IMPACTS OF SIXTEEN DIFFERENT BIOCHARS ON SOIL GREENHOUSE GAS PRODUCTION

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ABSTRACT

One potential abatement strategy to increasing atmospheric levels of carbon dioxide (CO_2) is to sequester atmospheric CO_2 captured through photosynthesis in biomass and pyrolysed into a more stable form of carbon called biochar. We evaluated the impacts of 16 different biochars from different pyrolysis/gasification processes and feed stock materials (corn stover, peanut hulls, macadamia nut shells, wood chips, and turkey manure plus wood chips) as well as a steam activated coconut shell charcoal on net CO_2, methane (CH_4) and nitrous oxide (N_2O) production/consumption potentials through a 100 day laboratory incubation with a Minnesota agricultural soil (Waukegan silt loam, total organic carbon = 2.6%); Wisconsin forest nursery soil (Vilas loamy sand, total organic carbon = 1.1%); and a California landfill cover soil (Marina loamy sand plus green waste-sewage sludge, total organic carbon = 3.9%) at field capacity (soil moisture potential = -33 kPa). After correcting for the CO_2, CH_4 and N_2O production of the char alone, the addition of biochars (10% w/w) resulted in different responses among the soils. For the agricultural soil, five chars increased, three chars reduced and eight had no significant impact on the observed CO_2 respiration. In the forest nursery soil, three chars stimulated CO_2 respiration, while the remainder of the chars suppressed CO_2 respiration. In the landfill cover soil, only two chars increased observed CO_2 respiration, with the remainder exhibiting lower CO_2 respiration rates. All chars and soil combinations resulted in decreased or unaltered rates of CH_4 oxidation, with no increases observed in CH_4 oxidation or production activity. Biochar additions generally suppressed observed N_2O production, with the exception being high nitrogen compost-amended biochar, which increased N_2O production. The general conclusions are: (1) the impact on trace gas production is both dependent on the biochar and soil properties and (2) biochar amendments initially reduce microbial activity in laboratory incubations. These preliminary results show a wide diversity in biochar properties that point to the need for more research.

Keywords: pyrolysis, black carbon, pyrolytic carbon, carbonization, biochar, greenhouse gas production

1. INTRODUCTION

One area in the renewable energy renaissance attracting significant attention is the use of biochar produced from the pyrolysis of vegetative biomass. Biomass sources such as agricultural residues or forestry wastes (e.g. fruit stones, nut shells, wood chips, sawdust, poultry litter, and corn stover) are excellent precursors for the production of bio-oil, biochar and biogas energy products [1-6]. This process releases energy and converts a portion of an easily degradable carbon (biomass) into a form that is more stable or recalcitrant (biochar), thus enabling the sequestration of atmospheric CO_2 [7,8]. Studies utilizing ^{14}C dating have shown that char in soils represents the oldest fraction of C in soils [9]. Therefore, by converting biomass into biochar, a long-term sink of atmospheric CO_2 could be realized [8,10] and contribute to carbon neutral energy production.

There have been limited studies to date detailing the impacts of biochar amendments on the resulting soil greenhouse gas production balance. For methane (CH_4) oxidation impacts there are field [11,12] as well as laboratory data [13]. However, these studies have very different conclusions. Complete suppression of CH_4 emissions from field plots in a tropical soil (Eastern Colombian Plains) following woody shrub (*Calliandra callothyrsus*) biochar amendments (15 g kg^{-1} in a grass stand and 30 g kg^{-1} in soybean) have been observed [11], as well as inferred increases in CH_4 oxidation activity relative to controls after

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application of mango tree biochar at rates of 8 and 20 t ha^{-1}[12]. On the other hand, laboratory incubations with varying amounts of hardwood sawdust (fast pyrolysis) biochar (2 to 60% C w/w) suppressed observed ambient CH_4 oxidation activity [13]. These contrary results could indicate differences in the impacts of various biochars, potential differences in soil responses or the difference between biochar source material and any combination of production conditions [e.g. 14]. Since biochar amendments alter soil physical properties, there also could be corresponding impacts on the reliability of flux chamber results from field plots due to differing chamber effects as a consequence of different soil physical properties [15].

