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Biochar-soil amendment for low-emission agriculture

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CHAPTER TWO: N₂O and CH₄ emission from soil amended with steam-activated biochar

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2.1 Introduction

Biochar has been reported to reduce emission of the potent greenhouse gasses (GHGs), nitrous oxide (N₂O) and methane (CH₄) from soils (*Singh et al.*, 2010; *Cayuela et al.*, 2013). Studies on the impact of biochar applications to soil further indicate that biochar quality (e.g. feedstock, pyrolysis conditions) is important but highly variable (*Joseph et al.*, 2010). More recently, post-production modifications of biochars have targeted to improve their properties with respect to nutrient retention. *Borchardet al.* (2012) showed that steam activation of biochar increased retention of NO₃-N by up to 55% compared to non-activated biochar. Activation by steam is also reported to increase the surface area from <10 m²/g to approximately 650 m²/g and pore size up to 14 Å (*Azargohar and Dalai*, 2008) depending on temperature and activation time.

The above process likely removes condensates of volatile compounds and increases biochar's pore space and size, surface area and adsorptive capacity for small molecules such as gasses and common solvents (*Rouquerol et al.*, 1999) and thus enhances diffusion of gasses and also the mobility and efficiency of microorganisms. These effects are also thought to alter the surface functional groups that affect the electro-chemical properties of biochar. Steam activation also enhances porosity (*Azargohar and Dalai*, 2008; *Enders et al.*, 2012;

Schimmelpfennig and Glaser, 2012) of the biochar that should increase soil aeration, which in turn affects the production of N₂O and CH₄. However, it has not been directly investigated whether steam activation has also an effect on N₂O and CH₄ emissions. The objective of this study was to investigate the effect of steam activation of biochar on the emission of N₂O and CH₄ from a highly weathered tropical upland soil.

2.2 Materials and Methods

Experimental design

The soil for the experiment was collected from Kapsengere on the southern Nandi hills in western Kenya (00° 09' 34''N and 34° 57' 37''E) at an elevation of 1750 m a.s.l. The area receives a mean annual rainfall of 2024 mm with mean annual temperature of 19°C. The soil is a humic Acrisol that was converted to agriculture around the year 1900 and has a low nutrient content. Soil used for the experiment was collected from a depth of 0.2 m, air-dried and sieved through a 2 mm sieve before being mixed with biochar to an equivalent rate of ~15 t/ha (2.6 kg of dry soil with 36 g of the biochar). Two source materials (maize stover and eucalyptus wood) were used to produce biochar. The feedstock was chopped and ground into 5 mm-sized particles and fed into a 60 L batch pyrolysis unit using Argon as a sweep gas at a flow rate of one liter per minute. For each feedstock, two pyrolysis temperatures (350°C and 550°C) were used to make biochar. The pyrolysis unit was programmed with a ramp temperature rate of 5°C per min and a maximum temperature dwell time of two hours before cooling. For each grade of biochar made, one part was steam activated (activated biochar) while the other was not (non-activated biochar) making a total of nine treatments (Table 2.1). Steam activation was done by injecting de-ionized water into the kiln after reaching maximum temperature. Water flow rate was 10 mL per minute for two hours.

Table 2.1: Experimental treatments

Treatment No.	Feed stock	Pyrolysis temperature (°C)	Steam activation
1	Maize stover	350	Activated
2			Non-activated
3		550	Activated
4			Non-activated
5	Eucalyptus wood	350	Activated
6			Non-activated
7		550	Activated
8			Non-activated
9	No biochar	-	-

Four replicated plastic pots (0.17 m *d* and 0.15 m *l*) per treatment were prepared and laid out in a completely randomized design in a greenhouse. Due to the inherent P deficiency of the soil, an equivalent of 1 kg / ha of triple super phosphate was added. The moisture content of the pots was maintained at 70% of water holding capacity by periodic weighing and replacement of water lost by evaporation. The mean temperature of the greenhouse ranged from 20°C to 35°C. The experiment was run for 34 days.

