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**Greening with black**

*Biochar-soil amendment for low-emission agriculture*

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## **7.1    Key findings**

This study was set out to improve our understanding of the role played by biochar in regulating the emission of greenhouse gases in agricultural soils. The five specific objectives stated in this study were addressed as follows: Objective 1 was to find out the extent to which biochar quality (feedstock, production temperature, and biochar pre-treatment) affect fluxes of N<sub>2</sub>O and CH<sub>4</sub>. The hypothesis was that surface chemistry of biochar, which is a function of its feedstock and production conditions, was responsible for its effect on soil-borne GHG emissions. It was observed (Chapter 2) that manipulating factors that affect surface chemistry of biochar resulted in changes in emission of CH<sub>4</sub> and N<sub>2</sub>O. Thus, the hypothesis is supported. This implies that surface chemistry and adsorption reactions play a significant role in the mechanisms regulating emission of CH<sub>4</sub> and N<sub>2</sub>O in soils. This is one of the direct ways in which biochar affects emission of these gasses.

The second objective was to find out how biochar quantity affects nitrogen transformation pathways and hence nitrous oxide emission in contrasting tropical agricultural soils. Nitrogen dynamics (nitrification, denitrification and ammonification) were hypothesized to be slowed by the presence of biochar due to the presence of organic functional groups and molecular retentions mechanisms. The results (Chapter 3) showed that biochar affects nitrogen dynamics differently in soils with different mineralogical composition. A more suppressive effect of biochar was observed in a Ferralsol (dominated by low-activity clays (mainly kaolinite, and a high content of sesquioxides) compared to an Acrisol (with high base saturation and high-activity clays). Neither soil mineralogy nor the biochar amount had a straightforward effect on N<sub>2</sub>O emissions. The gross N transformation did not correlate significantly with N<sub>2</sub>O emission,

suggesting biochar has a decoupling effect on the relation between N<sub>2</sub>O emission and mineral nitrogen. Instead, there seems to be a significant contribution of biochar to the final step of denitrification; the conversion of N<sub>2</sub>O to N<sub>2</sub> as observed in the effect of biochar on the N<sub>2</sub>O:N<sub>2</sub> ratio (Chapter 3). This observation suggests the existence of complex mechanisms possibly related to organo-mineral interactions and/or biochemical catalysis involved in biochar-amended soils.

The third objective sought to establish if there is a linkage between biochar and soil aggregation because fluxes of GHG are known to respond to soil aggregation (Khali et al., 2005; Uchida et al., 2008; Mangalassery et al., 2013; Pramanik et al., 2014; Nie et al., 2014). I envisaged that soil aggregation affects soils aeration, which in turn affects diffusion of gasses. Compacted soils have more restricted air movement and can increase formation of N<sub>2</sub>O due to lack of O<sub>2</sub>. The evidence generated by this thesis (Chapter 4) supports the assertion of the link between biochar and soil aggregation only when applied together with other easily mineralizable organic matter sources (such as *T. diversifolia* green manure).

Another important question that this study aimed to answer was whether biochar application to the soil can contribute to low-emission agriculture in tropical environments (Objective 4). It was found that biochar can reduce emission intensity of GHGs, increase SOC stocks and crop yield on a tropical soil. Therefore, the results confirm that biochar can have significant positive effect on low-emission agriculture. Greater net primary productivity in biochar-amended soils is the main reason for reduced CO<sub>2</sub>-eq.

The fifth and final objective aimed at finding out how long the residual effect of biochar remains relevant in the soil under tropical field conditions. It was found that the crop yield and

GHG mitigation benefits are maintained beyond three years, but they reduce steadily over time. This gradual decrease in the benefits of biochar are attributed to the gradual neutralization of initially active biochar surfaces charges, perhaps due to complexation and chelation in organo-mineral interactions with the soil-biochar matrix.