There are also limited studies on the impacts of biochar on N_2O production/consumption. A 50% reduction in N_2O emissions from soybean plots on acidic soils in the Eastern Colombian Plains has been observed [11] as well as an 85% reduction in laboratory N_2O production of rewetted soils containing 10% w/w municipal organic waste char compared to soils without biochar [16]. However, this effect was highly moisture dependent. A recent study also compared two different biomass source materials (green waste and a poultry litter) prepared at two different conditions (activated 550°C and non-activated 450°C) [17]. The suppression of N_2O activity was a function of biochar and is inconsistent across different biochars with short-term stimulation of N_2O production observed in the green waste non-activated biochar and reductions observed with the other chars [17]. Another recent study observed a reduction in laboratory N_2O production potential following biochar (fast pyrolysis hardwood sawdust) application to a Minnesota agricultural soil across multiple ranges from 2 to 60% C (w/w) at field moisture capacity [13]. The cause of these reductions is unclear. It has been postulated that the char stimulates N_2O reducing activity, thus reducing net N_2O production and the corresponding emissions [16].

However, these studies often involve a limited number of biochars and information from a single field or soil incubation study. Therefore, it is difficult to extrapolate these results to other soils and parent materials, complicating efforts to compare the impacts of different chars. As mentioned above, not all biochars are the same. The properties of the biochar vary as a function of the feedstock, particle size, temperature and rate of increase, residence time, pressures, and conditions of the starting material [14]. The purpose of this study is to document the impacts of 15 different types of chars (biochars and ashes) as well as a steam activated coconut charcoal on greenhouse gas (CO_2, CH_4, and N_2O) production balance across three diverse soil types (Minnesota agricultural soil, Wisconsin forest nursery soil and a California landfill cover soil).

2. MATERIALS AND METHODS

2.1. Materials

Soils. The physical properties of the three soils used in this experiment are given in Table 1. The agricultural soil was collected at the University of Minnesota's Research and Outreach Station in Rosemount, MN. The forest nursery soil was collected at the Hayward Wisconsin State Nursery (Hayward, WI) following seeding bed preparation. The landfill cover was collected from the Monterey Peninsula landfill (Marina, CA). The landfill soil was amended with green waste-sewage sludge compost at the site, which is the reason the total organic carbon (TOC) is higher than the typical soil series (0 to 2% TOC) as well as elevating the field capacity moisture content (Table 1). Soil texture and TOC were determined with the hydrometer method [18] and the loss on ignition method [19], respectively. Surface soil (0-5 cm) was collected from all sites, sieved to <2 mm and homogenized for the incubation study.

Biochars. A total of 16 different chars were evaluated in these laboratory incubations (Table 2). All these biochars were obtained and evaluated as received from the various suppliers[†]. The chars had a range of 1 to 86% carbon, 5 to 89% ash, 0.1 to 2.7% nitrogen, and a range of pyrolysis temperatures from 410 to 850°C. This group provides a cross-section of currently available biochars and ashes from biomass utilization. Biochar will be used to describe these materials, even though not all are biochars. BC-7 is a gasifier ash with the highest ash content (89%). In addition, some of the corn stover chars, despite the fact that the goal was to produce a biochar, have low C contents (24%) and high ash contents (54-70%). BC-14 is produced in a limited aerobic environment (not anaerobic as in the remainder of the biochars), and correspondingly possessed the highest oxygen content of all the chars. Of particular interest were the

[†] - Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

4 corn stover biochars (BC-4, 5, 11, 12). These four biochars were produced from the same corn stover feed stock, but experienced different pyrolysis conditions (Table 2). Proximal (ASTM D3172) and ultimate analyses (ASTM D3176) were performed by Hazen Research (Golden, CO) and BET surface area analyses were performed by the USGS (D. Rutherford, Boulder, CO) and Material Synergy (Oxnard, CA).

2.2. Methods

Greenhouse Gas Assessment Incubations. Triplicate incubations were conducted for each set as outlined in Table 3. The incubations were carried out at field capacity (soil moisture potential = -33 kPa) for each soil type (Table 1). Soil and char were manually mixed in the serum bottle prior to moisture addition. From preliminary investigations this technique was superior to mixing after moisture additions.

