CHARACTERIZATION OF BIOCHAR PREPARED FROM THREE DIFFERENT FEED STOCKS

A DESSERTATION SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF AGRICULTURE (SOIL SCIENCE)

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JULY, 2013

DECLARATION

I do hereby declare that this dissertation "CHARACTERIZATION OF BIOCHAR PREPARED FROM THREE DIFFERENT FEED STOCK" has been written by me and that it is the record of my own research work. It has neither in whole nor in part been presented for another degree elsewhere. Works of other researchers have been duly cited by reference to the authors and all assistance received also acknowledged.

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DEDICATION

This thesis is firstly dedicated to God Almighty, and to the indelible memory of my late parents, Mr. Owen Harris Zolue and Ms. Georgia K. Goneh, who work tirelessly in ensuring that I had the best of education but never lived to see how far I have come. May your souls rest in peace. Lastly, I dedicate this work to my Uncle, Jimmy Zolue, who was full of enthusiasm and total support from the birth of the idea for University's education. His clever and creative suggestions provided essential guidance.

ACKNOWLEDGEMENTS

I firstly want to give thanks to God Almighty for his blessing upon my life and for giving me strength; knowledge, wisdom and understanding that enable me realize my dream. I wish to express my sincere gratitude to Prof. G. N. N. Dowuona and Dr. E. K. Nartey for their patience, guidance, support and encouragement during the course of this work. I must also say I am grateful to you for reading through my work to enhance its scientific trustworthiness. You will forever be remembered. I am equally grateful to the Head of Department, Dr. T. A. Adjadeh and all senior members of the Department of Soil Science for their valuable support.

I wish to express my sincere gratitude to the Government of Liberia through the Ministry of Agriculture for securing a grant from the African Development Bank to finance my studies at the University of Ghana. May the glorious land of liberty continue to be ours.

I also wish to express my gratitude to all the laboratory technicians of the Department of Soil Science especially; Mr. Bernard Anipa, Mr. Julius Nartenor and Mr. Edmund Anum for the assistance offered me during the period of my laboratory work. I am indeed grateful.

May I also express thanks and appreciation to all my mates; Daniel Ansah Fianko, Brahene Sebastian Wisdom, Abigail Tettey, Eric Darko, Eric Koomson, Harris Yanquoi, and Emmanuel Atibila Nsobilafor their good spirit of comradeship.

On a personal note, I wish to thank Zainab Musa Shallangwa, J. Alexander Nyahn Jr., Mr. Maru Ali and all my colleagues from Liberia for always being there for me. May God give us long life.

ABSTRACT

Biochar-based soil management strategies in Ghana are new and are now being evaluated in the context of the country's agricultural system. Biochar produced from organic materials such as saw dust, rice husk and saw dust are being used in Ghana. These different feedstocks may have different physico-chemical properties which will influence the quality of the biochar produced when the feedstocks are carbonized and in turn govern their suitability for use in agriculture. A detailed characterization of biochar produced from rice straw, rice husk and saw dust was carried out in a bid to document the basic features of the products to ensure their safety and suitability for use as soil amendments. Rice husk and straw from the same plant material and saw dust from a saw mill were pyrolysed at 350 ^{o}C in a kiln at the Soil Research Institute of the Council of Science and Industrial Research, Kwadaso, Kumasi. These samples were air dried and parameters such as particle size distribution, bulk density, available water, electrical conductivity, pH in water and KCl, total oxidizable organic carbon, total nitrogen, total phosphorus, available phosphorus, and exchangeable basic cations and total elemental analysis were carried out. Over 70% of the rice straw and the rice husk biochar types were in the very small size fraction of between 63 µm and 250 µm. The saw dust biochar, however, had 63.7% of its size fraction in the coarse size regime of between 500 µm and 2500 µm. The bulk density values of the three biochar types were very low ranging between 0.19 Mg/m^3 and 0.23 Mg/m^3. Moisture content at field capacity was in the order of saw dust (9.55%) > rice straw (8.92%) > rice husk (7.70%). The rice straw biochar had the highest available moisture content of 3.39% which was almost 1.7 times higher than that of the saw dust biochar type. The rice straw had the highest pH of 10.5 as a result of its very high contents total Ca (10.44 mg/kg) and exchangeable Ca (7.63 cmol/kg) in addition to a high Si concentration of 170.8 mg/kg. The rice straw biochar

also had the highest EC of 3.57 dS/m due to its high exchangeable Na concentration. The total oxidisable organic carbon of 191.97 g/kg was highest in the rice straw biochar with the rice husk sequestering 136.23 g/kg and saw dust 115.8 g/kg. The saw dust biochar type was the lowest in N content. On account of the C:N ratios of 166.9 for the rice straw, 142 for the rice husk biochar and 156 for the saw dust biochar, the rice straw biochar type would be the most stable and hence sequester more carbon. Available P was very high in the rice straw as a result of the high Si content of the material and was found to be 2.5 and almost 3.8 times more than the total P in the rice husk and saw dust biochar types, respectively. The concentration of heavy metals Cu, Zn and more importantly Co and Pb were very low in all the three samples with concentrations below 0.5 mg/kg due to the near neutral to strongly alkaline pH regime of all the three biochar types. These very low levels of the heavy metals make the three biochar materials very safe for use as soil amendments without any toxicity hazards. The study has identified at a charring temperature of 350 ^{o}C, the rice straw biochar has high concentrations of Ca (10.44 mg/kg,) Mg (1.61mg/kg) and Si (170.8 mg/kg) and a high pH of 10.5 in both water and KCl and therefore has the potential of being used as an agricultural liming material.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

In many tropical environments where rainfall is high, weathering processes over time have resulted in soils with high amount of iron and aluminum oxides and oxy-hydroxides. Weathering and leaching have removed basic cations resulting in the formation of acidic soils characterized by low buffering capacity with potential aluminum release (Fisher and Jakoben, 2000). Such aluminum (Al) toxicity is one of the most important single factors limiting crop production in tropical soils (Sanchez, 2000). Acidification which accelerates with deforestation and intensified cultivation is also having a major impact on the increasing human population in Africa. Decreasing soil pH increases the instability of soil Al-minerals and thereby increases the concentration of total Al in soil solution. Speciation of Al depends on pH and a decrease in pH increases the relative amount of the plant toxic Al^{3+} ion relative to other Al-species (Matzner *et al*., 1998).

The highly weathered soils are mostly dominated by low activity clay minerals such as kaolinites and sesquioxides (Brady and Weil, 2001). These result in low and declining soil fertility which arises as a result of continuous cultivation where levels of soil replenishment, by whatever means, are too low to mitigate the process of soil nutrient mining, in instances where soil fertility is not restored by new inputs (Shisanya *et al*., 2009). Consequently, these soils have poor and declining soil fertility. Increasing cost of mineral fertilizers and its associated environmental effects, poor quality and low availability of organic amendments pose a serious

challenge to amending tropical soils. These tropical soils, therefore, remain low in productivity and require soil amendment.

Amendment of tropical soils in West Africa has been done mainly by the use of fertilizers, both inorganic and organic. The use of inorganic fertilizers in West Africa is not widespread because, they are not affordable to a majority of the farmers in the region. Furthermore, due to high price of imported fertilizers at farm gate and delays in delivery due to poor infrastructure, smallholder farmers often apply very low rates of inorganic fertilizer late in the growing season, leading to poor crop-yield responses (Heisey and Mwangi, 1996). Excess applications of inorganic fertilizers over the years have been one of the major contributing factors to environmental degradation in Africa (Bationo *et al*., 2006).

More often than not, the use of inorganic P fertilizer in acidic soils have not had the desired impact on soil productivity and crop yields because the soluble Al and Fe in and high levels of sesquioxides and kaolinite which tend to be protonated under those pH regimes sorb the added inorganic P (Nartey *et al*., 1997; Abekoe and Tiessen 1998). Thus application of inorganic fertilizers alone may not help to improve on the productivity of the soils. It has become imperative for the pH level of the soils to be increased to the desired range for optimum crop production.

Organic fertilizers though have continued to play an important role in maintaining soil structure, moisture control, and nutrient levels which gives it an added advantage over inorganic fertilizers, usage has not been popular under farm conditions because the material cannot supply all of the nutrients needed to sustain rapid yield growth. Organic matter is also slow in releasing nutrients to crops. Usage has not also been encouraging because ita application is mostly labour intensive and requires high application rate. With the high temperatures of the tropics,

decomposition rate of the material with a concomitant release of CO_2 is fast aggravating global warming thus leading to a short period for improvement in soil fertility (Sohi *et al.,* 2009). Organic matter addition buffers and thus though may add nutrients and make P more available under acidic conditions; it is unable to raise the pH of soils to any appreciable level for optimum crop production. It is, therefore, not suitable for use as a liming material.

Studies have shown that when organic materials are pyrolysed, the charred material increases in pH usually above 7 and persists in the soil for a long period of time (Lima *et al.,* 2002; Lehmann *et al*., 2003; Glaser *et al*., 2004; Steiner *et al*., 2007; Kimetu *et al*., 2008; Asai *et al*., 2009; Gaskin *et al*., 2008; Major *et al*., 2010). Spokas and Reicosky (2009) have report that pyrolysed charred organic material has the potential of increasing soil pH and decreasing aluminum toxicity. It has, therefore, become important to transform organic matter in to a more stable form that will persist longer in tropical soils and also help to reduce decomposition rate of the material and the frequency of application to soils. The remedy to this problem is biochar.