## **7.2 Mechanisms of biochar effect on GHG emissions**

### *Surface chemistry and adsorption reactions*

This thesis set out to investigate the mechanisms of biochar's influence on GHG emissions and its applicability to farm fields in tropical field conditions. The understanding of biochar mechanisms has improved after the investigations in this thesis. First, it has been found that surface chemistry generally plays a significant role as a mechanism for biochar effect on CH<sub>4</sub> and N<sub>2</sub>O from soils. N<sub>2</sub>O can break down by bonding with transitional metal cations since it can accept as well as donate electrons (Armor and Taube, 1971; Tolman, 2011). According to Sun et al. (2017), surface functional groups on biochar potentially facilitate electron transport through the carbon matrix. Surface chemistry of biochar is a function of feedstock and production conditions (Mukherjee et al., 2011; McBeath et al., 2015; Abas et al., 2018; Zhang et al, 2019).

Volatile matter content of biochar, also a consequence of production conditions, is correlated to CO<sub>2</sub> and N<sub>2</sub>O (Ameloot et al., 2013). Ameloot et al. (2013) also proposed that by providing microorganisms readily available substrate, increased emissions from biochar-amended soils may be observed. Overall, it can be inferred from these studies that to optimize biochar for reduced emissions, biochar produced at moderate temperatures (450 °C– 600 °C) is required.

### *Nitrogen dynamics and ion exchange*

The second mechanism investigated by my study is the role of biochar on nitrogen dynamics and associated N<sub>2</sub>O emissions. In the initial stages of biochar research, it was believed that the reduced availability of inorganic-N pools [NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>] (Table 1.1) is a precondition for reduced N<sub>2</sub>O emissions. These N forms are important precursors of soil nitrogen from which N<sub>2</sub>O is derived. However, the results of this thesis in the laboratory (Chapter 3) and under field conditions (Chapter 6) do not support the relationship between nitrogen dynamics as important predictor of biochar's role on GHG emission. It was also thought that NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> could be bound with biochar probably through ion exchange, surface complexation, hydrogen bonding, or Van der Waal's interactions (Essington, 2004). This decreases available mineral N that would otherwise be used during nitrification and denitrification (Clough and Condon, 2010; van Zwieten et al., 2010; Kameyama et al., 2012; Yao et al., 2012; Prommer et al., 2014). To date, contradictions remain concerning biochar-induced nitrogen dynamics and GHG emissions. For example, whereas Case et al. (2015) found that nitrification, denitrification, N immobilization and N<sub>2</sub>O emission all increased with biochar amendment, the effect of biochar on N availability could not explain N<sub>2</sub>O suppression.

In contrast, Edwards et al. (2018) recently found that biochar stimulated nitrification-derived N<sub>2</sub>O emissions when soil ammonium was high. Su et al (2019) found that although pH strongly correlated with abiotic N<sub>2</sub>O production, its contribution to gross emission was minute. Results of this thesis (Chapter 3) showed reduced N<sub>2</sub>O emission that is independent of mineral N dynamics. Since, soil biochar amendment has been found to increase the diversity of nirK and typical nosZ transcripts and relative gene and transcript copy numbers of the nosZ-encoded bacterial N<sub>2</sub>O reductase, microbial species that are specialized on direct N<sub>2</sub>O reduction (Harter et al., 2014; Harter et al., 2017), I suspect a mechanistic link between biochar and N<sub>2</sub>O

reductase, however the elucidation thereof remains a knowledge gap to be explored in future research.

### *Soil aggregation*

The third mechanism tested by my study is that biochar can improve soil physical properties (aggregation and aeration) and hence reduce anaerobic conditions that support N<sub>2</sub>O emission (Chapter 4). I hypothesized that biochar hastens build-up of macro-aggregates, improves aeration and this could reduce denitrification in soil micropores. Under integrated biochar-manure systems, the results of Chapter 4 support earlier evidence that biochar can increase soil aggregation (Liu et al., 2014; Obia et al., 2015).

However, Bandyopadhyay and Lal, (2014) observed that emissions of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> were significantly higher from the large macro-aggregates than from other aggregate size fractions, and that the contributions of the large macro-aggregates emissions towards those of bulk soil were significantly higher than those of micro-aggregates and the mineral fraction. Nie et al. (2014) also found higher C decomposition enzyme activities in micro-aggregates, but specific enzyme activity for N decomposition was higher in macro-aggregates. Mangalassery et al. (2013) reported a higher CH<sub>4</sub> flux in both macro- and micro-fractions, and no difference for N<sub>2</sub>O fluxes.