Biochar control incubations were conducted to assess the production/consumption of CH_4, CO_2 and N_2O solely from the biochar with and without water additions (1 and 2). These incubations allowed the correction of the soil + biochar incubations for the impact of the biochar, assuming that the behavior of the biochar was similar in both incubations [13]. These biochar + water incubations did not receive any microbial inocula, other than possible contamination (from spores and re-colonization) during storage. The 10% by weight biochar addition has been used in previous laboratory assessments (e.g. [13] and [16]).

Incubations were conducted in sterilized 125 mL serum vials (Wheaton Glass, Millville, NJ) and sealed with red butyl rubber septa (Grace, Deerfield, IL). Periodic gas samples were withdrawn from the incubations for analysis on a gas chromatographic-mass spectrometer (GC-MS) system to quantify gas production over a 100-d incubation period. However, if the O_2 level dropped below 15% during the incubation, the incubation was stopped and the rates of production were calculated up to this point to maintain comparison of aerobic conditions across all incubations. This does not impact the rate calculation since the production rate was typically constant ($R^2 >$ 0.90) for the 100 day incubation period of the biochar + soil incubations.

Gas Sampling and Analysis. To sample the incuba-tions, initially 5 mL of air (known composition) was injected into the sealed vials. 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 then injected into an autosampler vial that was previously helium-flushed for analysis. Concentrations from the GC were corrected for dilution from the 5 mL of air.

The samples were analyzed on a gas chromatograph/mass spectrometer (GC/MS) system described elsewhere [13]. Briefly, the GC 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). In this fashion the sampler was capable of injecting three independent sample loops onto three different analytical columns that are contained in a single gas chromatograph oven (Perkin Elmer, Waltham, Massachusetts, model Calrus 600).

The first column (60 µL loop) is a RT-Molesieve 5A (0.32mm x 30 m, Restek, Bellefonte, PA) with a 2.0 mL min^{-1} He flow rate. The second column (120 µL loop) is a RT-QSPLOT (0.32mm x 30 m, Restek, Bellefonte, PA), also with a 2 ml min^{-1} He flow rate. These two columns are connected to the mass spectrometer (Perkin Elmer, Waltham, MA, model 600T) through a diaphragm valve (Valco, Houston, TX, model DV22-2116) that permitted the selection of which effluent stream was sent to the detector. The third column (1.0 mL loop) is a CTR-1 (Grace; Deerfield, IL) with a 45 mL min^{-1} He flow rate that is connected to a thermal conductivity detector (TCD) and flame ionization detector (FID) in series.

The mass spectrometer quantifies neon (2.3 min; column 1), CO_2 (3.5 min; column 2), N_2O (4.0 min; column 2), CH_4 (8.0 min; column 1), and krypton (8.6 min; column 1). The TCD is used to quantify O_2 and N_2 and the FID is used as a supplemental quantification of CH_4. The column temperature program started at 35°C for 5 minutes then to 120°C at 20°C min^{-1} with a 0 min hold time for both columns. The system was calibrated using multiple traceable gas standards (Scott Specialty Gases; Troy, MI and Minnesota Oxygen Supply; Minneapolis, MN). Argon (100 ppm in He), used as an internal standard to correct for mass spectrometer drift, was injected with an additional sample valve (Valco, Houston, TX, model DV22-2116). Neon and krypton are used as tracers for vial injection problems.

Statistics. Results for the CO_2 and N_2O production and CH_4 oxidation activities were arithmetic means of triplicate samples. All greenhouse gas production rates were determined from the decrease or increase in concentration over time in the headspace of the incubation. Data were analyzed using an analysis of variance (ANOVA) procedure for independent samples to test for statistically significant differences using MINITAB (Minitab, Inc., State College, PA).

Table 1 Selected physical properties for the 3 soils used in this study.

Soil	Location	Soil Type	Sand	Silt (%)	Clay	pH	TOC (%)	Field Moisture Capacity, -33kPa (% w/w)
Agricultural	44.75° N; 93.07° W	Wauken silt loam (fine-silty over skeletal mixed, super active, mesic typic Hapludoll)	22	55	23	6.4	2.6	14.8
Forest Nursery	46.00° N; 91.30° W	Vials loamy sand (sandy, mixed, frigid, Entic Haplorthod)	84	9	7	6.8	1.1	12.0
Landfill Cover Soil	36.71° N; 121.76° W	Marina loamy sand (mixed, thermic Lamellic Xero-psamments) with green waste sewage sludge added	76	10	14	6.7	3.9	24.8

Notes: pH – determined in a 1:1 H_2O slurry. TOC – total organic carbon

Table 2 Selected physical properties for the 16 biochars evaluated in this study.

