UNIVERSITY OF CAPE COAST

EFFECTS OF CORN COB BIOCHAR ON THE PHYSICAL, CHEMICAL AND BIOLOGICAL PROPERTIES OF A HAPLIC ACRISOL, GHANA

BY

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DECLARATION

Candidate's Declaration

I hereby declare that this thesis is the result of my own original research and that no part of it has been presented for another degree in this University or elsewhere.

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Supervisors' Declaration

We hereby declare that the preparation and presentation of the thesis were supervised in accordance with the guidelines on supervision of thesis laid down by the University of Cape Coast.

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ABSTRACT

In this study, the effect of corn cob biochar on the soil physico-chemical and biological properties were investigated on a highly weathered tropical sandy loam. The study comprised four treatments with four replicates established in a randomized complete block design. Biochar was applied in two batches; corn cob biochar was first incorporated at rates of 10 t ha^{-1} (BC-10), 20 t ha^{-1} (BC-20), and 20 t ha^{-1} + triple super phosphate (BC-20+P) to study its effects on aggregate characteristics, water retention, gas transport and pore structure characteristics. Minimally disturbed soil samples from each of the 16 plots were sampled from the plots treated with the first batch of biochar at a depth of 0-20 cm. Metal core samplers were used for intact soil sampling. Incorporation of biochar decreased the tensile strength of the large aggregates (4–8 mm and 8–16 mm), but increased same in the smaller aggregates (1–2 mm). Soil friability and workability were significantly improved in the BC-20 and BC-20+P treatments. Soil water retention was measured within a pF range of 1 to 6.8. Application of 20 t ha^{-1} led to significant increase in soil water retention. The second batch had 50% of the first batch added to the respective initial biochar treatments. Thus, the total biochar application rates were 15 t ha^{-1} (BC-15), 30 t ha^{-1} (BC-30), and 30 t ha^{-1} + triple super phosphate (BC-30+P). Soil samples were randomly collected from 20 different spots of the plots treated with the second batch of biochar at 0 to 20 cm depth and the bulked soil samples from each treatment were analyzed. Biochar amendment resulted in a significant increase in the carbon lability index in the labile C pools. The carbon and nitrogen pool indices, as well as carbon and nitrogen management indices were increased with biochar amendment, especially in the BC-30 and BC-30+P treated plots. Incorporation of biochar at 30 t ha^{-1} had significant effects on soil microbial community composition, diversity and total PLFA. Dehydrogenase and urease enzyme activities increased with the increase of biochar application rate. In perspective, incorporation of biochar improved the soil physical, chemical and biological quality of the soil. This was manifested in the enhanced generic soil quality index calculated based on the integration of all the measured properties in the soils treated with the second batch of biochar application.

KEY WORDS

Aggregate characteristics

Gas transport

Labile carbon and nitrogen

Phospholipid fatty acids

Soil enzymes

Water retention

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DEDICATION

To my mother, wife and kids.

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LIST OF ABBREVIATIONS AND ACRONYMS

Notation	Name	Dimension
ASD	aggregate size distribution	
a_s	cross-sectional area of the soil	$[L^2]$
AC	active carbon	
BC	biochar	
BR	basal respiration	
CLi	carbon lability index	
CMI	carbon management index	
CPI	carbon pool index	
C_{PT}	convective percolation threshold	$[L^3\ L^{-3}]$
CT or CTRL	control	
d	equivalent pore diameter	[L]
DH	degree of humification	
D_o	diffusion coefficient in free air	$[L^2\ T^{-1}]$
D_p	soil gas diffusion coefficient	$[L^2\ T^{-1}]$
D_{PT}	diffusion percolation threshold	$[L^3\ L^{-3}]$
D_p/D_o	relative diffusion coefficient	
E	rupture energy	
ESP	mass specific rupture energy	
EC	electrical conductivity	
FA	fulvic acid	
FAME	Fatty Acid Methyl Ester	
GAB	Guggenheim-Andersen-de Boer	
GMWD	geometric mean weight diameter	

HA	humic acid	
HI	humification index	
HR	humification ratio	
IS	Instability index	
k_a	air permeability	$[L^2]$
kY	soil friability index	
Li	lability index	
M_g	amount of diffusing gas	
MBC	microbial biomass carbon	
MBN	microbial biomass nitrogen	
NLi	nitrogen lability index	
NMI	nitrogen management index	
NPI	nitrogen pool index	
OC	organic carbon	
p_a	air pressure	$[M\,L^{-1}\,T^{-2}]$
PCA	principal component analysis	
PLFA	phospholipid fatty acid	
PMC	potentially mineralizable carbon	
PO	pore organization	
POC	particulate organic carbon	
PON	particulate organic nitrogen	
qCO_2	specific maintenance respiration	
qR	respiratory quotient	
Q	volumetric flow rate	$[L^3\,T^{-1}]$
RDA	redundancy analysis	

SA	specific surface area	$[L^2]$
Salt-C	potassium sulfate field moist soil extractable carbon	
Salt-N	potassium sulfate field moist soil extractable nitrogen	
SB Q_{index}	soil biological quality index	
SC	structural coefficient	
SC Q_{index}	soil chemical quality index	
SI	stability index	
SOC	soil organic carbon	
SP Q_{index}	soil physical quality index;	
SQ_{index}	soil quality index	
TEC	total exchangeable carbon	
WDC	water dispersible clay	
MW-C	potassium sulfate microwaved field moist soil extractable carbon	
MW-N	potassium sulfate microwaved field moist soil extractable nitrogen	
MWD	mean weight diameter	
NMI	nitrogen management index	
W	soil workability	
WsMa	water stable macro-aggregates,	
WsMi	water stable micro-aggregates.	
x	distance [L] in the flow direction,	
Y	aggregate tensile strength	

Y_A	characteristic aggregate tensile strength	
ε	volumetric soil air content	$[L^3\ L^{-3}]$
f_g	air density	$[L\ T^{-1}]$
η	air viscosity	$[M\ L^{-1}\ T^{-1}]$,
ρ_b,	bulk density	$[M\ L^{-3}]$
Φ	total porosity	$[L^3\ L^{-3}]$
θ_p	plant available water content	$[L^3\ L^{-3}]$
Ψ	soil matric potential	$[F\ L^{-2}]$

CHAPTER ONE

GENERAL INTRODUCTION

1.1 Background and justification

In tropical regions, particularly sub-Saharan Africa (SSA), the problems which limit crop production including soil and water constraints remain unchanged. Biochar application for soil quality improvement is a relatively new concept in Ghana. Therefore, it is worthwhile to assess the impact of biochar on soil quality.

In the wake of rapid population growth and growing economies, topical issues including soil degradation, poor yields, food insecurity, climate change and energy demand necessitate identification and development of innovative ideas of sustainable management of farm lands. Expectations for agricultural soils to support plant growth and increase yields, whiles sequestering carbon (C) and producing biofuels are challenged by incessant heavy demands of the projected population increases (United Nations, 2011). According to FAO (2011), approximately 1 in 7 people are already food insecure. From the perspective of food production, the term 'food insecurity' simply implies to an urgent need to safeguard and effectively manage one of the most valuable resources in the world, "the soil".

Generally, most soils in Ghana are highly weathered and very susceptible to erosion. These weathered red soils are typical of similar highly weathered soils that occur throughout southern China (Zhang et al., 2017), tropical and sub-tropical South America, most parts of Africa and South East Asia. Therefore, if the weathered and degraded soils of Ghana can be successfully restored, managed and utilized for enhanced crop production, it would have wider implications for enhanced crop production in other countries.

Soils in the humid tropics have high productivity potential. However, the long-term inappropriate management of these soils has caused severe physical and chemical degradation, with a subsequent resultant effect on yields. High soil acidity (low pH), depletion of soil organic matter, soil erosion and deterioration in soil structure are the major degradative processes. To effectively restore and improve the physical and chemical fertility of these soils, and sustain arable cropping systems, environmentally sound and cost-effective soil management strategies need to be implemented to forestall further degradation of thc soils. Quite recently, considerable attention has been focused on the restoration and management of soil organic matter and soil structure in degraded soils worldwide. Degraded red soils of the humid tropics could be greatly ameliorated through increasing the content of organic carbon (C) (Du, Zhao, Wang, & Zhang, 2017) and improving soil aggregation. Since the launching of the Freedom from Hunger campaign by the FAO iin the early 1960s, maintainance of soil fertility through the use of imorganic fertilizers has now been rendered unsustainable due to its increasing cost. The use of organic wastes to improve and maintain soil fertility has been long emphasized to improve soil productivity.

Direct incorporation of plant residues into these soils may only have short-term impacts due to the relatively fast decomposition rate of fresh plant-derived organic matter in soils of the humid tropics. Accordingly, many scientists have recommended the conversion of crop residues and other agricultural waste products to biochar as a strategy to enhance the stock of soil organic matter (Li et al., 2016) to restore the fertility status of degraded soils, with multiple benefits for soil quality, enhanced crop yield and mitigation of greenhouse gases (Lehmann & Joseph, 2015).

Biochar is highly recalcitrant due to its high aromaticity and can sequester C for very long periods (Domingues et al., 2017; Qadeer et al., 2017). Therefore, application of biochar to soils as an amendment can be a potential pathway to improve and increase native soil organic carbon (SOC) and black C stabilization in cropping systems. The effect of corncob biochar application on aggregate-associated C concentration in an experimental field was studied by (Zhang et al., 2017). Their experiment lasted for a period of twelve months, and they observed a substantial accumulation of carbon in large macro aggregates, implying that biochar-derived C can be physically protected within these aggregate sizes. Many authors have studied the effect of biochar application on SOC decomposition in their quest to find solutions for enhancing soil C sequestration (Wang, Xiong, & Kuzyakov, 2016; Yang, Zhao, Gao, Xu, & Cao, 2017). That notwithstanding, previous studies have shown that biochar may both suppress and stimulate native SOC decomposition (Wang et al., 2016; Luo, Lin, Durenkamp, Dungait, & Brookes, 2017).

In this study, corn cob was pyrolyzed to produce corn cob biochar. In Ghana, more corn is produced annually than any other grain. After harvesting, residues such as corn cobs, corn husks, and stovers are either left on the farms to dry after which they are set ablaze yielding smoke-related environmental consequences. A better approach to solving this environmental challenge is to pyrolyze and convert these crop residues to biochar for subsequent application to soil. This approach offers not only an attractive solution to reducing air pollution from the burning of the corn residues, but it also promotes climate smart agriculture, and therefore serves as a favorable agricultural sustainability model for reutilizing crop residues. It also serves as a critical alternative strategy for improving waste management especially in Ghana.

1.2 Objectives

The main objective of the study was to assess the impact of corn cob biochar additions on the physico-chemical and biological properties of weathered tropical soil.

The specific objectives were to:

- determine the effects of biochar on aggregate characteristics strength, water retention and gas transport parameters in a biochar amended soil
- assess the impact of biochar on soil microbial community structure and diversity through phospholipid fatty acid profiling
- assess the impact of biochar application on soil carbon and nitrogen pools, as well as C and N management indices
- develop soil quality index following corn cob biochar application

The proposed project highlighted the significance of biochar application on the properties of a highly weathered tropical soil and soil quality that will help in a comprehensive soil management towards improved soil fertility and productivity. This will go a long way to improve agricultural production, enhance food security and improve the living standard of smallholder farmers living in rural areas where food production is predominantly their major source of income and livelihood. Extreme poverty and hunger will be reduced if agricultural production is enhanced. This PhD dissertation research may potentially contribute to ensuring sound soil management practices which may help in restoring the productivity and fertility status of the highly weathered soils in Ghana.

1.3 Hypotheses

The following hypotheses were tested:

- Hypothesis 1: Application of biochar improves the physical fertility of soils by increasing aggregate characteristics strength, water retention and pore structure characteristics.
- Hypothesis 2: Incorporation of biochar increases soil microbial biomass, microbial C and N, diversity and total phospholipid fatty acids.
- Hypothesis 3: Addition of biochar to soils increases microbial C and N pools as well as the quality of total organic carbon.

1.4 Dissertation outline

This thesis is organised in eight chapters. Chapter 1 comprises the background and justification as well as the objectives and the hypotheses of the study. Chapter 2 gives a general overview of some information by some authors (literature review) that is relevant to this study. Chapter 3 presents the site description, preparation and application of treatments, sampling and the general laboratory methods. Chapter 4 starts the discussion with the effect of biochar on soil physical properties. This chapter looks at how corn cob biochar affects aggregate characteristics of a tropical sandy loam. Chapter 4 further discusses the gas phase (pore size distribution) and soil moisture characteristics in the wet and dry regions of the soil moisture characteristics curve. The chapter further explains how corn cob biochar affects diffusive and convective gas flow. Chapter 5 focuses on how corn cob biochar affects soil biological and chemical properties. The chapter explains the effects of corn cob biochar on carbon and nitrogen labile pools, as well as carbon and nitrogen management and lability indices. Chapter 6 presents the effects of biochar on soil enzymes (urease and dehydrogenase enzyme activities) and microbial properties. The chapter further explains how microbial community structure, abundance and diversity are affected by corn cob biochar. Chapter 7 finalises the synthesis between the various experimental chapters, where a generic soil quality index is calculated based on all the measured soil properties (physical, chemical and biological) to elucidate the overall effect of corn cob biochar on the quality of a highly weathered soil of the humid tropics. The summary, conclusions and recommendations for further research are addressed in chapter 8.

There are two published papers (Appendix B) and three published conference posters (Appendix C) to support this thesis.

CHAPTER TWO

LITERATURE REVIEW

2.1 What is Biochar?

Biochar as a carbon-rich product made from the pyrolysis of biomass under oxygen-limited conditions and relatively low temperatures (Lehmann & Joseph, 2015). Owing to its inherent properties, scientific consensus exists that incorporation of biochar into soils can sustainably sequester carbon (C) and improve ancillary soil functions. Weng et al., (2017) describe biochar as a C-rich organic material produced during slow exothermic decomposition of biomass at temperatures ≤700 °C under zero oxygen or low oxygen conditions.

The use of biochar as a soil amendment has been suggested as a potential means to concomitantly improve soil functions and reduce emissions of greenhouse gases that would otherwise deplete the ozone layer, by converting a portion of biomass C into stable carbon fraction that has carbon sequestration value (International Biochar Initiative, 2012). The peculiar characteristics and usability of biochar depend largely on the feed stock used and also the pyrolysis conditions, such as temperature, time, heating rate, and level of oxygen (Calvelo Pereira et al., 2011). The by-products of pyrolysis of the biomass are biochar, syngas and bio-oil (Figure 1). These by-products are all potentially valuable; whereas the syngas and the bio-oil can be used as fuel, the biochar can be used as soil additive (Hansen et al., 2015).

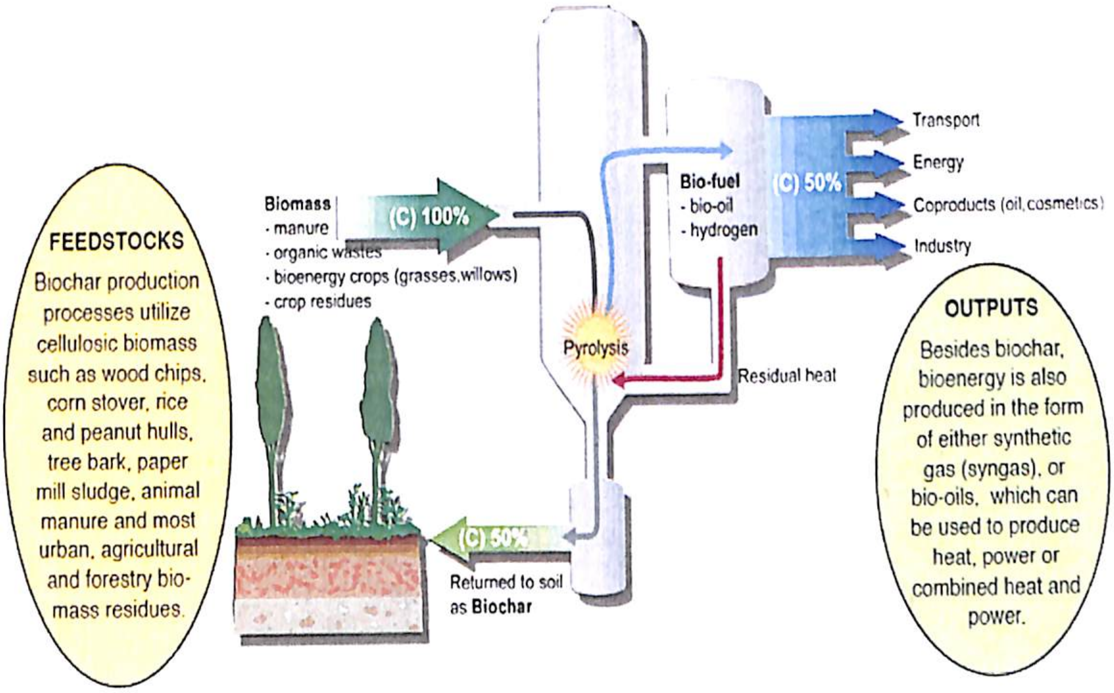


Figure 1: Biochar production process adapted from International Biochar Initiative (2012).

Biochar can be produced from a wide range of feedstock types such as woody materials, e.g., pine chips (Ronsse, van Hecke, Dickinson, & Prins, 2013); agricultural wastes, e.g., olive husk, corn cob, peanut hulls, and crop residues (Llorach-Massana, et al., 2017); green waste (Van Zwieten et al., 2010); animal waste (Lin et al., 2017); paper mill waste (Van Zwieten et al., 2010); and sewage sludge (Arazo, Genuino, de Luna, & Capareda, 2017). However, the pyrolysis temperature has an enormous effect on the stability of C in biochar than with the type of feedstock (Calvelo Pereira et al., 2011).

2.1.1 Properties of biochar

2.1.1.1 Chemical structure and surface characteristics

The arrangement of C in pyrogenic compounds formed during the thermal degradation process gives biochar its molecular structure. According to Xiao and Chen (2017), biochars contained highly condensed graphite-like structures, however, few clusters of aromatic rings have been observed in some other biochars. (Novak et al., 2014) posited that, due to the recalcitrant nature attributed to biochar by virtue of its condensed-chemical structure, biochar may have a less active role in the soil C and N. That notwithstanding, biochar may potentially involve in some chemical reactions presumably due to the presence of some unstable C groups, mainly at the surface of its chemical structure. Gaining an insight into the dominant forms of C in biochar is key to knowing the chemical behavior of biochars and its reactivity in the soil environment (Calvelo Pereira et al., 2011). The various C forms that are dominant in biochar include aliphatic, aromatic, carboxylate, and carbonyl forms (Novak, et al., 2009).

Table 1: *Total C Distribution (%) among Structural Groups in Biochars Pyrolysed from Different Feedstocks and at Different Temperatures as adapted from (Novak et al., 2009)*

Feedstock	Pyrolysis Temperature (°C)	Total C (%)		Carboxylate	Carbonyl	Sum
		Aliphatic	Aromatic			
Peanut hull	400	35	57	5	3	100
	500	12	82	3	3	100
Peacan shell	350	49	42	4	5	100
	700	29	58	14	0	100
Poultry litter	350	36	57	4	3	100
	700	n.a[b]	na	na	na	na
Switch grass	250	63	29	5	3	100
	500	12	82	3	3	100

[b]n.a. – not determined

Undoubtedly, a strong relationship exists between the pyrolysis temperature, and the chemical structure of biochars. Several authors (Kloss et al., 2012; Schimmelpfennig & Glaser, 2012) have affirmed that at high pyrolysis temperatures (400 – 700 °C), feedstock is converted into poly-condensed aromatic structures that contain high recalcitrant C. The concentration of C has been established to be directly proportional to pyrolysis temperature, thus, C concentration increases as pyrolysis temperature increases, whereas H and O concentrations gradually decrease (Novak et al., 2009). Therefore, an inverse relationship has been found to exist between pyrolysis temperatures and between H and O. Conversely, pyrolysis temperature also increases the ash (Kloss et al., 2012). On the other hand, biochar rich in C=O and C-H functional groups is formed at lower pyrolysis temperatures (250 – 400 °C). Comparatively, the yield recovery is high when pyrolysis occurs at lower temperature range, and the dominant organic compounds found in the biochar are aliphatic or less stable cellulose-like structures, which can easily be degraded by soil microbes.

The stability of biochar in the soil environment has been reported to have a positive correlation with the pyrolysis temperature (Wang et al., 2015). This finding was substantiated by Nguyen et al. (2008) who observed that, the loss of C from biochar produced at pyrolysis temperature of 350 °C during an incubation study was greater than that at 600 °C. This observation is attributed to the fact that, higher pyrolysis temperatures have the potential to increasingly change O-alkyl C to aryl and O-aryl furan like structures which would subsequently result in enhanced condensation of C structures (Kaal, Martínez Cortizas, & Nierop, 2009), and thus increase the stability of the biochar in the soil medium. More importantly, Nguyen et al., (2012) reported higher aromaticity and lower H/C and O/C ratios of both corn-derived and oak-derived BC at 600 °C than at 350 °C as a consequence of the peak pyrolysis temperature of pyrolysis (Table 2). Singh, Cowie, & Smernik (2012) studied the effect of pyrolysis temperature on biochar chemistry, and the authors reported that faster mineralization occurred in biochars produced at 400°C than in biochars produced at 550 °C.

The surface C of biochars is reportedly prone to conversion into nutrient exchange sites (Domingues et al., 2017) upon activation or weathering irrespective of the pyrolysis temperature. Thus, the propensity of the surface C of biochars to act as an exchange complex for cation exchange reactions is not altered or affected by pyrolysis temperatures.

Table 2: *Properties of Biochar depending on the Pyrolysis Temperature as adapted from Nguyen et al., (2012)*

Biomass type	Pyrolysis temperature	C/N	O/C	H/C	Aromaticity[a]
Corn stover	350°C	73	0.37	0.07	77.6
	600°C	86	0.21	0.03	85.2
Oak wood	350°C	759	0.26	0.06	61.8
	600°C	737	0.10	0.12	68.4

[a]Quantified using X-ray diffraction (XRD)

A wide range of functional groups such as heteroatoms (hydrogen, oxygen, nitrate, phosphorus and sulfur), acidic carboxyl groups and other basic functional groups (chromenes and pyrenes) can be found on the surface of biochar (Oh, Seo, Ryu, Park, & Lee, 2017). The presence of functional groups on the surface of biochar is largely dependent on feedstock type. Due to the presence of functional groups on biochar surface, most biochars have a strong surface area charge and therefore, a high cation exchange capacity (CEC) (Gai et al., 2014). This property makes biochar essentially useful in contaminant control and the release and retention of nutrients (Domingues et al., 2017).

The behavior of biochars relative to its polarity and, thus, its ability to potentially interact with water can be inferred by calculating the atomic ratios of C, H and O (Schimmelpfennig & Glaser, 2012). More importantly, these ratios have been set by International Biochar Initiative (2012) to standardize biochars where <0.7 for H/C_{org} is taken into consideration, C_{org} is the C associated to the charred structure (in this instance, inorganic C, if present, is not considered). Charred materials with (H/C) ≥0.7 are categorised as non-condensed aromatic structures like lignin (Schimmelpfennig & Glaser, 2012).

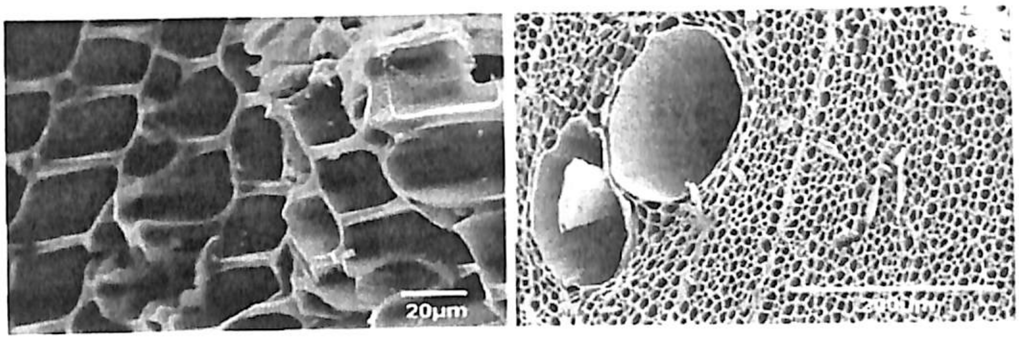
A relatively small variability in pH has been reported between biochars, with typical values above pH 7 (Zhelezova, Cederlund, & Stenström, 2017). The pH and electrical conductivity (EC) of biochars have been reported to be directly proportional with pyrolysis temperatures, and this is attributed to the accumulation of oxides of alkaline metals during the pyrolysis process (Gai et al, 2014). The high pH of biochar makes it potentially useful to raise the pH of acidic soils when incorporated into the soil (Chintala, Mollinedo, Schumacher, Malo, & Julson, 2014).

2.1.1.2 Physical characteristics

The physical characteristics of biochar is dependent on factors such as pyrolysis temperature, heating rates, and feedstock type and the pre- and post-handling of biochar, (Rafiq, et al., 2016). According to Lehmann & Joseph, (2009), the peak treatment temperature is the most important factor for physical alterations of the biochar product, followed by the heating rate and pressures.

The structure of biochar is amorphous, containing local crystalline structures of joint aromatic compounds (Han et al., 2017). The carbon skeleton formed during pyrolysis of organic materials gives biochar a distinct feature of having a high porosity, as a result of its sponge-like structure (Figure 2) (Zuolin Liu, Dugan, Masiello, & Gonnermann, 2017). The voids are formed in biochar as pores are categorized as macro- (>50μm), meso- (2-50μm) and micropores (<2μm) as seen in Figure 2. Comparatively, biochar has a large proportion of micropores (<2 x 10-3μm in diameter), and these micropores are responsible for the increasing surface area, that can reduce the mobility of soil water (Lehmann & Joseph, 2009). The high porosity results in biochar having a low bulk density than mineral soil, which when applied to the soil in sufficient rates can potentially reduce the total bulk density of the soil (Rogovska, Laird, Leandro, & Aller, 2017). Surface areas of biochar have been reported to range from 20 m^2g^{-1} up to 3000 m^2 g^{-1} (Guo, et al., 2002). The large surface area of biochar gives it the ability to enhance the ion exchange capacity and the sorption of nutrients (Sizmur, Fresno, Akgül, Frost,

& Moreno Jiménez, 2017). Moreover, the high surface area gives biochar the potential to adsorb large quantities of water due to the directly proportional relationship between water adsorption and surface area. The adsorption of water on the surface area of biochar is governed by the functional groups found in biochar (Sizmur et al., 2017). When incorporated into the soil, it is expected that biochar will increase the total soil surface area to enhance its water adsorption and ion exchange potential.



20µm 200µm

Figure 2: Scanning electron micrographs of biochar showing the highly porous structure, adapted from Lehmann & Joseph (2009).

The particle size distribution of biochar depends mostly on the feedstock type used in the pyrolysis process. Generally, wood-based biochars are reported to be of coarser structure than biochars obtained from crop residues which are of finer structure (Verheijen et al., 2014).

2.2 Effects of biochar on soil physical properties

The effects of biochar on soil physical properties depend on several factors, such as biomass or feedstock type, pyrolytic condition, application rate, and environmental condition (Mukherjee & Lal, 2013a). Soil physical properties such as aggregate characteristics, surface area, bulk density, soil structure, water holding capacity, pore volume and pore distribution

(Mukherjee & Lal, 2013) are key factors to soil fertility and plant growth and can be altered significantly by biochar amendment.

2.2.1 Soil tensile strength and friability

Tensile strength (TS) is the force per unit area required to fracture soil aggregates into smaller sizes. The tensile strength of soil is defined as the stress or force per unit area needed to cause soil to succumb to tension (Dexter & Kroesbergen, 1985). It is considered to be the most useful indicator of soil structural stability (Imhoff, da Silva, & Dexter, 2002). Tensile strength is a crucial and important mechanical property for investigating the structural stability of soil and thereby the resistance of soil aggregates against erosive forces (Dexter & Kroesbergen, 1985). It is a key soil physical property that determines the ease of producing a favorable seed-and root beds during tillage operations (Munkholm, 2011). The impact of biochar on soil strength is believed to emanate from the improved C storage potential of biochar amended soils due to a higher aromatic character and high C concentrations of biochar (Domingues et al., 2017). Several authors (Baranian Kabir, Bashari, Mosaddeghi, & Bassiri, 2017) have reported positive effects of organic carbon content on the strength of soil aggregates. In their studies, Blanco-Canqui & Lal (2007) observed that application of an organic amendment can increase the strength of soil aggregates in the 0- to 5-cm soil layer.

However, other authors have reported an inverse or no relationship between soil organic carbon content and aggregate tensile strength (Abid & Lal, 2009). Soil tensile strength is reported to decrease with increasing biochar concentration, evident in a hard-setting Australian Alfisol (Chan, Zwieten, Meszaros, Downie, & Joseph, 2008).

2.2.2 Soil aggregation

Soil aggregation is a natural process that involves the construction of secondary soil particles from primary particles exposed to physico-chemical and biological processes. The continuous bonding of soil particles by clay domains, polyvalent cations, and organic matter (OM), results in hierarchical soil aggregation. Incorporation of organic material causes an increased proportion of macro-aggregates and decreased proportion of micro-aggregates, resulting in increased water retention at low pF (suction) values (González-Pelayo, Andreu, Campo, Gimeno-García, & Rubio, 2006). Biochar is reported to be an effective amendment to induce soil aggregation (Busscher et al., 2010) and increase soil aggregate stability.

Soil aggregate stability is defined as the ability of soil aggregates to resist disruption when external forces are applied (Cosentino, Chenu, & Bissonnais, 2006). The stability of soil aggregates is key towards remediation of soils that are physically degraded. The organic carbon in soils with high aggregate stability does not easily succumb to decomposition and this promotes the sequestration of carbon in the long-term with a subsequent improvement in soil structural stability (Ouyang, Yu, & Zhang, 2014). Studies elucidating effects of biochar on soil aggregation are scarce (Mukherjee & Lal, 2013b). From literature, the existing studies have focused on soil stability of soil aggregates within different soils and for various types of biochar (Soinne, Hovi, Tammeorg, & Turtola, 2014). In a greenhouse experiment conducted by Hua, Lu, Ma, & Jin (2014), a significant increase in soil aggregate stability following the incorporation of biochar produced from straw was reported. On the contrary, Busscher, Novak, & Ahmedna (2011) reported a significant decrease in soil aggregation when biochar produced from peacan shells was applied, whereas Fungo et al. (2017) reported no effect of biochar on soil aggregate stability following an application of eucalyptus wood biochar pyrolyzes at 550°C to a *Typic Kandiudults* at a rate of 2.5 t ha^{-1}. No effect on aggregate stability has also been reported when rice-straw biochar was applied to an Ultisol (Peng, Ye, Wang, Zhou, & Sun, 2011). Undoubtedly, the above enumerated findings on biochar effects on soil aggregate stability are contrasting, thus emphasizing the need to quantify distinct soil and biochar properties for every situation (Khademalrasoul et al., 2014).

2.2.3 Water dispersible clay

According to Calero, Barrón, & Torrent (2008), clay dispersibility is the amount of clay that can be dispersed by water, which can subsequently affect the formation of soil aggregates and, in turn, promote soil erodibility. Application of organic amendments has been observed to decrease clay dispersibility (Paradelo, Oort, & Chenu, 2013). Increasing in soil pH, decreasing ionic strength of soil solution, the presence of monovalent cations (Na^+, K^+), and increasing soil water content are major factors that facilitate clay dispersion in soils (Soinne et al., 2014). Clay dispersibility has the potential to enhance the transportation of pollutants and nutrients that are attached to dispersed clay-sized particles to long distances, thus contributing to contamination of groundwater and eutrophication of receiving waterways (Soinne et al., 2014). Application of biochar to soils could influence clay dispersibility both negatively and positively (Khademalrasoul et al., 2014). Through its influence on soil moisture content, pH, zeta potential and ionic strength, biochar has the potential to speed up the dispersion of clay particles in soils. On the other hand, aging biochar forms biochar-mineral complexes (Lin, Munroe, Joseph, Kimber, & Van Zwieten, 2012) that enhance soil structural stability, which subsequently decreases the dispersion of clay particles in the soil environment.

2.2.4 Soil specific surface area

Specific surface area (SA) is critical with respect to the improvements in cation exchange capacity and sorption dynamics in soils. The surface area of soils is determined by soil particle size distribution, and mainly the clay content, and it can be estimated from the dry end of the soil water retention curve (Arthur et al., 2018; Arthur et al., 2013; Tuller & Or, 2005) or by the use of ethylene glycol monoethyl ether (EGME). Biochar has abundance of micropores (Fidel, Laird, & Parkin, 2017) that tend to increase the total specific surface area, which can facilitate nutrient and water retention, and filtering capacity of soils (Gamage, Mapa, Dharmakeerthi, & Biswas, 2016). The large surface area exhibited by biochar ultimately can result in an increase in total soil-surface area with positive effects on soil water- and nutrient-retention (Mia et al., 2017). The high surface area of biochar provides space for formation of bonds and complexes with cations and anions with metals and elements of soil on its surface which improves the nutrient retention capacity of soil (Domingues 2017; Mia, 2017). The total surface area of soil is an important physical parameter which controls essential functions of soil fertility such as water and nutrient holding capacity, aeration, and microbial activity (Jien & Wang, 2013). While many studies have reported on the surface area of biochars pyrolized from different feedstock types under a wide range of pyrolysis conditions, data available on surface area of biochar-amended soils is scanty. A long-term soil column incubation study indicated increases in specific surface area of an amended clayey soil from 130 to 150 $m^2 g^{-1}$ when biochar derived from mixed hardwoods was applied at rates of 0 to 20 $g kg^{-1}$ (Laird et al., 2010). Improvement in agronomic productivity of biochar-amended soils may be related to the higher surface area of the biochar-soil mixtures. Especially pores in the size of >0.2 μm on the inner biochar surface may host and retain plant available water and therefore increase the field capacity of the amended soil, resulting in a higher resilience of a soil against drought (Kammann & Graber, 2015).

2.2.5 Soil moisture retention

Soil moisture characteristics are among key indicators of soil physical quality. Laboratory procedures to measure soil moisture retention, involve intact soil cores either taken from the field or packed using bulk soil. Soil cores taken from the field are considered to have a more representative of the pore size distribution of the bulk soil, and therefore, reflect more realistic changes in moisture retention of the whole soil. Newly pyrolyzed biochar is initially hydrophobic (Xiao & Chen, 2017), as observed by hydrophobic molecule sorption, caused by chemical reactions during the pyrolysis process. As biochar undergoes oxidation, negatively charged functional groups bond to the surface of the biochar particle (Cheng et al., 2007), hence mitigating the hydrophobic behavior. Potential improvements in water holding capacity in biochar amended soils likely depend on biochar feedstock, charring conditions and soil properties (Novak et al., 2009). Barnes, Gallagher, Masiello, Liu, & Dugan (2014) found an improvement in water retention in sandy soil while improving drainage of clayey soil, by water movement through biochar pores or creation of interstitial biochar-soil space. However, blocking of pores by particulate soil organic matter may sometimes overlay these benefits (Prost et al., 2013).

In general, the application of all biochars increased the water holding capacity in all soils, indicating that the application of biochar can alter the soil physical properties. The addition of biochar to soils can have direct and indirect effects on the water retention. The soil pore network will especially determine the dimension of water retention in the soil, and will be affected by, for example, the inherent porosity of biochar, creating micropores (<0.002) in the soil (Baiamonte et al., 2015).

Studies revealed that the high inner surface area is one explanation for increasing soil water retention. An increased trend in the soil water retention capacity was found to have a positive correlation with pyrolysis temperature, and a higher water retention capacity was also found in woodchip biochar compared to biochar derived from dairy manure (Lei & Zhang, 2013). It is concluded, that a lower bulk density and higher surface area contributed to higher porosity and adsorption of water. Sun, Arthur, de Jonge, Elsgaard, & Moldrup, (2015) found an increasing water retention capacity in birch wood biochar treated sandy loam soil and attributed this phenomenon indirectly to the modified soil pore structure after biochar application. Sohi, Krull, Lopez-Capel & Bol (2010) pointed out that the increased water retention is one of the main reasons for increasing crop yields after biochar application.

2.2.6 Soil bulk density and total porosity

During pyrolysis of feedstocks, increasing temperature causes volatile organic compounds to be forced out (volatilized) by the rising temperature, resulting in significant increases in porosity and surface area (Huang et al., 2017) of the produced biochar. Comparatively, biochar is lightweight and less voluminous (with a bulk density of 0.3 and 0.43 Mg m^{-3} (Baronti et al., 2014) than agricultural soils with a bulk density of 1.0 – 1.5 Mg m^{-3} (Lal & Shukla, 2004). This property of biochar enhances its potential to decrease soil bulk (ρb) density (Wang et al., 2017). Several authors have reported well-established trends of decreasing bulk density with increasing rates of biochar application (Ahmed et al., 2017; Liu et al., 2017; Wang et al., 2017). Therefore, biochar, as an effective soil conditioner, has the potential to effectively provide relief for compacted agricultural soils. Reductions in the bulk density of soil following biochar amendment have been shown to be most distinctive in loamy or clayey soil, prone to soil compaction (Laird et al., 2010), with positive effects on the resilience of crops to drought (Baronti et al., 2014).

The total porosity and pore size distribution of soils are key soil characteristics with respect to water transmission and retention, soil aeration, and provision of habitat for soil microorganisms. With decreased soil ρb following biochar application, total porosity is hypothesized to increase (Rawal et al., 2016). Oguntunde, Fosu, Ajayi and van de Giesen (2004) reported over 10% increase in total porosity in twelve charcoal kiln sites relative to surrounding soils. A 6-week incubation study showed 6% and 12.7% reductions in ρb and the attendant increases in total porosity by 3% and 10.8% with biochar rates of 40 and 80 Mg ha^{-1} (Jones, Rousk, Edwards-Jones, DeLuca, & Murphy, 2012). Similar amendment rates of biosolids, mushroom compost, and green waste compost resulted in similar effects, but the biochar amendment produced the greatest impact on shifting the pore size distribution from macropores (> 30 μm) to micropores (0.1 – 29 μm).

With reduced bulk density and increased porosity, biochar has the potential to increase exchange of gases between the soil and the atmosphere. Zhang et al., (2012) reported a significant improvement in soil aeration when they amended a clayey soil with wheat straw biochar pyrolysed at 350-550 °C. Arthur & Ahmed (2017) reported an increase in relative gas diffusivity following an application of 3% w/w of rice straw biochar to a coarse-textured tropical soils three months after the incorporation of rice straw biochar. Due to its porous nature, incorporation of biochar into soils may increase the soils total pore space and subsequently influence other pore structure characteristics (Sun et al., 2015) such as pore connectivity and tortuosity and pore organization.

2.3 Effects of biochar on soil chemical and microbiological properties

The effects of biochar on some soil chemical, microbial and biological properties are numerated below:

2.3.1 Biochar and soil carbon dynamics

There are variations with regards to the effects of biochar application on soil carbon dynamics both in terms of magnitude of impact and the timing of impact. Despite the fact that some feed stock material may result in significant changes in soil carbon, there is the possibility that these changes may be mitigated over time, and their significance reduced in the soil ecosystem, barring any further disturbance over time. This, therefore, points to the fact that it is critically important to consider the feed stock type used in the production of biochar and time between disturbances to obtain a true picture of soil carbon dynamics, since a lot of processes in an intact agro ecosystem affect soil carbon storage, and with time will mitigate effects of disturbance. There is no uniformity relative to the effects of the application of biochar on carbon dynamics in every scenario. This is due to the fact that there are variations in different ecosystems with respect to soil type, type of feedstock material used and biochar application rates and to a large extent, the rate of soil disturbance. Moreover, soil carbon exists in multiple forms. Some forms of soil carbon are more sensitive to both disturbance and recent inputs (labile carbon), while others take a much longer time to replenish (recalcitrant carbon) (Gershenson, Bader, & Cheng, 2009)

Several distinct pools of soil carbon exist, and these pools are called fractions, with the shortest-lived carbon (<1-year-old) represented by microbial biomass and labile root exudates, which are easily decomposable simple organic compounds released by roots into soil. Medium-term carbon, several years to decades old, is represented by more complex organic materials. Ancient carbon, hundreds to thousands of years old, is represented by humins and humic acids, among other materials (Gershenson *et al.*, 2009).

The effects of the application of biochar as an amendment on soil carbon dynamics relates specifically to how management practices influence the net balance of carbon inputs and losses. To commence this analysis, highlighting the mechanisms though which carbon enters and exits the soil carbon pool is critical. Two main processes have been identified through which carbon enters the soil pool, and one principal process for soil carbon loss also observed. Carbon can either enter the soil through litter fall (decomposing woody and leafy material); a result of natural deposition or management activities where it is incorporated directly into mineral soil horizons or indirectly by way of surface organic matter, or it can enter the soil pool through rhizosphere processes, which include fine root death and root exudation (Gershenson *et al.*, 2009). Microbial decomposition, which is largely dependent on temperature, moisture, and substrate availability, plays a primary role in the loss of carbon from the soil (Wu et al., 2017).

A complex set of factors can affect soil carbon dynamics within soils. Potential exists for biochar to affect soil carbon dynamics by changing the rates of microbial decomposition, changing environmental conditions such as temperature and moisture, and changing the quality of litter inputs (more labile versus more recalcitrant inputs). Another important factor in decomposition of carbon in the context of biochar soil management is the stabilization of biochar carbon, which is becoming an interesting management practice worldwide (Gershenson *et al.*, 2009). If biochar is incorporated into soils, it can serve as an important long-term soil carbon pool, as well as increase overall soil quality (Randolph et al., 2017). Allaire et al., (2015), reported an increase in the overall soil C content after an incorporation of biochar into the soil. Biochar as a pure C source has the tendency to increase soil C stocks when applied to soil. Providing a rich source of C for microbes is another possible reason for observed increases in biological activities in salt-affected soils after biochar addition (Dai, Barberán, Li, Brookes, & Xu, 2017). However, previous studies on the effects of biochar on microbial biomass carbon (MBC) are inconsistent. While in some studies, biochar application significantly decreased soil MBC (Dempster, Gleeson, Solaiman, Jones, & Murphy, 2012), in other studies, there was no significant effect of biochar addition on soil MBC (Zavalloni et al., 2011). In contrast to the above mentioned observations, some other authors have found positive effects of biochar addition on microbial biomass studies (Gomez, Denef, Stewart, Zheng, & Cotrufo, 2014; Mierzwa-Hersztek, Klimkowicz-Pawlas, & Gondek, 2017). Generally, MBC highlights changes in SOC content and decomposition. Therefore, it can be stated that any processes and materials (inputs) which increase or decrease soil C content have the potential to influence soil microbial biomass and activity. Therefore, biochar, as a pure C source, can provide more C for the soil microbial community and increase MBC. Application of biochar to agricultural soils has been proposed as a means of increasing C storage in soil (that are inherently low in organic matter) and minimizing leaching of nutrients from these agricultural soils that are highly weathered (Domingues et al., 2017; Mia et al., 2017). Observed interaction effects between biochar C and available C (glucose C and plant residue C) on C mineralization have also been reported. The rate of decomposition of biochar is reported to increase after glucose addition (Luo et al., 2017). However, Liang, et al., (2010) and Zavalloni et al., (2011) reported no effect on biochar C mineralization with addition of plant residues. Other studies have reported relatively slow decomposition of added C in biochar-amended soils, which was attributed to decreasing C-use efficiency by soil microorganisms (Quilliam, Glanville, Wade, & Jones, 2013) and to stabilization of labile C.

Interestingly, application of fertilizer has also been found to greatly increase soil C content. A significant interaction between biochar and fertilization almost always gives a synergistic relationship between both treatments. For instance, in studying the effect of biochar on C dynamics, Allaire et al. (2015) observed that, full-N fertilization favored higher increases in soil C content. This finding was attributed to the fact that, the fertilizer application may have probably activated microbial activity and root development, both increasing biomass turnover. Another point worthy to be mentioned is that soil carbon is sensitive to soil type, (as higher clay content increases amounts of carbon adsorbed to soil surfaces), and soil structural characteristics, (such as soil aggregation, which provides physical protection from decomposition of soil organic matter) (Gershenson et al., 2009). All the above-mentioned factors enumerated can affect soil carbon dynamics in multiple, interrelated, and competing ways.

2.3.2 Biochar and soil nitrogen dynamics

In addition to the propensity to sequester C, biochar has been found to have agronomic benefits and to change the nitrogen (N) dynamics in soils (Fidel et al., 2017). There has been a growing interest in the potential of biochar on nitrogen dynamics since the biochar and N cycling review of Galloway et al., (2008). The anthropogenically induced global N cascade is resulting in enhanced fluxes of nitrous oxide (N2O), ammonia (NH3), and nitrate (NO3-) leaching (Galloway et al., 2008) as a consequence of the increasing intensification of agricultural systems. Therefore, in recent times, there has been a heightened interest in mitigation options to reduce environmentally harmful N fluxes. Biochar has been shown over the years to have potential in reducing inorganic-N leaching (Mia et al., 2017), N2O emissions (Yi et al., 2017), and ammonia volatilization, while also increasing biological nitrogen fixation (Rondon, Lehmann, Ramírez, & Hurtado, 2007).

2.3.2.1 Mitigation of nitrogen leaching using biochar

A lot of mechanisms have been proposed to throw more light on the apparent retention of N in soils amended with biochar and the reduction of N leaching. These mechanisms include adsorption of NH_3 or organic-N onto biochar, cation or anion exchange reactions, and enhanced immobilization of N as a consequence of labile C addition in the biochar (Clough, Condron, Kammann, & Müller, 2013).

Current scientific research has given clarity on potential role of biochars with respect to NO_3^- adsorption. Yao et al., (2010) evaluated 13 biochar materials to determine their potential to remove NO_3^- from solution. They observed that four biochars (bagasse, bamboo, peanut hull, and Brazilian pepperwood) produced at high temperature (600 °C) were able to remove between 0.12% to 3.7% of NO_3^- from a solution with variation in removal due to species of feedstock used. The potential biochars produced at higher temperature to remove NO_3^- as observed by Yao et al (2012) substantiates the earlier findings of Mizuta, Matsumoto, Hatate, Nishihara, & Nakanishi, (2004) who found that bamboo biochar produced at 900 °C had a high NO_3^- adsorption capacity.

A very informative study was undertaken by Kameyama, Miyamoto, Iwata, & Shiono, (2016) using sugarcane bagasse, where they determined NO_3^- adsorption properties of bagasse biochar produced at five pyrolysis temperatures (400–800 °C). A significant NO_3^- adsorption occurred at pyrolysis temperatures ≥700 °C. At high pyrolysis temperatures the biochars had high pH (8.7–9.8) and Kameyama *et al.* 2016 reasoned that the adsorption of NO_3^- was a result of base functional groups and not a result of physical adsorption since surface area and micropore volumes followed different trends when compared to observed NO_3^- adsorption. A similar study by Dempster et al., (2012) also showed that a *Eucalyptus* sp. biochar produced at 600 °C could adsorb NO_3^- when placed in an ammonium nitrate solution (10 g:100 mL), with up to 80% adsorbed after 24 h when the NO_3^- N concentration was 2.5 – 5 mg NO_3^-–N l^{-1} (0.02 – 0.04 mg NO_3^-–N per g biochar), decreasing to 38% at 50 mg NO_3^-–N l^{-1} although the adsorbtion rate had increased to 0.19 mg NO_3^-–N per g biochar.

From the afore-mentioned research works carried out by the various authors, it can be said that for a biochar to have the potential to adsorb NO_3^-, then the biochar feedstock material needs to be pyrolised at a temperature of at least 600 °C. Obviously, there is also a feedstock type effect on NO_3^- adsorption potentials and further research is needed to bring to light exactly how feedstock characteristics determine NO_3^- adsorption potentials given that high pyrolysis temperatures are deemed a prerequisite.

The practical implications of adding such a NO_3^- retentive biochar to a soil relative to reducing NO_3^- leaching needs to be queried. The significance of NO_3^- retention mechanism was studied by Yao et al., (2010) with respect to NO_3^- leaching, using two biochars with good NO_3^- retention properties (peanut hull and Brazilian pepperwood biochars made at 600 °C). These biochars were incorporated (2% by weight) into a sandy soil, in columns, and a nutrient solution (34.4, 10.0, and 30.8 mg l^{-1} of NO_3^-, NH_4^+, and phosphate ($PO4^{3-}$) was respectively applied. When the columns were flushed with 4 pore volumes of water over 4 days, it was observed that the biochar materials reduced NO_3^- leaching by 34% (Yao et al., 2010). Thus biochars produced at high temperature can reduce NO_3^- leaching. The disparities in the magnitude of the reduced NO_3^- leaching between laboratory and column studies may be possibly ascribed to the fact that column studies contain soil, with rates of biochar and NO_3^- concentrations that differ from the laboratory studies, and they have the potential for other loss pathways such as immobilisation and denitrification of NO_3^- to occur (Clough *et al*, 2013). That notwithstanding, other critical issues with respect to the potential for biochar to reduce NO_3^- leaching were also raised in the study of Kameyama *et al.*, (2016). The authors interrogated if adding biochar could significantly change a soil's physical characteristics relative to the hydraulic conductivity of the soil, and if so, could this affect the rate of NO_3^- leaching, negating or amplifying any effect of NO_3^- adsorption? And they also asked how permanent the adsorption of NO_3^- on to biochar was when incorporated in a soil?

The biochars physico-chemical characteristics such as pore size distribution, hydrophobicity and the rate of biochar addition can be used to answer the first question. Application of a bagasse biochar produced at 800 °C at a rate $\geq$5% by weight to a calcaric dark red soil increased the saturated hydraulic conductivity, with the effect likely to also be a function of the meso- and micro-pore fractions in the soil and biochar (Kameyama *et al., 2*016). Thus, application of biochar as a soil amendment could potentially increase the hydraulic conductivity of the soil, or preferential flow around larger particles, and thus lead to enhanced leaching of NO_3^-. Some authors, on the other hand have found that, amendment of soil with biochar increases water retention capacity and this may decrease leaching of NO_3^- (Dempster, *et al.*, 2012). Ideally, the water-holding properties of the soil should be known, and a biochar of suitable pore size distribution should be selected and applied at a rate not likely to enhance leaching (Clough et al, 2013). The permanence of adsorbed NO_3^- was also examined by Kameyama *et al.* (2016) by measuring NO_3^- transport in soil columns amended with the same NO_3^- adsorbing bagasse biochar (0%, 5%, or 10% by weight). They observed that when a 20 mg N l^{-1} solution of KNO_3 was applied to the soil columns the maximum concentration of NO_3^- in the effluent was approximately 5% less than in control (unamended soil), but the cumulative discharge of NO_3^- was similar in all treatments (Kameyama *et al.* 2016). The authors therefore concluded that NO_3^- was only weakly adsorbed onto biochar, that it could be desorbed by water infiltration, and that the net result may be an increased residence time for NO_3^- in the soil. Consequently, this may allow a greater opportunity for plant uptake of NO_3^-. Conclusively, the influence of biochar in curtailing NO_3^- leaching will primarily depend on its NO_3^- adsorption capacity (initial pyrolysis temperature and feedstock) and if anion or cation exchange capacities evolve with time in the soil, the biochar rate applied, the resulting rate of NO_3^- adsorption, the N loading of the given ecosystem, the resulting soil hydraulic characteristics, precipitation/irrigation events, soil type, plant and microbial N demand and potential biochar effects on these (e.g., changes in nitrification rates) (Clough *et al.*, 2013).

2.3.2.2 Immobilisation and ammonia volatilisation

A reduction in leaching of N has also been found in the absence of increased ion retention by biochars. Two switchgrass (*Panicum virgatum* L.) biochars produced at either 250 or 500 °C were placed in an Aridosol by Ippolito, Stromberger, Lentz & Dungan (2014) and subsequently, the cumulative NO_3^- leaching was determined at 34, 62, 92, and 127 days after the initiation of the experiment. Ippolito et al. (2014), found that less NO_3^- leached when biochar produced at the lowest temperature biochar was applied. This observation was attributed to the presence of more easily degradable C compounds at the lowest temperature and greater N immobilisation, thus reducing NO_3^- leaching (Ippolito et al., 2014). A 2M KCl extract of the incubated biochar-soil matrix also substantiated this reasoning with less NO_3^- present in the low temperature biochar-treated soils (Ippolito et al., 2012). Five biochar materials were incorporated into soil by Schomberg et al., (2012), and after a 127-day incubation period, reduced N leaching was observed. The observation was ascribed to the promotion of NH_3 losses by the biochar as a consequence of the elevated soil pH resulting from biochar addition (Schomberg et al., 2012). It is, therefore, considered worthwhile to examine the long-term net outcome of biochar in reducing leaching via N immobilisation, changes in nitrification, N sorption onto biochar or promotion of NH_3 volatilisation. Immobilisation of N may only happen for a short term following biochar application, and may lead to a delay in leaching of N (Clough et al., 2013).

2.3.2.3 Ammonium Adsorption and Leaching

Adsorption of NH_4^+ by biochar has been examined in a lot of scientific studies. For instance, Yao et al. (2012) observed that 9 of the 13 biochars tested in their sorption studies 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). Dempster *et al.* (2012) used *Eucalypt* sp. biochar pyrolysed at 600 °C and they observed that, the *Eucalypt* sp. biochar could adsorb 75% of the NH_4^+ in solution 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}, irrespective of the fact that the adsorption rate had increased to 0.25 mg $NH4^+$–N per g biochar. Placing NH_4^+ retentive biochars into soil has also been shown to affect the leaching of NH_4^+ (Clough *et al.*, 2013).

Soil solution NH_4^+ concentrations were found to have been affected at 20 cm depth when Ying Ding et al., (2010) added a bamboo charcoal (pyrolysed at 600 °C and added at 0.5% by weight to 0–10 cm depth) at a rate of 400 kg N ha^{-1} to a sandy silt soil, but no differences were observed at 40 cm depth after 70 days. Dempster et al. (2012) observed that when a biochar with cation exchange capacity (CEC) of ~10 cmolc kg^{-1} was added to a sandy soil (CEC of ~2 cmol $_{(+)}$ kg^{-1}) NH_4^+ leaching was reduced (15.0 to 12.9 mg pot^{-1}) 21 days after fertilization with ($(NH4)_2SO_4$; 40 kg N ha^{-1}). The explanation generally attributed to the adsorption of NH_4^+ onto biochar and the observed reductions in NH_4^+ leaching is the cation exchange capacity (CEC) of the biochar. The above-mentioned NH_4^+ retention was performed on fresh biochar materials which had relatively low CEC. In practical field applications, cation retention increases with biochar age and depends on climatic conditions (Zhelezova et al., 2017). The practical long-term importance of freshly made biochar in reducing NH_4^+ leaching therefore ought to be tested. However, the short-term practical impact of incorporating a new biochar material into soil on the total (soil + biochar) CEC can be inferred if both the soil's CEC, and the biochar's CEC and application rate are known (Clough et al., 2013). For instance, no effects of biochar (50 t ha^{-1}) on NH_4^+ adsorption was observed by Jones et al. (2012) in a three-year field trial. In sandy soils this biochar input may be significant in terms of CEC, but may also be insignificant, while for many soils that already contain higher levels of organic matter and clay the impact of biochar may be inconsequential (Clough et al., 2013).

Theoretically, ammonium held onto biochar surfaces due to cation exchange should be readily displaced with potassium chloride extraction. However, this was not observed when peanut hull biochar was exposed to NH_4^+ solutions, with ≤0.39% of the total sorbed NH_4^+ released (Prommer et al., 2014). Despite the fact that the exact mechanism for the retention of NH_4^+ was not identified, it was suggested in this study that physical entrapment of NH_4^+ in biochar pore structures may have been responsible (Saleh, Mahmoud & Rashad, 2012). With NH_4^+ ion having a diameter of 286pm and considering the fact that there is wide range of pore sizes in biochar materials, this observed phenomenon is entirely possible (Späth & König, 2010). It will, therefore, be imperative to study the mechanisms responsible for the adsorption of the various forms of N onto biochar surfaces and if possible, the effect of time on these mechanisms.

2.3.2.4 Dissolved Organic Nitrogen Retention and Leaching

Arguably, just a hand-full studies have critically examined dissolved organic-N (DON) leaching from soil and fewer still have paid attention to the role of biochar on this. No effect of biochar was observed on levels of DON leached from a sandy soil, which initially contained 18.8 mg N kg^{-1} in the 0 – 10 cm depth (actual values measured in treatments were not reported) in a study conducted by Dempster et al. (2012). It must, however, be emphasized that DON mainly carries a net negative charge. This, therefore, weakens the case for biochar having the potential to reduce leaching via adsorption of NO_3^- as argued by Dempster et al. (2012). The authors attributed the observed reductions in NO_3^- leaching to reduced rates of nitrification rather than NO_3^- adsorption, since the biochar was also known to inhibit nitrification (Dempster et al. 2012). This observation concurs with the findings of Kameyama et al. (2012), who found no differences in cumulative NO_3^- leaching from a sandy soil treated with a biochar known to be NO_3^- retentive over a shorter experimental duration.

2.3.2.5 Impacts of Biochar on Nitrogen Mineralization, Immobilisation and Nitrification

Soil carbon and nitrogen pools have a major impact on the rates of mineralization and immobilization in the soil. Generally, immobilization of N occurs as C:N ratio increases. Integration of biochar into the soil, therefore, adds another complexion to both the C and N pools in the soil. Slower mineralization of the biochar materials has been observed than the uncharred biomass (Knoblauch, Maarifat, Pfeiffer, & Haefele, 2011). Furthermore, application of biochar has been shown to decrease net N mineralization (Prommer et al., 2014), cause increased net N mineralization (Mia et al., 2017), have no effect on mineralization (Schomberg et al., 2012), decrease dissolved organic nitrogen (DON) or have little effect on DON (Prommer et al., 2014). Moreover, addition of biochar has been reported to have no effect on soil-N immobilization (Cheng, Cai, Chang, Wang, & Zhang, 2012) or promote immobilization (Wang et al., 2017).

Plant derived biochar embodied N has previously been assumed to be of low availability (Alburquerque et al., 2013) due to it being in heterocyclic structures. In an experiment conducted by Wang, Camps-Arbestain, Hedley, & Bishop, (2012), it was reported that acid hydrolysable N (amino acids, amino sugars and ammonia) found in manure-derived biochars decreased as pyrolysis temperature increased (from 250 to 550 °C) with a strong correlation between this acid hydrolysable N and CO_2 respiration, following biochar addition to soil, indicating that the total acid hydrolysable N represented the available N in the biochar.

According to Dai, Barberán, Li, Brookes & Xu (2017), fresh low pyrolysis temperature biochars can contain significant amounts of labile C that can be readily utilized by soil microorganisms which, when incorporated into the soil may have the tendency to render the microbially available soil N immobilized in the short term. This observation was demonstrated by Bruun, Müller-Stöver, Ambus & Hauggaard-Nielsen (2011) in an experiment in which wheat straw was pyrolysed at slow and fast temperatures. The wheat straw biochar produced at fast pyrolysis temperature resulted in a biochar that still contained a labile, un-pyrolysed carbohydrate fraction. When the slow and fast pyrolysis temperature biochars were applied to the soil the fast pyrolysis temperature biochar resulted in immobilisation of mineral N while the slow pyrolysis temperature biochar resulted in net N mineralization over a 65-day incubation period. Due to the fact that integration of biochar into soil involves multiple N pools, tracer studies are needed to study the gross N immobilisation and mineralization rates. ^{15}N labelling-tracing was used by Nelissen, Saha, Ruysschaert & Boeckx, (2014) to elucidate and model gross N dynamics following biochar (maize pyrolysed at 350 °C or 550 °C, C:N = 43 and 49, respectively) addition (10 g kg^{-1} soil) to a loamy sand (C:N = 9). In this study, the authors reported that gross N mineralization was stimulated by the application of biochar, with most of the N coming from a more recalcitrant fraction, whereas mineralization in the control was mainly from a labile N pool. This observation was ascribed to the biochar having a priming effect, *i.e.* stimulating microorgansims to mineralize recalcitrant soil organic matter (SOM) (Luo, et al., 2017). The authors finding was in accordance with the results of Schomberg *et al.* (2012) who also found differences in a recalcitrant N fraction when incubating several different biochars over 127 days. Increased turnover of SOM can emanate from the application of biochar as a result of priming effects, most likely induced by labile components of the biochar, and this may increase with increasing soil pH and decreasing pyrolysis temperature (Luo *et al.*, 2017). Thus, while biochar may contain bioavailable form of N, its mineralization and release will be dependent on how recalcitrant the biochar and soil N and C pools are, on the soil and biochar C:N ratio, the relative magnitude of the soil and biochar C and N pools, and the studied ecosystems (Clough et al., 2013).

Application of biochar to soils may have no effect on gross or net nitrification rates in agricultural soils (Cheng et al., 2012), but biochar addition to soils has been reported to enhance net nitrification in natural ecosystems as a result of the liming effects of biochar or the removal of inhibiting substances such as polyphenols or tannins (Castaldi et al., 2011). Volatile organic compounds associated with a biochar production can decrease nitrification activity (Clough & Condron, 2010). Wang et al. (2017) reported reduced nitrification in a peanut shell biochar amended agricultural soil because of the enhanced microbial activity and reduced the abundance of ammonia-oxidizing bacteria. In agricultural ecosystems, the lack of positive effects on net nitrification rates in biochar amended soils may be ascribed to the fact that, agricultural ecosystems are already characterized by high nitrification rates (DeLuca, MacKenzie, Gundale, & Holben, 2006). A study conducted by Nelissen et al., (2014) reported that addition of biochar stimulated gross nitrification in an agricultural soil. The authors attributed this observation to increased mineralization of NH_4^+ from the recalcitrant soil N pool, where the emission was larger than the simultaneous incorporation of NH_4^+ into the labile soil N pool. The authors, therefore, reasoned that the stimulation in gross nitrification was mainly due to an increase in the NH_4^+ substrate supply.

2.2.3 Effects of biochar on microbial biomass and activity in soils

2.2.3.1 Soil microbial biomass

The effects of biochar on soil microbial biomass (SMB) and activity can influence N transformations (Kammann et al., 2017). However, the impacts of biochar on soil microbial biomass and activity are still poorly understood, particularly beyond initial, short-term laboratory studies. Biochar has been reported to have induced large changes in SMB composition and activity, with beneficial effects on soil and/or plant productivity in the short term term (< one year) (Dai et al., 2017; Mierzwa-Hersztek et al., 2017). Biochar-induced changes in pH-value, generation of carbon-nutrient agglomerates in soil (Castaldi *et al.*, 2011) and sorption of toxic substances such as heavy metals or provision of an additional C-source (Mierzwa-Hersztek et al., 2017) may have resulted in these positive effects on soil microbial biomass following biochar application. Furthermore, biochar is observed to provide a habitat for mycorrhizal fungi, particularly by deliberate inoculation in the laboratory compared to the field (Quilliam et al., 2013). However, a decrease of microbial biomass following the soil application of biochar has also been observed, resulting in lower soil C and N turnover rates (Dempster et al., 2012).

Several authors have found positive effects of biochar on growth, root colonization and spore germination of mycorrhizal fungi (Salem, Kohler, Wurst, & Rillig, 2013) as well as on the activity and abundance of SMB (Bargmann, Martens, Rillig, Kruse, & Kücke, 2014). Conversely, negative effects of biochar application as an amendment to soils on mycorrhiza have also been reported, pointing to the occurrence of toxic compounds, mostly present in the water soluble carbon fraction (George, Wagner, Kücke, & Rillig, 2012). Corn cob derived biochar has been reported to increase microbial biomass and activity in soils, indicating the importance of biochar feedstock material for any effects on microorganisms (Steinbeiss, Gleixner, & Antonietti, 2009).

Apart from the feedstock material, the effect of biochar on SMB depends on the production process conditions, the time following the addition to soil and soil fertility status (Muhammad et al., 2014). The variations in biochar amelioration effects on SMB also depend on soil C content (Kimetu & Lehmann, 2010), soil texture, and soil management practices. Similarly, the response of soil microorganisms to biochar addition may vary with land use and agricultural management practices. Biochar application has been assessed for a wide range of soils including sands, sandy loams and sandy clay loams. Mixed responses from biochar application in soils that differed in soil fertility status and textural class include reductions in microbial biomass (Dempster et al., 2012), transient variation in bacterial or fungal growth, and increased microbial activity (Rutigliano et al., 2014). Inconsistent responses have been reported in microbial biomass and some components of microbial activity to the incorporation of biochar in soil (Dempster et al., 2012).