In Chapter 4, I found that when easily mineralizable SOM sources are available, biochar increased soil aggregation, which in turn is predicted to reduce emission of GHGs. This view is contradicted by the observation of Pramanik et al. (2014), who reported that cover crop applications increased N contents in smaller aggregates (<250 µm), which proportionately increased the N<sub>2</sub>O emission potential. Therefore, I have been able to verify that biochar can

indeed increase soil aggregation. However, our understanding of the correlation between biochar -induced aggregation and GHGs needs further investigation. It is even less clear if the response is the same for different soil types, a question. that remains to be answered. My suspicion is that the proportion of particle size fraction in the whole soil is the single most important factor determining whether a soil emits more or less N<sub>2</sub>O. The higher the proportion of macro-aggregates, the lower the emission of N<sub>2</sub>O and vice versa. This hypothesis needs to be tested by further studies. Another hypothesis that needs to be tested is whether soil mineralogy interacts with soil texture to affect N<sub>2</sub>O dynamics in the soil.

### **7.3 Practical potential of biochar**

#### *Emissions abatement*

Besides questions that target improving mechanistic understanding of the effect of biochar on GHG emissions, I have attempted to answer questions of a practical nature. The first is whether biochar can potentially reduce the CO<sub>2</sub>-equivalent under field conditions while providing yield improvement for farmers. The results of this thesis (Chapter 4 and 5) show that through the application of biochar in combination with carefully selected combinations of other soil amendments, a significant increase in crop yields can be realized while minimizing negative environmental consequences of agricultural practices.

Although yield benefits have already been reported in previous studies (Chan et al., 2007; Major et al., 2010; Zhang et al., 2012; Qiao-Hong et al., 2014), as have the GHG effect of biochar in agricultural systems (Rogovska et al., 2010; Feng et al., 2012; Cayuela et al., 2015), this thesis provides additional information on the combined benefits in both yield and environment dimensions. Now we know that both yield benefits and GHG mitigation can be achieved practically when biochar is integrated in agricultural systems in the tropics.

### *Build-up of SOM and structure*

The practical benefits of biochar application to field soils as observed in arise from the increased SOC, soil aggregation (Chapter 4) and lower emission intensities coupled with increased crop yield (Chapter 5). Since soil structure is a key factor for soil maintenance and for the physical and biological processes that it involves (Celik et al., 2004; Wortmann and Shapiro, 2008), the aggregate stability brought about by biochar carbon input are partly responsible for these benefits. Lower fertilizer input required under biochar amendment, (Chapter 5) provides an avenue for avoided emissions and reduces the cost of fertilizer for resource-constrained small-holder farmers in developing economies. This is consistent with previous studies on N-use efficiency of biochar systems showing that biochar systems require less fertilizer compared to systems with mineral fertilizer only (e.g. Zhang et al., 2012; Yoo et al., 2013). Alling et al. (2014) showed that biochar provides essential mineral nutrient required for plant growth in addition to improving soil buffer capacity. These additional benefits of biochar work together with soil physical, chemical and biological properties to improve crop yields.

This study has shown that when biochar is applied to a low-fertility soil, emission intensities can be reduced and crop yields can be increased. The results of this thesis concur with those of previous ones (e.g. Wang et al., 2013; Yang et al., 2017; Rodrigues and Horan, 2018), which found that overall, system-level emissions are a lower for pyrolysis-based systems compare to combustion counterparts. They noted, however, that these results are sensitive to biochar's ability to suppress N<sub>2</sub>O emissions and increase soil organic carbon, which are subject to high uncertainty. These observations imply that biochar is a promising option for achieving triple benefits of increasing carbon sequestration, increased crop yields and low-emissions in tropical agricultural systems.



#### 7.4 Further observations

This thesis found that biochar alone did not have an effect on emission intensity except where organic amendments were present (Chapter 4 and 5). Similarly, meta-analyses (Cayuela et al., 2014; Sagrilo et al., 2014; He et al., 2017) showed that whereas biochar does not affect CH<sub>4</sub>, it increases CO<sub>2</sub> emissions (Mean = 25±3%) and lowers N<sub>2</sub>O emissions (Mean = 41±7%). Nonetheless, a meta-analysis of yield-scaled greenhouse gas intensity (Lui et al., 2019) showed that biochar had no effect on greenhouse gas intensity when no nitrogen fertilizer was applied. The increase in CO<sub>2</sub> and CH<sub>4</sub> in biochar-amended soils is related to the increased metabolic activity of microbes from increased supply of mineralizable C supplied by the biochar, higher SOC status and the more active soil microbial activities (Smith et al., 2010; Jones et al., 2011; Zimmerman et al., 2011; Liu et al., 2016).

