



GHG impacts of biochar: Predictability for the same biochar



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ABSTRACT

One potential strategy to abate increasing atmospheric carbon dioxide (CO₂) levels is to sequester CO₂ as biochar, a structural form of carbon created through the pyrolysis of various biomass materials. Biochar may be applied to soils, but has resulted in variable impacts on net soil greenhouse gas (GHG) emissions, with results spanning from suppression to stimulation. This laboratory incubation study examined the impacts of the same hardwood biochar (fast pyrolysis at 550 °C) to elucidate driving variables affecting previously observed carbon dioxide (CO₂) fluctuations as well as nitrous oxide (N₂O), and methane (CH₄) production impacts across ten different US soils with and without biochar (10% w/w). Biochar application significantly impacted CO₂ ($P=0.04$) and N₂O ($P=0.03$) production following amendment across all soils, but there were no differences observed in CH₄ production/oxidation rates ($P=0.90$). Interestingly, the induced biochar GHG alterations were significantly correlated to the original GHG production activity in the control soil, suggesting a more universal response across various soils to the same biochar than has been previously hypothesized. After correcting for the amount of CO₂ released from the biochar itself [$24 \mu\text{g C g}_{\text{BC}}^{-1} \text{d}^{-1}$], there was no statistically significant alteration in the actual soil CO₂ mineralization rate for any soil. This suggests that the observed increase in CO₂ production was solely attributed to the abiotic CO₂ releases from the biochar. On the other hand, there was an average suppression of 63% in the N₂O production across all soils following biochar addition, which was again correlated to initial N₂O production activity. For this particular biochar, there are predictable impacts on the GHG production potential across various soils despite differences in soil chemistry, texture, and microbial communities.

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1. Introduction

The discovery and use of renewable energy sources is critical to the sustainability of the planet. One well known source is biomass, which has been historically used for energy and chemical production (Hawley, 1926). Biomass can originate from numerous sources; for example, in agriculture the generation of biomass waste is particularly high in sectors such as sugarcane production (Ribeiro and Raiher, 2013) and forestry product processing (Thompson et al., 2001). Energy from biomass is commonly associated with gasification, combustion, and its conversion to liquid biofuels (Voivontas et al., 2001). Additionally, biomass can be transformed through pyrolysis into biochar (Lehmann, 2007). The addition of the biochar products to soil has been speculated to

improve soil quality and increase carbon sequestration (Atkinson et al., 2010; Ameloot et al., 2013). In the context of global changes in temperature and atmospheric carbon balance, the ability to sequester carbon dioxide (CO₂) via biochar could be a viable mitigation strategy to lower atmospheric CO₂ levels (Goldberg, 1985; Lehmann, 2007).

By definition, biochar is a more stable form of carbon created through pyrolysis for carbon sequestration purposes (Sohi et al., 2010b; Spokas, 2010; Manyà, 2012). The use of biochar to increase soil carbon and fertility, while simultaneously reducing soil greenhouse gas (GHG) emissions has been a growing topic of study in recent years (Asai et al., 2009; Ameloot et al., 2013; Mašek et al., 2013). The capacity of biochar to sequester carbon is due to the transfer of atmosphere–biosphere cycling carbon to a slower cycling less microbial degradable structural form (Spokas, 2010; Zimmerman et al., 2011; Harvey et al., 2012). Due to its aromatic chemical nature, biochar is more recalcitrant to microbial decomposition than the original feedstock (Biederman and Harpole, 2013; Gurwick et al., 2013) and thereby postulated to

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exist for hundreds to thousands of years in the soil (Goldberg, 1985; Zimmerman, 2010; Castaldi et al., 2011; Zimmerman et al., 2011; Harvey et al., 2012; Ameloot et al., 2013; Mašek et al., 2013; Kuzyakov et al., 2014). However, recent studies also highlight its fragile physical nature, thereby physically disintegrating into suspended colloidal fractions (Jaffé et al., 2013; Spokas et al., 2014).

Biochar amendments to soil have the potential to reduce GHG emissions including CO₂, methane (CH₄), and nitrous oxide (N₂O) (Cayuela et al., 2010; Scheer et al., 2011); however the reported effects of biochar on GHG emissions are variable (Taghizadeh-Toosi et al., 2012a,b). Reductions in CO₂ production in biochar amended soils have been observed in some studies (Zimmerman et al., 2011; Harvey et al., 2012; Lentz et al., 2014), while no significant differences or stimulation in CO₂ production between control and biochar amended soils have been reported elsewhere (Spokas and Reicosky, 2009; Zimmerman et al., 2011). Likewise for CH₄, studies show suppressed CH₄ production (Rondon et al., 2007), while another reports observed increased CH₄ production (or reduced methanotrophic activity) (Spokas and Reicosky, 2009; Fungo et al., 2014). In contrast, the incorporation of biochar has more consistently reduced N₂O production in soils, with no clear indication of driving mechanism or responsible properties of the biochar (Cayuela et al., 2013).