Considering the wide influence of SMB on the soil nutrient cycling and on plant growth, it is imperative to identify the effects of biochar on soil microorganisms more succintly. However, there is limited scientific knowledge of the long-term effects of biochar on SMB to precisely predict SMB responses to biochar addition.

2.2.3.2 Soil microbial activity

Incorporation of biochar into soils promotes soil biological activity. In spite of the fact that biochar contains more recalcitrant C than other organic substrate such as compost and crop residues it has been shown that temporary release of labile C following biochar addition can considerably promote soil biological activity, but this effect could be short lived (Lehmann et al., 2011a).

The observed effects of biochar on soil microbiological activity are reported to result from at least three effects: alteration of phyico-chemical interactions, such as increased water and nutrient retention; electron donor provision; and provision of micro habitat that protects some microorganisms from predation.

2.2.3.2.1 Physico-chemical interactions

The incorporation of biochar into soil enhances the water holding capacity of the soil (Arthur and Ahmed 2017; Liu et al., 2017), nutrient adsorption capabilities (Zygourakis, 2017), dissolution-precipitation, acid-base reactions, redox reactions (Cayuela, et al., 2013) and cation retention (Domingues et al., 2017). The surface characteristics of biochar may exert positive impacts on soil nutrients and cations (Domingues et al., 2017), and the adsorption of nutrients onto biochar surface can lead to increased local nutrient concentrations for microbial community species (Yang Ding et al., 2016) and enhanced water retention which provide a conducive environment for microbes and enzymes to thrive and flourish to enhance soil ecosystem functionality.

2.2.3.2.2 Substrate provision

Generally, biochar is perceived as an inert soil material but evidence exists to show that biochar decomposes on two different timescales. In the initial stage, the labile C in biochar acts as substrates for soil biota. Consequently, soil microbial populations are affected by the quality of the applied biochar. The quality of biochar, in turn, depends on feedstock and pyrolysis conditions (Pandit, Mulder, Hale, Schmidt, & Cornelissen, 2017). Low molecular weight oxygenated volatile organic compounds (acids, alcohols and carbonyls) serve as substrates (Domingues et al., 2017) in low concentrations, but are toxic to microorganisms at higher concentrations (Zhu, Xiao, Shen, & Li, 2017) as are polycyclic aromatic hydrocarbons, cresols and xylenols (Xu & Zhou, 2017).

Enhanced microbial biomass respiration and respiration efficiency have been reported in response to biochar treatment (Mierzwa-Hersztek et al., 2017). Lower temperature biochars were observed by Dai et al., (2017) to have resulted in enhanced CO_2 evolution as a result of higher amounts of water-extractable organic carbon. Biochar mediated CO_2 evolution must also be considered in the context of greenhouse gas emissions with reports of increased methane and decreased nitrous oxide releases from rice paddy (Wang et al., 2017).

Remarkable differences in soil microbial community composition have been recorded in biochar amended soils, compared to similar, adjacent native soils (Mia et al., 2017; Mierzwa-Hersztek et al., 2017). Therefore, it is clear that application of biochar as a soil amendment affects microbial ecology beyond the timescale of adsorbed residuals metabolism. It must be emphasized that, changes in the soil microbial population following applications of biochar as an organic amendment varies according to biochar type (electron donors), rate of application, frequency of application and duration of application (longer term effects) (Johannes Lehmann et al., 2011b).

2.2.3.2.3 Habitat provision

Pores in biochar can provide support surfaces for microbial colonisation which, together with enhanced water holding capacity, can afford a suitable habitat for microorganisms (Dai et al., 2017; Yang, Zhao, Gao, Xu, & Cao, 2016). The ability of biochar to support larger numbers of microbes with higher respiration rates was studied by Jien & Wang, (2013) and Domingues et al., (2017). In their study, the authors observed a significant positive response from biochar, with its relatively high surface area and adsorption capacity. These observations made by the authors therefore presuppose that, a high surface area in combination with high water retention serve as a panacea for an increased microbial abundance. Also, the two materials supported distinct population types as demonstrated by phospholipid fatty acid analysis. The disparities reported in the biochar and activated carbon with respect to microbial ecology remain unresolved although they may result from pore size variations affording protection from fungal grazers (Warnock et al., 2010), or effecting pH and local concentrations of pore gases.

Enzyme activities should be considered paramount in reviewing soil microbial responses to biochars. Bailey, Fansler, Smith & Bolton Jr, (2011) examined enzyme activity (ß-glucosidase, ß-N-acetylglucosaminidase, leucine aminopeptidase and lipase) in the presence of *Panicum virgatum* biochar in three soil types (Palouse silt loam, Quincy sand and Warden sandy loam). The authors, however, recorded inconsistent results with both increased (enzyme function chemical enhancement) and decreased (substrate sorption) activities. A lot of studies, therefore, have to be done to elucidate the activities of enzyme and their effects on soil microbial response following biochar additions to soils of the humid tropics.

2.4 Biochar Management and Soil Nutrient Availability

Applications of biochar to soils have been reported to substantially increase the availability of total nitrogen concentrations and phosphorus as well as other major cations (Lehmann, Gaunt, & Rondon, 2006). The application of bio-char (charcoal or biomass-derived black carbon (C)) to soil is proposed as a novel approach to establish a significant, long-term, sink for atmospheric carbon dioxide in terrestrial ecosystems. Apart from positive effects in both reducing emissions and increasing the sequestration of greenhouse gases, the production of biochar and its application to soil will deliver immediate benefits through improved soil fertility and increased crop production. Conversion of biomass C to biochar C leads to sequestration of about 50% of the initial C compared to the low amounts retained after burning (3%) and biological decomposition (< 10–20% after 5–10 years), therefore yielding more stable soil C than burning or direct land application of biomass. This efficiency of C conversion of biomass to biochar is highly dependent on the type of feedstock, but is not significantly affected by the pyrolysis temperature (within 350–500 °C common for pyrolysis). Existing slash-and-burn systems cause significant degradation of soil and release of greenhouse gases and opportunies may exist to enhance this system by conversion to slash-and-char systems. Our global analysis revealed that up to 12% of the total anthropogenic C emissions by land use change (0.21 Pg C) can be off-set annually in soil, if slash-and-burn is replaced by slash-and-char. Agricultural and forestry wastes such as forest residues, mill residues, field crop residues, or urban wastes add a conservatively estimated 0.16 Pg C yr^{-1}. Biofuel production using modern biomass can produce a bio-char by-product through pyrolysis which results in 30.6 kg C sequestration for each GJ of energy produced. Using published projections of the use of renewable fuels in the year 2100, bio-char sequestration could amount to 5.5–9.5 Pg C yr^{-1} if this demand for energy was met through pyrolysis, which would exceed current emissions from fossil fuels (5.4 Pg C yr^{-1}). Bio-char soil management systems can deliver tradable C emissions reduction, and C sequestered is easily accountable, and verifiable (Lehmann et al., 2006). The Cation exchange capacity and soil pH have been found to increase following the application of biochar (Pandit et al., 2017; Wang et al., 2017; Zhelezova et al., 2017). Increases in the availability of nutrient for plants is the result of both the direct nutrient additions by the biochar and greater nutrient retention (Domingues et al., 2017), but it can also be inferred that partly, the higher nutrient availability of nutrients in biochar amended soils is a resultant effect of changes in soil microbial dynamics (Degrune et al., 2017).

The availability of nutrients in biochar amended soils will culminate into increases in crop yield. Increases in yield have frequently been reported that are directly attributable to the addition of biochar over a control without biochar (Xiao et al., 2016). The immediate beneficial effects of biochar additions for nutrient availability are largely due to higher potassium, phosphorus, and zinc availability, and to a lesser extent, calcium and copper (Johannes Lehmann et al., 2011a). The long term beneficial effects of biochar applications on plant nutrient availability include an improvement in the stabilization of soil organic matter, concurrent slower release of nutrient from added organic matter, and an improvement in the cation exchange capacity of the soil which ultimately results in better retention of all cations, which subsequently increases crop productivity.

The effect of biochar applications on crop productivity depends on the rate of biochar application. Invariably, nitrogen limitation is the reason for a substantial decrease in yields at high application rates, as nitrogen availability decreases through immobilization by microbial biomass at high C:N ratios (Lehmann et al., 2006), although other growth-limiting factors may be responsible as well. With increasing rates of application, plant response at a given site is positive until some maximum is reached, above which growth response is negative (Lehmann et al., 2006).

Moreover, the response of plant yields to biochar applications is dependent on the properties of the biochar, soil properties (greater response occurs on nutrient-deficient, sandy soils), concurrent nutrient and organic matter additions, and plant species. Leguminous crops have been reported to thrive well under greater biochar applications as compared to gramineae species, since they can compensate for limited nitrogen availability by increased biological nitrogen fixation (BNF) (Lehmann et al., 2006). Incorporations of nutrients into the soil from inorganic or organic sources (fertilizers) are usually significant for high plant productivity and enhance the positive response of the bio-char amendment.

Biochar soil management, with associated increases in nutrient availability and pH, not only enhances crop yields and decreases risk of crop failure, but also opens new possibilities for cropping, i.e., high-value crops can be produced on sites that would normally not be suitable for production (Lehmann *et al.*, 2011). Improving soil health by applying biochar to highly weathered soils in the humid tropics that are inherently low in soil fertility will result in having nutritious and easily marketable produce. This resultant positive effect can improve cash returns which will ultimately enhance the livelihood resilience and health of peasant farmers who currently only have access to poor soils. Enhancement of the livelihood resilience of small holder farmers in rural areas who depend solely on agricultural for their livelihood is possible not only through increased plant yields, but also through increased quality and variety of the crops grown.

2.5 Soil Fertility and Crop Productivity in Soils Amended with Biochar

A number of soil properties have a major impact on soil fertility. Soil fertility involves a complex balance of biotic and abiotic factors that are spatially and temporally dynamic. Application of biochar to soils may produce immediate effects on soil properties such as water retention, or microbial activity (Domingues et al., 2017; Arthur and Ahmed 2017; Dai et al., 2017), but the magnitude of the effect depends on soil type (Mia et al., 2017).

For biochar added to soil to adequately revitalize nutrient-impoverished soils, there should be noted increases in the quantities of plant-available nutrients and the nutrition retention capacity of the soil (Sohi et al., 2010). To elucidate the interactions between soil and biochar, there is the need to critically consider how these effects of biochar on the soil ecosystem vary geographically and temporally. Microbial diversity changes when organic amendments are added to the soil (Zheng et al., 2016a). The turnover processes of soil microbial communities and their interaction with organic and inorganic plant nutrient are complex (Zak, Holmes, White, Peacock, & Tilman, 2003) and have a profound effect on soil functions and its fertility. Research has suggested that incorporation of biochar into soil can have a significant impact on microbial C metabolism and population dynamics (Jaiswal et al., 2017). Several explanations for these effects have been reported, such as biochar sorption, including the presence of volatile organic compounds (VOCs) that can inhibit or stimulate microbial mineralization reactions or affect plant–microbial interactions (Spokas et al., 2012), variability in biochar's susceptibility to mineralization (Zimmerman, Gao, & Ahn, 2011), microbial habitat through pH modifications, beneficial micropores on the biochar for microbial habitat (Warnock et al., 2010), or the presence of critical nutrients for microbial growth and metabolic energy transfer reactions. The above-mentioned explanations highlight the importance of understanding the biochar-soil microbes interactions, and this knowledge is fundamental in enhancing soil health with subsequent increase in crop production. There are a greater number of increased yield results reported following the incorporation of biochar into highly weathered or degraded soils having limited fertility and productivity (Jeffery et al., 2017). A majority of the yield improvements have been realized from traditional kiln-formed hardwood charcoal or chars that possess plant nutrients (e.g., high N content in poultry manure biochar) (Spokas et al., 2012). Several potential reasons exist for this apparent improved performance of traditional hardwood charcoal biochar. Firstly, biochars from fast pyrolysis units have been extremely variable (Spokas et al., 2012). It has been suggested that incomplete conversion of the biomass feedstock due to thermal limitations and irreproducibility of heat transfer is the cause of this variability (Bruun et al., 2011). Deenik, McClellan, Uehara, Antal, & Campbell (2010) also reported variable volatile matter content in fast pyrolysis biochars. This therefore translates to differences between batches of biochar produced, rendering them potentially unique irrespective of the fact that similar production conditions are used in producing the batches of biochar. Furthermore, there are variations that exist not only in biochar quality as a function of the production process, but also these variations are linked to the post-production storage or activation (Nuithitikul, Srikhun, & Hirunpraditkoon, 2010). Activation can occur when the biochar is cooled with water or when the hot biochar is exposed to atmospheric oxygen during cooling. Surface oxidation of biochar, even at ambient conditions, alters surface chemical groups (Cheng et al., 2012), which subsequently influences the potential interactions with soil nutrient. It must however be emphasized that, more often than not, the post-production handling of the biochar is not reported. There is therefore the need to effectively report biochar post-production handling and storage conditions.

A lot of authors have reported positive responses for net primary crop production, grain yield and dry matter following biochar applications to soils (Xiao et al., 2016). Two recent meta-analyses revealed an overall 10-12 % increase in plant and crop productivity due to biochar addition to soil with the most positive results for soils with a coarse texture and neutral to acidic pH (Biederman & Harpole, 2013; Jeffery, Verheijen, van der Velde, & Bastos, 2011). This is consistent with other findings, indicating that biochar has the most positive effects on plant yield in soils exhibiting a low cation exchange capacity, low carbon content and low pH (Crane-Droesch, Abiven, Jeffery, & Torn, 2013).

The impact of biochar on crop productivity largely depends on the characteristics of soil, the climate of the planting area, feedstock type, pyrolysis conditions, and dosage of biochar addition (Jeffery et al., 2017). This actually accounts for the reason why researchers find different results in some field experiments. For instance, positive results suggested that application of biochar as an organic amendment improved crop yield (Zheng, Wang, Deng, Herbert, & Xing, 2013). Olive-tree pruning-derived biochar amendment positively correlated with a higher yield but the nutrient content was not obviously affected (Olmo, Alburquerque, Barrón, Campillo, Gallardo et al., 2014). In a study conducted in Kaoma, Zambia, application of maize cob-derived biochar significantly increased maize yield by over 100% in different soils (Cornelissen, et al., 2013). Oguntunde et al. (2004), investigated the effect of charcoal residue on maize yield in Ghana, and they reported that grain and biomass yield of maize increased by 91% and 44%, respectively on charcoal site soils compared to adjacent field soils.

Contrary to the above-mentioned observations, some authors suggested that the application of biochar to soil did not promote plant yields. Low charcoal additions (0.5 t ha^{-1}) have shown marked impact on various plant species, whereas higher rates seemed to inhibit plant growth (Ogawa, Okimori, & Takahashi, 2006). A substantial decrease in crop yield has been reported by some authors when a higher dosage of biochar was applied (Borchard, Siemens, Ladd, Möller, & Amelung, 2014). For instance, Rajkovich et al. (2012) carried out a pot experiment in a greenhouse and observed that animal manure biochar and food waste biochar decreased the yield of corn at a high application rate (7%), while lower rates of application (2%, 0.5%) of biochar could increase the yield. A study conducted in Mkushi in Zambia, revealed that neither maize cob nor wood biochar affected the maize yields (Cornelissen et al. 2013). A three-year field experiment was conducted by Jones et al. (2012) and they reported that biochar made from commercial wood chip had a little effect on maize yield in the first year, but enhanced maize yield in the third year.

The impact of biochar application is seen most in highly degraded acidic or nutrient depleted soils (Jeffery et al., 2017). Crop yields, particularly on tropical soils can be increased if biochar is applied in combination with inorganic or organic fertilizers.

2.6 Potential Responsible Mechanisms for Biochar Yield Responses

A complex interaction between biochar and fertilizer relative to yield response has been reported (Yu et al., 2016). Applications of biochar as an organic soil amendment to poor soils have been cited to enhance soil cation exchange capacity (CEC) properties (Jeffery et al., 2017). It must however be emphasized that, not all biochar–soil interactions cause an increase in CEC because little or no changes in CEC have also been reported after certain biochar additions to soils (Nguyen et al., 2008) that have been linked to other parameters along the biochar production chain. Some studies have found that application of biochar to soils may alter pH levels and the availability of soil nutrients such as Ca or Mg, which were found to limit maize growth in highly weathered tropical soils (Major, Rondon, Molina, Riha, & Lehmann, 2010), or the availability of Boron and Molybdenum, which are important cofactors in biological N fixation, while decreasing the concentrations of acidic cations (exchangeable Al^{3+} and H^{+}). Other explanations for biochar's crop yield impact have ranged from N immobilization leading to decreased N availability due to the high C:N biochar ratios (Fidel et al., 2017), liming effects of the biochar (Jeffery et al., 2017), reduced plant availability of macronutrients due to pH changes, and direct sorption of soil nutrients (Gai et al., 2014).

The impact of biochar applications on a variety of soil types at ten different locations was studied by Insam (2001). In their study, the authors observed increases in yield in soils with low P availability and improved plant response to additional fertilizers with biochar additions. However, these findings are not universal; even fertilizer plus biochar additions have resulted in suppressed yields in some cases (Spokas el al., 2012). It can, therefore, be inferred that, soil nutrient status alone will not suffice to explain all the crop responses observed following biochar application. However, it could be important after biochar amendments to weathered and low N- and P-containing soils due to fertilization (Spokas el al., 2012).

Other potential mechanisms responsible for the impact of biochar on agronomic yield have also been documented. Studies have shown altered rates and timing of seed germination as a function of biochar additions (Rillig et al., 2010). Variations in germination and consequentially emergence of new seedlings that are capable of independent existence could influence plant growth and yield due to the timing of precipitation and accumulation of thermal time. In other words, plant seeds that are concomitantly sown in biochar-amended and non–biochar-amended soils that emerge at different times are also temporally equivalent to a varying planting date (Spokas et al., 2012). Variations in planting date in field plots have been observed to have an effect on plant growth and yield due to the timing of precipitation and accumulation of growing degree days (Egli & Bruening, 1992). Biochar can also sorb, release, or catalyze transformations of compounds that affect plant and microbial growth (Spokas el al., 2012). Quite recently, much attention is focused on the role of volatile organics (VOCs) in soil microbial and plant signaling which is seen as an emerging field of study (Insam & Seewald, 2010). In some cases, these VOCs may be sorbed by biochar particles (Dutta et al., 2017), whereas at other times VOCs may be emitted from biochars (Ghidotti, Fabbri, & Hornung, 2017). Plant allelopathic reactions are reported to emanate from this release or sorption of VOCs, and may inhibit or stimulate microbial functionality and positive or negative plant effects (Deenik *et al.*, 2010). However, these chemical effects are reported to be dependent on the properties of soil, soil microbes, plant, and the applied biochar (Spokas el al., 2012). This, therefore, implies that, the role of biochar in sorbing or releasing inhibitory chemicals could then be used to explain seemingly contradictory results observed in yield responses to biochar application, because the yield response can be inferred to be a function of the respective concentration thresholds for the specific soil microbe or plant.

Improvements in plant yield induced by biochar additions are further complicated by the occasional delayed response, with negative or no impact in the initial year (Sorensen & Lamb, 2016) followed by yield increases of varying degrees in subsequent years. These delayed responses are hypothesized to occur due to aging of the biochar (e.g., oxidation or other chemical alteration) (Singh, Hatton, Singh, Cowie, & Kathuria, 2010). Chemical or thermal biochar activation significantly changes the surface chemistry of biochar (Nuithitikul *et al.*, 2010). Chemisorption of oxygen by biochar particles also alters the surface chemistry and microbial degradability (Cheng et al., 2007), which could potentially affect biochar nutrient availability. These abiotic chemisorption reactions occur at ambient conditions which have only received limited attention in the biochar literature (Jones et al., 2012; Zimmerman et al., 2011). These reactions that are observed in the post processing of biochar can, therefore, have the potential to immensely change the 'potency' of the biochar and resulting observed impacts. This, again, highlights the need to report postproduction handling and storage of the biochar material. From the afore mentioned reactions, it can be said that the impact of biochar on soil fertility may be either positive or negative depending on the soil type, quality of the feedstock and rate of the biochar applied. An application of high-nutrient biochar that exceeds recommended fertilization rates may unbalance soil nutrient levels (Ippolito et al., 2014), produce little improvement in soil nutrient retention, and increase nutrient leaching potentials. Improvements in soil nutrient following biochar applications may take some time to be observed. It is most likely to envision a delay in soil improvements if a particular element is enclosed in a chemical ring structure because the kinetics of surface functional group oxidation and cleavage of ring structures would be rate limiting (Yao et al., 2010). However, a majority of the existing studies have been limited to less than 3 years, which may not be enough time for the soil nutrient cycle to be affected (Spokat et al., 2012).

Conclusively, it can be summarized that the responses of plants to the application of biochar are the net result of production (e.g., feedstock and pyrolysis conditions) and postproduction (storage or activation) conditions. The production and post-production processes have the potential to impart unique properties to each batch of biochar, irrespective of the fact that the batches of biochar are produced from the same pyrolysis unit and biomass feedstock. As a result of the lack of universal biochar properties and characterization reported in biochar studies, full elucidation of the processes responsible for yield response following biochar additions from literature studies is unfeasible and requires additional detailed studies (Lehmann et al., 2011a), particularly highlighting biochar production and postproduction handling. The processes or mechanisms by which biochar enhances the growth and yield of plants are debatable, but this knowledge gab needs to be filed since it is crucial to fully optimize the use of biochar for agronomic purposes.

2.7 Summary

Biochar has the potential to increase crop yield and provide ancillary benefits of increasing fertilizer use efficiency and microbial community structure to enhance soil biota for efficient ecosystem functionality. Application of biochar to soils also has the potential to promote climate-smart agriculture through carbon sequestration and mitigation of greenhouse gas emissions. The use of locally produced agricultural waste-recycled biochar can, therefore, be used as an amendment to improve soil quality and support economic crop production in the higly weathered tropical soils. Potential research opportunities, therefore, exist with respect to the effect of biochar on soils of the humid tropics, with special emphasis on the stability of biochar in tropical soils, incorporation method, feedstock type, pyrolytic temperature, and fertilizer application rate and fertilizer use efficiency.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Description of the Study Area

The research was conducted at the University of Cape Coast Teaching and Research farm in the coastal savanna agro ecological zone of Ghana (Figure 3). The area is characterized by high rainfall (1400 mm per annum) with a bimodal pattern. The major rainy season starts in April and ends in mid-July with a peak in the month of June. The minor season commences from September to mid-November with a peak in the month of September. A short dry spell separating the two rainy seasons occurs from mid-July to mid-August. The main dry season is from November to March. Temperatures are high throughout the year with mean monthly temperatures ranging from 20 °C in June to 28 °C in April. The soil is a well-drained sandy loam developed on sandstones, shales and conglomerates and classified as a *Haplic Acrisol* (WRB, 2015). Soil chemical properties prior to establish the experiment were pH 6.1, electrical conductivity 200 μS cm^{-1}, total organic carbon 9.3 g kg^{-1}, total nitrogen 0.73 g kg^{-1}, with total phosphorus, potassium and magnesium contents of <0.4, 11.9, and 9.3 mg 100 g^{-1}, respectively, (Amoakwah, Frimpong, & Arthur, 2017).

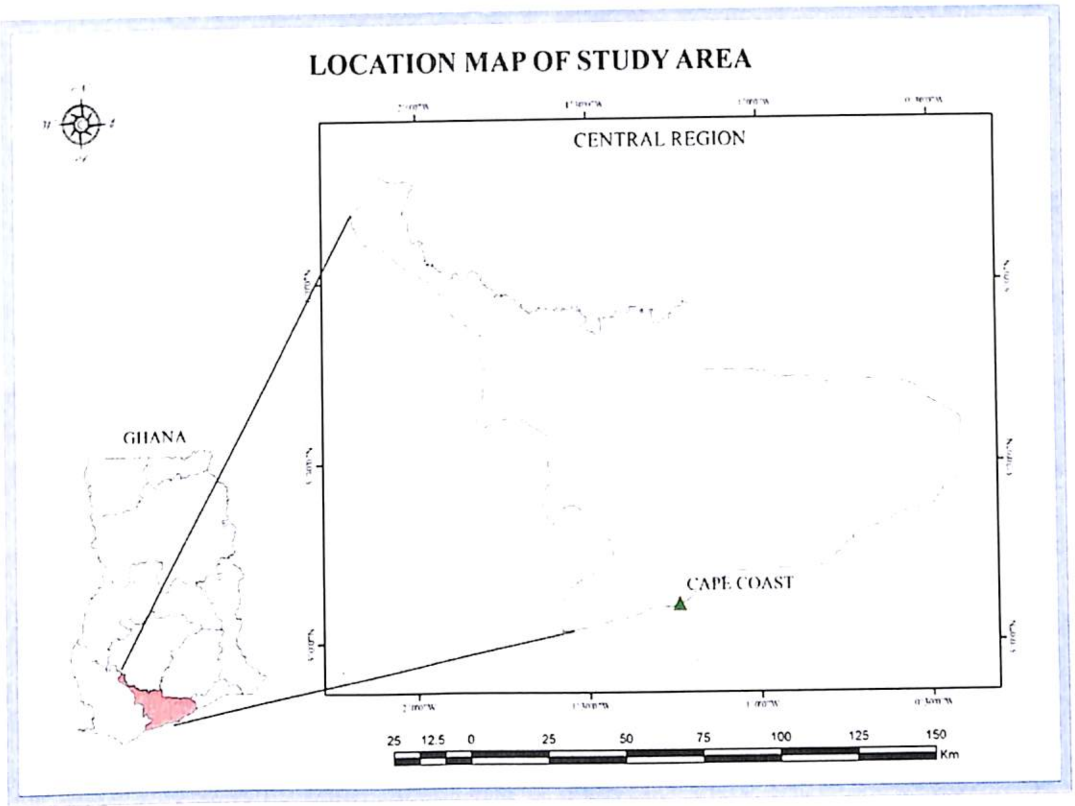


Figure 3: Location of the study area.

3.2 Production and Basic Properties of Biochar

The biochar that was used in the experiment was produced from waste corn cob feedstock pyrolyzed at 500-550 °C in a Lucia stove reactor for a period of 48 hours. The biochar particles were homogenized by milling to a <2 mm particle size. Biochar chemical properties include: 85.3% dry-matter, 38.8% total carbon, 0.9% total nitrogen, 10.2 pH, 3.31 mg kg^{-1} polycyclic aromatic hydrocarbons, 3150 mg kg^{-1} phosphorus, with calcium, magnesium, potassium, and sodium of 8.7, 4.5, 31.8 and 2.2 g kg^{-1}, respectively (Amoakwah et al., 2017).

3.3 Field Layout

The study involved sixteen (16) plots each measuring 3 m × 6 m (18 m^2), with pathways of 0.6 m between plots and 1 m between blocks. The study comprised four treatments with four replicates established in a randomized complete block design. The field was ploughed and then harrowed to achieve fine tilth, followed by the removal of stubble and weeds. On each plot, beds were raised up to 15 cm above the soil surface to facilitate drainage.

The 2-mm sieved biochar was applied to the field plots at rates of 0, 10 t ha^{-1} and 20 t ha^{-1}, and 20 t ha^{-1} with P (P-enriched biochar). These rates corresponded to 0, 0.34 and 0.68% (w/w) of biochar for the respective plots. Due to the low pH levels in most tropical soils, Al^{3+} and Fe^{2+} (sesquioxides) predominate in the soil solution. These acidic cations have the tendency to sorb available P, making P unavailable in the soil solution. The P-enriched biochar was added as a treatment primarily to protect the added P from being sorbed by the P-sorbing constituents in the soil solution. The P-enriched biochar was prepared by mixing 50 kg P_2O_5 ha^{-1} (Triple super phosphate) with 0.34% (w/w) of biochar. The mixture was stored for seven days before it was applied to the field. The treatments are denoted by CT, BC-10, BC-20, and BC-20+P for the 0, 10 t ha^{-1} and 20 t ha^{-1}, and 20 t ha^{-1} with P (P-enriched biochar), respectively.

Biochar (with and without P fertilizer) was broadcast on the soil surface of the treatment plots and incorporated into the soil by ploughing with a hoe to a depth of about 20 cm on 7th November 2015. To maintain consistency, ploughing (the same hoe treatment) was done on the control plots each time biochar was incorporated in the biochar treatment plots. Three weeks after biochar application to the soil, okra seeds were sown directly by putting two seeds in each hole created with a dibber at a depth of 4 cm and at a spacing of 60 cm × 60 cm. Two weeks after germination when the plants were about 8 cm tall, the plants were thinned to one plant per stand. Pre-planting fertilizer application of 50 kg P_2O_5 ha^{-1} in the form of triple superphosphate was done directly on the plots with the treatments without the P slurry. The plants were side dressed with 100 kg N ha^{-1} (sulphate of ammonia) and 100 kg K_2O ha^{-1} applied in two splits, two weeks after germination and at fruit set.

After the end of one growing season, 50% of the biochar application rate for the respective treatments was added to the initial application rates on 25th September 2016. Thus, 5 t ha^{-1} of corn cob biochar was added to the plot treated with 10 t ha^{-1}, and 10 t ha^{-1} was applied to the plots treated with 20 and 20 + P treated plots, yielding a total of 15 t ha^{-1} (0.51% w/w), 30 t ha^{-1} (1.03% w/w) and 30 t ha^{-1} (1.03% w/w) + P respectively. The treatments after the end of the okra growing season are accordingly denoted as CT, BC-15, BC-30 and BC-30+P for the 0, 15 t ha^{-1}, 30 t ha^{-1} and 30 t ha^{-1} + P (P-enriched biochar). The basis for the split application was because the amount of biochar received at the beginning of the experimental period was not enough to achieve the full respective application rates. Hence, the biochar was applied in batches.

3.5 Soil Sampling

Soil samples were collected on 21st May, 2016 from the plots that received the first batch of biochar, when the okra plants had reached physiological maturity. A spade was used to extract bulk, minimally disturbed soil samples from each of the 16 plots (four replicates from each of the CT, BC-10, BC-20 and BC-20+P treated plots) at a depth of 0-20 cm for aggregate characteristics measurements. In addition, bulk samples from each plot were taken from the middle of each plot, avoiding visibly compacted areas of the field due to human traffic for soil texture, pH, electrical conductivity and total organic carbon analyses.

On 16th January, 2017, soil samples from a depth of 20 cm soil layer were randomly collected by soil auger (5 cm diameter) from the sixteen plots that received the second batch of corn cob biochar (four replicates from each of the CT, BC-15, BC-30 and BC-30+P treated plots). From each corresponding plot, a spade was used to sample soil aggregates to determine the aggregate protected carbon and nitrogen and water stable aggregate measurements. The soil samples were sealed in plastic ziploc bags and transported to The Ohio State University within 2 days after sampling. In the laboratory, the aggregates were carefully spread on clean sheets and were allowed to air-dry at room temperature.

CHAPTER FOUR

EFFECTS OF BIOCHAR ON SOIL PHYSICAL PROPERTIES

4.1 Aggregate Characteristics, Water Retention and Gas Transport

4.1.1 Introduction

Soils of the humid tropics are often highly weathered and are typically characterized by low pH, low cation exchange capacity, and low inherent soil fertility. The problem is further exacerbated by intensive and long-term cultivation, which results in soil degradation due to soil acidification, soil organic carbon (SOC) depletion and severe soil erosion (Meyer, Poesen, Isabirye, Deckers, & Raes, 2011). The decrease in SOC caused by long-term cultivation decreases the aggregate stability of the soil and increases its erosivity (Annabi, Bissonnais, Villio-Poitrenaud, & Houot, 2011) and degradation of soil structure. These negative impacts may be aggravated if crop production is conducted on lands with low productivity and high proneness to soil physical degradation, a frequent situation in many agroecosystems of Ghana. There is, therefore, the need to improve aggregate strength and soil structural complexity of soils of the humid tropics through the incorporation of soil organic amendments. Soil aggregation is a key indicator of soil quality because it mediates microbial feedbacks of C and N cycling in soils (Demisie, Liu, & Zhang, 2014). Similarly, soil structure is an important soil quality factor that can influence crop productivity as it affects storage and movement of soil water, nutrients, and gases within the soil matrix. For agriculture purposes, a healthy soil structure is viewed as that which shows a combination of well-developed soil aggregates and pore systems (Bronick & Lal, 2005), enhancing the exchange of gases between soil and atmosphere. Soil structure also determines the ability of soils to carry out essential ecosystem functions and services such as turnover of organic matter, provision of optimal conditions for microbial activity, and C sequestration (Gregory, et al., 2007; Lal & Shukla, 2004). Application of biochar to soil has been reported in previous studies to improve soil aggregate stability (Obia, Mulder, Martinsen, Cornelissen, & Børresen, 2016) by increasing the cation exchange capacity of soils (Jien & Wang, 2013), thereby preventing clay dispersion and associated disruption of soil aggregates (Fungo et al., 2017). In a study conducted by Obia et al. (2016), application of corn cob biochar at rates of 0.8 to 2.5 w/w% to a tropical sandy soil increased total porosity and available water capacity by 2 to 3% respectively. Studies by Sun et al. (2013) showed that birchwood biochar improved soil pore structure indices such as pore tortuosity and pore organization by enhancing convective gas transport and increasing the ratio of macroporosity to total porosity.

Although, previous studies have reported the effect of biochar application on the volume and architecture of soil pores, the mechanisms underlying these changes are yet to be fully understood (Atkinson, Fitzgerald, & Hipps, 2010; Lehmann et al., 2011). Further, for soils of the humid tropics, research on the effects of biochar on gas transport parameters and soil water retention characteristics is relatively limited (Mukherjee & Lal, 2013a). Moreover, there is paucity of information regarding the effects of biochar application on soil aggregate characteristics in highly weathered soils of the humid tropics. Thus, there is a knowledge gap on the effect of biochar application on aggregate tensile strength, aggregate stability, soil friability, soil workability and clay dispersibility of soils of the humid tropics under field conditions. Therefore, the objectives of the study were:

- to elucidate the effect of corn cob biochar (with or without phosphorus) on the aggregate characteristics: soil tensile strength, friability, soil aggregate stability, clay dispersibility and soil workability of a highly weathered tropical sandy loam.
- to examine the mechanisms underlying the effect of corn cob biochar on soil water retention, air flow by convection and diffusion, and derived soil structure indices under a series of controlled matric potentials.

4.1.2 Materials and methods

4.1.2.1 Determination of soil aggregate characteristics

4.1.2.1.1 Soil aggregate stability

Soil samples extracted by the spade were gently broken along natural planes of failure to obtain aggregates of < 8 mm. These aggregates were air dried at room temperature, after which each sample was kept in a zip lock bag. The De Leenheer & De Boodt (1995) method was used to determine the aggregate stability of the samples. Briefly, for dry sieving, about 300 g of the 8-mm sieved air-dried samples were sieved again over a set of seven sieves (0.30, 0.50, 1.00, 2.00, 2.83, 4.76, and 8.00 mm). Thereafter, another 300 g of soil was sieved over the same set of sieves while immersed in water (wet sieving) (Figure 4).

Figure 4: The wet sieving machine.

The fractions remaining on each sieve for both the dry and wet sieving was used to estimate the stability index. Details of the methodology are described in Leroy et al., (2008). The stability index (SI) was used to classify the aggregate stability of treatments based on Eqs. (1), and (2).

$$MWD = \frac{\sum m_i \times d_i}{\sum m_i} \quad [1]$$

$$Instability\ Index\ (IS) = MWD_{dry} - MWD_{wet} \quad [2]$$

where MWD is the mean weight diameter (mm), m_i is the mass of aggregate fraction i (g), and d_i, the mean diameter of fraction i (mm). The stability index (SI) was estimated as SI = 1/IS.

4.1.2.1.2 Clay dispersibility

Subsamples of approximately 10 g of air-dried aggregates of 1-2 mm were taken for the determination of clay dispersibility as outlined by Pojasok & Kay, (1990). Cylindrical plastic bottles with the soil subsample and 80 mL artificial rainwater (0.012 mM $CaCl_2$, 0.150 mM $MgCl_2$ and 0.121 mM NaCl; pH 7.82; EC 2.24×10^{-3} S m^{-1}) were rotated end-over-end (33 rpm, 23-cm diam. rotation) for 2 min (Figure 5). After shaking, the samples were removed and left undisturbed for sedimentation for 4 hours and 38 minutes, allowing particles >2 m to settle. Subsequently, the suspension containing particles ≤2 m, i.e., the dispersed clay, was siphoned off by pipette and transferred into a beaker. Ten milliliters of the suspension was then transferred to a pre-weighed glass vial followed by oven drying at 105 °C for 24 hours. The weight of the dispersed clay was determined after oven-drying the suspension. The dispersible clay content was scaled by the clay content and reported as "mg clay per g clay" since it is generally known that increasing clay content enhances the amount of dispersible clay in soils.

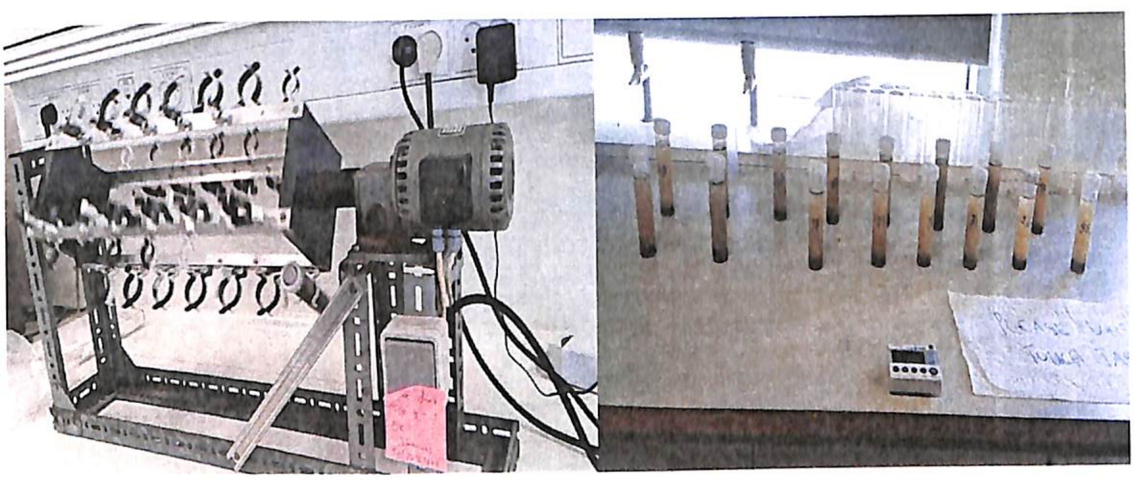


Figure 5: End-over-end shaking method.

4.1.2.1.3 Soil tensile strength

Aggregates in the size classes of 1 – 2mm, 2 – 4mm, 4 – 8mm and 8–16mm for the tensile strength test were obtained from air-dried soil carefully fragmented by hand during the drying process (Elmholt, Schjønning, Munkholm, & Debosz, 2008). Tensile strength of air-dry aggregates of all four size classes was measured as detailed by (Munkholm, Schjønning, & Petersen, 2001). In brief, the aggregates were crushed individually between two parallel plates in an indirect tension test. Fifteen (15) individual randomly selected aggregates for each combination of treatment, replicate, aggregate size, were tested (4 treatments × 4 replicates each × 4 aggregate size fractions × 15 aggregates = 960 tests). Aggregates were individually weighed before crushing. Individual fracturing forces were obtained by crushing aggregates between two flat parallel plates (Figure 6) in an indirect tension test (Dexter & Kroesbergen, 1985). The machine was calibrated with a constant displacement rate of 0.03 mm s^{-1} for all the tests. The compressive force was measured with a load cell (0–100 N).

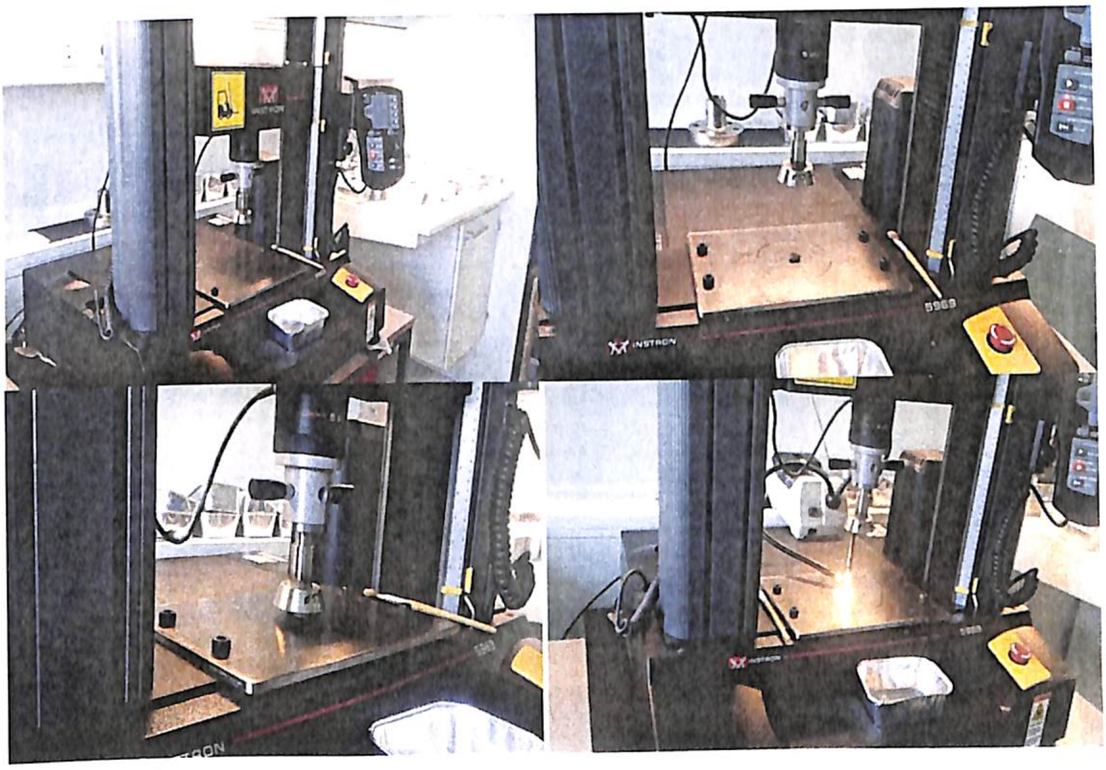


Figure 6: Instron for the indirect tension test for the soil tensile strength analysis.

Aggregate failure was detected when a continuous crack or a sudden drop in the force reading was observed (Dexter & Kroesbergen, 1985). After the test, the water content was determined by oven-drying subsamples of soil aggregates at 105 °C for 24 hours.

The aggregate tensile strength (Y, kPa) was calculated from the equation:

$$Y = \frac{0.576 \times F}{d^2} \qquad [3]$$

where F (N) is the polar force required to fracture the aggregate and d (m) is the mean aggregate diameter. The mean diameter of all aggregates was estimated from the average of the upper and lower sieve mesh sizes of the respective aggregate size classes (thus, 1.5 mm, 3 mm, 6 mm and 12 mm for 1 – 2 mm, 2 – 4 mm, 4 – 8 mm and 8 – 16 mm aggregate size classes respectively). The effective diameter (*d*) of each aggregate was adjusted using the aggregate's mass (Dexter & Kroesbergen, 1985). In this study, *d* was estimated from:

$$d = d_i \left(\frac{m_o}{m_i} \right)^{\frac{1}{3}} \qquad [4]$$

where, d_i is the mean diameter of the aggregates calculated from the respective aggregate size classes, m_o is the dry mass of individual aggregates and m_i is the mean dry mass for batches of 15 aggregates of each treatment.

4.1.2.1.4 Rupture Energy

The rupture energy, E, was derived by calculating the area under the stress-strain curve:

$$E \approx \sum_i F(s_i)\Delta s_i \qquad [5]$$

where $F(s_i)$ is the mean force at the i^{th} subinterval and Δs_i is the displacement length of the i^{th} subinterval. The mass-specific rupture energy, E_{sp}, was calculated as:

$$E_{sp} = \frac{E}{m} \qquad [6]$$

where *m* is the mass of the aggregate. For all the aggregate size classes (1 to 2 mm, 2 to 4 mm, 4 to 8 mm and 8 to 16 mm), the *m* was measured for each individual aggregate tested for tensile strength.

4.1.2.1.5 Soil friability

Soil friability is the tendency of a mass of soil to crumble into a certain size range of smaller aggregates under applied stress (Utomo & Dexter, 1981). Soil friability index was found as the slope of the graph of the natural logarithm of the tensile strength (kPa) of the aggregates against the natural logarithm of the aggregate volume (m^3).

Friability was classified according to Imhoff et al., (2002): F < 0.1 = not friable, 0.1– 0.2 = slightly friable, 0.2 – 0.5 = friable, 0.5– 0.8= very friable and >0.8 = mechanically unstable.

4.1.2.1.6 Soil workability

Soil workability (W) is a combination of friability (F) and the inverse of the mean of tensile strength (Y) as suggested by Arthur, Tuller, Moldrup, & Wollesen de Jonge, (2014):

$$W = F \times \left(\frac{1}{Y}\right) \qquad [7]$$

Thus, this parameter combines friability and the energy needed to fragment the clods. A small workability value signifies unsuitability for soil fragmentation at a given energy input and vice versa.

4.1.2.2 Soil water retention and gas transport characteristics

For soil water characteristics measurments, 100-cm^3 intact soil cores were first weighed and subsequently placed in a sandbox for the measurment of the wet region of the soil water charactistics curve.

4.1.2.2.1 Wet region measurements

Measurement of wet region water retention was performed in the laboratory at constant temperature of 20 °C. The 32 intact cores were placed in a sand box (Figure 7) and saturated with water from underneath, drained and saturated again prior to imposition of suction levels. Suction was applied successively after saturation to establish matric potentials (ψ) of −10, −30, −50, and −100 cm H_2O (pF 1, 1.5, 1.7, and 2.0).

Figure 7: Sand box for the regulation of matric potential between pF 1 and 2.0.

Thereafter, samples were moved to a suction plate apparatus (Figure 8) to successively establish matric potentials of between −300, and −500 (corresponding to pF 2.5, 2.7), cm H_2O, and lastly to a Richard pressure plate (Figure 9) at −1000 cm H_2O (corresponding to pF 3.0) according to the methodology described by Dane & Hopmans, (2002).

Figure 8: Suction plates for regulation of matric potential at pF 2.5 and 2.7.

Figure 9: Richard plate apparatus for regulation of matric potential at pF3.0.

4.1.2.2.2 Dry region measurements

The dry end of the soil water retention curve (from pF 3.8 to 5.0) was measured with a temperature compensated WP4-T dewpoint Potentiameter (METER Group Inc., Pullman, WA, USA (Figure 10). At equilibrium, the temperatures of the device and sample were measured in the chamber and subsequently converted to water activity, a_w (relative humidity). The well-known Kelvin equation was then used to convert the a_w to matric potential (ψ). First, air-dry subsamples from replication plots were oven dried to determine the prevailing water content. Based on the prevailing water content, increasing amounts of water was added to each air-dry subsample to roughly correspond to matric potentials between pF 3.8 and 5.0. A total of eighty (20 from each treatment) subsamples were used for this. To avoid evaporation losses, the moistened soil samples were sealed in Ziploc bags and stored in the refrigerator for 4 weeks to allow equilibration. After the equilibration period, two consecutive soil water potential measurements were taken with the WP4-

T. The samples were oven dried at a temperature of 105 °C for 24 hours to determine the gravimetric water content.

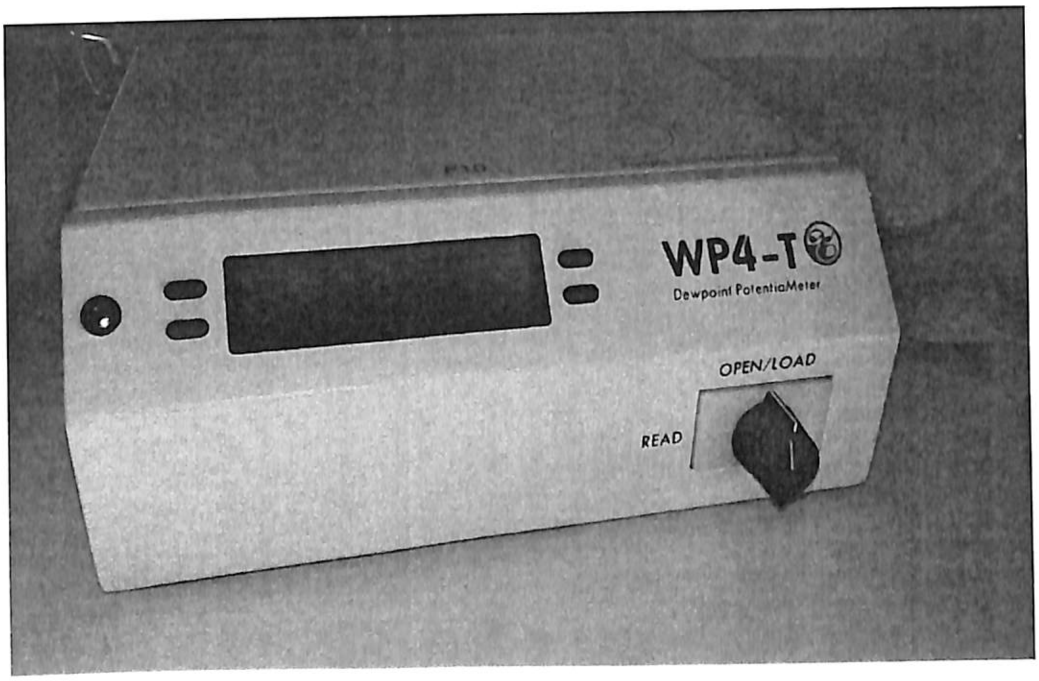


Figure 10: WP4-T Dew point potentiometer for water retention determination at pF 3.8 and 5.0.

For the water retention between pF 5.0 and 6.8, a Vapor Sorption Analyzer (METER Group Inc., Pullman, WA, USA) was used (Figure 11). Briefly, 3 g of an air-dry subsample was placed in the instrument and the matric potential and soil mass simultaneously measured.

Figure 11: Vapor Sorption Analyzer for determinnation of water retention at matric potential of pF 5.0 and 6.8.

Measurements for each sample were done in duplicate and samples were oven dried afterwards to obtain the gravimetric water content. For further details on the measurement procedure, consult Arthur et al. (2014) and Likos, Lu, & Wenszel, (2011).

Specific surface area (SA) was estimated from the measured water retention between pF 5.0 and 6.8 using the theoretical Guggenheim-Andersen-de Boer sorption isotherm equation as suggested by Timmermann, (2003) and evaluated by Arthur et al., (2017). After obtaining the monolayer water content (M_0, kg kg^{-1}) from the GAB modeling of the dry region water retention data, the SA was obtained by the following relation, $SA = M_0NA/w_M$, where N is Avogadro's number (6.02×10^{23} mol^{-1}), A is the area covered by one water molecule (10.8×10^{-20} m^2) and w_M is the molecular weight of water (0.018 kg mol^{-1}).

4.1.2.2.3 Air permeability

Flow of air by convection in an unsaturated soil is simply the movement of air molecules in the soil medium in response to a pressure gradient. The ability of a porous medium (eg soil) to conduct air by convection is generally termed air permeability (Ka) (Ball & Schjønning, 2002). This is the estimate of the intrinsic permeability, and it follows Darcy's Law, which states that the rate of fluid flow through a porous column is directly proportional to the permeability or the pressure gradient (Ball & Schjønning 2002). This is given by the equation:

$$f_g = \left(\frac{k_a(\varepsilon)}{\eta}\right)\left(\frac{dp_a}{dx}\right) \qquad \text{[Eq. 8]}$$

where f_g is the air density [L T^{-1}], η is the air viscosity [M L^{-1} T^{-1}], p_a is the air pressure [M L^{-1} T^{-2}], x is the distance [L] in the flow direction, and ε is the volumetric soil air content [L^3 L^{-3}]. The flux can be expressed as the volumetric flow rate, Q [L^3 T^{-1}], per unit area perpendicular to flow, as [L^2], through a path length, L [L]. In a tube of radius r and length L, Q can be calculated from Poiseuille's law. Solving for Ka gives the following equation:

$$k_a = \frac{Q\eta}{a_s}\frac{L_e}{\Delta P_a} \qquad \text{[Eq. 9]}$$

where a_s is the cross-sectional area [L^2], and L_e is the length of the sample [L], Pa=hgρ

In the laboratory, air permeability, k_a, was measured by the Forchheimer approach (Figure 12) described by Schjønning & Koppelgaard, (2017) on cores that were equilibrated at matric potentials of −30, −50, −100, −300, −500 and −1000 cm H_2O. Briefly, four corresponding values of pressure difference, ΔP at values around 5, 2, 1 and 0.5 hPa, were applied across the soil sample placed in an air permeameter, and the resulting air flow, Q was measured. For the purpose of quality control, a 'standard' test (with actual pressure difference, P_a <400 Pa, at target air flow, Q_t =3 ml min^{-1}) was performed prior to soil samples measurement, in two series of steps. First, the system identifies corresponding actual air flow, Q_a, and P_a values, where P_a is requested to be within ±10% of the target pressure difference, P_t = 5 hpa. Second, the system finds corresponding values of Q_a and P_a for three additional levels of ΔP = ~2, ~1, and ~0.5 hPa. By measuring at the highest pressure difference of 5 hPa prior to measuring the lower values, the risk that changes in ΔP during a measurement loop will affect water films was curtailed (Schjønning & Koppelgaard, 2017) . Darcy's law was then used to calculate k_a in a steady state.

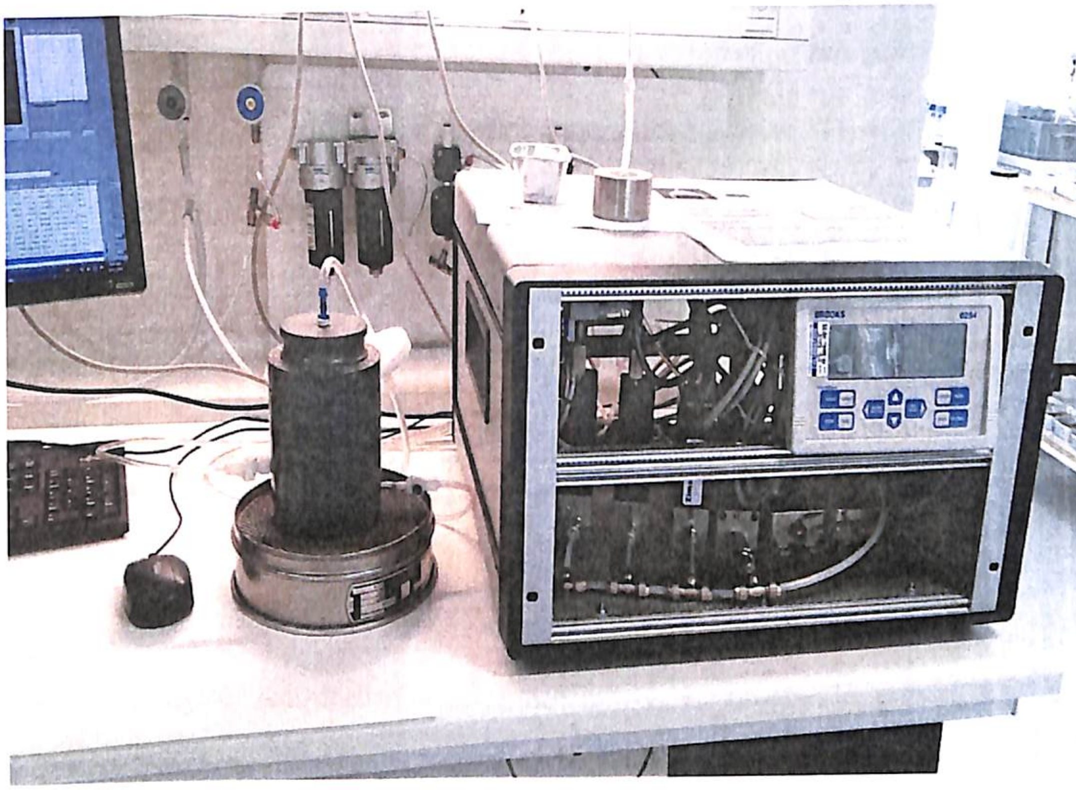


Figure 12: Air permeability chamber for the determination of movement of gas by convection.

4.1.2.2.4 Gas diffusivity

The diffusive transport of gas through the porous media (soil) is facilitated by a concentration gradient within the soil matrix, from a high concentration to a low concentration. The Fick's Law is used to describe one-dimensional diffusion of gases in oil. Fick asserted that diffusion is a dynamic molecular process, and this made him propose the laws of diffusion by means of analogy with the Fourier Law of head conduction. Fick's Law is given by the equation:

$$\frac{M_g}{a_s t} = f_g = -D_p\left(\frac{\partial C_g}{\partial x}\right) \qquad \text{[Eq. 10]}$$

where M_g is the amount of diffusing gas [M], a_s is the cross-sectional area of the soil [L^2], t is time [T], f_g is the gas flux density [M L^{-2} T^{-1}], C_g is the bulk concentration of the gaseous phase [M L^{-3}], x is the soil distance [L], and D_p

is the soil gas diffusion coefficient [$L^2 T^{-1}$] which is often scaled by Do (where Do [$L^2 T^{-1}$] is the diffusion coefficient in free air) and denoted as the relative diffusion coefficient, Dp/Do, or soil gas diffusivity (Freijer, 1994).

The unsteady state of a gas according to Rolston & Moldrup, (2002) is non-reactive (physically, chemically and biologically), and it is described by the combination of Fick's first law and the continuity equation:

$$\varepsilon\left(\frac{\partial C_g}{\partial t}\right) = D_p\left(\frac{\partial^2 C_g}{\partial x^2}\right) \qquad \text{[Eq. 11]}$$

where ε is the volumetric soil air content [$L^3 L^{-3}$].

The gas diffusion measurement was done on soil cores already equilibrated at matric potentials (ψ) of -30, -50 and -100, -300 cm, -500 and -1000 cm H_2O. In the laboratory, the soil gas diffusivity measurement was done at room temperature (20°C) on 100-cm^3 intact soil cores at six matric potentials. The experimental setup that was initially suggested by Taylor (1950) and subsequently improved further by Schjønning (1985) was used for the measurement of gas diffusion (D_p/D_0). Firstly, the gas diffusivity chamber (Figure 13) was made oxygen-free by flushing with 100% N_2 gas. The top of the soil core was exposed to the atmosphere to allow atmospheric air to enter into the chamber through the soil sample. Subsequently, O_2 was measured by an electrode mounted on the chamber wall. The O_2 diffusion coefficient in soil (D_p) was calculated as proposed by Rolston and Moldrup (2002). There was a relative small variation in the time taken for each measurement due to differences in the applied matric potentials, and this difference in the measuring time was considered small enough to neglect the O_2 depletion resulting from microbial consumption (Schjønning et al., 1999).

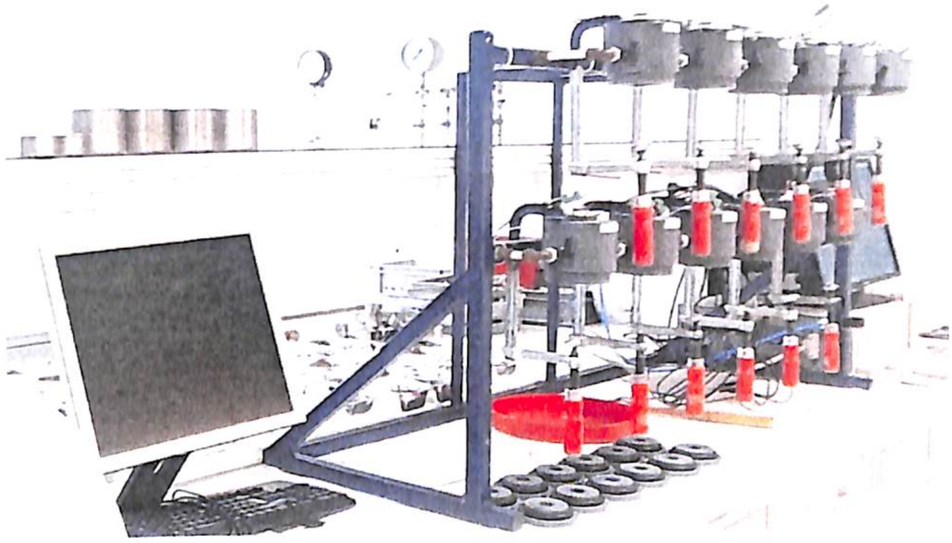


Figure 13: Gas tight chamber for soil gas diffusivity measurments.

4.1.3 Models

The pore size distributions of the soils were derived from the water retention data based on the capillary rise equation by approximating the relationship between Ψ and the equivalent pore diameter (d, μm) by:

$$d = \frac{3000}{\Psi} \qquad \text{[Eq. 12]}$$

Pore structure (continuity, complexity, and distribution) was estimated using models based on either D_p/D_O or ka and ε. The logarithmic form of the exponential model proposed by Marshall (1959) and Millington (1959) was used to relate D_p/D_o and ε:

$$\log\left(\frac{D_p}{D_o}\right) = \log(m_d) + N_d \log(\varepsilon) \qquad \text{[Eq. 13]}$$

where m_d and N_d are fitted parameters. Because of the fact that D_p/D_o value of 10^{-4} is considered as an indication of zero diffusion through a continuous air-filled pore space (Broecker & Peng, 1974), the ε at that point is considered to be the diffusion percolation threshold

$$\left(D_{PT} = 10^{-[\log(m_d)+4]/N_d}, m^3 m^{-3}\right) \quad \text{[Eq. 14]}$$

or an estimate of the volume of pores blocked to exchange of air as reported in previous studies (Schjønning 2002b).

Similarly, k_a was related to ε by the logarithmic form of a simple exponential model proposed by Ball, O'Sullivan, & Hunter (1988):

$$\log(k_a) = \log(m_c) + N_c \log(\varepsilon) \quad \text{[Eq. 15]}$$

where m_c and N_c are fitted parameters. An estimate of the permeability percolation threshold

(C_{PT}, m^3 m^{-3}) was obtained by assuming that a soil with k_a of 1.0 μm^2 is effectively impermeable (Ball et al., 1988). It must be emphasized that this k_a threshold may not be applicable to all situations due to the fact that, it is not directly based on critical limits for soils functions.

The applicability of C_{PT} in relation to D_{PT} was assessed for treated and untreated soils. The optimal value of k_a for each of the four soil groups based on the treatments (CTRL, BC-10, BC-20, and BC-20+P) was estimated using the relation

$$\left(C_{PT} = 10^{-[\log(m_c)+x]/N_c}\right) \quad \text{[Eq. 16]}$$

where x is the log (k_a) value at which C_{PT} best fit the physically based D_{PT}.

To further assess the differences in pore connectivity and tortuosity after biochar incorporation, two indices from the literature were estimated: the soil pore organization (PO) of which gives an indication of the pore size distribution, and continuity which is an empirical index of pore continuity/pore organization (PO, μm^2) (Groenevelt, Kay, & Grant, 1984):

$$PO = \frac{k_a}{\varepsilon} \qquad [Eq. 17]$$

4.1.4 Data analyses and statistics

Statistical analyses were performed using Sigma Plot 11 (Systat Software Inc., San Jose). All data obtained were checked for normality and homogeneity of variance. Analyses of variance (ANOVA) was used to test for differences between biochar-treated and untreated soils, and the Holm-Sidak post-hoc test was used to differentiate between any two given treatments. Logarithmic transformation was performed on the aggregate tensile strength and soil volume data to yield normality prior to analyses. The test for statistical significance of treatment effects was done at $p<0.05$, unless otherwise stated. Statistical significance is indicated by lower case letters beside the mean values. Results are given as mean ± standard error (SE) in tables and figures.