The unexpected results showing that N dynamics do not affect N<sub>2</sub>O emissions may be because the main source of N<sub>2</sub>O from soils is microbial-mediated (Cayuela et al., 2013; Van Zwieten et al., 2014) and soil N is important for microbial activity. Many biological processes in soil utilize nitrogen directly or indirectly. Besides, several studies show that biochar accelerates soil N transformations, thereby increasing soil N bio-availability (van Zwieten et al., 2014). However, some studies have shown that biochar limits availability of NO<sub>3</sub><sup>-</sup>, (Kameyama et al., 2012; Yao et al., 2012), which is a major precursor for denitrification and N<sub>2</sub>O emission. This leaves questions as to the main mechanism for biochar's role on nitrogen dynamics and N<sub>2</sub>O emission.

Another unexpected result of this thesis is the observation that biochar application rate did not affect N<sub>2</sub>O emission in the incubation study (Chapter 3). Previous studies show a consistent positive correlation between biochar rate and N<sub>2</sub>O emission (Cayuela et al., 2014; Laghari et

al., 2015; Mandal et al., 2018; Lan et al., 2019). Biochar studies have used highly variable application rates ranging from < 0.5% to >10%. The biochar rate of 2% and 4% w/w used in the incubation study (Chapter 3) was based on the average value for most studies at the time. This point to the inconsistencies still remains concerning the range within which the application rate can be responsive. For example, two separate studies (Sun et al., 2014 and Xiao et al., 2016), both using forest soils, applied widely different rates (30 t ha<sup>-1</sup> and 5 t ha<sup>-1</sup>) observed comparable reductions in N<sub>2</sub>O emissions (~26%). According to Jin et al. (2019), from the point of view of crop yields and economic benefits, about 11 t ha<sup>-1</sup> biochar is the optimal biochar application rate for the local farmers in China, while Pandit et al. (2018) has proposed 15 t ha<sup>-1</sup> in Nepal. Even then, this is still a high application rate for most farmers in tropical Africa.

Notwithstanding improvement in crop yields in biochar amended-soils, biochar can achieve low-emission agriculture if careful combinations of biochar and other soil amendments are applied. Noteworthy is that nitrogen is a resource that needs to be included in biochar systems because of biochar's ability to immobilize N (Zhu et al., 2019; Li et al., 2019; Jin et al., 2019) to the extent that even the little nitrogen available in low-N soils such as those in the tropics. Information on the effect of biochar on GHG emission over time is largely lacking. However, previous evidence on crop yield (Glaser et al., 2002; Lehmann and Rondon, 2006; Steiner et al., 2007; Cornellison et al., 2018) supports the observed decreasing trend in a biochar effect.

The greatest challenge that remains for biochar in agricultural systems is how to access adequate materials and design appropriate production technologies to avail biochar to resource-constrained farmers for soil application (Singh, et al., 2014; Kavitha et al., 2018). Torres-Rojas et al (2011) estimated that in western Kenya, the amount of biomass available to an average household can produce an average of 0.46 t ha<sup>-1</sup> y<sup>-1</sup> of biochar if they use an improved "First-

generation pyrolytic cook stove” to reduced wood energy consumption. This will require up to five years to achieve the rate of 2.5 t ha<sup>-1</sup> that was used in my study.

Nevertheless, results in Chapter 5 suggest that it is possible to continue realizing yield benefits for up to three years after a single dose of biochar. As observed in Chapter 2, the production conditions for biochar significantly influence the quality, and hence the resultant benefits. Previous studies using biochar for soil amendment used application rates ranging from two to ten tons per hectare. These are large quantities that are hardly available to an average farmer. The argument is that there are several materials available for biochar production such as sugarcane bagasse from sugar factories, sawdust from carpentry workshops. At the moment, these materials are considered waste and pose challenges for disposal. Moving feedstock from the gardens to where the pyrolysis takes place constitutes a large proportion of the production cost. Therefore, developing technologies for efficient conversion of such materials can improve access to biochar for soil application.