Biochar #	Source Material	Source	Pyrolysis Temp (°C)	C	N	Ash (%)	O	H	Surface Area (m^2g^{-1})	Moisture (%)
BC-1	Corn Stover (Australia)	Best Energies	815	44.7	0.5	54.7	1.2	1.6	4.38	2.6
BC-2	Pine wood chip	EPRIDA	465	74.5	0.3	5.6	8.9	3.2	0.10	5.3
BC-3	Peanut hulls	EPRIDA	481	59.0	2.7	15.3	12.4	1.9	1.01	7.8
BC-4	Corn stover (IA)	Iowa State University	500	24.6	0.6	69.1	4.6	1.1	4.20	2.7
BC-5	Corn stover (IA)	EPRIDA	410	42.1	1.0	53.7	11.3	1.6	2.23	3.8
BC-6	Biosource™	Char C Group	465	42.7	2.2	*NA*	*NA*	*NA*	63.50	15.0
BC-7	Turkey manure + woodchip	SWROC – Univ. of MN (gasifer ash)	850 (*)	1.4	0.1	89.1	3.0	0.5	4.78	3.9
BC-8	Oak/Hickory	USDA-ARS (David Laird)	*NA*	69.1	0.7	14.1	9.3	2.2	19.20	6.4
BC-9	Pine woodchip	EPRIDA	465	71.2	0.2	9.3	11.4	3.0	0.19	7.2
BC-10	Peanut hulls (aged compared to B-3)	EPRIDA	481	60.2	0.9	14.5	10.3	0.9	286.0	16.2
BC-11	Corn stover (IA)	EPRIDA	505	65.7	1.2	54.2	4.2	1.4	17.30	5.3
BC-12	Corn stover (IA)	EPRIDA	515	50.7	1.0	73.7	0	0.8	9.85	2.7
BC-13	Activated coconut shell charcoal	Willinger Bros. (steam activation)	450	83	0.4	12	0	0	960	5.5
BC-14	Wood Pellets	Chip Energy	*NA*	69	0.1	6	20	3.3	24	5.6
BC-15	Hardwood char	Lump charcoal	*538*	53	0.4	27	10	2.6	7.2	6.3
BC-16	Macadamia shell	Biochar Brokers (EternaGreen™)	*NA*	84	0.6	2	2	2.3	0.4	9.5

Notes: *NA* indicates that the data is not available and (*) BC-7 is a gasifier ash versus a pyrolysis char.

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Table 3 Description of incubations conducted for each type of biochar with the following combinations of soil, biochar and water.

Set #	Biochar Amount (g)	Soil	Water (mL)
1	0.5	None	0
2	0.5	None	1.0
3	0.5	Agricultural soil (5g)	0.74
4	0.5	Forest nursery soil (5g)	0.60
5	0.5	Landfill cover soil (5g)	1.24
6	None	Agricultural soil (5g)	0.74
7	None	Forest nursery soil (5g)	0.60
8	None	Landfill cover soil (5g)	1.24
9, Control	None	None	1.0

If significant differences existed among the factors, as indicated by the F-ratio, the Tukey's Honest Significant Difference (HSD) test was performed to determine which pair-wise interactions were significantly different at the $P<0.05$ levels.

3. RESULTS

3.1. Greenhouse Gas Production/Consumption of Biochar-Alone

CO_2. Table 4 presents the observed consumption/ production potential of the biochar only incubations with and without water additions. For CO_2, when water was added all values were significantly different than the control incubations (serum bottle, water, and septa). We observed CO_2 production or release in 15 of the 16 biochars evaluated. The only biochar that did not release or sorb CO_2 was the steam activated coconut shell charcoal (BC-13; Table 4). In addition, one biochar (BC-7) sorbed CO_2 during the period of the incubation (within 5 days the ambient CO_2 was non-detectable; <10 ppm) with the rate of disappearance of -76 µg CO_2 g_{char}^{-1} d^{-1} [dry] versus -99.2 µg CO_2 g_{char}^{-1} d^{-1} [wet]. Addition of moisture statistically increased production of CO_2 in 8 of the 13 chars that had production of CO_2 in the dry state (Table 4).