4.1.5 Results and discussion

4.1.5.1 Aggregate characteristics

4.1.5.1.1 Biochar effect on soil texture and chemical properties

Soil texture at the field site was classified as a sandy loam with soil organic carbon (SOC) approximately 1.03% for the control plots. The variability (standard error) of the soil texture within the plots ranged from 0.8 to 1.8 for clay, 0.2 to 0.4 for silt, and 0.8 to 1.8 for the sand fraction. There was no effect of applied biochar on soil texture (Table 3).

Table 3: *Effect of Corn Cob Biochar on Soil Textural and Chemical Properties*

Treatment	Clay	Silt	Sand	OC	Ph	EC
	% by weight					$\mu S\ cm^{-1}$
CTRL	19^{ns}	8^{ns}	73^{ns}	1.03^{a}	5.9^{bc}	309^{a}
BC-10	18	9	73	1.39^{ab}	6.2^{ac}	76^{b}
BC-20	18	8	74	1.71^{b}	6.5^{a}	61^{b}
BC-20+P	19	9	72	1.32^{ab}	6.3^{a}	66^{b}

Different letters within a column indicate that treatments are significantly different (Holm Sidak test; $p<0.05$), *ns* denote lack of a statistically significant difference among treatments. CTRL, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 ha^{-1}(P-enriched biochar) respectively.

Addition of corn cob biochar significantly ($p < 0.05$) increased the SOC compared to the control. There was a significant increase of 26%, 40% and 22% in the SOC when application rates of 10 t ha^{-1}, 20 t ha^{-1} and 20 t ha^{-1}+P of biochar was applied respectively. Interestingly, no significant differences were observed in the mean concentrations of SOC among the BC-10 and BC-20+P treatments. The highest SOC content was observed for the BC-20 treatment plots. The increase in SOC following the application of biochar agrees with the findings of Zolfi-Bavariani, Ronaghi, Ghasemi-Fasaei, & Yasrebi (2016) who reported a three-fold increase in SOC after applying poultry-derived biochar (2% w/w) on a calcareous loamy soil. Similarly, Khademalrasoul et al. (2014) observed up to a two-fold increase in

SOC after the application of swine biochar to a sandy loam soil at rates of 1, 2, and 5 kg m^{-2}.

Soil pH increased significantly by 0.3, 0.6 and 0.4 units for the BC-10, BC-20, and BC-20+P, respectively, compared to the CTRL. This finding was in agreement with the results of Hairani, Osaki, & Watanabe (2016) who showed an increase in soil pH by 0.15 to 0.25 units in a Gleyic Fluvisol amended with fine wood biochar at a rate of 35 t ha^{-1}. Novak et al. (2014) also reported an increase of 5.6 to 6.6 in soil pH following the application of hard wood biochar at a rate of 22.4 Mg ha^{-1} dry weight to a loamy sand acidic Ultisol. Additionally, Jien & Wang (2013) observed an increase in soil pH from 3.5 to 5.1 with increasing rates of biochar application following the application of waste wood biochar applied at the rates of 2.5 and 5% (w/w) to a highly weathered Typic Paleudult. The increase in soil pH is attributable to the liming potential of biochar due to the high pH (10.2) of the added biochar (Jien & Wang, 2013).

Application of corn cob biochar decreased the electrical conductivity (EC) of the soil by 75%, 80% and 79% in the BC-10, BC-20 and BC-20+P treated plots respectively, compared to the control. The decrease in soil EC found in this study in the biochar amended soils contradicted the findings of Yang et al. (2016) and Chintala et al., (2014) who observed an increase in EC following the application of corn stover and switchgrass biochar, respectively, to an acidic clayey soil at rates of 20 g kg^{-1}, 40g kg^{-1} and 60g kg^{-1}. Statistically, there was no difference in EC values among the different BC treatments. Chathurika et al. (2016) recorded no significant change in EC after the application of woodchip biochar at rates of 10 g kg^{-1} (or 1% w/w) and at 20 g kg^{-1} (or 2% w/w) to Almasippi loamy sand and a Newdale clay loam respectively. Similarly, Paneque, Rosa, Franco-Navarro, Colmenero-Flores, & Knicker (2016) also recorded no significant difference in EC when pine wood and woodchip biochar were applied to a sandy loam Calcic Cambisol at rates of 1.5 and 15 t ha^{-1}. The disparities in the effect of biochar on EC suggest that the effect of biochar on soil properties is dependent on the pyrolysis conditions and feedstock type used.

4.1.5.1.2 Water dispersible clay (WDC)

Soil clay dispersibility is an important measure of structural stability in soils. Since clay dispersibility in soils is strongly influenced by the clay content (Getahun, Munkholm, & Schjønning, 2016), the dispersible clay content was scaled with the clay content. In this study, there was a trend of increasing clay dispersibility (WDC) with increasing rates of biochar application (increase of 8%, 12% and 9% was observed in the BC-10, BC-20, and BC-20+P amended plots, respectively as compared to CTRL), although the observed differences were not significant due to the large variations within the plots for each treatment (Figure 14).

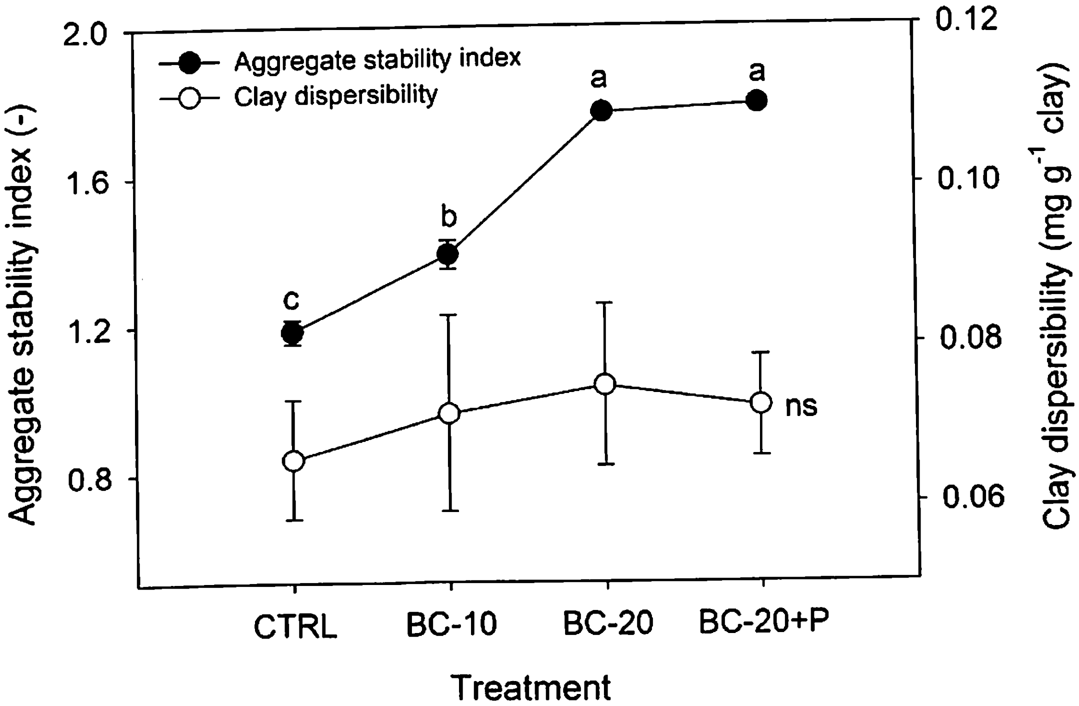


Figure 14: Corn cob biochar effects on aggregate stability index and dispersible clay content. CTRL, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

This increasing trend in WDC found in the biochar-amended soils was consistent with findings made by Hansen et al. (2015) who reported a significant increase in WDC when wood gasification biochar was incorporated at a rate of 5% (w/w) into a sandy loam soil. Contrasting reports of the overall effect of biochar on WDC has been reported in the literature. Khademalrasoul et al. (2014) argued that biochar may influence WDC negatively and positively. Through its influence on soil pH, ionic strength, zeta potential, and moisture content, biochar can also accelerate clay dispersion in soils. Hansen et al. (2015) reported that straw gasification biochar had no effect on WDC while Khademalrasoul et al. (2014) and (Soinne et al., 2014) reported an increase in WDC in soils amended with birch-wood biochar and wood chips biochar, respectively. On the other hand, aging biochar forms biochar-mineral complexes that have the potential to decrease WDC by increasing soil structural stability (Kumari, Moldrup, Paradelo, Elsgaard, & de Jonge, 2016). The trend of increasing WDC in the corn cob biochar amended soils can be attributed to higher soil pH and lower EC. Soinne et al. (2014) observed an increase in WDC in fine-textured soils (silty clay loam and clay, respectively), as well as in a coarse-textured soil amended with a mixture of Norway spruce and Scots pine chips at rates of 15 and 30 t ha^{-1}. Khademalrasoul et al. (2014) attributed the higher WDC for the biochar-amended soils to the high pH and low electrical conductivity. In this study, no significant correlation was observed between EC and WDC, but WDC strongly correlated positively (r = 0.99^{*}, p = 0.006) with soil pH (Table 4).

Table 4: *Pearson's Correlation Coefficients between Some Soil Physico-Chemical Properties (n=4)*

	EC	WDC	SI	SOC
Ph	−0.95*	0.99**	0.92*	0.91
EC		−0.94*	−0.81	−0.81
WDC			0.88	0.95*
SI				0.73
SOC				

EC, electrical conductivity; SI, aggregate stability index; WDC, water dispersible clay content; SOC, soil organic carbon. *significant correlation between two properties at p<0.10. ** significant correlation between two properties at p<0.05.

For WDC, the type and concentration of cations in the soil solution are decisive factors. The presence of monovalent cations (e.g., K^{+}) in the soil solution can increase zeta potential by increasing the net negative charge of the clay-minerals surfaces, and thus enhance clay dispersibility. A decrease in surface charge to more negative values is the primary reason for clay dispersion (Nguyen et al., 2008). Soil pH affects WDC by changing the surface charge of the clay particles through protonation and deprotonation reactions of variable charge sites. An increase in pH results in a deprotonation reaction which increases the zeta potential by increasing the surface charge. An increase in soil pH facilitates an interaction between OH^- ions and the edge sites of clay minerals and this makes them neutral or negatively charged (Nguyen et al., 2008) resulting in higher dispersibility. From our study, application of corn cob biochar increased soil pH with a resultant effect on increased clay dispersion. Our observation is in agreement with Nguyen et al. (2008) who reported a positive correlation between soil pH and surface charge, with a resultant effect on clay dispersion. Even in soils with high amount of permanent negatively charged clay minerals, the effect of pH on dispersion is a common finding, but it is most pronounced in kaolinitic soils with relatively high amounts of variably charged sites (Kaya, Ören, & Yükselen, 2006).

4.1.5.1.3. Aggregate Stability

Stability of soil aggregate is critical for maintaining the soil's resistance to mechanical stresses such as the impacts of rainfall and surface runoff. When soil aggregates disintegrate, the finer particles produced are easily transported by soil erosion forces (wind and water), settle later in soil pores, clog them and lead to formation of soil crusts. The clogging of soil pores subsequently promotes surface run-off by reducing the infiltration capacity of soils, enhancing water erosion with its attendant negative effect on soil fertility. Hence, aggregate stability is an important factor in soil erosion

(Besalatpour, Ayoubi, Hajabbasi, Mosaddeghi, & Schulin, 2013). Aggregates with a higher stability do not easily disintegrate and promote long-term carbon sequestration and soil structural stability (Ouyang et al., 2014). The effect of biochar on soil aggregate stability has yielded mixed results due to a range of methodological, temporal and material factors (Soinne et al., 2014). In this study, application of biochar significantly increased the stability index of the soil aggregates by 15%, 33% and 34% in the BC-10, BC-20, and BC-20+P amended plots respectively as compared to the CTRL (Fig. 14). This observation is in accordance with the observation of Burrell, Zehetner, Rampazzo, Wimmer, & Soja (2016) when they applied woodchip biochar at a rate of 3% by weight to three agricultural soils (Planosol, Chernozem and Cambisol). The observation from this study is also in line with the findings of Khademalrasoul et al. (2014) who indicated that black carbon in the soil acts as a binding agent between aggregates and increases the aggregate stability. The increasing trend of aggregate stability index (SI) in the biochar treated plots can partly be related to the slightly higher amount of soil organic carbon that was recorded in the biochar amended plots (Table 3). The incorporation of organic materials to soils increases soil aggregate stability through an increase in soil organic carbon. The improved SOC content of the soil might have improved the conditions of the soil in the biochar amended plots, thus creating a conducive environment for mycorrhizal fungi (Fletcher et al., 2014) and improving soil aggregate stability. Moreover, application of the corn cob biochar increased soil aggregate stability possibly due to internal cohesion through the binding of mineral particles and carbon (Soinne et al. 2014). Application of organic amendments to the soil can potentially increase soil aggregation because of binding agents, for example, exopolysaccharides obtained from turnover of the organic amendments (Papadopoulos, Bird, Whitmore, & Mooney, 2009). Tsai, Liu, Chen, Chang, & Tsai (2012) suggested that the aromatic nature of biochar may function as a bond between soil particles. The effect of the corn cob biochar on aggregate stability may be linked to organic carbon functional groups on the biochar surfaces and labile carbon released from the char into the soil system. Therefore, it can be speculated that high concentration of humic acids resulting from the breakdown of biochar particles in the soil matrix might also account for the significantly more stable aggregates in the biochar treated plots.

Increase in the electrolyte concentration (EC) promotes flocculation by shrinking the diffuse double layers of soil colloids. However, application of biochar rather decreased the EC in this study. Therefore, the observed increase in SI in the biochar amended treatments could partly be attributed to the fact that other aggregation mechanisms in the soil matrix as discussed above were responsible for the stability of the aggregates regardless of the decrease (leaching) of soluble salts in the treated plots. The corn cob biochar surfaces may have attracted labile organic matter, thus offering substrates for soil microorganisms, which subsequently might have built further aggregates through the extraction of mucilage (Liang et al., 2010).

4.1.5.1.4 Tensile strength

Tensile strength is an important soil property relevant for assessing the structural stability of a soil and its resistance against erosive forces (Watts & Dexter, 1998). Further, it is considered important in identifying management practices for sustainable crop production (Abid & Lal, 2009). Dexter &

Kroesbergen, (1985) affirmed that tensile strength is probably the most useful measure of strength of individual soil aggregates because it is a very sensitive indicator of the condition of a soil. In this study, application of BC-10 did not have any effect on tensile strength in the 1–2 mm aggregates as compared to the CTRL. However, application of BC-20 and BC-20+P resulted in a significant increase in the tensile strength of the 1-2mm aggregates as compared to the CTRL and BC-10 (Fig. 15).

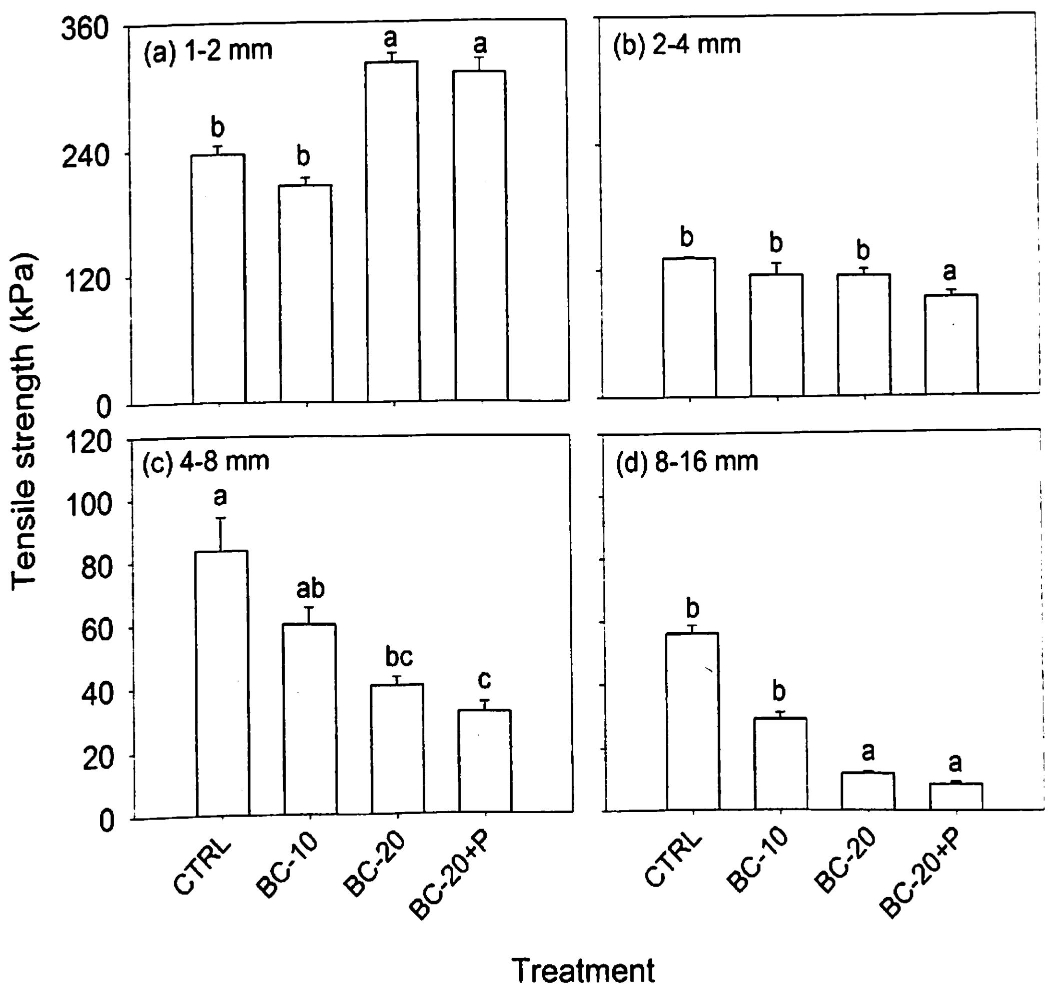


Figure 15: Effects of different application rates of corn cob biochar on tensile strength of various air-dried aggregate classes. CTRL, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively. Note the different x-axis scales for ab and cd.

The significant increase in tensile strength in the 1–2 mm aggregates is because corn cob biochar increases the water content within the aggregates. This implies that the relatively few pre-existing micro-cracks in the aggregates were not fully active to reduce air-pressure within the aggregates or to allow in-flow of air from surrounding air-filled pores. The relatively high water content in the B-20 and BC-20 + P relative to the control and the BC-10 curtailed the expansion and elongation of micro-cracks and this is believed to have adversely affected crack growth with a resultant increase in aggregate tensile strength in the smaller aggregates. It must however be noted that application of corn cob biochar in our study significantly decreased the tensile strength of soil aggregates in the large aggregates (4–8 and 8–16 mm). Other authors (Abu- Hamdeh, Abo- Qudais, & Othman, 2006; Munkholm et al., 2001) have also noted that aggregate tensile strength of natural or well managed soils decreases with increasing aggregate size. This is due to the fact that, there is an improved structural pore networks in well managed soils with an appreciable amount of pre-existing micro cracks in the large aggregates which can join to form arrays of continuous fracture surfaces upon exposure to mechanical stress (eg. tillage). The disparity in the effect of the applied biochar in the smaller aggregate size and the larger aggregate sizes could be ascribed to different interactions between the biochar particles and the different aggregate sizes. Khademalrasoul et al. (2014) affirmed that for larger particles, soil particles bond and interact with biochar particles, whereas no biochar-soil bonding occurs between biochar particles and smaller aggregate sizes. The tendency for a more systematic decrease in the tensile strength observed in the larger aggregates contradicts other studies which found opposite trends (Blanco-Canqui & Lal, 2007; Khademalrasoul et al., 2014).

The decrease in tensile strength for the large aggregates after biochar application may be attributed to the high SOC with increasing biochar application rates. Increasing the rate of biochar might have promoted crack growth and activated the pre-existing micro cracks in the large aggregates, and this ultimately gave the aggregates the propensity to elongate under mechanical stresses. The application of the corn cob biochar might have also increased the structural quality of the soil which all culminated into decreasing the tensile strength of the aggregates as the size class gets larger.

In this study, there was a systematic decrease in specific rupture energy for the larger aggregates as compared to the smaller aggregates in all the treatments (Figure 16). Soil specific rupture energy gives an indication on the strength of dry aggregate, and it is an indicator of the resistance and resilience of a soil when it is subjected to mechanical stress or manipulation. Soil resistance describes the ability of a system to retain its functional capacity upon imposition of stress, whereas soil resilience is the capacity of the soil to return to an equilibrium following displacement in response to disturbances or recover its initial function upon removal/reduction of the applied stress (Gregory et al., 2007).

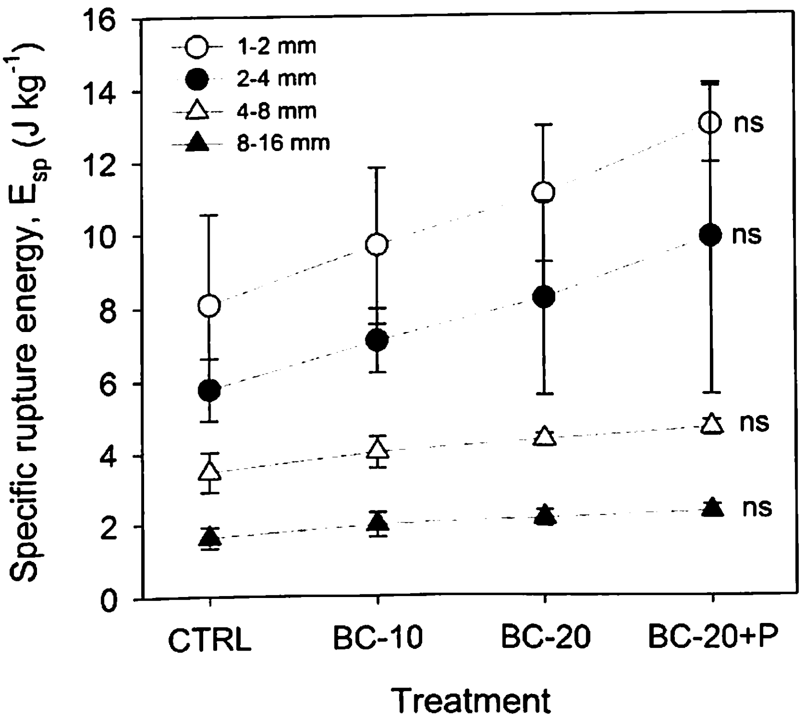


Figure 16: Effects of different application rates of corn cob biochar on specific rupture energy of various air-dried aggregate classes. CTRL, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

A similar observation was made by Schjønning, P. et al. (2012) who ascribed this finding to a collapse of the soil structural hierarchy as aggregate size increased. The implication is that, comparatively, the smaller aggregates are more resistant and resilient to stress (mechanical), and for that matter, more energy would be required to break the smaller aggregates than to break the larger aggregates. Statistically, no significant differences were observed among the specific rupture energy of the different aggregate sizes and the treatments.

4.1.5.1.5 Friability and workability index

Utomo & Dexter (1981) defined friability as the tendency of an unconfined soil to break down and crumble under applied stress into a particular size range of smaller fragments. Soil friability is also characterized by an ease of fragmentation of undesirably large aggregates/clods into undesirable small elements and a difficulty in fragmentation of minor aggregates into undesirable small elements (Munkholm 2011b). Friability (k_Y or k_E) was quantified by relating the tensile strength (*Y*) or specific rupture energy (*E*) of aggregates to their sizes (volume) (Figure 17).

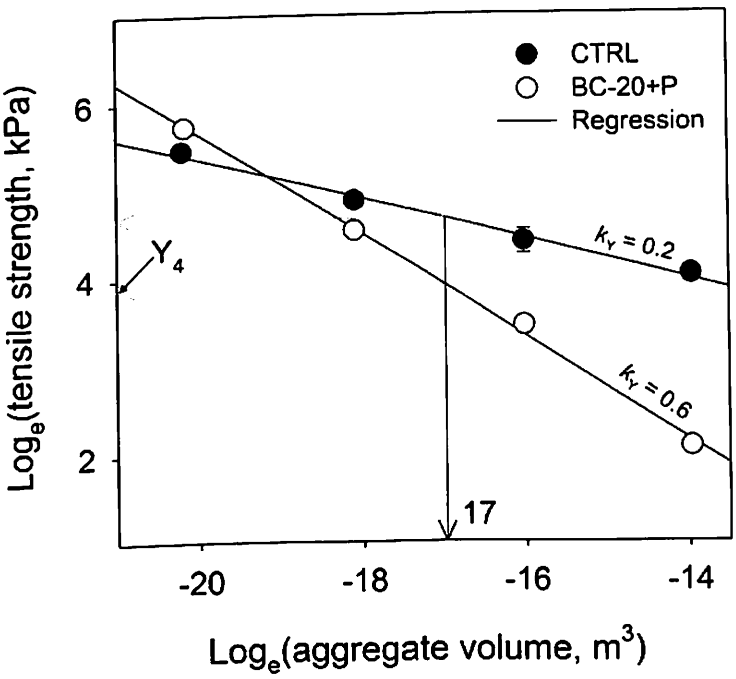


Figure 17: Log$_e$ aggregate tensile strength, Y, (kPa) as a function of log$_e$ aggregate volume, V (m3) for air-dry aggregates. Soil friability index, kY, determined as the slope of the regression equation is shown for each soil. Estimation of the median size soil aggregate class (4-mm = 17 m^3) of air-dry aggregates is also shown.

Soil aggregate friability strength was therefore characterized by soil friability index (k_Y or k_E) and the characteristic aggregate tensile strength (Y_4). The aggregate size class 4 mm was selected because it is the median size of the tested aggregates in this study. An example of derived k_Y and Y_4 for CTRL and BC-20+P is presented in Figure 17. A similar approach was used to derive k_E.

For all treatments, both k_Y and k_E increased significantly with increasing biochar application rates. Since there was a strong linear relationship between k_Y and k_E for the four treatments (Figure 18), only k_Y is discussed hereafter.

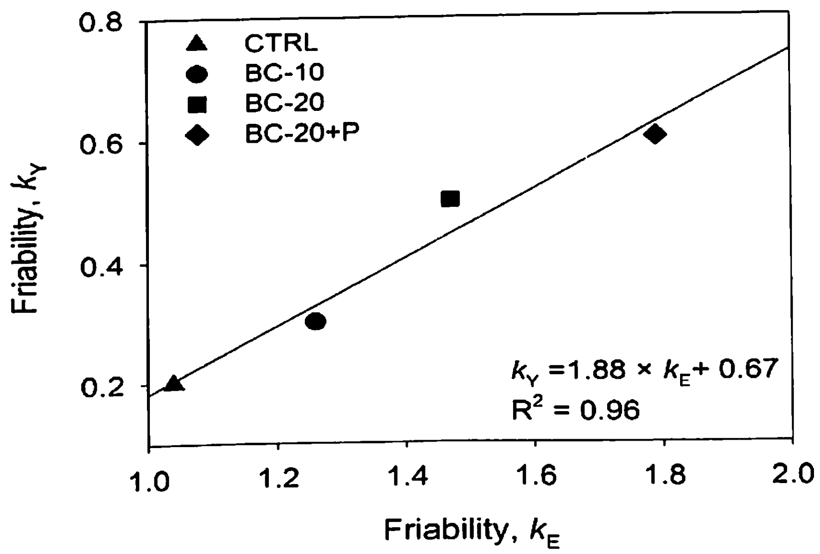


Figure 18: Linear relationship between indices of friability based on either aggregate tensile strength, kY, or specific rupture energy, kE, for each soil. CTRL, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5.

Biochar significantly increased k_Y by 28%, 57% and 60% in the 10tha^{-1}, 20 t ha^{-1} and 20 t ha^{-1} + P biochar treated plots respectively compared to the control plots (Table 5).

Table 5: *Aggregate Friability (kY and kE), Characteristic Aggregate Strength (Y4) and Workability (W) for Control and Biochar Treatments*

Treatment	k_Y	k_E	Y_4 (kPa)	W (×10^3)
CTRL	0.23^c	1.04^c	107	2.16
BC-10	0.32^b	1.26^b	77.3	4.08
BC-20	0.53^a	1.56^{ab}	61.8	8.63
BC-20+P	0.58^a	1.83^a	50.4	11.5

k_Y, friability derived from tensile strength; k_E, friability derived from specific rupture energy.

Different letters indicate that slopes (friability) are significantly different (p<0.05) between biochar treatments. CTRL, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

Statistically, no difference in the k_Y or k_E was observed in the BC-20 and BC-20+P treatments, however there was a significant difference in friability index between the BC-10 and the other biochar treatments. According to the classification index by Imhoff et al., (2002), the CTRL and BC-10 are classified as "friable", whereas the BC-20 and BC-20+P fall under the "very friable" category. The larger friability values observed after biochar application is attributable to the larger SOC contents of the biochar treatments. Soils with large contents of SOC tend to be more friable and easier to till than small-content SOC soils (Arthur et al., 2014). Further, there was a trend of decreasing soil strength (Y_4) with increasing biochar application. The CTRL had Y_4 roughly 1.5 to 2 times that of the biochar-treated soils, and this was clearly due to the larger SOC for the biochar treatments. Earlier studies confirm that aggregates from soils with low SOC tend to harden and cement (Défossez et al., 2014) as they dry yielding larger Y_4 values (Arthur et al., 2014).

Soil workability is defined as the ease with which soil can be physically manipulated for the purposes of cultivation (Arthur et al., 2014). The soil workability index gives the degree with which the soils (treated or untreated) can be tilled. The soils from the untreated plots produced a lower workability index than soils from the biochar amended plots, indicating that more energy will be required to fragment the aggregates in the control plots (Table 5).

The relatively poor ability of the aggregates to be physically manipulated could be attributed to the low SOC which resulted in low soil structural stability with low micro pores and with fewer cracks (Watts &

Dexter, 1998). Soil workability index increased with increasing biochar rates. Addition of organic material to the soil improves the soil structure, soil aggregates and total soil porosity with a substantial amount of micro cracks, which increase the friability, and workability of the soil. Generally, soil workability also increased with increasing SOC content (Arthur et al., 2014). Thus, corn cob biochar application has the potential to significantly improve soils from the perspective of soil tillage and the creation of a suitable seed bed for germination and plant growth.

4.1.5.2 Water retention and gas transport

4.1.5.2.1 Effects of biochar on soil bulk density

Biochar application decreased soil bulk density but the decreases observed were not statistically significant among the different treatments. Hence, total porosity values for the control and biochar treatments were similar (Table 6). Soil bulk density which is considered to be the main driving force of soil physical properties depicts the potential function of the soil with regards to soil aeration, water infiltration, structural support and water and gaseous movement. Results from the study showed that, although not statistically significant, biochar application appears to lower soil bulk density with minimal effect on total porosity. Previous authors have reported substantial decrease in soil bulk density after the incorporation of different kinds of biochar to different soil types. For example, Arthur & Ahmed, (2017) applied 3% w/w of rice straw biochar to a coarse-textured tropical soil and reported a significant (32%) decrease in bulk density, three months after the incorporation of rice straw biochar. This was translated into a 22% and 16% increase in total porosity after 3 months and 15 months of biochar application respectively. Further, in an incubation experiment that lasted for 120 days, Randolph et al. (2017) recorded a significant decrease in bulk density following the application of wood chips and plant residues biochar pyrolysed at three different pyrolytic temperatures (350 °C, 500 °C and 700 °C) and at an application rate of 2% w/w to sandy clay loam soils. Sun et al., (2015) affirmed that the porous nature and lower density of biochar compared to mineral soil, was responsible for the potential decrease in soil bulk density when they added birch wood biochar pyrolyzed at 500 °C to a sandy loam at application rates of 10 and 50 Mg ha^{-1}. The lack of significant increases in bulk density in our study could be attributed to the low rate of biochar application (a maximum of 0.68%) to our soil. The added biochar may not have been enough to substantially dilute the mineral fraction of the soil.

Table 6: *Effect of Corn Cob Biochar on bulk density, total porosity and plant availabe water*

Treatment	ρ_b	Φ	θ_p
	Mg m^{-3}	m^3 m^{-3}	
CT	1.52 ±0.01[a]	0.43 ±0.01[a]	0.09 ±0.01[a]
BC-10	1.49 ±0.02[a]	0.44 ±0.02[a]	0.10 ±0.01[a]
BC-20	1.45 ±0.03[a]	0.45 ±0.03[a]	0.12 ±0.01[a]
BC-20+P	1.49 ±0.03[a]	0.44 ±0.03[a]	0.12 ±0.01[a]

§ρ_b, bulk density; Φ, total porosity, θ_p, plant available water content. Different letters indicate that means are significantly different ($p<0.05$).

4.1.5.2.2 Soil water retention

The soil water contents found in the various treatments at the different matric potentials are shown in Figure 19a. There was no significant difference between the biochar treatments and CT when matric potential was ≤ pF 1.5.

Between pF 2.0 and 3.0, the BC-20 and BC-20+P treatments had significantly higher water contents than the BC-10 and CT (Figure 19a). Consequently, the biochar treatments showed similar macro- and meso-porosity (pores larger than 30 μm) as the CT (Figure 19b).

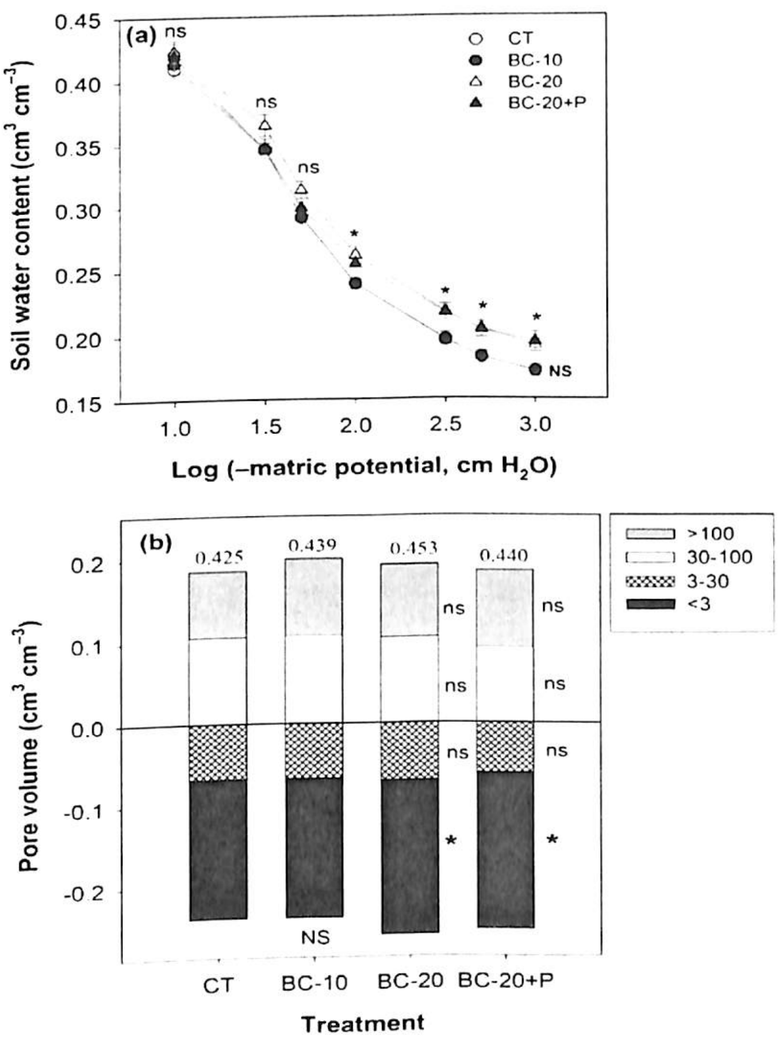


Figure 19: Corn cob biochar effect on (a) soil water retention and (b) pore size distribution. "NS" indicates no significant difference between BC-10 and CT. Values on top of bars are total pore volumes. "*" indicates significant difference between the water content or pore size class of the BC-20 and BC-20+P treatment compared to the CT. "ns" indicates no significant difference between the water content or pore size class of the BC treatment and the control. CT, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 t ha^{-1}, respectively.

Conversely, the BC-20 and BC-20+P had significantly larger proportions of micropores (pores <3 μm) than the CT. The BC-10 had a similar trend for both the water retention curve and the pore size fractions compared to the CT. Plant available water content increased only slightly (6 to 12%) for the BC treatments relative to the CT. Crop growth, microbial activities and gas exchange dynamics are important processes that are significantly influenced by the ability of the soil to retain water. For the sandy loam in this study, corn cob biochar application at 20 t ha^{-1} showed significant increase in soil water contents at lower matric potentials (pF 2.0–3.0), but at an application rate of 10 t ha^{-1}, no noticeable effect of biochar on soil water retention occurred, possibly due to the low application rate. Precluding all instances of biochar hydrophobicity, an increase in water retention in the soil at a given matric potential after the application of biochar is one of the easily recognizable beneficial effects of biochar. For instance, Randolph et al. (2017) noted a significant increase in water retention after the incorporation of woodchips and plant residues biochars at a rate of 2% w/w to a sandy clay loam. Similarly, Ulyett, Sakrabani, Kibblewhite, & Hann (2014) reported a significant increase in water retention at a matric potential of −5 kPa when a deciduous mixed wood biochar pyrolysed at 600 °C was added to a sandy loam at a rate of 60 t ha^{-1}. The authors ascribed the increase in soil water retention to the intrinsic high surface area of the biochar. Karhu, Mattila, Bergström and Regina (2011) recorded an increase in gravimetric soil water content determined following the incorporation of birch wood biochar pyrolyzed at temperature of 400 °C at an application rate of 9 t ha^{-1} to a silty loam. The authors attributed this increase in water retention to increase in total porosity which led to a corresponding increase in water retention in small pores, and thus increasing the water retention of the soil. The use of pore size distribution to infer soil structure changes induced by different phenomena is becoming common in soil science (Dal Ferro, Sartori, Simonetti, Berti, & Morari, 2014). Different sizes of pores present in the soil medium present distinct and well-defined functions in the soil. According to Pires et al. (2017), pores with size (equivalent cylindrical diameter (ECD)) > 50 μm are classified as transmission pores and <0.50 μm as residual and bonding pores. The transmission pores are responsible for air movement and drainage of excess water, whereas the residual pores are responsible for the retention and diffusion of ions in soil solutions. Lal and Shukla (2004) classified pores with ECD between 0.50 μm and 50 μm as intermediate pores, that are responsible for the release and retention of water against gravity. Biochar at all rates did not produce any significant changes in three of the four pore size fractions considered (3 to <100 μm) of the sandy loam soils. However, BC-20 and BC-20+P significantly increased the very fine pores (< 3 μm) compared to the CT. This is important particularly for storage of water for plant uptake. Although plant available water content (θ_p) was not significantly affected by biochar application, there was a trend of increasing θ_p with increasing biochar rates. For some plants, this marginal increase is particularly important during critical growth periods. Earlier studies that reported significant increases in θ_p were due to an increase in the fraction of smaller pores (0.1–10 μm) and a decrease in the larger pore size fraction. For example, Liu et al. (2016) observed increase in smaller pores (0.1–10 μm) relative to the larger pores (10–1000 μm) when they applied 16 t ha^{-1} of commercial straw biochar pyrolyzed at 500 °C to a loamy soil. Abel et al. (2013) reported an increase in the smaller pore size fractions and a decrease in the larger fractions when they applied biochar pyrolyzed from maize (mix of whole plant) at a temperature of 750 °C and at rates of 1, 2.5 and 5 wt%. (Glab Tomasz, Palmowska Joanna, Zaleski Tomasz, & Gondek Krzysztof, 2016) also found an increased volume of small pores (<50 μm in diameter) and a decreased volume of larger pores (50 - 500 μm) when they applied biochar pyrolyzed from miscanthus and winter wheat at 300 °C and at application rates of 0.5, 1, 2 and 4% to loamy sand. In our study, although the BC-20 and BC-20+P treatments had an increased fraction of small pores, they also had numerically higher fraction of large pores, resulting in marginal effect on the θ_p.

4.1.5.2.3 Specific surface area

The soil specific surface areas (SA) of the BC-20 and BC-20+P were 53 and 24 %, respectively, larger than that of CT. Surprisingly, the BC-10 treatment recorded ~23.8% reduction in soil surface area relative to the CT. These observed differences in SA were all not statistically significant (Figure 20).

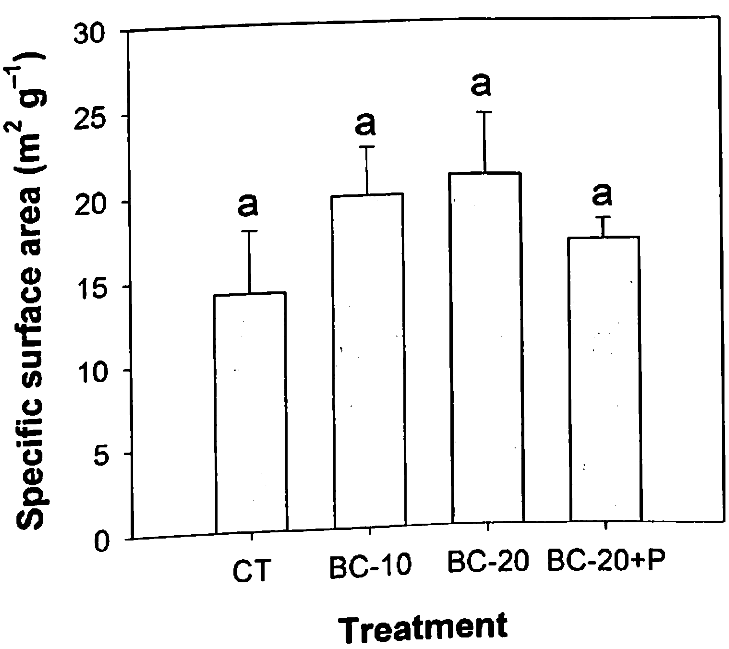


Figure 20: The soil specific surface area (derived from dry-region soil water retention) as affected by biochar. CT, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 t ha^{-1}, respectively.

The soil specific surface area (SA), which was derived from dry-region water retention data (pF 5 to 6.7), is an important property that influences numerous physico-chemical soil properties, and it is determined by the amount of clay and organic matter present in the soil. One of the notable effects of biochar incorporation into soils is an increase in OC, and this has been reported by several authors (Zhang et al., 2017; Zhu, Xiao, Shen, & Li 2017). Results from the study showed that, addition of BC resulted in a significant increase in OC in the BC-20 and BC-20+P soils. Organic carbon is positively related to soil surface area (Kaiser & Guggenberger, 2003) through organo-mineral associations. Therefore, the greater SA found in the BC-20 and BC-20+P treated soils compared to the CT could be attributed to the effect of increased OC after biochar incorporation.

4.1.5.2.4 Air filled porosity and gas transport

Corn cob biochar application had no effect on the relationship between the total air-filled porosity (the difference between the total porosity and water content) and the air connected porosity (the pores that are connected in the soil matrix to the atmospheric air). The results showed that all the treatments (CT, BC-10, BC-20 and BC-20+P) were clustered around the 1:1 line (Figure 21).

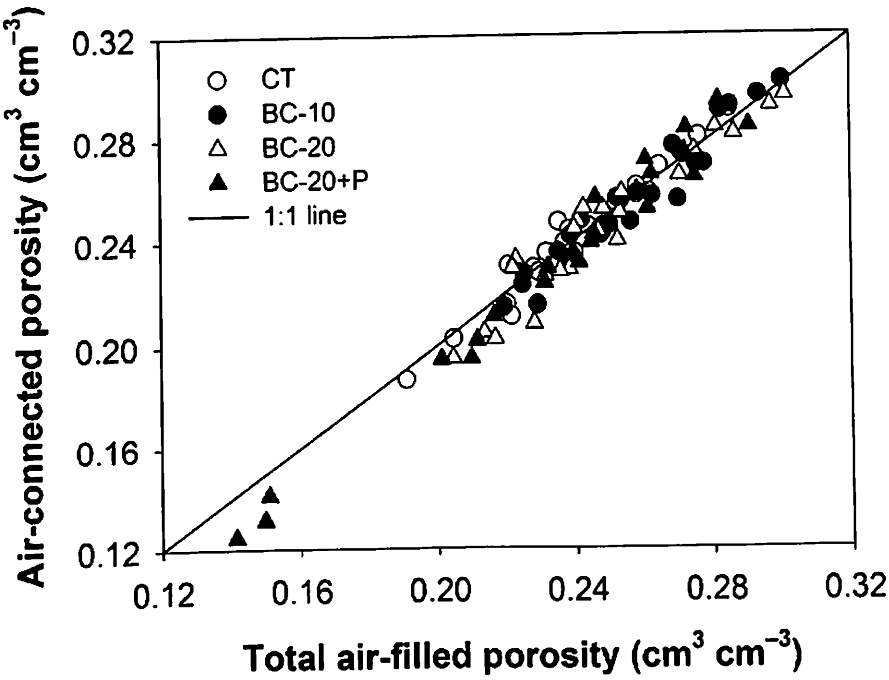


Figure 21: *Relationship between total air-filled porosity (calculated from soil-water retention data) and air-connected porosity measured by a pycnometer. CT, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 t ha^{-1}, respectively.*

4.1.5.2.5 Air movement by conduction and diffusion

The soil's ability to conduct air by diffusion expressed by relative gas diffusivity as a function of matric potential is shown in Figure 22a.

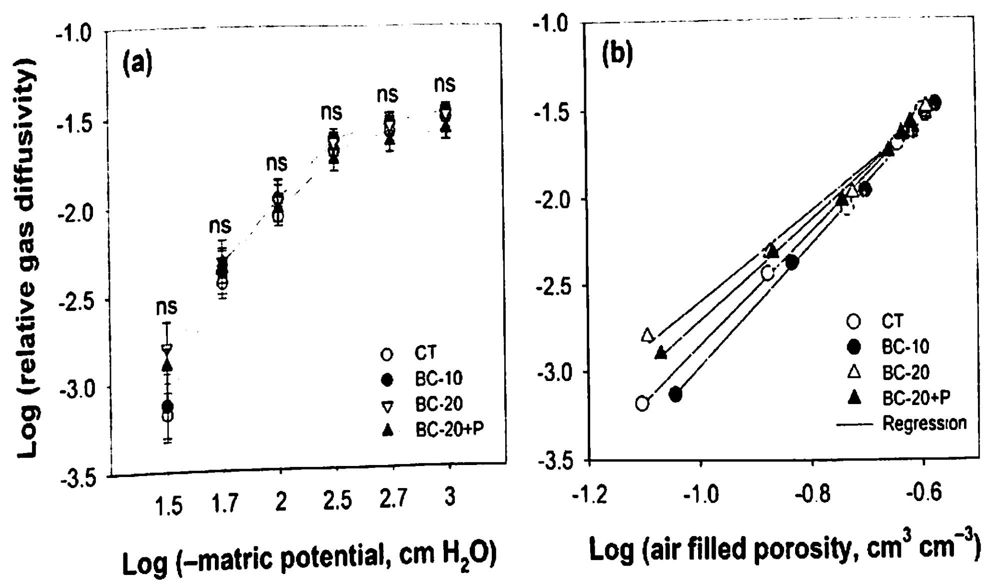


Figure 22: Relative gas diffusivity (log-scale) as a function of (a) matric potential (in pF units) and (b) total air-filled porosity. "ns" indicates no significant difference between treatments for a given matric potential. CT, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 t ha^{-1}, respectively.

Relative gas diffusivity increased with increasing air-filled porosity (decreasing matric potential) for all treatments (Figure 22b). No significant differences were observed between relative gas diffusivity values of the biochar treatments, nor between the biochar treatments and the CT, irrespective of the total porosity of the various treatments. Soil air permeability increased with decreasing matric potential in all the treatments (Figure 23a). Though not significant, the BC treatments tended to have larger air permeability values than the CT at matric potentials between 1.5 and 2.0. The $\log_{10}$ of air permeability as a function of $\log_{10}$ air-filled porosity for all treatments is presented in Figure 23b.

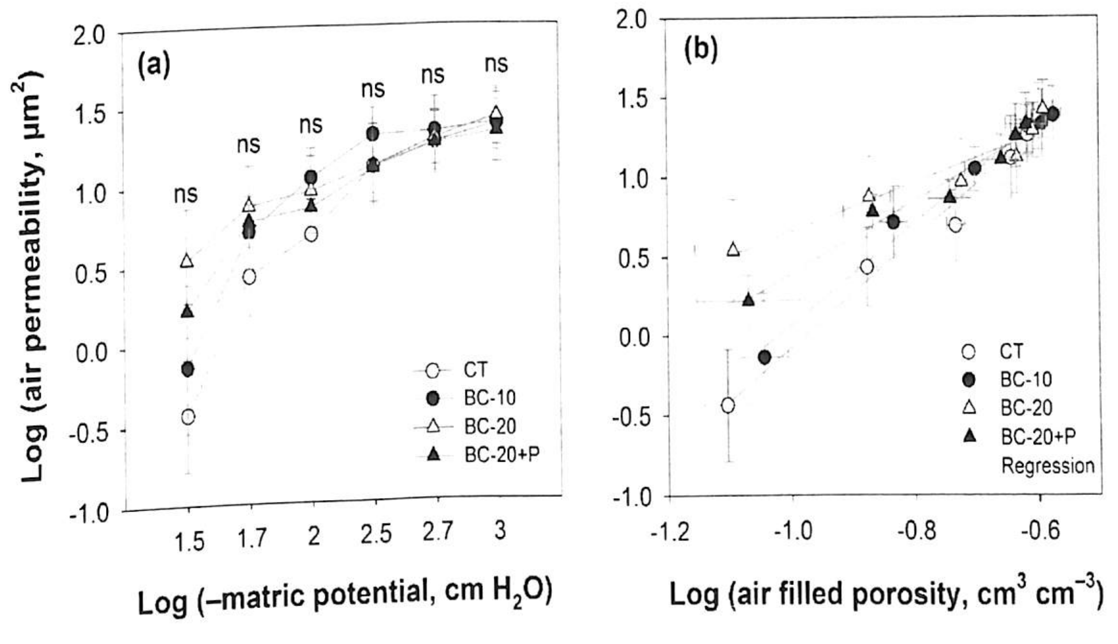


Figure 23: Soil air permeability (log-scale) as a function of (a) matric potential (in pF units) and (b) total air-filled porosity. "ns" indicates no significant difference between treatments for a given matric potential. CT, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 t ha^{-1}, respectively.

For all the treatments, air permeability increased with increasing air-filled porosity. At low air-filled porosities, there was a tendency for larger permeability values for the BC-20 treatments compared to the CT and BC-10 treatments. Transport of gas in the soil is a very important factor that influences soil aeration and respiration by plant roots. Gas transport characteristics have the potential to affect soil physical quality and crop productivity. Therefore, the quantification of gas transport parameters is important in effective management of physically degraded soils. The ability of soil to conduct air through the pores can be quantified by relative gas diffusivity, D_p/D_o which is driven by concentration gradients, and air permeability, k_a which is driven by pressure gradients. Relative gas diffusivity and air permeability are crucial gas transport parameters that provide insight into gas exchange by diffusion and convection processes, respectively (Arthur et al., 2013). According to Baral, Arthur, Olesen & Petersen (2016), these two parameters are indicators of soil function, and are important for greenhouse gas emissions. Arthur et al. (2013) also affirmed that these two properties are critical for soil aeration and transport of volatile compounds in the soil medium. Relative gas diffusivity (D_p/D_0) increased non-linearly with an increase in pF for all the treatments (Figure 22a). The observed increase in D_p/D_0 as pF increases is attributed to a directly proportional relationship between pF and air-filled porosity. This observation corroborated the findings of Arthur & Ahmed (2017) who reported a larger D_p/D_0 at -10kPa than -3 kPa due to larger air filled porosity at -10 kPa. Thus, an increase in air filled porosity resulted in a corresponding increase in D_p/D_0 (Figure 22b). At higher pF values, diffusion of gases in the soil is higher; conversely, higher water contents at lower pF values limit oxygen diffusion (Schjønning, Thomsen, Petersen, Kristensen, & Christensen, 2011).

The D_p/D_0 affects the availability of atmospheric O_2 for intrinsic soil microbes capable of degrading a variety of soil pollutants under aerobic is ascribed to the development of more connected pores as the soil dries out at higher pF values. At a pF of 1.5, the soils that received the highest biochar application rates (BC-20 and BC-20+P) conducted a relatively higher amount of air than the both the CT and BC-10 treated soils. This observation may be attributed to a reduced air-filled porosity in the CT and BC-10 treated soils (Figure 5b) as the amount of water at this matric potential occupied a substantial amount of pores and blocked potential flow pathways in the CT and BC-10 treated soils. When this happens, air movement in the soil will be essentially impeded, hence, air permeability will be low or almost negligible. Generally, an increasing trend in k_a was observed in the BC treated soils. This observation contradicts the findings of Arthur and Ahmed (2017) who reported a decrease in k_a 15 months after rice straw biochar application. The authors attributed their observation to an increase in water retention with a subsequent reduction in macropore fraction after the biochar application. A significant decrease in k_a was also reported by Wong, Chen, Ng and Wong, (2016), when they applied peanut shell biochar pyrolysed at 500°C to clayey soil at application rates of 5, 10 and 15%. The authors attributed this observation to a decreased soil inter-pores at a high biochar application, suggesting that k_a is mainly governed by inter-aggregate pores at low biochar content. The possible reason to our observation is that, the corn cob biochar applied did not significantly increase the water content to warrant the presence of blocked pores. Hence, there was a considerable fraction of the air-filled pores that were relatively active in conducting air in the soil matrix.

4.1.5.2.6 Pore structural complexity and gas percolation thresholds

To elucidate the effect of corn cob biochar on soil structure, the soil pore organization (PO) was evaluated to compare the structural complexity between the biochar treated soils and the CT. The PO parameter gives an indication of the structural differences in differently managed soils (Deepagoda et al., 2013), as smaller PO values are attributed to more tortuous pore structure (and thus higher structural complexity), implying an improved pore continuity than large PO values. From the study, PO was computed at two matric potentials (pF 2 and pF 3) at which Dp/Do and k_a were measured (Table 7).

Table 7: *Biochar Effects on Soil Pore Organization (PO) at pF 2 and pF 3, on Slopes of Log–Log Plots of Relative Gas Diffusivity and Air Permeability vs. Air-Filled Porosity (Nd and Nc, respectively) and on the estimates of the Diffusion Percolation Threshold (D_{PT}, m^3 m^{-3}), Permeability Percolation Threshold (C_{PT}, m^3 m^{-3})*

Treatment	PO_{pF2}	PO_{pF3}	N_d	N_c	D_{PT}	C_{PT}
CT	48^{ns}	166^{ns}	3.24^{ns}	3.40^{ns}	0.044^{ns}	0.054^{ns}
BC-10	74	169	3.49	3.17	0.051	0.046
BC-20	88	145	2.58	1.51	0.029	0.008
BC-20+P	48	144	2.87	2.25	0.036	0.024

"ns" denotes no significant difference among the treatments

No significant difference was observed in soil PO between the biochar treated soils and the CT at both matric potentials. At pF 2, no distinct pattern could be seen in PO between the CT and the biochar treated soils. However, PO was lower in the BC-20 and BC-20+P treatments at pF 3. Comparatively, soil PO computed at pF 2 was lower than that of pF 3. This is probably because at low pF, the length of convection pathway is high due to low pore continuity and an increase in apparent tortuosity. Amendment of the soils with biochar showed no clear trend in soil pore organization (PO) with application rate. For BC-10 and BC-20, PO_{pF2} was about two times that of CT whereas BC-20+P was identical to the CT. At pF3, PO was numerically similar among all treatments.

Similarly, other indicators of soil structural complexity (N_c and N_d) were not affected significantly by the application of corn cob biochar. Further, biochar incorporation did not have any significant effect on the fraction of the air-filled pores that are inactive in diffusion (denoted by D_{PT}), though there was a reduction of 34% and 18% in D_{PT} in the soils that received the highest biochar application rates (BC-20 and BC-20+P, respectively) relative to the CT (Table 7). There was an increase of 25% in D_{PT} in the biochar treatment (BC-10) as compared to the CT, even though this increase was not statistically different from the CT soil. Furthermore, corn cob biochar application did not have a significant effect on the convection percolation threshold (C_{PT}). Irrespective of the reduction in C_{PT} by 15%, 85% and 54% in the BC-10, BC-20 and BC-20+P respectively, as compared to the CT, there was no significant difference in C_{PT} between the biochar treatments and the CT.

The diffusion of gases in water has been reported by several authors to be slower than that in air by a factor of 10^4 (Moldrup, Olesen, Yoshikawa, Komatsu, & Rolston, 2004; Thorbjorn, Moldrup, Blendstrup, Komatsu, & Rolston, 2008). Based on this premise, Arthur et al. (2013) posited that a relative gas diffusivity value of 10^{-4} may be considered as a threshold for diffusion through connected air-filled pores. Any value below the threshold value implies that diffusion occurs in the water phase. Therefore, it can be inferred that the air-filled porosity at which the D_p/D_o threshold occurs is the diffusion percolation threshold, denoted by D_{PT}, from Eq. [4]. According to Arthur et al. (2013), the D_{PT} value expresses the fraction of air-filled pores that are not active in diffusion due to the fact that these pores are blocked by water or they are embedded in aggregates. Though not statistically significant, the soils treated with BC-20 and BC-20+P recorded lower D_{PT} values relative to the CT (Table 7). This observation implies that, most of the pores in the BC-20 and BC-20+P soil were actively involved in diffusive gas transport, giving a further indication that the biochar treated soils have lower structural complexity than the CT. This assertion is further substantiated by the low PO values obtained at pF 3 for the BC-20 and BC-20+P soils.

Similar to D_{PT} is a convection percolation threshold C_{PT}, which is suggested by Ball et al., (1988) to exist when air permeability (k_a) = 1.0µm. On the average, D_{PT} was observed to be higher than C_{PT} in the biochar amended soils. This was not expected considering the diverse pore domains that dictate convective and diffusive gas flows. Comparatively, convective flow preferentially occurs in macropores that are well drained, whereas flow of gas by diffusion takes place in virtually all pores, giving it a higher probability of yielding a lower D_{PT} values than C_{PT}. Our findings contradict the observation made by Masís-Meléndez, de Jonge, Chamindu Deepagoda, Tuller, & Moldrup, (2015) who reported lower values in D_{PT} than C_{PT}. This observation from our study may be attributed to a relatively larger water content in the network of arterial pores that directly influence gas diffusion along the axes of the cores in the biochar amended soils, hence, the lower D_{PT}

values observed in the BC treatments relative to the C_{PT} values. The relatively lower C_{PT} values observed in the BC treated soils may also be due to an increase in air-filled pore space (drained macropores) that led to a subsequent increase in the interconnected pathways for a convective gas transport in the BC amended soils.

4.1.6 Summary and Conclusions

This study assessed how corn cob biochar applied at 0 [CTRL], 10 t ha^{-1} [BC-10] and 20 t ha^{-1}, [BC-20] and 20 t ha^{-1} with P (P-enriched biochar) [BC-20+P] to a tropical sandy loam affected several aggregate characteristics and demonstrated the following:

- Increasing the rate of corn cob biochar improved the water stability of the aggregates compared to the CTRL, despite the absence of a significant effect on the dispersible clay content.
- For smaller aggregates (1–2 mm), tensile strength for BC-20 and BC-20+P treatments was significantly higher than the CTRL and BC-10, with an opposite trend observed for larger aggregates (4–8 mm and 8–16 mm).
- Corn cob biochar significantly improved soil friability and the ease of tillage quantified with a workability index.

In perspective, the adoption and incorporation of biochar may ultimately ameliorate the rate of degradation in highly weathered soils and salvage the decline in soil physical quality in tropical soils by curtailing the potential effect of soil erosion. Furthermore, the study demonstrated that addition of 10 t ha^{-1} and 20 t ha^{-1} of corn cob biochar to a tropical sandy loam has moderate impacts on soil water retention, air flow by convection and diffusion, and derived soil structure indices. Specifically:

- Higher water content was observed for the 20 t ha^{-1} biochar treatments relative to the control treatment only for matric potentials larger than pF 2.0; due to an increase in fine pores in the biochar treatments (< 3 μm).
- Despite modest increases in plant available water and soil specific surface area, biochar did not significantly affect these properties.
- Soil air permeability and gas diffusion as a function of air- filled porosity was not significantly affected by biochar application. Consequently, soil structure complexity was statistically similar for all treatments.

The observations mentioned above were made for corn cob biochar with relatively small rates of application, hence the lack of significant differences in the gas transport and pore structure characteristics. Further and/ or complimentary studies with higher biochar application rates and possibly, with different types of biochar and soil types are recommended to elucidate general biochar effects on soil functions in tropical ecosystems.

4.2 Biochar Effects on Soil Aggregate Stability and Aggregate-Associated Properties

Ancilliary studies were conducted to assess the effect of incremental changes in biochar application rates on water stable aggregates and some aggregate-associated properties. This study was conducted on the soils treated (with 15 t ha^{-1} and 30 t ha^{-1} with and without phosphate fertilizer). This study was necessitated to test the hypothesis that, increasing the rate of biochar will enhane the formation of aggregates.

4.2.1 Introduction

In spite of the potential benefits of biochar on soil aggregation, there have been some contrasting results on effect of biochar on macro and micro soil aggregates dynamics. Sun & Lu (2014) reported an increase in macro-aggregate formation after incorporation of biochar to clayey soils. On the contrary, Pronk, Heister, Ding, Smalla, & Kögel-Knabner (2012) observed a negative effect of biochar on the amount of macro-aggregates >2 mm in an artificial soil. The contrasting observations made in these two different studies may be ascribed to differences in the biochar reactivity (i.e., the amount of reactive functional groups) that strongly depend on pyrolytic conditions and feedstock type (Keiluweit, Nico, Johnson, & Kleber, 2010). Moreover, soil aggregate formation is tightly linked to the activity of the decomposer community (Guillou, Angers, Maron, Leterme, & Menasseri-Aubry, 2012). According to Grunwald et al. (2016), an increase in microbial activity can lead to less aggregate formation as a result of the intensified decomposition of organic binding agents. Conversely, soil aggregation formation is promoted due to the production of microbially derived binding agents when microbial activity is enhanced.

The location of SOC within the aggregates and its chemical characteristics, which affect the rate of its decomposition and thus its sequestration and aggregation potential, have not received much attention (Fungo et al., 2017). The effect of Soil organic carbon dynamics and its chemical composition can be analyzed by Fourier transform infrared (FTIR) spectroscopy, which characterizes the status of SOC decomposition in soils (Hansen et al., 2015). This technology has been widely utilized by several authors to study the chemical composition of SOC fractions (Calderón, Haddix, Conant, Magrini-Bair, & Paul, 2013; Soriano-Disla, Janik, Rossel, Macdonald, & McLaughlin, 2014). However, there is a knowledge gap on the association between organic functional groups, aggregate-associated C and aggregation in biochar amended soils. The objective of this work was to assess the distribution of soil aggregates, size fractions and aggregate-associated structural properties following corn cob biochar application.

4.2.2 Materials and methods

4.2.2.1 Aggregate size distribution (ASD), Mean weight diameter (MWD) and Geometric mean weight diameter (GMWD)

About 200 g of air-dried bulk soil was taken per plot. Larger clods where broken by hand along planes of natural weakness. The broken aggregates were passed through a stack of three sieves; 8 mm sieve on top, 5mm sieve in the middle and a base with no opening (blind sieve) at the bottom. The aggregate size between 5 mm and 8 mm were collected. The large aggregates retained on the top 8 mm sieve were again crush until about 100 g of soil aggregates between 5 mm and 8 mm were obtained for each treatment. Plant materials or roots from each sample were removed and the samples were stored in zip lock bags and labeled for analysis.

A wet sieving method that comprised of four sets of the U.S. Standards Sieve stack was used to determine aggregate size distribution (ASD) and mean weight diameter (MWD). Each set comprised of seven different size sieves ranging from 5mm (top), 2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm and

0.053 mm (bottom). All four sets hanged on an oscillator beam and were dropped into a bucket underneath. Each bucket has a measuring scale sticking on its inner wall for measuring water level. This whole unit was attached to a regular shaker tray that pooled back and forth the oscillator unit. Briefly, 51 g of air-dried aggregates were placed on the top sieve stack (5 mm) in each set and lowered to the level of the water surface to moisten the soil aggregates through capillary action, followed by 10 minutes of gentle submersion cycles (48 cycles per minute), with a stroke length of 10 cm. Thereafter, the soil on each sieve was transferred to a beaker, and was left to stand for 24 h, after which it was dried for 24 h at 60 °C and weighed. The MWD (mm) was calculated using the formula:

$$MWD = \sum_{i=1}^{n} w_i . \bar{x}_i \qquad \text{[Eq. 18]}$$

where x_i is the average diameter of the opening of two consecutive sieves, and w_i is the weight ratio of aggregates remaining on the $_i$th sieve. For the determination of ASD, the weight ratio of soil in each sieve (5 mm, 2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm and 0.053 mm) was attributed to the total weight of aggregates in the corresponding aggregate size class.