Biochar is cited to be capable of sequestering nitrogen within its aromatic structure during the pyrolysis process (Smith et al., 1988; Hilscher and Knicker, 2011) and decreasing levels of N₂O production following soil applications (Huang et al., 2004; Yanai et al., 2007). Therefore, biochar may act as an agent for mitigating nitrogen losses and potentially serve as a slow-release N-fertilizer in agricultural soils (Laird et al., 2010; Taghizadeh-Toosi et al., 2012a; Clough et al., 2013). There is also the hypothesis that biochar reduces N₂O emissions in soils with high denitrification activity and potentially could increase N₂O emissions in soils dominated by nitrification production (Sánchez-García et al., 2014; Cayuela et al., 2015). However, the exact mechanisms behind these reductions and their duration in soils are not fully known (Cayuela et al., 2013; Clough et al., 2013).

The variability in GHG production following biochar amendments has been linked to a number of factors. The heterogeneity among biochar properties is one such factor contributing to the observed differences. Depending on the biomass material,

pyrolysis conditions and post-production processing (Mészáros et al., 2007; Keiluweit et al., 2010; Harris et al., 2013), biochars can vary in both the numbers and type of associated chemical moieties (Singh et al., 2010; Uchimiya et al., 2013) and contain unique mixtures of sorbed volatile organic compounds (Spokas et al., 2011; Quilliam et al., 2012). Furthermore, the inherent variability of soil properties at all scales (e.g., Parkin, 1987) may impact soil-biochar-microbial interactions (Jaiswal et al., 2014) and consequently the GHG production (Cayuela et al., 2013; Cornelissen et al., 2013; Van Zwieten et al., 2014).

At present, the GHG mitigation potential of biochar is difficult to estimate because the mechanisms of the GHG suppression have not yet been fully elucidated (Lehmann et al., 2011; Ameloot et al., 2013; Cayuela et al., 2013). Attempts at deriving unified mechanisms of biochar interactions (Jeffery et al., 2011; Biederman and Harpole, 2013; Liu et al., 2013) have been restricted in part by the variability among biochars studied as well as the variability among soils. It has been known for some time that dissimilar soils have different biochar mineralization potentials (Potter, 1908); however, only a limited number of studies have examined multiple soil types. Therefore, the objective of this study is to evaluate GHG emissions (CO₂, N₂O, and CH₄) in 10 US soils with and without the identical biochar amendment through a laboratory assessment. This will allow an investigation into potential correlations to soil properties across different soils and elucidate potential mechanisms behind biochar GHG suppression or enhancement by reducing the variability due to different site specific climatic conditions (e.g. air and soil temperatures, soil moisture).

2. Materials and methods

2.1. Soil sampling

Surface soils (0–5 cm depth) from 10 locations across the US were selected for this study. A random grab soil sample from 0–5 cm was taken from at least 3 locations within a 2 m radius and then homogenized to comprise each of the 10 soil samples. This depth interval typically contains the maximum soil microbial activity for the soil profile (Panettieri et al., 2014). The soil samples were air dried, ground and sieved through a 2-mm sieve. Following this the samples were stored until time of analysis

Table 1
Soil properties.

Soil location	Soil taxonomy	OM ^a %	CEC ^b ppm	pH	P	K	Ca	Mg	S	Na	Zn	Mn	Fe	Cu	B
Forest soils															
Minnesota – F (MN-F)	Mixed, frigid Spodic Udipsamment	2.10	3.10	4.90	145	52	318	38	23	17	2	25	447	1.3	0.20
Wisconsin – F (WI-F)	Sandy, mixed, frigid, Entic Haplorthod	0.50	1.10	6.89	55	22	128	27	18	16	0	16	76	1.3	0.10
Agricultural soils															
California (CA)	Coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents	1.30	9.60	7.50	98	112	1816	262	19	25	14	78	75	22	0.70
Florida (FL)	Siliceous, hyperthermic Mollic Psammaquents	0.90	3.90	7.30	73	21	894	29	13	17	4	7	118	4	0.20
Minnesota – A (MN-A)	fine-silty over skeletal, mixed, superactive, mesic Typic Hapludoll	4.80	16.90	6.10	60	156	2568	507	12	25	4	119	190	3	1.00
South Carolina (SC)	Fine, kaolinitic, thermic Typic Paleaquults	1.30	2.40	6.20	69	106	300	73	11	16	6	14	99	2	0.10
Idaho (ID)	Coarse-silty, mixed, superactive, mesic Durinodic Xeric Haplocalcid	1.50	19.0	7.60	18	176	345	152	1	62	2	15	6	2	0.10
Illinois (IL)	Fine-silty, mixed, superactive, mesic Typic Endoaquolls	4.30	15.80	6.30	21	152	2552	472	18	22	2	60	144	3	0.60
Michigan (MI)	Coarse-loamy, mixed, mesic Typic Hapludalfs	1.80	8.10	5.80	31	104	1172	208	12	25	2	61	196	2	0.20
Pennsylvania (PA)	Fine-loamy, mixed, active, mesic Ultic Hapludalfs	2.80	9.10	6.50	39	103	1810	126	9	20	1	202	118	2	0.40

^a OM, organic matter.

^b CEC, cation exchange capacity (cmol_c/dm³).

Table 2
Biochar properties.