Biochar has been defined as charred organic matter, produced with the intent to deliberately apply to soils to sequester carbon and improve soil properties (Lehmann and Joseph, 2009). Biochar as a soil conditioner has also been defined as a porous carbonaceous solid produced by thermo chemical conversion of organic materials in an oxygen depleted atmosphere with physico-chemical properties suitable for the safe and long-term storage of carbon in the environment and for soil improvement (Shackley and Sohi, 2010). Biochar is noted to have numerous characteristics and uses. These include, serving as a soil conditioner by making nutrients more available to plants and improving soil structure, providing habitat for soil microorganisms, which in turn may aid in making some nutrients available to crops (Sohi *et al.,* 2009). The high surface area and pore structure of biochar provides a habitat for soil

microorganisms, which in turn may aid in making some nutrients available to crops (Lehmann and Joseph, 2009). Biochar also provides an indirect nutrient effect by reducing leaching of nutrients that otherwise would not be made available to crops. As a soil enhancer, biochar makes soil more fertile, boosts food security, preserves cropland diversity, and reduces the need for some chemical and fertilizer inputs. It improves water quality by helping to retain nutrients and agrochemicals in soils for use by plants and crops, resulting in less pollution.

Biochar production offers a simple, sustainable tool for managing agricultural wastes. This can be achieved by converting agricultural waste into a powerful soil enhancer that can preserve cropland diversity and discourage deforestation. Sustainable biochar can be used now to help combat global warming by holding carbon in soil and by displacing fossil fuel use (IBI, 2009). For soils that require liming, there is growing evidence that biochar may provide similar benefits of improving soil pH balance (Collins, 2008). The quantity of biochar however, that needs to be applied relative to liming may be high (Yanai *et al*., 2007). The substitution of biochar for lime can provide for net carbon benefit compared to standard liming and be cheaper.

Research has shown that the stability of biochar in soil greatly exceeds that of un-charred organic matter. Biochar retains nitrogen emissions of nitrous oxide hence the potency of the greenhouse gas may be reduced. Turning agricultural waste into biochar also reduces methane (another potent greenhouse gas) generated by the natural decomposition of organic matter. To achieve an advanced process for improving product yields from pyrolysis of selected biomass, it is important to undertake proper characterization. As such, the physical and chemical properties of biochar have to be determined so as to fully ascertain the mechanism by which these biochar produced from different feed stocks can improve upon the productivity of agricultural soils.

1.2 Justification

In rice growing areas of Ghana, rice husk and straw abound and in almost all regions of Ghana, there are mountains of saw dust as a result of wood processing from saw mills. These materials are hardly used as source of organic matter to soils because of their high C:N ratio (Chan and Xu, 2009). The rice husk and saw dust 'mountains' in Ghana breed rodents. Disposing of these organic materials has been through burning aerobically which cause environmental pollution. Aerobic burning of organic matter has been noted to account for a 10% global methane emissions and 1% nitrous oxide emissions (Crutzen and Andreae. 1990). However, when these organic materials are charred anaerobically, they could serve as valuable soil conditioners to improve upon the productivity of soils. In Asia, rice husk, rice straw and saw dust are pyrolysed into biochar and added to improve upon the physical and chemical properties of soils (Shackley *et al.*, 2011; Sokchea *et al.*, 2012).

Biochar-based soil management strategies in Ghana are new and are now being evaluated in the context of the country's agricultural system. According to Sohi et al (2009), to agronomically use biochar, its properties (physical and chemical) must be measured so as to fully ascertain the mechanism by which the material is able to improve upon the productivity of agricultural soils. There is, therefore, a compelling need to determine and understand the physical and chemical properties of the material.

Biochar produced from organic materials such as saw dust, rice husk and saw dust are being used in Ghana. These different feedstocks may have different physico-chemical properties. It is therefore, likely that these different physico-chemical properties will influence the quality of the biochar produced when the feedstocks are carbonized and may in turn govern their suitability for use agronomically. It has become imperative to do a detailed characterization

of biochar produced from rice straw, rice husk and saw dust so as to document their respective basic features to ensure their safety for use as soil amendments. It is also appropriate to quantify the key properties that may give rise to the beneficial qualities of biochar from these feedstocks.

The objectives of this study were therefore to:

(a) determine the differences in the physical and chemical properties of biochar produced from three different feed stocks namely rice straw, rice husk and sawdust.

(b) assess the suitability of rice straw, rice husk and saw dust biochar types as potential liming materials based on their respective calcium, magnesium and silicon concentration.

1.3 Research hypothesis

H_O: There is no difference amongst the physical and chemical properties of biochar produced from different feedstocks namely; rice straw, rice husk and saw dust

H_A: There is difference amongst the physical and chemical properties of biochar produce from different feedstocks namely; rice straw, rice husk and saw dust.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Origin of biochar

Biochar was initially linked to the exploration and archaeological study of early human settlement and soils. These early studies of soils being enriched from what appears to be the deliberate mixing of burned biomass in soils around human settlements helped spark more recent interest in biochar. These deposits of enriched soils, known as *terra preta* in the Amazon region of South America, have a fascinating history of scientific study of their own (Lehmann *et al.*, 2003).

More current studies of biochar are focused on its role in a growing demand for biomass-based energy sources that can mitigate greenhouse gas emissions and slow climate change. In addition, biochar has the potential to enhance soil quality and soil carbon sequestration. A secondary source of interest in biochar comes from the growing need to develop low-cost and healthier biomass-fuelled stove technology.

2.2 Biochar

Biochar is a fine-grained, highly porous charcoal substance that is distinguished from other charcoals in its intended use as a soil amendment. Biochar is charcoal that has been produced under conditions that optimize certain characteristics such as high surface area per unit of volume and low amounts of residual resins deemed useful in agriculture. The particular heat treatment of organic biomass used to produce biochar contributes to its large surface area and its characteristic ability to persist in soils with very little biological decay (Lehmann and Rondon, 2006).

Biochar is produced by the combustion of biomass under oxygen-limited conditions. The term biochar was originally associated with a specific type of production, known as 'slow pyrolysis'. In this type of pyrolysis, oxygen is absent, heating rates are relatively slow, and peak temperatures relatively low. However, the term biochar has since been extended to products of short duration pyrolysis at higher temperatures known as 'fast pyrolysis and novel techniques such as microwave conversion.

There is a wide variety of char products produced industrially. For applications such as activated carbon, char may be produced at high temperature, under long heating times and with controlled supply of oxygen. In contrast, basic techniques for manufacture of charcoal (such as clay kilns) tend to function at a lower temperature, and reaction does not proceed under tightly controlled conditions. Traditional charcoal production should be more accurately described as 'carbonization' which involves smothering of biomass with soil prior to ignition or combustion of biomass whilst wet.

Drying and roasting biomass at even lower temperatures is known as 'torrefaction' (Arias *et al.*, 2008). A charred material is also formed during 'gasification' of biomass, which involves thermal conversion at very high temperature (800°C) and in the partial presence of oxygen. This process is designed to maximize the production of synthesis gas ('syngas'). Materials produced by torrefaction and gasification differ from biochar in physico-chemical properties, such as particle pore size and heating value (Sohi *et al*., 2009) and have industrial applications, such as production of chemicals (methanol, ammonia, urea) rather than agricultural applications.

In order to differentiate biochar from charcoal formed in natural fire, activated carbon, and other black carbon materials, it is important to give a clear definition of each since all their products are obtained from the heating of carbon-rich material.

2.2.1 Char

This is a solid product arising from thermal decomposition of any natural or synthetic organic material. Examples are char from forest fire and soot resulting from the incomplete combustion of fossil hydrocarbon.

2.2.2 Charcoal

Charcoal is produced from the thermal decomposition of wood and related organic materials and is mainly for use as an urban fuel for heating and cooking. It is also traditionally used as soil amendment for control of odour (Okimori *et al.,* 2003). Temperatures in traditional kilns approach 450-500°C, which is similar to that of industrial pyrolysis but with lower yields. The conversion of feedstock dry mass may be as low as 10% compared to 35% using more formal production technology. Also, all heat as well as gaseous and liquid co-products are lost during the combustion process.

2.2.3 Activated carbon

Activated carbon is manufactured by heating carbonaceous material at a high temperature (above 500°C) and over long (>10 hours) periods of time. The resulting material is characterised by a very high adsorptive capacity. It is not used as a soil amendment but has been applied for cleansing processes, such as water filtration and adsorption of gas, liquid or solid contaminants (Tomaszewski *et al.,* 2007).

2.2.4 Black carbon

Black carbon: a general term that encompasses diverse and ubiquitous forms of refractory organic matter that originate from incomplete combustion (Baldock and Smernik 2002). The diversity of burning conditions results in black carbon occupying a continuum of material.

2.3 Pyrolysis

Pyrolysis is the heating of biomass feedstock under controlled conditions to produce combustible synthesis gas ('syngas'), and oil ('bio-oil') that can be burnt to produce heat, power, or combined heat and power. Biochar, the third combustible product produced in pyrolysis, is the solid charred and carbon-rich residue. Pyrolysis has a requirement for initial energy, in the same way as in straight combustion. Some heat in the flame is used to initiate combustion of new feedstock.

The potential advantage of pyrolysis-derived bioenergy over other bioenergy strategies in terms of greenhouse gas emissions results not only solely from the retention of up to 50% of the feedstock carbon in stable biochar, but from indirect savings that may result from the use of biochar in agriculture, specifically the soil (Gaunt and Lehmann 2008). The pyrolysis process greatly affects the qualities of biochar and its potential value to agriculture in terms of agronomic performance or in carbon sequestration.

