Greening with black

Biochar-soil amendment for low-emission agriculture

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1.1 Climate Change, Agriculture and Food Security

Climate change mitigation is a top priority goal of the 21st century. Whereas climate change affects agriculture through changes in temperature and the amount and variability of rainfall, agriculture affects climate change through alteration in soil cover and emission of greenhouse gases. This interconnectedness between agriculture and climate change poses a significant global contest when addressing the food security challenge. Ultimately, addressing the food security challenge implies dealing with the feedbacks between climate change and agriculture. Although climate change is predicted to affect food security in many parts of the world, its effect is estimated to be greater in the already vulnerable farming communities in sub-Saharan Africa (SSA). The impact of climate change therefore has wide ramifications on the livelihood to many people. Addressing climate change is therefore a prudent way to ensure livelihood sustainability in Africa.

1.2 Agriculture and greenhouse gas emissions

Increase in anthropogenic greenhouse gas (GHG) concentrations between 1951 and 2010 are the most likely cause of rise in mean surface temperature globally (Bindolf et al., 2013). Estimates from the Intergovernmental Panel on Climate Change (IPCC, 2014) show that in 2011, the concentrations of carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) were, respectively, 40%, 150%, and 20%, higher than the amounts before the industrial revolution. The concentrations of these gases have all increased since 1750 due to human activity (IPCC, 2014). Agriculture contributes 24% of total greenhouse gas emissions (Ciais et al. 2013), and is the leading contributor (56%) of non-carbon dioxide greenhouse gases (CH₄...
and N₂O (IPCC, 2014). The major sources of agricultural emissions are the heavy use of nitrogen fertilizers, cultivation of rice paddies, and emissions from livestock. Whereas agricultural soils contribute to GHG emissions, they can also mitigate climate change through direct and indirect GHG abatement such as sequestration of carbon (C) as soil organic matter (SOM), depending on the management practices.

According to Ciais et al. (2013), anthropogenic N₂O emissions are 1.7 to 4.8 TgN (N₂O) yr⁻¹ from the application of nitrogen fertilizers in agriculture. In highly-weathered low-fertility soils of the humid tropics of sub-Saharan Africa, continuous use of nitrogen fertilization and supplementation with green manure is common practice, and is an important soil management strategy (Mucheru-Muna et al., 2007). However, the use of these amendments risks increasing N₂O emissions due to decomposition of organic matter or the provision of excess mineral nitrogen to support denitrification (Jarecki et al., 2009; Peterson and Sommer, 2011). Therefore, climate-responsive innovations that increase food production while sequestering soil carbon and reducing N₂O are needed to reduce the impact of agriculture on the climate system.

1.3 Biochar and greenhouse gas emissions from agricultural soils

Biochar has been proposed as a climate-smart strategy to address the Climate-Agriculture nexus. Several studies have shown that biochar can improve soil fertility (through nutrient additions, improved aeration and moisture storage, reducing leaching of nutrients through leaching, improving nutrient uptake by plants), increase soil carbon sequestration and reduce emission of CH₄ and N₂O from agricultural soils (Zhu et al., 2014; Ding et al., 2016). Owing to the wide variability in these properties, the effects of biochar remain inconsistent and therefore inadequate to make robust recommendation for soil management. Whereas some
studies report mitigation of GHGs from soils following biochar amendment, others report increased emissions. Moreover, the mechanisms underpinning the response remains poorly understood. Further investigations are needed to elucidate the biogeochemical mechanisms responsible for observed disparity in emissions responses in biochar amended soils.

1.4 Mechanisms and controversy surrounding biochar effects on GHGs in soils

1.4.1 Methane

Several studies have shown that biochar can reduce CH$_4$ emission from soils as well as increase oxidation of atmospheric CH$_4$ (Zhang et al., 2010; Yoo and Kang, 2011; Case et al., 2014), suggesting that it can be a good management option to reduce methane concentrations in the atmosphere (Liu et al., 2014; Schimmelpfennig et al., 2014). At the same time, several other studies report the opposite, i.e. increased emissions of CH$_4$ from biochar-amended soils (Spokas, 2013; Singla and Inubushi, 2014), thereby raising questions as to whether biochar increases or mitigates atmospheric CH$_4$.

