Drury, C. F. (2007). Residual soil nitrogen in soil landscapes of Canada as affected by land use practices and Agricultural policy scenarios. *Land Uses Policy,* 24: 89-99.

Yao, F. X., Arbestain, M. C., Virgel, S., Blanco, F., Arostegui, J., Maciá-Agulló, J. A., Macías, F. (2013). Simulated geochemical weathering of a mineral ash-rich biochar in a modified soxhlet reactor.*Chemosphere* 2010, *80*, 724 - 732. *Agronomy*, *3* 339

Yao, Z., Zheng, X., Dong, H., Wang, R., Mei, B. and Zhu, J. (2012). A 3-year record of N2O and CH4emissions from a sandy loam paddy during rice seasons as affected by different nitrogenapplication rates. *Agric. Ecosyst. Environ.* 2012, *152*, 1–9.

Yariv, S. and Cross, H. (2002) _Organo-clay complexes and interactions.‘ (MarcelDekker: New York).

Yeboah, E., Ofori, P., Quansah, G., Dugan, E. and Sohi, S. (2009). Improving soil productivity through biochar amendments to soils. *African Journal of Environmental Science and Technology* 3.

KNUST

Zhang, A. F., Bian, R. J., Pan, G. X., Cui, L. Q., Hussain, Q., Li, L. Q., Zheng, J. W., Zheng, J. F., Zhang, X. H., Han, X. J. (2013). Effects of biochar amendment on soil quality, crop yield andgreenhouse gas emission in a chinese rice paddy: A field study of 2 consecutive rice growingcycles. *Field Crops Res.* 2012, *127*, 153–160.*Agronomy* 2013, *3* 335.

Zhang, A. F., Cui, L. Q., Pan, G. X., Li, L. Q., Hussain, Q., Zhang, X. H., Zheng, J. W., Crowley, D. (2010). Effect of biochar amendment on yield and methane and nitrous oxide emissions from a rice paddy from Tai Lake plain, China. Agr Ecosyst Environ 139:469 - 475.

Zhang, A., Cui, L., Pan, G., Li, L., Hussain, Q., Zhang, X., Zheng, J., Crowley, D. (2013). Effect of biochar amendment on yield and methane and nitrous oxide emissions from a rice paddy from tai lake plain, china. *Agric. Ecosyst. Environ.* 2010, *139*, 469–475. © 2013 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/3.

Zhanga, A., Biana, R., Pana, G., Cuia, L., Hussaina, Q., Li, L., Zhenga, J., Zhenga, J., Zhanga, X., Hana, X. and Yua, X. (2012). Effects of biochar amendment on soil quality, crop yield and greenhouse gas emission in a Chinese rice paddy: A field study of 2 consecutive rice growing cycles. Field Crops Res. 127:153-160.

Zhen, L. and Routray, J. K. (2003). Operational Indicators for Measuring Agricultural Sustainability in Developing Countries. Environmental Management. 32(1): 34–46.

Zimmerman, A. R. (2010). Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). *Environ. Sci. Technol.* 2010, *44*, 1295–1301.

Zimmerman, A. R. (2012). Environmental stability of biochar. In *Biochar and Soil Biota*; Ladygina, N., Rineau, F., Eds.; CRC Press: Boca Raton, FL, USA, 2012.

Zimmerman, A. R., Gao, B. and Ahn, M. Y. (2011). Positive and negative carbon mineralization primingeffects among a variety of biochar-amended soils. *Soil Biol. Biochem.* 2011, *43*, 1169 - 1179.

Zwieten, V. L, Kimber, S., Morris, S., Chan, Y. K., Downie, A., Rust, J., Joseph, S. and Cowie, A. (2010). Effect of biochar from slow pyrolysisi of papermill waste on agronomic performance and soil fertility. Plant. Soil 327:235-246.

KNUST
NYANSAPO W ɔ SANE NO BADWENMA