The process and process-parameters, mainly temperature and furnace residence time, are important in the quality of the product. The process and process conditions, however, also interact with feedstock type in determining the nature of the product. These variables together influence the chemical, biological and physical properties, which limit the potential use for biochar products. Each category of pyrolysis process is characterized by a contrasting balance

among biochar, bio-oil and syngas as shown in Table 2.1. The precise ratio in these products may vary between plants, and may be optimized at a particular installation (Demirbas, 2004).

It is critical that maximising the production of biochar relative to mass of initial feedstock (Demirbas, 2006), is always at the expense of usable energy in the liquid or gaseous form. Although a greenhouse gas mitigation strategy may favour maximising the biochar product (Gaunt and Lehmann 2008), the balance that is realised is a function of market and engineering constraints.

Table 2.1. Fate of initial feedstock mass between products of pyrolysis processes

Process	Process Liquid (bio-oil)	Solid (biochar)	Gas (syngas)
FAST PYROLYSIS Moderate temperature (~500 °C) Short hot vapour residence time (<2s)	75% (25% water)	12%	13%
INTERMEDIATE PYROLYSIS Low-moderate temperature, Moderate hot vapour residence time	50% (50% water)	25%	25%
SLOW PYROLYSIS Low-moderate temperature, Long residence time	30% (70% water)	35%	35%
GASIFICATION high temperature (>800 °C) Long vapour residence time	5% tar 5% water	10%	85%

Source: (IEA, 2007).

2.3.1 Slow pyrolysis

Slow pyrolysis can be divided into traditional charcoal making and more modern processes. It is characterized by slower heating rates, relatively long solid and vapour residence times and usually a lower temperature than fast pyrolysis, typically 400°C (Bridgwater *et al*, 1999). The target product is often the char, but this will always be accompanied by liquid and gas products although these are not always recovered. Slow pyrolysis can also be defined as the thermal conversion of biomass by slow heating at low to medium temperatures (450 to 650°C) in the absence of oxygen, with the simultaneous capture of syngas (David *et al*,. 2006).

Traditional processes, using pits, mounds or kilns, generally involve some direct combustion of the biomass, usually wood, as heat source in the kiln. Liquid and gas products are often not collected but escape as smoke with consequent environmental issues (Antal and Grønli, 2003). Feedstock's in the form of dried biomass pellets or chips of various particle sizes are fed into a heated furnace and exposed to uniform heating, generally through the use of internal or external heating as retort furnace or kilns, respectively.

2.3.2 Fast pyrolysis

Fast pyrolysis is characterized by high heating rates and short vapour residence times. This generally requires a feedstock prepared as small particle sizes and a design that removes the vapours quickly from the presence of the hot solids. There are a number of different reactor configurations that can achieve this including ablative systems, fluidized beds, stirred or moving beds and vacuum pyrolysis systems. A moderate temperature of around 500°C is usually used (Ensyn, 2009). Very rapid feedstock heating leads to a much greater proportion of bio-oil and less biochar.

The time taken to reach peak temperature of the endothermic process (the 'resistance time') is approximately one or two seconds, rather than minutes or hours as is the case with slow pyrolysis. The lower operating temperature also enhances the overall conversion efficiency of the process relative to slow pyrolysis. Maintaining a low feedstock moisture content of around 10% and using a fine particle size of < 2mm permits rapid transference of energy despite relatively moderate peak temperatures of around 450°C (and in the range 350 to 500°C). In many systems, the transfer is further increased by mechanically enhancing feedstock contact with the heat source or maximising heat source surface area.

Various technologies have been used and proposed or tested including: fixed beds, augers, ablative methods, rotating cones, fluidized beds and circulating fluidized beds. Surface charring must be continuously removed during reaction to prevent pyrolysis of particle interiors being inhibited by its insulating effect. Bio-oil is condensed from the syngas stream under rapid cooling, with the combustion of syngas providing the pyrolysis process heat. The bio-oil is a low grade product with a calorific value, on a volume basis, approximately 55% that of regular diesel fuel. It is unsuitable as a mainstream liquid transport fuel even after refining, and is most suitable as a fuel-oil substitute (BEST Energies, 2009).

2.3.3 Intermediate pyrolysis

The term intermediate pyrolysis is used to describe biomass pyrolysis in a certain type of commercial screw-pyrolyser, the Haloclean reactor (Hornung *et al*, 2006). This reactor is designed for waste disposal of electrical and electronic component residues by pyrolysis. When used for biomass it has performance similar to slow pyrolysis techniques, although somewhat quicker.

2.4 Biochar feedstock

Feedstock is the term conventionally used for the type of biomass that is pyrolysed and turned into biochar. In principle, any organic feedstock can be pyrolysed, although the yield of solid residue (char) respective to liquid and gas yield varies greatly along with physic-chemical properties of the resulting biochar.

Feedstock is, along with pyrolysis conditions, the most important factor controlling the properties of the resulting biochar. Firstly, the chemical and structural composition of the biomass feedstock relates to the chemical and structural composition of the resulting biochar and, therefore, is reflected in its behavior, function and fate in soils. Secondly, the extent of the physical and chemical alterations undergone by the biomass during pyrolysis (e.g. attrition, cracking, microstructural rearrangements) is dependent on the processing conditions mainly temperature and residence times (Sjöström, 1993; Demirbas, 2004).

A wide variety of feedstocks can be used depending on location, cost, and availability. Therefore, the relative proportion of each component will determine the extent to which the biomass structure is retained during pyrolysis, at any given temperature. The type of feedstock used for pyrolysis is more important where biochar is to be applied as a soil conditioner (Day *et al*., 2005; Das *et al*., 2008; Gaunt and Lehmann, 2008).

Feedstocks currently used at a commercial-scale or in research facilities include wood chip and wood pellets, tree bark, crop residues (including straw, nut shells and rice hulls), switch grass, organic wastes including distillers' grain, bagasse from the sugarcane industry and olive waste (Yaman, 2004), chicken litter (Das et al., 2008), dairy manure, sewage sludge (Shinogi *et al.*, 2002) and paper sludge. The elemental ratios of carbon, oxygen and hydrogen are key feedstock parameters in commercial use and the quality of fuel products (Friedl *et al.*, 2005).

The feedstocks which are favoured for bio-oil and fuel-gas are those that have low mineral and N content. These include wood and biomass from energy crops, including short-rotation woody plants (such as willow), high productivity grasses (such as *Miscanthus* sp.), and a range of other herbaceous plants. They may also include abundant, available and low-cost agricultural byproducts, including cereal straw.

The proportions of hemi-cellulose, cellulose and lignin content determine the ratios of volatile carbon (in bio-oil and gas) and stabilized carbon (biochar) in pyrolysis products. Feedstock's with high lignin content produce the highest biochar yields when pyrolysed at moderate temperatures - approximately 500 ^{o}C (Demirbas, 2006). Charring of agricultural waste products such as nut shells and rice hulls for energy production may be advantageous compared to disposal as waste by some other means (Demirbas, 2006)

2.5 Carbonization

Carbonization is a number of pyrolysis processes that most closely resemble traditional, basic methods of charcoal manufacture, and which produce biochar of the highest carbon content. The auto-thermal carbonization process is the small-scale method widely used in rural communities around the world. The process is optimized for the solid products of pyrolysis, but condensed gases provide an industrial product known as 'wood vinegar', which as well as providing the basis for food flavouring ingredients, is considered to have a fertilizer value to plants. The auto-thermal process as the most realistic option has been proposed for the participation of local communities in using biochar to build soil fertility, especially in developing countries. It is lower in cost, and easier and simpler than pyrolysis systems where ratios of solid, liquid and syngas products have to be optimized (Okimori *et al.*, 2003; Ogawa *et al*., 2006).

2.6 Properties of Biochar

The combined heterogeneity of the feedstock and the wide range of chemical reactions which occur during processing, give rise to a biochar product with a unique set of structural and chemical characteristics (Antal and Gronli, 2003; Demirbas, 2004). According to Sohi *et al.*, (2009), it is important that the properties of biochar such as pH, volatile compound content, ash content, water holding capacity, bulk density, pore volume, and specific surface area measured so as to have an assessment for the use of the material, agronomically.

2.6.1 Structural composition

Thermal degradation of cellulose between 250 and 350ºC results in considerable mass loss in the form of volatiles, leaving behind a rigid amorphous C matrix. As the pyrolysis temperature increases, so does the proportion of aromatic carbon in the biochar, due to the relative increase in the loss of volatile matter (initially water, followed by hydrocarbons, tarry vapours, H_2, CO and CO_2), and the conversion of alkyl and O-alkyl C to aryl C (Baldock and Smernik, 2002). Around 330 ºC, polyaromatic graphene sheets begin to grow laterally, at the expense of the amorphous C phase, and eventually coalesce. Above 600 ºC, carbonization becomes the dominant process. Carbonization is marked by the removal of most remaining non-C atoms and consequent relative increase of the C content, which can be up to 90% (by weight) in biochars from woody feedstock's (Antal and Gronli, 2003; Demirbas, 2004).

Biochar is comprised of stable carbon compounds created when biomass is heated to temperatures between 300 to 1000°C under low (preferably zero) oxygen concentrations. The structural and chemical composition of biochar is highly heterogeneous, with the exception of pH, which is typically > 7. Some properties are pervasive throughout all biochars, including the

high C content and degree of aromaticity, partially explaining the high levels of biochar's inherent recalcitrance. Nevertheless, the exact structural and chemical composition, including surface chemistry, is dependent on a combination of the feedstock type and the pyrolysis conditions (mainly temperature) used (Sohi *et al.*, 2009). These same parameters are key in determining particle size and pore size macro, meso and microspore; distribution in biochar.