Soil-atmosphere exchange of CH$_4$ in biochar amended soils is determined by the interaction of several factors, including biochar properties (i.e., feedstock, pyrolysis temperature and quantity) and soil properties (soil texture, soil organic matter content, soil pH, and soil moisture) (Lehmann et al., 2011; Castaldi et al., 2011; Feng et al., 2012; Fungo et al., 2014). Some of the mechanisms proposed include: (i) increased diffusivity of the biochar-amended soil together with reduced (buffered) fluctuations in soil moisture (Karhu et al., 2011), (ii) adsorption of NH$_3$ thereby lowering the NH$_4^+$ concentrations (Taghizadeh-Toosi et al., 2012); (iii) changes in the Archaeal methanogenic or bacterial methanotrophic community and activity (Feng et al., 2012; Khan et al., 2013).
Given the conflicting information in the scientific literature, it is unclear how the various factors, alone and combined, produce the observed effect. There is a need for an assessment in order to improve our understanding of the dominant factors (van Zwieten et al., 2015). To put the study in context, we highlight the principle processes and organisms responsible for production and consumption in the soil, and how introduction of biochar can affect them.

**CH$_4$ production and consumption in soils**

Atmospheric CH$_4$ results from either biogenic, thermogenic or pyrogenic sources (Ciais et al., 2013). Biogenic fluxes arise largely from the biological process in which organic matter decomposition by specialized bacteria under anaerobic conditions (Ciais et al., 2013). Two groups of micro-organisms present in the soil perform the two principle processes of methane production (methanogenesis) and consumption (methanotrophism) (Hanson and Hanson, 1996; Frarrel et al., 2013a).

Methanogenic *Archaea* (Methane-producing microbes) is a phylogenetically diverse group within several unique features, including acting as cofactors and unusual membrane lipids (Bratin et al., 1992; Hanson and Hanson, 1996). Methanogenesis happens only in the absence of oxygen, or where predominantly reducing conditions prevail, with no oxidizing agents such as Fe$^{2+}$, NO$_3^-$, or SO$_4^{2-}$. Methanogens are also highly sensitive to oxygen, temperature (about 20–40°C), and pH (4.0–8.0) (Serrano-Silva et al., 2014). Methanogens are obligate methanogenic deriving energy from the reduction of more oxidized forms of carbon atoms (such as methanol, acetate or methylamine; Cassidy et al., 1996) to form methane and transform carbon dioxide to methane. Furthermore, methanogens utilize a very narrow range of substrates and some can even fix N$_2$ (Jones, 1998; Frarrell et al., 2013b).
Methanotrophs (Methane-oxidizing bacteria) are ubiquitous, phylogenetically and physiologically diverse (Bratin et al., 1992; Hanson and Hanson, 1996). They are obligate methanotrophic and cannot use other substrates (Topp and Hanson, 1991). Methane is oxidized to carbon dioxide through the intermediate Using methanol, formaldehyde, and formate sequential providing energy for Methanotrophs using formadehyde and the primary source of carbon and O2 and the terminal electron accepter (Zheng et al., 2014). The enzyme Methane monooxygenase is the responsible catalyst for this reaction (Hornibrook, et al., 2009).

According to Schnell and King (1995), soils can consume methane as long as they are sufficiently porous to allow diffusion of oxygen to take place. Methanotrophs utilize various aliphatic and aromatic molecules, and are sensitive to many of the same inhibitors (Frarrell et al., 2013b).

**Effects of biochar on CH$_4$ in the soil**

Following the addition of biochar to the soil, a myriad of physical-chemical and biological processes acts interactively to determine the amount and rate of methane fluxes at the soil-atmosphere interface. A simplified model of the critical relationships between biochar and CH$_4$ fluxes is represented in Figure 1.1. In brief, the soil environment can be divided into three components; (1) The microbial community – performs a sequence of biological processes resulting in the production or consumption of CH$_4$; (2) The soil matrix (soil-biochar surfaces) – regulates the supply of substrates, toxins, and reaction surfaces for chemical species and microbes; and (3) The soil micro-environment – mainly soil solution and air, controls the movement of ions and molecules within the soil, and gas exchange between the soil and the atmosphere.
Processes affecting CH$_4$ fluxes that can arise from the addition of biochar into the soil include the following: (i) Biochar may contain a number of organic molecules some of which may be utilized by methanogens, including highly specific one such as acetates, alcohols and methylamines (Frarrel et al., 2013); (ii) Biochar is thought to offer better protection of microbes against predators because of its pore structure (Saito and Marumoto, 2002; Thies and Rillig, 2009; Lehmann et al., 2011); (iii) Biochar may remove organic molecules that could be toxic to microorganisms, such as phenols (De Luca et al., 2009) or produce others such as ethylene (Spokas et al., 2010); (iv) Encapsulation of soil organic matter, including microbes, may reduce decomposition and mineralization or protect microbes from predators; (v) Complexation and/or chelation between biochar surfaces (phenolic hydroxyl and acid groups) and essential trace metals can affect the availability and reactivity of methanogenic as well as methanotrophic activities (Baldock and Smernik, 2002; Bolan et al., 2012; Glaser et al., 2000); (vi) Surface adsorption on biochar may reduce the toxicity of free ammonium to methanotrophs (Berglund et al., 2004; Lee et al., 2005; Lehmann et al., 2006). The observed response in the above-mentioned processes is a function of the quality of biochar, soil properties and the soil microenvironment (Van Zweiten et al., 2015).
1.4.2 Nitrous oxide