The GMWD was calculated as follows:

$$GMWD = \exp \frac{\sum_{i=1}^{n} w_i . \log x_i}{\sum_{i=1}^{n} w_i . x} \qquad \text{[Eq. 19]}$$

where n is the number of aggregate size range (mm), and w_i is the weight of aggregates in a size class of average diameter x_i.

4.2.2.2 Water stable macro and micro-aggregates

The water stable macro aggregates (expressed as a percentage) were determined by finding the weight ratio of soil in the sieves between 0.25 mm-5mm to the total weight of the aggregates (51 g). Similarly, the water stable micro-aggregates (expressed as a percentage) were determined by the weight ratio of soil with a diameter from 0.053 mm-0.125 mm.

4.2.2.3 Structural coefficient (SC)

This was determined as follows:

$$SC = \frac{WsMa}{WsMi} \qquad \text{[Eq. 20]}$$

where $WsMa$ is the water stable macro-aggregates, and $WsMi$ is the water stable micro-aggregates.

4.2.3 Results

4.2.3.1 Aggregate size distribution and Macro and micro aggregate stability

The investigation of the aggregate size distribution in the soils following the incorporation of biochar showed that, the micro aggregates recorded the greatest proportion of the soil aggregates in all the treatments; thus, most of the aggregates fell in the 0.125 and 0.053 mm size class for all treatments (Figure 24).

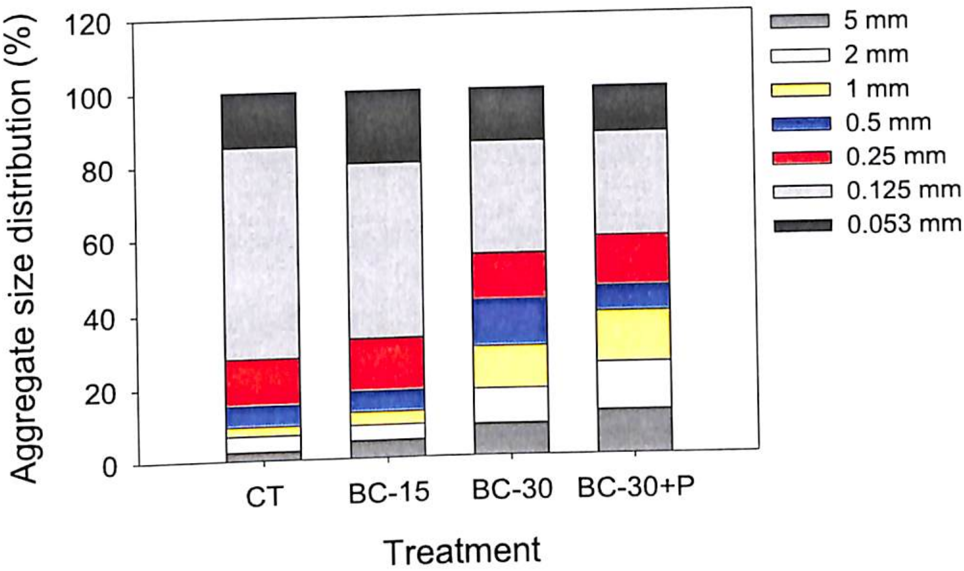


Figure 24: Corn cob biochar effects on aggregate size distribution. CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5, respectively.

In general, application of biochar increased the proportion of the water stable macro aggregates (>0.25 mm), and this effect was quite pronounced in the BC-30 and BC-30+P. In the 5 mm aggregate size class, application of corn cob biochar significantly increased the proportion of macro aggregates by 263.29 and 405.06% in the BC-30 and BC-30+P treated soils compared with the CT ($p<0.01$). Application of BC-15 did not have a significant effect on water stable macro aggregate in all the aggregate size classes (0.25-5 mm) relative to the CT. In the 2mm aggregate size fractions, the BC-30 and BC-30+P significantly increased ($p<0.01$) the proportion of water stable aggregates by 115.40 and 189.73% respectively. A significant increase of 334.21 and 416.17% in the macro aggregates ($p<0.01$) was also recorded in the respective BC-30 and BC-30+P treated soils in the 1 mm aggregate size fraction. In the 0.5 mm aggregate, no significant difference was observed in the water stable aggregates in the biochar treated soils and the CT, except the BC-30 which recorded a significant increase ($p<0.05$) in water stable aggregates by 118.38% relative to the CT. Corn cob biochar application did not have any significant effect on the water stable aggregates in the 0.25 mm irrespective of the application rate. Generally, application of biochar significantly decreased the proportion of the water stable micro aggregates, in the 0.125 mm ($p<0.01$) and 0.053 mm ($p<0.05$) size fractions. The decrease in the micro aggregates was dominant in the soils that received the highest application rates. BC-30 recorded a significant decrease of 45.90 and 18.0% in the 0.125 and 0.053 mm aggregate size classes respectively, whereas a BC-30+P recorded 50.09 and 15.69% reduction in water stable micro aggregates in the 0.125 and 0.053 mm aggregate size fractions, respectively.

Application of corn cob biochar resulted in a significant increase in the water macro aggregate stability (aggregates between 0.25 and 5 mm) relative to the CT (Figure 25).

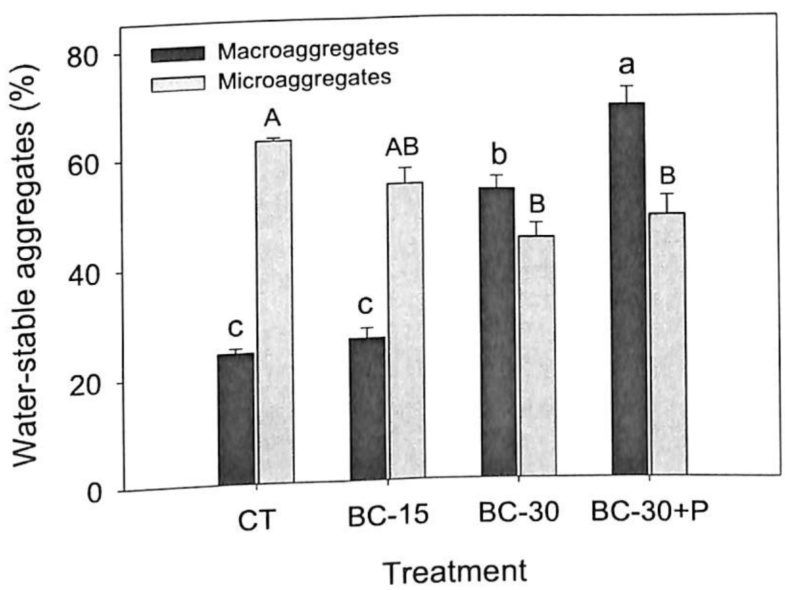


Figure 25: Effects of different application rates of corn cob biochar on the stability of macro and micro aggregates of a tropical sandy loam. CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

Biochar applied at a rate of 15 t ha^{-1} did not have any significant effect on the stability of water stable macro aggregates. However, biochar applied at a rate of 30 t ha^{-1} resulted in a significant increase in the stability of macro aggregates by 117.94 and 182.76% in the BC-30 and BC-30+P treated soils, respectively compared to the CT. Among the biochar treatments, the order of the effect of biochar on macro aggregate stability was BC-30+P>BC-30>BC-15. Conversely, application of biochar resulted in a significant reduction in micro aggregate stability. A reduction of 13.74, 29.45 and 23.17% in micro aggregate stability was recorded in the BC-15, BC-30 and BC-30+P compared to the CT. Among the biochar treatments, no significant difference was observed between BC-30 and BC-30+P. Moreover, there was no statistical difference between BC-30 and BC-15. However, there was a significant difference between BC-30+P and BC-15.

4.2.3.2 Water stable macro and micro-aggregate stocks

Application of biochar at a rate of 30 t ha^{-1} resulted in a significant increase in the water stable macro aggregate stock ($p<0.01$) (Table 8).

Table 8: *Effects of Corn Cob Biochar on Bulk Density, Macro and Micro-Aggregate Stocks and Geometric Mean Weight Diameter (GMWD)*

Treatment	Bulk density ($g\ cm^{-3}$)	Macro aggregate stock ($Mg\ ha^{-1}$)	Micro aggregate stock ($Mg\ ha^{-1}$)	GMWD
CT	1.53 ± 0.00a	735.26 ± 27.55c	62.72 ± 0.51a	0.46± 0.01b
BC-15	1.44 ± 0.02b	756.99 ± 55.34c	54.10 ± 2.91b	0.50 ± 0.02b
BC-30	1.38 ± 0.03b	1461.58 ± 65.10b	44.25 ± 2.54c	0.58 ± 0.03a
BC-30+P	1.38 ± 0.03b	1896 ± 88.56a	48.19 ± 3.54c	0.66 ± 0.03a

An increase of 97.82 and 156.66% in the water stable macro aggregates was observed in the BC-30 and BC-30+P treated soils respectively relative to the CT. No significant difference was observed between BC-15 and CT. Among the biochar treatments, significant differences in their effects on water stable macro aggregate stock were observed. The magnitude of the impact of the biochar treatments on the macro aggregate stock was in the order of BC-30+P>BC-30>BC-15.

Conversely, application of corn cob biochar resulted in a significant decrease ($p<0.01$) in the water stable micro aggregate stock by 18.28, 30.24 and 35.95% in the BC-15. BC-30 and BC-30+P treated soils respectively compared to the CT (Table 8). Among the biochar treatments, there was no difference between BC-30 and BC-30+P. However, significant differences existed between the 30 t ha^{-1} treatments (BC-30 and BC-30+P), and the BC-15. Thus, increasing biochar application rate resulted in a significant decrease in the water stable micro aggregate stock.

4.2.3.3 Mean weight diameter and structural coefficient

The effects of corn cob biochar application on mean weight diameter and structural coefficient are presented in Figure 26.

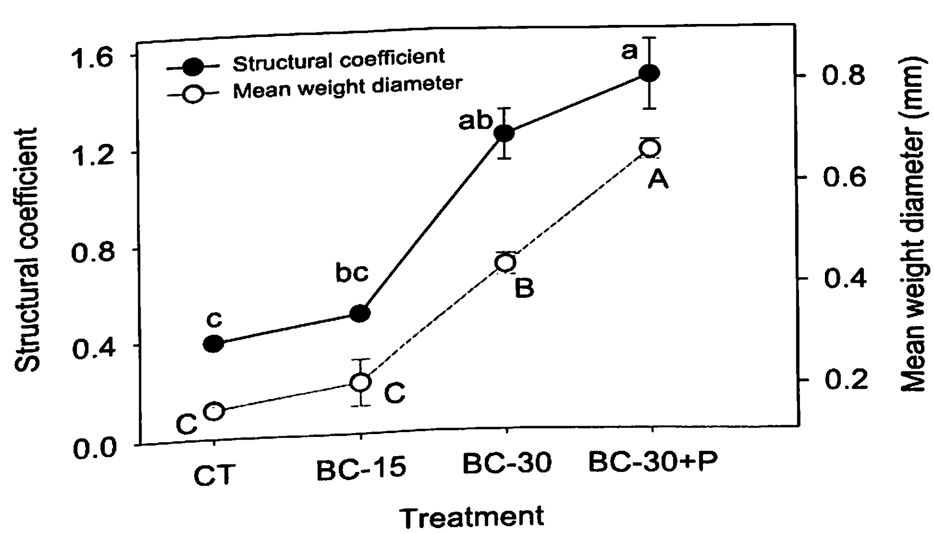


Figure 26: Effects of different application rates of corn cob biochar on the mean weight diameter and structural coefficient. CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1} respectively.

Incorporation of corn cob biochar at a rate of 30 t ha^{-1} resulted in a significant increase in the mean weight diameter (MWD) of the soils ($p<0.01$). No statistical difference was observed between the CT and BC-15. However, there was a significant increase in MWD by 152.94 and 288.24% in the BC-30 and BC-30+P treated soils. The magnitude of the effect of corn cob biochar on MWD was in the order of BC+P>BC-30>BC-15, and this order was significant between the biochar treatments. This led to a subsequent significant increase in the geometric mean weight (GMWD) following biochar application at a rate of 30 t ha^{-1} ($p<0.01$) (Table 8). A significant increase of 152.94 and 288.24% in GMWD was recorded in the BC-30 and BC-30+P treated soils. Among the biochar treatments, no significant difference was observed between BC-30 and BC-30+P. However, BC-30 and BC-30+P were significantly different from BC-15. Despite an increase of 23.53% in GWMD of the BC-15 treated soils relative to the CT, there was no statistical difference between them. The magnitude of the effect of the various treatments on GMWD was in the order of BC-30=BC-30+P>BC-15=CT. This suggests that, increasing rates of biochar can potentially increase the stability of the soil.

Biochar incorporated at a rate of 30 t ha^{-1} resulted in a significant increase in structural coefficient by 215.39 and 274.36% in the respective BC-30 and BC-30+P treated soils relative to the CT ($p<0.01$) (Figure 26). Statistically, there was no difference between BC-15 and CT, despite an increase of 25.64% in structural coefficient in the BC-15 treated soils. Among the biochar treatments, no significant difference was observed between BC-30 and BC-30+P. However, the effect of BC-30 and BC-30+P on SC was significantly higher than that of BC-15. Thus, increasing the rate of biochar application resulted in a corresponding increase in SC in a tropical sandy loam.

4.2.3.4 Bulk density

Corn cob biochar application significantly decreased ($p<0.01$) the bulk density of the soil (Table 8). A decrease of 5.88% was observed in the BC-15 treated soils, whereas a decrease of 9.8% in bulk density was recorded in both BC-30 and BC-30+P treated soils relative to the CT. No significant difference in bulk density was observed among the biochar treatments.

4.2.4 Discussion

4.2.4.1 Aggregate size distribution and aggregate stability dynamics

The greatest proportion of the soil aggregates were found in the micro aggregates, with the CT soils having significantly higher proportions of the micro aggregates as compared to the biochar treatments. This observation is in agreement with Zhang et al. (2017), who reported a significant increase in the micro aggregates in the reference soils relative to the biochar treatment when they applied wheat-straw derived biochar pyrolysed at 350-550 °C to a silty clay loam at a rate of 16 t ha^{-1}. Comparatively, biochar application significantly increased the proportion of aggregates in the larger size classes (>0.25mm) than the CT. This observation led to a significant increase in water stable macro aggregates especially in the soils treated with 30 t ha^{-1} of biochar (BC-30 and BC-30+P). This observation is in agreement with the studies conducted by Hartley, Riby, & Waterson (2016) who reported a significant increase in soil macro aggregation following the incorporation of biochar pyrolysed from 'oversize' woody biomass at a temperature of 430-440 °C, and applied to a sandy soil at a rate of 5% v/v. The increase in water stable macro aggregates may be attributed to oxidized carboxylic acid groups on biochar particles (Glaser et al., 2002), interacting with soil minerals, especially in the macro aggregates. Ouyang, et al. (2014) reported a significant increase in soil macro aggregate formation in a 90-d biochar incubation study, with little effect on micro aggregation; they opined that biochar served as a habitat for microbial growth facilitating macro aggregation, which is akin to the effect of corn cob biochar applied at 30 t ha^{-1} in this study. Furthermore, the increase in macro aggregate stability may be attributed to the high C:N ratio of biochar, which might have created favorable conditions to fungi (Bossuyt et al., 2001), which have been reported to play a more important role in macro aggregate formation than bacteria. Organic materials are directly responsible for the formation of macro aggregates (Six, Bossuyt, Degryze, & Denef, 2004) through the actions of fungal hyphae and microbial extracellular polysaccharide gums in the soil matrix. Complexation processes resulting from organic functional groups and/or microbial activity (Hartley et al., 2016) are the most likely mechanisms that result in the formation or macro aggregates in biochar amended soils.

The significant effect of corn cob biochar on the stability of macro aggregates is not surprising as biochar amendment has been reported to be beneficial in soils that have poor physical characteristics such as sandy soils (Abujabhah, Bound, Doyle, & Bowman, 2016). However, Unger, Killorn, & Brewer (2011) suggested that, the effect of biochar on the physical properties (eg. Macro aggregate stability) of these poor soils will depend on the type of biochar, as chemical composition differs with different feedstocks.

In this study, application of biochar applied at a rate of 30 t ha^{-1} (BC-30 and BC-30+P) significantly decreased micro aggregation (0.125-0.053 mm) relative to the CT. This observation conformed to the findings of Zhang et al. (2017) who reported a significant decrease in micro aggregation by 21.3% when they applied a wheat straw biochar at a rate of 16 t ha^{-1} to a silty clay loam. The relatively smaller percentage of macro aggregates in the CT and BC-15 treated soils, compared to the BC-30 and BC-30+P treated soils, is a result of the breakdown of soil structure in both CT and BC-15. This breakdown in macro aggregates was reflected in the micro aggregate amounts in both CT and BC-15. In both treatments, there are larger proportions of micro aggregates compared to BC-30 and BC-30+P treated soils. Microbial community diversity and time are the major factors influencing the formation of micro aggregate formation (Handayani, Coyne, & Tokosh, 2010). According to Handayani et al. (2010), micro aggregate formation becomes dominant when plant and microbial communities become less productive and more diverse in the soil medium. The larger amount of micro aggregates in CT and BC-15 indicates lower aggregate stability in these soils. Thus, when aggregates breakdown, finer particles are produced which are easily carried away by rain water or wind, which upon re-sedimentation, have the tendency to clog soil pores, decreasing aeration and leading to the formation of soil crusts. This sealing effect facilitates surface run off (Besalatpour et al., 2013), and thus promotes further water erosion. Moreover, a relatively higher rate of biochar applied to the soil enhanced the interaction between biochar and the <0.053mm soil particles. This therefore caused cementation of the minute particles to form micro-aggregates (0.125-0.053 mm) for subsequent macro aggregate formation. Therefore, the number of macro aggregates in the BC-30 and BC-30+P increased as compared to CT and BC-15, while the number of micro aggregates was determined by the net effect of the micro aggregate formation and upward aggregation of micro aggregates to macro aggregates (Dong, Guan, Li, Lin, & Zhao, 2016), and thus a reduction in micro aggregates in the BC-30 and BC-30+P amended soils. Tisdall & Oades (1981) affirmed that macro aggregates are formed by micro-aggregates through organic adhesion.

The increase in macro aggregation in the BC-30 and BC-30+P treated soils led to a subsequent significant increase in water stable macro aggregate stock ($p<0.01$). Conversely, the higher micro aggregation in the BC-15 and the CT relative to the BC-30 and BC-30+P resulted in a significant increase in water stable micro aggregates stock ($p<0.01$) in the reference soil and the BC-15. Our results contradict the findings of Al-Faiyz (2017) who found no effect of biochar on aggregation. For instance, Fungo et al. (2017) attributed the lack of aggregate formation to the fact that, aggregates formed in the early stages could have been disintegrated due to tillage at planting and weeding, as soil tillage has been reported to break the soil aggregates. That notwithstanding, other authors (Liu et al., 2014; Sun & Lu, 2014) have reported a significant increase in aggregation following the application of biochar. The disparities in the effect of biochar on aggregate formation may have probably occurred due to time of soil sampling after biochar application, application rate of biochar, soil texture and feedstock type used. For example, Liu et al. (2014) reported a significant increase in aggregation when wheat straw biochar pyrolysed at 350 °C was applied to red soil at a rate of 40 t ha^{-1}, but not at 20 t ha^{-1}. Sun and Lu

(2014) equally reported an increase in aggregation when straw biochar was applied at a rate of 90 t ha^{-1} to a clayey soil but no difference in aggregate formation was observed with wood chips biochar applied to the same soil at similar application rate.

4.2.4.2 Aggregate and structural stability indices

Mean weight diameter (MWD) and Geometric mean weight diameter (GMWD) are important parameters of aggregate stability. As an index of structural stability of soil aggregates, a high MWD and GMD value gives an indication of the predominance of the larger, more stable aggregates over the smaller, less stable fractions. Application of corn cob biochar at a rate of 30 t ha^{-1} significantly increased the mean MWD and GMWD of the soil, indicating that incorporation of biochar can reduce the breakage of soil macro aggregates (Dong et al., 2016). Our observation is in agreement with previous studies that biochar amendment increased the MWD (Zhang et al., 2017, Dong et al., 2016). In an incubation experiment, Sun and Lu (2014) recorded a significant increase in MWD and GMWD when a clayey soil was amended with biochar pyrolysed from straw and wastewater-sludge at a temperature of 500°C, and applied at rates of 20, 40, and 60 g biochar kg $soil^{-1}$. Soil structural coefficient is the proportion of the macro aggregates compared to the micro aggregates, and it gives an indication of the soil aggregate stability. Corn cob biochar applied at a rate of 30 t ha^{-1} significantly increased the soil physical structural stability. A significant positive correlation was observed between SC and both MWD ($r=0.94$, $p<0.01$) and GMWD ($r=0.89$, $p<0.01$) which indicates that the stability of soil aggregates was reflected in the MWD, and this has been reported in previous studies (Gelaw, Singh, & Lal, 2015; Hontoria et al., 2016). Thus, larger SC, MWD and GMD values for the biochar-amended soils exhibits a further significant enhancement in soil aggregate.

4.2.5 Conclusions

Application of biochar at 30 t ha^{-1} significantly enhanced macro aggregate formation and the stability of water stable macro aggregates especially in the BC-30 and BC-30+P treated soils. Increasing the rate of biochar application improved the aggregate structural stability indices which gives an indication of the predominace of macro aggregates that have the potential of reducing erosion in the biochar treated soils. In perspective, increasing the rate of corn cob biochar have the potential to reduce the rate of erosion by promoting the formation of macro aggregates in a tropical sandy loam.

CHAPTER FIVE

EFFECTS OF BIOCHAR ON SOIL BIOCHEMICAL PROPERTIES

5.1 Soil Carbon and Nitrogen Lability, Organic Carbon Partition and Composition

5.1.1 Introduction

The TOC, as the composite indicator of soil quality, is crucially important in providing energy and substrates and maintaining the bio-diversity and ecosystems efficiency to support agricultural resiliency and food security (Aziz, Mahmood, & Islam, 2013). While the TOC is composed of both humic and non-humic C fractions, each of these C fractions makes its particular contribution towards soil quality based on its chemical composition and lability, biochemical turnover, and physico-chemical stability (Stevenson, 1994). The non-humic C pool is composed mainly of polysaccharide and protein-like compounds (Flaig, Beutelspacher, & Rietz, 1975). Based on classical extraction of TOC by alkaline and acidic solutions, the humified fraction is categorized into three fractions, namely HA, FA, and humin, respectively (Stevenson, 1994). Both humic and non-humic C fractions originate during and/or after organic residues decomposition and subsequent polymerization of metabolites into the complex and heterogenic nature of the TOC with distinct functional groups, elemental composition, and physico-chemical properties (Jeffery et al., 2011).

Several studies have reported that TOC is not a very consistent, sensitive and early indicator to detect short-term changes in soil C cycling in response to management practices, due to its inherent background biochemical complexity and physico-chemical stability with clays and calcium (Salinas-

Garcia, Hons, Matocha, & Zuberer, 1997; Stevenson, 1994). It is reported that that there are continual humification processes undergoing in new TOC formation and/or native TOC content mediated through complex microbial and biochemical reactions and consequently, labile C compounds are converted into recalcitrant compounds or vice-versa (Zech et al., 1997). Maintaining a steady source of labile C pool than that of absolute amount of TOC is far more important to support soil functions (Aziz et al., 2013; Islam & Weil, 2000).

Carbon and nitrogen contents are stoichiometrically linked in SOM and play a crucial role in global C and N cycles to regulate agroecosystem services. However, the C: N stoichiometry in SOM under terrestrial ecosystems is greatly influenced by management practices. Cropping system productivity and sustainability are highly reliant on the dynamics of SOM, including the turnover of labile C and N and the renewal of stabilized C and N pools (Weil & Magdoff, 2004). According to Schmidt et al. (2011), the labile pool is small (typically <20% of the total), but extremely important to rapid cycling of C and nutrients for microbes and plants, soil aggregation, and C and N sequestration (Weil & Magdoff, 2004). Labile C and N in SOM is considered as a quality indicator that is more sensitive and can be detected even with the slightest change in total C and N contents (Li et al, 2016). It is highly responsive to changes in C and N inputs and provides a measurable index before changes in C and N contents (Stockmann et al., 2013). This presupposes that the influence of changes in soil management following an application of chemical fertilizer or soil amendments can be noticed sooner in the labile C and N pools rather than in the total C and N contents. Therefore, the influence of C and N lability in soil quality and crop productivity cannot be over emphasized.

Application of biochar has been reported in previous studies as one of the soil amendments in sustainable agriculture (Jeffery et al., 2011; Lehmann et al., 2006) to potentially sequester C (Spokas, 2013; Zhang et al., 2014). Labile soil C and N dynamics are key variables that are pivotal in soil quality (SQ) assessments. Understanding these dynamics will provide a better insight into how biochar application influences soil C: N.

The objectives of the study were to (1) investigate whether humic- and non-humic characteristics exhibited early, consistent and measurable changes in TOC sensitivity to biochar amendment and determine if differences translated into soil C storage by different rates of biochar application, (2) determine the effects of corn cob biochar on C and N lability indices, C and N pool indices and C and N management indices, and (3) to identify key factors regulating the patterns of labile C and N pools in response to biochar application in a highly weathered soil under humid tropical climates.

5.2 Materials and Methods

5.2.1 Soil biological and chemical analyses

Basal respiration, an indicator of antecedent biological activity was measured using an invitro method. In this method, soils were incubated for 31 days under static conditions at 25 ^{o}C. A 20 g of 2 mm sieved field-moist soil was placed into a 1 L Mason jar along with 5.0 ml of 0.5 M NaOH solution to trap CO_2 and 5.0 ml of deionized water in a separate container for the purpose of maintaining moist and humid environment inside the jar for normal bacteria growth. Three blanks were included in the experimental set-up.

Figure 27: Incubator for basal respiration studies

After 30 days, the NaOH solution was titrated with 0.5 M of standard hydrochloric acid (HCl) and basal respiration was calculated as follows:

$$BR = \frac{[(B-T)\times M\times 12\times 1000]}{W\times d} \qquad \text{[Eq. 21]}$$

where BR is basal respiration in (mg CO_2 kg^{-1} of soil day^{-1}), B is the volume (ml converted to L) of 0.5 M HCl required to neutralize the NaOH in the blank titration, T is the volume (ml converted to L) of 0.5 M HCl required to neutralize the NaOH in the sample vials from the soil incubation, M is the molarity of HCl, W is the weight of the soil sample in g converted to kg, 12 is the moles conversion to g of CO_2, d is the number of days the samples were incubated, and 1000 is the g converted to mg equivalent. Total amount of CO_2 released from the incubated soil was divided by the TOC concentration to calculate the potentially mineralizable C (PMC).

The soil extraction procedure proposed by Islam & Weil (1998) was adapted for the determination of NO_3^- and NH_4^+ contents in the soil samples. Briefly, field moist soil was gently screened through a 2 mm sieve to eliminate stones, plant debris and large organic substances. Soil that passed through the 2 mm sieve was collected for further extraction and subsequent analyses. A 10 g of the sieved field-moist soil was weighed into a 50 ml centrifuge tube. 25 ml of potassium sulphate (K_2SO_4) solution was added and the samples were placed in a rack of a horizontal shaker and shaken for 1 h at 25 oscillations per minute. After shaking, the samples were centrifuged for 5 minutes at 2000 rpm. The supernatants were filtered through Fisher Q2 filter paper into 25 ml scintillation vials. These extracts were used to determine available NO_3^- and NH_4^+ using an Astoria Pacific Auto Analyzer equipped with two dedicated cartridges and photovoltaic detectors, one each for NO_3^- and NH_4^+. The two cartridges were 305-A-023-A00 for NH_4^+-N and 305-A173-A01 for NO_3^--N. The difference between the initial available nitrogen (NH_4^+ and NO_3^-) and available nitrogen at the end of the incubation period was used to calculate the potentially mineralizable N (PMN). The specific maintenance respiration (qCO_2) rates, as measures of soil microbial catabolism, were calculated as BR rates over soil microbial biomass concentration (Anderson & Domsch, 1989). Total carbon (TC) and TN concentrations were determined on finely-ground (<125 μm) oven-dried soil by using the Elementar® automated CNS dry combustion analyzer.

Active carbon was determined by the proced [illegible]

Stine, Gruver, [illegible]

[illegible] was burnt in a muffle furnace at 480 °C for 2 hr. and the POM concentration was calculated by the loss on ignition method. Another sample of the sand associated POM was ground by a ceramic mortar and pestle and analyzed for POC and PON concentration by using the Elementar® automated CNS dry combustion analyzer. Microbial biomass carbon and nitrogen concentration g of the sieved field-moist soil was weighed into a 50 ml centrifuge tube. 25 ml of potassium sulphate (K_2SO_4) solution was added and the samples were placed in a rack of a horizontal shaker and shaken for 1 h at 25 oscillations per minute. After shaking, the samples were centrifuged for 5 minutes at 2000 rpm. The supernatants were filtered through Fisher Q2 filter paper into 25 ml scintillation vials. These extracts were used to determine available NO_3^- and NH_4^+ using an Astoria Pacific Auto Analyzer equipped with two dedicated cartridges and photovoltaic detectors, one each for NO_3^- and NH_4^+. The two cartridges were 305-A-023-A00 for NH_4^+-N and 305-A173-A01 for NO_3^--N. The difference between the initial available nitrogen (NH_4^+ and NO_3^-) and available nitrogen at the end of the incubation period was used to calculate the potentially mineralizable N (PMN). The specific maintenance respiration (qCO_2) rates, as measures of soil microbial catabolism, were calculated as BR rates over soil microbial biomass concentration (Anderson & Domsch, 1989). Total carbon (TC) and TN concentrations were determined on finely-ground (<125 μm) oven-dried soil by using the Elementar® automated CNS dry combustion analyzer.

Active carbon was determined by the procedure adopted from Islam, Stine, Gruver, Samson-Liebig, & Weil, (2003). In brief a 5.0 g air-dried soil was weighed into a 50 ml centrifuge tube containing 20 ml of 0.02 M of $KMnO_4$ and placed onto a high speed shaker for 2 minutes. Samples were then centrifuged at 2000 rpm for 5 minutes. A 0.5 ml supernatant solution was carefully drawn and placed into another set of pre-arranged centrifuge tubes containing 40 ml of deionized water, and then brought to 45 ml volume. These tubes were capped and subjected to a quick mix to obtain uniform color distribution. Quantitation was made based on the assumption that the bleaching of the KMnO4 color was proportional to the amount of active C in the soil.

$$AC = (0.02\,M(a + b \times absorbance)) \times (9000\,mg\,cmol^{-1}) \times \left(\frac{0.02\,L}{0.005\,kg\,OD\,soil} \right) \quad \text{[Eq. 22]}$$

where AC is active carbon in mg kg^{-1}, 0.02M is the initial $KMnO_4$ solution concentration, *a* is the intercept and *b* is the slope of the standard curve, 9000 is the mg C (i.e. 0.75 moles) oxidized by 1 mole MnO_4 changing from Mn^{+7} to Mn^{+2}, 0.02 L is the volume of $KMnO_4$ solution reacted, 0.005 is the kg of soil used and OD is oven dry.

Immediately after measuring AC, 10-mL of the $KMNO_4$ reacted solution was taken and placed in plastic tubes, and 0.2-mL of 1 M citric acid solution was subsequently added. The mixture was shaken to decolorize, and active nitrogen (AN) concentrations were determined by using the Shimadzu® automated total dissolved C and N analyzer.

Particulate organic matter (POM) was collected after dispersing the 2 mm sieved air-dried soil with 0.5% $(NaPO_3)_6$ solution. The dispersed soil suspension was passed through a 53 μm sieve to collect sand associated POM followed by washing with running distilled water and oven-drying at 65 °C until a constant weight was obtained. A portion of the sand associated POM was burnt in a muffle furnace at 480 °C for 2 hr. and the POM concentration was calculated by the loss on ignition method. Another sample of the sand associated POM was ground by a ceramic mortar and pestle and analyzed for POC and PON concentration by using the Elementar® automated CNS dry combustion analyzer. Microbial biomass carbon and nitrogen concentration was determined with the rapid microwave irradiation and extraction method (Islam & Weil 1998).

5.2.2 Extraction, fractionation, and analysis of humic and non-humic C fractions

The extractions of HA and FA of the soil total organic C (TOC) were carried-out by a modified procedure (Ghosh & Schnitzer, 1979; Navarrete, Tsutsuki, & Navarrete, 2011). Briefly, a 1.0 g oven-dried equivalent (ODE) sample of air-dried soil in a 50 mL plastic tube was shaken with 15 mL of 0.1 M NaOH solution (~pH 12.2) under continuous shaking at 250 rpm for a 24 hr. period. After shaking, the soil suspension was centrifuged at 3000 rpm for 10 min and filtered to obtain soil free extracted C (TEC) aliquot. The procedure was repeated thrice. The TEC aliquots were combined (~ 45 mL) and slowly acidified with concentrated H_2SO_4 to ~ pH 2 and allowed to stay over-night for coagulation and precipitation of HA from the FA. The tubes were then centrifuged at 3000 rpm for 10 min for complete precipitation and separation of the HA from the FA. The FA in solution was separated from the precipitated HA by filtration using 0.4 μm Millipore membrane (filter paper). The precipitated HA was re-dissolved in 45 mL of 0.1 M NaOH and purified from silica and ash contents by repeated dialysis in water. A 5 mL sample of filtered HA or FA aliquot was diluted to the 20 mL volume in a glass tube with 15 mL of distilled deionized water. The total C in the diluted HA and FA samples was determined by using the Shimadzu® total dissolved organic C and N analyzer.

The non-humic glucose equivalent C was determined in both HA and FA aliquots by the anthrone-sulfuric acid method (Brink, Dubach, & Lynch, 1960). Briefly, 1 mL of diluted HA or FA aliquot was taken into a 25 mL plastic tube with 5 mL of cold anthrone-sulfuric acid reagent mixture. The mixture in the tube was slowly vortex for mixing followed by heating in a boiling water-bath for 10 min. After cooling, the absorbance of the aliquot as against the glucose C standard solutions was measured at 607 nm by using a Shimadzu® spectrophotometer. The concentration of the anthrone reactive glucose equivalent C was subtracted from both HA and FA fractions. Humin, the most stabilized residual fraction of TOC was calculated after subtracting the TEC concentration from the TOC concentration.

Several quotients as measures of humification characteristics of TOC, such as humification index (HI), humification ratio (HR), and degree of humification (DH) were calculated (Aziz et al., 2013; Saviozzi, Levi-Minzi, & Riffaldi, 1994).

$$HI(\%) = \left[\frac{(Glucose\ equivalent\ total\ non-humic\ C)}{TOC}\right] \times 100 \quad \text{[Eq. 23]}$$

$$HR(\%) = \left[\frac{(Glucose\ free\ HA + FA)}{TOC}\right] \times 100 \quad \text{[Eq. 24]}$$

$$DH(\%) = \left[\frac{(Glucose\ free\ HA + FA)}{TEC}\right] \times 100 \quad \text{[Eq. 25]}$$

For spectroscopic analyses, the HA-C and FA-C fractions were adjusted to pH 7 and their optical densities were measured by a Shimadzu® spectrophotometer at visible wavelength (400 – 700 nm) with 50 nm intervals. The optical densities and wavelength values were log-transformed for for log-log relationship, and the slope of each relationship was calculated (Ghosh & Schnitzer, 1979). The optical densities of soil free extracts measured at 465 and 665 nm were used to calculate the E_{465}/E_{665} ratios (Chen, Senesi, & Schnitzer, 1977).

5.2.3 Calculation of carbon stocks and stratification

The TOC, TEC, HA, FA, humin, and non-humin C stocks were calculated by multiplying their concentration by the concurrently measured ρb values and depth. Stratification of extracted C fractions was calculated by dividing their C values under various treatments by the respective values of that C fraction in the control (reference) treatment soil (Franzluebbers, 2002). The use of the reference soil to calculate for C stratification assessment is important, so that similar soils under various treatments can be compared systematically.

5.3 Results

5.3.1 Labile carbon and nitrogen concentrations

Corn cob biochar application resulted in a significant increase in active carbon (AC) by 196, 253 and 270% in the BC-15, BC-30 and BC-30+P treated soils respectively, compared to the CT ($p<0.01$) (Table 9). Among the biochar treatments, the BC-15 treatment had significantly lower AC than the BC-30 treatments. A similar trend was observed in active nitrogen (AN) following corn cob biochar application.

A significant increase ($p<0.05$) of 91, 140 and 200% in particulate organic carbon (POC) was observed in the BC-15, BC-30 and BC-30+P treated soils, respectively, compared with the CT (Table 9). The POC contents of all the biochar treated soils were statistically similar. Incorporation of biochar did not have any significant effect on particulate organic nitrogen (PON) ($p=0.30$).

Table 9: *Effects of Corn Cob Biochar on Total Carbon (TC), Total Nitrogen (TN), Active Carbon (AC), Active Nitrogen (AN), Particulate Organic Carbon (POC) and Particulate Organic Nitrogen (PON)*

Treatment	TC (g kg^{-1})	TN (g kg^{-1})	AC (mg kg^{-1})	AN (mg kg^{-1})	POC (mg kg^{-1})	PON (mg kg^{-1})
CT	8.74 ± 0.79b	0.62 ± 0.08c	141.11± 1.54c	27.88±2.28c	1.83 ± 0.92b	0.17 ± 0.06^{ns}
BC-15	11.70±1.10ab	0.92 ± 0.08bc	418.28 ± 7.96b	39.64±2.92b	3.50 ± 1.09a	0.16 ± 0.05
BC-30	13.64 ± 1.09a	1.39 ± 0.19ab	497.68± 0.55a	57.27±3.05a	4.39 ± 2.04a	0.27 ± 0.05
BC-30+P	13.51 ± 0.79a	1.46 ± 0.21a	521.86±28.60a	61.99±0.70a	5.49 ± 1.35a	0.25 ± 0.02

§Means separated by same lower case letter in each column were not significantly different among the treatments at $p \leq 0.05$

There was a significant increase ($p < 0.01$) in potentially mineralizable carbon (PMC) by 1.5- and 1.7-fold in the soils treated with BC-30 and BC-30+P respectively, compared with the CT (Table 10). No significant difference was observed between BC-15 and CT. Statistically, the PMC contents in the BC-30+P and BC-30 amended soils were similar, and both treatments had higher PMC than the BC-15 soils.

Application of biochar resulted in a significant increase ($p < 0.04$) in microbial biomass C by 4.5-, 8.2-, and 8.3-fold in the BC-15, BC-30 and BC-30+P amended soils, respectively, compared with the CT (Table 10). The MBC contents in the BC-30 and BC-30+P treated soils were statistically similar. A 2.7-fold increase ($p < 0.01$) in microbial biomass N (MBN) content was recorded in the soils amended with BC-30 and BC-30+P (Table 10), while the BC-15 was statistically similar to the CT. The MBN content in the soils amended with 30 t ha^{-1} of biochar (BC-30 and BC-30+P) was significantly higher than the BC-15 amended soils.

Table 10: *Effect of Corn Cob Biochar on Microbial Biomass Carbon (MBC), Microbial Biomass Nitrogen (MBN), Respiratory Quotient (qR), Specific Maintenance Respiration (qCO_2), Potentially Mineralizable Carbon (PMC) and Potentially Mineralizable Nitrogen (PMN) in a Tropical Sandy Loam*

Treatment	MBC	MBN	qR	qCO_2	PMC	PMN
	(mg kg^{-1})	(mg kg^{-1})	(%)	(µg CO_2 mg^{-1} C d^{-1})	(mg kg^{-1})	(mg kg^{-1})
CT	39.7 ± 5.9c	20.5 ± 3.6b	0.5 ± 0.1c	419 ± 69a	5.4 ± 0.5c	1.7 ± 0.3b
BC-15	177.4 ± 7.7b	29.1 ± 2.0b	1.6 ± 0.2b	141.1±13b	6.6 ± 1.0bc	1.6 ± 0.2b
BC-30	324.6±27.5a	55.1 ± 4.0a	2.5 ± 0.3a	112 ± 8b	8.1±0.6ab	2.0 ± 0.1a
BC-30+P	328.5±34.5a	55.7 ± 2.1a	2.5 ± 0.3a	120 ± 15b	9.1 ± 0.8a	2.1 ± 0.4a

§Means separated by the same lower case letter in each column were not significantly different among the treatments at $p \leq 0.05$.

5.3.2 Carbon lability, pool and management indices

Application of corn cob biochar significantly ($p<0.01$) increased the carbon lability index (CLi) of the active carbon (AC) in all the biochar treated soils relative to the control (**Table 11**).

Table 11: *Effect of Corn Cob Biochar on Active Carbon (AC), Microbial Biomass Carbon (MBC), Particulate Organic Carbon (POC) and Potentially Mineralizable Carbon (PMC) Lability Index in a Tropical Sandy Loam*

	Carbon Lability Index (CLi)			
Treatment	AC	MBC	POC	PMC
CT	1.0b	1.0b	1.0 b	1.0 ^{ns}
BC-15	2.4 ± 0.2a	2.5 ± 0.29a	1.2 ± 0.4b	0.9 ± 0.2
BC-30	2.4 ± 0.2a	2.6 ± 0.21a	2.0 ± 0.5a	1.0 ± 0.1
BC-30+P	2.5 ± 0.2a	2.8 ± 0.30a	2.5 ± 1.0a	1.0 ± 0.2

§Means separated by same lower case letter in each column were not significantly different among the treatments at $p\leq0.05$.

Among the biochar treatments, no significant difference was observed with respect to the CLi of the AC. The CLi of the microbial biomass carbon (MBC) was significantly higher ($p<0.01$) by 2.5-fold, 2.6-fold and 2.8-fold in the BC-15, BC-30 and BC-30+P treated soils, respectively as compared with the CT. Similarly, there was no significant difference in CLi of the MBC in all the biochar treatments.

A significant increase of 1.2-fold, 2.0-fold and 2.5-fold in CLi particulate organic carbon (POC) was recorded in the BC-15, BC-30 and BC-30+P treated soils, respectively relative to the CT ($p<0.05$). On the contrary, no significant difference was observed in the CLi of the potentially mineralizable carbon (PMC) between the biochar treated soils and the CT ($p>0.5$). Comparatively, the CLi of the MBC was the highest, followed by AC and POC, with PMC recording the lowest values of CLi in all the biochar treated soils.

Application of biochar at a rate of 30 t ha^{-1} resulted in a significant increase ($p<0.05$) in the carbon pool index (CPI) (a measure of total organic carbon sequestration) by 64 and 56% in the BC-30 and BC-30+P treated soils respectively, compared to the CT (Figure 28). However, the CPI values of the BC-30 and BC-30+P amended soils were statistically similar. Similarly, no statistical difference was observed in CPI between the BC-15 amended soils and the CT.

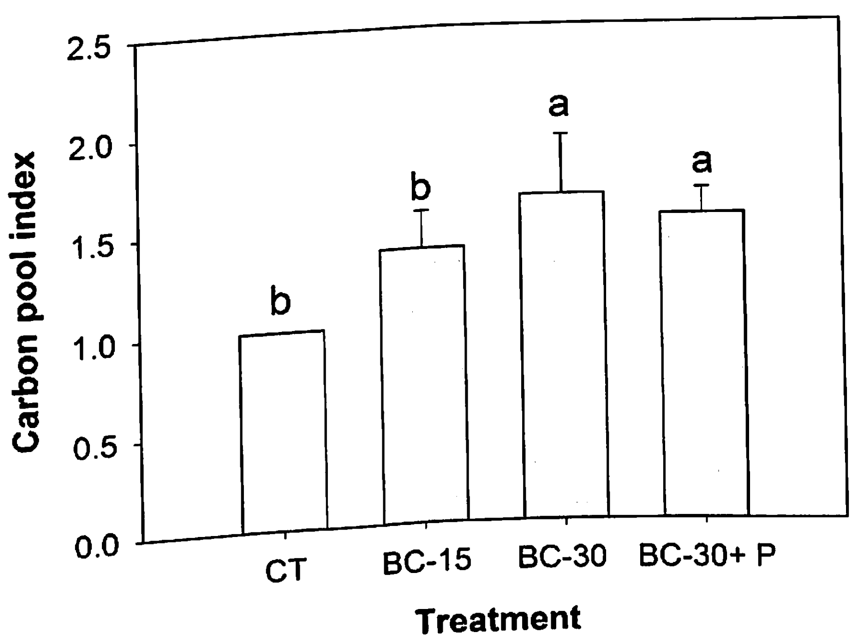


Figure 28: Carbon pool index following corn cob biochar application. CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1} respectively.

The carbon management index (CMI) (a composite indicator of both total carbon sequestration and lability) of the AC significantly increased by 159, 206 and 224% in the BC-15, BC-30 and BC-30+P treated soils relative to the CT ($p<0.01$) (Figure 29).

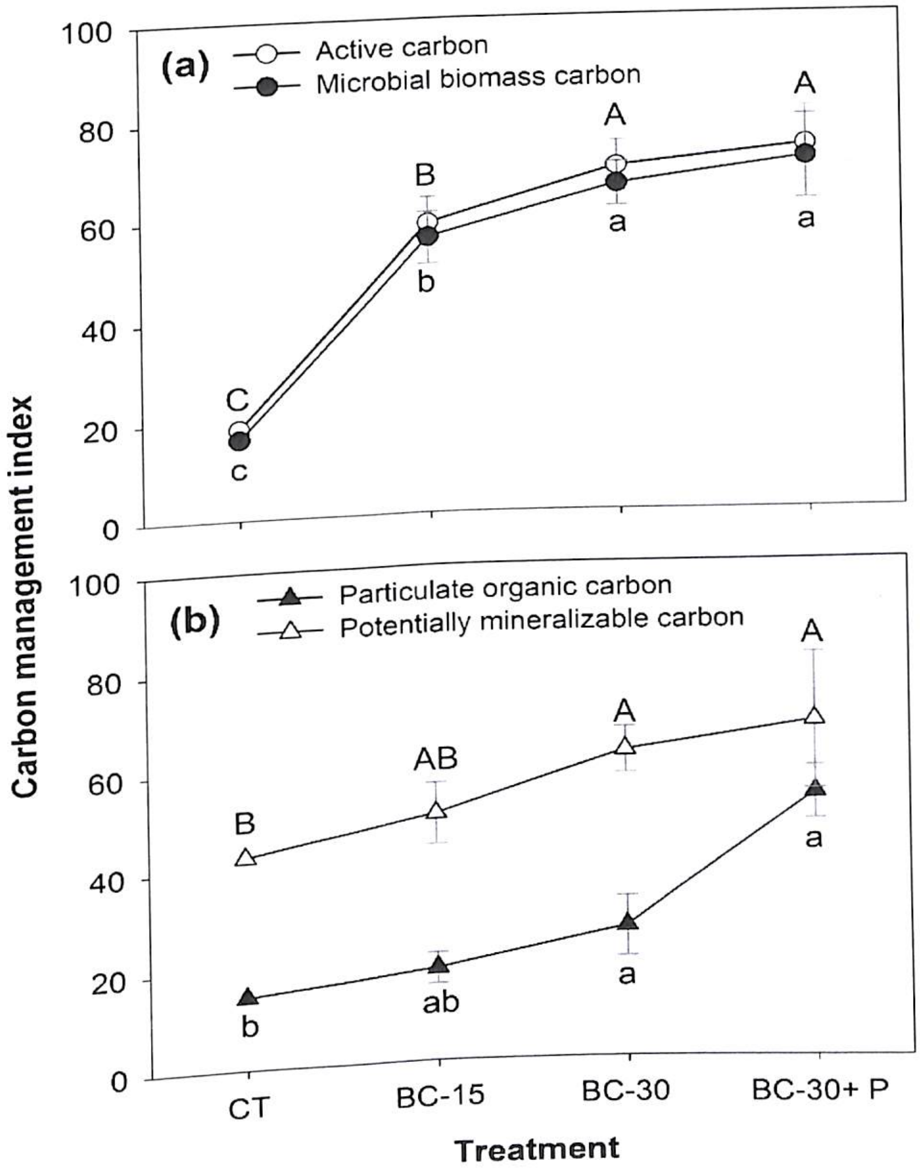


Figure 29: Carbon management index calculated based on active carbon, microbial biomass carbon, particulate oragnic carbon and potentially mineralizable carbon. CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1} respectively.

Statistically, the CMI of all the biochar-amended soils was similar.

A similar trend was observed when MBC was used as a measure of the CMI. A percentage increase ($p<0.05$) of CMI by 64 and 78 in BC-30 and BC-

30+P amended soils, respectively was observed when PMC was used as a measure of CMI relative to the CT. However, there was no statistical difference between the CMI in the BC-15 amended soils and the CT. Among the biochar treated soils, there was no difference in CMI based on the PMC.

The CMI of the POC in all the biochar treated soils was not statistically different from that of the CT ($p>0.5$). Generally, among the carbon labile pools, the CMI ranked from highest values to lowest values as AC>MBC>PMC>POC.

5.3.3 Nitrogen lability, pool and management indices

Incorporation of corn cob biochar did not have any significant effect on the nitrogen lability index (NLi) of the active nitrogen (AN) ($p=0.87$), particulate organic nitrogen (PON) ($p>0.50$) and potentially mineralizable nitrogen (PMN) ($p>0.5$). For the microbial biomass nitrogen (MBN) ($p<0.05$) (Table 12), NLi increased by 21 and 18% in the BC-30 and BC-30+P treated soils respectively, compared to the CT.

Table 12: *Effect of Corn Cob Biochar on Active Nitrogen (AN), Microbial Biomass Nitrogen (MBN), Particulate Organic Nitrogen (PON) and Potentially Mineralizable Nitrogen (PMN) Lability Index in a Tropical Sandy Loam*

	Nitrogen Lability Index (NLi)			
Treatment	AN	MBN	PON	PMN
CT	1.0 ^{ns}	1.0b	1.0 ^{ns}	1.0 ^{ns}
BC-15	0.9 ± 0.1	0.9 ± 0.2b	0.8 ± 0.13	0.6 ± 0.1
BC-30	0.9 ± 0.1	1.2 ± 0.2a	0.7 ± 0.13	0.6 ± 0.1
BC-30+P	1.0 ± 0.2	1.2 ± 0.2a	0.9 ± 0.25	0.5 ± 0.2

§Means separated by same lower case letter in each column were not significantly different among the treatments at $p\leq0.05$.

Statistically, there was no difference in NPI in the BC-15 treated soils and the CT. However, incorporation of biochar at 30 t ha^{-1} resulted in a significant increase ($p<0.05$) in the nitrogen pool index (NPI) by 139 and 137% in the BC-30 and BC-30+P amended soils, relative to the CT (Figure 30).

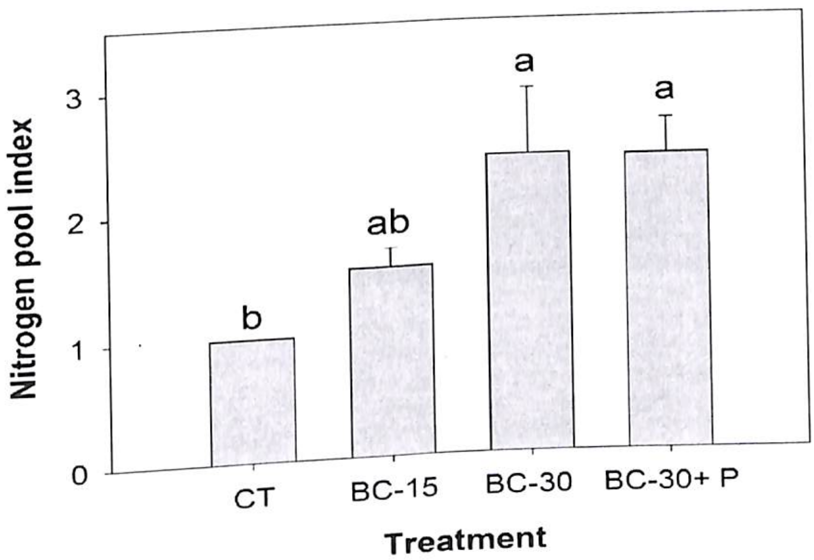


Figure 30: Nitrogen pool index following corn cob biochar application. CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1} respectively.

The various labile nitrogen pools were respectively used as a measure of nitrogen management index (NMI). A significant increase of 104 and 123% in NMI of the AN was respectively recorded in the BC-30 and BC-30+P amended soils ($p<0.01$) (Figure 31). No difference in NMI was observed in the BC-15 treated soils and the CT.

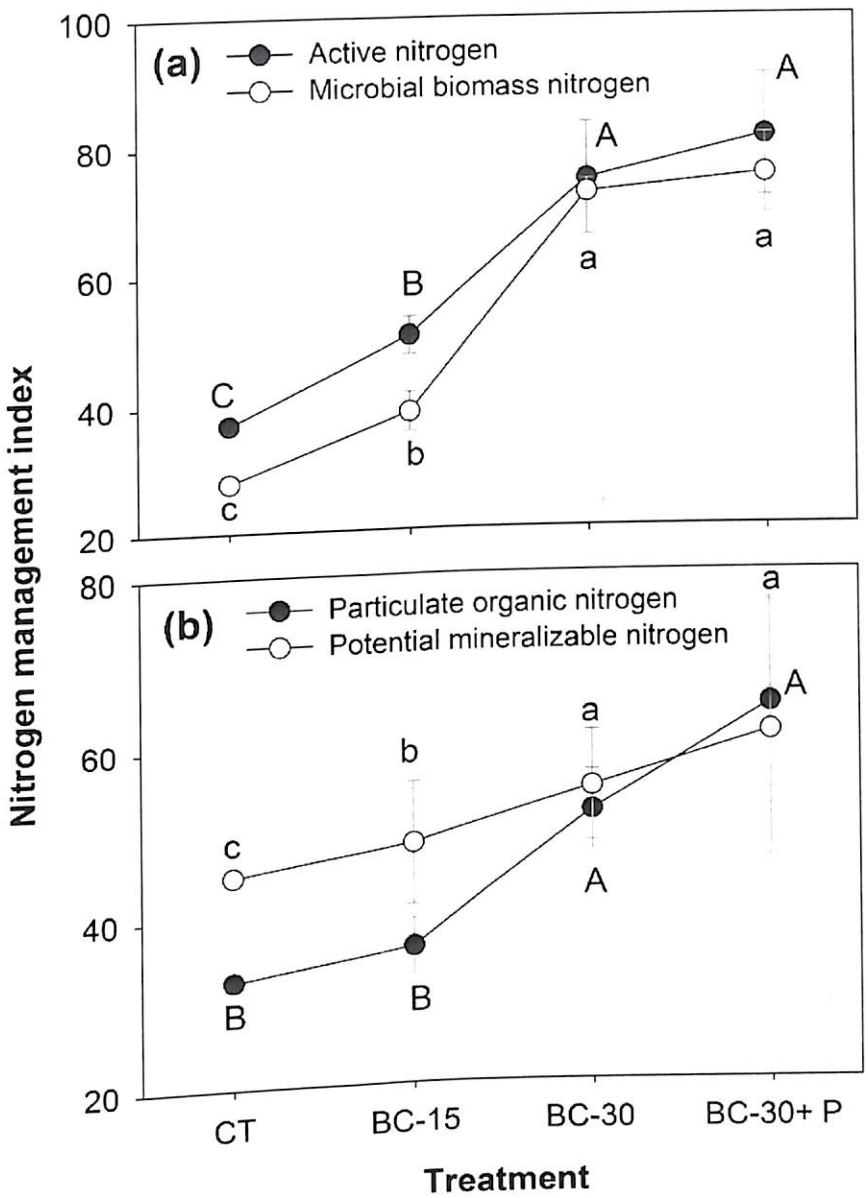


Figure 31: Nitrogen management index calculated based on active nitrogen, microbial biomass nitrogen, particulate oragnic nitrogen and potentially mineralizable nitrogen. CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1} respectively.

A similar pattern was observed when MBN was used as a measure of NMI. The NMI of the PON recorded a significant increase of 29 and 60% in the BC-30 and BC-30+P treated soils, relative to the CT ($p<0.05$). Statistically, no difference was observed in NMI between the BC-15 treated soils and the CT.

When PMN was used as a measure of NMI, there was no difference between the biochar treated soils and the CT ($p>0.5$). Generally, among the nitrogen labile pools, the NMI ranked from highest values to lowest values was in the order of AN>MBN>PMN>PON.

5.4 Discussion

5.4.1 Labile carbon and nitrogen concentrations

Application of corn cob biochar significantly increased labile carbon content of the soils, and this effect was much pronounced in the soils treated with 30 t ha^{-1} of biochar. This observation is in agreement with the study of Zhang et al. (2017) who reported a significant increase in the labile carbon pool following an incorporation of straw biochar pyrolysed at 350 – 550 ^{o}C into a silty clay loam at a rate of 16 t ha^{-1}.

Labile C and N refer to the fractions of SOM that have a high activity and are therefore sensitive to management practices and highly susceptible to oxidation and decomposition (Chen et al., 2007). Labile organic C and N fractions are characterized as dissolved organic carbon and nitrogen, active carbon and nitrogen, potentially mineralizable carbon and nitrogen, particulate organic carbon and nitrogen, and microbial biomass carbon and nitrogen (Jiang et al., 2017).

Particulate organic carbon is dominated by crop remains and microbial and faunal debris and represent an energy source for microorganisms and a reservoir of labile TOC and plant nutrients (Christensen, 2001); it is therefore highly sensitive to management practices.

The increase in POC in the biochar amended soils may be explained by the possibility that a significant portion of biochar had been localized in the particulate organic matter, resulting in higher POC content (Tian et al., 2016). The increase in POC in this study clearly indicates that incorporation of biochar may have a higher potential for improving soil quality of the tropical sandy loam because particulate organic carbon is associated with nutrient cycling (Liebig, Varvel, Doran, & Wienhold, 2002), SOM sequestration (Carter & Gregorich, 2010), and the formation and stability of soil macro-aggregates.

The study showed that biochar application at rates of 30 t ha^{-1} led to increased MBC compared to the unamended control. The increase in MBC reflected in the relatively higher soil basal respiration values and exponential reduction in the specific maintenance respiration rates in the biochar amended treatments than in the control (Figure 32).

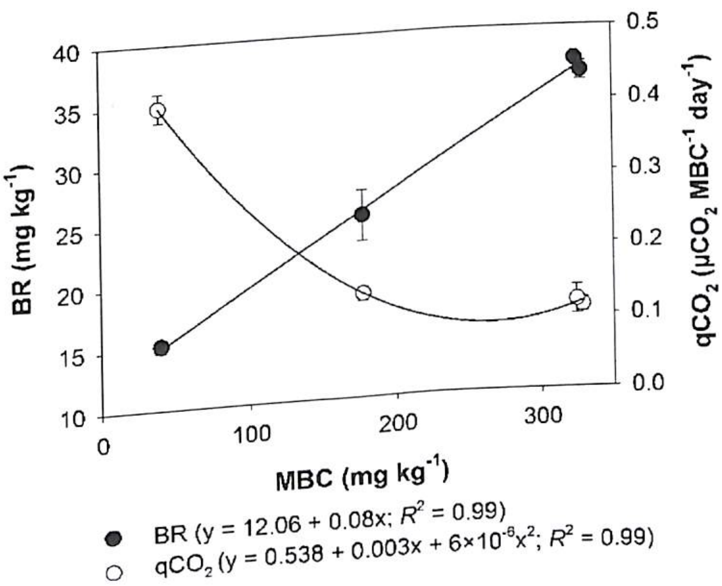


Figure 32: Relationships between basal respiration and microbial biomass carbon; and between specific maintenance respiration and microbial biomass carbon.

This implies a higher microbial C efficiency in the BC-30 and BC-30+P amended soils, compared with the CT. Contrary to our findings, Lu et al., (2014), reported no effect of corn straw biochar on MBC in a laboratory experiment where corn straw biochar pyrolysed at 555 °C was applied to sandy loam at a rate of 15 t ha^{-1}. In their study, the soil sample was sieved to a particle size of <2 mm, hence the biochar reacted with only micro aggregates. In field experiments, incorporated biochar has the tendency to react with micro, meso and macro aggregates, hence its impact on some soil properties (e.g., MBC) may be high.

Soil microbial biomass carbon is the living component of TOC and plays a key role in nutrient cycling and the decomposition and transformation of TOC in the soil medium (Bin Liang, Yang, He, & Zhou, 2011). MBC also serves as a useful indicator of changes in soil C stabilization and nutrient dynamics following soil management practices (Fierer, Strickland, Liptzin, Bradford, & Cleveland, 2009). In the present study, corn cob biochar addition potentially increased labile C inputs, which resulted in a significant increase in MBC concentrations in accordance with the findings of (Biederman & Harpole, 2013).

In this study, biochar additions resulted in a significant increase in AC relative to the control. This indicates that a higher rate of organic matter decomposition and nutrient cycling would accelerate the conversion of nutrients from organic to inorganic forms through mineralization (Wang et al., 2015), possibly due to high biological activity in the biochar amended soils. This observation is further supported by the significant increase in the soil basal respiration (BR) and increased respiratory quotient (qR) which is indicative of increased biological activity and carbon use efficiency, respectively. Carbon mineralization is often more enhanced in less stressed ecosystems due to the abundance and higher activity of soil microbes. The biochar amended soils in this study are considered to be less stressed due to a substantial decrease in the specific maintenance respiration (qCO_2) rates (high microbial efficiency), and therefore, decomposition of organic matter and subsequent increases in AC would be high in the biochar treated soils as compared to the control.

Potentially mineralizable carbon (PMC) in soil is a measure of easily decomposable carbon and considered an important pool of soil organic matter. The increased PMC in the biochar amended soils could also be ascribed to high biological activity where substrates such as PMC accumulates (Takata, Funakawa, Akshalov, Ishida, & Kosaki, 2007) and enhances the microbial bioavailability of carbon in mineral soil ecosystems.

Corn cob biochar application equally resulted in a significant increase in active nitrogen (AN) and microbial biomass nitrogen (MBN). The increases in AN and MBN relate to the enhanced TN in the biochar amended soils and enhanced microbial activity exemplified by the high qR and greater biological efficiency (low qCO_2). These suggest enhanced active and microbial N content of the labile fractions of TON in the biochar treated soils. Potentially mineralizable N is a measure of the active fraction of soil organic N, which is mainly responsible for the release of soil mineral N through microbial activities. The significant increase in PMN in the soils treated with 30 t biochar ha^{-1} may be due to the increase in microbial activity, which could have increased the decomposition rate and enhanced release of easily decomposable fraction of the TN. However, biochar application did not alter the particulate organic nitrogen pools of the soil organic nitrogen. Among the labile N pools, MBN may be considered as an early and sensitive indicator of changes in N accumulation and lability in response to biochar application in a tropical sandy loam due to its high nitrogen lability index as compared to the rest of the tested labile N pools (AN, PMN and PON).

5.4.2 Carbon pool and management index

The carbon pool index (CPI), which is a measure of total organic carbon concentration significantly increased when corn cob biochar was applied to the tropical sandy loam at 30 t ha^{-1} (Figure 28). This finding is in agreement with a previous study by Demisie, Liu, & Zhang (2014). Zhang et al. (2017) also reported a significant increase in CPI following incorporation of straw-derived biochar pyrolysed at 350-550 °C into a silty clay loam textured soil at a rate of 16 t ha^{-1}. The increase in CPI in the 30 t ha^{-1} amended soil suggests that corn cob biochar could potentially increase soil organic carbon sequestration (Weng et al., 2017) and improve the overall soil quality (Fernández-Ugalde, Gartzia-Bengoetxea, Arostegi, Moragues, & Arias-González, 2017). This observation is supported by the enhanced organic carbon content in the BC-30 and BC-30+P amended soils, and the positive correlation between TOC and CPI ($r = 0.80$, $p < 0.01$). In this study, CPI values greater than 1 ($CPI > 1$) were estimated in soils amended with biochar at a rates[1] of BC-30 and BC-30 + P, which according to Demisie et al. (2014), indicates organic C accumulation.