Gas measurements

Measurements of N₂O and CH₄ were conducted using the static chamber method. A cuvette (cylindrical chamber) made from stainless steel (0.15 m *d* and 0.185 m *l*) was fitted with two openings to allow air to flow in and out during measurement. The openings were connected to the inlet and outlet points of a photo-acoustic infrared multi-gas monitor (INNOVA 1312-5, Lumasense Technologies A/S, Ballerup, Denmark) by two 0.7 m-long Teflon tubes as inflow and outflow to the cuvette. The multi-gas monitor was calibrated and set to compensate the cross-interference of gases and water vapor with NH₃, N₂O and CO₂. The calibration of the gas monitor was done by Lumasense Technologies, Denmark two weeks before the experiment. To overcome the problem of cross-interference, a filter carousel was installed in the monitor and an algorithm that computes the interference CH₄ on N₂O was included. Inside the cuvette,

air humidity and temperature were determined by a digital thermo-hygrometer (PCE-313 A, Paper-Consult Engineering Group, Meschede, Germany). This was attached to the cuvette from the outside and only the sensor reached inside the cuvette through a tight screw connector made of PVC. The concentration of the gas in the chamber was determined at time 0, 2, 4 and 6 minutes after chamber closure.

Soil and biochar analysis

Elemental analysis was done by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Ciros, CCD, Spectro, Germany) after sample extraction using modified dry-ashing technique (Enders et al., 2012). The pH was measured in triplicate in 1:20 soil:deionized water after shaking at 200 rpm for 24 h. Percentage of volatile material, ash content, and elemental (C, H, O, N, and S) content were determined on an oven dry-weight following the ASTM D 3172 and 3176 standard methods. Soil and biochar properties were determined in four replicates. The properties of the soil and biochar used in the experiment are shown in Table 2.2.

Statistical analysis

Cumulative gas fluxes were obtained by calculating the area of trapezia under the flux-time curve and summing the results while assuming linear changes in measurements between time intervals. Treatment effects (n=4) were tested using multivariate analysis of variance and individual treatments separated at 5% level of significance using Wilk's lamda. Partial Eta-square (Table 3) indicates the proportion of total variability attributable to the respective factor. The interpretation is similar to that of R^2 in univariate regression analysis (Levine and Hullett, 2002). The CO₂-e of each treatment was calculated as the sum of the individual gas fluxes

multiplied by their corresponding “global warming potential”, considering the CO₂-equivalent of 298 for N₂O and 25 for CH₄ over a 100-year time horizon (see *Zhang et al.*, 2012).

Table 2.2: Chemical properties of soil and biochar used in the pot experiment

Characteristic	Soil	Maize Stover				Eucalyptus			
		350		550		350		550	
		None	Steam	None	Steam	None	Steam	None	Steam
pH	6.2	9.3	9.3	10.0	10.0	7.5	7.0	9.5	10.2
P	108.7	1.91	2.70	3.22	2.96	0.14	0.11	0.21	0.34
K	0.82	25.40	27.78	39.70	14.53	0.88	1.09	3.44	4.44
Ca	0.57	4.84	4.34	6.57	12.05	4.72	4.49	6.03	6.59
S	nd	0.72	0.84	0.90	0.59	0.08	0.05	0.09	0.07
Na	nd	1.09	0.63	0.45	1.17	1.68	1.91	2.05	1.95
Mg	0.11	2.55	2.58	3.29	5.62	1.12	1.29	1.88	1.94
Fe	5.29	3.02	3.31	4.86	0.26	0.00	0.42	0.06	0.11
Al	6.52	4.57	5.04	7.29	0.16	0.06	0.03	0.01	0.02
Mn	nd	0.19	0.17	0.25	0.09	0.20	0.26	0.36	0.40
Cu	nd	0.08	0.03	0.06	0.12	0.02	0.03	0.15	0.11
Ti	nd	0.08	0.07	0.10	0.00	0.00	0.00	0.00	0.00
Ni	nd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sr	nd	0.05	0.05	0.07	0.02	0.04	0.04	0.05	0.06
B	nd	0.00	0.01	0.01	0.00	0.03	0.02	0.03	0.01
Zn	14.6	0.09	0.21	0.11	0.06	0.14	0.25	0.07	0.04
Ba	nd	0.10	0.09	0.13	0.01	0.08	0.09	0.12	0.12
C (%)	nd	67.1	57.5	67.7	78.97	67.1	61.6	83.2	87.7
N (%)	nd	0.78	0.71	0.51	0.58	0.23	0.22	0.19	0.13
O (%)	nd	14.0	26.6	14.0	6.4	27.1	32.3	10.8	7.3
H (%)	nd	3.51	3.63	1.94	3.86	3.84	3.71	2.37	2.45
*Volatile matter (%)	nd	32.2	31.0	14.1	12.0	35.1	34.6	12.2	11.5
Ash (%)	nd	14.6	11.6	15.8	10.2	1.7	2.2	3.5	2.4
Molar C:N	nd	85.5	81.3	133.9	136.3	287.8	282.9	438.8	681.3
Molar H:C	nd	0.05	0.06	0.03	0.05	0.06	0.06	0.03	0.03
Molar O:C	nd	0.21	0.46	0.21	0.08	0.40	0.52	0.13	0.08

*Material lost when moisture-free biochar is heated to 950°C. Units for the elements are in mg g-soil⁻¹. nd=Not determined.