## **7.5 General conclusions and recommendations**

### ***Conclusions***

The evidence from this thesis has demonstrated that biochar application generally increases emission of CO<sub>2</sub> and CH<sub>4</sub> but largely reduces N<sub>2</sub>O emission from agricultural soils. Similarly, it has emerged from this study, that removing volatile matter from biochar through steam activation can increase N<sub>2</sub>O emission. Activation of biochar using steam enhanced its capacity to suppress CH<sub>4</sub> and N<sub>2</sub>O emission, and the effect of steam activation is dependent on production conditions (feedstock and pyrolysis temperature) of the biochar. Based on this knowledge, pyrolysis systems should be tailor-made to produce “designer” biochar, which has specific chemical properties matched to overcome limitations of tropical soils. I also found no

direct linkage between soil nitrogen dynamics in the laboratory and in the field, indicating that this is not a major factor in regulating N<sub>2</sub>O suppression by biochar both in the short-term (days) and long-term (years). Furthermore, biochar application rate did not affect N<sub>2</sub>O emission. As a practical benefit of biochar to farmers, this thesis has revealed that biochar can achieve low-emission agriculture by increasing soil C sequestration and crops yields if careful combinations of biochar and other soil amendments are applied. Biochar soil-amendment can contribute to reducing GHG intensity by up to 65% depending on how other soil amendments are managed. The contribution of biochar on reducing GHG emissions decreases over time but can continue for more than three years under tropical field conditions. Over the six consecutive seasons that a field trial was conducted, the effect had reduced by more than half.

### ***Recommendations***

While a large body of evidence supports the positive effect of biochar on reducing GHG emissions, improved yield and soil carbon sequestration, significant uncertainty remains since several studies still show no or negative results, particularly under field conditions. Multi-location field trials involving a wide range of biochar and soil properties should be undertaken to improve accuracy of the estimated effects of biochar on various agronomic and environmental benefits. Such trials should be monitored over a long time (5-10 years) to fill the knowledge gap concerning the long-term effects of biochar application under field conditions. Furthermore, field trials comparing various combinations of soil amendments should be used to determine the optimum soil management regimes that make biochar application economically feasible for low-income farmers.

Comparing the pore structure, organic by-products, and surface functional groups of biochars produced under a range of conditions is required to develop production parameters for biochar

for specific agronomic requirements. Such studies should aim at developing stoichiometric models combining a wide range of properties in order to improve the predictability of the response of biochar when applied in soils amendments.

Although numerous studies emphasize denitrification as the major source of  $N_2O$  emission from soil, the role of the nitrification pathway needs to be investigated in light of the fact that biochar increases nitrification rate. This potential pathway for  $N_2O$  emission in biochar amended soils should be explored further use of  $^{15}N$  tracer techniques combined with nitrification inhibitors and direct  $N_2$  measurements in order to distinguish pathways for  $N_2O$  and  $N_2$  production. Besides, other abiotic pathways for  $N_2O$  production from soils such as breakdown of hydroxylamine and reduction of nitrate need to be studied under different soil types.

Further microbiological studies need to be undertaken to identify the relationships between microbial-mediated processes and the denitrification pathways. Biochemical (enzyme activity) and genetic (gene abundance) studies have been conducted and relationships with  $N_2O$  emission identified but the mechanism linking them remains elusive. The tendency for  $N_2O$  to act as an electron acceptor as well as donor may be the critical stage at which  $N_2O$  is broken down to  $N_2$  under the catalytic influence of biochar surface chemistry. There is a need to use levelled  $N_2O$  in non-soil systems to investigate conditions for formation and breakdown of  $N_2O$  with or without biochar. This will shade light on the role of biochar in the reduction of  $N_2O$  to  $N_2$ .

The economics of biochar production from a wide range of feedstock such as saw dust, sugarcane bagasse and municipal biomass waste application, including its inclusion in global

carbon markets remains an important area for further investigation. It will also be useful to investigate the possibility of improving biochar behavior in Biochar-Fertilizer blending. Social studies to establish perception and acceptability of biochar use in soil fertility management among small-holder farmers in developing countries are necessary. Such studies should consider the socio-economic environment and farming systems where biochar will be applied.