Short Communication

N$_2$O and CH$_4$ emission from soil amended with steam-activated biochar

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Abstract

Steam-activation increased CH$_4$ emission of stover biochar but decreased it for wood biochar by 14%–70%. Biochar generally increased CH$_4$ emission but reduced N$_2$O emission by 10%–41%. Emission of N$_2$O was 17% lower for maize-stover biochar compared to *Eucalyptus*-wood biochar, and 3% lower for 350°C compared to 550°C pyrolysis temperature. Emission of CH$_4$ was 21% higher for activated stover biochar compared to *Eucalyptus*-wood biochar and 10% lower for 350°C compared to 550°C pyrolysis temperature. No difference in net CO$_2$ equivalent was observed among biochar grades.

1 Introduction

Biochar has been reported to reduce emission of the potent greenhouse gasses (GHGs), N$_2$O and CH$_4$, 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. *Borchard* et al. (2012) showed that steam activation of biochar increased retention of NO$_3^-$-N by up to 55% compared to nonactivated biochar. Activation by steam is also reported to increase the surface area from < 10 m^2 g^{-1} to ≈ 650 m^2 g^{-1} and pore size up to 14 Å (*Azargohar* and *Dalai*, 2008) depending on temperature and activation time. This 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 and organo-mineral properties of biochar-soil matrix. 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 N$_2$O and CH$_4$. However, it has not been directly investigated whether steam activation has also an effect on N$_2$O and CH$_4$ emissions. The objective of this study was to investigate the effect of steam activation of biochar on the emission of N$_2$O and CH$_4$ from a highly weathered tropical upland Humic Acrisol.

2 Materials and methods

The soil for this experiment was collected from Kapsengere on the S Nandi hills in W Kenya (00°09′34″ N; 34°57′37″ E) at an elevation of 1750 m asl. 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 passed through a 2-mm sieve before being mixed with biochar to an equivalent rate of ≈ 15 t ha^{-1} (2.6 kg of dry soil with 36 g of the biochar). Two source materials (maize stover and *Eucalyptus* wood) were used to produce the 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 1 L min^{-1}. For each feedstock, two pyrolysis temperatures (350°C and 550°C) were used to make the biochar. The pyrolysis unit was programmed with a ramp temperature rate of 5°C min^{-1} and a maximum temperature dwell time of 2 h before cooling. For each grade of biochar made, one part was steam-activated (activated biochar) while the other was not (nonactivated biochar), making a total of 9 treatments (Tab. 1). Steam activation was done by injecting de-ionized water into the kiln after reaching maximum pyrolysis temperature. Water flow rate was 10 mL min^{-1} for 2 h.

Four replicated plastic pots (∅ 0.17 m, height 0.15 m) per treatment were prepared and laid out in a completely randomized design in a greenhouse. Due to the inherent P defi-

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Table 1: Experimental treatments.

Treatment No.	Feed stock	Pyrolysis temperature / °C	Steam activation
1	maize stover	350	activated
2			nonactivated
3		550	activated
4			nonactivated
5	*Eucalyptus* wood	350	activated
6			nonactivated
7		550	activated
8			nonactivated
9	no biochar	–	–

ciency of the soil, an equivalent of 1 kg ha^{-1} 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 d.

2.1 Gas measurements

Measurements of N_2O and CH_4 were conducted using the static chamber method. A cuvette (cylindrical chamber) made from stainless steel (⌀ 0.15 m, length 0.185 m) 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 multigas 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 multigas monitor was calibrated and set to compensate the cross-interference of gases and water vapor with NH_3, N_2O, and CO_2. The calibration of the gas monitor was done by Lumassence Technologies, Denmark 2 weeks before the experiment. To overcome the problem of cross-interference, a filter carouse was installed in the monitor and an algorithm that computes the interference CH_4 on N_2O 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 min after chamber closure.

2.2 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-to-deionized water after shaking at 200 rpm for 24 h. Percentage of volatile material, ash content, and elemental (C, H, O, N, and S) contents were deter-

mined on an oven-dry weight following the ASTM D 1762-84 and 3176 standard methods. Briefly, Organic C was quantified by pretreating 1 g of biochar samples with 38% HCl. Initial removal of carbonates was achieved by fuming the samples with concentrated HCl to prevent physical loss before transfer into silver capsules. The capsules were held upright in a porcelain spot plate (#60430, CoorsTek, Inc., Golden, CO, USA) and placed on a digestion block preheated to 80°C in a fume cupboard and covered with an inverted Nalgene™ (Thermo Fisher Scientific, Waltham, MA, USA) lid. A 40-mL aliquot of 38% HCl was put into a 25 mm × 150 mm borosilicate tube (#9825-25, Corning Life Sciences, Corning, NY) that was placed into the block under the cover. Samples were fumed overnight and retrieved the next day after all HCl had evaporated. Carbonate dissolution was completed by drop-wise additions of 38% HCl followed by drying at 80°C prior to preparing the capsules for analysis. Hydrogen (H) was determined by combustion using a Hekatech HT Oxygen Analyzer interfaced to a PDZ Europa 20–20 isotope ratio–mass spectrometer (Sercon Ltd., Cheshire, UK). Total O was derived by difference. Soil and biochar properties were determined in four replicates. The properties of the soil and biochar used in the experiment are shown in Tab. 2.