\( \text{N}_2\text{O} \) production in soils

\( \text{N}_2\text{O} \) originates mainly from agricultural soils through nitrification and denitrification. Nitrification is a two-step process and includes: (i) the oxidation of \( \text{NH}_3 \), and (ii) the oxidation of \( \text{NO}_2^- \) (Subbarao et al., 2006). Step (i) is rate-determining, and is mediated by autotrophic ammonia–oxidizing prokaryotes while conversion of \( \text{NH}_3 \) to hydroxylamine is catalyzed by ammonia monooxygenase in autotrophic oxidation of \( \text{NH}_3 \) (Francis et al., 2007; Hayatsu et al., 2008). In step (ii), hydroxylamine oxidoreductase oxidizes hydroxylamine to \( \text{NO}_2^- \). During ammonia oxidation, \( \text{N}_2\text{O} \) is always emitted (Poth and Focht, 1985).

Denitrification involves sequential bacteria-mediated steps that start with reduction of \( \text{NO}_3^- \) or \( \text{NO}_2^- \) to NO, then to \( \text{N}_2\text{O} \), and finally to \( \text{N}_2 \). Each step is catalyzed by highly specialized reductase enzymes that include, respectively, nitrate reductase, nitrite reductase, nitric oxide...
reductase, and nitrous oxide reductase (Lashof and Ahuja, 1990; Kim and Bruce, 2008). The catalytic action of nitrite reductase in reducing NO$_2^-$ to NOx, is crucial in the denitrification process since it results in production of N$_2$O as a product (Zhang et al., 2009). The rate of N$_2$O production in the above step is controlled by several factors, including concentration of (NO$_3^-$ and NH$_4^+$), soil temperature, organic carbon content, and aeration (Farquharson and Baldock, 2008; Kim and Bruce, 2008).

**Effect of biochar on N$_2$O production**

The mechanisms for reduction of N$_2$O emission revolve around the following two fundamental principles; (i) inhibition of N$_2$O-forming processes (denitrification, nitrification and nitrifier denitrification), and (ii) Inhibition of the reduction of N$_2$O to N$_2$ by nitrous oxide reductase (N$_2$O-R) and complexation of nitrous oxide by soil/biochar particles. Theoretically, these processes can take place simultaneously in the soil. Biochar addition to soil can thus influence some of these processes that contribute to the fluxes of N$_2$O (Fig. 1.2). The potential effects of biochar on N$_2$O emission are summarized in Table 1.1.

![Figure 1.2: Processes hypothetically influencing N$_2$O emission from soil after addition of biochar](image)

<table>
<thead>
<tr>
<th>Table 1.1: Potential effects of biochar on N$_2$O emission</th>
<th>Effect of biochar on N$_2$O emission</th>
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8
Table 1.1: Processes and mechanisms for the effects of biochar on emission of N\(_2\)O in soils