Feedstock	Hardwood sawdust
Pyrolysis temperature (°C)	550
pH	7.1
% C _{total}	63.9
% C _{inorganic}	2.1
% C _{organic}	61.8
% N	0.44
% O	11.8
% H	3
% Ash	21.1
% VM ^a	26.1
% FC ^b	52.8
SSA ^c (m ² g ⁻¹)	0.8

Note: All composition percentages are based on oven-dried (105 °C) weight basis.

^a VM, volatile matter.

^b FC, fixed carbon.

^c SSA, specific surface area by BET N₂ adsorption method (Brunauer et al., 1938).

(lab temperature). Agricultural soils were collected from Minnesota, Florida, South Carolina, Idaho, Illinois, Pennsylvania, Idaho, Michigan, and California and forest soils from Minnesota and Wisconsin, which together represent a range of potential soil properties (Table 1). Soils were analyzed for typical micro- and macro- nutrient contents by a commercial soil testing laboratory (A&L Laboratories, Memphis, TN) (Table 1).

2.2. Biochar

The biochar used in this study was prepared from hardwood sawdust under fast pyrolysis conditions (550 °C; Dynamotive Energy Systems; Vancouver, Canada). The biochar is a very finely grained biochar (<0.3 mm) which facilitates uniform mixing with the soil. This particular biochar was selected since it has been shown to significantly reduce N₂O emissions (Spokas et al., 2009) and nitrate leaching in previous studies (Ippolito et al., 2014). The biochar underwent proximate analysis (ASTM D1762, Hazen Research; Golden, CO), ultimate analysis (ASTM D3176, Hazen Research; Golden, CO) and surface area analysis (BET, N₂, Material Synergy; Oxnard, CA) (Table 2). The biochar was applied at a rate of 10% w/w to all soils in this experiment. The 10% by weight biochar addition has been used in previous laboratory studies (Ippolito et al., 2014); although an unrealistic application rate for agronomic soils, it provides a measurable impact of biochar additions on GHG production (Spokas et al., 2009).

2.3. GHG incubations

Quadruplicate incubations were conducted for each soil (S) with and without biochar (B). For each soil type, the treatments were:

1. (S + B) = Soil (5 g) + Biochar (0.5 g) + DI water.
2. (S) = Soil (5 g) + DI water.
3. (BC) = Biochar Control: 1 g BC + 0.3 mL DI water.

The amount of DI water that was added was sufficient to bring each soil up to field capacity (−33 kPa). There were no differences in the amount of water added to the biochar incubations for each soil type, since there were no significant differences observed in the water holding capacity of any soil (drained from saturated state; data not shown). Soils and biochar were manually mixed in 125 mL serum bottles prior to water addition. Then, soils were pre-incubated for 7 days prior to the start of the incubation to

ensure re-establishment of stabilized microbial dynamics, and avoid the initial spike in GHG production following rewetting (Franzuebbers et al., 1996; Lamparter et al., 2009). Biochar control incubations were conducted to assess the production or consumption of CO₂, N₂O and CH₄ from the biochar itself in an aerobic environment. DI water was added to these incubations, since previous data has shown that the presence of moisture increases the abiotic release of CO₂ from biochar (McBain et al., 1933; Zimmerman, 2010; Jones et al., 2011).

All incubations were conducted in pre-sterilized serum vials (Wheaton Glass, Millville, NJ) and sealed with red butyl rubber septa (Grace, Deerfield, IL). Gas samples were periodically withdrawn from the incubations for analysis on a gas chromatographic system to quantify gas production over a 45-d incubation period. Gas samples were taken at different time intervals throughout the incubation, with biweekly reading for the first two weeks, then weekly for the remainder of the experiment. O₂ headspace levels remained >15% throughout the incubation, ensuring aerobic conditions. The gas chromatographic system consisted of a headspace sampler (Agilent, Foster City, CA, model 7694) that was modified with the addition of a 10-port diaphragm sample valve (Valco, Houston, TX, model DV22-2116). Initially, 5 mL of lab air (known composition) was injected into the sealed vials to allow the withdrawal of a 5 mL headspace sample without altering headspace gas pressure. The syringe was flushed 3 times to allow for adequate mixing of the serum bottle headspace. Five mL of gas was then pulled back into the syringe and subsequently injected into an autosampler vial that was previously helium-flushed for analysis. Concentrations from the GC were mathematically corrected for dilution from the 5 mL of air and converted to a mass basis by the ideal gas law. The GC system used was previously described in Spokas and Bogner (2011). The rate of production of each gas was calculated as the linear increase in the gas concentration as a function of time ($R^2 > 0.90$) for the 45 day incubation period.

2.4. Ammonia, nitrate and nitrite

At the conclusion of the experiment (day 45), two of the replicate GHG incubations were extracted with 2 M KCl for 1 h at a soil to liquid ratio of 1:5. After settling for 0.5 h, extracts were centrifuged and filtered (no. 42; Whatman, Maidstone, UK). Filtrates were then stored (−20 °C) until analysis. Filtrate samples were analyzed for ammonium-N [NH₄⁺-N] and the sum of nitrite-N and nitrate-N [NO₂⁻-N + NO₃⁻-N] using a flow-through injection analyzer (Lachat, Milwaukee, WI). Filtrates were then analyzed solely for nitrite-N [NO₂⁻-N] and the amount of nitrate-N was calculated by difference.