Biochar's physical and chemical characteristics may significantly alter key soil physical properties and processes and are, therefore, important to consider prior to its application to soil. The physical and chemical properties determine the suitability of each biochar for a given application, as well as define its behaviour, transport and fate in the environment. Dissimilarities in properties between different biochar products emphasises the need for a case-by-case evaluation of each biochar product prior to its incorporation into soil at a specific site. Research aimed at fully evaluating the extent and implications of particle and pore size distribution of biochar on soil processes and functioning is essential. The influence on mobility and fate of biochar is equally important (Gaskin *et al*., 2008).

2.6.2 Particle size distribution

Initially, particle size distribution in biochar is influenced mainly by the nature of the biomass feedstock and the pyrolysis conditions (Cetin *et al*., 2004). Shrinkage and attrition of the organic material occur during processing, thereby generating a range of particle sizes of the final product. The intensity of such processes is dependent on the pyrolysis technology (Cetin *et al*., 2004). Particle size distribution in biochar also has implications for determining the suitability of each biochar product for a specific application (Downie *et al*., 2009), as well as for the choice of the most adequate application method. In addition, health and safety issues relating

to handling, storage and transport of biochar are also largely determined by particle size distribution.

Wood-based feedstocks generate biochars that are coarser and predominantly xylemic in nature, whereas biochars from crop residues (e.g. rye, or maize) and manures offer a finer and more brittle structure (Sohi *et al*., 2009). Downie *et al.* (2009) have further provided evidence of the influence of feedstock and processing conditions on particle size distribution in biochar.

Generally, particle size has been found to decrease as the pyrolysis heat treatment temperature increased (450 -700 ºC range) in saw dust and wood chippings due to a reduction of the biomass material resistance to attrition during processing (Downie *et al*., 2009). For higher heating rates (e.g. 105-500ºC sec^{-1}) and shorter residence times, finer feedstock particles (50-2000 μm) are required in order to facilitate heat and mass transfer reactions, resulting in finer biochar material (Cetin *et al*., 2004). In contrast, slow pyrolysis (heating rates of 5-30ºC min^{-1}) can use larger feedstock particles, thereby producing coarser biochar (Downie*et al.*, 2009). Increasing the proportion of larger biochar particles can also be obtained by increasing the pressure from atmospheric to 5, 10 and 20 bars during processing, which results in both particle swelling and clustering, due to melting i.e. plastic deformation followed by fusion (Cetin *et al*., 2004).

2.6.3 Chemical composition and surface chemistry

Biochar composition is highly heterogeneous, containing both stable and labile components (Sohi *et al.*, 2009). Carbon, volatile matter, mineral matter (ash) and moisture are generally regarded as its major constituents (Antal and Gronli, 2003).

The relative proportion of biochar components determines the chemical and physical behaviour and function of biochar as a whole (Brown, 2009), which in turn determines its suitability for a site specific application, as well as transport and fate in the environment (Downie, 2009). For example, coarser and more resistant biochars are generated by pyrolysis of wood-based feedstock's (Winsley, 2007). In contrast, biochars produced from crop residues (e.g. rye, maize), manures and seaweed are generally finer and less robust (lower mechanical strength). The latter are also nutrient-rich, and therefore, more readily degradable by microbial communities in the environment (Sohi *et al.*, 2009).

The ash content of biochar is dependent on the ash content of the biomass feedstock. Grass, grain husks, straw residues and manures generally produce biochar with high ash contents, in contrast to that from woody feedstock's (Demirbas, 2004).

Moisture is another critical component of biochar (Antal and Gronli, 2003), as higher moisture contents increase the costs of biochar production and transportation for unit of biochar produced. Keeping the moisture content up to 10% (by weight) appears to be desirable (Bridgwater and Peacocke, 2000). In order for this to be achieved; pre-drying the biomass feedstock may be a necessity, which can be a challenge in biochar production.

According to Sohi *et al.* (2009), the high carbon contents and strong aromatic structure of biochar largely account for its chemical stability. The pH of biochar shows little variability among products, and is typically greater than 7. Total carbon content in biochar has been found to range between 172 - 905 g kg^{-1}, although organic carbon often accounts for <500 g kg^{-1}, as reviewed by Chan and Xu (2009) for a variety of source materials. Total N varies between 1.8 and 56.4 g kg^{-1}, depending on the feedstock (Chan and Xu, 2009). Despite seemingly high, biochar total N content, the nutrient may not be necessarily beneficial to crops, since N is mostly

present in an unavailable form (mineral N contents < 2 mg kg^{-1}; Chan and Xu, 2009). Nuclear magnetic resonance (NMR) spectroscopy has shown that aromatic and heterocyclic N-containing structures in biochar occur as a result of biomass heating, converting labile structures into more recalcitrant forms (Almendros *et al.*, 2003). The C:N ratio in biochar has been found to vary widely between 7 and 500 (Chan and Xu, 2009), with implications for nutrient retention in soils.

Total P and total K in biochar range broadly according to feedstock, with values between 2.7 - 480 and 1.0 - 58.0 g kg^{-1}, respectively (Chan and Xu, 2009). Interestingly, total ranges of N, P and K in biochar are wider than those reported in the literature for typical organic fertilizers. Most minerals within the ash fraction of biochar are thought to occur as discrete associations independent of the carbon matrix, with the exception of K and Ca (Amonette and Joseph, 2009). Typically, each mineral association comprises more than one type of mineral ((Amonette and Joseph, 2009).

The complex and heterogeneous chemical composition of biochars is extended to its surface chemistry, which in turn explains the way biochar interacts with a wide range of organic and inorganic compounds in the environment. Aldehyde -(C=O) H, carboxyl -(C=O)OH) and NO_2, occur predominantly on the outer surface of the graphene sheets and surfaces of pores (van Zwieten et al., 2009). Some of these groups act as electron donors, while others as electron acceptors, resulting on coexisting areas which properties can range from acidic to basic and from hydrophilic to hydrophobic (Amonette and Joseph, 2009). Some functional groups also contain other elements, such as N and S, particularly in biochars from manures, sewage sludge and rendering wastes.

Different processing conditions (temperature of 700 ^{0}C or 450 ^{0}C) explained differences in N contents among three biochars from poultry litter (Lima and Marshall, 2005; Chan *et al.*,

2007). As the pyrolysis temperature rises, so does the proportion of aromatic carbon in the biochar, while N contents peak at around 300^0C (Baldock and Smernik, 2002). In contrast, low processing temperatures (< 500^0C) favour the relative accumulation of a large proportion of available K, Cl (Yu *et al*., 2005), Si, Mg, P and S (Schnitzer *et al.*, 2007). Therefore, processing temperatures < 500 ^{o}C favour nutrient retention in biochar (Chan and Xu, 2009), while being equally advantageous in respect to yield (Gaskin *et al.*, 2008). Nevertheless, it is important to stress that different permutations of those processing conditions, including temperature, may affect differently each source material. This emphasises the need for a case-by-case assessment of the chemical and physical properties of biochar prior to its application into soil.

Relating the adverse effect of a particular constituent (or its concentration) of biochar to a desirable biochar application rate is difficult, as the exact biochar composition is often not provided in the literature. The review of relevant literature has indicated that the full knowledge on the composition of biochar as a soil amendment, and the way it is influenced by those parameters, as well as the implications for soil functioning, is still scarce (Ameloot, *et al.*, 2013). Partially, this can be explained by the fact that most characterisation work has involved charcoals with high carbon and low ash content, as required by the increasingly demanding market for activated carbon. Another factor is the wide variety of processing conditions and feedstock's available.

2.6.4 Pore size distribution and connectivity

Biochar pores are classified into three categories (Downie *et al*., 2009), according to their internal diameters (ID): macrospores (ID >50 nm), mesopores (2 nm< ID <50 nm) and micropores (ID <2 nm). These categories are orders of magnitude different to the standard

categories for pore sizes in soil science. The elementary porosity and structure of the biomass feedstock is retained in the biochar product formed (Downie *et al*., 2009). The vascular structure of the original plant material, for example, is likely to contribute for the occurrence of macropores in biochar, as demonstrated for activated carbon from coal and wood precursors (Downie *et al*., 2009). In contrast, micropores are mainly formed during processing of the parent material.

Macrospores have been identified as a 'feeder' to smaller pores while micropores effectively account for the characteristically large surface area in charcoals (Brown, 2009). The development of microporosity in biochar is linked to an increase in structural and organisational order and is favoured by higher temperatures and retention times, as previously demonstrated for activated carbon (Lua *et al*., 2004).

Lua *et al*. (2004) observed a peak in surface area of pistachio-nut shell char at low heating rates (10^{o}C), whereas higher heating rates resulted in a decrease in surface area. In particular, the lignocellulosic composition of the parent material largely determines the rate of its thermal decomposition, and therefore, the development of porosity (Gonzaléz *et al*., 2009). In the case of charcoals from almond tree pruning, a greater volume of meso and macrospores was obtained, which was accounted for by the slow decomposition rate of such precursor during the initial stages of pyrolysis (Gonzaléz *et al*., 2009).