<table>
<thead>
<tr>
<th>Biochemical process</th>
<th>Reaction mechanisms</th>
<th>Citation</th>
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<tr>
<td>Organic N mineralization</td>
<td>• Retention of inorganic N on biochar surfaces through surface adsorption and microbial immobilization</td>
<td>Berglund et al., (2004); Novak et al., (2010); Bruun et al., (2011); Dempster et al. (2011); Knowles et al., (2011); Ippolito et al., (2012); Nelissen et al., (2012), Nelissen et al. (2015); Nelissen et al. (2014)</td>
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<tr>
<td>Ammonia volatilization</td>
<td>• Adsorption of NH(_3) to biochar depending on biochar surface area and CEC of the soil</td>
<td>Lee et al. (2005); Lehmann et al. (2006)</td>
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<td></td>
<td>• Adsorption of NH(_4^+) and NH(_3)</td>
<td>Van Zwieten rt al. 2010); Kizito et al. (2014); Wang et al. (2015)</td>
</tr>
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<td>Nitrification</td>
<td>• Biochar exerts a direct effect on the activity of ammonia oxidizers and nitrifies by altering NH(_4^+) availability.</td>
<td>Dempster et al. (2011); Knowles et al., (2011); Ippolito et al., (2012); Nelissen et al., (2014); Nelissen et al. (2015); (Castaldi et al., 2011; Wang et al., 2015; He et al, 2018)</td>
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<td></td>
<td>• Biochar-induced changes in soil pH and other physico-chemical properties on the functioning of ammonia oxidizers and nitrifiers at a community level.</td>
<td>Yanai et al. (2007); Wu et al. (2012)</td>
</tr>
<tr>
<td>Denitrification</td>
<td>• Enhancing NO(_3^‐) immobilization in microbial biomass and uptake by plants,</td>
<td>Cayuela et al. (2013)</td>
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<td></td>
<td>• Increasing soil pH</td>
<td>Tryon (1948); Liang et al. (2006); Cheng et al. (2008); Van Zwieten et al. (2014); Su et al., (2019)</td>
</tr>
<tr>
<td></td>
<td>• Promoting soil aeration by reducing bulk density and increasing porosity</td>
<td>Yanai et al. (2007)</td>
</tr>
<tr>
<td></td>
<td>• Increasing nosZ gene expression which encodes the nitrous oxide reductase that reduces N(_2)O to N(_2)</td>
<td>Ducey et al. (2013); Harter et al. (2014); He et al. (2018)</td>
</tr>
<tr>
<td></td>
<td>• Catalyzing electron transfer</td>
<td>Cayuela et al. (2013)</td>
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**Inhibition of N\(_2\)O formation**

Some studies (e.g., Deluca et al., 2006) have demonstrated that addition of biochar increased the rate of nitrification significantly. However, these authors did not show whether the fluxes of N\(_2\)O reduced correspondingly. Although they hypothesize that increased nitrification might have resulted in increased N\(_2\)O emission, this process is not necessarily present in the soil. This is because N\(_2\)O may not be produced if sufficiently oxic conditions prevail. Van Zwietens et al. (2008) showed that the nitrification rate was not affected by the presence of biochar, suggesting that nitrifier activity is not affected by biochar. Being a highly porous material, addition of biochar to the soil will increase pore space and soil aeration and aggregation and water-holding
capacity. Increased aeration does not favour production of N$_2$O. Although there is evidence of an inverse relationship between pH and N$_2$O emission (Bergaust et al., 2010; Liu et al., 2010; Raut et al., 2012; Su), the responsible mechanism is not understood. These studies postulate that low pH interferes with the assembly of the enzyme N$_2$O-reductase.

*Reduction of N$_2$O to N$_2$*

Van Zwieten et al. (2008) postulated that the reduction in N$_2$O emission with biochar application was due to removal of the native soil organic carbon that acts as substrate for heterotrophic denitrifiers. On the other hand, it is also possible that the adsorption of soil organic carbon may enhance its accessibility to microorganisms that flourish on, or around biochar particles. Biochar addition to soil could modify the availability of NH$_4^+$-N, which is also used by some microbes as an energy source instead of CH$_4$ while using O$_2$ as an electron acceptor (Bykova *et al.*, 2007). In such cases, the CH$_4$ uptake into the soil will be reduced while allowing more oxygen to be available hence less denitrification.

Biochar contains a number of functional groups that include hydroxyl, methyl, carboxylic and alkene groups (Li *et al.*, 2013; Stella-Mary *et al.*, 2016). With increasing charring temperature, mass cleavage of O-alkylated groups and anomeric O-C-O carbons occurs prior to the production of fused-ring aromatic structures (Li *et al.*, 2013; Stella-Mary *et al.*, 2016). The composition of these functional groups may modify the activity of denitrifyers and therefore the amount of N$_2$O emitted from the soil. The interactions that exist between biochar-biochar surfaces and biochar-soil surfaces may result in the adsorption and/or complexation of some important bio-molecules responsible for N$_2$O formation or direct interaction with N$_2$O itself. Enhancing enzymatic reduction of N$_2$O to N$_2$ by biochar is an alternative mechanism by which
biochar reduces emission of N\textsubscript{2}O. It is possible that increased pH favours activity of reductase enzymes through improved access to substrates and/or cofactors.