2.5. Statistical analysis

Results for the CO₂, N₂O, and CH₄ production rates were reported as the arithmetic means of the four replicates, while ammonia-N, nitrate-N and nitrite-N results were averages of duplicate samples. The average GHG production rates and extractable nitrate concentration between control and biochar treatments were analyzed across the different soil types using one-way ANOVAs with post-hoc Tukey's test to analyze for significant interactions among the soil types. The assumption of normality was verified with the Kolmogorov–Smirnov test and homogeneity of variance was confirmed with the Bartlett test. Linear regression analyses were used to further explore relationships among soil variables. Significance was defined as $p \leq 0.05$, unless otherwise indicated. R statistical software was used for all analyses (R Core Team, 2014).

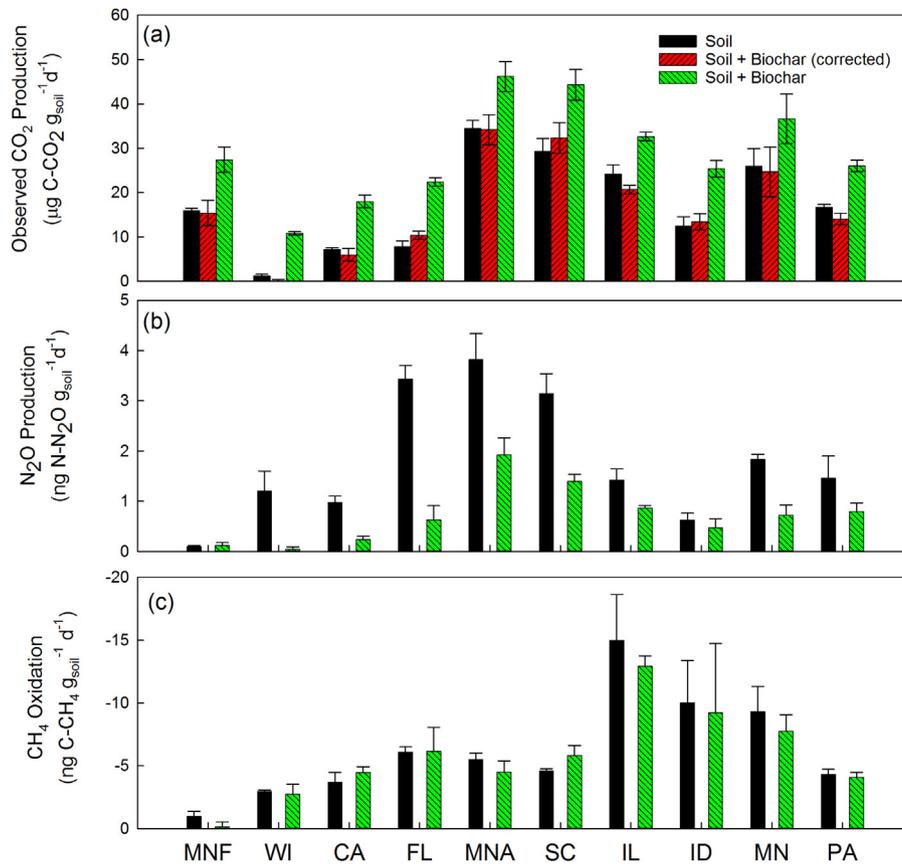


Fig. 1. Observed cumulative production rates of (a) CO_2 , (b) N_2O and (c) CH_4 from soils with and without biochar over the 45 day incubation. Error bars represent one standard deviation of the quadruplicate samples. The symbol is the location abbreviation (Table 1), MN-F: Minnesota Forest; WI-F: Wisconsin Forest; CA: California; FL: Florida; MN-A: Minnesota Agriculture; SC: South Carolina; IL: Illinois; ID: Idaho; MI: Michigan; and PA: Pennsylvania.

3. Results

3.1. GHG production impacts

Fig. 1 presents the observed average cumulative rates of CO_2 , N_2O and CH_4 production in the various soils with and without biochar. In order to account for production of CO_2 from the biochar itself, the subtraction of a biochar control (with no soil) was used (Spokas et al., 2009). The biochar in this study produced $24 \mu\text{g C g}_{\text{BC}}^{-1} \text{d}^{-1}$. This rate suggests a loss of $\sim 4.4 \text{ mg C g}_{\text{BC}}^{-1} \text{yr}^{-1}$ from abiotic oxidation (or $0.4\% \text{ C yr}^{-1}$). Contrary to the observed CO_2 production in the biochar control, no significant N_2O or CH_4 production/consumption was observed. Therefore, no biochar correction was applied to the CH_4 and N_2O production data. After applying this correction for the BC production, no significant differences between the control and biochar amended soils were observed (Fig. 1a), despite the fact that there were significant differences in the uncorrected CO_2 production rates ($P=0.038$).

Statistically significant differences between the biochar and non-amended soils for N_2O production were observed across all soils ($P=0.027$). N_2O production from soils without biochar were observed to be highest in FL, MN-A and SC soils (3.43 ; 3.8 and $3.1 \text{ ng N g}^{-1} \text{d}^{-1}$, respectively; Fig. 1b) and lowest in the MN-F soil ($0.1 \text{ ng N g}^{-1} \text{d}^{-1}$; Fig. 1b).