2.6.5 Cation exchange capacity and pH

The CEC variation in biochars ranges from negligible to around 40 cmol $kg^{-1}$and has been reported to change following incorporation into soils (Lehmann, 2007). This may occur by a

process of leaching of hydrophobic compounds from the biochar (Briggs *et al*., 2005) or by increasing carboxylation of C via abiotic oxidation (Cheng *et al*. 2006; Liang *et al*., 2006).

Considering the very large heterogeneity of its properties, biochar pH values are relatively homogeneous, that is to say they are largely neutral to basic. Chan and Xu (2009) reviewed biochar pH values from a wide variety of feedstocks and found a mean of pH 8.1 in a total range of pH 6.2 – 9.6. The lower end of this range seems to be from green waste and tree bark feedstocks, with the higher end from poultry litter feedstocks.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Sample preparation

Biochar from three feed stock namely, sawdust, rice husk and rice straw were carbonized at a kiln temperature of 350 ^{o}C at the Soil Research Institute of the Council for Scientific and Industrial Research, Kwadaso, Kumasi. These samples were air dried for about one week and transported to the Department of Soil Science, University of Ghana for laboratory analyses.

3.2 Laboratory analyses

3.2.1 Particle size distribution

Fifty grams each of the biochar prepared from rice husk, sawdust and rice straw was weighed into 2.5mm sieves which had been under laid with other sieves of decreasing diameter of 2mm, 1mm, 0.5 mm, 0.25 mm, 0.125 mm, 0.09 mm and 0.063 mm on a Retsch VS 1000 mechanical shaker. The biochar samples were then shaken continuously at 50 rpm for 5 min. The various size distributions of each of the three biochar types were then weighed and expressed as a percentage of the total 50 g mass of biochar taken.

3.2.2 Bulk density

Bulk density was estimated by determining the mass of oven dried biochar that could occupy a particular volume of container (Jones *et al*., 2011). A quantity of each of the biochar types was dried in an oven at 105 ^{0}C till a constant mass was attained and kept in a desiccator to avoid absorption of moisture from the atmosphere. This took about 48 hours. Each of the samples was poured to fill a 250 cm^{3} measuring cylinder amidst intermittent gentle tapping to

ensure good packing to the 250 cm^3 mark. The mass of each biochar sample to fill the 250 cm^3 volume was then determined by weighing. The bulk density was then calculated from the mass of biochar divided by the total volume of biochar.

3.2.3 Available water

The moisture content of the three samples was measured at field capacity (1/3 bar or 33 kPa) and at wilting point (15 bar or 1500 kPa) using the pressure plate method (Eilers, 1978). The biochar samples were placed in the appropriate rings, leveled properly and saturated with water for 24 hours. After 24 hours, the rings bearing the biochar samples were mounted in the extractor and the outflow tube connected. The lid was mounted properly and the clamps of the pressure membrane screwed down. The outflow tube was connected to a 100 mL conical flask for the collection of water. The pressure in the extractor was turned on with a pressure unit and maintained at1/3 bar.

After a minute, water from the pressure plate cell started flowing into the conical flask. The water level in the conical flask or collector was noted for several hours. After 3 days, the water in the collector stop rising. The same pressure was then maintained for three more days and it was ensured that there was no further rise of the conical flask water. This then showed that equilibrium had been attained. The biochar samples were taken out and weighed immediately. The biochar samples were replaced again in the cell for continuation of the experiment at different suction value, 15 bar. After a period of five days the samples were taken out for drying in the oven. The dry weight of the samples and moisture content and different pressure stages were computed. The difference in moisture content at 33 kPa and 1500 kPa was estimated as the available moisture content of each biochar sample.

3.2.4 Electrical conductivity

One gram of biochar from each feedstock i.e. rice straw, rice husk, and saw dust was weighed into a beaker and 20 mL of distilled water added, to give a biochar water ratio of (1:20). This ratio was used to ensure enough volume of supernatant for immersion of electrode. The mixture was then stirred several times for about 30 min and left to stand for about an hour to allow most of the suspension to settle and also for the suspension temperature to equilibrate with the temperature in the instrument room.

The electrical conductivity was then determined using the "Solu Bridge" electrical conductivity meter at cell constant K = 1.06 at 25 ^{0}C. The electrode was then rinsed with distilled water and then immersed into the partly settled suspension and the reading on the conductivity meter recorded.

3.2.5 pH in water

One gram of biochar (from each feedstock) rice straw, rice husk and saw dust was weighed into a beaker and 20 mL of distilled water added, to give biochar water ratio of (1:20). This ratio was used to ensure enough volume of supernatant for immersion of electrode. The mixture was then stirred several times for about 30 minutes and left to stand for about an hour to allow most of the suspension to settle and also for the suspension temperature to equilibrate with the temperature in the instrument room. The glass electrode pH meter- CG818, Schott Great was standardized using two solutions of pH 7 and 9. The electrode was then rinsed with distilled water and then immersed into the partly settled suspension and the reading on the pH meter recorded. The determination of pH of the samples was repeated using 1 M KCl solution according to the protocol outlined.

3.2.6 Total oxidizable carbon

The oxidizable carbon was determined using the wet oxidation method of Walkley and Black(1934). This method involves the reduction $Cr_2O_7^{2-}$ ion by the carbon and the unreduced $Cr_2O_7^{2-}$ measured by titration with ammonium ferrous sulphate.

Hundred milligrams of finely grained sieved biochar (0.5 mm) was weighed in triplicates into 500 mL Erlenmeyer flask. Ten mL of 1.0 M potassium dichromate (K_2Cr_2O7) followed by 10 mL of concentrated H_2SO_4 was added to the biochar. The flask was then swirled making sure that the solution was in contact with all the particles of the biochar and allowed to stand for about an hour. Two hundred mL of distilled water was added after which 7 mL of 85% orthophosphoric acid and few drops of Barium diphenyl-4 sulphonate indicator were added. The solution was then titrated against 0.5 M acidified ammonium ferrous sulphate solution to a green end point.

A standardization titration of the $K_2Cr_2O_7$ with the ferrous ammonium sulphate was done and the amount of organic carbon calculated by subtracting the number of moles of unreduced $K_2Cr_2O_7$ from the number of moles of $K_2Cr_2O_7$ present in the standardized titration. The concentration of oxidizable carbon in each of the samples was calculated indirectly from the number of moles of unreduced dichromate consumed by the ammonium ferrous sulphate.

3.2.7 Total nitrogen

Total nitrogen was determined by a modified Kjeldahl digestion method. The nitrogen in the sample was converted to ammonium by digestion with concentrated sulphuric acid using selenium as catalyst and addition of K_2SO_4 to raise the boiling point of the mixture. The ammonium formed was determined by distilling the digest with a strong alkali (40% NaOH) and titration with a standard acid.

Air dried biochar of 0.2 g was weighed in triplicates into Kjeldahl digestion flasks. The catalyst and K_2SO_4 were added followed by 5 mL concentrated H_2SO_4. The mixture was digested for about 30 minutes and the digest after cooling, transferred into a 100mL volumetric flask and made up to volume with deionized water. A 5 mL aliquot was then pipetted into a Markham distillation apparatus and 5mL of 40% NaOH added and rinsed with deionized water to about 100 mL. A 5 mL boric acid solution to which few drops of mixed indicator (0.13 g of methyl red + 0.666 of methylene blue dissolved in 100 mL of 95% ethanol) had been added were put into a conical flask to trap the liberated ammonia. The distillate was then back titrated with 0.01 M HCl solution. Similar procedure was adopted for a blank which had no biochar sample to account for traces of N if any, in the reagents and water used. The concentration of N in the biochar was estimated from the number of moles of HCl consumed in the reaction with ammonium borate formed when the ammonia was trapped in boric acid.

3.2.8 Total phosphorus

Total phosphorous was determined by digesting 0.2 g of biochar with 25 mL of a mixture of concentrated HNO_3 and 60% $HClO_4$ in the ratio of 1:1.5. Distilled water was added to the digest, filtered and made up to volume in a 100 mL volumetric flask with distilled water.

Phosphorus in the digest was determined as described by the Murphy and Riley (1962) method. An aliquot of 5 mL of the sample solution was taken into a 50 mL volumetric flask and a drop each of P-nitro phenol and 4 M ammonium hydroxide were added until a yellow colour developed. Then, 8 mL of a solution containing concentrated sulphuric acid, ammonium molybdate, potassium antimony tartrate, and ascorbic acid were added. The content was topped up to the 50 mL mark with distilled water. The concentration of phosphorus was then determined on a Philips' UV spectrophotometer at a wavelength of 712 nm. The P content of the

samples in triplicates was then read with the spectrophotometer, with which further calculations were made using the formula:

$$P\ (mg/kg) = \frac{(SP\ Reading) x Vol.of\ Extract}{Volue\ of\ aliquot\ x\ weight\ of\ Biochar} X \frac{10^6}{1000} \ldots\ldots\ldots \quad [1]$$

Where SP is sample reading

3.2.9 Available phosphorus

Available phosphorus was determined by the Olsen method (1965). One gram of biochar sample was weighed into an extraction bottle and 50 mL of sodium bicarbonate solution was added and shaken for 30 minutes on a mechanical shaker. The biochar-extractant mixture was filtered through a Whatman No.42 filter paper. A 10 mL aliquot was taken and 10 mL sulphuric acid (H_2SO_4) added and centrifuged at 3000 rpm for 15 minutes. The concentration of the P in each sample was then determined after colour development using the Murphy and Riley method as described in section 3.2.8. The intensity of the colour at a wavelength of 712 nm was measured with the spectrophotometer and recorded. The P was calculated using the formula in Section 3.2.8.