1.5 Research problem

Whereas numerous studies have been conducted, the complexity of the interaction among multiple processes, as described in the previous paragraphs, make our understanding of the role of biochar in regulating GHG emissions incomplete, with several contradictions in the observed effects. Furthermore, most studies on biochar have relied on short-term laboratory investigations, raising questions as to the applicability of the findings to practical situations in field settings and the residual effect of biochar. Cognizant of the abovementioned knowledge gaps, this study was set out to investigate the following specific objectives:

1.6 Objectives of the study

The overall objective of this study was to improve our understanding of the effect of biochar amendment on processes and mechanisms governing the emission of GHG from a variety of tropical soils. The specific objectives of the study were;

1. To determine the effect of biochar quality (feedstock, production temperature, and biochar pre-treatment activation) on the fluxes of N\textsubscript{2}O and CH\textsubscript{4}

2. To evaluate the role of biochar in nitrogen transformation and associated emission of N\textsubscript{2}O and N\textsubscript{2}

3. To assess the influence of biochar on soil aggregate distribution under field conditions under conventional tillage practices

4. To quantify emission intensity, carbon stocks and crop yield in a low-fertility soil under various management options
5. To analyze the residual effect of biochar on soil mineral nitrogen, NH$_3$ and N$_2$O in a field soil three years after application of organic and mineral resources

### 1.6 Significance of the study

Results from this study will be helpful in designing soil fertility management practices such as reducing the use of nitrogen fertilizers. Efforts are underway to include biochar in carbon-trading schemes. The information in this thesis can be helpful in providing indications as to the timeframe within which biochar can stay in the soil while providing benefits for farmers. The wide-scale use of biochar as a climate-smart agricultural practice will depend on the comprehensive scientific understanding of the processes it influences after application to agricultural soils. The net magnitude of these processes and their interaction has to be assessed mechanistically and for their practical significance. These processes must be seen to produce practical benefits to farmers in terms of crop yields while maintaining their carbon sequestration and emission reduction potential. The fast-changing climate coupled with the high population growth lays urgency to these investigations since they are likely to provide immediate and long-lasting solutions to the climate change-agriculture-food security nexus.

### 1.7 Study area

This study was conducted using soils from western Kenya, a region where sustainable soil management is extra important because the soils in this region are highly weathered and low in nutrients due to the continuously high temperatures. However, information on appropriate management options is chronically lacking. The farming in western Kenya is representative of many areas in sub-Saharan Africa. That is to say, farming is primarily small-scale (farms averaging 0.3 to 3 hectares in size), with about 75% of total agricultural output produced on rain-fed agricultural lands, and the systems are highly integrated (many enterprises in spatial
mixtures on the same piece of land) (Government of Kenya, 2012). The area receives bimodal rainfall, with long rains occurring from March to June and the short rains from August to November, totaling 1500–1800 mm annually (Fig. 1.3). Long-term mean temperature ranges between 22 and 24 °C. The geology of the survey area consists of rocks and sediments of Precambrian to recent times. The system of rock covers in the area is characterized by granites. The granite is not uniform throughout. It has variations which include syenites, granodiorites, dolerites and rhyolites (GoK, 1984).

Some of the processes that make tropical soils different from temperate ones are as follows: (a) Ionization of water is four times as high as at 10°C, (b) Silica is eight times as soluble, (c) Dissolution proceeds much quicker, (d) Less CO$_2$ penetrates the soil, (e) The hydrolytic power of the solution is much higher, (f) Soil water is less viscous, (g) More water penetrates deeper in the soil (Buring, 1970). Two soil types were used; Acrisol and Feralsols . All of these soils are characterized by a high content of 1:1 type clays, a presence of highly insoluble minerals such as quartz sand and sesquioxides, and a low cation exchange capacity (CEC).
Figure 1.3: Location of the study site in western Kenya; (a) Location of Kenya relative to the world map; (b) Elevation map of Kenya showing the western highlands; (c) The climate zones indicating the Equatorial climate in the study site; (d) A satellite map showing the vegetation structure.