No significant differences were observed in the CH_4 production rates ($P=0.897$) across all soils due to the high standard deviations. Total methane flux was the lowest in the ID, WI-F, and MI soils (-1.2 and $-0.93 \text{ ng C g}^{-1} \text{d}^{-1}$, respectively) both with and without biochar. A negative methane flux indicates net soil methane oxidation activity.

3.2. Ammonia, nitrate and nitrite

The available inorganic N at the conclusion of the 45 day laboratory incubations did vary among soils. The FL soil was the only soil with a statistically significant higher ammonia level following the addition of biochar (186%), with the MN forest soil was the only soil with a 46% lower availability. The remaining 8 soils had no significant difference in ammonia availability following biochar addition.

On the other hand, there was 43–96% lower nitrate availability in the biochar treatments compared to the controls across the

Table 3

Values for ammonia, nitrate, and nitrite ($\text{mg N kg}_{\text{soil}}^{-1}$) in soils with (S+BC) and without (S) biochar after the 45 day incubation.

Soil location	Ammonia		Nitrate		Nitrite	
	S	S+BC	S	S+BC	S	S+BC
Forest soils						
Minnesota – F	628.33 a	337.50 b	18.83 a	16.90 a	15.00 a	16.38 a
Wisconsin – F	0.54 a	1.3 a	12.4 a	0.5 b	<10	<10
Agricultural soils						
California	18.08 a	20.42 a	1615.83 a	1249.17 a	14.27	<10
Florida	17.14 a	31.92 b	419.17 a	35.25 b	13.93 a	14.10 a
Minnesota – A	35.42 a	22.25 a	1537.50 a	834.17 b	<10	<10
South Carolina	25.17 a	29.58 a	700.83 a	227.50 b	<10	<10
Idaho	6.54 a	5.21 a	32.42 a	6.42 b	<10	<10
Illinois	22.58 a	21.08 a	1061.67 a	600.00 b	16.08 a	15.53 a
Michigan	28.75 a	22.17 a	763.33 a	411.67 a	17.25 a	17.67 a
Pennsylvania	17.58 a	17.21 a	678.33 a	386.67 a	<10	<10

Note: Within each variable for the soil and the (soil + biochar) followed by the same letter are not significantly different ($p > 0.05$) by Student's *t*-test.

Table 4
Pearson correlations between GHG production potential with and without biochar compared to soil attributes.

	OM	CEC	pH	P	K	Ca	Mg	S	Na	Zn	Mn	Fe	Cu	B	CO ₂	N ₂ O	CH ₄	BC_CO ₂	BC_N ₂ O	
OM	0.89**																			
CEC	-0.35	-0.01																		
pH	-0.31	-0.43	-0.24																	
P	0.80**	0.86**	-0.16	-0.4																
K	0.82**	0.98***	0.15	-0.44	0.81**															
Ca	0.86**	0.96***	-0.03	-0.4	0.87**	0.90***														
Mg	-0.13	-0.16	-0.18	0.61	-0.26	-0.2	-0.06													
S	0.53	0.80*	0.06	-0.3	0.72*	0.78*	0.78*	-0.12												
Na	-0.17	0.13	0.48	0.36	0.25	0.2	0.17	0.13	0.4											
Zn	0.54	0.58	0.02	-0.34	0.53	0.65	0.39	-0.46	0.5	0										
Mn	0.22	-0.07	-0.85**	0.6	-0.09	-0.18	-0.08	0.48	-0.08	-0.29	-0.12									
Fe	-0.18	0.19	0.58	0.27	0.18	0.29	0.19	0.28	0.48	0.92***	0.09	-0.32								
Cu	0.76*	0.89**	0.14	-0.11	0.74*	0.89**	0.88**	-0.03	0.75*	0.4	0.54	-0.08	0.42							
B	0.69*	0.55	-0.54	-0.29	0.76*	0.42	0.58	-0.44	0.39	-0.1	0.25	0.21	-0.34	0.37						
CO ₂	0.44	0.45	0.13	-0.25	0.45	0.43	0.45	-0.64	0.26	0.16	0.17	-0.24	-0.1	0.48	0.63					
N ₂ O	-0.31	-0.35	-0.22	-0.12	-0.38	-0.48	-0.21	0.22	-0.15	-0.48	-0.42	0.09	-0.37	-0.4	-0.17	-0.36				
CH ₄	0.6	0.47	-0.49	-0.16	0.69*	0.36	0.49	-0.46	0.33	0.02	0.18	0.23	-0.27	0.32	0.97***	0.70*	-0.32			
BC_CO ₂	0.55	0.48	-0.04	-0.34	0.59	0.42	0.52	-0.65	0.25	0.05	0.22	-0.21	-0.23	0.47	0.78*	0.95***	-0.26	0.79*		
BC_N ₂ O	-0.4	-0.55	-0.35	-0.1	-0.48	-0.66	-0.43	0.09	-0.38	-0.61	-0.44	0.16	-0.58	-0.65	-0.12	-0.38	0.94***	-0.23	-0.25	

P < 0.05 indicates a significant difference.