2.3 Results and Discussion

Overall, biochar addition to soil reduced N₂O but increased emission of CH₄ (Fig. 2.1a). All of the activated biochars showed lower emissions of N₂O compared to the non-activated biochar by 10-41%, except the 350°C wood biochar which showed no difference due to activation (Fig. 2.1a). This may be due to removal of sorbed labile carbon from volatile condensates, and

improving diffusion of toxic oxygen (*Case et al., 2012*) thereby allowing for more effective N₂O reductase enzyme and thus lower N₂O emission from soil. The electron shuttle role proposed by *Cayueta et al. (2013)* for biochar's role on N₂O reduction to N₂ may be due to organic rather than mineral matter interactions. Further investigation into the complexity and distribution of organic functional groups is necessary to better understand impact on of biochar emission of GHGs.

Activated stover-derived biochar increased CH₄ emission by approximately 14-70% but a reverse effect of similar magnitude was observed for activated wood-derived biochar (Fig. 2.1b). There seems to be significant difference in pore structure between stover and wood derived biochar to explain this disparity in CH₄ emission following steam activation. Some studies (*Steinbeiss et al., 2009; Feng et al., 2012*) have suggested that the continuous porous structure of biochar increases retention of CH₄ and thus provide “hot spots” for methanotrophic proliferation. *Spokas et al. (2011)* reported that volatile organic carbon composition of biochar, linked with others, result in both stimulative and inhibitive effects in plant and microbial systems.

A multivariate analysis showed that feedstock, temperature and steam activation of biochar all have significant effect on emission of both N₂O and CH₄ (Table 2.3). Presence of biochar could catalyze N₂O reduction to N₂ as end-product by acting as an electron shuttle (*Cayueta et al., 2013*). By increasing the pore volume and size (*Azargohar and Dalai, 2008*) and altering surface functional groups, activation of biochar may affect its pH buffer capacity, specific chemical toxins, metal complexes and precipitation products resulting from its addition to soil. All these very likely processes are not clearly understood and thus warrant further investigation. Results further show that feedstock, temperature and activation explained 32, 10 and 56% of

differences in N₂O while 22%, 22% and 21% of variations in missions of CH₄ emissions were explained by feedstock, temperature and steam activation, respectively (Table 3). Emission of N₂O is lower by 17% if maize stover biochar is activated compared to Eucalyptus wood biochar, and 3% lower if pyrolysis temperature is 350°C compared to 550°C. CH₄ emission is higher by 21% if activated biochar was made from maize stover compared to Eucalyptus wood and 10% lower if the pyrolysis temperature was 350°C compared to 550°C.