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 (Tab. 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 CO_2 equivalent of each treatment was calculated as the sum of the individual gas fluxes multiplied by their corresponding "global-warming potential", considering the CO_2 equivalent of 298 for N_2O and 25 for CH_4 over a 100-y time horizon (see *Zhang* et al., 2012).

3 Results and discussion

Overall, biochar addition to soil reduced N_2O but increased emission of CH_4 (Fig. 1). All of the activated biochars showed lower emissions of N_2O compared to the nonactivated biochar by 10%–41%, except the 350°C wood biochar which showed no difference due to activation (Fig. 1a). This may be due to removal of sorbed labile C from volatile condensates, and improving diffusion of toxic oxygen (*Case* et al., 2012) thereby allowing for more effective N_2O reductase enzyme and thus lower N_2O emission from soil. The "electron-shuttle" role proposed by *Cayuela* et al. (2013) for biochar's effect on N_2O reduction to N_2 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 CH_4 emission by ≈ 14%–70% but a reverse effect of similar magnitude was observed for activated wood-derived biochar (Fig. 1b). There seems to be significant difference in pore structure between

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Table 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.

stover- and wood-derived biochar to explain this disparity in CH_4 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 CH_4 and thus provide "hot spots" for methanotrophic proliferation. *Spokas* et al. (2011) reported that volatile-organic-C 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 N_2O and CH_4 (Tab. 3). Presence of biochar could catalyze N_2O reduction to N_2 as end-product by acting as an electron shuttle (*Cayuela* 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 addi-

tion 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 N_2O while 22%, 22%, and 21% of variations in missions of CH_4 emissions were explained by feedstock, temperature, and steam activation, respectively (Tab. 3). Emission of N_2O 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. Emission of CH_4 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.

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
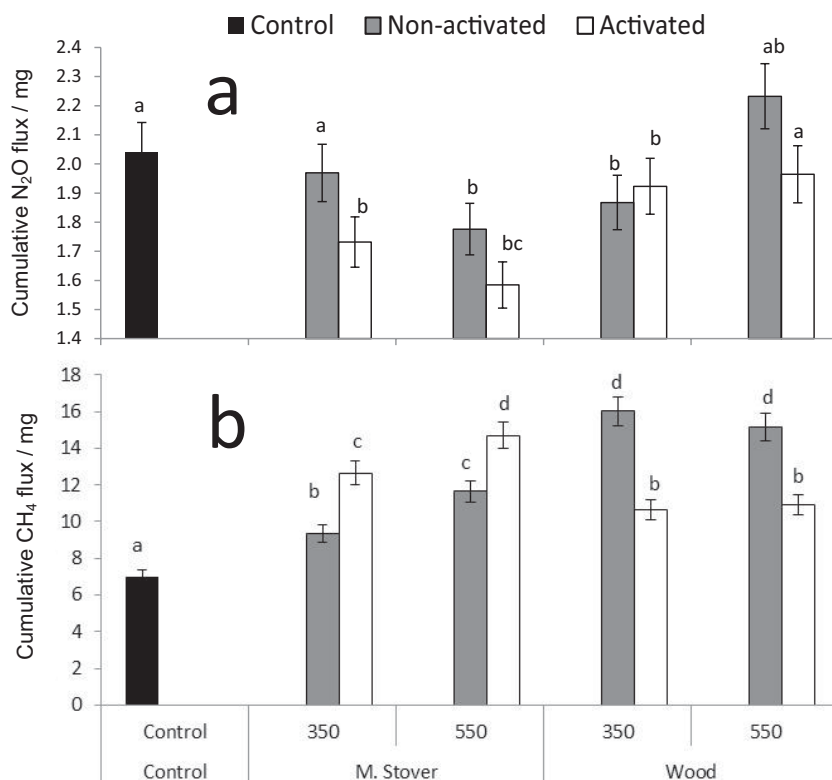
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Figure 1: Cumulative emissions of N_2O (a) and CH_4 (b) over 34 d and as affected by biochar quality (feedstock, pyrolysis temperature, and steam activation). Different letters indicate significant differences between the treatments at $P < 0.05$. Error bars are standard errors ($n = 4$).

studies (*McBaim,* 1926; *Hitoshi* et 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 Fe and Cu, which are known to play important roles in denitrification enzymes. Formation of complexes similar to that observed with Ru may occur in soils, favoring 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 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 nonactivated biochar made from *Eucalyptus* wood at 550°C showed a significantly higher CO_2 equivalent (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 CO_2-e; sd = 3.48). None of the other treatments differed in their CO_2-e from the control.

4 Conclusions and recommendations

We conclude that steam activation of *Eucalyptus*-wood-derived biochar enhances biochar's capacity to suppress CH_4 and N_2O 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.

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