MB, microbial biomass; OM, organic matter; CEC, cation exchange capacity.

7 statistically significant reductions (Table 3). The MN-F, CA, and PA soils possessed no difference in nitrate availability as a function of biochar addition. In addition, there were no statistically significant differences observed in nitrite concentration in any soil following the 45 d incubations between the control and biochar treatments (Table 3).

3.3. Correlation analysis

Correlation analysis of the observed GHG production rates (control and the uncorrected biochar rates), final inorganic-N availability, and the corresponding soil properties were then conducted (Table 4). Examining solely the GHG production rates (last 6 rows), soil OM content was correlated with control rate CO₂ (CO₂) (R=0.69). In addition, there were two significant correlations observed between K with control rate CO₂ and the biochar CO₂ (B_CO2) production. However, the more significant results were the significant correlations between the mean GHG production rates of the control (unamended soils; CO₂, N₂O, and CH₄) versus the production rates of the biochar amended soils (BC_CO₂, BC_N₂O, and BC_CH₄) with the Pearson's correlation coefficient (R) ranging from 0.94 to 0.97 (P < 0.001; Table 4). There were significant linear relationships for all three GHG gases with biochar related to their associated control rate:

$$CO_2 \quad [CO_{2\text{Biochar}} = 0.944 \quad (CO_{2\text{control}}) + 11.14 \mu\text{g C g}_{\text{soil}}^{-1} \text{d}^{-1}; R^2 = 0.97; P < 0.001],$$

$$N_2O \quad [N_{2O\text{Biochar}} = 0.3709 \quad (N_{2O\text{control}}) - 0.05 \text{ ng N g}^{-1} \text{d}^{-1}; R^2 = 0.63; P < 0.0058], \text{ and}$$

$$CH_4 \quad [CH_{4\text{-Biochar}} = 0.714 \quad (CH_{4\text{-control}}) - 1.02 \text{ ng C g}^{-1} \text{d}^{-1}; R^2 = 0.90; P < 0.0001] \text{ (Fig. 2)}.$$

Incidentally, the rate of CO₂ production of the biochar blank (0.5 g biochar in control) is very close to the value of the intercept from the linear regression between the control and biochar CO₂ production rates (11.14 μg C g_{soil}⁻¹ d⁻¹; Fig. 2a). Similarly, the negligible N₂O (0.05 ng N g⁻¹ d⁻¹; Fig. 2b) and CH₄ intercept values (-1.02 ng C g⁻¹ d⁻¹; Fig. 2c) are consistent with the insignificant N₂O or CH₄ flux observed in the biochar only controls.

From the linear regression between control and biochar-amended rates (Fig. 2b), N₂O production following biochar addition was suppressed by an average of 63%. This suppression was statistically significant in 60% of the soils (WI-F, CA, FL, MN-A, SC, and PA). The soils that did not show a statistically significant suppression were also those with the lowest basal rate of N₂O production in the soil control (<1.5 ng N g⁻¹ d⁻¹).

4. Discussion

The chemical, physical and biological properties of soil, which can be altered by biochar application, directly influence soil-plant-atmosphere processes. For example, biochar has been reported to increase soil pH for acidic soils and in turn impact the availability soil nutrients (Lentz and Ippolito, 2012). Additionally, several studies have shown higher productivity rates in biochar amended soils related to improved soil conditions (Chan et al., 2007; Glaser et al., 2009). Asai et al. (2009) observed an increase in yield due to an increase in plant-available P content, and Laird et al. (2010) noted an increase in soil extractable P, K, Mg, and Ca in soil treated with biochar. Biological alterations in soil following the addition of biochar can include changes in the composition and abundance of the biological community, as well as enzyme activities (Lehmann et al., 2011). It is commonly reported in literature that GHG production is highly associated with such soil attributes (Sohi et al., 2010a); thus, it may be important to consider potential alterations in soil characteristics (Yao et al., 2010;