The increase in CPI in the biochar amended soils resulted in a corresponding increase in CMI (Figure 29) which is in agreement with the findings of Demisie et al. (2014) and Zhange et al. (2017). The carbon management index (CMI) is a composite indicator of both TOC sequestration and lability, and can be used to monitor differences in soil C dynamics among treatments. The CMI expresses the soil quality in terms of increments in the total C content and in the proportion of labile C fraction compared to the control which arbitrarily has a CMI of 100 (Demisie et al., 2014). In highly weathered soils of the humid tropics, the low TOC content negatively affects soil properties and productivity; therefore, balanced organic matter turnover is necessary for sustainable soil management and carbon sequestration.

From the study, the higher CMI values observed in the biochar amended soils are related to both the amount and quality of TOC and TN accumulated over time, thus slowly modifying the size of the labile C pool in the soil. These results are in agreement with other studies that reported that the impact of organic amendments alone and/or with chemical fertilization significantly increased the CMI and NMI relative to the chemical fertilization alone or the control (Gong, Yan, Wang, Hu, & Gong, 2009; Verma & Sharma, 2007).

5.4.3 Nitrogen pool and management index

Because Carbon and nitrogen are stoichiometrically linked, incorporation of corn cob biochar equally resulted in a significant increase in the nitrogen pool index (NPI) (Figure 30), primarily due to the significant increase in total nitrogen induced by the addition of biochar as compared to the unamended soils. Thus, the increase in NPI is primarily due to expected CN stoichiometry in the enhanced soil organic matter (SOM), and therefore, biochar addition could potentially increase N sequestration as a result of an observed positive correlation between NPI and TON ($r = 0.89$; $p < 0.01$). Any changes in quantitative and qualitative aspects in the total organic carbon content are expected to reflect in the total nitrogen content of SOM with a subsequent increase in the NPI.

The enhanced NPI in the biochar amended soils resulted in an increase in the nitrogen management index (NMI) in these soils (Figure 31). This may be ascribed to the significant increase in the soil organic carbon and nitrogen and enhanced labile N pools. This suggests that the biochar amended soils may have greater quantity and quality of soil organic matter available for decomposition by the soil microbial community (Jiang, Xu, Hao, & Dong, 2017) relative to the control soils. When the NMI of AN was plotted (Y axis) against the CMI of AC, a significant 1:1 relationship was observed between them. The CMI of AC linearly and significantly accounted for 82% of the variability in the NMI of AN and vice-versa (Figure 33a). A similar plot between NMI of MBN and CMI of AC equally yielded a significant 1:1 relationship between them. However, the CMI of AC linearly accounted for 75% of the variability in the NMI of AN (Figure 33b).

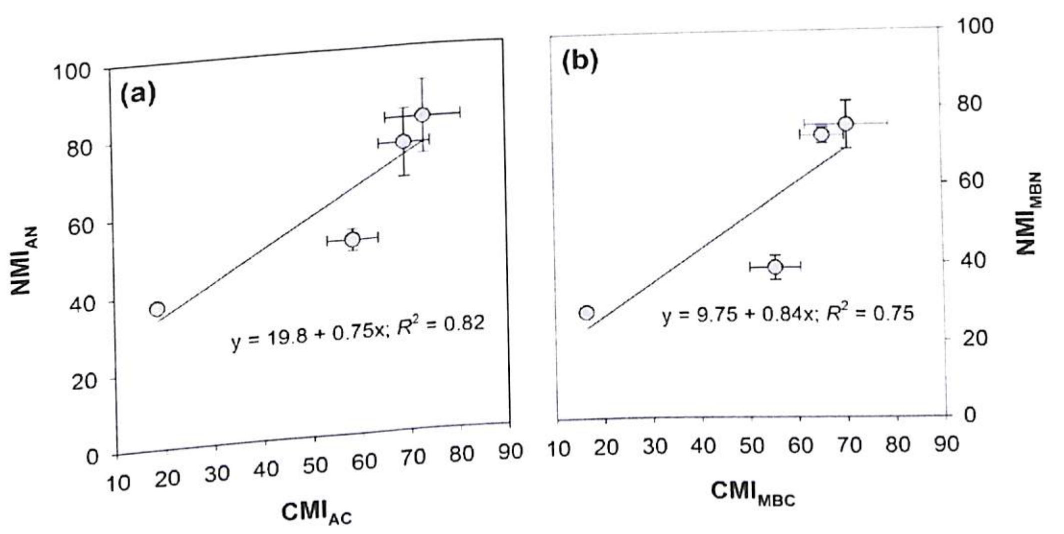


Figure 33: Relationship between (a) nitrogen management index of active nitrogen and carbon management index of active carbon; and (b) between nitrogen management index of microbial biomass nitrogen and carbon management index of microbial biomass carbon.

5.5 Organic Carbon Partition and Composition

5.5.1 Results

5.5.1.1 Soil Total- and Extracted Organic Carbon Fractions

Significant differences were observed in the concentrations of TOC and extracted C fractions by the effects of biochar application (Table 13). Soils amended with 30 t biochar ha^{-1} with- and without P amendments (BC-30 and BC-30+P) had the highest concentration of TOC (by 57 to 62 %), as compared to the control soil. Among the biochar treatments, the concentration of the humin C fraction which is the most stabilized fraction of TOC was higher in the BC-30 (by 32%) and BC-30+P (by 38%) treatments than in the BC-15 (by 17.9%). The Control soil had the lowest humin C concentration (0.79%), with no significant difference between the Control and BC-15 treated soils.

Application of biochar significantly increased the TEC concentration by 88.8, 116.7 and 131%, respectively in the BC-15, BC-30 and BC-30+P amended soils relative to the control soil (Table 13). Comparatively, a higher concentration of the HA was observed than the FA concentrations in all biochar treatments. The biochar amendments significantly increased the HA concentrations as compared to the control. The FA concentration was highest in the BC-30+P (193%) and BC-30 (183%) treatments than in the other treatments. Thus, increasing biochar application rates increased the FA concentrations. The concentration of $T_{glucose}$ was significantly higher in the 30 Mg ha^{-1} (0.37 to 0.43 g kg^{-1}), with a lower concentration (0.22 g kg^{-1}) observed in the 15 Mg biochar ha^{-1} amended soils. A non-significant difference in $T_{glucose}$ content was observed between the BC-15 and the control soils (Table 13).

Table 13: *Biochar Effects on the Concentrations of Soil Total- and Extracted Organic Carbon Fractions (mean values are presented with standard error)*

Biochar Trt.	TOC (gkg^{-1})	TEC (gkg^{-1})	FA (gkg^{-1})	H A (gkg^{-1})	T_{glucse} ($g\ g^{-1}$)	Humin ($g\ kg^{-1}$)
Control	8.7±0.8b≠	2±0.1b	0.3±0.01c	1.6±0.1b	0.1±0.02b	6.7±0.2b
BC-15	11.7±1.1ab	3.7±0.6a	0.6±0.1b	2.9±0.6a	0.2±0.02b	8±0.3b
BC-30	13.6±1.1a	4.4±0.3a	0.9±0.04a	3.1±0.3a	0.4±0.04a	9.2±0.9a
BC-30+P	14.1±1.7a	4.5±0.4a	0.9±0.1a	3.2±0.4a	0.4±0.1a	9.6±1.4a

TOC = Total organic carbon; TEC = Total exchangeable carbon; FA = Fulvic acid; HA = Humic acid; $T_{glucose}$=Total glucose equivalent carbon. ≠ Means separated by same lower case letter in each column were not significantly different among the treatments at $p \leq 0.05$.

Biochar positively influenced the proportion of FA to HA ratios, with the highest FA: HA (53%) observed in 30 t biochar ha^{-1} treatment. The control plot recorded the least FA: HA, with no significant difference between the control and the BC-15 soils. A significantly higher TEC/TOC ratio was observed in the BC-30+P soils (39%) compared to a lower proportion in the control plots (Table 14). Among the biochar treatments, there was no significant difference in the TEC/TOC ratio. Similarly, a lack of significant difference in TEC/TOC was observed in BC-30, BC-15 and the control soils. While the FA/TEC was highest in the 30 Mg ha^{-1} soils, the HA/TEC ratio was highest in 15 t ha^{-1} and the control soils. No significant difference was observed in $T_{glucose}$/TEC among the biochar treatments.

Table 14: *Biochar Effects on the Percent Distribution of Soil Total- and Extracted Organic Carbon Fractions (mean values are presented with standard error)*

Biochar Trt.	TEC/ TOC	FA/ TEC	FA/ HA	HA/ TEC	$T_{glucose}$/ TEC
Control	0.23±0.03b≠	0.15±0.05b	0.19±0.02b	0.79±0.03a	0.06±0.1^{ns}
BC-15	0.32±0.03ab	0.17±0.06ab	0.22±0.02ab	0.77±0.05ab	0.06±0.1
BC-30	0.31±0.02ab	0.20±0.09a	0.30±0.04a	0.71±0.06b	0.09±0.1
BC-30+P	0.35±0.05a	0.20±0.06a	0.30±0.03a	0.70±0.07b	0.1±0.2

TOC = Total organic carbon; TEC = Total exchangeable carbon; FA = Fulvic acid; HA = Humic acid; $T_{glucose}$=Total glucose equivalent carbon. ≠ Means separated by same lower case letter in each column were not significantly different among the treatments at $p \leq 0.05$.

Biochar application significantly influenced the TOC distribution when expressed on a mass per unit area basis (Table 15). The TOC stocks were significantly higher in the plots amended with 30 t biochar ha^{-1} than in the control and BC-15 treated plots. The TOC stocks in the BC-15 treated plots were not significantly different from the control soil. In contrast to TOC, application of biochar significantly increased the TEC stocks. Like TEC, the humin stocks showed a similar pattern in response to biochar application (Table 15). A similar trend was also observed in the HA stocks as affected significantly by the biochar application. Similarly, biochar application significantly increased the FA stocks, however, the increases in FA stocks in the BC-30 and BC-30+P treated soils were significantly higher than that of the BC-15 treated soils. The plots treated with 30 t biochar ha^{-1} increased the

$T_{glucose}$ stocks, with an increase of 194 and 243% in the BC-30 and BC-30+P treated plots, respectively compared to the control. The increase in $T_{glucose}$ stocks in the BC-15 amended soils was statistically similar to that of the control plots.

Table 15: *Biochar Effects on the Stocks of Soil Total- and Extracted Organic Carbon Fractions (mean values are presented with standard error)*

Biochar Trt.	TOC ($t\ ha^{-1}$)	TEC ($t\ ha^{-1}$)	FA ($t\ ha^{-1}$)	HA ($t\ ha^{-1}$)	$T_{glucose}$ ($t\ ha^{-1}$)	Humin ($t\ ha^{-1}$)
Control	26.8±2.4b≠	6±0.3b	0.9±0.04c	4.8±0.3b	0.4±0.1b	20.7±2.6b
BC-15	33.7±3.2ab	10.7±1.8a	1.7±0.17b	8.4±1.7a	0.6±0.1b	23±2a
BC-30	37.7±3.0a	11.8±0.9a	2.3±0.10a	8.4±0.8a	1±0.3a	25.9±2.4a
BC-30+P	37.3±3.8a	12.5±1.2a	2.4±0.16a	8.9±1.1a	1.2±0.2a	24.7±3.8a

TOC = Total organic carbon; TEC = Total exchangeable carbon; FA = Fulvic acid; HA = Humic acid; $T_{glucose}$=Total glucose equivalent carbon.

≠ Means separated by same lower case letter in each column were not significantly different among the treatments at $p \leq 0.05$.

5.5.1.2 Stratification of soil organic carbon fractions

A significantly higher stratification (by 55 to 56%) of TOC was observed in the 30 $t\ ha^{-1}$ of biochar treated soils followed by the plots treated with 15 $t\ ha^{-1}$ (34%) when compared with the CT (Table 16). Like TOC, a similar pattern on humin and $T_{glucose}$ stratification was observed. The total exchangeable carbon (TEC) stratification was significantly higher in all the biochar treated plots relative to the CT. Though no significant differences were observed in the TEC stratification among the biochar treatments, an increasing TEC stratification trend was observed in the order of BC-30+P>BC-30>BC-15. The $T_{glucose}$ stratification was highest in the BC-30 (by 209%) and BC-30+P (by 262%) treated soils compared to the CT.

Table 16: *Stratification of Soil Organic Carbon Fractions in response to Varying Rates of Biochar Application (mean values are presented with standard error)*

Biochar Treatment	TOC	TEC	FA	HA	$T_{glucose}$	Humin
	(Values were divided by the values at 20cm of the reference soil)					
Control	1b≠	1b	1c	1b	1b	1b
BC-15	1.3±0.13ab	1.9±0.31a	2±0.2b	1.9±0.37a	1.8±0.20b	1.2±0.10ab
BC-30	1.5±0.12a	2.2±0.16a	2.8±0.1a	2 ±0.20a	3.1±0.30a	1.4±0.13a
BC-30+P	1.6±0.16a	2.3±0.22a	3±0.2a	2.1±0.27a	3.6±0.54a	1.3±0.20a

TOC = Total organic carbon; TEC = Total exchangeable carbon; FA = Fulvic acid; HA = Humic acid; $T_{glucose}$=Total glucose equivalent carbon. ≠ Means separated by same lower case letter in each column were not significantly different among the treatments at $p \leq 0.05$.

5.5.1.3 Spectral characteristics of total- and extracted organic carbon fractions

The humification index (HI), as one of the indicators of TOC quality, was significantly increased by the application of biochar at 30 t ha^{-1}, with an increase of 50 and 69% in the BC-30 and BC-30+P amended soils, respectively, compared to the CT. Among the biochar treatments, the lower HI was observed in the plots treated with BC-15 with no difference between this treatment and the CT. The humification ratio was significantly impacted upon by the incorporation of biochar at all rates, with an increase of 35, 31 and 41% in the BC-15, BC-30 and BC-30+P treated plots respectively relative to the CT. In contrast, the degree of humification (DH) of TOC was impacted differently by the biochar treatments. The DH was significantly higher) in the

CT and BC-15 amended soils, than in the soils treated with BC-30 and BC-30+P (Figure 34). There was no difference in DH in the BC-30 and BC-30+P treated plots.

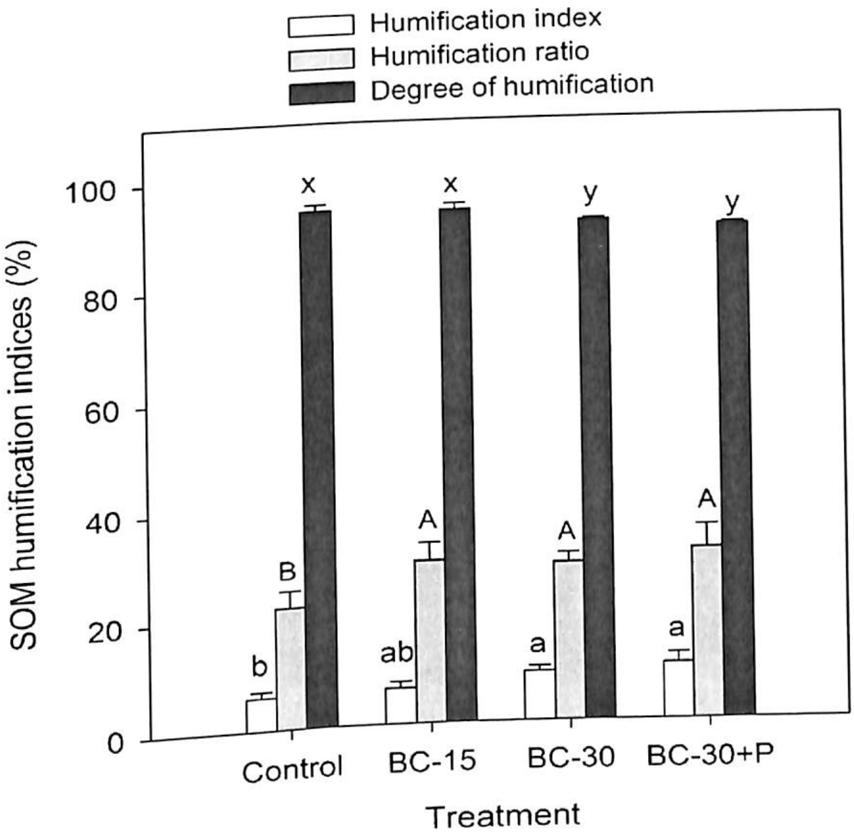


Figure 34: Biochar effects on humification characteristics of soil total organic carbon. Mean values are presented with standard error (BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively).

The slope of log optical density vs. log wavelength was significantly smaller in the BC-30 and BC-30 +P treated soils, compared to the CT and BC-15 amended soils. No significant difference was observed in the slope between the Control and BC-15 soils (Figure 35).

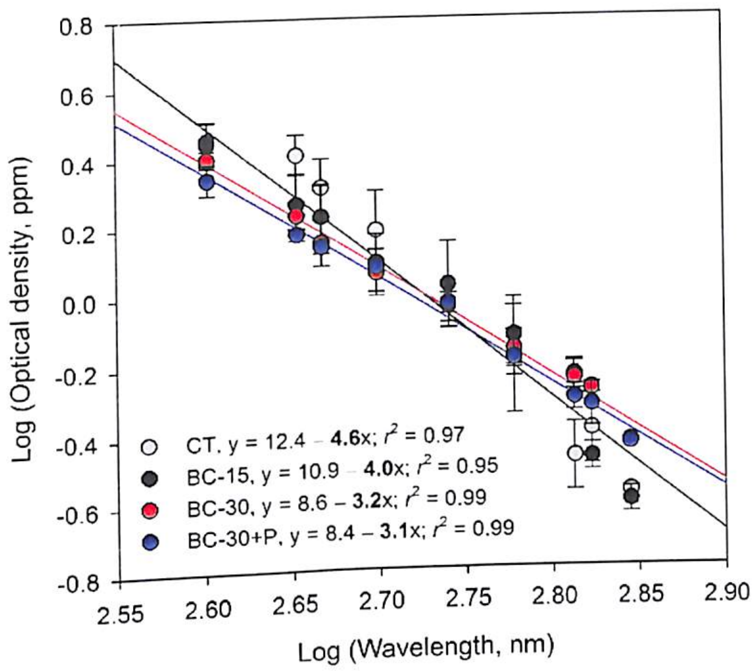


Figure 35: Slopes calculated from the relationship between log wavelength and log optical densities of humic and fulvic acid carbon fractions. Mean values are presented with standard error (BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively).

Spectral analysis showed higher values of E_4/E_6 for the FA (5 to 5.1) in the CT and BC-15 treated soils than that of the HA (2.8 to 3) in the BC-30 and BC-30+P amended soils (Figure 36).

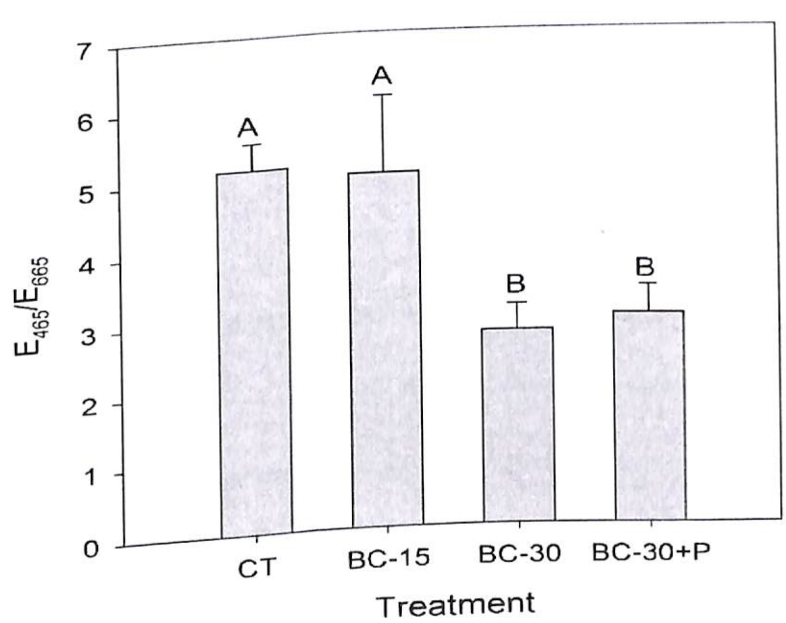


Figure 36: Biochar effects on $E_{465}/E_{66}5$ of humic and fulvic acids carbon fractions (BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively).

5.5.2 Discussion

The significant increase in TOC in the plots treated with 30 tha^{-1} of biochar could be attributed to the higher aromatic character and high C concentration (Domingues et al., 2017) of the added biochar, which might have impacted positively on the TOC content of the treated soils. Through its interactions with minerals and other organic compounds in soil (Fernández-Ugalde et al., 2017), the applied likely biochar promoted macro aggregate formation which protected the native and applied C from microbial decomposition (Hartley et al., 2016), hence increasing the TOC content. Furthermore, the increase in the TOC content could be ascribed to a slower decomposition of the relatively high amount of biochar in the BC-30 and BC-30+P treated soils primarily due to the high amount of recalcitrant C in biochar and the dominance of energy efficient fungal food webs (Aziz et al., 2013) as a result of the high CN ratio of biochar. Consequently, transformation of the biochar derived C through humification into TOC is believed to be far more efficient in the plots treated with 30 t ha^{-1} of biochar as compared with the control plots.

The relatively low FA/TEC in the CT as compared to the BC-30 and BC-30+P treated plots may be ascribed to significant losses of labile FA. This is substantiated by the less FA concentrations observed in the CT soils, which was expected primarily due to greater utilization of more labile FA by inefficient bacteria-dominated food webs and concomitant loss of soluble labile FA by leaching and runoff (Schnitzer, 2000). In contrast, improved aggregate properties in the BC-30 and BC-30+P treated plots might have (Amoakwah et al., 2017) enhance the resistance of the soil against erosive forces to have subsequently curtailed the loss of labile FA through leaching and runoff.

The humified C fractions of soil organic matter (SOM) have been reported to undergo variable stabilization processes through complex and close physico-chemical interactions with calcium or clays, or by physical protection within soil aggregates (Stevenson, 1994). Comparatively, among the humified C fractions, the FA concentration was greatly influenced more by agronomic practices (e.g. application of organic amendments) than that of the HA, humin and TOC (Zalba & Quiroga, 1999). The relatively higher concentrations of the FA in the BC-30 and BC-30+P treated soils is related to an accumulation of low molecular weight aliphatic C compounds from the added biochar that are perhaps weakly associated with cations or clays (Stevenson, 1994). The FA has lower molecular weight than HA, and therefore, it is more polar and labile than the HA, and due to its sensitivity to agronomic practices, it can be used as an early indicator when evaluating changes in TOC quality than the HA.

The substantial increase in HA-C in the biochar treated soils gives an indication of a significant accumulation of aromatic C in the soil. Humic acid has a high molecular weight and therefore degrades slowly in the soil. An accumulation of HA-C in the biochar amended soils therefore implies that C is sequestered in passive form. Consequently, nutrient accumulation will be potentially enhanced through an increase in the cation exchange capacity (Wang et al., 2017). Also, there will be improvements in soil structure (Daoyuan, Fonte, Parikh, Six, & Scow, 2017) and invrease in water holding capacity (Liu et al., 2017; Yu, Harper, Hoepfl, & Domermuth, 2017), while reducing erosion. The significantly higher concentrations of glucose equivalent non-humic C compounds in the BC-30 and BC-30+P treated soils is possibly ascribed to the increased release and translocation of nonstructural carbohydrates from the applied biochar.

The stratification of TOC and extracted C fractions generally increased with increasing the biochar application rate, primarily due to the relatively high amount of C input (Yousaf et al., 2017) from the applied biochar. Also, the high stratification of TOC and C fractions in the BC-30 and BC-30+P treated soils could be attributed to high respiration quotient and low specific maintenance respiration rate in the biochar treated plots which indicates high ecosystem functionality and less stressed ecosystem (Islam & Weil, 2000). Thus, the TOC higher stratification therefore reflects a relatively less stressed environment that leads to better soil quality with enhanced ecosystem services. The 30 t ha^{-1} of biochar amended soils would be expected to provide greater and diverse quantities of crop residues to the soils, which would subsequently increase the content and lability of TOC, and enhance soil health.

The significantly higher FA/HA values in the BC-30 and BC-30+P treated soils indicate a relatively higher proportion of low molecular weight aliphatic C compounds with a higher degree of aromatization (Stevenson, 1994). The high molecular weight aromatic C, heavily substituted with hydroxyl and carboxyl functional groups are typical of higher FA/HA ratios and dominant in biologically diverse and active soils (Islam, Mulchi, & Ali, 2000). In contrast, the lower FA/HA values in the CT and the BC-15 treated soils reflect leaching and loss of labile FA-C due to the susceptibility of these soils to erosion and leaching as a result of low TOC content.

Humification index (HI) reflects the presence of non-humic organic carbon that is less condensed, less aromatic, easily metabolized, and therefore easily decomposable and labile. A significantly higher HI in the BC-30 and BC-30+P treated soils therefore suggests that biochar amendment might have significantly increased the aliphatic TOC quality. However, the proportionate increase in the aliphatic C was far less than that of the aromatic C. This observation is accentuated by the high humification ratio (HR) values in the plots treated with 30 t ha^{-1} of biochar. The HR is directly related to the content of humified organic matter, and therefore the high HR values in the BC-30 and BC-30+P amended soils indicate a more humidified nature of the TOC in this soil (Saviozzi et al., 1994). Application of biochar at a rate of 30 t ha^{-1} resulted in a significant decrease in the degree of humification (DH). Degree of humification is a measure or indicator of the rate of decomposition of soil organic matter in the soil medium. The decrease in SOM humification degree may be attributed to the increase in aggregate stability (Amoakwah et al 2017) and enhanced macro aggregate-associated C that is protected in the macro aggregate colloidal particles from rapid decomposition by opportunistic soil microbes. In this sense, incorporation of biochar at a rate of 30 t ha^{-1} decreased the decomposition rate of SOM with positive effects on its degree of humification. This has the potential to subsequently improve the physical, chemical and biological properties of the soil. Zech et al., (1997) reported that the humification of SOM is characterized by increases in carboxyl C, alkyl C, and aromatic C (mainly phenolic groups) and a decrease in O-alkyl C. The changes that occur in SOM during the humification process is therefore related to the preferential preservation of more recalcitrant organic compounds such as phenolic structures in the BC-30 and BC-30+P treated soils. Conversely, the increase in the DH in the CT and BC-15 treated soils reflects the breakdown of soil aggregates which exposes soil carbon to rapid microbial degradation, with subsequent loss of the labile components of SOM through catabolism and leaching processes, and reduced ecosystem services.

Spectroscopic analysis provides useful insight into the qualitative nature of the soil TOC in the HA-C and FA-C fractions (Islam et al., 2000). The slope of the log optical density vs. log wave length graphs serves as a direct index of the particle size or molecular weight of C compounds in TOC (Khan, 1959). A relatively gentle (lower) slope suggests the dominance of high molecular weight aromatic HA-C fraction, and this supports the theory that states that the slope decreases with increasing molecular weight of organic C compounds (Kahn, 1959). The significantly lower slopes in the BC-30 and BC-30+P may be ascribed to the lower ratio of E_{465}/E_{665} which suggests that TOC is dominated by high molecular weight humic acid-like substances with an increasing proportion of aromatic chain structures and higher degree of aromatic condensation (Chen et al., 1977). The E_4/E_6 ratio therefore serves as an indicator of humification processes (Stevenson, 1994) to influence TOC quality in soils. Higher proportions of aromatic phenolic acids and phenolic polymers are typical of the humid acid fraction of soils with relatively higher organic carbon content (Yavitt & Fahey, 1985) as observed in the plots treated with 30 t ha^{-1} of corn cob biochar. The above observations could suggest that the BC-30 and BC-30+P treatments may have enhanced the dominance of energy efficient biochemical pathways responsible for the increased aromatic TOC quality with a simultaneous decrease in aliphaticity.

5.6 Conclusions

Corn cob biochar application to a highly weathered tropical sandy loam significantly improved the soil biological and chemical properties over the control. Total microbial biomass pool increased with greater biological efficiency (high qR and BR, and low qCO_2), increased TOC and TN accumulation, all of which are indicators of improved soil quality. The study also showed that corn cob biochar application significantly enhanced the lability of C and N especially in the at 30 t biochar ha^{-1} amended treatments. Furthermore, TOC and TN lability and C and N management indices calculated based on microbial biomass C and N, potentially mineralizable C and N, active C and N, and particulate organic C and N concentrations were significantly higher in the 30 t ha^{-1} biochar-amended soils than in the control soils. The study showed that, among the tested labile C and N pools, the active C and N pools were the most sensitive indicators to detect early and consistent changes in soil organic matter accumulation and C and N lability in response to biochar application in a weathered tropical soil.

Biochar applied to a highly weathered tropical sandy loam significantly increased the TOC content and quality, especially with BC-30. Increasing the rate of biochar increased the concentrations of both HA and FA, however the concentrations of HA were comparatively higher than FA. The stratification of TOC and extracted C fractions were also increased with increasing biochar application rates. Though biochar increased both aliphatic and aromatic quality of TOC, the spectroscopic analysis from the comparatively gentle slopes of the log optical density vs. log wavelength, coupled with the lower E_{465}/E_{665} support a suggestion that the BC-30 and BC-

30+P treatments favored high molecular weight aromatic quality of TOC in the treated soils. The accumulation of aromatic C gives an indication that C may have been sequestered in passive form which buttresses the C sequestration potential of biochar amendment. The significant increase in aromatic TOC quality in the plots treated with 30 t ha^{-1} of biochar gives an implication that soil organic carbon is progressively stored in passive form through gradual humification of labile C pools into recalcitrant C with time. In perspective, biochar applied in the right rate may potentially enhance the stability of soil organic carbon by improving the aromatic TOC quality. Biochar as a soil amendment has the potential to enhance C sequestration in a tropical agro ecosystem.

CHAPTER SIX

EFFECTS OF BIOCHAR ON SOIL ENZYMES AND MICROBIAL PROPERTIES

6.1 Introduction

In recent times, there has been a growing interest in incorporating biochar to improve soil fertility and productivity (Korai et al., 2018), to sequester carbon, and restore ecological services provided by highly weathered and nutrient-poor soils in sub Saharan Africa. Application of biochar to soils has therefore been proposed as a method for the long-term storage of organic carbon in the soil, and to simultaneously provide agronomic benefits due to the enhancement of soil properties (Naeem et al., 2018). Variable effects on the composition and abundance of soil microorganisms and micro flora have been reported following the application of biochar as a soil amendment (Lehmann et al., 2011).

Decomposition of biochar, which is associated with complex biochemical processes in the soil medium, is facilitated by several external factors in agro-ecosystems, such as the availability of nutrients and energy sources as well as the microbial abundance and activity (Wang et al., 2016). Lanza, Rebensburg, Kern, Lentzsch, & Wirth (2016) suggested that it is crucial to study the mechanisms of biochar decomposition in order to clearly appreciate the feasibility of its application in a soil system. In this context it is crucial to analyze the effects of biochar on soil microbial activity and community composition. Several studies have reported an overall increase of various taxa of microorganisms such as Gram-positive and Gram-negative bacteria (Ameloot et al., 2013), actinobacteria (Prayogo, Jones, Baeyens, &

Bending, 2014) and fungi (Steinbeiss, Gleixner, & Antonietti 2009) following the application of biochar as a soil amendment. Application of biochar may provide a habitat for soil microorganisms (Quilliam et al., 2013) and enhance soil ecological characteristics such as water retention capacity or soil buffering capacity which may be ideal for microbial growth (Karhu et al., 2011). According to Watzinger et al. (2014), biochar may be a source of energy and nutrient for soil fauna, and thus biochar may interact with soil trophic chains in the soil-plant continuum. Conversely, biochar application has been reported to reduce the growth of soil microorganisms during the early stages after amendment (Mitchell, Simpson, Soong, & Simpson, 2015). This variation in biochar effects on microorganisms' abundance and community composition has been ascribed to differences in soil type (Chen et al., 2017).

Soil microorganisms play a crucial role in the decomposition of organic matter and soil nutrient biogeochemical cycling in agro-ecosystems (Cusack, 2013). Diversity of soil microbial communities is therefore considered paramount in maintaining soil health and enhancing soil productivity.

According to Zhao et al., (2016), different microbial groups are responsible for specific functions during the decomposition of organic residues. For instance, bacteria are dominant in the initial stage of the decomposition process, whereas fungi dominate in the later stages of organic residue decomposition (Marschner, Crowley, & Rengel, 2011). Generally, addition of organic materials to the soil facilitates microbial activity and induces changes in the composition of soil microbial community structure in an agro ecosystem (Liu et al., 2017). Thus, the incorporation of biochar to top soil may stimulate the activities of bacteria and fungi (Bamminger et al., 2014).

Soil extracellular enzymes are proximate agents of organic matter formation and decomposition, and they are catalysts that play a critical role in modulating the responses of agroecosystems to changes in abiotic and biotic conditions. Enzymes are synthesized and secreted by soil microorganisms (Zhao et al., 2016) and are involved in the biogeochemical cycling of nutrients in the soil (Burns et al., 2013). Gaining insights into the impact of biochar on the activities of soil enzymes has been identified as critical research priority (Lehmann et al., 2011c). However, only a few studies have analyzed the response of soil enzymes to soil environment under different rates of biochar in a highly weathered soil of the humid tropics (Fungo et al., 2017; Zhang et al., 2017). In recent times, some studies have reported that incorporation of biochar to soil has the potential of increasing the activities of soil enzymes related to nutrient (N and P) cycling, and decreasing the activities of soil enzymes involved in C cycling (Bailey et al., 2011). On the other hand, other studies have also reported inconsistent results that suggest that, addition of biochar to soils has variable effects on enzyme activities (Sun, Li, Chen, Wang, & Xiong, 2014).

Little is known about the effects of biochar addition on soil biological processes involved in C and N dynamics and on soil microbial composition in a tropical agroecosystem. The soil microbial community structure is sensitive to environmental changes (Zhao et al., 2016), and therefore, it might be sufficient to use these as indicators of soil quality changes. This study therefore aims to elucidate the response of soil enzymes and microbial composition in soils of the humid tropics to corn cob biochar application at different rates.

6.2 Materials and Methods

6.2.1 Enzyme activities

Two enzymes were analyzed using the colorimetric method by Hu et al. (2014). The activity of urease was quantified by the determination of ammonium released from a slurry containing soil, urea solution (10%) and citrate buffer (pH 7) after incubation at 37 °C for 24 h. The urease enzyme activity was expressed in mg ammonium per 100 g of soil (dry weight).

Dehydrogenase enzyme activity was determined with the reduction of triphenyltetrazolium chloride (TTC) to triphenylformazan (TPF) as described by Serra-Wittling, Houot & Barriuso (1995). Briefly, a 3 g soil sample was incubated in 3 ml water and 3 ml 3% 2, 3, 5-triphenyl-tetrazolium chloride (TTC) at 37 °C for 24 h in darkness. After, 10 ml of methanol was added, and the suspension was then homogenized and filtered through a glass fiber filter, and the filter was washed with methanol until the reddish color (triphenyl formazan) caused by the reduced TTC disappeared from the filter, and the volume adjusted to 100 ml. The optical density at 485 nm was compared to those of TPF standards.

6.2.2 Phospholipid fatty acid analysis

Phospholipid fatty acid analysis was performed as described by Frostegaard & Baath (1996). Lipids were extracted from soil with a single-phase mixture of chloroform, methanol and aqueous citrate buffer (Bligh and Dyer reagent). The organic, lipid-containing phase was collected and the lipids were separated into neutral, glyco- and phospholipid fractions using silicic acid columns. The phospholipids were then converted to their methyl-esters by alkaline methanolysis to be detected by GC-FID (Figure 37).

Figure 37: Gas chromatograph (GC) equipped with a HP Ultra 2 capillary column and a flame ionization detector for the determination of Fatty Acid Methyl Ester (FAME) concentrations.

Methyl nonadecanoate served as an internal standard, which allowed calculation of Fatty Acid Methyl Ester (FAME) concentrations (Zelles, 1999). The FAME detection and quantification were performed with a Hewlett-Packard 5890 Series II gas chromatograph (GC) equipped with a HP Ultra 2 capillary column and a flame ionization detector. The measurement was done with the MISystem, Version 5 (MIDI Inc., Newark, DE), using the D1 method. The GC temperature program ramped from 170 to 270°C at 5°C min^{-1}. The reports generated by the MISystem software provided peak areas (response) and peak names (according to the peak match with the D1 method library). Standard nomenclature for the FAMEs includes the number of C atoms counted from the omega (ω) end (i.e., opposite the carboxyl end), followed by the number of double bonds after the colon; *cis* conformations are designated with the suffix c, and the prefixes i and a are given for iso- and anteiso-branched FAMEs, respectively.

The suffix 10 methyl indicates a methyl group at the 10th C atom, while OH stands for hydroxy and cyc for cyclopropane groups. The FAME compounds 18:2ω6,9c and 18:1ω9c served as fungal biomarkers (Kaur, Chaudhary, Kaur, Choudhary, & Kaushik, 2005). The proportion of fungal FAMEs was calculated as a percentage of the total FAMEs, where fungal FAMEs were summed with bacterial FAMES (15:0, a15:0, i15:0, i16:0, 16:1ω7c, 16:1ω9c, 17:0, a17:0, i17:0, 17:0cyc, 17:1ω8c, 18:1ω5c, 18:1ω7c, 19:0cyc). Markers for Gram positive (G+) bacteria were a15:0, i15:0, i16:0, a17:0 and i17:0. Selected monounsaturated and cyclopropane FAMEs served as indicators for Gram negative (G−) bacteria: 16:1ω7c, 18:1ω7c, 17:0cyc and 19:0cyc (Zelles, 1999).

The Shannon diversity index (H') was calculated and used as an indication of the diversity of the soil microbes (Shannon, 1948).

6.2.3 Statistical Analysis

Statistical analyses were performed using SigmaPlot 11 (Systat Software Inc., San Jose). Normality and homogeneity of variance were checked on all obtained data. Principal Component Analysis (PCA) and Redundancy Analysis (RDA) were performed using R version 3.3.1 (2016). To test the relationship between the soil factors and PLFA, we used analyses of variance (ANOVA) permutation test using 1000 permutations on the RDA. Analyses of variance was also used to test for differences between control and biochar-amended soils, and the Holm-Sidak post-hoc test was used to differentiate between any two given treatments. We used $p<0.05$ as a criterion for statistical significance of treatment effects unless otherwise stated. Statistical significance is indicated by lower/upper case letters beside the mean values. Results are given as mean ± standard error (SE) in tables and figures.

6.3 Results

6.3.1 Soil characteristics after corn cob biochar application

6.3.1.1 Microwaved and salt extractable C

Corn cob biochar application significantly increased microwaved extractable C following biochar application on all treated plots ($p<0.01$) (Table 17). Microwaved extractable C increased by 211, 482 and 510% in BC-15, BC-30 and BC-30+P treated soils respectively. No significant difference in microwaved extractable C content was observed between BC-30 and BC-30+P treated soils, both of which differed significantly from BC-15

Biochar application resulted in a significant increase, by 145% and 224%, of salt extractable C in the plots that received the highest biochar application rates (BC-30 and BC-30+P respectively) compared with the CT treatment (Table 17). Statistically, BC-30 and BC-30+P were similar as was BC-15 and the CT treatment.

6.3.1.2 *Microwaved and salt extractable N*

The biochar treatments significantly increased microwaved extractable N by 27, 99 and 105% in BC-15, BC-30 and BC-30+P treated soils respectively compared to the control ($p < 0.01$) (Table 17). Thus the highest concentration of microwaved extractable N was observed in the B-30+P treated soils. However, there was no statistical difference observed between BC-30+P and BC-30, both of which had significantly higher microwaved extractable N than the BC-15 treatment.

Similarly, increasing biochar application rates resulted in a significant increase in salt extractable N by 11.5, 25.7 and 36.4% in BC-15, BC-30 and BC-30+P amended soils respectively relative to the control ($p < 0.01$) (Table 17). Statistically, there was a significant difference between the plots that received 15 t ha^{-1} and 30 t ha^{-1} biochar.

Tabel 17: Effects of Different Rates of Corn Cob Biochar on Soil Chemical Properties at 0-20 Cm Depth (mean values were presented with standard error)

Biochar treatment	pH_{Water} (1:2.5)	Ec ($\mu S\ cm^{-1}$)	TC ($g\ kg^{-1}$)	TN ($g\ kg^{-1}$)	MW-C ($mg\ kg^{-1}$)	Salt-C ($mg\ kg^{-1}$)	MW-N ($mg\ kg^{-1}$)	Salt-N ($mg\ kg^{-1}$)
CT	5.4±0.1c$^{\neq}$	421±3.7a	8.7±0.8b	0.6±0.1c	14.3±1.0c	6.1±1.4b	21.8±1.9c	10.7±0.1d
BC-15	6.2±0.02b	210 ±0.9b	11.7±1.1ab	0.9± 0.1b	44.5±1.3b	7.5± 0.8b	27.7±0.9b	12.0±0.4c
BC-30	6.6 ±0.1a	111 ±3.6c	13.7 ±1.1a	1.4±0.2ab	83.2±4.4a	14.8±2.8ab	43.2±1.9a	13.6±0.4b
BC-30+P	6.7±0.01a	110 ±2.0c	14.1 ±1.4a	1.5 ±0.2a	87.3±1.6a	19.6±5.9a	44.7±1.1a	14.6±0.1a

EC = Electrical conductivity; TC = Total organic carbon; TN = Total organic nitrogen; Salt-C =Potassium sulfate field moist soil extractable carbon; MW-C = Potassium sulfate microwaved field moist soil extractable carbon, MW-N = Potassium sulfate microwaved field moist soil extractable nitrogen; Salt-N = Potassium sulfate field moist soil extractable nitrogen. $^{\neq}$Different letters indicate that means are significantly different among biochar treatments ($p \leq 0.05$).

6.3.1.3 Microbial biomass C and biomass N

An increasing rate of biochar application resulted in a significant increase of microbial biomass C (MBC) by 347, 718 and 728% in the BC-15, BC-30 and BC-30+P soils respectively relative to the control soil ($p < 0.04$) (Table 18). Among the biochar application rates, no difference was observed in both BC-30 and BC-30+P treatments. However, the effect of BC-15 on MBC was significantly lower than BC-30 and BC-30+P.

Microbial biomass N (MBN) contents were significantly raised by 169 and 172% when the soils were amended with BC-30 and BC-30+P, respectively ($F = 35.2$, $p < 0.01$; Table 18). There was no difference in MBN when the BC-15 was compared to the CT.

Table 17: *Effects of Different Rates of Corn Cob Biochar on Soil Microbial Biomass and Associated Biological Properties at 0-20 cm Depth (mean values are presented with standard error)*

Biochar Treatment	MBC ($mg\ kg^{-1}$)	MBN ($mg\ kg^{-1}$)	MBC:MBN	qCO_2 ($\mu g\ CO_2\ mg^{-1}\ C\ d^{-1}$)	PMC ($mg\ kg^{-1}$)
CT	39.7± 5.9c[≠]	20.5±3.6b	1.9±0.8b	415±69a	5.4±0.5c
BC-15	177.4±7.7b	29.1±2b	6.1±0.7a	141±13b	6.6±0.9bc
BC-30	324.6±27.5a	55.1±4a	5.9±0.6a	112±8b	8.1±0.6ab
BC-30+P	328.5±34.5a	55.68±2.1a	5.8±0.6a	120±15b	9.1±0.8a

MBC = Microbial biomass carbon; MBN = Microbial biomass nitrogen; qCO_2 = Specific maintenance respiration; PMC = Potentially mineralizable carbon. ≠Different letters indicate that means are significantly different among biochar treatments ($p \leq 0.05$).

6.3.1.4 Potentially mineralizable C

Corn cob biochar application improved the Potentially mineralizable C (PMC) content of the soil (Table 18). This effect was more pronounced at higher biochar application rates. Statistically, no difference was observed between BC-15 and CT. However, there was a significant increase in PMC by 50 and 69% in BC-30 and BC-30+P amended soils respectively compared with the CT ($p < 0.01$). The PMC of the BC-30+P treatment was similar to BC-30 but different from BC-15.

6.3.1.5 Respiratory quotient (qR), qN, and specific maintenance respiration (qCO_2)

Incorporation of corn cob biochar significantly increased the respiratory quotient (qR) in all the biochar treated soils compared to CT ($p < 0.01$). Soils amended with BC-15, BC-30 and BC-30+P recorded a percentage increase in qR by 234, 423 and 426 respectively compared to CT (Figure 38a). Among the biochar treatments, no significant difference was observed between BC-30 and BC-30+P. The proportion of MBN in TN denoted by qN, was significantly impacted on by the added biochar (Figure 38b). A 2-fold increase in qN was observed on the soils treated with BC-15, whereas 3-fold increase was recorded in the BC-30 and BC-30+P treated soils relative to the CT ($p<0.01$).

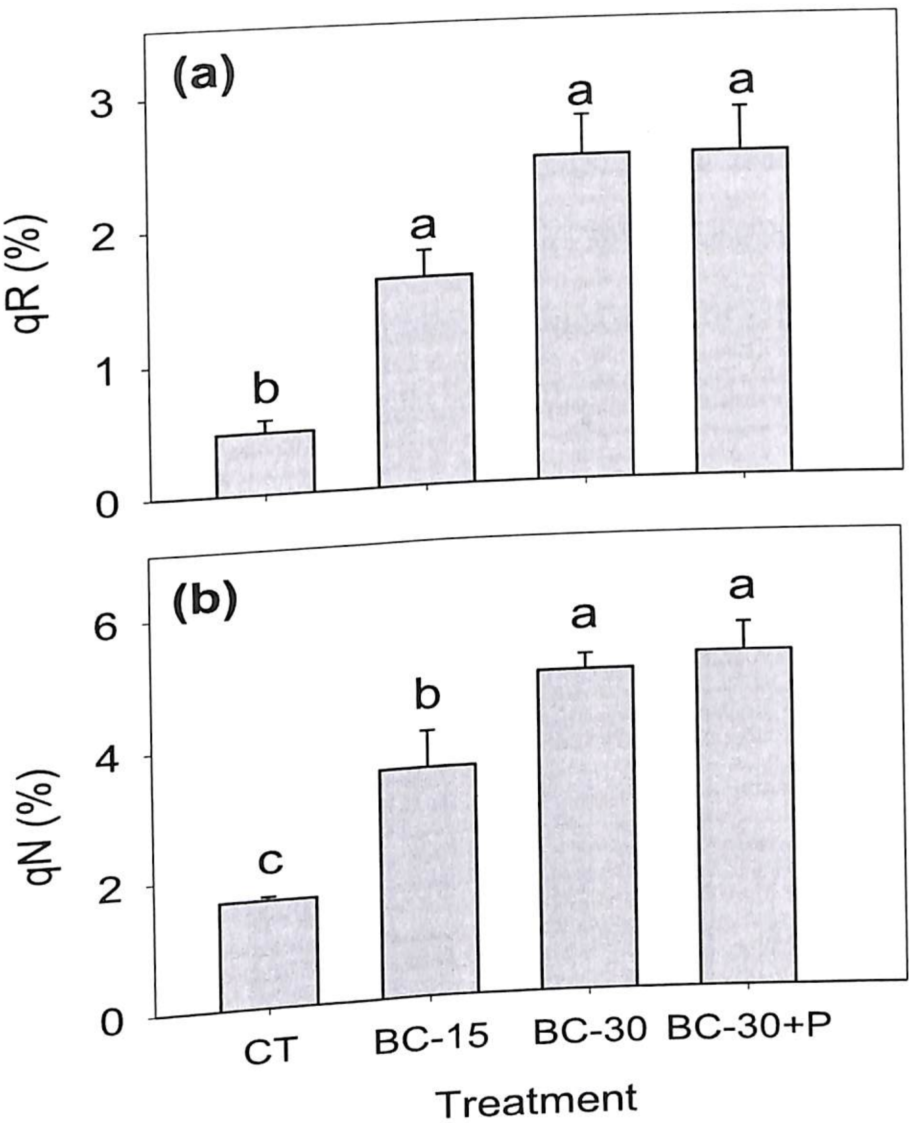


Figure 38: Effects of different application rates of corn cob biochar on (a) the proportion of microbial biomass carbon in total carbon (respiratory quotient) and (b) the proportion of microbial biomass nitrogen in total nitrogen. CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1} respectively.

Specific maintenance respiration (qCO_2) significantly decreased ($P<0.01$) in all the biochar amended soils relative to the control (Table 18). A reduction of 66.0, 73.0 and 71.1% was recorded in BC-15, BC-30 and BC-30+P treated soils, respectively, compared to the control. No difference was observed among the biochar treatments, implying that application of biochar as low as 15 t ha^{-1} could result in a significant reduction in qCO_2 in a tropical sandy loam.

6.3.1.6 Soil basal respiration (BR)

Incorporation of biochar significantly increased the basal respiration rates by 64, 138 and 144% in the BC-15, BC-30 and BC-30+P treatments ($p<0.01$) compared to the control (Figure 39). Among the biochar treatments, BC-15 had lower respiration rates compared to the BC-30 and BC-30+P which had similar BR.

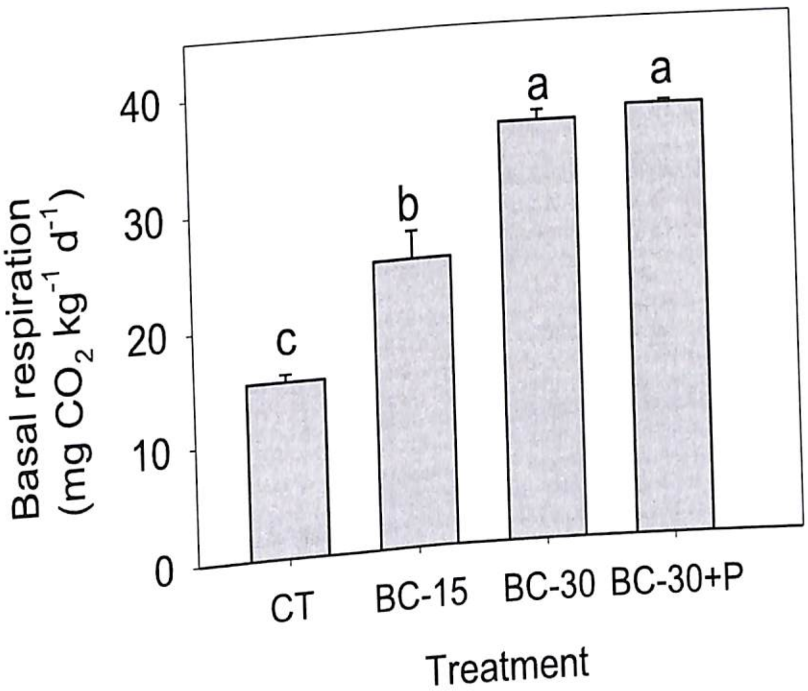


Figure 39: Corn cob biochar effects on basal respiration. CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

6.3.1.7 Soil enzyme activities and phospholipid fatty acid profiling for soil microbial community and diversity analysis

The potential activities of two enzymes (dehydrogenase and urease) involved in C and N cycling were determined following biochar incorporation to a tropical sandy loam. The activities of both enzymes increased significantly after biochar application with an observable effect of application rate. Incorporation of biochar at a rate of 30 t ha^{-1} significantly increased (p < 0.01) urease enzyme activity by 52 and 62% in BC-30 and BC-30+P amended soils compared to the control (Figure 40a). No statistically significant difference in urease enzyme activity was observed between BC-15 and the control.

Similarly, application of corn cob biochar significantly enhanced soil dehydrogenase enzyme activity in all treatments (p<0.01) (Figure 40b). Dehydrogenase activity increased by 50%, 221%, and 238% in BC-15, BC-30 and BC-30+P treated soils, respectively, relative to the control, but the effects of BC-30 and BC030+P on dehydrogenase enzyme activity were not significantly different from each other.

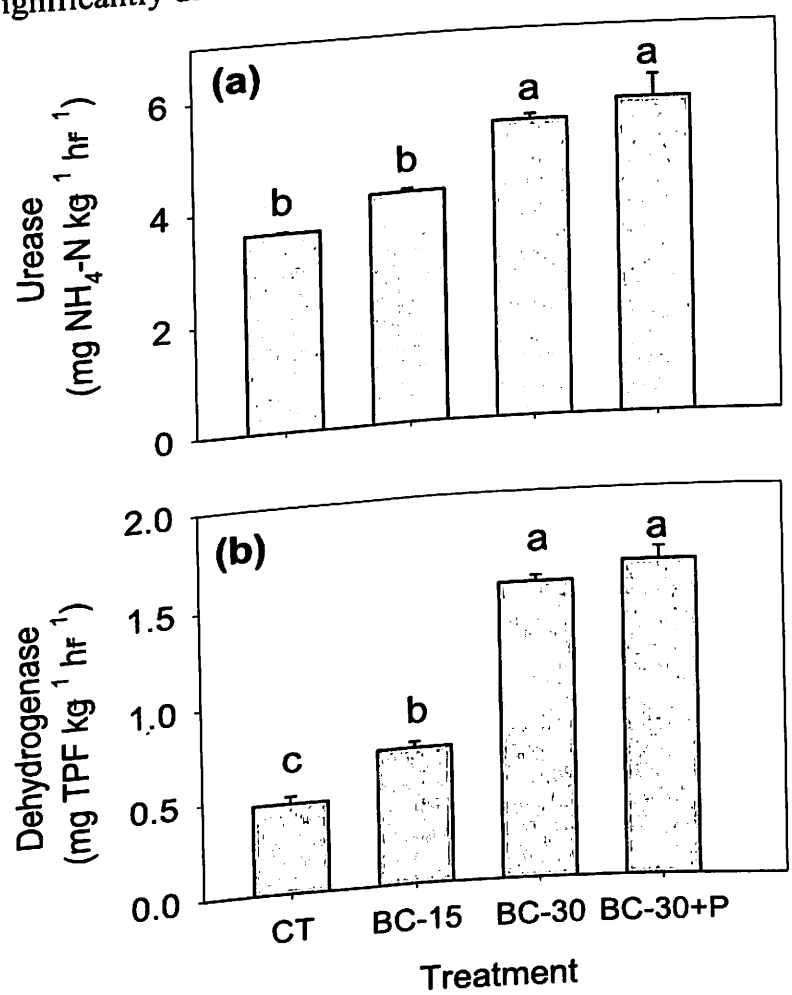


Figure 40: Corn cob biochar effects on (a) urease and (b) dehydrogenase enzyme activities. CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

A total of 17 PLFAs were detected and used as a measure of microbial biomass and the abundance of the various taxonomic microbial groups in the treated and untreated soils (Table 19).

Table 18: *Phospholipid Fatty Acid (PLFA) Markers Used for the Taxonomic Soil Microbial Groups*

Taxonomic group	Specific PLFA markers
Actinobacteria	16:0 10-methyl, 17:0 10-methyl, 18:0 10-methyl
Bacteria	15:0, 17:0,
Gram$^-$ bacteria	16:1 ω7c, 17:0 cyclo, 19:0 cyclo ω8c, 18:1 ω7c,
Gram$^+$ bacteria	15:0 iso, 15:0 anteiso, 16:0 iso, 17:0 iso, 17:0 anteiso
Fungi	18:2 ω6c, 18:1 ω9c
Arbuscular mycorrhiza fungi	16:1 ω5c

In all the plots that received biochar treatments, there was a significant increase in the abundance of arbuscular mycorrhiza by 82, 351 and 358% in the BC-15, BC-30 and BC-30+P treated plots respectively compared to the control ($p<0.01$). Soil fungal abundance also increased significantly in all the biochar amended plots by 222, 452 and 521% ($p<0.01$) following the respective incorporation of BC-15, BC-30 and BC-30+P into the soil. Incorporation of corn cob biochar at a rate of 30 t ha^{-1} significantly increased the abundance of Gram positive (Gram+) bacteria by 73 and 91% ($p < 0.01$), Gram negative (Gram–) bacteria by 50 and 58% ($p < 0.01$), actinobacteria by 79 and 89% ($p < 0.01$), bacteria by 250 and 263% ($p<0.01$) and total bacteria by 68 and 81% ($p<0.01$) in BC-30 and BC-30+P amended soils, respectively, compared to the control (Table 20)

Table 19: *Phospholipid Fatty Acid (PLFA) Concentrations for Different Functional Groups of Soil Microbial Community in the Biochar Treated- and Untreated Soils (mean values were presented with standard error)*

Bochar	Taxonomic group					
Treatment	Actinobacteria	Bacteria	Gram-	Gram+	Fungi	AMF
CT	6.9±0.7b[‡]	0.5±0.2b	12.2±0.4c	13.2±0.6b	2.1±0.3d	1.1±0.02c
BC-15	9.7±0.2ab	1.4±0.1a	15.3±0.5bc	17±0.4b	6.7±0.5c	2±0.08b
BC-30	12.3±1.3a	1.8±0.2a	18.1±1.1ab	22.9±1.7a	11.5±0.3b	4.9±0.04a
BC-30+P	13±1.6a	1.9±0.2a	19.3±1.5a	25±2.7a	12.9±0.2a	5±0.04a

AMF = Arbuscular mycorrhiza fungi. [‡]Different letters indicate that means are significantly different among biochar treatments ($p < 0.05$).

Compared to the CT, application of 30 t ha^{-1} corn cob biochar significantly increased ($p < 0.05$) the total PLFA concentrations in the treated soils while the BC-15 treatment was statistically similar to the CT (Figure 41).

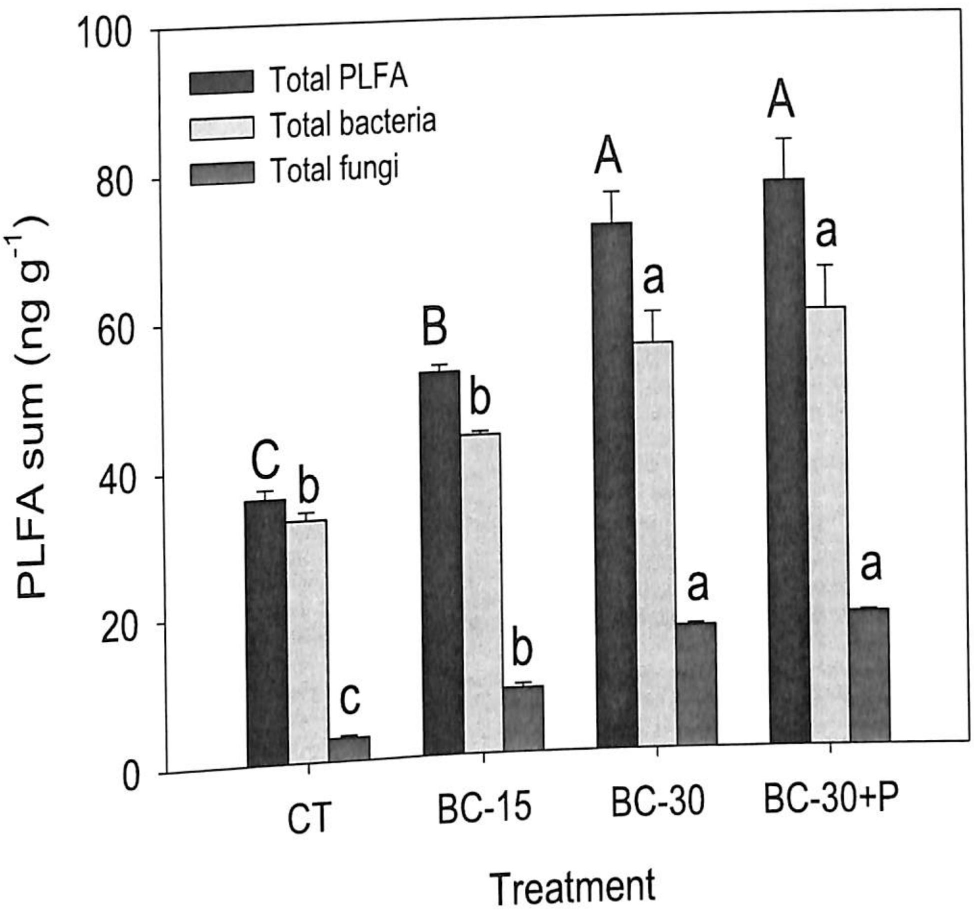


Figure 41: Effects of different application rates of corn cob biochar on total PLFA and sum of bacteria and fungi. CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1} respectively.

Increasing corn cob biochar application rate also had a corresponding positive effect on the abundance of total fungi and bacteria in the soil (Figure 42). The ratios of Gram + to Gram- bacteria, as well as Fungi to bacteria were significantly increased in plots treated with BC-30 and BC-30+P compared to the control ($p<0.01$) (Figure 42).

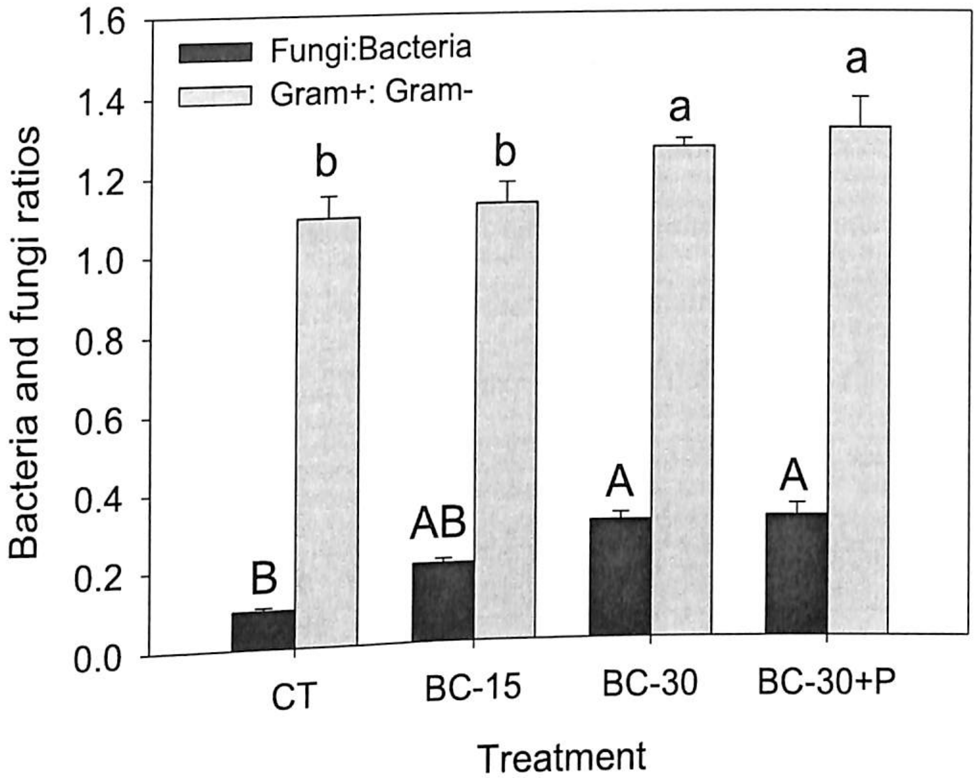


Figure 42: Microbial parameters revealed by the PLFA profiles generated from the treated and untreated soils. CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

Invariably, application of 15 t ha^{-1} was not statistically different from the control when comparing its microbial composition. For all functional groups of microbial communities, which included arbuscular mycorrhizal fungi (AMF), gram-/+ bacteria, fungi, and bacteria, the highest concentrations of PLFA was found in the soils treated with 30 t ha^{-1} of biochar (BC-30 and BC-30+P).

Microbial diversity was based on the identified fatty acids in the respective treatments. Except the gram positive in which no significant difference was observed in the diversity index in the biochar treated plots and the CT, there was a significant increase in the diversity indices of actinobacteria ($p < 0.01$) and Gram- ($p < 0.01$) in the plots treated with 30 t ha^{-1} of biochar (Figure 43a). The bacteria that were neither Gram-, Gram+ nor actinobacteria were classified as "other bacteria", and their diversity was much pronounced ($p < 0.01$) in the BC-30 and BC-30+P treated soils. Similarly, arbuscular mycchoriza fungi and "other fungi" were more diversified in the plots amended with 30 t ha^{-1} of biochar (Figure 43a). Comparatively, the Shannon diversity index showed that total bacteria and fungi were more diversified in the biochar treated plots relative to the CT (Figure 43b), with the highest diversity observed in the BC-30 and BC-30+P treated soils. Generally, application of biochar increased both bacteria and fungi fatty acids diversity.