The largest accumulation of CO_2 was observed in the macadamia nut biochar (BC-16; 4475 µg CO_2 g_{char}^{-1} d^{-1}), followed by the compost-amended char (BC-6; 1022 µg CO_2 g_{char}^{-1} d^{-1}). It should be noted that BC-16 was the freshest biochar (tested less than 2 months from production versus 1 to 2 yrs for the other chars) and BC-6 was a composite biochar + high N compost mixture. The exact make-up of BC-6 is not fully known due to the proprietary nature of the pine wood chips biochar + compost amendment.

CH_4. For CH_4, there were only 3 chars (BC-3, BC-4 and BC-6) that sorbed or oxidized CH_4 at low rates in the wet state (-2.6, -2.6 and -4.1 ng CH_4 g_{soil}^{-1} d^{-1}, respectively) and there were four chars that had observable CH_4 production rates (BC-10, 14, 15 and 16). Note the difference in the units from the CO_2 production (µg CO_2) compared to methane and nitrous oxide (ng of gas).

N_2O. For N_2O, three biochars had production of N_2O that was statistically different from the control (BC-5, 6 and 13; Table 4). However, this difference was observed only following moisture additions in BC-5 and 6. There was only minor detectable sorption or disappearance of N_2O from the headspace in the remaining incubations. BC-6 had the highest N_2O production, again hypothesized to be related to the presence of the compost.

O_2. All chars had oxygen (O_2) consumption that was statistically different from the control incubation when wet (Table 4). In general, there was increased O_2 consumption with moisture additions. BC-16 had the highest rate of oxygen consumption (-1611 µg O_2 g_{char}^{-1} d^{-1}), probably linked to the fresh nature of that char. One interesting note is that BC-13 had observable consumption of O_2 (-125 µg O_2 g_{char}^{-1} d^{-1}) but no observable production of CO_2 (Table 4).

3.2. Greenhouse Gas Production/Consumption of Soil + Biochar

CO_2. The effects of biochar additions on CO_2 respiration are shown in Figure 1. In order to properly account for the impacts of the gas production of the soil + biochar system, control incubations with biochar alone with and without water amendments were conducted (Table 4). This "abiotic" effect has been observed by others [13,20,21] and needs to be used as a correction for the soil incubations [13]. This correction was calculated with Eq. 1, where $CO_2^{biochar+soil}$ is the total CO_2 production from the soil + biochar + water incubation (µg CO_2) at time t_d (Set 3,4 or 5 in Table 3), $CO_2^{biochar}$ is the total CO_2 production (µg) at time t_d for the biochar + water incubation (Set 2 in Table 3) and t_d is the time of sampling (days).

$$CO_2 \text{Production Rate Corrrected} = \frac{\left(CO_2^{biochar+soil} - CO_2^{biochar}\right)}{5g_{soil}(t_d)} \quad \text{(Eq. 1)}$$

Rates of CO_2 evolution/consumption from the biochar itself are occasionally greater than the magnitude for the CO_2 respiration of the control soils (agricultural soil: 26 µg CO_2 $g_{soil}^{-1}d^{-1}$; forest nursery soil: 2 µg CO_2 g_{soil}^{-1} d^{-1}; landfill soil: 160 µg CO_2 g_{soil}^{-1} d^{-1}), which further justifies the above correction. Assuming that the behavior of the char is the same in the soil + water (Sets 3,4 and 5 in Table 3) and water incubations (Set 2 in Table 3), Eq. (1) will correct the data for the char-alone production. The above correction is shown for CO_2, but the other gases were dealt with in the same way.

The importance of applying the correction for the char-alone CO_2 production is clearly seen (Figure 1A2), with some of the corrected CO_2 production changing from stimulated respiration to no significant difference (e.g. BC-4, 5, 10, and 12). All discussion of the CO_2 production potentials of the soil + biochar incubations will be based on these corrected values.