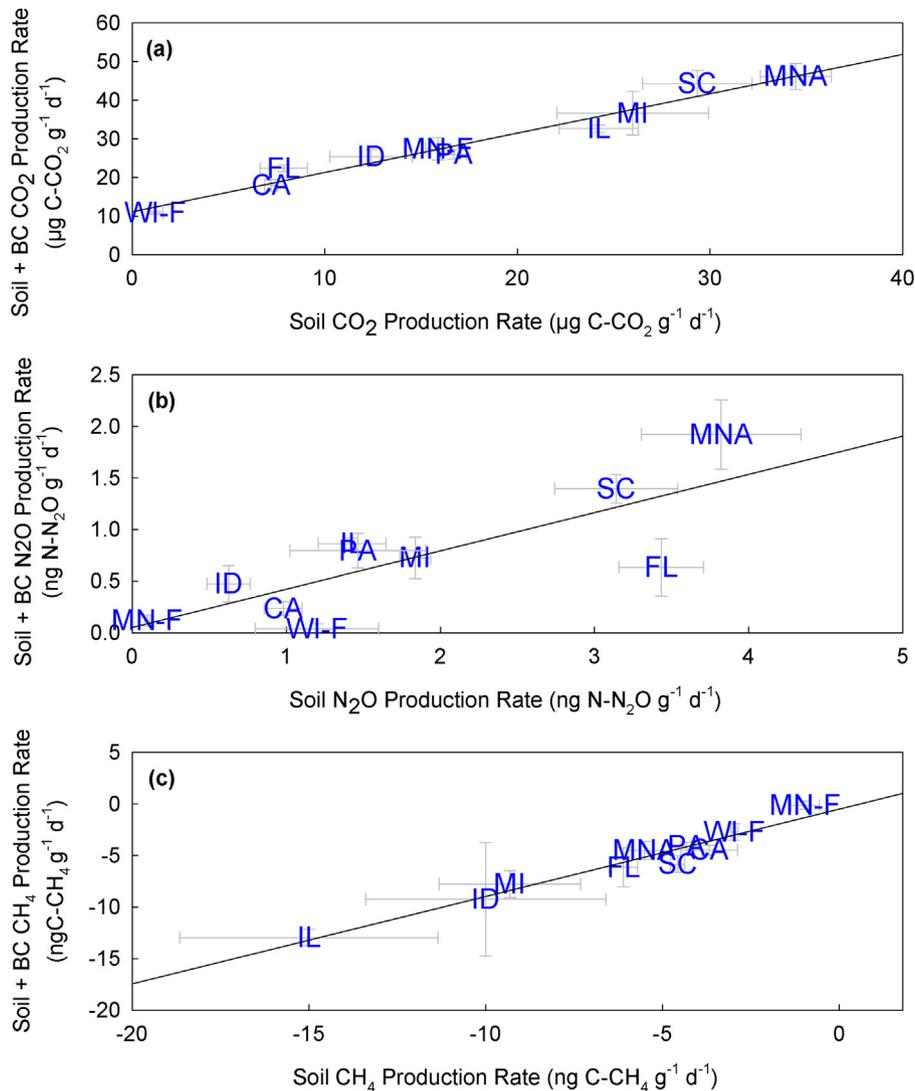


Fig. 2. Observed relationships between the biochar amended and control incubations for (a) CO₂, (b) N₂O, and (c) CH₄ production between all soil types. Error bars represent corresponding one standard deviation of the associated rates. The symbol is the location abbreviation (Table 1), MN-F: Minnesota Forest; WI-F: Wisconsin Forest; CA: California; FL: Florida; MN-A: Minnesota Agriculture; SC: South Carolina; IL: Illinois; ID: Idaho; MI: Michigan; and PA: Pennsylvania.

Jones et al., 2012; Spokas, 2013; Zheng et al., 2013). However, studies with the same biochar added to multiple soils are lacking.

Our results demonstrate that with the identical biochar addition to soil, GHG dynamics may be less tightly linked to soil properties (i.e. CEC, microbial biomass & community structure), but may be driven by the biochar–nitrate interaction (Cayuela et al., 2013). This is supported by the linear relationships observed between the control and biochar amended soil GHG production rates (Fig. 2). Since biochar's impact on GHG production is correlated across different soil types suggests that these impacts would be driven by the biochar properties and not influenced as greatly by soil chemical and microbial differences. These linear relationships observed for CO₂, N₂O, and CH₄ production show that a single biochar reacts more uniformly across different soil chemistries and microbial activities than currently hypothesized (e.g., Sohi et al., 2010a). Therefore, the impact of biochar on a soil's GHG production could potentially be predicted based on its original, un-amended GHG production activity. The mechanisms responsible for these observed correlations with a soil's initial GHG production, however, remain ambiguous.

Increases in CO₂ production in soils following biochar application could be due to the abiotic production from chemisorptions of

oxygen to the surface of biochar (Puri et al., 1958) or microbial biomass already present on the biochar. Either of these would explain the positive intercept (Fig. 2a) of the biochar control incubation. Given the linear response observed for all the soils evaluated here, we hypothesize that the majority of this effect is due to abiotic processes stimulated by the biochar addition, particularly supported by the fact that the biochar control resulted in a similar production rate for a 0.5 g of biochar. Such processes would be influenced by biochar characteristics, which vary with feedstock conditions, pyrolysis temperature and post-production handling conditions. For example, Ameloot et al. (2013) observed greater net C mineralization from low temperature biochars compared to the control and the treatments with high temperature biochars and Sigua et al. (2014) observed a significant impact with particle size. Additionally, greater CO₂ and N₂O production were found in low temperature (350 °C) compared to high temperature (700 °C) biochar (Ameloot et al., 2013), which has been correlated to the degree of incomplete carbonization (Fabbri et al., 2012). Thus, mineralization rates and production of CO₂ present different behaviors according to individual biochar properties and it is unlikely that an average biochar factor for CO₂ production will be determined. The time elapsed since the production of a biochar

also influences its ability to impact the GHG production in soils as a result of decomposition, weathering, or microbial activity (Spokas, 2013; Borchard et al., 2014). This hinders our ability to extract information from meta-analyses across all biochars, since different processes are likely active with different biochars. We need to understand the mechanism of interaction allowing us to normalize the observed responses.