3.2.10 Exchangeable cations

A 2 g biochar was weighed into an extraction bottle and 50 mL of 1 M ammonium acetate (NH4OAc, pH 7) was added. The bottle was shaken in a mechanical shaker for one hour and the contents filtered through a Whatman No. 42 filter paper into clean empty bottles. Exchangeable calcium and magnesium in the extract were determined using the Atomic Absorption Spectrophotometer (AAS) with exchangeable Na and K being determined by flame photometry.

3.2.11 Total elemental analysis

Total elemental analysis of the three biochar samples were done by the wet digestion method. Fifty milligrams each of the three biochar materials which had been oven dried and ground was weighed into digestion vessels and wetted with a few drops of de-ionised water. Five millilitres of concentrated HNO_3 and 4 mL of 48% HF and 1.0 mL of HCl were added. The contents were put on a digestion block and digested slowly amidst intermittent swirling to ensure complete digestion when the solution became colorless.

Upon complete digestion, the digest was allowed to cool, de-ionised water added and decanted carefully and made up to volume in a 100 mL volumetric flask, capped and shaken thoroughly. The total concentration of Si, Fe, Zn, Cu, Pb, Co, Mn, Mg, and Ca levels were determined on a Perkin Elmer AAS.

3.3 Data Analyses

The various physico-chemical parameters of the biochar determined were subjected to analysis of variance to determine if differences existed among the three biochar samples.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Physical Properties

4.1.1 Particle Size distribution

The particle size distribution of the three biochar samples is presented in Table 4.1. The smallest size fractions of between 63 and 125 µm was 36.9%, 42.6% and 20.9%, respectively for the rice straw, rice husk and sawdust biochar types. It is also apparent that 53.8% and 51% of the size fraction is between 125 and 250 µm for the rice straw and the rice husk biochars, respectively. The saw dust biochar on the other hand had about 38% of its particles between 125 µm and 250 µm. The largest proportion of 63.7% of the saw dust biochar was in the coarser size regime of between 500 µm and 2500 µm. In that same coarse size regime of between 500 µm and 2500 µm, the rice straw and rice husk biochars had only 26.3% and 24.7% size fraction, respectively. In general, the saw dust can be said to be coarser than its rice counterparts.

Wood-based feedstocks generate biochars which have been found to be coarser and predominantly xylemic in nature, whereas biochars from crop residues such as cereal have a finer and more brittle structure (Sohi *et al*., 2009; Downie *et al.*, 2009). Saw dust is a byproduct of sawn logs from woody trees with high cellulose, hemicellulose, polyphenol and lignin contents whereas rice straw and husk are from herbaceous rice plants with lower lignin and polyphenol contents Attrition during the charring process will hence be higher in the rice based feedstocks (Cetin *et al.*, 2004). It is therefore, not surprising that the cereal based biochar types i.e. rice straw and rice husk are finer in texture than their saw dust counterpart.

The finer nature of rice husk and rice straw than the saw dust biochar has implication for agriculture. The rice based materials will have larger specific surface area which will result in more chemical reactive surfaces when amended to soils. The ability to hold and release nutrients will as a matter of consequence be greater.

Table 4.1. Particle size distributions of the three biochar types.

Particle Size (µm)	Rice straw	Rice husk	Saw dust
	----------% size distribution----------		
2500 µm	2.7	2.7	4.4
2000 µm	8.3	8.3	12.7
1000 µm	5.0	5.1	5.8
500 µm	10.3	8.6	40.8
250 µm	36.4	27.6	24.9
125 µm	17.4	23.5	13.1
90-63 µm	19.5	19.1	7.8

4.1.2 Bulk density

The bulk density values of the three biochar types are presented in Table 4.2. The rice straw biochar type has a statistically lower bulk density value of 0.19 Mg/m^3 than the rice husk and the saw dust. The rice husk and saw dust biochar types have similar bulk density values of 0.22 and 0.23 Mg/m^3, respectively. The lower bulk density of the rice straw than the rice husk could be due to the more fibrous nature of the straw than the husk. The fibrous straw with its more porous nature would be lighter with a concomitant lower density. In being amended to soils therefore, the rice straw biochar will be more prone to losses by wind and water.

Generally all the three materials are very light and therefore as soil amendment, will have to be incorporated and mixed very well with the soil to avoid losses through water and wind erosion. Surface application will not be ideal as they will float on water should the soil be irrigated.

4.1.3 Moisture content of the biochar

The capacities of the three biochar types to hold moisture at 33 kPa and 1500 kPa and their respective available moisture contents are provided in Table 4.3. At field capacity (FC), there

Table 4.2. Bulk density of the biochar types.

Biochar type	Mg/m^3
Rice Straw	0.19
Rice Husk	0.22
Saw Dust	0.23
LSD	0.01

Table 4.3. Moisture content of the three biochar types.

Biochar type	FC† (1500 kPa (%)	WP‡ (33 kPa)	AWC§
	----------(%)----------		
Rice Straw	8.92b	5.53b	3.39a
Rice Husk	7.70c	5.45b	2.22b
Saw Dust	9.85a	7.86a	1.99b
LSD	0.55	0.54	0.25

†FC = field capacity; ‡WP = Wilting point; §AWC = Available water.

Means followed by different letters are significantly different at p = 0.05.

are clear differences among the three biochar types in the amount of moisture they can hold. Moisture content at FC is in the order of saw dust (9.85%) >rice straw (8.92%) > rice husk (7.70%). At wilting point (WP), however, the rice based biochar types had similar moisture contents of between 5.45% and 5.53% with the saw dust biochar type having the highest

moisture content of 7.86%. Under severe drought conditions, therefore, application of saw dust biochar to soil should be the preferred choice.

It is worthy of note that despite the superior nature of saw dust biochar in terms of the volume of moisture it can hold at both FC and WP, it is not the best when availability of moisture to crops is of prime interest. The rice straw biochar instead, has the highest available moisture content of 3.39% which is almost 1.7 times higher than that of the saw dust. For water availability to crops therefore, rice straw ought to be the choice for amendment. Perhaps the more porous nature of the straw imparts onto the material, the ability to hold more water for plant usage. From Table 4.3 it is also realized that there is no difference statistically between saw dust and rice husk in terms of moisture availability.

4.2 Chemical properties

Analytical data on selected chemical properties of the biochar materials are presented in Table 4.4. Discussion of the individual properties made in the sub-sections below.

4.2.1 pH

The pH of the biochar types in both water (pH_w) and KCl (pH_{KCl}) is shown in Table 4.4. In both media, pH was strongly alkaline with highest value of 10.5 in the rice straw biochar type. In water, the rice husk biochar had a neutral pH of 6.8 which increased to a slightly alkaline regime 8.12 in KCl. The saw dust on the other hand, in water recorded a neutral pH of 7.3

Table 4.4. Some chemical properties of the three biochar types.

Biochar Type	EC(dS/cm)	pH_W	pH_{KCl}	*AP(mg/kg)	†TP(ppm)	‡TN(g/kg)	±TOC(g/kg)	C/N
Rice Straw	3.57**a**	10.50	10.51	1375**a**	4864**a**	1.15**a**	191.97**a**	166.9
Saw Dust	2.56**b**	7.31	8.60	89**b**	363**c**	0.74**c**	115.80**c**	156.0
Rice Husk	0.18**c**	6.81	8.12	126**b**	549**b**	0.96**b**	136.23**b**	141.9
LSD	0.034			109.7	12.9	0.05	5.782	

Means followed by different letters are significantly different at p = 0.05

*AP = Available Phosphorus

†TP = Total Phosphorus

‡TN = Total Nitrogen

±TOC = Total Organic Carbon

which changed to a slightly alkaline pH of 8.6 in KCl. The change in pH values, that is ΔpH = pH KCl –pH H_2O are positive 1.29 and 1.31, respectively for the saw dust biochar and rice husk biochar. The positive ΔpH of the saw dust and rice husk biochar types is an indication that as variable charged materials, the two have net positive charges (Evangelou, 1998). Thus the anion exchange capacities of saw dust and rice husk biochar are likely to be higher than that of the rice straw biochar type. Adsorption of anions such as nitrates, phosphates and sulphates nonspecifically, for later release to crops may be enhanced should the two materials be added to highly weathered and sandy soils. The neutral pH of the two materials is an added advantage as they are likely to make P one of the most limiting nutrients in tropical soils more available. The rice husk and the saw dust biochar types with their net positive charges could also be used as chemical filters to remove anionic contaminants from the environment. Incorporation of these two materials to soil could minimize leaching of nitrates with a decrease in groundwater pollution.

4.2.2 Electrical conductivity

The electrical conductivity (EC) values of the three biochar types follow similar trends as the pH. The rice straw biochar has the highest EC value of 3.57 dS/m with the saw dust biochar being 2.56 ds/m and the rice husk biochar the lowest EC of 0.18 dS/m. From the EC values, it is clear that all the materials are not saline. However, the rice straw biochar which has the highest EC of 3.57 dS/m and pH of 10.5 is approaching the critical limit of 4 dS/m for salinity (Evangelou, 1998). It is therefore, advisable for this material not to be used in soils with moderate to high sodium content as it may lead to salinization of the soils. Caution must be exercised in using the rice straw biochar on near to neutral soils as frequent application may lead

to salinity build up. The saw dust and rice husk biochar types could be used on near to neutral soil with the rice straw biochar being used as amendment of acidic soils where solubility of Na and salinity are not likely to be high.