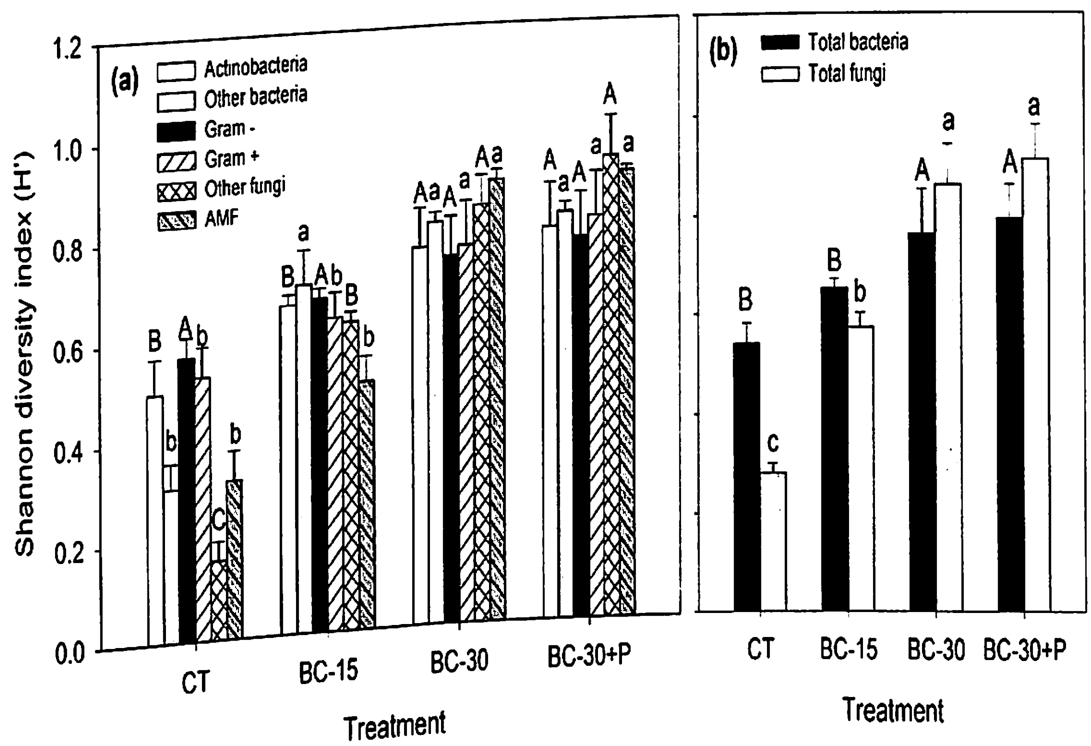


Figure 43: Corn cob biochar effects on the Shannon diversity index of bacteria and fungi taxonomic groups (a) and total fungi and bacteria (b). CT denotes control; BC-15, 30, and 30+P denote biochar treatments with 15 t ha^{-1}, 30 t ha^{-1}, and 30 t ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

Principal component analysis (PCA) was performed on the data using soil factors as variables. The results of the PCA are presented in Figure 44.

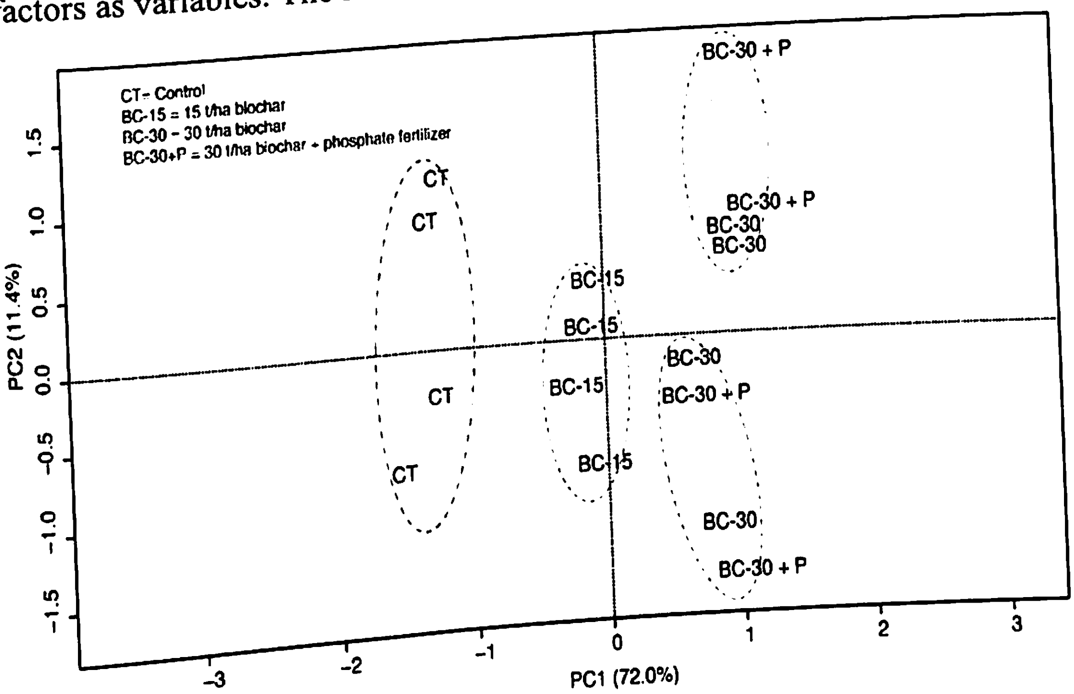


Figure 44: Principal component analysis (PCA) of microbial community activities from different treatments

The first and second PCA accounted for 72.0 and 11.4% of the variation, respectively. The PCA separated the treatments into three clusters. The first two clusters, CT and BC-15 were clustered in negative PC1. The third cluster composed of BC-30 and BC-30+P which were clustered in positive PC1. These results show that soil factors can separate CT and BC-15 from BC-30 and BC-30+P. Redundancy analysis (RDA) was used to determine the soil factors that had a significant impact on the PLFA. To test the relationship between the soil factors and PLFA, we used ANOVA permutation using 1000 permutations on the RDA. There was a significant difference at $P < 0.05$ indicating that soil factors do explain PLFA (Table 1, Appendix A).

Figure 45 displays RDA space and the blue vectors show the soil factor variables that fall along the RDA space. The four most important soil factors (qR, MBC, MBN, and BR) are longest vectors along the RDA axis in explaining variation along the axis (Figure 45).

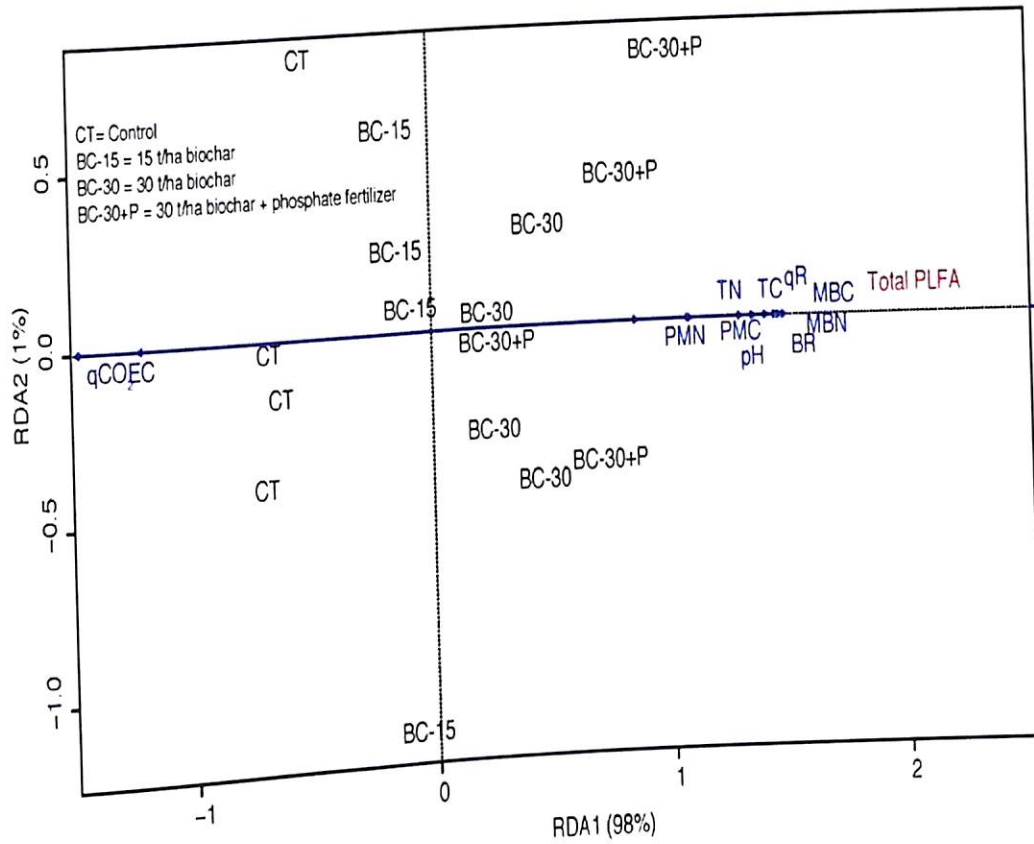


Figure 45: Redundancy analysis (RDA) of the correlations between soil parameters. Arrows indicate the impact of soil parameters on Total PLFA. Abbreviations: BR; Basal respiration, MBC; Microbial biomass carbon, MBN; Microbial biomass nitrogen, PMC; Potentially mineralizable carbon, PMN; qR; Respiratory quotient, qCO_2; Specific maintenance respiration, EC; Electrical conductivity, pH-H_2O; pH-water, TC; Total carbon, and TN; Total Nitrogen.

6.4 Discussion

6.4.1 Effects of biochar on soil microbial biomass

Increase of soil microbial biomass following the incorporation of biochar has been widely reported in laboratory (Ameloot et al., 2013; Zhang et al., 2017) and field studies (Jones et al., 2012). Zheng et al. (2016) reported a significant increase in microbial biomass carbon following an incorporation of wheat straw biochar pyrolyzed at 350-550°C to a sandy loam at a rate of 20 and 40 t ha^{-1}. The increase in MBC in the biochar amended soils may be attributed to the overall improvement in TC and TN, decrease in nutrient leaching (Major et al., 2010), as well as an increase in pH (Lu et al., 2015) which may provide a favorable habitat for beneficial soil microbes (Liu et al., 2017). Also, the labile C in biochar could serve as a microbial substrate (Ameloot et al., 2013; Farrell et al., 2013) and potentially be a key driver for microbial growth. However, Xu, Tan, Wang, & Gai (2016) reported the absence of an effect of maize straw biochar on MBC and MBN following an application of varying rates (40, 80 and 160 t ha^{-1}) of biochar pyrolysed at 500°C to a Fluvo-aquic soil. Dempster et al. (2012) reported a significant decrease in MBC when 25 t ha^{-1} of eucalyptus biochar pyrolzed at 600°C was applied to a sandy soil. The increase in MBC in our study could potentially reflect the increased microbial biomass.

In this study, prior to soil incubation, residual plant roots were removed from the soil, and therefore, soil basal respiration was equal to soil microbial respiration. Application of biochar enhanced soil respiration which is in agreement with the findings of Xu et al. (2016) and Zhang et al. (2017). The increase in soil respiration rates of the biochar amended soils can be related to an improved soil structure, which might have subsequently resulted in enhanced aeration and increased microbial activity. This result implies that application of corn cob biochar has the potential to improve microbial activity due to the labile (active) C and N in biochar which subsequently enhanced the C and N contents in the biochar amended soils (Xu et al., 2016). This observation however contradicts the findings of Zheng et al. (2016a) who found a significant reduction in soil respiration in wheat straw biochar-amended soils in a tropical Chinese sandy loam. Castaldi et al. (2011)

and Schimmelpfennig, Müller, Grünhage, Koch & Kammann (2014) reported no significant changes in soil respiration following biochar amendment in field condition. In some instances, soil respiration was even depressed in Miscanthus bioenergy croplands after miscanthus-derived biochar pyrolyzed at 550 – 600 °C was applied to a silty clay loam at a rate of 9.5 t ha^{-1} (Schimmelpfennig et al., 2014). In an incubation experiment where corn stover biochar pyrolysed at 350-550 °C was added to a silty loam at a rate of 10 t ha^{-1}, Herath et al. (2015) reported that the added biochar could exert a negative instead of a positive priming effect on native soil organic matter decomposition, at least in some soil types.

The potential of biochar to sequester C has been subjected to careful scrutiny based on observations of short term priming effect of biochar incorporation on native soil organic carbon (SOC) decomposition, leading to temporary increases in soil respiration rates. Wardle, Nilsson and Zackrisson (2008) first addressed this issue after finding an 8% decrease in forest SOC decline following application of biochar to a forest soil, which could be explained by the substantially increased soil respiration rates in the first year after biochar application. A much higher soil respiration rate of 28% on average of 46 observations from laboratory and short-term field studies was reported by Sagrilo, Jeffery, Hoffland & Kuyper (2015) following biochar addition. However, it must be emphasized that the results from this study did not substantiate their conclusion from relatively lab-biased studies. The variant results on biochar effects on soil respiration may be explained by the following reasons. Firstly, different laboratory and field protocols used for soil respiration measurements could contribute to the different observations reported in different studies. In a meta-analysis conducted by Sagrilo et al. (2015), it was observed that most of the studies estimated soil CO_2 effluxes by incubating soils in the laboratory. Invariably, the biochars and (most especially) soils used in the studies were normally milled into very fine particles, instead of soil aggregates found in the natural field. Therefore, there are virtually no aggregates to physically protect the carbon substrates which render them highly accessible to soil microbes, and which subsequently resulted in a much higher soil respiration rate following biochar addition, compared to field studies (Ahmad et al., 2011; Troy, Lawlor, O' Flynn, & Healy, 2013). Under field conditions, however, the organic substrates could be physically protected in soil macro aggregates and/or well bound to soil mineral particles (Brodowski, Amelung, Haumaier, Abetz, & Zech, 2005; Liang et al., 2010), limiting their access by soil microorganisms. Secondly, the relatively conducive conditions with consistent ambient temperature and soil moisture in laboratory incubation studies could also enhance soil microbial growth and facilitate active response to exotic carbon input. Moreover, different biochar application rates could be another factor that mediate the response of soil basal respiration to biochar application. The biochar application rates (15 and 30 t ha^{-1}) used in this study were relatively high enough to elicit a positive response relative to soil respiration rate. In the meta-analysis of Sagrilo et al. (2015), high soil respiration was positively correlated with extremely high rates of applied biochar (up to 480 t ha^{-1}).

That notwithstanding, application of biochar at extremely high rates could be impractical due to cost and access to readily available feedstocks, which already militate against farmers' adoption of biochar directly in their production (Clare, Barnes, McDonagh, & Shackley, 2014).

6.4.3 Respiratory quotient and specific maintenance respiration

Specific maintenance respiration is the amount of oxygen consumed by microbes which is an indication of metabolic stress. Application of biochar has been reported in previous studies to increase air permeability and gas diffusion in soils (Arthur & Ahmed, 2017), which by extension increases the O_2 concentrations in biochar amended soils. The increased O_2 availability therefore suggests that, microbes could potentially gain access to previously inaccessible O_2 which in return stimulates enhanced microbial activities. It is therefore not surprising that there was a significant reduction in qCO_2 following BC application. Also, the control soil which showed a high qCO_2 recorded lower TN and TC contents compared with the biochar treated soils. This pattern further substantiates the fact that nutrient limitation played a critical role in affecting the differences among soils in response of the microbial biomass to biochar application (Kolb, Fermanich, & Dornbush, 2009). The relatively high qCO_2 in the control soil points towards a stressed and disturbed condition than the BC treated soils. The less stressed ecosystem in the BC-amended soils also implies an increased abundance of fungi, as soil fungi tend to increase under undisturbed conditions (Gottshall, Cooper, & Emery, 2017). This observation is further supported by a significant increase in the proportion of MBC to MBN (Table 18). Thus, an increase in the ratio of MBC to MBN (microbial CN ratio) enhances the abundance of fungi. This observation is further supported by the significant increase in Fungi:Bacteria ratio in the biochar amended soils (Figure 42). The increase in microbial biomass C and N in the biochar amended soils resulted in a significant decrease in qCO_2 which implies a potential increase in microbial efficiency in the biochar treated soils compared with the untreated soils.

Respiratory quotient (qR) is a reflection of "microbial efficiency" (Zheng et al., 2016) and has been widely used as a bio indicator of disturbance and ecosystem development (Bardgett & Saggar, 1994). Application of corn cob biochar significantly enhanced qR which contradicts the finding of Zheng et al. (2016) following application of wheat straw biochar pyrolysed at 350-500°C to a sandy loam at 20 and 40 t ha^{-1}. In this study, the increased qR found in the biochar treated soils is in agreement with Xu et al., (2016), and it suggests increased microbial biomass population which indicates enhanced ecosystem functionality. The high respiratory quotients in the biochar amended soils also suggest that the microbes in the soils likely produce less cell mass per unit of C degraded than those in untreated soil, thus there is an increase in microbial C use efficiency and therefore helped enhance the SOC retention in the biochar amended soil. This is substantiated by the power function relationship between qR and qCO_2 (Figure 46).

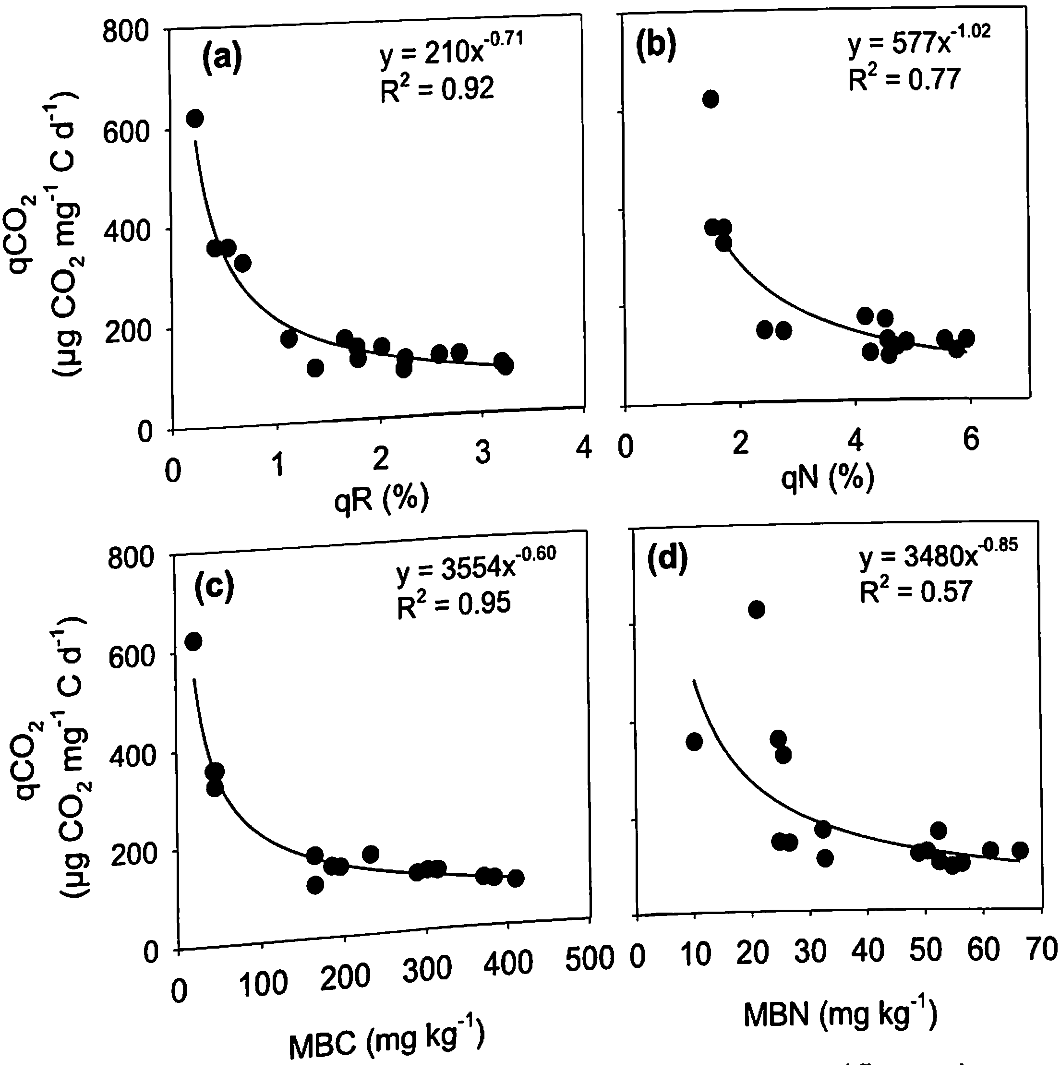


Figure 46: Power function relationship between specific maintenance respiration (qCO2) and qR, qN, microbial biomass carbon (MBC) and microbial biomass nitrogen (MBN)

Increasing the proportion of the microbial biomass C to total organic C exponentially decreased the specific maintenance respiration rate. Thus, application of biochar increased the microbial efficiency as result of an increase in bioenergetic status of microbial biomass.

Conversely, the lower respiratory quotient in the CT may be attributed to the low activities of the microorganisms compared to the BC treated soils or a shift of SOC towards a more recalcitrant form against microbial degradation (Six, Frey, Thiet, & Batten, 2006) in the CT. This explanation may be substantiated by the significantly lower dehydrogenase and urease enzyme activities in CT compared with the BC treated soils. Dehydrogenase is an intracellular enzyme that participates in oxidative phosphorylation in microorganisms (Insam, 2001) and is assumed to be linked to microbial respiratory processes. This enzyme according to Serra-Wittling et al. (1995), has often been correlated with organic C availability in soils.

6.4.4 Effects of corn cob biochar on microbial enzyme activities

Soil enzymes primarily mediate the rate of soil organic matter decomposition and nutrient cycling processes (Nannipieri et al., 2012). The activities of enzymes which can be used to reflect microbial activity (Huang et al., 2017) responded sensitively to the corn cob biochar treatments in our study. Urease activity significantly increased in the BC-treated soils relative to the CT which is in agreement with a study conducted by Zhang et al. (2017) who applied straw-derived biochar pyrolysed at 350-550°C at varying rates of 8 and 16 t ha^{-1} to a silty clay loam and recorded a significant increase in urease activity by 41.2 and 44.3%, respectively. The increase in the activity of urease could be attributed to the fact that the biochar might have increased the activity of specific enzymes related to N utilization (Huang et al., 2017) in soil which was substantiated by the study of Bailey et al. (2011). A significant correlation (Table 2 Appendix A) between MBC and urease enzyme was observed ($r=0.93$, $p<0.01$), and this may be ascribed to the release of more urease by soil microbial biomass (Zhang et al., 2017) which might have improved the transformation of nitrogen in the soil. Dempster et al. (2012) further asserted that incorporation of biochar potentially promotes nitrogen transformation in soils, which might be related to urease activity. In a 90-day incubation study, Wang et al., (2015) recorded a significant increase in urease enzyme activity following the application of maize straw biochar pyrolysed at 450°C applied at varying rates of 0.5 to 5% by weight to a light loamy soil.

Soil dehydrogenase enzymes are the major representatives of the oxidoreductase enzymes class (Gu, Wang, & Kong, 2009). Dehydrogenases are one of the most important enzymes in the soil environment, and are used as an indicator of overall soil microbial activity (Salazar, Sánchez, Alvarez, Valverde, Galindo et al., 2011), due to the fact that they occur intracellular in all living microbial cells (Yuan & Yue, 2012), and they are tightly linked with microbial oxidoreduction processes (Moeskops, Sukristiyonubowo, Buchan, Sleutel, Herawaty et al., 2010). Soil dehydrogenase enzymes play a key role in the biological oxidation of soil organic matter (OM) (Zhang et al., 2010) by transferring hydrogen (H^+) from organic substrates to inorganic acceptors.

Incorporation of corn cob biochar significantly enhanced dehydrogenase enzyme activity which is in agreement with a previous study (Awasthi et al., 2017). The increase in dehydrogenase activity in the BC-amended soil could be ascribed to a suspected increase in water content as reported in several studies (Arthur & Ahmed, 2017; Zuolin Liu et al., 2017; Ulyett et al., 2014). Low water availability has been reported to inhibit soil dehydrogenases by lowering intracellular water potential, and thus by reducing hydration and dehydrogenase enzymes activity (Wall & Heiskanen, 2003). Periods of soil water limitation may potentially affect microbial communities through dehydration. Wolinska & Stępniewska, (2011) affirmed that the most common environmental stress for soil microorganisms is perhaps drought.

Thus, soil dehydrogenase enzyme activity is significantly influenced by soil water content.

Moreover, the increased dehydrogenase activity in the BC-amended soils could also be ascribed to increased organic matter content in the treated soils relative to the CT. Soil organic matter (SOM) has significant effects not only on soil enzymes activities but also on the activities of soil microbes. Soil organic matter is considered as an indicator of soil quality (similarly like dehydrogenases) (Salazar et al., 2011) because of its property of being a nutrient sink and source that can potentially enhance soil physico-chemical properties, and also enhance soil biological activity. According to Fontaine, Mariotti, & Abbadie, (2003), the quality and amount of SOM in the soil is important as it affects the supply of energy for microbial growth and enzyme production. Evidently, there is a strong positive correlation between soil enzymatic activity and soil OM content (Table 2 Appendix A). The increased SOM contents in the BC-amended soils might have provided enough substrate to support higher microbial biomass, hence higher enzyme production (Yuan and Yue, 2012). Some authors have reported a strong connection between soil dehydrogenase enzyme activity and SOM content (Pascual, Garcia, Hernandez, Moreno, & Ros, 2000).

Wolińska and Stępniewska, (2011) reported a high correlation coefficient between urease and dehydrogenase enzymatic activies and total organic carbon content, which suggested a significant role of these intracellular enzymes in the transformations of basic components of SOM. In a study conducted by Pascual, Garcia, Hernandez, Moreno and Ros (2000), the authors observed that soils characterized with low soil microbial and biological activity (e.g. low microbial biomass carbon and low soil respiration rate), also showed the lowest values of dehydrogenase and urease activity. Soil dehydrogenase enzyme accelerates the decomposition of SOM, which is reflected in soil respiration and CO_2 effluxes from the rizosphere (Zhang et al., 2010), substantiating the fact that dehydrogenase enzyme is positively correlated with OM content. Correlation analysis revealed that dehydrogenase enzyme activity correlated positively with soil basal respiration ($r=0.94$; $p<0.01$) and total carbon ($r=0.62$; $p<0.05$) (Table 2 Appendix A).

Several studies have reported that application of biochar to soils can potentially sorb a wide range of organic and inorganic molecules which may affect enzyme activities by sorbing enzymes and/or their substrates (Jin, 2010). Contrary to this, a correlation analysis from our study showed that the two enzymes were positively correlated with MBC, MBN, TC, TN and PMC (Table 2 Appendix A) which were enhanced in the biochar treated plots. These results indicate that the potential of biochar to sorb enzymes and reduce their activities may be dependent on the type of biochar, type of soil, soil nutrient content and the specific enzyme. Further research is, however, needed to understand the mechanisms behind the sorption of soil enzymes by biochar.

6.4.5 Response of soil microbial community profiling and diversity to biochar application

In this study, application of corn cob biochar to a tropical sandy loam increased the total PLFA compared with the untreated soil, due to the increase in soil organic carbon (C) and nitrogen (N) following the incorporation of biochar, as total PLFA correlated positively with TC and TN (Table 3 Appendix A). Our observation is in agreement with the findings of Chen et al.

(2017) who reported an increase in total PLFA after incorporating fine bamboo stick biochar pyrolyzed at 700°C for 4 hours, and applied to a sandy loam at 3 and 9% wt/wt. The soil C and N are considered to be the main energy and nutrient sources for microbial growth (Zhao et al., 2016). Previous studies have suggested that microbial community composition is enhanced by soil organic amendments, and that this effect is related to the soil C (Ai, Liang, Sun, Wang, & Zhou, 2012; Bowles, Acosta-Martínez, Calderón, & Jackson, 2014) because of organic matter mineralization which increases the growth and activity of soil microorganisms (Wang et al., 2015) and enhances microbial biomass carbon (MBC), microbial biomass nitrogen (MBN), and basal respiration (BR) and respiratory quotient (qR).

The idea behind redundancy analysis (RDA) is to apply regression to examine how much of the variation in one set of variables explains the variation in another set of variables. Results from the RDA showed that the four most important soil factors that had a significant impact on the total PLFA are qR, MBC, MBN, and BR (Figure 45).

The potential mechanisms of the effects of biochar on soil microorganisms include (i) provision of a C substrate, (ii) production or adsorption of substances that stimulate (Bamminger et al., 2014) or inhibit soil microbes (Dempester et al., 2012), and/or (iii) provision of a suitable habitat for microbial growth and protection from predators (Quilliam et al., 2013). Total bacteria and fungi in the soil amended with 30 t ha^{-1} (BC-30 and BC-30+P) showed a significant increase, which is contrary to the results of Demptster et al (2012), who applied 5 and 25 t ha^{-1} of eucalyptus biochar pyrolysed at 600°C for 24 hours, and applied to sandy soil. In a 90-day incubation experiment, Wang et al (2015) equally reported a decrease in the total PLFA and relative abundance of bacteria and fungi following the application of maize straw biochar pyrolysed at 450°C to light loamy soil at varying rates of between 0.5 to 5% by weight.

The fungi bacteria ratio has been used as an indication of C sequestration potential with a higher fungal diversity (higher ratio) implying greater C storage in soil (Strickland & Rousk, 2010). Based on interpretation of data, a ratio of less than 0.05 indicates a very poor soil health while 0.30 and above indicates very good soil health. The fungi: bacteria ratio significantly increased with increasing rate of biochar application. Soils treated with BC-30 and BC-30+P recorded fungal:bacterial ratio of 0.30, which gives an indication that, application of corn cob biochar enhanced the soil health of the tropical sandy loam when applied at 30 t ha^{-1}.

Application of biochar directly impacted the diversity and abundance of soil bacteria and fungi by strongly affecting soil pH and soil organic C content. The increase in C increased the microbial biomass carbon and nitrogen, specific maintenance respiration and respiratory quotient, which were the strongest predictors of microbial community attributes in this study. Our findings also mimic observed global patterns in MBC, MBN, qR and BR which have been found to increase in tandem with soil C contents (Xu, Thornton, & Post, 2013). These results suggest that soil microbial communities and diversities are limited or enhanced by C in tropical soils and align with the hypothesis indicating that soil C content is a major driver of the abundance and diversity of soil bacteria and fungi (Siciliano et al., 2014). The increase in bacteria community abundance and diversity might also be attributed to the increase in soil pH in the biochar treated plots. Previous findings have highlighted soil pH as a major predictor of bacterial richness and diversity across a wide range of ecosystem types (Lauber, Hamady, Knight, & Fierer, 2009). Linear increases in bacteria diversity with pH have been found mainly in soils with pH values of 6.5 (Fierer & Jackson, 2006; Lauber et al., 2009). Our findings showed pH values of 6.6 and 6.7 in the BC-30 and BC-30+P treated soils respectively, which are approximately the same as the reported pH value ideal for higher bacteria abundance and diversity. This observation thus indicates the importance of soil pH as a driver of bacterial diversity patterns as reported by previous large-scale studies (Fierer & Jackson, 2006; Lauber et al., 2009). These results support the notion that soil pH drives changes in bacterial composition in terrestrial agroecosystems (Fierer & Jackson, 2006; Lauber et al., 2009). Other studies have reported a negative relationship between soil pH and fungal abundance and diversity. However, our results give a contrasting effect of soil pH on fungi diversity, indicating that other environmental or soil factors might have been the most favorable and major predictors of fungi richness and diversity in a tropical agroecosystem.

6.5 Conclusions

Application of biochar at 30 t ha^{-1} had a profound significant effect on enzyme activities and soil microbial properties by increasing the soil basal respiration and respiratory quotient, with decreased specific maintenance respiration rates which all culminated into increasing the microbial activity of the BC-30 and BC-30+P amended soils. Furthermore, high rates of biochar had significant effects on soil microbial community composition, diversity and total PLFA. Incorporation of biochar at a rate of 30 t ha^{-1} enhanced the abundance and diversity of bacteria and fungi acids. Among the soil factors, the ones that contributed most to the abundance of soil microbes in the BC-30 and BC-30+P treated soils were BR, qR, MBC and MBN.

CHAPTER SEVEN

EFFECTS OF CORN COB BIOCHAR ON SOIL QUALITY

7.1 Introduction

The term "soil quality" is commonly used in relation to the two critical soil functions of productivity and protection of environmental quality (Wander & Drinkwater, 2000). This therefore implies that soil quality can be defined as the ability of the soil to support crop growth and effectively produce crops in a sustainable manner without compromising on environmental quality. In this regard, soil plays a crucial role in providing essential services for plant growth, for partitioning and balancing the movement of water and gases in the soil matrix and the atmosphere, and as an effective buffer for the environment (Acton, & Padbury, 1993). In agriculture, management practices focus primarily on enhancement of soil biological, physical and chemical properties which have a paramount effect on soil productivity.

Despite the numerous reported benefits of biochar application to soils, little is known about its impact on the quality of the soils of the humid tropics. Most of the studies done on biochar in tropical soils take into consideration some selected properties without aggregating these properties into an index of soil quality with regards to specific soil functions. The aim of this research was to use the inductive approache to develop soil quality indices to study the impact of corn cob biochar on the quality of weathered tropical sandy loam.

7.2 Materials and Methods

7.2.1 Modeling soil quality

Modeling soil quality requires the selection of soil properties that are sensitive to short-term management practices, and are, therefore, considered nitrogen (PMN), respiratory quotient (qR), specific maintenance respiration (qCO_2), total phospholipid fatty acids (total PLFA), total bacteria and total fungi. Application of biochar resulted in significant increases in the soil biological quality indices by 1.6-, 2.3- and 2.4-folds in the plots treated with BC-15, BC-30 and BC-30+P treatments, respectively (Table 21).

Significant differences in soil biological quality indices existed among the biochar treatments, with the highest index recorded in the plots treated with 30 t ha^{-1} biochar. Thus, increasing the rate of biochar application significantly impacted on the soil biological quality. No significant difference was observed in soil biological quality in the BC-30 and BC-30+P amended soils.

The soil electrical conductivity (EC), pH, total organic carbon (TOC) and nitrogen (TON), particulate organic carbon (POC) and nitrogen (PON), active carbon (AC), humic acid extractable carbon (HA-C), fulvic acid extractable carbon (FA-C), glucose and humin concentrations were integrated to calculate the soil chemical soil quality. All the biochar treated plots contributed to a significant increase in soil chemical quality. However, incorporation of biochar at a rate of 30 t ha^{-1} significantly increased the chemical soil quality by 2.3 to 2.4 fold, with the BC-15 treated soil having a 1.8-fold increase in soil chemical quality relative to the control (Table 21).

The soil physical quality index was calculated by using the soil mean weight diameter (MWD), geometric mean weight (GMWD), macro aggregate stability (MaAS), micro aggregate stability (MiAS), structural coefficient (SC) and bulk density (ρb). The soil physical quality was significantly improved in the BC-30 and BC-30+P treated soils, with a 2.2 to 2.6-fold increase compared to the CT. The plots treated with 15 t ha^{-1} biochar did not result in a significant increase in the soil physical quality (Table 21). Statistically, both BC-30 and BC-30+P treatments had similar impact on the soil physical quality index despite a seemingly higher value observed in the BC-30+P treated soils.

Table 20: *Effects of Corn Cob Biochar on Soil Biological, Chemical, Physical, and Overall Inductive Soil Quality Indices*

Treatment	SB $_{index}$	SC Q_{index}	SP Q_{index}	Inductive S_{index}
CT	36.6±1.7c	33.1±3.1c	24.9±2.3b	31.6±3.6c
BC-15	57.7±2.1b	59.4±1.8b	31.7±3.8b	49.6±2.1b
BC-30	84±3.4a	74.4±5.3a	55±5.9a	71.1±6.3a
BC-30 + P	87±4.7a	77.3±8.2a	65.4±5.6a	76.7±5.8a

SB Q_{index} = Soil biological quality index; SC Q_{index} = Soil chemical quality index; SP Q_{index} = Soil physical quality index; Inductive SQ_{index} = Inductive soil quality index. ≠Different letters indicate that means are significantly different among biochar treatments ($p \leq 0.05$).

All the soil quality indicators, comprising of the biological, chemical and physical properties mentioned above were integrated to calculate the inductive soil quality index for the respective treatments. The inductive sol quality index responded positively to the incorporation of biochar at all rates (Table 21). Among the biochar treatments, the highest inductive soil quality index was observed in the plots treated with 30 t ha^{-1}, with a significant 2.3- to 2.4-fold increase relative to the CT.

7.3.1 Identification of key soil quality predictors

Principal component analysis (PCA) was performed on the data using soil factors as variables. The PCA separated the treatments into three clusters. The first two clusters, CT and BC-15 were clustered in negative PC1. The third cluster composed of BC-30 and BC-30+P which were clustered in positive PC1. These results showed that soil factors could separate CT and

BC-15 from BC-30 and BC-30+P. Redundancy analysis (RDA) was used to determine the soil factors that had a significant impact on the soil biological, chemical and physical quality.

7.3.1.1 Principal Component Analyses on Soil Biological Quality index (SB Qindex)

The results of the PCA on SB Q_{index} are presented in Figure 47.

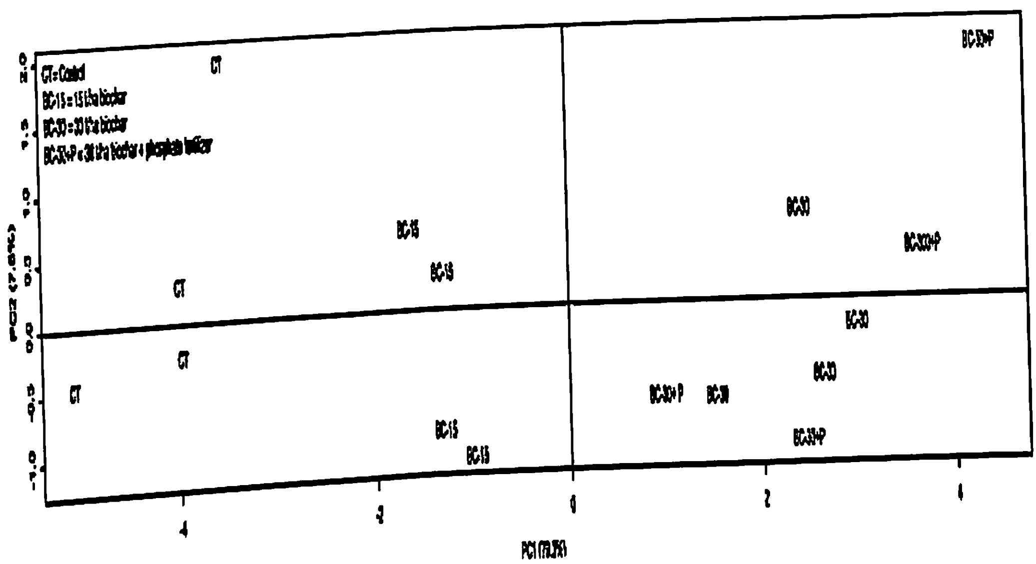


Figure 47: Principal component analysis (PCA) of soil biological properties from different treatments

The first and second PCA accounted for 79.3 and 7.6% of the variation, respectively. The PCA separated treatments into three clusters. The first two clusters, control and BC-15 were clustered in negative PC1. The third cluster composed of BC-30 and BC-30+P was clustered in positive PC1. These results show that soil factors can separate CT and BC-15 from BC-30 and BC-30+P.

7.3.1.2 Redundancy analysis on Soil Biological Quality index (SB Q_{index})

To test the relationship between the soil factors and SB Q_{index}, ANOVA permutation test was used by running 1000 permutations on the RDA. There was a significant difference at $P < 0.05$ indicating that soil factors explained SB Q_{index} (Table 4 Appendix A). Figure 2B displayed RDA space and the blue vectors showed soil factor variables fell along the RDA space. The four most important soil factors (total bacteria, total PLFA, total Fungi and MBC) were the longest vectors along the RDA axis in explaining variation in along the axis (Figure 48).

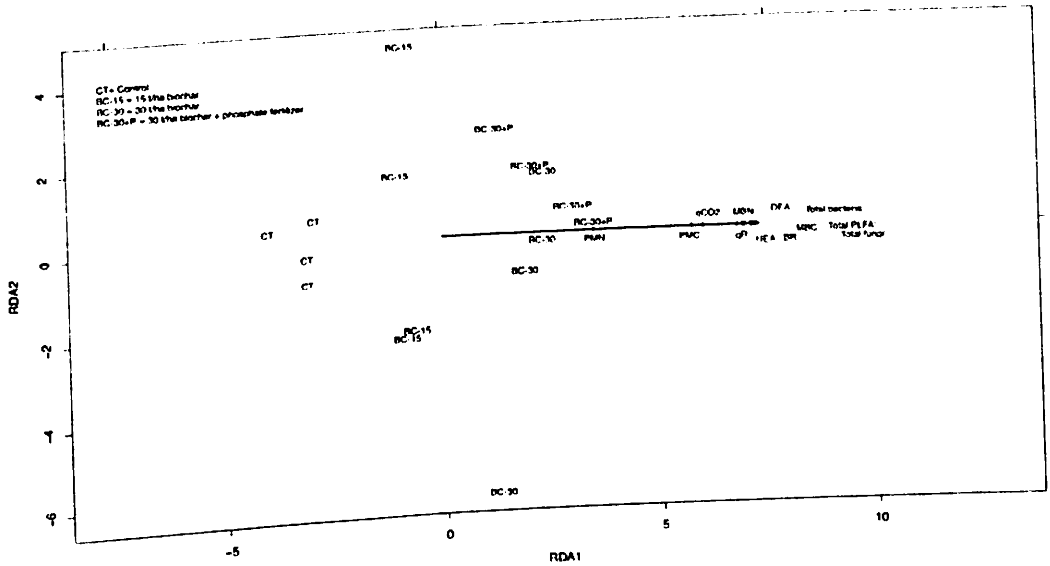


Figure 48: Redundancy analysis (RDA) of the correlations between soil biological parameters. Arrows indicate the impact of soil parameters on soil biological quality index. Abbreviations: PMC; Potentially mineralizable carbon, PMN; Potentially mineralizable nitrogen, MBC; Microbial biomass carbon, MBN; Microbial biomass nitrogen, qCO_2; Specific maintenance respiration, qR; Respiratory quotient, UEA; Urease enzyme activity, DEA; Dehydrigenase enzyme activity, PLFA; Phospholipid fatty acids.

7.3.1.3 Principal component analysis on Soil Chemical Quality index (SC Qindex)

The results of the PCA on SC Q_{index} are presented in Figure 49.

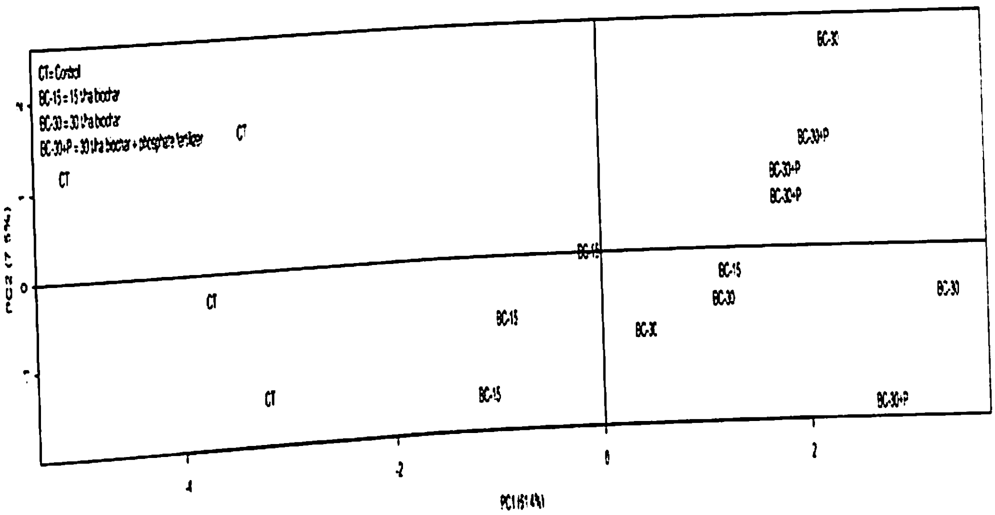


Figure 49: Principal component analysis (PCA) of soil chemical properties from different treatments.

The first and second PCA accounted for 61.4 and 7.5% of the variation, respectively. The PCA separated treatments into three clusters. The first two clusters, control and BC-15 were clustered in negative PC1, except 1 BC-15 that was in positive PC1. The third cluster composed of BC-30 and BC-30+P was clustered in positive PC1. These results showed that soil factors could separate CT and BC-15 from BC-30 and BC-30+P.

7.3.1.4 Redundancy analysis on Soil Chemical Quality index (SC Qindex)

To test the relationship between the soil factors and SC Q_{index}, ANOVA permutation test was used by running 1000 permutations on the RDA. There was a significant difference at $P < 0.05$ indicating that soil factors explained SC Q_{index} (Table 5 Appendix A). Figure 50 displayed RDA space and the blue vectors show soil factor variables fell along the RDA space.

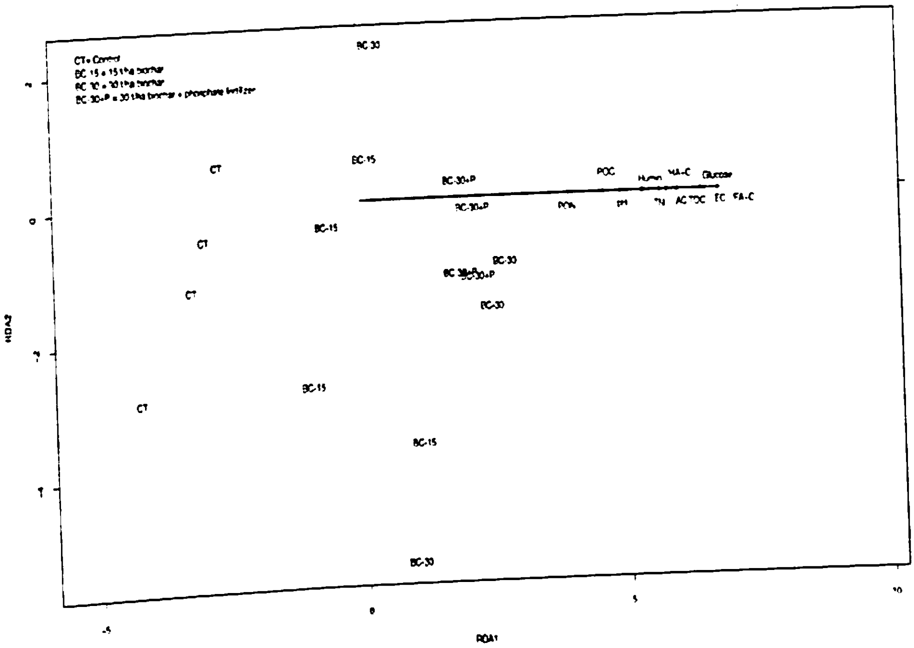


Figure 50: Redundancy analysis (RDA) of the correlations between soil biological parameters. Arrows indicate the impact of soil parameters on soil chemical quality index. Abbreviations: POC; Particulate organic carbon, PON; Particulate organic nitrogen, TN; Total nitrogen, TOC; Total organic carbon, EC; Electrical conductivity, FA-C; Fulvic acid carbon, HA-C; Humic acid carbon.

The four most important soil factors (Glucose, FA-C, EC, and TOC) were longest vectors along the RDA axis in explaining variations in along the axis (Figure 50).

7.3.1.5 Principal Component Analyses on Soil Physical Quality index (SPindex)

The results of the PCA on SP Q_{index} are presented in Figure 51

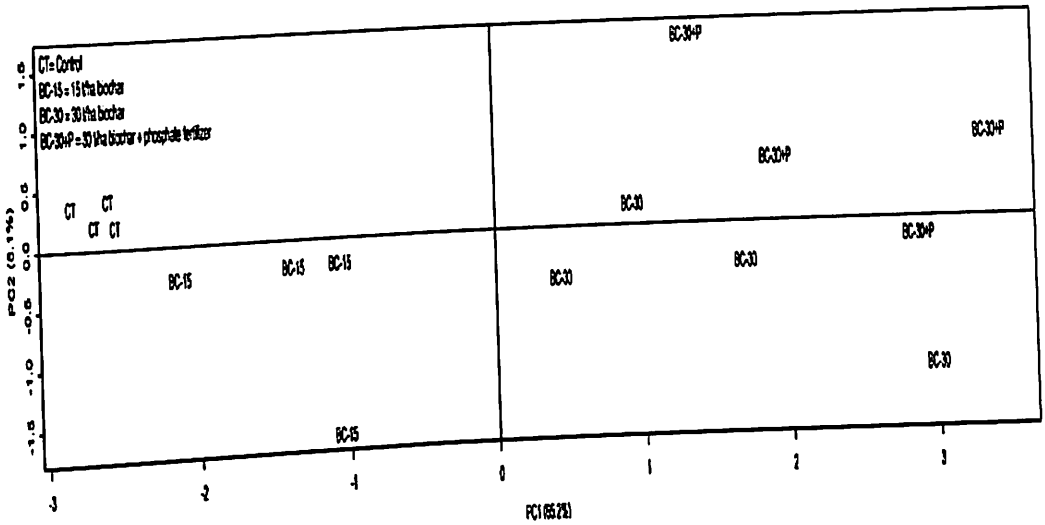


Figure 51: Principal component analysis (PCA) of soil physical properties from different treatments.

The first and second PCA accounted for 65.2 and 8.1% of the variations, respectively. The PCA separated treatments into three clusters. The first two clusters, control and BC-15 were clustered in negative PC1. The third cluster composed of BC-30 and BC-30+P was clustered in positive PC1. These results showed that soil factors could separate CT and BC-15 from BC-30 and BC-30+P.

7.3.1.6 Redundancy analysis on Soil Physical Quality index (SP Qindex)

To test the relationship between the soil factors and SP Qindex, ANOVA permutation test was used by running 1000 permutations on the RDA. There was a significant difference at $P < 0.05$ indicating that soil factors explained SP Qindex (Table 6 Appendix A). Figure 52 displayed RDA space and the blue vectors showed soil factor variables fell along the RDA space.

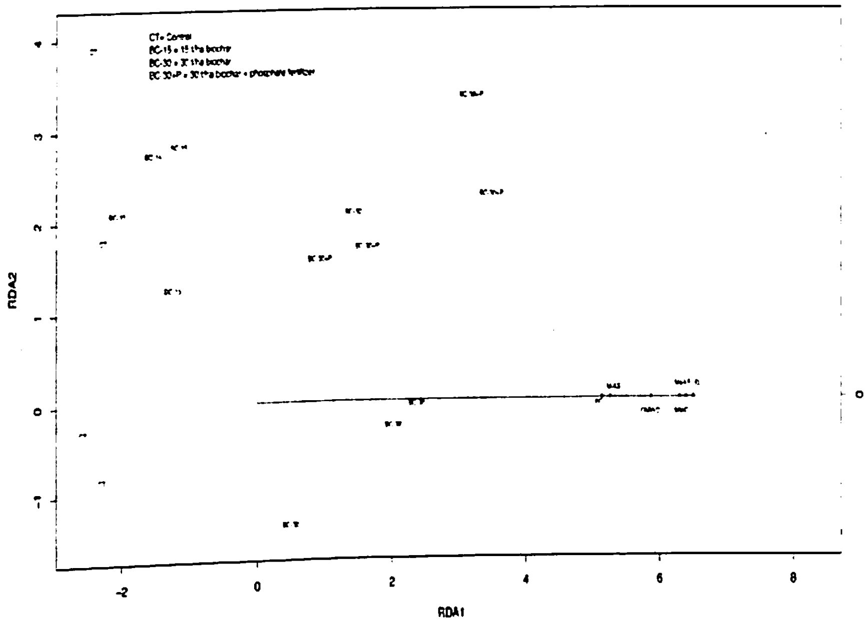


Figure 52: Redundancy analysis (RDA) of the correlations between soil biological parameters. Arrows indicate the impact of soil parameters on soil physical quality index. Abbreviations: BD; Bulk density, MiAS; Micro aggregate stability, MaAS; Macro aggregate stability, GMWD; Geometric mean weight diameter, MWD; Mean weight diameter, SC; Structural coefficient.

The four most important soil factors (SC, MaAS, MWD, GMWD) were longest vectors along the RDA axis in explaining variations along the axis (Figure 52).

7.4 Discussion

In this study, application of biochar at 30 t ha^{-1} significantly enhanced the inductive soil quality due to a reduction in electrical conductivity (ECe) and pronounced increases in basal respiration (BR), dehydrogenase enzyme activity (DEA), microbial biomass carbon (MBC), respiratory efficiency (qR), total phospholipid fatty acids (PLFA) and total fungi as shown by the redundancy analysis. A number of studies reported that application of biochar to soils can increase soil microbial biomass carbon, and may also affect the soil biological community composition (PLFA), which in turn affects nutrient cycling, plant growth, SOC mineralization and soil quality (Lehmann et al., 2011). The increased in the soil quality index may be attributed to the enhanced retention of SOC in the biochar amended soils due to the high microbial efficiency and enhanced ecosystem functionality as depicted by the high respiratory quotient (qR) in the biochar amended soils (BC-30 and BC-30+P). Results from the redundancy analysis shows that fungi are important predictor of soil quality, and this is attributed to the carbon storage potential of soils with high fungi diversity and abundance.

From the study, the increase in soil quality was also highly predicted by microbial activity indicated by high soil basal respiration and dehydrogenase enzyme activity. Dehydrogenase enzymes are among the most important enzymes in the soil environment, and are used as an indicator of overall soil microbial activity (Salazar et al., 2011), because they occur intracellularly in all living microbial cells (Yuan & Yue, 2012). Soil dehydrogenase enzymes facilitates SOM decomposition which is reflected in high soil basal respiration rates from the rhizosphere (Zhang et al., 2010). This therefore substantiates the fact that dehydrogenase enzyme is positively correlated with SOM content, and for that matter, soil quality.

7.4.1 Relationship among soil quality indices

The soil quality index was regressed on soil biological quality, soil chemical quality and soil physical quality to evaluate their respective contribution as sensitive and early indicators of the overall soil quality. Among the soil quality indices, the soil biological quality greatly contributed to enhancing the quality of the amended soil. When plotted one to one, the soil biological quality accounted for 95% of the soil quality index variability linearly (Figure 53).

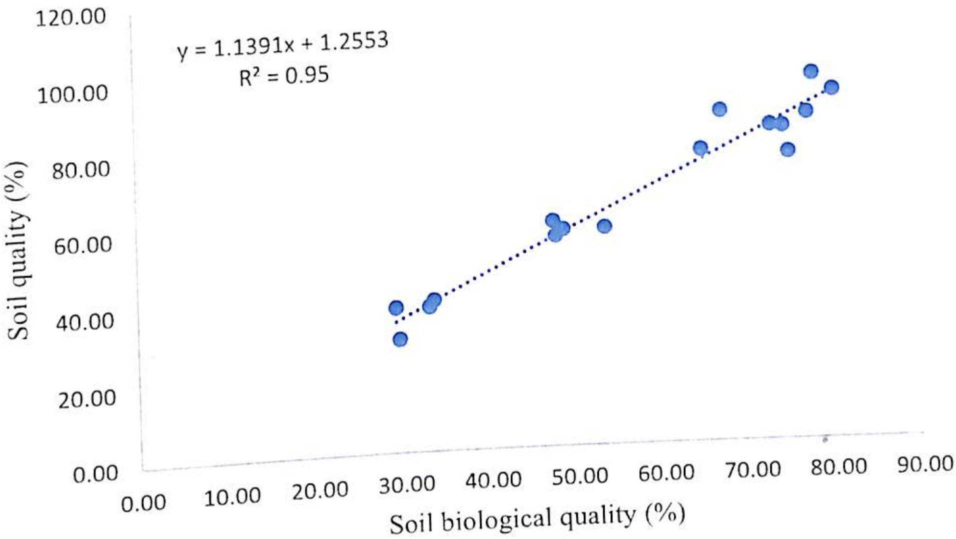


Figure 53: Relationship between soil biological quality and overall soil quality.

Thus, an improvement in soil biological quality improved the overall soil quality. The soil chemical and physical quality indices respectively accounted for 82 (Figure 54) and 80% (Figure 55) variability of the soil quality index.

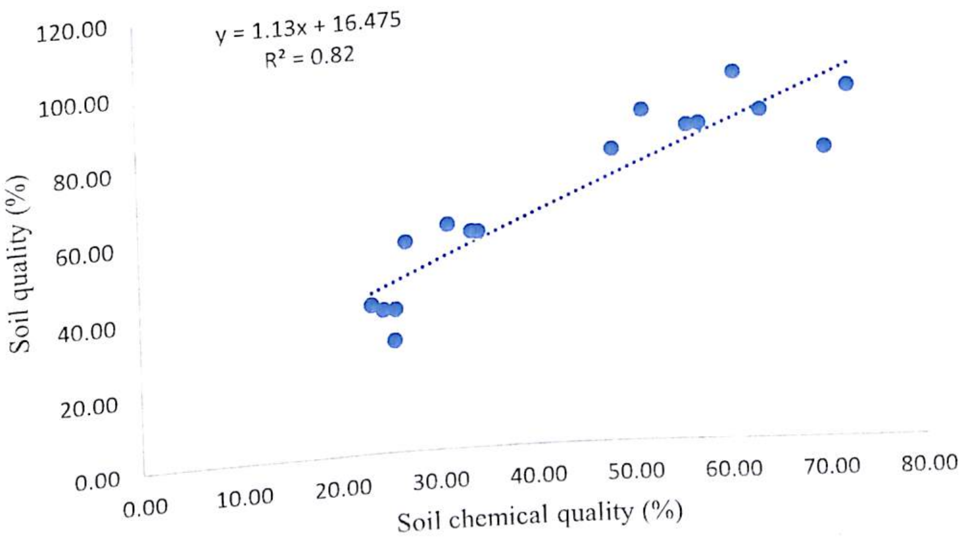


Figure 54: Relationship between soil chemical quality and overall soil quality.

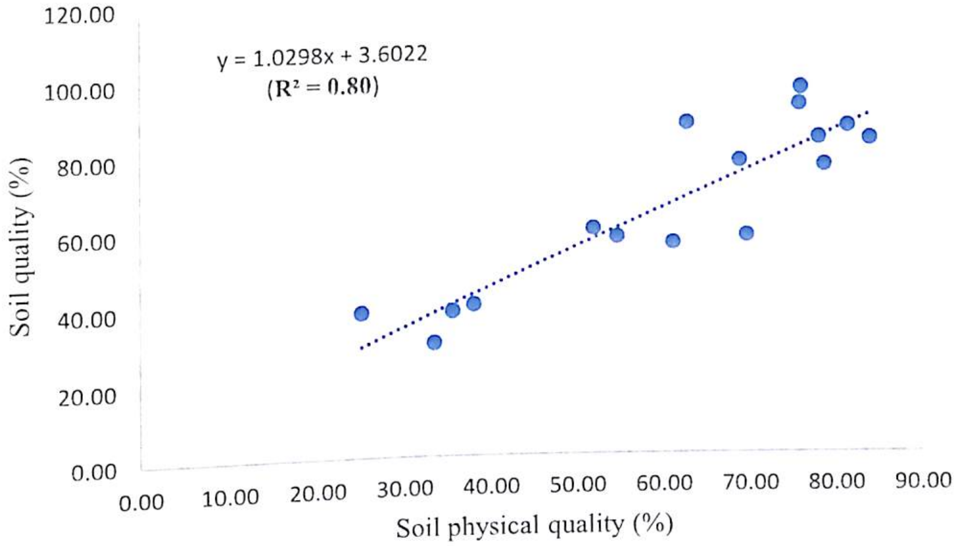


Figure 55: Relationship between soil physical quality and overall soil quality.

The soil biological quality also accounted for 82 and 80% of the variability in soil physical quality and soil chemical quality respectively (Figure 56 and Figure 57).

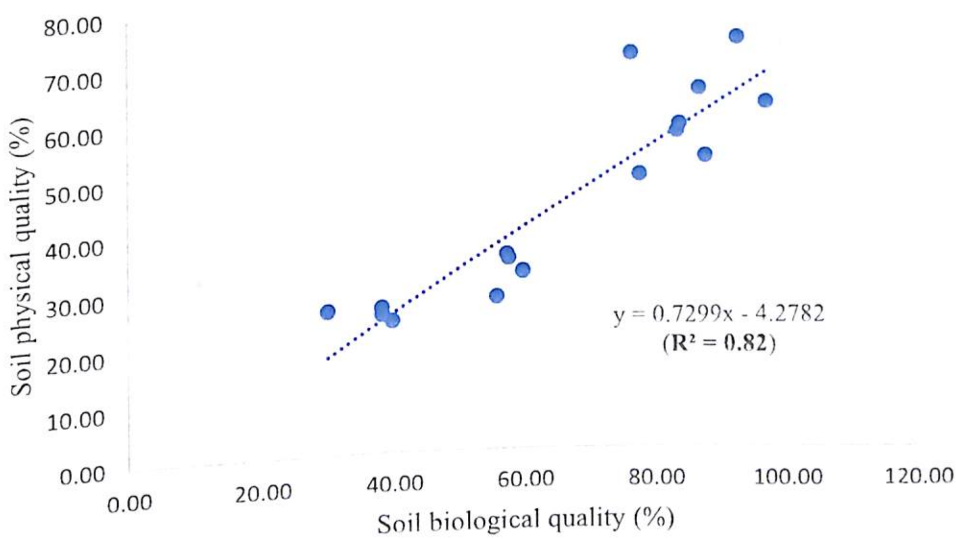


Figure 56: Correlation between soil biological quality and physical quality.

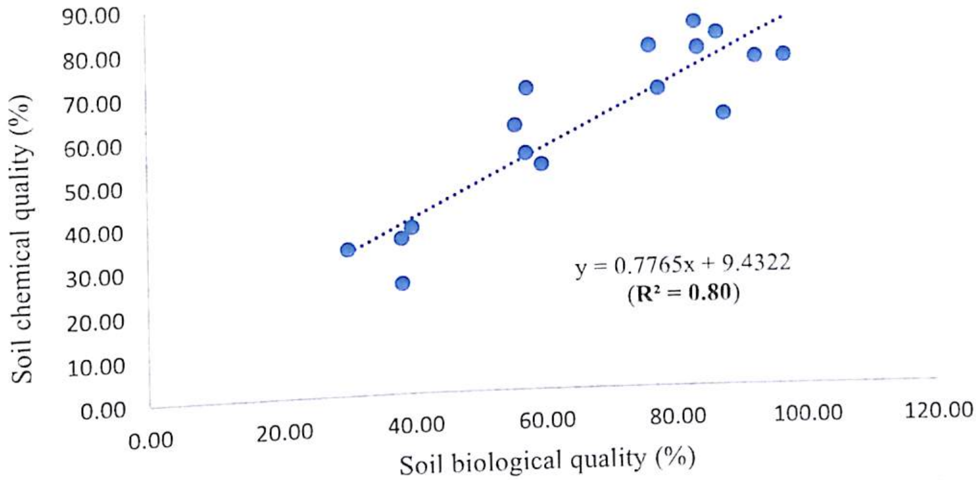


Figure 57: Correlation between soil chemical quality and biological quality

A highly significant linear relationship of soil biological quality with soil quality index suggests that among the soil biological, chemical and physical quality indices, the soil biological quality index is a consistent and, sensitive and early indicator of changes in soil quality long before the changes are detected in the other soil quality indicator properties. This observation is further corroborated by Bünemann et al., 2018; Schloter, Nannipieri, Sørensen, & van Elsas, (2018) who opined that changes in soil biological activities or biochemical processes may be used as early indicators of changes in soil quality. The soil biological quality is greatly responsible among other properties, for decomposition of organic residues, facilitating nutrient cycling in the soil, metabolizing labile carbon, synthesizing humic substances, enhancing macro aggregation and structural stability, and protection of organic matter as particulate organic matter (Melero, López-Garrido, Murillo, & Moreno, 2009; Schloter et al., 2018). Therefore, an improvement in the soil biological properties relates to improvement in the soil chemical and physical properties and subsequently, an enhancement in the overall soil quality (Aziz et al., 2013). This is further substantiated by the significant relationship of soil biological quality with soil chemical and soil physical quality, which justifies the role of soil biology to enhancing the other soil properties.