BC-6 did cause the soil + biochar incubations to go anaerobic (<15% O_2) after 15 d and BC-16 caused anaerobic conditions after 20 d. For the analysis used here, the rate of CO_2 production for BC-6 was calculated between days 0-15 and BC-16 was calculated between days 0-20. The rest of the incubations remained aerobic (>15% O_2) throughout the incubation period (100 d). For the agricultural soil (Figure 1A1 and 1A2), two biochars (BC-1 and 11) suppressed CO_2 respiration and five chars (BC-3, 6, 14, 15 and 16) that significantly stimulated CO_2 respiration compared to the soil controls and nine with no significant alteration (BC-2, 4, 5, 7, 8, 9, 10, 11, 12, and 13). For the agricultural soil, the two chars that suppressed respiration were derived from corn stover (Table 2). For the forest nursery soil (Figure 1B1 and 1B2), four chars (BC-1, 7, 14, and 15) stimulated CO_2 respiration (corrected) and eight chars suppressed respiration (BC-2, 3, 4, 5, 6, 8, 9 and 16), with four having no significant effects (BC-10,11,12 and 13). For the landfill cover soil (Figure 1C), the majority of the chars suppressed CO_2 respiration. However, there were two chars that increased CO_2 respiration (BC-6 and 14) with one illustrating non-significant alterations (BC-16). The remainder of the thirteen biochars suppressed CO_2 respiration in the landfill cover soil.

CH_4. The effects of the biochar additions on CH_4 oxidation/production are shown in Figure 2. Recognize that what was measured was the net result of soil CH_4 oxidation and CH_4 production. The majority of chars decreased observed net CH_4 oxidation rates in the agricultural and landfill soils (Figure 2A and 2C) and also reduced the rate of CH_4 production observed in the forest nursery soils (Figure 2B). For the agricultural soil (Figure 2A), five chars (BC-10, 13, 14, 15, and 16). did not significantly affect the observed oxidation rate However, the remainder of the chars all significantly reduced net CH_4 oxidation rates as well as altering the soil from a net CH_4 sink to net CH_4 production. For the forest soil (Figure 2B), char additions universally suppressed the observed CH_4 production. Note that the control forest nursery soil was a net CH_4 producing soil (Figure 2B: + 41.8 ng CH_4 g_{soil}^{-1} d^{-1}).

For the landfill soil, a dramatic suppression was observed in the CH_4 oxidation activity (Figure 2C). This is of particular importance since the landfill cover soil possessed the highest CH_4 oxidation capacities of the soils evaluated. Certain char additions (BC-3, 4, 5, 6, 11, and 16) caused the landfill cover soil to become a net producer of CH_4. The addition of chars typically reduced the observed net CH_4 oxidation rates in agricultural and landfill soils as well as reduced net CH_4 production observed in the forest nursery soils (Figure 2).

The chars made from the same feedstock (Iowa corn stover: BC-4, 5, 11 and 12) have very different responses in soil CO_2 production despite the fact that the char is from the same feedstock and similar pyrolysis temperatures (Table 2). BC-4 and 5 had elevated CO_2 production (160 µg CO_2 g_{char}^{-1} d^{-1}), whereas BC-11 and 12 had lower production (8 and 6 µg CO_2 g_{char}^{-1} d^{-1}, respectively). These results show the importance of knowing the pyrolysis production characteristics and suggest a need for standards in the description of pyrolytic carbon.

N_2O. The effects of the biochar additions on N_2O production are shown in Figure 3. The majority of chars decreased observed N_2O production rates. However, in the agricultural soil (Figure 3A) BC-6 and BC-16 dramatically increased the observed N_2O production by 295% and 1627%, respectively. For the forest nursery soil, BC-6 and BC-3 increased observed N_2O production rates, whereas in the landfill cover soil BC-6 and BC-14 increased observed N_2O production.

Table 4 Production (+) or consumption (-) rate of CO_2, CH_4, N_2O and O_2 from the various chars (without soil) in the dry and wet state.