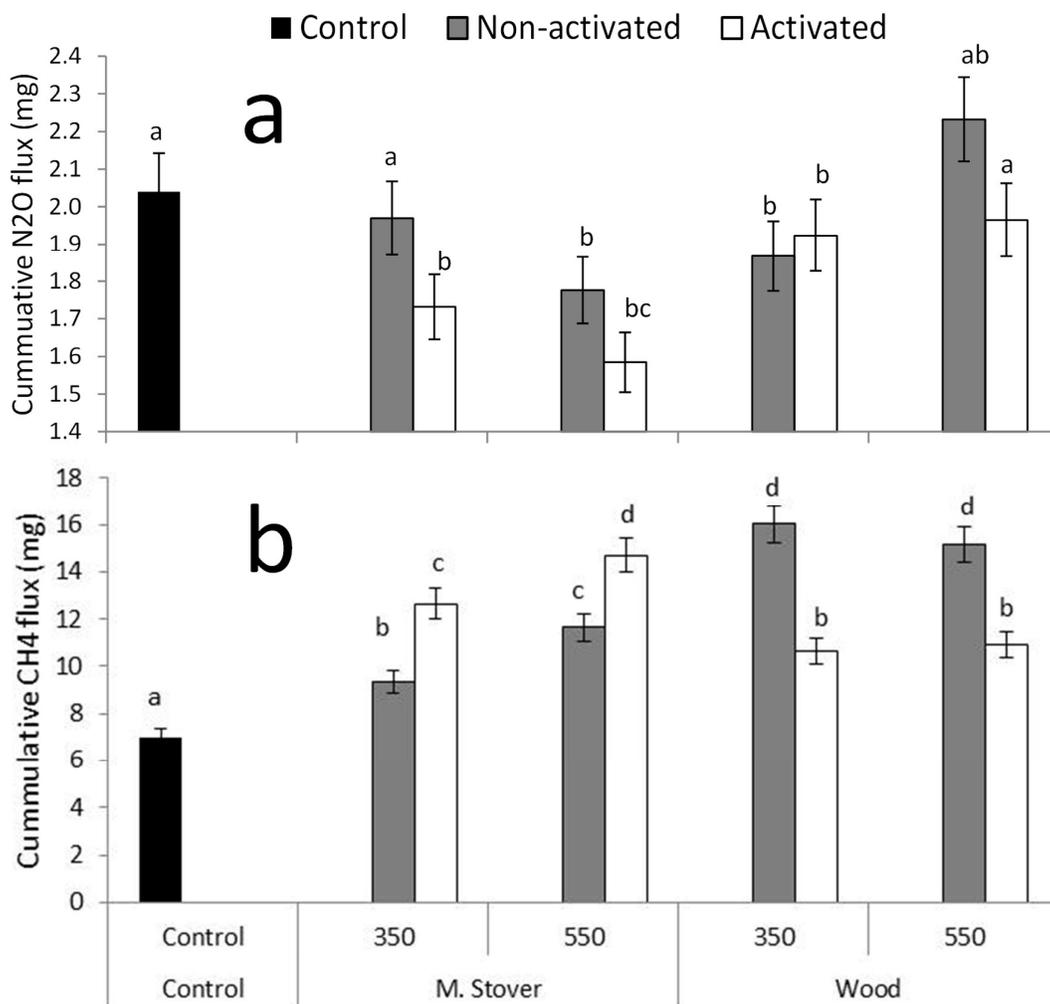


Fig. 2.1: Cumulative emissions of nitrous oxide (a) and methane (b) over 34-days and as affected by biochar quality (feedstock, pyrolysis temperature and steam activation). Different

letters indicate significant differences between the treatments at $P < 0.05$. Error bars are standard errors ($n=4$).

Important to note is that steam activation explained a large part (56%) of variation in N_2O emissions, suggesting a crucial role of either surface area, pore size and volume or surface functional groups on N_2O production and/or reduction. Sorption behavior of N_2O on biochar has been reported in earlier studies (*McBain, 1926; Hitoshiet al., 2002*). N_2O , having both N and O heteroatoms, normally serves as a good ligand in metal ions and is expected to have ligand properties somewhat similar to those of NO or N_2 (*Dong-Heon, 2006*). Although the N_2O coordination adducts reported in literature are scarce, one notably well-characterized N_2O coordination complex is known. Spectral evidence suggests the existence of N_2O plus $[Ru(NH_3)_5(N_2O)]^{2+}$, which is in equilibrium with N_2O (*Armor and Taube, 1971*). Ruthenium (Ru) is a d-block element like iron and copper, which are known to play important roles in denitrification enzymes. Formation of complexes similar to that observed with Ru may occur in soils, favouring the observed reduction in N_2O but this area requires more research. Feedstock, pyrolysis temperature and activation may all affect the speciation and abundance of metals and therefore requires more research.

Table 2.3: Effect size indices (partial eta-squared) for feedstock, pyrolysis temperature and steam activation on emission of CH_4 and N_2O from soil

Source of variation	Partial eta-squared	
	CH_4	N_2O
Feedstock	0.22	0.32
Pyrolysis temperature	0.22	0.10
Steam activation	0.21	0.56
Error	0.35	0.08

Only non-activated biochar made from eucalyptus wood at $550^\circ C$ showed a significantly higher CO_2-e (0.39 kg CO_2-e) of the combined effect of N_2O and CH_4 emissions from soil

compared to an unamended control (0.31 kg CO₂-e; sd=3.48). None of the other treatments differed in their CO₂-e from the control.

2.4 Conclusions and Recommendations

We conclude that steam-activation of eucalyptus wood-derived biochar enhances biochar's capacity to suppress CH₄ and N₂O emission. The effect of steam activation is dependent on feedstock and pyrolysis temperature of the biochar. Further investigation into the pore structure, organic by-products, surface functional groups and especially the surface metal species of biochar following activation will cast more light on responsible mechanisms.