7.5 Conclusions

Soil quality is an integrated function of soil biological, chemical and physical properties. Results from the study showed that soil biological quality, soil chemical quality and soil physical quality improved significantly in the biochar treated soils. Among the biochar treatments, the BC-30 and BC-30+P performed best in improving the soil quality properties and soil quality over time. A significant relationship between soil quality index and soil biological quality gives an indication that soil biological quality can be used as a sensitive and early indicator of a tropical sandy loam soil quality evaluation in response to biochar amendment application or sustainable soil management practices. Furthermore, a robust and routine measurement of soil biological quality properties can be used as an early indicator of soil quality in a tropical agro ecosystem.

CHAPTER EIGHT

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

8.1 Summary

The entire research focused on elucidating the effects of corn cob biochar on the fertility of highly weathered tropical sandy loam. The research specifically dealt with the effect of biochar on soil physical properties (e.g. aggregate characteristics strength, water retention and gas transport parameters), soil microbiological properties (e.g. soil microbial community structure and diversity) and soil chemical properties (e.g. carbon and nitrogen pools).

In experiment 1 (Chapter 4), the impact of biochar on aggregate characteristics such as aggregate stability, clay dispersibility, aggregate tensile strength, soil friability and workability was assessed. The study also assessed the effect of corn cob biochar on water retention at several matric potentials, gas transport parameters (air permeability and gas diffusion) and pore structure characteristics (convective and diffusion percolation threshold). The study showed that the stability of soil aggregates was significantly improved in the soils treated with 20 t ha^{-1} (with and without P). Secondly, aggregate tensile strength of the smaller aggregates (1-2 mm) was significantly higher with increasing biochar application rate. Furthermore, increasing the rate of corn cob biochar application improved soil friability and workability. The study further demonstrated that incorporation of biochar at 20 t ha^{-1} to a tropical sandy loam may potentially reduce the rate of soil physical degradation by improving the stability of soil aggregates.

In this study, incorporation of biochar at 10 and 20 t ha^{-1} moderately improved water retention, gas transport parameters and pore structure characteristics. Biochar applied at 20 t ha^{-1} resulted in an increase in the fine pores which subsequently led to an increase in water retention at matric potentials larger than pF 2.0.

The study demonstrated that increasing the rates of biochar subsequently increased the proportion of aggregates in the larger size fractions (>0.25mm) leading to an increase in the water stable macro aggregates in the plots treated with 30 t ha^{-1} (with and without phosphate fertilizer). Increasing the rates of biochar significantly enhanced the indices of structural stability (structural coefficient, mean weight diameter and geometric mean weight) which indicated the predominance of larger, more stable aggregates in the BC-30 and BC-30+P treated plots.

In experiment 2 (Chapter 5), a study was conducted to elucidate the impact of corn cob biochar on soil chemical properties. Carbon (C) and nitrogen (N) lability, C and N pool and C and N management indices were calculated based on the labile C and N pools of total C and N. The study showed that increasing the rate of biochar application resulted in a significant increase in the labile C and N fractions. Among the tested labile C and N pools, the active C and N fractions were observed to be the most sensitive indicators to detect early changes in soil organic matter accumulation and C and N lability in response to corn cob biochar application.

Incorporation of biochar at 30 t ha^{-1} enhanced the quality and content of soil organic carbon which concomitantly increased the humic and fulvic acid fractions of total organic carbon. The BC-30 and BC-30+P treatments favored the accumulation of high molecular weight aromatic quality of TOC which suggests that C may have been sequestered in passive form. In perspective, biochar applied 30 t ha^{-1} may potentially enhance the stability of SOC by improving the aromatic TOC quality.

In experiment 3 (Chapter 6), the effect of corn cob biochar on soil microbiological properties and enzyme activities was assessed. In this study, it was observed the BC-30 and BC30+P treatments had a profound effect on enzyme activities and soil microbial properties. The study demonstrated an increase in the soil respiration and respiratory quotient, with decreased specific maintenance respiration rates which indicated a substantial increase in soil microbial activities in the BC-30 and BC-30+P treated plots. Furthermore, biochar applied at 30 t ha^{-1} impacted significantly on soil microbial community composition and total phospholipid fatty acids. The diversity and abundance of fungi and bacteria was enhanced in the BC-30 and BC-30+P treated soils relative to the rest of the treatments. Principal component and redundancy analyses carried out showed that among the soil factors, the ones that contributed most to the abundance of soil microbes in the BC-30 and BC-30+P treated soils were soil basal respiration, respiratory quotient, microbial biomass carbon and nitrogen.

Chapter 7 focused on the integration of all the measured soil properties to assess the overall effect of corn cob biochar on soil quality. The study demonstrated that, among the treatments, the BC-30 and BC-30+P performed best to improving the soil quality properties and soil quality over time. From the study, a significant relationship was observed between soil quality index and soil biological quality which therefore indicates that, soil biological quality may be potentially used as a sensitive and early indicator of soil quality evaluation in response to biochar application or sustainable soil management practices in a tropical sandy loam.

In perspective, application of corn cob biochar has the propensity to increase the fertility and productive capacities of weathered soils of the humid tropics.

8.2 Conclusions

The study demonstrated that incorporation of corn cob biochar into a weathered tropical sandy loam enhanced the physical fertility by improving the aggregate characteristics strength, water retention and pore structure characteristics of the soil. Application of biochar to highly weathered soils of Ghana may potentially improve the water retenting capacity of the soils, enhance gas transport by convection and diffusion and improve soil structure to help salvage the decline in soil physical quality by reducing the potential effects of soil erosion.

In addition, corn cob biochar increased soil microbial biomass, microbial community structure and diversity, and total phospholipid fatty of the soil used in this study. In perspective, adoption and incorporation of biochar to the highly weathered soils of Ghana may enhance ecosystem functions and efficiency. Lastly, the various C and N pools, and the quality of total organic carbon were enahnced in the biochar amended soils. Biochar application has the potential to enhance carbon sequestration in a tropical agro ecosystem. This approach promotes climate smart agriculture and therefore serves as a favorable agricultural sustainability model for value addition on crop residues. It also serves as a critical alternative strategy for improving waste management especially in Ghana.

8.3 Recommendation

Further research should be conducted to elucidate the long-term effect of corn cob biochar on water retention and gas transport parameters in highly weathered soils of in Ghana. It is recommended that periodic sampling should be done on the field where this research was conducted to investigate the distribution of carbon and nitrogen with depth in the biochar amended soils.

The usefulness of other feed stock types for the production of biochar should be thoroughly explored in a long-term field experiments to elucidate their potential impacts on soil physical, chemical and biological properties.

Also, different pyrolytic temperatures should be thoroughly investigated to determine which temperature works best for which feedstock type in order to maximise the potential impacts of biochar in the humid tropical soils.

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APPENDICES

APPENDIX A

STATISTICAL TABLES

Table 1: *Results of analysis of variance permutation test for redundancy analysis*

	df	Variance	F	Pr > F
Model	11	320.1	17.9	0.014
Residual	4	6.5		

Table 2: *Pearson's Correlation Coefficients between Soil Properties*

	BR	UEA	DEA	MBC	MBN	MBC: MBN	PMC	qR	qCO_2	EC	pH	TC	TN
BR	1	0.88**	0.94**	0.93**	0.89**	0.68*	0.78**	0.87**	-0.77**	-0.94**	0.92**	0.68**	0.79**
UEA		1	0.9**	0.93**	0.89**	0.68*	0.77**	0.85**	-0.68**	-0.84**	0.81**	0.65**	0.82**
DEA			1	0.89**	0.95**	0.49	0.71**	0.83**	-0.65**	-0.89**	0.85**	0.62*	0.75**
MBC				1	0.88**	0.76**	0.69**	0.95**	-0.81**	-0.93**	0.9**	0.66**	0.80**
MBN					1	0.4	0.66**	0.81**	-0.66**	--0.86**	0.82**	0.62**	0.68**
MBC:MBN						1	0.56*	0.77**	-0.82**	-0.74**	0.75**	0.55	0.60*
PMC							1	0.84**	-0.06*	-0.66**	0.64**	0.46	0.42
qR								1	-0.08**	-0.87**	0.64*	0.4	0.43
qCO_2									1	0.87**	-0.83**	-0.57	-0.57*
EC										1	-0.98**	-0.72**	-0.75**
pH											1	0.71**	0.72**
TC												1	0.74
TN													1

BR = Basal respiration, UEA = Urease enzyme activity, DEA = Dehydrogenase enzyme activity, MBC = Microbial biomass carbon, MBN = Microbial biomass nitrogen, PMC = Potentially mineralizable carbon, qR = respiratory quotient, qCO_2 = Specific maintenance respiration, EC = Electrical conductivity, TC = Total carbon, TN = Total nitrogen. Significant correlations are highlighted with asterisk $*p < 0.05$; $p** < 0.01$

Table 3: *Correlations coefficients of microbial properties and soil environmental factors*

Biochemical parameters	Total PLFA	Gram$^-$	Gram$^+$	Total bacteria	Fungi	Bacteria:Fungi	Gram$^+$:Gram$^-$	Fungi:Bacteria
BR	0.91**	0.83**	0.81**	0.84**	0.97**	0.60*	0.57**	0.90**
UEA	0.93**	0.88**	0.91**	0.89**	0.91**	0.60*	0.72**	0.74**
DEA	0.93**	0.83**	0.87**	0.86**	0.97**	0.62*	0.69*	0.87**
MBC	0.89**	0.82**	0.82**	0.82**	0.93**	0.60*	0.63*	0.86**
MBN	0.90**	0.81**	0.86**	0.83**	0.94**	0.53*	0.73**	0.84**
MBC:MBN	0.57*	0.55*	0.47	0.53*	0.60*	0.52*	0.24	0.61*
PMC	0.67**	0.63*	0.61*	0.63*	0.68**	0.26	0.42	0.59*
qR	0.83**	0.79**	0.77**	0.78**	0.85**	0.53*	0.56*	0.77**
qCO_2	-0.73**	-0.70**	-0.65*	-0.68*	-0.77**	-0.51*	-0.44	-0.75**
EC	-0.89**	-0.81**	-0.79**	-0.82**	-0.95**	-0.67*	-0.58*	-0.91**
pH	0.86**	0.80**	0.75**	0.79**	0.91**	0.75**	0.49	0.88**
TC	0.66*	0.59*	0.58*	0.60*	0.72**	0.63*	0.41	0.71**
TN	0.80**	0.800*	0.74**	0.76**	0.78**	0.55*	0.47	0.65*

BR = Basal respiration, UEA = Urease enzyme activity, DEA = Dehydrogenase enzyme activity, MBC = Microbial biomass carbon, MBN = Microbial biomass nitrogen, PMC = Potentially mineralizable carbon, qR = respiratory quotient, qCO2 = Specific maintenance respiration, EC = Electrical conductivity, TC = Total carbon, TN = Total nitrogen. Significant correlations are highlighted with asterisk *$p < 0.05$; $p^{**} < 0.01$

Table 4: *Results of ANOVA Permutation Test for RDA*

	df	Variance	F	Pr > F
Model	12	485.48	51037576	0.001
Residual	3	0.000		

Table 5: *Results of ANOVA Permutation Test for RDA*

	df	Variance	F	Pr > F
Model	11	366.13	1.667e+31	0.001
Residual	4	0.001		

Table 6: *Results of ANOVA Permutation Test for RDA*

	df	Variance	F	Pr > F
Model	6	313.62	2.4126e+31	0.001
Residual	9	0.001		

APPENDIX B:

PUBLISHED PAPERS

Paper 1.

E. Amoakwah, K.A. Frimpong, D. Okae-Anti, E. Arthur. Soil water retention, air flow and pore structure characteristics after corn cob biochar application to a tropical sandy loam. Geoderma 307 (2017) 189-197. http://dx.doi.org/10.1016/j.geoderma.2017.08.025

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Soil water retention, air flow and pore structure characteristics after corn cob biochar application to a tropical sandy loam

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ABSTRACT

Soil structure is a key soil physical property that affects soil water balance, gas transport, plant growth and development, and ultimately plant yield. Biochar has received global recognition as a soil amendment with the potential to ameliorate the structure of degraded soils. We investigated how corn cob biochar contributed to changes in soil water retention, air flow by convection and diffusion, and derived soil structure indices in a tropical sandy loam. Intact soil cores were taken from a field experiment that had plots without biochar (CT), and plots each with 10 t ha^{-1} (BC-10), 20 t ha^{-1} without or with phosphate fertilizer (BC-20 and BC-20 + P respectively). Soil water retention was measured within a pF range of 1 to 6.8. Gas transport parameters (air permeability, k_a, and relative gas diffusivity, D_p/D_0) were measured between pF 1.5 and 3.0. Application of 20 t ha^{-1} led to significant increase in soil water retention compared to the CT and BC-10 as a result of increased microporosity (pores < 3 μm) whereas for soil specific surface area, biochar had minimal impact. No significant influence of biochar was observed for k_a and D_p/D_0 for the BC treatments compared to the CT despite the larger values for the two properties in the 20 t ha^{-1} treatments. Although not significant, the diffusion percolation threshold reduced by 34% and 18% in the BC-20 and BC-20 + P treatments, respectively, compared to the CT. Similarly, biochar application reduced the convection percolation threshold by 15 to 85% in the BC-amended soils. The moderate impact of corn cob biochar on soil water retention, and minimal improvements in convective and diffusive gas transport provides an avenue for an environmentally friendly disposal of crop residues, particularly for corn cobs, and structural improvement in tropical sandy loams.

1. Introduction

Soil structural stability, which is defined as the spatial heterogeneity of the different components or characteristics of soil (Dexter, 1988), has enormous effects on plant growth and development, through its effects on soil water balance, and soil workability. Soil structure is a key soil quality factor that can influence crop productivity as it affects storage and movement of soil water, nutrients, and gases within the soil matrix. For instance, soil structure determines the characteristics of water movement in the soil ecosystem, and can thus influence the dissolution and availability of nutrients to growing plants. For agriculture purposes, a healthy soil structure is viewed as that which shows a combination of well-developed soil aggregates and pore systems (Bronick and Lal, 2005), enhancing the exchange of gases between soil and atmosphere. Soil structure also determines the ability of soils to carry out essential ecosystem functions and services such as turnover of organic matter, provision of optimal conditions for microbial activity, and C sequestration (Gregory et al., 2007; Lal and Shukla, 2004). Soil pores occurring within (intra) soil aggregates and between (inter) aggregates serve as pathways for soil water and air movement. The movement of water and gas in the soil profile is influenced not only by the amount of pores and their sizes but also by the pore connectivity and tortuosity (Osozawa, 1998), which is to a large extent related to the geometric characteristics of soil pore structure. Soils with low oxygen diffusivity (below a threshold value of 0.02) restrict root development (Deepagoda et al., 2011), which results in stunted growth and poor yield in crops. The interaction between soil self-organizing processes such as renewal of soil gases and solution by exchange with the environment (Targulian and Krasilnikov, 2007) and management strategies such as incorporation of organic amendments determines the extent of pore structure development (Sun et al., 2013).

Several authors have reported improvements in plant yield following biochar application (Biederman and Harpole, 2013; Blackwell et al., 2009; Jeffery et al., 2014). The improved crop yields found in biochar amended soils is partly attributed to positive improvement in soil physical and hydraulic parameters, such as decreased soil

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penetration resistance, and bulk density (Busscher et al., 2011) and increased water-holding capacity (Kinney et al., 2012). Also, biochar has high porosity and specific surface area, which can affect the total pore space and gas transport at the soil-atmosphere interface and within the soil ecosystem (Sun et al., 2013). In a study conducted by Obia et al. (2016), application of corn cob biochar at rates of 0.8 to 2.5 w/w% to a tropical sandy soil increased total porosity and available water capacity by 2 to 3% respectively. Studies by Sun et al. (2013) showed that birch wood biochar improved soil pore structure indices such as pore tortuosity and pore organization by enhancing convective gas transport and increasing the ratio of macroporosity to total porosity. Comparatively, biochar has a lighter density than mineral soil, and this property of biochar has been reported by Sun et al. (2015) to significantly increase the total pore spaces of soil. Abel et al. (2013) reported increased total pore volume in the soil medium following the incorporation of 1–5 wt% biochar produced from maize feedstock (mixture of whole plant). Although several studies report beneficial effects of biochar application, detrimental effects may also occur. Most biochars have high pH, with the potential to increase soil pH, and this can potentially increase clay dispersibility due to a dominance of repulsive forces between clay minerals (Roth and Pavan, 1991), and in turn result in decreased aggregation and disruption of soil structure. Kumari et al. (2017) found increased content of water dispersible colloids (WDC) following application of birch wood biochar; an observation they attributed to increased soil pH and decreased electrical conductivity in the biochar-treated soils. Busscher et al. (2010) reported a significant decrease in soil aggregation when biochar produced from pecan shells was applied, whereas Fungo et al. (2017) reported absence of an effect of biochar on soil aggregate stability following application of 2.5 t ha^{-1} eucalyptus wood biochar pyrolyzed at 550 °C to a Typic Kandiudult. Similarly, rice-straw biochar, when applied to an Ultisol, had no effect on soil structural stability (Peng et al., 2011). Undoubtedly, the above enumerated findings on biochar effects on soil aggregate stability are contrasting, thus emphasizing the need to quantify distinct soil and biochar properties for every situation (Khademalrasoul et al., 2014).

Previous studies have reported the effect of biochar application on the volume and architecture of soil pores, however, the mechanisms underlying these changes are yet to be fully understood (Atkinson et al., 2010; Lehmann et al., 2009). Further, for soils of the humid tropics, research on the effects of biochar on gas transport parameters and soil water retention characteristics is relatively limited (Mukherjee and Lal, 2013). Therefore, the objectives of the study were to examine the mechanisms underlying the effect of corn cob biochar on soil water retention, air flow by convection and diffusion, and derived soil structure indices under a series of controlled matric potentials.

2. Materials and methods

2.1. Study area and soil characteristics

The research was conducted at the University of Cape Coast Teaching and Research farm located in the coastal savanna agro ecological zone of Ghana (5°07′N, 1°17′W). The area has two seasons; a rainy season where most rainfall events are recorded between April and October, with June being the wettest month (average rainfall of 327 mm), and a dry season where a long dry spell is recorded between November and March, with March being the hottest month (with a maximum temperature of 31 °C). The area is generally characterized by high rainfall (1400 mm per annum) with mean monthly temperatures ranging from 24 °C to 28 °C. The soil is well-drained sandy loam (18, 9 and 73% by weight of clay silt and sand, respectively) developed on sandstones, shales and conglomerates and classified as a *Haplic Acrisol* (IUSS Working Group WRB, 2015). The chemical properties of the soil in the study area prior to biochar application include the following: 0.93% soil organic carbon, 0.073% total nitrogen, total phosphorus, potassium and magnesium contents were < 0.4, 11.9 and 9.3 mg 100 g^{-1}, respectively, soil pH of 6.1 and an electrical conductivity of 200 μS cm^{-1}.

2.2. Field experimentation and sampling

2.2.1. Biochar properties

The biochar was produced from corn cob feedstock pyrolyzed in a reactor (Lucia stove) with a temperature of 500–550 °C. The biochar produced was sieved to a < 2 mm particle size to obtain a relatively high surface area to improve its reactivity in the soil. The biochar had 85.3% dry matter, 38.8% total carbon, 0.9% total nitrogen, pH of 10.2, 3.31 mg kg^{-1} polycyclic aromatic hydrocarbons, 3150 mg kg^{-1} phosphorus, with Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} of 8690, 4510, 31,800 and 2160 mg kg^{-1}, respectively (Amoakwah et al., 2017).

2.2.2. Field layout

The study adopted the randomized complete block design with thirty-two (32) plots (four treatments with eight replications for each treatment), with each plot measuring 3 m × 6 m (18 m^2). In order to achieve fine tilth, the field was ploughed and harrowed twice, followed by the removal of stubble and weeds. The plots were raised to 15 cm above the natural soil surface to enhance drainage and accommodate access pathways (0.6 m) between plots. Three levels of biochar were used in this study; 10 t ha^{-1} and 20 t ha^{-1}, and 20 t ha^{-1} with P (P-enriched biochar), corresponding to 0, 0.34 and 0.68% respectively. The P-enriched biochar was prepared by mixing 50 kg P_2O_5 ha^{-1} (Triple super phosphate) with 0.68% of biochar. This treatment was included to examine whether pre-treating biochar with P will minimize P fixation by aluminum (Al^{3+}) and hence promote P availability. Investigation into P fixation was not included here since it was not within the scope of this paper. Prior to biochar application, a subsample of the corn cob biochar stock was oven-dried to determine the prevailing water content.

On 7th November 2016, biochar (with and without P fertilizer) was applied by broadcasting on the soil surface of the treatment plots and incorporating it into the soil by plowing to a depth of about 20 cm. To maintain consistency in the treated and untreated plots, all the plots (control and treated) were tilled with a hoe after the biochar application. Hereon, the treatments are denoted by CT, BC-10, BC-20, and BC-20 + P for the 0, 10 t ha^{-1} and 20 t ha^{-1}, and 20 t ha^{-1} with P, respectively. Soil sampling was done on 21st May 2016.

2.3. Soil sampling

Metal core samplers (0.034 m length, 0.061 m in diameter, 100 cm^3 sample volume) were used for intact soil sampling from a depth of 0–20 cm. The sampling for all treatments was done in the center of the plot within rows, avoiding visibly compacted areas. Eight replicate samples were taken for each treatment. At the same locations, disturbed bulk samples were taken for other measurements (texture, organic matter, pH, dry region water retention, etc.)

2.4. Laboratory measurements

2.4.1. Soil texture and organic carbon content

Soil texture was determined by a combination of sieving and hydrometer methods (Gee and Or, 2002). Determination of soil total carbon content was done through the oxidation of carbon to CO_2 at a temperature of 1800 °C with a FLASH 2000 organic elemental analyzer, which was coupled to a thermal conductivity detector (Thermo Fisher Scientific, MA, USA). Since carbonates were absent in the soils, the soil total carbon was considered as soil organic carbon (SOC).

2.4.2. Soil pH and electrical conductivity

Soil pH was determined by mixing 8 ml of air dried soil and 30 ml of deionized water (which corresponds to a soil-water ratio of approximately 1:2.5). Soil pH and EC were subsequently measured by inserting a combined pH and electrical conductivity (EC) electrode into the supernatant (Thomas, 1996).

2.4.3. Soil water retention

2.4.3.1. Wet region measurements. Measurement of wet region water retention was performed in the laboratory at constant temperature of 20 °C. The 32 intact cores were placed in a sand box and saturated with water from underneath, drained and saturated again prior to imposition of suction levels. Suction was applied successively after saturation to establish matric potentials (ψ) of − 10, − 30, − 50, and − 100 cm H_2O (pF 1, 1.5, 1,7, and 2.0; (Schofield, 1935)). Thereafter, samples were moved to a Richard pressure plate apparatus to successively establish matric potentials of − 300, − 500, and − 1000 cm H_2O (corresponding to pF 2.5, 2.7, and 3.0 respectively) according to the methodology described by Dane and Hopmans (2002). At selected potentials, the same soil samples were used for gas transport measurements (described in air permeability and gas diffusion sections below).

2.4.3.2. Dry region measurements. The retention curve from pF 3.8 to 5.0 was obtained with a temperature compensated WP4-T dewpoint Potentiameter (METER Group Inc., Pullman, WA, USA). First, air-dry subsamples from replication plots were oven dried to determine the prevailing water content. Based on the prevailing water content, increasing amounts of water was added to each air-dry subsample to roughly correspond to matric potentials between pF 3.8 and 5.0. A total of eighty (20 from each treatment) subsamples were used for this. To avoid evaporation losses, the moistened soil samples were sealed in Ziploc bags and stored in the refrigerator for 4 weeks to allow equilibration. After the equilibration period, two consecutive soil water potential measurements were taken with the WP4-T. The samples were oven dried at a temperature of 105 °C for 24 h to determine the gravimetric water content.

For the water retention between pF 5.0 and 6.8, a Vapor Sorption Analyzer (METER Group Inc., Pullman, WA, USA) was used. Briefly, 3 g of an air-dry subsample was placed in the instrument and the matric potential and soil mass simultaneously measured. Measurements for each sample were done in duplicate and samples were oven dried afterwards to obtain the gravimetric water content. For further details on the measurement procedure, please consult Arthur et al. (2014) and Likos et al. (2011).

Specific surface area (SA) was estimated from the measured water retention between pF 5.0 and 6.8 using the theoretical Guggenheim-Andersen-de Boer sorption isotherm equation as suggested by Timmermann (2003) and evaluated by Arthur et al. (2017). After obtaining the monolayer water content (M_0, kg kg^{-1}) from the GAB modeling of the dry region water retention data, the SA was obtained by the following relation, $SA = M_0NA/w_M$, where N is Avogadro's number (6.02×10^{23} mol^{-1}), A is the area covered by one water molecule (10.8×10^{-20} m^2) and w_M is the molecular weight of water (0.018 kg mol^{-1}).

2.4.4. Air permeability

Air permeability, k_a, was measured by the Forchheimer approach described by Schjønning and Koppelgaard (2017) on cores that were equilibrated at matric potentials of − 30, − 50, − 100, − 300, − 500 and − 1000 cm H_2O. Briefly, four corresponding values of pressure difference, ΔP at values around 5, 2, 1 and 0.5 hPa, were applied across the soil sample placed in an air permeameter, and the resulting air flow, Q was measured. For the purpose of quality control, a 'standard' test (with actual pressure difference, P_a < 400 Pa, at target air flow, Q_t = 3 ml min^{-1}) was performed prior to soil samples measurement, in two series of steps. First, the system identifies corresponding actual air flow, Q_a, and P_a values, where P_a is requested to be within ± 10% of the target pressure difference, P_t = 5 hPa. Second, the system finds corresponding values of Q_a and P_a for three additional levels of ΔP = ~2, ~1, and ~0.5 hPa. By measuring at the highest pressure difference of 5 hPa prior to measuring the lower values, the risk that changes in ΔP during a measurement loop will affect water films was curtailed (Schjønning and Koppelgaard, 2017). Darcy's law was then used to calculate k_a in a steady state.

2.4.5. Gas diffusion

The experimental setup that was initially suggested by Taylor (1950) and subsequently improved further by Schjønning (1985) was used for the measurement of gas diffusion (D_p/D_0). Firstly, the gas diffusivity chamber was made oxygen-free by flushing with 100% N_2 gas. The top of the soil core was exposed to the atmosphere to allow atmospheric air to enter into the chamber through the soil sample. Subsequently, O_2 was measured by an electrode mounted on the chamber wall. The O_2 diffusion coefficient in soil (D_p) was calculated as proposed by Rolston and Moldrup (2002). The gas diffusion measurement was done on soil cores already equilibrated at matric potentials (ψ) of − 30, − 50 and − 100, − 300 cm, − 500 and − 1000 cm H_2O. There was a disparity in the time taken for each measurement due to differences in the applied matric potentials, and this difference in the measuring time was considered small enough to neglect the O_2 depletion resulting from microbial consumption (Schjønning et al., 1999).

2.4.6. Bulk density, porosity, and plant available water

After completing the wet region water retention, air permeability and gas diffusion measurements, the samples were oven-dried at 105 °C for 24 h. The weight of each sample was subsequently recorded at each matric potential and after oven drying. The total soil porosity was estimated from the measured bulk density (ρ_b) and a particle density of 2.65 Mg m^{-3}. The volumetric soil water content (θ, m^3 m^{-3}) at each matric potential was taken as the respective difference in weight of the oven-dried samples multiplied by the bulk density (ρ_b). At each matric potential, air-filled porosity (ε, m^3 m^{-3}) was calculated as the difference between the total porosity and volumetric water content (θ, m^3 m^{-3}). The plant available water content (θp, m^3 m^{-3}) was calculated as the difference between the water content at pF 2.5 and pF 4.2.

2.5. Models

The pore size distributions of the soils were derived from the wet region water retention data based on the capillary rise equation by approximating the relationship between Ψ and the equivalent pore diameter (d, μm) (Schjønning, 1992):

$$d = \frac{3000}{\Psi} \quad (1)$$

Pore structure (continuity, complexity, and distribution) was estimated using models based on either gas diffusivity (D_p/D_0) or air permeability (k_a) and (air-filled porosity (ε). The logarithmic form of the exponential model proposed by Marshall (1959) and Millington (1959) was used to relate D_p/D_0 and ε:

$$\log\left(\frac{D_p}{D_o}\right) = \log(m_d) + N_d \log(\varepsilon) \quad (2)$$

where m_d and N_d are fitted parameters. Because of the fact that D_p/D_0 value of 10^{-4} is considered as an indication of zero diffusion through a continuous air-filled pore space (Broecker and Peng, 1974), the ε at that point is considered to be the diffusion percolation threshold, (D_{PT}, m^3 m^{-3})

$$D_{PT} = 10^{-[\log(m_d)+4]/N_d} \quad (3)$$

or an estimate of the volume of pores blocked to exchange of air as reported in previous studies (Schjønning et al., 2002).

Similarly, k_a was related to ε by the logarithmic form of a simple exponential model proposed by Ball et al. (1988):

$$\log(k_a) = \log(m_c) + N_c \log(\varepsilon) \tag{4}$$

where m_c and N_c are fitted model parameters representing soil structural complexity. An estimate of the permeability percolation threshold (C_{PT}, $m^3\ m^{-3}$) was obtained by assuming that a soil with k_a of 1.0 μm^2 is effectively impermeable (Ball et al., 1988).

The applicability of C_{PT} in relation to D_{PT} was assessed for treated and untreated soils. The optimal value of k_a for each of the four soil groups based on the treatments (CT, BC-10, BC-20, and BC-20 + P) was estimated using the relation

$$C_{PT} = 10^{-[\log(m_c)+x]/N_c} \tag{5}$$

where x is the log (k_a) value at which C_{PT} best fit the physically based D_{PT}.

To further assess the differences in pore connectivity and tortuosity after biochar incorporation, the soil pore organization (PO, μm^2) which gives an indication of the pore size distribution was considered for two matric potentials (-100 and -300 cm H_2O) (Groenevelt et al., 1984)

$$PO = \frac{k_a}{\varepsilon} \tag{6}$$

2.6. Data analysis and statistics

Statistical analyses were done using SigmaPlot 11 (Systat Software Inc., San Jose). All the data obtained were checked for normality and homogeneity of variance. Differences between the control and biochar treatments were tested using analyses of variance (ANOVA), after which the Holm-Sidak post-hoc test was used to differentiate between any two given treatments. We used $p < 0.05$ as a criterion for statistical significance of treatment effects, unless otherwise stated. Results are presented as mean ± standard error (SE) in tables and figures.

3. Results

3.1. Soil texture and organic carbon

The particle size distribution and soil organic carbon contents of the treatment plots are presented in Table 1. There was minimal variability within the treatments in terms of soil texture; standard errors for texture ranged from 0.8 to 1.8 for clay, 0.2 to 0.4 for silt, and 0.8 to 1.8 for the sand fraction (Table 1). Among the biochar treatments, only BC-20 treated soils recorded a significant increase of 66% in soil organic carbon (SOC) relative to the CT. The SOC in the BC-10 and BC-20 + P treated soils were statistically similar (Table 1).

3.2. Soil pH and electrical conductivity (EC)

Application of corn cob biochar significantly increased the soil pH by 0.6 and 0.4 units for the BC-20 and BC-20 + P amended soils respectively, relative to the CT. Conversely, incorporation of biochar significantly decrease the EC by 75%, 80% and 79% in the BC-10, BC-20 and BC-20 + P amended plots respectively, compared to the control.

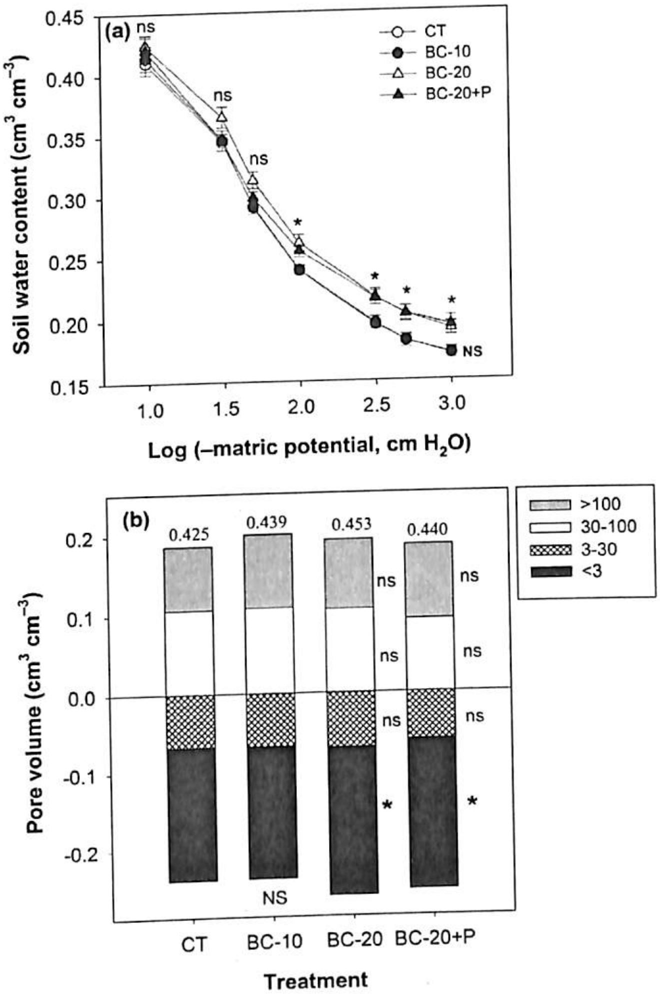

Fig. 1. Corn cob biochar effect on (a) soil water retention and (b) pore size distribution. "NS" indicates no significant difference between BC-10 and CT. Values on top of bars are total pore volumes. "*" indicates significant difference between the water content or pore size class of the BC-20 and BC-20 + P treatment compared to the CT. "ns" indicates no significant difference between the water content or pore size class of the BC treatment and the control. CT, control; BC-10, 20, and 20 + P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 t ha^{-1}, respectively.

3.3. Soil bulk density, water retention and specific surface area

Statistically, the bulk density and total porosity in the biochar treated soils were similar to that of the CT (Table 1). The soil water contents found in the various treatments at the different matric potentials are shown in Fig. 1a. There was no significant difference between the biochar treatments and CT when matric potential was ≤ pF 1.5. Between pF 2.0 and 3.0, the BC-20 and BC-20 + P treatments had significantly higher water contents than the BC-10 and CT (Fig. 1a).

Table 1
Effect of corn cob biochar on soil texture, chemical and physical properties.

Treatment	Clay	Silt	Sand	OC	pH	EC	ρ_b	Φ	θ_p
	% by weight				(–)	$\mu S\ cm^{-1}$	$Mg\ m^{-3}$	$m^3\ m^{-3}$	
CT	19 ± 1.8^a	8 ± 0.4^a	73 ± 1.8^a	1.03 ± 0.08^a	5.9 ± 0.1^{bc}	309 ± 46^a	1.52 ± 0.01^a	0.43 ± 0.01^a	0.09 ± 0.01^a
BC-10	18 ± 0.9^a	9 ± 0.3^a	73 ± 1.1^a	1.39 ± 0.18^{ab}	6.2 ± 0.2^{ac}	76 ± 4^b	1.49 ± 0.02^a	0.44 ± 0.02^a	0.10 ± 0.01^a
BC-20	18 ± 0.8^a	8 ± 0.2^a	74 ± 0.8^a	1.71 ± 0.12^b	6.5 ± 0.2^a	61 ± 8^b	1.45 ± 0.03^a	0.45 ± 0.03^a	0.12 ± 0.01^a
BC-20 + P	19 ± 1.6^a	9 ± 0.3^a	72 ± 1.9^a	1.32 ± 0.09^{ab}	6.3 ± 0.1^a	66 ± 8^b	1.49 ± 0.03^a	0.44 ± 0.03^a	0.12 ± 0.01^a

§OC, organic carbon; EC, electrical conductivity, ρ_b, bulk density; Φ, total porosity, θ_p, plant available water content. Different letters indicate that means are significantly different ($p < 0.05$).

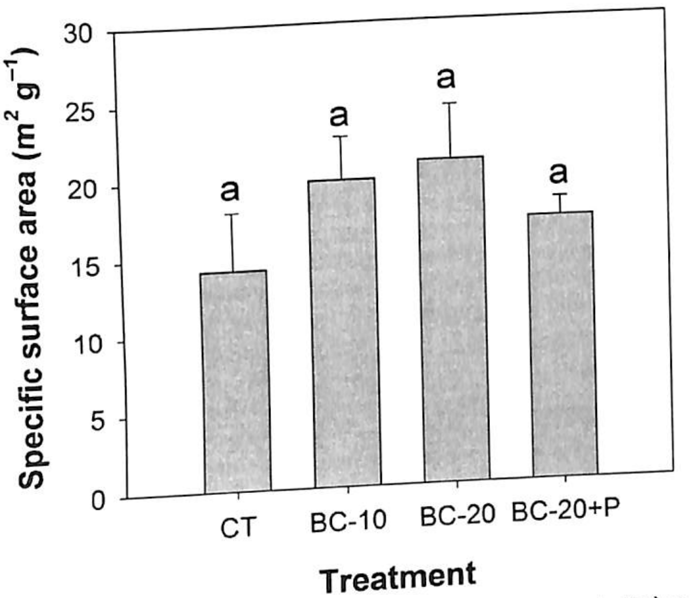

Fig. 2. The soil specific surface area (derived from dry-region soil water retention) as affected by biochar. CT, control; BC-10, 20, and 20 + P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 t ha^{-1}, respectively.

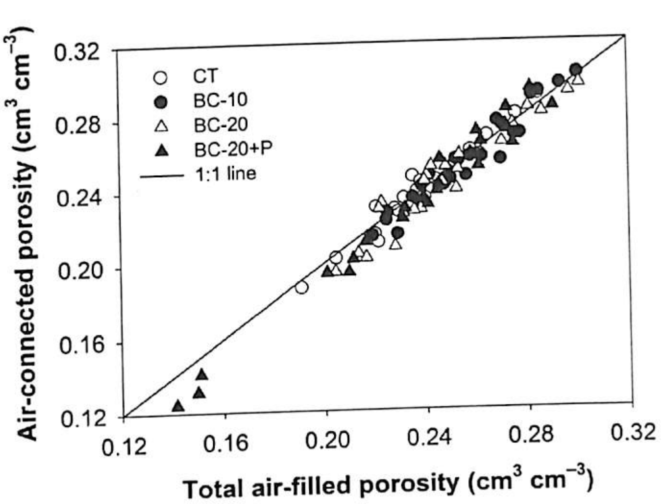

Fig. 3. Relationship between total air-filled porosity (calculated from soil-water retention data) and air-connected porosity measured by a pycnometer. CT, control; BC-10, 20, and 20 + P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 t ha^{-1}, respectively.

Consequently, the biochar treatments showed similar macro- and meso-porosity (pores larger than 30 μm) as the CT (Fig. 1b). Conversely, the BC-20 and BC-20 + P had significantly larger proportions of micropores (pores < 3 μm) than the CT. The BC-10 had a similar trend for both the water retention curve and the pore size fractions compared to the CT. Application of biochar had little impact on the plant available water content (Table 1). Similarly, biochar application did not have any significant effect on the soil specific surface areas (SA) (Fig. 2).

3.4. *Air filled porosity and gas transport*

Corn cob biochar application had no effect on the relationship between the total air filled porosity (the difference between the total porosity and water content) and the air connected porosity (the pores that are connected in the soil matrix to the atmospheric air). The results showed that all the treatments (CT, BC-10, BC-20 and BC-20 + P) were clustered around the 1:1 line (Fig. 3). The soil's ability to conduct air by diffusion expressed by relative gas diffusivity as a function of matric potential is shown in Fig. 4a. Relative gas diffusivity increased with increasing air filled porosity (decreasing matric potential) for all treatments (Fig. 4). No significant differences were observed between relative gas diffusivity values of the biochar treatments, nor between the biochar treatments and the CT, irrespective of the total porosity of the various treatments (Fig. 4). Soil air permeability increased with decreasing matric potential in all the treatments (Fig. 5a). Though not significant, the BC treatments tended to have larger air permeability values than the CT at matric potentials between 1.5 and 2.0. The $\log_{10}$ of air permeability as a function of $\log_{10}$ air-filled porosity for all treatments is presented in Fig. 5b. For all the treatments, air permeability increased with increasing air-filled porosity. At low air-filled porosities, there was a tendency for larger permeability values for the BC-20 treatments compared to the CT and BC-10 treatments.

3.5. *Soil structural indicators*

Amendment of the soils with biochar showed no clear trend in soil pore organization (PO) with application rate. For BC-10 and BC-20, PO_{pF2} was about two times that of CT whereas BC-20 + P was identical to the CT. At pF3, PO was numerically similar among all treatments. Similarly, other indicators of soil structural complexity (N_c and N_d) were not affected significantly by the application of corn cob biochar. Further, biochar incorporation did not have any significant effect on the fraction of the air-filled pores that are inactive in diffusion (denoted by D_{PT}), though there was a reduction of 34% and 18% in D_{PT} in the soils that received the highest biochar application rates (BC-20 and BC-20 + P, respectively) relative to the CT (Table 2). There was an increase of 25% in D_{PT} in the biochar treatment (BC-10) as compared to the CT, even though this increase was not statistically different from the CT soil. Furthermore, corn cob biochar application did not have a significant effect on the convection percolation threshold (C_{PT}). Irrespective of the reduction in C_{PT} by 15%, 85% and 54% in the BC-10, BC-20 and BC-20 + P respectively, as compared to the CT, there was no significant difference in C_{PT} between the biochar treatments and the CT.

4. Discussion

4.1. *Biochar and soil water retention*

4.1.1. *Soil density and porosity*

Soil bulk density which is considered to be the main driving force of soil physical properties depicts the potential function of the soil with regards to soil aeration, water infiltration, structural support and water and gaseous movement. Results from the study showed that, application of biochar did not change the soil bulk density and total porosity. Previous authors have reported substantial decrease in soil bulk density after the incorporation of different kinds of biochar to different soil types. For example, Arthur and Ahmed (2017) applied 3% w/w of rice straw biochar to a coarse-textured tropical soil and reported a significant (32%) decrease in bulk density, three months after the incorporation of rice straw biochar. This was translated into a 22% and 16% increase in total porosity after 3 months and 15 months of biochar application respectively. Further, in an incubation experiment that lasted for 120 days, Randolph et al. (2017) recorded a significant decrease in bulk density following the application of wood chips and plant residues biochar pyrolyzed at three different pyrolytic temperatures (350 °C, 500 °C and 700 °C) and at an application rate of 2% w/w to sandy clay loam soils. Sun et al. (2015) affirmed that the porous nature and lower density of biochar compared to mineral soil, was responsible for the potential decrease in soil bulk density when they added birch wood biochar pyrolyzed at 500 °C to a sandy loam at application rates of 10 and 50 Mg ha^{-1}. The lack of significant increases in bulk density in our study could be attributed to the low rate of biochar application (a

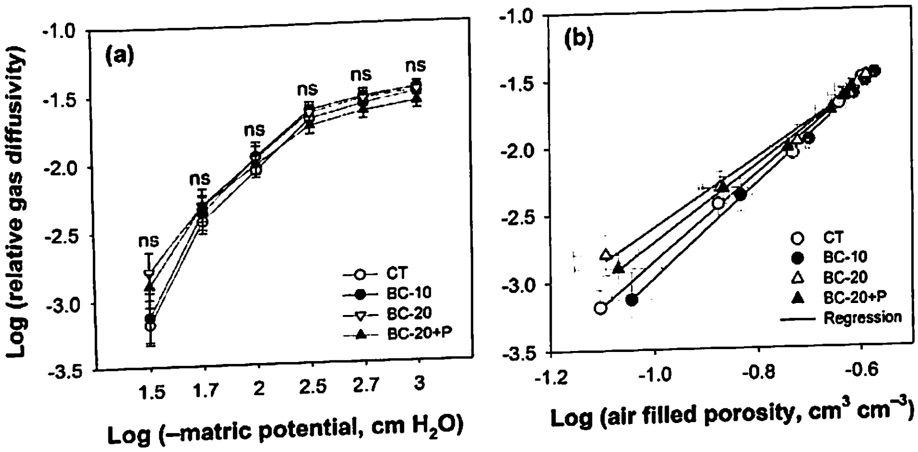

Fig. 4. Relative gas diffusivity (log-scale) as a function of (a) matric potential (in pF units) and (b) total air-filled porosity. "*ns*" indicates no significant difference between treatments for a given matric potential. CT, control; BC-10, 20, and 20 + P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 t ha^{-1}, respectively.

maximum of 0.68%) to our soil. The added biochar may not have been enough to substantially dilute the mineral fraction of the soil.

4.1.2. Water retention and pore size distribution

Crop growth, microbial activities and gas exchange dynamics are important processes that are significantly influenced by the ability of the soil to retain water. For the sandy loam in this study, corn cob biochar application at 20 t ha^{-1} showed significant increase in soil water contents at lower matric potentials (pF 2.0–3.0), but at an application rate of 10 t ha^{-1}, no noticeable effect of biochar on soil water retention occurred, possibly due to the low application rate. Precluding all instances of biochar hydrophobicity, an increase in water retained in the soil at a given matric potential after the application of biochar is one of the easily recognizable beneficial effects of biochar. For instance, Randolph et al. (2017) noted a significant increase in water retention after the incorporation of woodchips and plant residues biochars at a rate of 2% w/w to a sandy clay loam. Similarly, Ulyett et al. (2014) reported a significant increase in water retention at a matric potential of − 5 kPa when a deciduous mixed wood biochar pyrolyzed at 600 °C was added to a sandy loam at a rate of 60 t ha^{-1}. The authors ascribed the increase in soil water retention to the intrinsic high surface area of the biochar. A similar observation was made by Głąb et al. (2016) when they applied straw biochar produced at a pyrolytic temperature of 300 °C from miscanthus (*Miscanthus giganteus*) and winter wheat (*Triticum aestivum* L.) at application rates of 0.5%, 1%, 2%, and 4% to a loamy sand. In addition, Karhu et al. (2011) recorded an increase in gravimetric soil water content determined following the incorporation of birch wood biochar pyrolyzed at temperature of 400 °C at an application rate of 9 t ha^{-1} to a silty loam. The authors attributed this increase in water retention to increase in total porosity which led to a corresponding increase in water retention in small pores, and thus increasing the water retention of the soil. The use of pore size distribution to infer soil structure changes induced by different phenomena is becoming common in soil science (Dal Ferro et al., 2014). Different sizes of pores present in the soil medium present distinct and well defined functions in the soil. According to Pires et al. (2017), pores with size (equivalent cylindrical diameter (ECD)) > 50 μm are classified as transmission pores and < 0.50 μm as residual and bonding pores. The transmission pores are responsible for air movement and drainage of excess water, whereas the residual pores are responsible for the retention and diffusion of ions in soil solutions. Lal and Shukla (2004), classified pores with ECD between 0.50 μm and 50 μm as intermediate pores, that are responsible for the release and retention of water against gravity. Biochar at all rates did not produce any significant changes in three of the four pore size fractions considered (3 to < 100 μm) of the sandy loam soils. However, BC-20 and BC-20 + P significantly increased the very fine pores (< 3 μm) compared to the CT. This is important particularly for storage of water for plant uptake. Although plant

Table 2
Biochar effects on soil pore organization (PO) at pF 2 and pF 3, on slopes of log–log plots of relative gas diffusivity and air permeability vs. air-filled porosity (N_d and N_c, respectively) and on the estimates of the diffusion percolation threshold (D_{PT}, m^3 m^{-3}), permeability percolation threshold (C_{PT}, m^3 m^{-3}).

Treatment	PO_{pF2}	PO_{pF3}	N_d	N_c	D_{PT}	C_{PT}
CT	48^{ns}	166^{ns}	3.24^{ns}	3.40^{ns}	0.044^{ns}	0.054^{ns}
BC-10	74	169	3.49	3.17	0.051	0.046
BC-20	88	145	2.58	1.51	0.029	0.008
BC-20 + P	48	144	2.87	2.25	0.036	0.024

"ns" denotes no significant difference among the treatments.

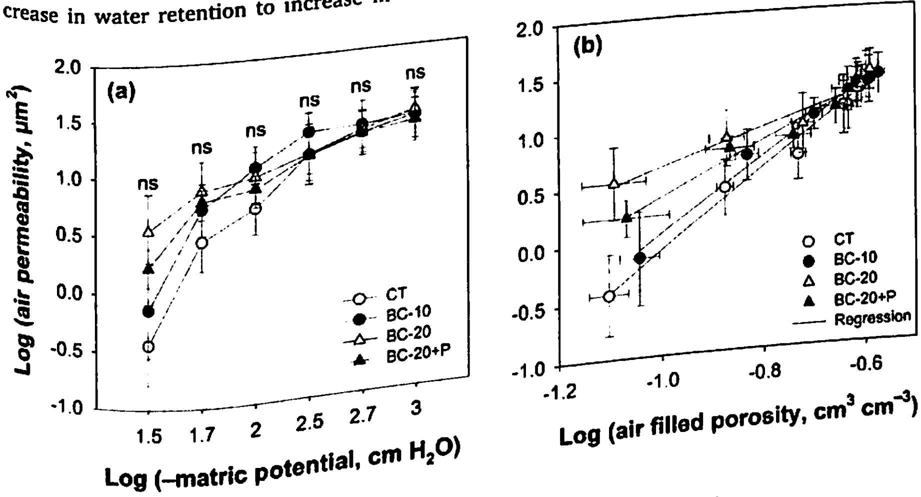

Fig. 5. Soil air permeability (log-scale) as a function of (a) matric potential (in pF units) and (b) total air-filled porosity. "*ns*" indicates no significant difference between treatments for a given matric potential. CT, control; BC-10, 20, and 20 + P denote biochar treatments with 10, 20 t ha^{-1}, and 20 t ha^{-1} + 50 kg P_2O_5 t ha^{-1}, respectively.

available water content (θ_p) was not significantly affected by biochar application, there was a trend of increasing θ_p with increasing biochar rates. For some plants, this marginal increase is particularly important during critical growth periods. Earlier studies that reported significant increases in θ_p were due to an increase in the fraction of smaller pores (0.1–10 μm) and a decrease in the larger pore size fraction. For example, Liu et al. (2016) observed increase in smaller pores (0.1–10 μm) relative to the larger pores (10–1000 μm) when they applied 16 t ha^{-1} of commercial straw biochar pyrolyzed at 500 °C to a loamy soil. Abel et al. (2013) reported an increase in the smaller pore size fractions and a decrease in the larger fractions when they applied biochar pyrolyzed from maize (mix of whole plant) at a temperature of 750 °C and at rates of 1, 2.5 and 5 wt%. Głąb et al. (2016) also found an increased volume of small pores (< 50 μm in diameter) and a decreased volume of larger pores (50–500 μm) when they applied biochar pyrolyzed from miscanthus and winter wheat at 300 °C and at application rates of 0.5, 1, 2 and 4% to loamy sand. In our study, although the BC-20 and BC-20 + P treatments had an increased fraction of small pores, they also had numerically higher fraction of large pores, resulting in marginal effect on the θ_p.

4.1.3. Specific surface area

The soil specific surface area (SA), which was derived from dry-region water retention data (pF 5 to 6.8), is an important property that influences numerous physico-chemical soil properties, and it is determined by the amount of clay and organic matter present in the soil. One of the notable effects of biochar incorporation into soils is an increase in OC, and this has been reported by several authors (e.g., Zhang et al., 2017; Zhu et al., 2017). Results from the study showed that, addition of BC resulted in a significant increase in OC in the BC-20 and BC-20 + P soils. Despite this, there was no significant increase in the SA of the amended soils compared to the control soil possibly due to the relatively short period between the time of biochar application and soil sampling (197 days after biochar application). The SA of soils is controlled primarily by the amount of clay and clay mineralogy (Pennell, 2002) with minimal contribution from soil organic matter for soils with clay content greater than ~20%. As the soil used in the study had clay ~19%, the increases in OC may not be enough to contribute significantly to changes in SA. This explains the contrasting results found in Arthur and Ahmed (2017) where they applied rice straw biochar to a sand-textured soil (clay < 3%) and reported significantly increased SA in the biochar treatments compared to the control.

4.2. Biochar effect on soil air movement and structural complexity

4.2.1. Air movement by conduction and diffusion

Transport of gas in the soil is a very important factor that influences soil aeration and respiration by plant roots. Gas transport characteristics have the potential to affect soil physical quality and crop productivity. Therefore, the quantification of gas transport parameters is important in effective management of physically degraded soils. The ability of soil to conduct air through the pores can be quantified by relative gas diffusivity, D_p/D_o which is driven by concentration gradients, and air permeability, k_a which is driven by pressure gradients. Relative gas diffusivity and air permeability are crucial gas transport parameters that provide insight into gas exchange by diffusion and convection processes, respectively. According to Baral et al. (2016), these two parameters are indicators of soil function, and are important for greenhouse gas emissions. Relative gas diffusivity (D_p/D_0) increased non-linearly with an increase in pF for all the treatments (Fig. 4a). The observed increase in D_p/D_0 as pF increases is attributed to a directly proportional relationship between pF and air-filled porosity. This observation corroborates the findings of Arthur and Ahmed (2017) who reported a larger D_p/D_0 at − 10 kPa than − 3 kPa due to larger air filled porosity at − 10 kPa. Thus, an increase in air filled porosity resulted in a corresponding increase in D_p/D_0 (Fig. 4b). At higher pF values, diffusion of gases in the soil is higher; conversely, higher water contents at lower pF values limit oxygen diffusion (Schjønning et al., 2011).

The D_p/D_0 affects the availability of atmospheric O_2 for intrinsic soil microbes capable of degrading a variety of soil pollutants under aerobic conditions (Davis et al., 2009). The critical D_p/D_0 limits for adequate soil aeration has been reported to be within the range of 0.005–0.02 (Stepniewski, 1981). A study by Schjønning et al. (2006) concluded that the threshold value of D_p/D_0 for adequate diffusion of oxygen in the soil is 0.005. Albeit not significant, at pF 1.7, whereas the CT treatment was in the anaerobic range (D_p/D_0 < 0.005), the BC-treated soils had D_p/D_0 values ≥ 0.005. This suggests that, at relatively low pF values, as occurs in wet humid areas, biochar has the potential to facilitate gaseous exchange within the soil ecosystem to enhance soil microbial activity and root respiration. Among the biochar treated soils, BC-10 recorded the highest mean value of D_p/D_0 (0.035) at pF 3. This could be ascribed to the fact that, due to the comparatively high application rates (20 t ha^{-1}), and by virtue of the fact that the biochar were ground (to a particle size of < 2 mm), some of the biochar particles might have filled some of the air-filled pore spaces as the water content decreased. However, the magnitude of the purported infilling of the air-filled pore spaces by the ground biochar in BC-20 and BC-20 + P was not enough to counteract the ability of the soils to facilitate gaseous movement, as D_p/D_0 values of 0.033 and 0.028 (which are above the critical D_p/D_0 value for adequate aeration) were recorded in BC-20 and BC-20 + P respectively.

Air permeability (k_a) controls the movement of air through the soil via convective flow in response to a pressure gradient, and it is a soil physical property that is strongly related to the soil total porosity, pore size distribution, continuity and tortuosity; thus, k_a is sensitive to structural changes as it is directly related to soil structural characteristics. Air permeability increased with increasing pF among the BC treated soils and the CT (Fig. 5a). This is ascribed to the development of more connected pores as the soil dries out at higher pF values. Generally, an increasing trend in k_a was observed in the BC treated soils, particularly at pF < 2.5. This observation contradicts the findings of Arthur and Ahmed (2017) who reported a decrease in k_a 15 months after rice straw biochar application. The authors attributed their observation to an increase in water retention with a subsequent reduction in macropore fraction after the biochar application. A significant decrease in k_a was also reported by Wong et al. (2016), when they applied peanut shell biochar pyrolyzed at 500 °C to clayey soil at application rates of 5, 10 and 15%. The authors attributed this observation to a decreased soil inter-pores at a high biochar application, suggesting that k_a is mainly governed by inter-aggregate pores at low biochar content. The possible reason to our observation is that, the corn cob biochar applied did not significantly increase the water content to warrant the presence of blocked pores. Hence, there was a considerable fraction of the air-filled pores that were relatively active in conducting air in the soil matrix.

4.2.2. Pore structure and gas percolation thresholds

To elucidate the effect of corn cob biochar on soil structure, the soil pore organization (PO) was evaluated to compare the structural complexity between the biochar treated soils and the CT. The PO parameter gives an indication of the structural differences in differently managed soils (Chamindu Deepagoda et al., 2013), as smaller PO values are attributed to more tortuous pore structure (and thus more complex structure), implying an improved pore continuity than large PO values. From the study, PO was computed at two matric potentials (pF 2 and pF 3) at which D_p/D_0 and k_a were measured (Table 2). No significant difference was observed in soil PO between the biochar treated soils and the CT at both matric potentials. At pF 2, no distinct pattern could be seen in PO between the CT and the biochar treated soils. However, PO was lower in the BC-20 and BC-20 + P treatments at pF 3. Comparatively, soil PO computed at pF 2 was lower than that of pF 3. This is probably because at low pF, the length of convection pathway is high due to low pore continuity and an increase in apparent tortuosity.

The diffusion of gases in water has been reported by several authors to be slower than that in air by a factor of 10^4 (Moldrup et al., 2004; Thorbjorn et al., 2008). Based on this premise, Arthur et al. (2013) posited that a relative gas diffusivity value of 10^{-4} may be considered as a threshold for diffusion through connected air-filled pores. Any value below the threshold value implies that diffusion occurs in the water phase. Therefore, it can be inferred that the air-filled porosity at which the D_p/D_0 threshold occurs is the diffusion percolation threshold, denoted by D_{PT}, from Eq. (3). According to Arthur et al. (2013), the D_{PT} value expresses the fraction of air-filled pores that are not active in diffusion due to the fact that these pores are blocked by water or they are embedded in aggregates. Though not statistically significant, the soils treated with BC-20 and BC-20 + P recorded lower D_{PT} values relative to the CT (Table 2). This observation implies that, most of the pores in the BC-20 and BC-20 + P soil were actively involved in diffusive gas transport, giving a further indication that these biochar treated soils may have lower structural complexity than the CT. This assertion is further substantiated by the low PO values obtained at pF 3 for the BC-20 and BC-20 + P soils.

Similar to D_{PT} is the convection percolation threshold C_{PT}, which is suggested by Ball et al. (1988) to exist when air permeability (k_a) = 1.0 µm. On the average, D_{PT} was observed to be higher than C_{PT} in the biochar amended soils. This was not expected considering the diverse pore domains that dictate convective and diffusive gas flows. Comparatively, convective flow preferentially occurs in macropores that are well drained, whereas flow of gas by diffusion takes place in virtually all pores, giving it a higher probability of yielding a lower D_{PT} values than C_{PT}. Our findings contradict the observation made by Masís-Meléndez et al. (2015) who reported lower values in D_{PT} than C_{PT}. This observation from our study may be attributed to a relatively larger water content in the network of arterial pores that directly influence gas diffusion along the axes of the cores in the biochar amended soils, hence, the lower D_{PT} values observed in the BC treatments relative to the C_{PT} values. The relatively lower C_{PT} values observed in the BC treated soils may also be due to an increase in air-filled pore space (drained macropores) that led to a subsequent increase in the interconnected pathways for a convective gas transport in the BC amended soils.

5. Conclusions and recommendations

This study demonstrated that addition of 10 t ha^{-1} and 20 t ha^{-1} of corn cob biochar to a tropical sandy loam has moderate impacts on soil water retention, and no clear effect on air flow by convection and diffusion, and derived soil structure indices. Specifically:

- Larger water contents was observed for the 20 t ha^{-1} biochar treatments relative to the control treatment only for matric potentials larger than pF 2.0; due to an increase in fine pores in the biochar treatments (< 3 µm).
- Corn cob biochar application did not significantly affect the bulk density, total porosity, plant available water and specific surface area of the soil.
- Soil air permeability and gas diffusion as a function of air-filled porosity was not significantly affected by biochar application. Consequently, soil structure complexity was statistically similar for all treatments.

The observations mentioned above were made for corn cob biochar with relatively small application rates and short residence time (197 days) between application and soil sample collection; hence the lack of significant differences in the gas transport and pore structure characteristics. Further and/or complimentary studies with higher biochar application rates and possibly, with different types of biochar and soil types, and over a longer time period are recommended to elucidate general biochar effects on soil functions in tropical ecosystem.

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Paper 2.

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Corn Cob Biochar Improves Aggregate Characteristics of a Tropical Sandy Loam

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Most tropical soils are highly weathered and are vulnerable to soil erosion because of their poor aggregate characteristics. Soil aggregate characteristics are critical indicators of soil structural stability, and they have the propensity to influence soil physical behavior and functioning. In this study, we investigated the effect of corn cob biochar on the aggregate characteristics of a highly weathered tropical sandy loam. Biochar was incorporated at rates of 10 Mg ha^{-1} (BC-10), 20 Mg ha^{-1} (BC-20), and 20 Mg ha^{-1} + triple super phosphate (BC-20+P) and the stability, strength, and friability of soil aggregates evaluated. Biochar increased soil organic C (SOC) by 28 to 66% and decreased electrical conductivity (EC) relative to the untreated soil. The fraction of water-stable aggregates was significantly improved by 27 to 53% in biochar treatments compared with the control. Biochar decreased the tensile strength of the large aggregates (4–8 and 8–16 mm), but increased same in the smaller aggregates (1–2 mm) and consequently led to significant improvements in soil friability and workability in the BC-20 and BC-20+P treatments. In perspective, incorporation of biochar may offer the potential to arrest the rate of degradation in highly weathered tropical soils and salvage the decline in their physical quality by minimizing the effects of soil erosion.

Abbreviations: BC-10, biochar incorporated at a rate of 10 Mg ha^{-1}; BC-20, biochar incorporated at a rate of 20 Mg ha^{-1}; BC-20 +P, biochar incorporated at a rate of 20 Mg ha^{-1} + triple super phosphate; E_{sp}, specific rupture energy; EC, electrical conductivity; MWD, mean weight diameter; SOC, soil organic C; WDC, water dispersible clay; Y, aggregate tensile strength.

Core Ideas

- **Amount of water-stable aggregates increased after biochar amendment.**
- **Biochar decreased tensile strength of soil aggregates larger than 4 mm.**
- **Strength of smaller aggregates (<2 mm) increased after biochar application.**
- **Soil friability and workability increased with increasing biochar application rate.**

Soils of the humid tropics are often highly weathered and are typically characterized by low pH, low cation-exchange capacity, and low inherent soil fertility. The problem is further exacerbated by intensive and long-term cultivation, which results in soil degradation because of soil acidification, SOC depletion, and severe soil erosion (De Meyer et al., 2011). The decrease in SOC caused by long-term cultivation decreases the aggregate stability of the soil and increases its erosivity (Annabi et al., 2011). The benefits of applying organic amendments such as manure and compost to soils to enhance their organic matter contents and increase soil biological activities and nutrient supply to growing plants have been acknowledged worldwide. However, benefits derived from the application of such organic amendments to soils of the humid tropics are typically short-lived as a result of high rates of soil organic matter decomposition because of high temperatures and high amounts of rainfall (Ghosh et al., 2015). There is therefore, the need to apply other soil organic amendments that are more stable in the soil in an environmentally sound and cost-effective manner to enhance soil quality and increase crop yields.

In this regard, biochar application for agricultural purposes is gaining considerable attention globally. Biochar is a carbon-rich byproduct obtained from pyrolysis, that is, incomplete thermal decomposition of organic materials under low or no oxygen conditions at relatively low temperatures (<700°C; Castellini et al., 2015).