Compared to the control soils, observed CH₄ concentrations were not significantly different with biochar additions to soils in this study. Other studies have reported a reduction in CH₄ production or increasing CH₄ oxidation with the addition of biochar (Laird, 2008). However, this inconsistency could be related to differences in biochar chemical and physical factors leading to changes in soil redox state or the differences in sorbed organic compounds and inorganic constituents are known stimulants or inhibitors of methane oxidation (Hubley et al., 1975; Hazeu and Bruyn, 1980). Furthermore, the aerobic conditions in this experiment would not favor CH₄ production (methanogens).

For all of the soils in this study, there was a reduction in N₂O production rate and typically a reduction in extractable nitrate with the addition of this hardwood fast pyrolysis biochar. Sorption of ammonia and nitrate to biochar has been cited as a possible mechanism for the suppression of soil N₂O production and nitrate leaching (Laird, 2008). Other studies have observed increases in gene abundance with N-fixation and denitrification (Ducey et al., 2013). Given the fact that the suppression observed here was correlated across different soils with different N₂O production potentials, we hypothesize that direct effects on microbial populations are not a likely explanation for this biochar. Similar to the result of this study, others have observed the ability of biochar to decrease total N₂O productions to be independent of soil texture and mineralogy, but highly correlated with initial soil nitrate concentrations and dissolved organic C (Cayuela et al., 2013), which would be assessed in this study through the initial GHG production activity. In addition, Lin et al. (2014) also could not link biochar's N₂O suppression to any microbial group through the use of selective microbial inhibitors, supporting an abiotic mechanism for the interaction of a macadamia nut shell biochar. These findings along with the results observed here, suggest that biochar participates in abiotic reduction of nitrate/nitrite to N₂(g). This mechanism is typically dismissed as a trivial contributor in soils (i.e., Nelson and Bremner, 1970). Nevertheless, these chemical interactions could be more important in biochar amended soils, analogous to observations of N₂O production in Antarctica soils (Samarkin et al., 2010) and the critical role of iron in moderating nitrogen transformations (Zhu et al., 2013).

The abiotic transformations of nitrite/nitrate by the charcoal-cation metal systems have been known for some time (Moraghan and Buresh, 1977; Hansen et al., 1996; Huang and Zhang, 2004; Huang et al., 2009). These reactions include the chemical conversion of nitrate/nitrite directly to N₂ gas, which could be an important process when evaluating alterations in biochar N₂O mitigation and reduction in nitrate leaching. In other words, biochar additions might increase the importance of direct chemical reaction pathways terminating in N₂ formation (Zhu et al., 2013; Dhakal et al., 2014), thus reducing the reliability of the N₂O:N₂ ratio that has been used as evidence of increased microbial denitrification. Furthermore, a potential negative consequence of this chemical interaction is that instead of nitrate being sorbed to the biochar and available through desorption, it might be removed from the soil system entirely. This could explain the reduced nitrate in final biochar extractions, and the reduction of N in existing leaching experiments (e.g. Laird, 2008). This reduction in available nitrate in biochar amended soil also could lead to decreases in plant growth and explain the historical suggestions to co-apply biochar with a synthetic or organic fertilizer (Priestley,

1770; Davy, 1856; Blake, 1893). In the long-term, biochar is hypothesized to promote improved fertilizer availability (Raynbird, 1847; Davy, 1856; Terne, 1882; Khan et al., 2008); although complete understanding of these mechanisms and long-term effects are lacking.

Biochars are complex heterogeneous materials on many levels; it has different surface chemistries, diverse microbial populations and its responses to nitrate and ammonium sorption could differ as a result of these and other chemical variations (Asada et al., 2006; Seredych et al., 2010, 2011; Long et al., 2011). The sorption and reaction potential of biochar with nitrogen depends on the surface oxygen groups (Fujitsu et al., 1993; Seredych and Bandosz, 2007; Huang et al., 2008; Shafeeyan et al., 2011) as well as the retention/trapping of dissolved nitrogen species in biochar micropores (Kameyama et al., 2012). Thereby, greater concentrations of surface oxygen groups on biochar with aging (Qian and Chen, 2014) could result in a biochar with decreased carbon sequestration potential (Spokas, 2013; Naisse et al., 2015; Qian and Chen, 2014) and increased reactivity with inorganic N forms.

5. Conclusion

This study examined the universality in potential GHG mitigation due to the same biochar application. The addition of this hardwood biochar reduced both the production of N₂O and extractable nitrate concentrations across a variety of soils studied. These corresponding reductions are hypothesized to be the result of biochar-nitrate interactions (chemical reaction and not sorption), since this would explain both the observed suppression of N₂O and nitrate following biochar addition. Our results show that in the short term, the alteration in GHG production is more uniform than hypothesized from compiling existing studies using different soils and different biochars, depending solely on original GHG production rates. This study provides insight that the inconsistent effects across existing biochar studies partly result from variability in biochar properties, and care should be utilized when comparing biochar effects across different studies. Comparing dissimilar biochars confounds our ability to synthesize results from different studies, due to the variability in the functionality and mechanistic differences between biochars. While the results from this study show that applying an identical biochar to different soils can result in predictable impacts on GHG production, these relationships are likely different for various biochars.

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