4.2.3 Total oxidizable organic carbon

The total oxidisable organic carbon of the three materials as shown in Table 4.4 is in the order of rice straw > rice husk > saw dust. The 191.97 g/kg, 136.23 g/kg and 115.8 g/kg, respectively for the rice straw, rice husk and saw dust biochar is in consonance with organic carbon contents obtained by Chan and Xu (2008) for a variety of biochar materials.

The proportions of hemi-cellulose, cellulose and lignin content determine the ratios of volatile carbon (in bio-oil and gas) and stabilized carbon (biochar) in pyrolysed products. Feedstocks with high lignin content produce the highest biochar yields when pyrolysed at moderate temperatures, approximately 500 °C (Fushimi *et al*., 2003; Demirbas, 2006). It was, expected that the saw dust biochar which came from woody plant species and is more lignified would have the highest organic carbon content. The higher significant levels of organic carbon in the two rice biochar types than their saw dust counterpart could be as a result of the lower kiln temperature of 350 ^{o}C used in the carbonization process for the three materials.

Thermal degradation of cellulose between 250 and 350 ºC results in considerable mass loss in the form of volatiles, leaving behind a rigid amorphous C matrix. As the pyrolysis temperature increases, so does the proportion of aromatic carbon in the biochar, due to the relative increase in the loss of volatile matter (initially water, followed by hydrocarbons, tarry vapours, H_2, CO and CO_2), and the conversion of alkyl and O-alkyl C to aryl C (Baldock and Smernik, 2002). Above 600 ºC, carbonization becomes the dominant process. Carbonization is

marked by the removal of most remaining non-C atoms and consequent relative increase of the C content, which can be up to 90% (by weight) in biochars from woody feedstock's (Antal and Gronli, 2003; Demirbas, 2004). It, therefore, stands to reason that the rice straw and the rice husk biochar types have higher organic carbon contents than the saw dust type as they are less lignified and hence must have lost most of their respective non-carbon contents with a concomitant increase in carbonisation by the 350 ^{o}C kiln temperature employed.

The rice straw biochar being highest in oxidizable carbon implies that it should be the preferred material among the three for carbon sequestration at a charring temperature of 350 ^{o}C. This is because the rice straw biochar would convert a lot more atmospheric carbon into a more stable form of carbon than the rice husk and saw dust biochar types.

4.2.4 Total nitrogen

The total nitrogen contents of the three biochar types were 1.15 g/kg, 0.96 g/kg and 0.74 g/kg for rice straw, rice husk and saw dust, respectively. Statistically, the saw dust biochar type was the lowest in N content and this agrees with findings of Fushimi et al. (2003) and Demirbas (2006) who noted that biochar types from woody plant species have low N contents.

The relatively higher total nitrogen value observed for rice straw and rice husk compared to saw dust biochar type might be due to the more plant uptake of N from application of nitrogenous fertilizers which is common in rice cultivation. The higher total N in the rice straw biochar than the rice husk biochar is a confirmation of the fact that more N is needed for vegetative growth than seed formation.

The C:N ratios of the three biochar types as presented in Table 4.4 are 166.9 for the rice straw, 142 for the rice husk biochar and 156 for the saw dust biochar. On application to soils, the

rice straw biochar type would have the highest stability and hence sequester more carbon because degradation would be slowest. The rice husk biochar type at a charring temperature of 350 ^{o}C would have the highest degradability and hence the least stable on application to soils.

4.2.5 Total and available phosphorus

The total phosphorus (TP) concentration of the e three biochar shows that rice straw biochar had the highest TP accumulation of 4864 mg/kg with the rice husk biochar accumulating only 549 mg/kg TP. The lowest TP content of 363 mg/kg was observed in the saw dust biochar. Even though the straw and husk came from the same rice plant, the straw biochar has strikingly a higher TP content which is almost 9 times more than the TP in rice husk biochar. Phosphorus is utilized by cereals in the strengthening of structural tissues, particularly straws (Brady and Weil, 2002). It is therefore, not surprising that the rice husk biochar has the highest accumulation of TP. The exceptionally high TP in the rice straw biochar type could also be in indication that the rice plant from which the material was harvested may have received heavy dose of P application.

Available P concentration in the three biochar types also followed a similar pattern as total P with the rice straw having the highest available P content of 1375 mg/kg. In fact this available P level in the rice straw which is 28.26% of the total P is 2.5 and almost 3.8 times more than the total P in the rice husk and saw dust biochar types, respectively. The high available P contents of the rice husk biochar are as a result of its high TP.

Most tropical soils are highly weathered and dominated by sesquioxides and kaolinite. Consequently P availability is low. Addition of rice straw biochar with its high pH high organic carbon, TP and available P contents, especially to acidic tropical soils holds promise for P availability. The high pH will reduce the acidity and with the high organic carbon, high total and

available P, P availability could be enhanced. It may be interesting to conduct an experiment to ascertain the combined effect of application of rice straw biochar and inorganic P fertilizers on productivity of highly weathered acidic P deficient soils.

4.2.6 Exchangeable bases

The concentration of the exchangeable bases Ca, Mg, K and Na in the three biochar types are presented in Table 4.5. The highest exchangeable Ca and Mg levels of 7.63 cmol/kg and 1.73 cmol/kg, respectively was observed in the rice straw biochar. These high levels of the two exchangeable cations may account for the strikingly high pH of the material. The sum of Ca and Mg in the saw dust biochar (1.91 cmol/kg) was higher than that of rice husk biochar (1.22 cmol/kg) explaining the higher pH of the saw dust than the rice husk biochar.

The Na levels were exceptionally high in the rice straw (30 cmol/kg), more than 16.6 times and 22.7 times the levels found in the rice husk and saw dust biochar types, respectively. The very high level of exchangeable Na in the rice straw accounts for its high EC of 3.56 dS/m. The higher exchangeable Na in the saw dust biochar than the rice husk biochar is also in consonance with its higher EC. In general, the sum of bases was highest in the rice straw followed by the saw dust biochar with the lowest sum of bases in the rice husk biochar and this trend ties in well with the pH values of the three biochar materials.

4.2.7 Total elemental analysis

The total Ca, Mg, Fe, Zn, Cu, Pb, Co and Si concentrations in the three biochar types are shown in Figure 4.1. From the figure, it is clear that the concentration of total basic cations (Ca

Table 4.5. Exchangeable bases in the three biochar types.

Biochar Type	Ca	Mg	K	Na	Sum of Bases
----------cmol/kg----------					
Rice Straw	7.63a	1.73a	1.48a	30a	40.84
Rice Husk	0.36c	0.86b	0.78c	1.32c.	3.32
Saw Dust	1.23b	0.68b	1.13b	1.81b	4.85
LSD		0.15	0.66	0.06	0.12

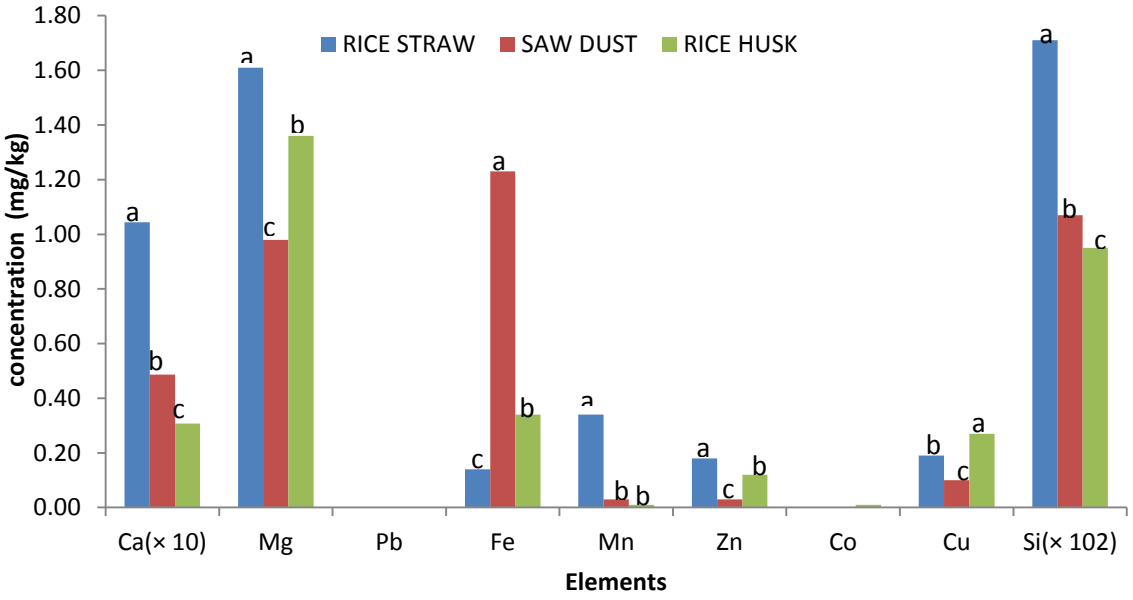

Figure 4.1. Concentration of the various total elements in the three biochar types.

and Mg) are highest in the rice straw with Ca being highest with a content of 10.4 mg/kg. The Ca content in the straw is more than twice that found in the saw dust and more than thrice the content in the rice husk biochar. The high Ca and Mg contents of the rice straw biochar also explain the high exchangeable forms of the cations in the material (Table 4.4).

The high levels of total basic cations, particularly Ca may, in part, account for the very high pH of 10.5 in both water and KCl observed for the rice straw biochar. The high total Ca and Mg content of the rice straw biochar coupled with its high pH makes the material a good choice for use as a liming material. The high level of Ca may exchange for Al at the exchange site of acid soils thereby decreasing exchangeable acidity.