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Several authors have reported beneficial effects derived from the application of biochar to soils including improved physicochemical properties of soil, enhanced SOC levels, increased fertilizer-use efficiency, and increased crop production, particularly in long-term cultivated soils in subtropical and tropical regions (Ghosh et al., 2015; Bass et al., 2016; Gamage et al., 2016). The impact of biochar on soil aggregate properties such as fraction of water-stable aggregates, clay dispersibility, and aggregate tensile strength relative to soil management in humid tropics cannot be over emphasized. However, few studies have reported the effects of biochar on aggregate strength and mechanical properties of tropical soils that are crucial for tillage (seed bed preparation) and plant growth.

Cosentino et al. (2006) defined soil aggregate stability as the ability of soil aggregates to resist disruption when external forces are applied and Calero et al. (2008) defined clay dispersibility as the amount of clay that can be dispersed by water. High clay dispersibility reduces soil aggregation, thereby increasing soil erodibility. Ouyang et al. (2013) argued that soil organic matter within aggregates with a higher stability does not easily decompose and hence water-stable aggregates promote long-term C sequestration and soil structural stability. Biochar application to soils increases the water-stable aggregates and decreases the turbidity and the release of small-sized soil particles (Liu et al., 2012; Soinne et al., 2014). According to Khademalrasoul et al. (2014), biochar addition may influence clay dispersibility either negatively or positively in that the added biochar can accelerate clay dispersion in the soil through its influence on soil pH, ionic strength, zeta potential, and moisture content. On the contrary, biochar aging in soil promotes biochar–mineral complexes, resulting in an improved structural stability and a decrease in clay dispersibility (Lin et al., 2012).

Tensile strength of aggregates, which is the force per unit area required to cause the disruption of aggregates, is a sensitive indicator of the soil structural condition and reflects the effects of natural factors, as well as land use and management (Dexter and Watts, 2000). Knowledge of the mechanical strength of soils is crucial from the point of view of root growth and soil tillage. Another important soil mechanical parameter is the friability index which is related to tensile strength and aggregate size (Utomo and Dexter, 1981). It is a key soil physical property that determines the ease of producing favorable seed-and-root beds during tillage operations (Munkholm, 2011). Guimarães et al. (2009) established a positive correlation between SOC content in the topsoil and soil friability because of the effect of SOC on soil structural hierarchy, whereas the opposite was found for the subsoil.

There is paucity of information regarding the effects of biochar application on soil aggregate characteristics (e.g., tensile strength, aggregate stability, soil friability, soil workability, and clay dispersibility) in highly weathered soils of the humid tropics. Therefore, the study aims to contribute to knowledge on how corn cob biochar impacts on the characteristics of the aggregates of a tropical sandy loam. We hypothesize that corn cob biochar applied to a tropical sandy loam will improve aggregate strength and increase aggregate friability via an increased C content

Table 1. Particle-size distribution and chemical properties of top soil (0–20 cm) prior to start of experiment.

Clay	Silt	Sand	OC	Total N	Total P	K	Mg	pH	EC
——% by weight——					——mg 100 g^{-1}——				μS cm^{-1}
18	9	73	0.93	0.073	<0.4	11.9	9.3	6.1	200

Table 2. Characteristics of corn-cob biochar used in the study.†

DM	OM	TC	TN	pH	P	K	Ca	Mg	Fe	Na	ΣPAHs
——g 100 g^{-1}——					——mg kg^{-1}——						
85.3	61.5	38.8	0.9	10.2	3150	31800	8690	4510	3920	2160	3.31

† DM, dry matter; OM, organic matter; TC, total carbon; TN, total nitrogen, PAH, polyaromatic hydrocarbons (calculated as the mathematical sum of 19 PAHs). Sigma (ΣPAHs) denotes the sum of the PAHs.

MATERIALS AND METHODS

Description of the Study Area

The field work was done at the University of Cape Coast Teaching and Research farm located in the coastal savanna agroecological zone of Ghana (5°07′ N lat., 1°17′ W long.). The area is characterized by high rainfall (1400 mm per annum) with a bimodal pattern. Temperatures are high throughout the year with mean monthly temperatures ranging from 24°C in August to 28°C in April. The soil is well-drained sandy loam developed on sandstones, shales and conglomerates and classified as a Haplic Acrisol (FAO, 1977). Details of the particle-size distribution and chemical properties of the investigated soil are presented in Table 1

Field Experimentation and Sampling

Biochar Production and Preparation

The biochar was produced from corn cob feedstock in a reactor, with a pyrolytic temperature of 550°C for 48 h. The biochar was sieved to < 2 mm to obtain biochar with a relatively high surface area for enhanced reactivity in the soil matrix. The chemical and physical characteristics of the biochar used in the study are presented in Table 2.

Field Layout

The study involved 16 plots, each measuring 3 m × 6 m (18 m^2), with pathways of 0.6 m between plots. The study comprised four treatments with four replications each. The field was plowed and harrowed to achieve fine tilth, followed by the removal of stubble and weeds. On each plot, beds were raised up to 15 cm above the soil surface to facilitate drainage. The 2-mm sieved biochar was applied to the field plots at rates of 0, 10 Mg ha^{-1} and 20 Mg ha^{-1}, and 20 Mg ha^{-1} with P (P-enriched biochar). These rates corresponded to 0, 0.34, and 0.68% (w/w) of biochar for the respective plots. Because of the low pH levels in most tropical soils, Al^{3+} and Fe^{2+} (sesquioxides) predominate in the soil solution. These acidic cations have the tendency to sorb available P, making P unavailable in the soil solution. The P-enriched biochar was added as a treatment primarily to protect the added P from being sorbed by the P-sorbing constituents in the soil solution. The P-enriched biochar was prepared by mixing 50 kg P_2O_5 ha^{-1} (Triple super phosphate) with 0.68%

(w/w) of biochar. The mixture was stored for 7 d before it was applied to the field. The treatments are denoted by CTRL, BC-10, BC-20, and BC-20+P for the 0, 10 Mg ha^{-1} and 20 Mg ha^{-1}, and 20 Mg ha^{-1} with P (P-enriched biochar), respectively.

Biochar (with and without P fertilizer) was broadcast on the soil surface of the treatment plots and incorporated into the soil by plowing with a hoe to a depth of about 20 cm. Biochar application rates were split into two; The first 50% of the biochar rates were applied on 7 Nov. 2015, and the remaining 50% of the rates were applied on 29 Jan. 2016. To maintain consistency, plowing (the same hoe treatment) was done on the control plots each time biochar was incorporated in the biochar treatment plots. Three weeks after the second biochar application to the soil, okra (*Abelmoschus exculentus*) seeds were sown directly at two seeds per hole with a dibber to a depth of 4 cm and at a spacing of 60 cm × 60 cm. Two weeks after germination, the plants were thinned to one plant per stand.

Soil Sampling

Soil samples were collected on 21 May 2016, when the okra plants reached physiological maturity. A spade was used to extract bulk, minimally disturbed soil samples from each of the 16 plots at a depth of 0 to 20 cm for aggregate stability measurements. In addition, bulk samples were taken from the middle of each plot, avoiding visibly compacted areas of the field due to human traffic. A total of 16 soil samples were obtained (4 treatments with 4 replications per each treatment).

Laboratory Measurements

Soil Texture and Organic Carbon Content

The particle-size distribution of the soil was determined by sieving following the standard hydrometer method (Gee and Or, 2002). The content of total C was quantified by the oxidation of C to CO_2 at 1800°C with a FLASH 2000 organic elemental analyzer coupled to a thermal conductivity detector (Thermo Fisher Scientific). Total C was considered as SOC since there were no carbonates present.

Soil pH and Electrical Conductivity

For soil pH, 25 mL of deionized water was added to 10 g of air dried soil (corresponding to soil/water ratio of approximately 1:2.5) and the mixture was mechanically shaken for 10 min and left to settle for another 10 min. A combined pH and EC electrode was then used to measure soil pH and EC (Thomas, 1996).

Soil Aggregate Stability

The samples extracted by the spade were gently broken along natural planes of failure to obtain aggregates of <8 mm. These aggregates were air dried at room temperature, after which each sample was kept in a zip lock bag. The De Leenheer and De Boodt (1959) method was used to determine the aggregate stability of the samples. Briefly, for dry sieving, about 300 g of the 8-mm sieved air-dried samples were sieved again over a set of seven sieves (8.00, 4.76, 2.83, 2.00, 1.00, 0.50, and 0.30 mm). Thereafter, another 300 g of soil was sieved over the same set of sieves while immersed in water (wet sieving). The fractions remaining on each sieve for both the dry and wet sieving were used to estimate the mean weight diameter (MWD). The MWD (mm) was estimated with Eq. [1]. Details of the methodology are described in Leroy et al. (2008).

$$MWD=\frac{\sum m_i \times d_i}{\sum m_i} \quad [1]$$

where MWD denotes the mean weight diameter (mm) of the aggregates, m_i is the mass of aggregate fraction i (g), and d_i, the mean diameter of the aggregate fraction i (mm). The stability index (SI) which was used to classify the aggregate stability was estimated as:

$$SI=\frac{1}{MWD_{dry}-MWD_{wet}} \quad [2]$$

Clay Dispersibility

For determining clay dispersibility, 10 g of air-dried aggregates was used. The method we used was a modified version of what is described in Pojasok and Kay (1990). In brief, cylindrical plastic bottles with the aggregates and 80 mL of artificial rainwater (0.012 mM $CaCl_2$, 0.15 mM $MgCl_2$, and 0.121 mM NaCl; pH of 7.82; EC of 2.24×10^{-3} S m^{-1}) were rotated end-over-end (33 rpm, 23-cm diam. rotation) for 2 min. After shaking, the samples were removed and left undisturbed for sedimentation for 4 h and 38 min, allowing particles >2 µm to settle. Subsequently, the suspension containing particles £2 µm, that is, the dispersed clay, was siphoned off by pipette and transferred into a beaker. Ten milliliters of the suspension was then transferred to a preweighed glass vial followed by oven drying at 105°C for 24 h. The mass of the dispersed clay was calculated from the oven dry mass considering the original sample mass. The dispersible clay content was scaled by the clay content and reported as "mg clay per g clay" since increasing clay content enhances the amount of dispersible clay in soils.

Soil Tensile Strength

Aggregates in the size classes of 1 to 2, 2 to 4, 4 to 8, and 8 to 16 mm for the tensile strength test were obtained from air-dried soil carefully fragmented by hand during the drying process (Elmholt et al., 2008). Tensile strength of air-dry aggregates of all four size classes was measured as detailed by Munkholm et al. (2001). In brief, the aggregates were crushed individually between two parallel plates in an indirect tension test. Fifteen individual randomly selected aggregates for each combination of treatment, replicate, aggregate size, were tested (4 treatments × 4 replicates each × 4 aggregate-size fractions × 15 aggregates = 960 tests). Aggregates were individually weighed before crushing. The force necessary to fracture the aggregates was derived by crushing aggregates between two flat parallel plates in an indirect tension test as described by Dexter and Kroesbergen (1985). A constant displacement rate of 0.03 mm s^{-1} and a load cell of 0 to 100 N was used for all the tests. The point of failure for each aggregate was detected when a continuous crack or a sudden drop in the force reading was observed (Dexter and Kroesbergen, 1985). All samples were placed in the oven at 105°C for 24 h to determine the water content.

Thereafter, aggregate tensile strength (Y, kPa) was calculated from Eq. [3] (Dexter and Watts, 2000):

$$Y=\frac{0.576\times F}{d^2} \quad [3]$$

where F (N), and d (m) denote the polar force required to fracture the aggregate and the mean aggregate diameter, respectively. The mean diameter of all aggregates was estimated from the average of the upper and lower sieve mesh sizes of the respective aggregate-size classes (thus, 1.5, 3, 6, and 12 mm for 1- to 2-, 2- to 4-, 4- to 8-, and 8- to 16-mm aggregate size classes, respectively). For each aggregate, the effective diameter used for Eq. [3] was estimated from Eq. [4] following Dexter and Kroesbergen (1985).

$$d=d_i\left(\frac{m_o}{m_i}\right)^{\frac{1}{3}} \quad [4]$$

where, d_i is the mean diameter of the aggregates calculated from the respective aggregate size classes, m_o is the dry mass of individual aggregates and m_i is the mean dry mass for batches of 15 aggregates of each treatment.

Rupture Energy

The energy at rupture (E) for each aggregate was obtained by computing the area under the stress-strain curve according to Vomocil and Chancellor (1969),

$$E\approx\sum_i F(s_i)\Delta s_i \quad [5]$$

where $F(s_i)$ is the mean force at the i^{th} subinterval and Δs_i is the displacement length of the i^{th} subinterval. The mass-specific rupture energy, E_{sp}, was obtained by normalizing E with the aggregate mass (m):

$$E_{sp}=\frac{E}{m} \quad [6]$$

For all the aggregate-size classes (1–2, 2–4, 4–8, and 8–16 mm), m was measured for each individual aggregate tested for tensile strength.

Soil Friability

Soil friability index was taken as the slope of the plot of the natural logarithm of the tensile strength (kPa) of the aggregates against the natural logarithm of the aggregate volume (m^3). Friability of the treatments was classified according to the ranges provided by Imhoff et al. (2002). To evaluate differences in soil friability among treatments, parallel lines analyses were conducted to determine if the regression slopes were significantly different from each other.

Soil Workability

Soil workability (W) represents the ease with which a soil can be tilled. Quantitatively, it can be obtained by a combination of friability (F) and tensile strength (Y) as suggested by Arthur et al. (2014):

$$W=F\times\left(\frac{1}{Y}\right) \quad [7]$$

Generally, soils with large values of W are easier to till and vice versa for soils with small W values.

Data Analyses and Statistics

Statistical analyses were performed using SigmaPlot 11 (Systat Software Inc., San Jose, CA). All data obtained were checked for normality and homogeneity of variance. Analyses of variance (ANOVA) was used to test for differences between biochar-treated and untreated soils, and the Holm-Sidak post-hoc test was used to differentiate between any two given treatments. Logarithmic transformation was performed on the aggregate tensile strength and soil volume data to yield normality prior to analyses. We used $p < 0.05$ as a criterion for statistical significance of treatment effects unless otherwise stated. Statistical significance is indicated by lowercase letters beside the mean values. Results are given as mean ± standard error (SE) in tables and figures.

RESULTS

Corn Cob Biochar Effects on Soil Properties

Soil Texture and Chemical Properties

Soil texture at the field site was classified as a sandy loam with SOC of approximately 1.03% for the control plots. There was no effect of applied biochar on soil texture (Table 3). Hereon, the treatments are denoted by CTRL, BC-10, BC-20, and BC-20+P for the 0, 10 Mg ha^{-1} and 20 Mg ha^{-1}, and 20 Mg ha^{-1} with P (P-enriched biochar), respectively

For SOC, there was a statistically significant difference among some of the treatments as determined by one-way ANOVA [$F(3, 12) = 5.07, p = 0.017$]. A Holm-Sidak post hoc test revealed that SOC was significantly (66%) larger for BC-20 than CTRL ($p = 0.002$). The BC-10 and BC-20+P treatments showed nonsignificant increases of 35% ($p = 0.062$) and 35% ($p = 0.125$), respectively, compared with the CTRL. There was no significant differences in the SOC among the biochar treatments, despite the relatively large SOC value of the

Table 3. Effect of corn-cob biochar on soil textural and chemical properties.

Treatment	Clay	Silt	Sand	OC	pH	EC
		g 100g^{-1}				µS cm^{-1}
CTRL	19 (1.8)^{ns}†	8 (0.4)^{ns}	73 (1.8)^{ns}	1.03 (0.08)^{b}	5.9 (0.03)^{bc}	309 (46)^{a}
BC-10	18 (0.9)	9 (0.3)	73 (1.1)	1.39 (0.18)^{ab}	6.2 (0.09)^{ac}	76 (4.2)^{b}
BC-20	18 (0.8)	8 (0.2)	74 (0.8)	1.71 (0.12)^{a}	6.5 (0.17)^{a}	61 (7.6)^{b}
BC-20+P	19 (1.6)	9 (0.3)	72 (1.9)	1.32 (0.09)^{ab}	6.3 (0.06)^{a}	66 (8.4)^{b}

† Numbers in brackets indicates standard error of the mean. Different letters within a column indicate that treatments are significantly different (Holm-Sidak test; $p < 0.05$), ns denote lack of a statistically significant difference among treatments. CTRL, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 Mg ha^{-1}, and 20 Mg ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

BC-20 treatment compared with BC-10 and BC-20+P. Soil pH was significantly different among some of the treatments [$F(3, 12) = 5.75, p = 0.011$]. There was a significant increase in soil pH by 0.6 and 0.4 units for the BC-20 ($p = 0.002$), and BC-20+P ($p = 0.008$), respectively, compared with the CTRL (Table 3). Corn cob biochar significantly ($p < 0.001$) decreased soil EC by 75, 80, and 79% in the BC-10, BC-, and BC-20+P plots respectively, compared with the CTRL (Table 3).

Soil Aggregate Characteristics after Biochar Application

Aggregate Stability and Water Dispersible Clay

The incorporation of corn cob biochar had a significant [$F(3, 12) = 138.7, p < 0.001$] effect on the stability of the soil aggregates among some of the treatments (Fig. 1). The aggregate stability indices for the CTRL, BC-10, BC-20, and BC-20+P treatments were 1.17, 1.48, 1.77, and 1.79, respectively representing increases of 27, 52, and 53% for the biochar treatments compared with the CTRL. Thus, the effect of biochar on soil aggregate stability was more pronounced with an increasing rate of biochar application. Despite a surprising trend of increasing water dispersible clay (WDC) content with biochar application rate, there was no statistically significant difference among treatments [$F(3, 12) = 0.169, p = 0.915$].

Air-Dried Aggregate Water Content

There was a general trend of increasing soil water content with biochar application rate for all the aggregate-size classes (Table 4). However, only the 1- to 2-mm aggregates recorded a significant increase in water content among some of the treatments [$F(3, 12) = 6.15, p = 0.009$]. The BC-20 and BC-20+P treatments had significantly larger aggregate water contents than the CTRL ($p = 0.008$ and 0.003, respectively). There was no difference in the water content of the 1- to 2-mm aggregates in both the CTRL and BC-10 ($p = 0.388$). Among the biochar treatments, no significant difference in water content was observed.

Tensile Strength and Rupture Energy

The aggregate tensile strength (Y) for 1- to 2-mm aggregates differed significantly among some of the treatments [$F(3, 12) = 39.4, p < 0.001$] with mean values of 237, 206, 322, and 313 kPa respectively, for the CTRL, BC-10, BC-20, and BC-20+P treatments(Fig. 2a). The increase in Y was significant for the BC-20 ($p < 0.001$) and BC-20+P ($p < 0.001$) treatments when compared with the CTRL. Among the biochar treatments, BC-20 and

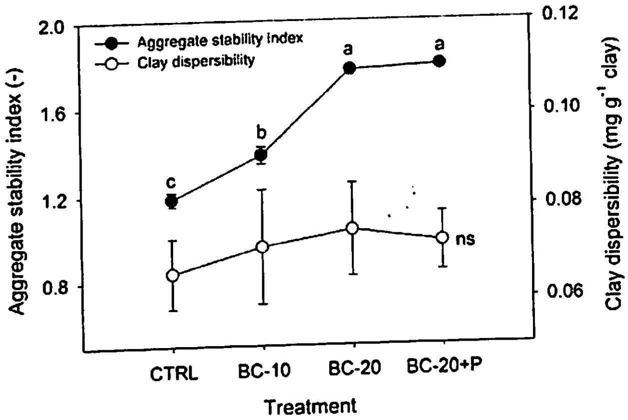

Fig. 1. Corn cob biochar effects on aggregate stability index and dispersible clay content. CTRL, control; BC-10, BC-20, and BC-20+P denote biochar treatments with 10, 20 Mg ha^{-1}, and 20 Mg ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

BC-20+P were statistically similar ($p = 0.466$) but different from BC-10. For the 2- to 4-mm aggregates, a trend of decreasing Y with increasing rates of biochar was observed in the biochar treated plots as compared with the CTRL. However, no significant difference in Y was observed in the CTRL, BC-10, and BC-20 plots (Fig. 2b). Comparatively, BC-20+P recorded a significantly lower tensile strength (94 kPa) compared with the CTRL ($p = 0.002$). For the 4- to 8-mm aggregates, Y differed significantly among some of the treatments [$F(3, 12) = 16.7, p < 0.001$]. Specifically, BC-20 and BC-20+P treatments had significantly ($p < 0.001$) higher Y compared with CTRL. The BC-10 treatment was statistically similar to the CTRL and BC-20 treatments (Fig. 2c). For the largest aggregates (8–16 mm), all biochar treatments exhibited significantly lower Y than the CTRL [$F(3, 12) = 161.2, p < 0.001$].

Specific rupture energy (E_{sp}) exhibited trends similar to what was observed earlier for Y. For all treatments, smaller aggregates required larger energies at the point of aggregate rupture/failure compared with larger aggregates (Fig. 3). Furthermore, increasing biochar rates tended to increase the E_{sp}, particularly for the smaller aggregates, these increases were, however not significant.

Indices of Aggregate Friability, Workability, and Characteristic Strength

Friability (k_Y or k_E) was quantified by relating the tensile strength (Y) or specific rupture energy (E) of aggregates to their sizes (volume; Fig. 4). An example of how the friability indices were obtained for the CTRL and BC-20+P treatments is pre-

Table 4. Aggregate water content for the various aggregate size classes (%), friability (k_Y [kPa m^{-3}] and k_E [J kg^{-1} m^{-3}]), characteristic aggregate strength (Y_4) and workability (W) for control and biochar treatments.

Treatment	Aggregate water content (g 100g^{-1})				k_Y	k_E	Y_4	W (×10^3)
	1–2 mm	2–4 mm	4–8 mm	8–16 mm				
CTRL	0.88 (0.24)^{b}†	0.88 (0.13)^{ns}	1.01 (0.21)^{ns}	0.75 (0.14)^{ns}	0.23^{c}	1.04^{c}	107	2.16
BC-10	1.14 (0.13)^{ab}	1.14 (0.13)	1.01 (0.21)	1.00 (0.21)	0.32^{b}	1.26^{b}	77.3	4.08
BC-20	1.78 (0.15)^{a}	1.27 (0.33)	1.27 (0.15)	1.26 (0.15)	0.53^{a}	1.56^{ab}	61.8	8.63
BC-20+P	1.91 (0.25)^{a}	1.40 (0.24)	1.14 (0.25)	1.67 (0.46)	0.58^{a}	1.83^{a}	50.4	11.5

† Numbers in brackets indicates standard error of the mean. k_Y, friability derived from tensile strength; k_E, friability derived from specific rupture energy. Different letters for k_Y and k_E indicate that slopes (friability) are significantly different ($p < 0.05$) between biochar treatments. *ns* denote no significant differences between treatments. CTRL, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 Mg ha^{-1}, and 20 Mg ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

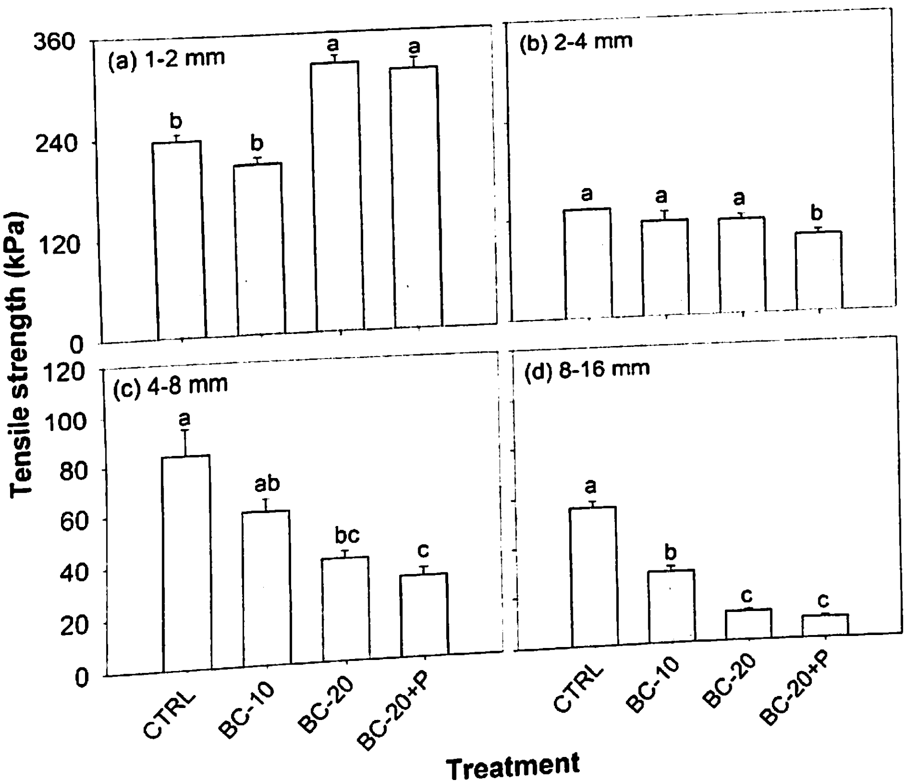

Fig. 2. Effects of different application rates of corn cob biochar on tensile strength of various air-dried aggregate classes. CTRL, control; BC-10, BC-20, and BC-20+P denote biochar treatments with 10, 20 Mg ha^{-1}, and 20 Mg ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively. Note the different *x* axis scales for *ab* and *cd*.

sented in Fig. 4. Friability obtained from the tensile strength values is denoted k_Y and that from the specific rupture energy values is denoted k_E. For the two examples presented BC-20+P has more friable aggregates (based on k_Y) than CTRL because the strength of the BC-20+P aggregates decrease sharply with aggregate volume. In addition, Fig. 4 also shows the estimation of the characteristic aggregate strength (Y_4) as the strength of a 4-mm aggregate (which corresponds to an aggregate volume of 17 m^3). The aggregate-size class 4 mm was selected because it is the median size of the tested aggregates in this study.

The k_Y, k_E, and Y_4 values for the CTRL and biochar treatments are provided in Table 4. Expectedly the two indices of friability agreed well with each other (Table 4, Fig. 5) and one can easily be predicted from the other with a high degree of accuracy. Based on the classification index of Imhoff et al. (2002) for k_Y, the CTRL and BC-10 are classified as "friable", whereas the BC-20 and BC-20+P fall under the "very friable" category.

Based on results of the parallel lines analyses, biochar application significantly increased k_Y by 39, 130, and 152% for the BC-10, BC-20, and BC-20+P relative to CTRL ($p < 0.001$; Table 4). Among the biochar treatments, k_Y was significantly higher in the BC-20 ($p = 0.0016$) and BC-20+P ($p = 0.0021$) treatments than the BC-10. Similarly, k_E was significantly higher in the biochar treated plots compared with the CTRL ($p < 0.05$). Corn cob biochar significantly increased k_E by 22, 50, and 76% in the BC-10 ($p < 0.033$), BC-20 ($p = 0.0155$), and BC-20+P ($p = 0.010$), respectively, compared with the CTRL. Statistically, there was no

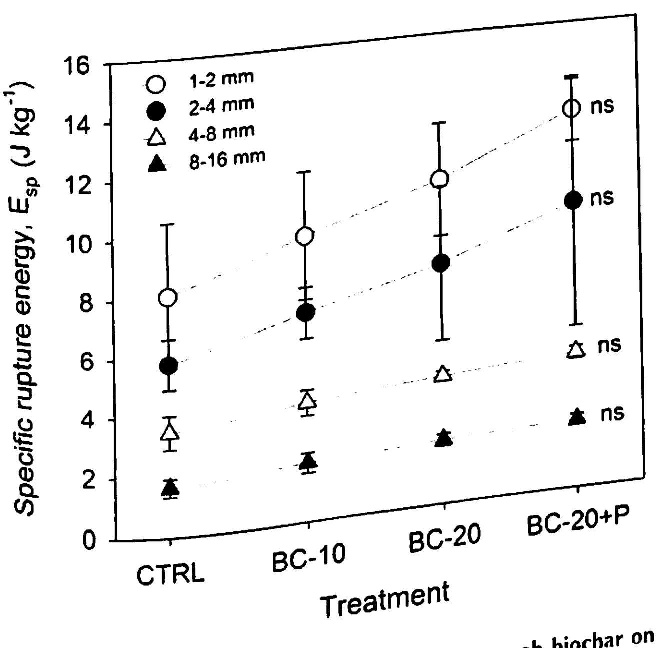

Fig. 3. Effects of different application rates of corn cob biochar on specific rupture energy of various air-dried aggregate classes. CTRL, control; BC-10, 20, and 20+P denote biochar treatments with 10, 20 Mg ha^{-1}, and 20 Mg ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

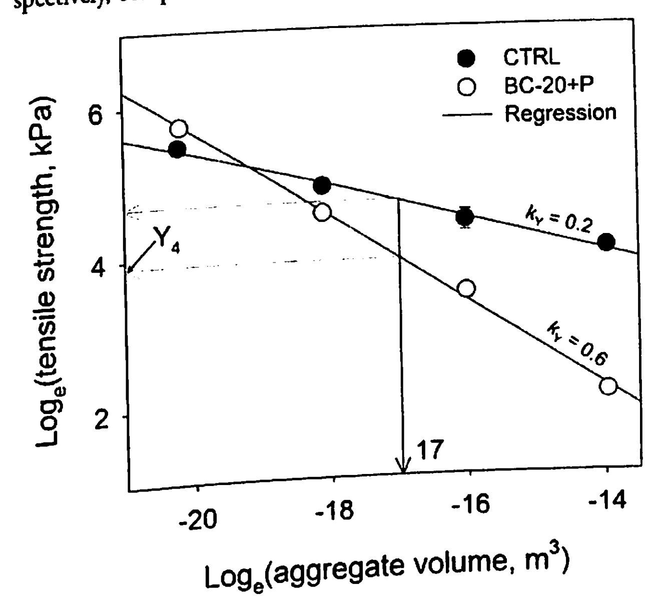

Fig. 4. Log$_e$ aggregate tensile strength, *Y*, (kPa) as a function of log$_e$ aggregate volume, V (m^3) for air-dry aggregates. Soil friability index, k_Y, determined as the slope of the regression equation is shown for each soil. Estimation of the median size soil aggregate class (4 mm = 17 m^3) of air-dry aggregates is also shown.

difference in k_E between BC-20 and BC-20+P treatments (p = 0.254). Similarly, no significant difference was observed in k_E in the BC-20 and BC-10 treatments (p = 0.100). However, there was a significant difference in k_E between BC-10 and BC-20+P (p = 0.035).

Characteristic aggregate strength decreased by 28, 42, and 53% in the BC-10, BC-20, and BC-20+P treatments, respectively, compared with the CTRL. Conversely, biochar increased the soil workability (W) by 89, 300, and 432% in the BC-10, BC-20, and BC-20+P treatments, respectively, relative to the CTRL (Table 4).

DISCUSSION

Soil Chemical Properties after Biochar Application

The increase in SOC following the application of biochar agrees with the findings of Zolfi-Bavariani et al. (2016) who reported a three-fold increase in SOC after applying poultry-derived biochar (2% w/w) on a calcareous loamy soil. Similarly, Khademalrasoul et al. (2014) observed up to a two-fold increase in SOC after the application of swine manure biochar to a sandy loam soil at rates of 1, 2, and 5 kg m^{-2}. The increase in pH following the incorporation of biochar in this study is in agreement with the results of Hairani et al. (2016) who showed an increase in soil pH by 0.15 to 0.25 units in a Gleyic Fluvisol amended with fine wood biochar at a rate of 35 Mg ha^{-1}. Novak et al. (2016) also reported an increase from 5.6 to 6.6 in soil pH following the application of hard wood biochar at a rate of 22.4 Mg ha^{-1} dry weight to a loamy sand acidic Ultisol. Additionally, Jien and Wang (2013) observed an increase in soil pH from 3.5 to 5.1 with increasing rates of biochar application following the application of waste wood biochar applied at the rates of 2.5 and 5% (w/w) to a highly weathered Typic Paleudult. The increase in soil pH is attributable to the liming potential of biochar because of the high pH (10.2) of the added biochar (Jien and Wang, 2013). The decrease in soil EC found in this study in the biochar amended soils contradicts the findings of Yang et al. (2016) and Chintala et al. (2014) who observed an increase in EC following the application of corn stover and switchgrass biochar at rates of 20, 40, and 60 g kg^{-1}, respectively, to an acidic clayey soil. Statistically, there was no difference in EC values among the different biochar treatments. Chathurika et al. (2016) recorded no significant effect in EC after the application of woodchip biochar at rates of 10 g kg^{-1} (or 1% w/w) and at 20 g kg^{-1} (or 2% w/w) to Almasippi loamy sand and a Newdale clay loam, respectively. Similarly, Paneque et al. (2016) also recorded no significant difference in EC when pine wood and woodchip biochar were applied to a sandy loam Calcic Cambisol at rates of 1.5 and 15 Mg ha^{-1}.

Soil Aggregate Characteristics after Biochar Application

Aggregate Stability and Clay Dispersibility

Stability of soil aggregate is critical for maintaining the soil's resistance to mechanical stresses such as the impacts of rainfall and surface runoff (Cañasveras et al., 2010). When soil aggregates disintegrate, the finer particles produced are easily transported by soil erosion forces (wind and water), settle later in soil pores, clog them, and lead to formation of soil crusts (Yan et al., 2008). The clogging of soil pores subsequently promotes surface run-off by reducing the infiltration capacity of soils, enhancing water erosion with its attendant negative effect on soil fertility. Thus, aggregate stability is an important factor in soil erosion (Besalatpour et al., 2013). Aggregates with a higher stability do not easily disintegrate and promote long-term C sequestration and soil structural stability (Ouyang et al., 2013). The effect of biochar on soil aggregate stability has yielded mixed results because of a range of methodological, temporal, and material factors (Soinne et al., 2014; Sun and Lu, 2014). In this study, application of corn cob biochar increased the stability index of the soil aggregates but surprisingly had no significant effect on clay dispersibility. The improved aggregate stability agrees with Burrell et al. (2016) when they applied woodchip biochar at a rate of 3% (w/w) to three agricultural soils (Planosol, Chernozem, and Cambisol). Our observation is also in line with the findings of Khademalrasoul et al. (2014) who indicated that black C in the soil acts as a binding agent between aggregates and increases the aggregate stability. The increasing trend of aggregate stability index (SI) in the biochar treated plots can be related partly to the slightly larger amount of SOC that was recorded in the biochar amended plots (Table 3). The incorporation of organic materials to soils increases soil aggregate stability through an increase in SOC (Hartley et al., 2016). The improved SOC content of the soil may have improved the conditions of the soil in the biochar amended plots, thus creating a conducive environment for mycorrhizal fungi (Fletcher et al., 2014), thus improving soil aggregate stability. Moreover, biochar increased soil aggregate stability possibly because of internal cohesion through the binding of mineral particles and C (Soinne et al., 2014; Sun and Lu, 2014). Application of organic amendments to the soil can potentially increase soil aggregation because of binding agents, for example, exopolysaccharides obtained from turnover of the organic amendments (Papadopoulos et al., 2009). Tsai et al. (2012)

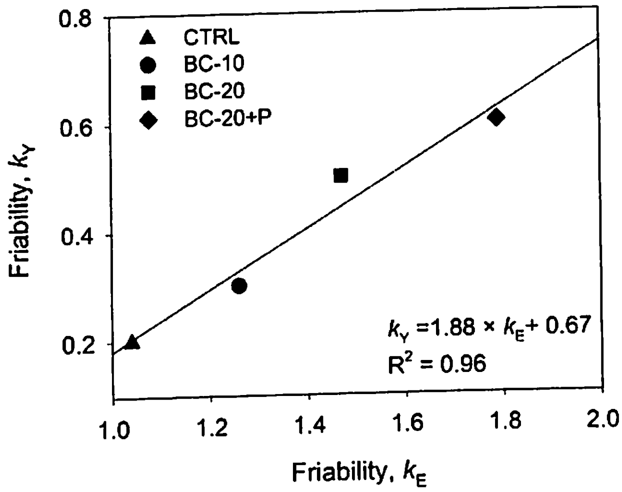

Fig. 5. Linear relationship between indices of friability based on either aggregate tensile strength, k_Y, or specific rupture energy, k_E, for each soil. CTRL, control; BC-10, BC-20, and BC-20+P denote biochar treatments with 10, 20 Mg ha^{-1}, and 20 Mg ha^{-1} + 50 kg P_2O_5 ha^{-1}, respectively.

also suggested that the aromatic nature of biochar may function as a bond between soil particles. The effect of the corn cob biochar on aggregate stability can also be linked to organic C functional groups on the biochar surfaces and labile C released from the char into the soil system (Hartley et al., 2016). Increase in the electrolyte concentration promotes flocculation by shrinking the diffuse double layers of soil colloids. However, application of biochar rather decreased the EC in this study. Therefore, the observed increased aggregate stability in the biochar amended treatments could partly be attributed to the fact that other aggregation mechanisms in the soil matrix as discussed above were responsible for the stability of the aggregates regardless of the decrease (leaching) of soluble salts in the treated plots. The lack of a significant effect of biochar on WDC was surprising partly because of the clear increase in aggregate stability and also the larger SOC for the biochar treatments. The discrepancy between the two indicators of structural stability is likely because of scale—the stability index that quantifies aggregate stability incorporates organic matter–mineral dynamics for a larger range of aggregates (0.3 to 8 mm). While for WDC, the aggregate-size class of 1 to 2 mm was used for experimentation and as reported by Arthur et al. (2014), for soils with low SOC, cementation effects arising from encrusted clay could decrease WDC compared with soils with larger SOC contents. Contrasting reports of the overall effect of biochar on WDC has been reported in the literature. For instance, Hansen et al. (2016) reported that straw gasification biochar had no effect on WDC while Khademalrasoul et al. (2014) and Soinne et al. (2014) reported an increase in WDC in soils amended with birch-wood biochar and wood chips biochar, respectively. Khademalrasoul et al. (2014) argued that biochar may influence WDC negatively and positively in that through its influence on soil pH, ionic strength, zeta potential, and moisture content, biochar can accelerate clay dispersion in soils. Soinne et al. (2014) observed an increase in WDC in fine-textured soils (silty clay loam and clay, respectively), as well as in a coarse-textured soil amended with a mixture of Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) chips at rates of 15 and 30 Mg ha^{-1}. Khademalrasoul et al. (2014) attributed the higher WDC for the biochar-amended soils to the high pH and low electrical conductivity. In this study, no significant correlation was observed between EC and WDC, but WDC strongly correlated positively ($r = 0.99^*$, $p = 0.006$) with soil pH (Table 5) despite the absence of a clear effect of biochar on WDC.

Table 5. Pearson correlation coefficients between some physicochemical soil properties ($n = 4$).†

	EC	WDC	SI	SOC
pH	-0.95*	0.99**	0.92*	0.91
EC		-0.94*	-0.81	-0.81
WDC			0.88	0.95*
SI				0.73
SOC				

*significant correlation between two properties at $p < 0.10$.
** significant correlation between two properties at $p < 0.05$.
† EC, electrical conductivity; SI, aggregate stability index; WDC, water dispersible clay content; SOC, soil organic carbon.

Tensile Strength and Specific Rupture Energy

Tensile strength is an important soil property relevant for assessing the structural stability of a soil and its resistance against erosive forces (Watts and Dexter, 1998). Further, it is considered important in identifying management practices for sustainable crop production (Abid and Lal, 2009). Application of high rates of biochar (BC-20 and BC-20+P) in this study increased the tensile strength of the smaller aggregates. The significant increase in tensile strength in the 1- to 2-mm aggregates is because corn cob biochar increased the water content within the aggregates (Table 4). This implies that the relatively few preexisting micro-cracks in the aggregates were probably not fully active to reduce air-pressure within the aggregates or to allow in-flow of air from surrounding air-filled pores. The relatively high water content in the B-20 and BC-20 + P relative to the control and the BC-10 curtailed the expansion and elongation of micro-cracks and this is believed to have adversely affected crack growth with a resultant increase in aggregate tensile strength in the smaller aggregates. It must however be noted that application of corn cob biochar in our study significantly decreased the tensile strength of soil aggregates in the large aggregates (4–8 and 8–16 mm). Other authors have also noted that aggregate tensile strength of natural or well-managed soils decreases with increasing aggregate size (Munkholm et al., 2001; Abu-Hamdeh et al., 2006). This may be because of an improved structural pore network in well managed soils with an appreciable amount of preexisting micro cracks in the large aggregates which join to form arrays of continuous fracture surfaces on exposure to mechanical stress (e.g., tillage). The disparity in the effect of the applied biochar in the smaller aggregate size and the larger aggregate sizes could be ascribed to different interactions between the biochar particles and the different aggregate sizes. Khademalrasoul et al. (2014) affirmed that for larger particles, soil particles bond and interact with biochar particles, whereas no biochar-soil bonding occurs between biochar particles and smaller aggregate sizes.

The decrease in tensile strength for the large aggregates after biochar application may be attributed to the high SOC with an increase in biochar application rates which probably improved the soil structural porosity. This is because application of biochar has the tendency to increase the aggregate and structural stability of the soil, which in turn increases soil porosity primarily as a result of increased activity by soil fauna. Increasing the rate of biochar might have promoted crack growth and activated the preexisting micro cracks in the large aggregates, and this ultimately gave the aggregates the propensity to elongate under mechanical stresses. The corn cob biochar applied in this study might have also increased the structural quality of the soil which all culminated into decreasing the tensile strength of the aggregates as the size class gets larger.

Soil E_{sp} gives an indication on the strength of dry aggregate strength, and it is an indicator of the resistance and resilience of a soil when it is subjected to mechanical stress or manipulation. Soil resistance describes the ability of a system to retain its functional capacity on imposition of stress, whereas soil resilience is the capacity of the soil to return to an equilibrium following displacement in response to disturbances or recover its initial function on removal/

reduction of the applied stress (Gregory et al., 2007). In this study, there was a systematic increase in specific rupture energy for the smaller aggregates as compared with the larger aggregates in all the treatments (Fig. 3). A similar observation was made by Schjønning et al. (2012) who ascribed this finding to a collapse of the soil structural hierarchy as aggregate-size increases. The implication is that, comparatively, smaller aggregates are more resistant and resilient to mechanical stress, and as a result, more energy is required to break them compared with larger aggregates. Statistically, no significant differences were observed between the specific rupture energy of the different aggregate sizes and the treatments.

Aggregate Friability and Workability

Utomo and Dexter (1981) defined friability as the tendency of an unconfined soil to break down and crumble under applied stress into a particular size range of smaller fragments. Soil friability is also characterized by an ease of fragmentation of undesirably large aggregates/clods and a difficulty in fragmentation of minor aggregates into undesirable small elements (Munkholm, 2011). For all treatments, both k_Y and k_E increased significantly with increasing biochar application rates. Since there was a strong linear relationship between k_Y and k_E for the four treatments (Fig. 5), only k_Y is discussed from hereon.

The larger friability values observed after biochar application is attributable to the larger SOC contents of the biochar treatments. Soils with large contents of SOC tend to be more friable and easier to till than small-content SOC soils (Arthur et al., 2014). Further, there was a trend of decreasing characteristic soil strength (Y_4) with increasing biochar application. The CTRL had Y_4 roughly 1.5 to 2 times that of the biochar-treated soils, and this was clearly because of the larger SOC for the biochar treatments. Earlier studies confirm that aggregates from soils with low SOC tend to harden and cement (Défossez et al., 2014) as they dry, yielding larger Y_4 values (Arthur et al., 2014).

Soil workability is defined as the ease with which soil can be physically manipulated for the purposes of cultivation (Arthur et al., 2014). The soil workability index gives the degree with which the soils (treated or untreated) can be tilled. The soils from the untreated plots produced a lower workability index than soils from the biochar-amended plots, indicating that more energy will be required to fragment the aggregates in the control plots (Table 5). The relatively poor ability of the aggregates to be physically manipulated could be attributed to the low SOC which resulted in low soil structural stability with low micro pores and with fewer cracks (Watts and Dexter, 1998). Soil workability index increased with increasing biochar rates. Addition of organic material to the soil improves the soil structure, soil aggregates and total soil porosity with a substantial amount of micro cracks that increases the friability and workability of the soil. Generally, soil workability also increased with increasing SOC content (Arthur et al., 2014). Thus, corn cob biochar application has the potential to significantly improve soils from the perspective of soil tillage and the creation of a suitable seed bed for germination and plant growth.

CONCLUSIONS

This study assessed how corn cob biochar applied at 0 (CTRL), 10 Mg ha^{-1} (BC-10), and 20 Mg ha^{-1} (BC-20), and 20 Mg ha^{-1} with P (P-enriched biochar; BC-20+P) to a tropical sandy loam affected several aggregate characteristics and demonstrated the following:

- Increasing the rate of corn cob biochar improved the water stability of the aggregates compared with the CTRL, despite the absence of a significant effect on the dispersible clay content.

- For smaller aggregates (1–2 mm), tensile strength for BC-20 and BC-20+P treatments was significantly higher than the CTRL and BC-10, with an opposite trend observed for larger aggregates (4–8 mm and 8–16 mm).

- Corn cob biochar significantly improved soil friability and the ease of tillage quantified with a workability index.

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APPENDIX C

CONFERNECE PROCEEDINGS

2017 Tropentag International conference, Germany.

Emmanuel Amoakwah*, Emmanuel Arthur, Kwame Agyei Frimpong and Rafiq I. Khandakar.

Corn cob biochar improves the aggregate characteristics of a tropical sandy loam.

20th to 22nd September, 2017.

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Corn Cob Biochar Improves Aggregate Characteristics of a Tropical Sandy Loam

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ntroduction

Biochar, as a soil amendment, has received global attention. However, little is known about its effect on aggregate characteristics of weathered tropical soils.

Objective

To elucidate the effect of corn cob biochar on the aggregate characteristics soil tensile strength, friability, soil aggregate stability, clay dispersibility and soil workability of a highly weathered tropical sandy loam.

laterials and methods

Figure 1. Location map

Field layout

- RCBD
- 4treatments with 4 four replications each
- 16 plots (3 m × 6 m each)

Figure 2. Field Layout

3iochar preparation

Feed stock: Corn cob

Pyrolytic temperature: 550°C

iochar dose

10 t ha^{-1} (0.17% (w/w)) and 20 t ha^{-1} (0.34% (w/w)) and 20 t ha^{-1} with P (P-enriched biochar).

reatments

The treatments are denoted by CT, BC-10, BC-20, and BC-20+P for the 0, 10 t ha^{-1} and 20 t ha^{-1}, and 20 t ha^{-1} with P respectively.

Soil sampling

- 197 days after biochar was applied, a spade used to extract bulk, minimally disturbed soil samples from each of the 16 plots at a depth of 0-20 cm for aggregate stability measurements.
- Bulk samples were taken from the middle of each plot, avoiding visibly compacted areas of the field due to human traffic.

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is work was funded by the Danish International evelopment Agency (Ministry of Foreign Affairs of enmark) as part of the project "Green Cohesive ricultural Resource Management, WEBSOC", DFC oject no: 13-01AU.

Abstract

Most tropical soils are highly weathered and are vulnerable to soil erosion due to their poor aggregate characteristics. Soil aggregate characteristics are critical indicators of soil structural stability, and they have the propensity to influence soil physical behavior and functioning. In this study, we investigated the effect of corn cob biochar on the aggregate characteristics of a highly weathered tropical sandy loam. Biochar significantly increased soil organic carbon by 22-40% relative to the untreated soil with a surprising trend of increasing water dispersible clay as biochar rate increased. Amount of water stable aggregates was significantly improved by 15 – 34% in biochar treatments compared to control. Incorporation of biochar decreased the tensile strength of the large aggregates (4–8 mm and 8–16 mm), but increased same in the smaller aggregates (1–2 mm). Soil friability and workability were significantly improved in the BC-20 and BC-20+P treatments.

Aggregate tensile strength (Y, (kPa))

Figure 3. Instron for Y measurement

- Aggregates in the size classes of 1–2, 2–4, 4–8, and 8–16 mm for the tensile strength test were obtained from air-dried soil.
- In brief, the aggregates were crushed individually between two parallel plates in an indirect tension test. Fifteen (15) individual randomly selected aggregates for each combination of treatment, replicate, aggregate size, were tested (4 treatments × 4 replicates each × 4 aggregate size fractions × 15 aggregates = 960 tests).
- A constant displacement rate of 0.03 mm s^{-1} and a load cell of 0–100 N was used for all the tests. The point of failure for each aggregate failure was detected when a continuous crack or a sudden drop in the force reading was observed (Dexter and Kroesbergen, 1985).

Y (kPa) was calculated from Eq. [1]

$$Y = \frac{0.576 \times F}{d^2} \quad [1]$$

where F (N), and d (m)denote the polar force required to fracture the aggregate and the mean aggregate diameter, respectively.

For each aggregate, the effective diameter used for was estimated from Eq. [4] following (Dexter and Kroesbergen, 1985).

$$d = d_i\left(\frac{m_o}{m_i}\right)^{\frac{1}{3}} \quad [2]$$

where, d_i is the mean diameter of the aggregates calculated from the respective aggregate size classes, m_o is the dry mass of individual aggregates and m_i is the mean dry mass for batches of 15 aggregates of each treatment.

Soil friability

Soil friability index was taken as the slope of the plot of the natural logarithm of the tensile strength (kPa) of the aggregates against the natural logarithm of the aggregate volume (m^3).

Rupture Energy

The energy at rupture (E) for each aggregate was obtained by computing the area under the stress-strain curve according to eq. 3..

$$E \approx \sum_i F(s_i)\Delta s_i \quad [3]$$

The specific rupture energy was computed from eq. [4]:

$$E_{sp} = \frac{E}{m} \quad [4]$$

where $F(s_i)$ is the mean force at the i^{th} subinterval and Δs_i is the displacement length of the i^{th} subinterval.

Soil workability (W)

obtained from eq. [5]:

$$W = F \times \left(\frac{1}{Y}\right) \quad [5]$$

Aggregate stability

Figure 4. Wet and dry sieving machine

The stability index (SI) was used to classify the aggregate stability of treatments based on Eq.[6], [7] and [8].

$$MWD = \frac{\sum m_i x d_i}{\sum m_i} \quad [6]$$

$$IS = MWD_{dry} - MWD_{wet} \quad [7]$$

$$SI = \frac{1}{IS} \quad [8]$$

Clay dispersibility

Figure 5. End-over-end shaking method

- 10 g of air-dried aggregates used.
- In brief, cylindrical plastic bottles with the aggregates and 80 mL artificial rainwater (0.012 mM $CaCl_2$, 0.15 mM $MgCl_2$ and 0.121 mM NaCl; pH 7.82; EC 2.24 × 10^{-3} S m^{-1}) were rotated end-over-end (33 rpm, 23-cm diam. rotation) for 2 min.

Results and discussion

Table 2. Particle size distribution and chemical properties of top soil (0-20 cm) prior to start of experiment.

Clay	Silt	Sand	OC	Total N	Total P	K	Mg	pH	EC
% by weight					mg 100 g^{-1}				µS cm^{-1}
18	9	73	0.93	0.073	<0.4	11.9	9.3	6.1	200

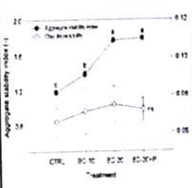

Figure 5. Corn cob biochar effects on aggregate stability index and dispersible clay content

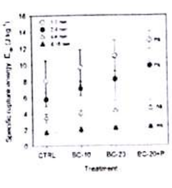

Figure 7. Effects of different application rates of corn cob biochar on specific rupture energy of various air-dried aggregate classes.

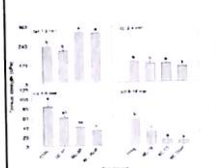

Figure 6. Effects of different application rates of corn cob biochar on tensile strength of various air-dried aggregate classes.

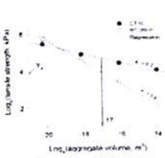

Figure 8. Log$_e$ Y, (kPa) as a function of log$_e$ aggregate volume, V (m^3) for air-dry aggregates. Soil friability index, k_Y, determined as the slope of the regression equation is shown for each soil. Estimation of the median size soil aggregate class (4-mm = 17 m^3) of air-dry aggregates is also shown.

Table 3. Aggregate friability (k_Y and k_E), characteristic aggregate strength (Y_4) and workability (W) for control and biochar treatments

Treatment	k_Y	k_E	Y_4 (kPa)	W (×10^3)
CTRL	0.23^c	1.04^c	107	2.16
BC-10	0.32^b	1.26^b	77.3	4.08
BC-20	0.53^a	1.56^{ab}	61.8	8.63
BC-20+P	0.58^a	1.87^a	50.4	11.5

k_Y, friability derived from tensile strength; k_E, friability derived from specific rupture energy Different letters indicate that slopes (friability) are significantly different ($p<0.05$) between biochar treatments.

Conclusion

- Increasing the rate of corn cob biochar improved the water stability of the aggregates compared to the CT, despite the absence of a significant effect on the dispersible clay content.
- For smaller aggregates (1–2mm), tensile strength for BC-20 and BC-20+P treatments was significantly higher than the CT and BC-10, with an opposite trend observed for larger aggregates (4–8 mm and 8–16 mm).
- Corn cob biochar significantly improved soil friability and the ease of tillage quantified with a workability index.

Reference

Dexter, A.R., and B. Kroesbergen. 1985. Methodology for determination of tensile strength of soil aggregates. Journal of Agric. Engineering Research 31:139-147.

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2017 ASA, CSSA, and SSSA International Annul meeting, Tampa, Florida, USA.

Emmanuel Amoakwah*, Emmanuel Arthur, Kwame Agyei Frimpong and Rafiq I. Khandakar.

Corn cob biochar effect on tropical soil aggregate stability and aggregate-associated carbon and nitrogen contents.

http:/scisoc.confex.com/crops/2017am/webprogram/start.html

OHIO AGRICULTURAL RESEARCH AND DEVELOPMENT CENTER

2017 ASA, CSSA & SSSA International Annual Meetings| Florida, U.S.A.

Corn Cob Biochar Effects on Tropical Soil Aggregate Stability and Aggregate-Associated C and N Contents.

Emmanuel Amoakwah[1,2*], Emmanuel Arthur[3], Kwame Agyei Frimpong[2] and Rafiq I. Khandakar[1]

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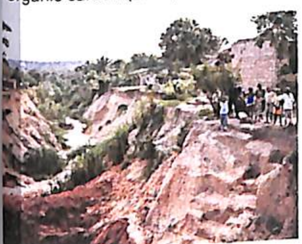
[2]Department of Soil Science, College of Agriculture and Natural Sciences, School of Agriculture, University of Cape Coast, PMB, Cape Coast, Ghana.

[3]Department of Agroecology, Faculty of Science and Technology, Arhus University, Blichers Allé 20, Postbox 50, DK-8830 Tjele, Denmark.

1. Introduction

Soils of the humid tropics are susceptible to accelerated erosion, which consequently affects soil quality in response to loss of soil organic carbon (SOC) via erosion.



- Loss of SOC from the upper fertile horizon.
- Land physically degraded.
- Lands rendered less productive.

1A. Impact

- Productivity affected with low crop yield.
- Increase food insecurity and poverty.

How do we restore and improve soil quality by increasing and/or maintaining SOC contents

1B. Solution

Environmentally-sound and cost effective soil management strategy?

Pyrolysed

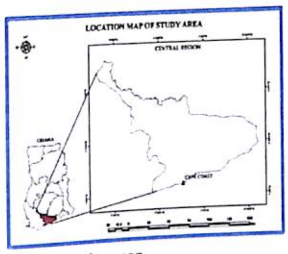
Crop residues

Biochar

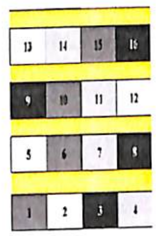
2. Objective

To assess the distribution of aggregate size fractions, aggregate stability, and aggregate-associated C and N contents following corn cob biochar amendments.

3. Materials and methods



Location map



Field layout
- RCBD
- 4treatments with 4 four replications each
- 16 plots (3 m × 6 m each)

Biochar preparation
- Feed stock: Corn cob
- Pyrolytic temperature: 550°C

Biochar dose
- 15 t ha^{-1} (0.51% (w/w)) and 30 t ha^{-1} (1.03% (w/w)) and 30 t ha^{-1} with P (P-enriched biochar).

Treatments
- The treatments are denoted by CT, BC-15, BC-30, and BC-30+P for the 0, 15 t ha^{-1} and 30 t ha^{-1}, and 30 t ha^{-1} with P respectively.

Soil sampling
- Biochar was applied on 7th November 2015. On 16th January, 2017, a spade used to extract bulk, minimally disturbed soil samples from a depth of 0-20 cm for aggregate stability measurements.

Aggregate stability

Wet and dry sieving machine

$$MWD = \frac{\sum m_{i \times d_i}}{\sum m_i}$$

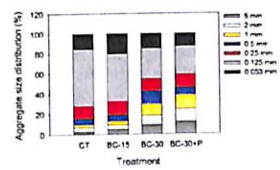
Aggregate-associated C and N determination

The air-dried soil aggregate size fractions were finely-milled prior to the analysis.

Acknowledgments

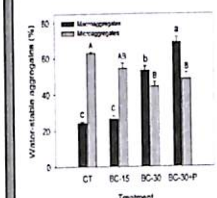
This work was funded by the Danish International Development Agency (Ministry of Foreign Affairs of Denmark) as part of the project "Green Cohesive Agricultural Resource Management, WEBSOC", DFC project no: 13-01AU.

4. Results and discussion

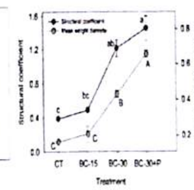


Corn cob biochar effects on aggregate size distribution

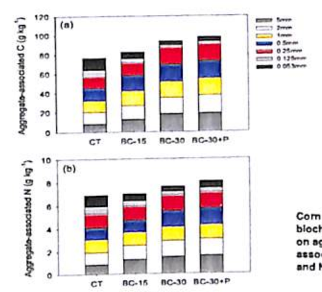
Treatment	Bulk density (g cm^{-3})	Macro aggregate stock (Mg ha^{-1})	Micro aggregate stock (Mg ha^{-1})
CT	1.53 ± 0.00a	735.26 ± 27.55c	62.72 ± 0.51a
BC-15	1.44 ± 0.02b	756.99 ± 55.34c	54.10 ± 2.91b
BC-30	1.38 ± 0.03b	1461.58 ± 65.10b	44.25 ± 2.54c
BC-30+P	1.38 ± 0.03b	1896 ± 88.56a	48.19 ± 3.54c



Effects of different application rates of corn cob biochar on the stability of macro and micro aggregates of a tropical sandy loam.



Effects of different application rates of corn cob biochar on the mean weight diameter and structural coefficient.



Corn cob biochar effects on aggregate-associated C and N (g kg^{-1}).

5. Conclusion

- Increasing the rate of corn cob biochar improved the macro aggregate stocks and enhanced the water stable macro aggregates.
- Increasing biochar application rate significantly enhanced the stability of the aggregates by increasing the mean weight diameter and structural coefficient.
- Corn cob biochar significantly improved aggregate-associated C and N in the macro aggregates

2017 ASA, CSSA, and SSSA International Annul meeting, Tampa, Florida, USA.

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Biochar effects on microbial community profiling of a tropical sandy loam.

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2017 ASA, CSSA & SSSA International Annual Meetings| Florida, U.S.A.

Biochar effects on microbial community profiling of a tropical sandy loam

Emmanuel Amoakwah[1,2*], Emmanuel Arthur[3], Kwame Agyei Frimpong[2] and Rafiq I. Khandakar[1]

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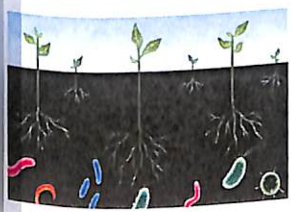
1. Introduction

- Tropical soils experience high temperatures, humidity and intense rainfall.
- Consequent leaching of nutrients
- Low pH (acidity problem)
- Low organic matter content
  - ➢Affects microbial community structure and biological activity.
- Low soil fertility and crop productivity

Economically feasible and sound environmental strategy?

Biochar proposed as one of the amendments to improve soil biology, enzyme activities and microbial community structure.



Soil microbes play critical roles in
- ❖OM decomposition
- ❖Nutrient cycling

Microbial diversity has paramount importance in maintaining soil health to enhance soil productivity.

B. The Game

Environmentally-sound and cost effective soil management strategy?

Crop residues

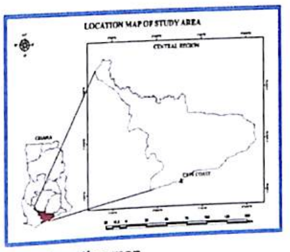
Pyrolysed

Biochar

2. Objective

To study the response of soil enzymes and microbial composition in soils of the humid tropics to biochar application at different rates.

3A. Materials and methods



Location map

Field layout
- RCBD
- 4treatments with 4 four replications each
- 16 plots (3 m × 6 m each)

Biochar preparation
- Feed stock: Corn cob

Pyrolytic temperature: 550°C

Biochar dose
- 15 t ha^{-1} and 30 t ha^{-1} and 30 t ha^{-1} with P (P-enriched biochar).

Treatments
- The treatments are denoted by CT, BC-15, BC-30, and BC-30+P for the 0, 15 t ha^{-1} and 30 t ha^{-1}, and 30 t ha^{-1} with P respectively.

Soil sampling
- Biochar was applied on 7th November 2015. On 16th January, 2017, soil samples from a depth of 20cm soil layer were randomly collected by soil auger (5 cm diameter) from the sixteen plots.

Acknowledgments

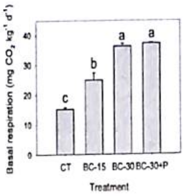
This work was funded by the Danish International Development Agency (Ministry of Foreign Affairs of Denmark) as part of the project "Green Cohesive Agricultural Resource Management, WEBSOC", DFC project no: 13-01AU.

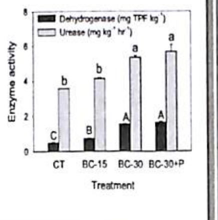
3B. Microbiological properties

Basal respiration, microbial biomass, enzyme activities and phospholipid fatty acids (PLFA), and metabolic quotients.

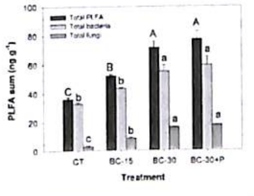
FAME detection and quantification

4. Results and discussion





Treatment	MBC (mg kg^{-1})	MBN (mg kg^{-1})	qCO2	PMC (mg kg^{-1})
CT	39.7 ± 5.88c	20.5 ± 3.55b	0.4 ± 0.07a	5.4 ± 0.53c
BC-15	177.4 ± 7.65b	29.1 ± 2.01b	0.1 ± 0.01b	6.6 ± 0.95bc
BC-30	324.6 ± 27.54a	55.1 ± 3.97a	0.1 ± 0.01b	8.1 ± 0.60ab
BC-30+P	328.50 ± 34.49a	55.68 ± 2.11a	0.12 ± 0.02b	9.1 ± 0.81a



5. Conclusion

- Soil microbial biomass and enzyme activities increased with high rates of corn cob biochar.
- Application of biochar at 30 t ha^{-1} significantly enhanced soil basal respiration and respiratory quotient, and decreased specific maintenance respiration.
- High rates of biochar had significant effects on soil microbial community structure and total PLFA.

APPENDIX D

PAPERS READY TO BE SUBMITTED FOR PUBLICATION

1. Biochar effects on soil microbial biomass, community profiling, and respiration and enzyme activities. To be submitted to *Journal of Agriculture, Ecosystem and Environment*.

2. Organic carbon and nitrogen partitioning in highly weathered tropical soils by corn cob biochar amendments. To be submitted to *Soil Science Society of America Journal*.

3. Does biochar influences soil carbon and nitrogen lability and sequestration in highly tropical soils? To be submitted to *Soil Biology and Biochemistry*.

4. Biochar amendments improve aggregate size distribution, structural properties, and carbon and nitrogen protection in highly weathered tropical soils. To be submitted to *CATENA*.

5. Greenhouse gas emissions in response to biochar amendments of highly weathered tropical soils. In preparation. To be submitted to *Soils and Tillage Research*.

6. Biochar improves soil quality and crop productivity. To be submitted to *Soils and Tillage Research*.