The concentration of heavy metals Cu, Zn and particularly Co and Pb are very low in all the three samples with concentrations below 0.5 mg/kg. These very low levels of the heavy metals make the three biochar materials very safe for use as soil amendments without any toxicity hazards. The biochar materials all have pHs between 6.8 and 10.5. These neutral to strongly alkaline pH may explain the trace to very low levels of heavy metals in the biochar materials.

The Fe concentration in the saw dust biochar of 1.23 mg/kg was the highest with the rice straw having the lowest concentration of 0.14 mg/kg. The very low level of Fe in the rice straw biochar is as a result of its high alkaline pH. Iron is an acidic cation and hence will not predominate in alkaline medium.

The silicon concentration of the biochar materials were in the order of rice straw biochar > rice husk > saw dust. Just as was observed for Ca, the rice straw had the highest Si content of 170. 8 mg/kg Si which is 63 mg/kg and 76 mg/kg higher than the contents in the rice husk and saw dust biochar types. Silicon is a nutrient in rice production and this explains the relatively higher levels of the rice biochar types than their saw dust counterpart. The higher Si content of the rice straw may be due to the nutrient being absorbed by the rice plant in addition to Ca and P for strengthening of the skeletal stem tissue (Purseglov, 1972).

The pK1 of silicic acid (H_4SiO_4) is between 9.6 and 9.8 (Nartey *et al.*, 2000). This pK value is just 0.7 pH units lower than the pH of the rice straw biochar. A large proportion of Si in the rice straw biochar when applied to the soil may therefore be in the conjugate base form, $H_3SiO_4^-$. This species of Si in addition to the acid, H_4SiO_4 have higher abilities to be adsorbed onto surfaces of sesquioxides and kaolinite than the available plant forms of P, $H_2PO_4^-$ and HPO_4^{2-} (Tisdale *et al.*, 2002) Addition of rice straw to highly weathered tropical soil may therefore enhance P availability. The presence of the H_4SiO_4 and its conjugate base $H_3SiO_4^-$ in the rice straw which has a high TP content of 4864 mg/kg may account for the very high available P content of 1375 mg/kg.

4.3 Suitability for liming

An agricultural liming material has been defined as any substance that can supply Ca and Mg as cations in combination with carbonates, hydroxyls, oxides and silicates as anions (Brady and Weil, 2002). From the total analyses, it is seen that the rice straw biochar has the highest concentrations of Ca (10.44 mg/kg,) Mg (1.61mg/kg) and Si (170.8 mg/kg). The material also has a high pH of 10.5 in both water and KCl. It is, therefore clear that the rice straw is a suitable biochar for use as an agricultural liming material. Considering the readily availability of rice straw and some cheap improvised local methods of biochar production being employed, the use of rice straw biochar may be the panacea to the acidic problems of highly weathered tropical soils. Experiments will, however, have to be conducted to calculate the $CaCO_3$ equivalent of the rice straw biochar. This is to help estimate the amount of the material to apply and evaluate its competitiveness in terms of cost in comparison with the traditional liming materials.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATION

The work has shown that there are differences in the physical and chemical properties when rice husk, rice straw and saw dust are pyrolysed at a temperature of 350 ^{o}C. It is apparent from the study that over 70% of the rice straw and the rice husk biochars were in the very small size fraction of between 63 µm and 250 µm. The saw dust biochar on the hand had the proportion of 63.7% of the material in the coarse size regime of between 500 µm and 2500 µm.

The bulk density values of the three biochar types were very low ranging between 0.19 Mg/m^3 and 0.23 Mg/m^3. Generally all the three materials are very light and therefore as soil amendment, will have to be incorporated and mixed very well with the soil to avoid losses through water and wind erosion. Surface application will not be ideal as they will float on water should the soil be irrigated.

Moisture content at field capacitywas in the order of saw dust (9.55%) > rice straw (8.92%) > rice husk (7.70%). At wilting point (WP), however, the rice based biochar types had similar moisture contents of between 5.45% and 5.53% with the saw dust biochar type having the highest moisture content of 7.86%. Under severe drought conditions, therefore, application of saw dust biochar to soil should be the preferred choice. The rice straw biochar had the highest available moisture content of 3.39% which was almost 1.7 times higher than that of the saw dust making rice straw the preferred choice of material in terms of water availability to crops.

There were significant differences in pH among the three biochar types with the rice straw recording the highest value of 10.5 in both water and KCl as a result of its very high contents total Ca of 10.44 mg/kg and exchangeable Ca of 7.63 cmol/kg in addition to a high Si concentration of 170.8 mg/kg. The saw dust had a pH of 8.12 in water with the rice husk

recording a neutral pH of 6.8 in water. The change in pH values, that is ΔpH = pH KCl –pH H_2O were positive for the rice husk and saw dust biochar types indicating that the two materials could be used as sorbents for anions. The rice straw biochar also had the highest EC value of 3.57 dS/m due to its high exchangeable Na concentration.

The total oxidisable organic carbon of 191.97 g/kg was highest in the rice straw biochar with the rice husk sequestering 136.23 g/kg and saw dust 115.8 g/kg at a kiln temperature of 350 ^{o}C. The saw dust biochar type was the lowest in N content. On account of the C:N ratios of 166.9 for the rice straw, 142 for the rice husk biochar and 156 for the saw dust biochar the rice straw biochar type would be the most stable and hence sequester more carbon.

Total and available P were particularly high in the rice straw biochar with the material accumulating respective levels of 4864 mg/kg and 1375 mg/kg. The high available P in the rice straw which was as a result of the high Si content of the material was found to be 2.5 and almost 3.8 times more than the total P in the rice husk and saw dust biochar types, respectively.

The concentration of heavy metals Cu, Zn and particularly Co and Pb are very low in all the three samples with concentrations below 0.5 mg/kg due to the near neutral to strongly alkaline pH regime of all the three biochar types. These very low levels of the heavy metals make the three biochar materials very safe for use as soil amendments without any toxicity hazards.

The study showed that the rice straw biochar has the highest concentrations of Ca (10.44 mg/kg,) Mg (1.61 mg/kg) and Si (170.8 mg/kg). The material also has a high pH of 10.5 in both water and KCl and therefore has the potential of being used as an agricultural liming material.

5.1 Recommendations

It is recommended that further studies be carried out in the laboratory to determine the $CaCO_3$ equivalence of the rice straw biochar. This is to help estimate the amount of the material to apply and evaluate its competitiveness in terms of cost in comparison with the traditional liming materials. The study should also be extended to the field thereafter to ascertain the efficacy of the rice straw biochar type as a liming material and also its effect on soil productivity by evaluating the growth and yield of an added test crop.

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APPENDIX

Analysis of variance

Variate: AP_mg_kg

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	85119.487	42559.743	38151.16	<.001
Residual	6	6.693	1.116		
Total	8	85126.180			

Analysis of variance

Variate: Ca

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	88.496257	44.248128	29571.04	<.001
Residual	6	0.008978	0.001496		
Total	8	88.505235			

Analysis of variance

Variate: Co

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	4.067E-05	2.033E-05	91.50	<.001
Residual	6	1.333E-06	2.222E-07		
Total	8	4.200E-05			

Analysis of variance

Variate: Cu

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	4.250E-02	2.125E-02	3608.89	<.001
Residual	6	3.533E-05	5.889E-06		
Total	8	4.254E-02			

Analysis of variance

Variate: EC_S_cm

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	22435162.2	11217581.1	37860.58	<.001
Residual	6	1777.7	296.3		
Total	8	22436939.9			

Analysis of variance

Variate: Fe

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	2.01597156	1.00798578	11022.93	<.001
Residual	6	0.00054867	0.00009144		
Total	8	2.01652022			

Analysis of variance

Variate: K

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	0.735022	0.367511	351.87	<.001
Residual	6	0.006267	0.001044		
Total	8	0.741289			

Analysis of variance

Variate: Mg

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	0.598627	0.299313	41.73	<.001
Residual	6	0.043033	0.007172		
Total 8 0.641660					

Analysis of variance

Variate: Mn

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	0.2038136	0.1019068	693.77	<.001
Residual	6	0.0008813	0.0001469		
Total	8	0.2046949			

Analysis of variance

Variate: Na

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	1.618E+03	8.088E+02	2.443E+05	<.001
Residual	6	1.987E-02	3.311E-03		
Total	8	1.618E+03			

Analysis of variance

Variate: TN_g_kg

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	1.759E-03	8.796E-04	1077.07	<.001
Residual	6	4.900E-06	8.167E-07		
Total	8	1.764E-03			

Analysis of variance

Variate: TOC_g_kg

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	0.9325087	0.4662543	556.68	<.001
Residual	6	0.0050253	0.0008376		
Total	8	0.9375340			

Analysis of variance

Variate: TP_mg_kg

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	1538.7089	769.3544	6294.72	<.001
Residual	6	0.7333	0.1222		
Total	8	1539.4422			

Analysis of variance

Variate: Zn

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	3.458E-02	1.729E-02	4322.11	<.001
Residual	6	2.400E-05	4.000E-06		
Total	8	3.460E-02			

Analysis of variance

Variate: pHKCl

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	23.3692667	11.6846333	36262.66	<.001
Residual	6	0.0019333	0.0003222		
Total	8	23.3712000			

Analysis of variance

Variate: pHW

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Biochar_Type	2	9.5524667	4.7762333	39078.27	<.001
Residual	6	0.0007333	0.0001222		
Total	8	9.5532000			