	Dry				Wet (1 mL water)			
BC	CO_2 (ug CO_2 g_{char}^{-1} d^{-1})	CH_4 (ng CH_4 g_{char}^{-1} d^{-1})	N_2O (ng N_2O g_{char}^{-1} d^{-1})	O2 (ug O_2 g_{char}^{-1} d^{-1})	CO_2 (ug CO_2 g_{char}^{-1} d^{-1})	CH_4 (ng CH_4 g_{char}^{-1} d^{-1})	N_2O (ng N_2O g_{char}^{-1} d^{-1})	O2 (ug O_2 g_{char}^{-1} d^{-1})
None	0.2 (0.1)	-0.1 (0.2)	-0.6 (0.1)	-0.12 (3.6)	1.6 (0.3)	-0.1 (0.2)	-0.5 (0.1)	-0.15 (3.5)
1	2.4 (0.1) *	0.3 (0.1)	-1.1 (1.8) *	-17.0 (10.0)*	22.7 (2.4) *	0.3 (0.2)	-0.8 (0.6)	-22.9 (2.0)*
2	2.6 (0.7) *	0.2 (0.1)	-0.3 (0.1)	-9.5 (5.8)*	30.9 (1.1) *	0.3 (0.4)	-0.4 (1.3)	-25.5 (10.4)*
3	2.2 (0.5) *	-2.5 (0.3) *	-0.3 (0.1)	-11.4 (4.3)*	168.5 (23.5) *	-2.6 (0.6) *	0.0 (0.1)	-39.3 (12.7)*
4	3.6 (0.3) *	-2.2 (0.5) *	-0.9 (0.2) *	-12.1 (8.8)*	162.4 (15.0) *	-2.6 (0.6) *	-0.4 (0.5)	-55.33 (24.1)*
5	12.0 (1.0) *	0.5 (0.3)	-0.8 (0.6)	-23.0 (8.2)*	165.9 (6.9) *	0.5 (0.1)	0.9 (0.6)	-83.3 (20.7)*
6	781.4 (300.0) *	2.8 (0.6) *	-0.6 (0.1) *	-241 (15.0)*	1,022.4 (109.0) *	-4.1 (0.9) *	5.7 (2.3) *	-255.3 (8.5)*
7	-76.0 (1.5) *	0.0 (0.1)	-1.0 (1.1)	-19.3 (6.1)*	-99.2 (5.9) *	0.2 (0.1)	0.0 (1.1)	-31.1 (14.8)*
8	-8.0 (0.9) *	0.3 (0.2)	-0.8 (0.8)	-22.1 (19.7)	59.1 (3.9) *	0.3 (0.1)	-0.8 (0.9)	-20.2 (6.5)*
9	4.2 (0.1) *	0.3 (0.2)	-1.0 (0.4)	-11.1 (7.5)*	12.7 (3.4) *	0.2 (0.1)	-1.3 (0.6) *	-25.5 (9.2)*
10	11.6 (5.8) *	-0.3 (0.0)	-1.1 (0.6)	-11.9 (6.0)*	139.4 (4.7) *	5.6 (2.3) *	-0.8 (0.6)	-10.4 (4.1)*
11	8.0 (0.7) *	0.3 (0.1)	-1.4 (0.9)	-5.6 (8.2)	7.9 (0.7) *	0.2 (0.1)	-0.5 (1.5)	-22.3 (7.9)*
12	3.2 (0.4) *	0.2 (0.3)	-1.3 (0.2) *	-3.3 (8.1)	5.5 (1.2) *	0.4 (0.5)	-0.8 (0.4)	-22.5 (7.9)*
13	0.4 (0.6)	1.5 (0.6) *	3.1 (1.5) *	-38.0 (44.0)	1.6 (0.2)	0.4 (0.6)	2.0 (1.4) *	-125.0 (77.0)*
14	10.0 (0.9) *	0.2 (1.2)	0.5 (1.0)	-23.0 (14.0)*	675.0 (144.0) *	3.2 (1.5) *	-2.8 (2.7)	-167.9 (94.0)*
15	27.6 (1.6) *	0.6 (1.4)	-0.4 (0.1)	-71.8 (35.0)*	140.0 (9.4) *	1.3 (0.7) *	-1.9 (1.3) *	-112.5 (25.9)*
16	533.0 (310.4) *	57.6 (14.4) *	-1.6 (2.0)	-281.7 (163.5)*	4,474.6 (594.6) *	73.8 (10.0) *	-6.8 (0.9) *	-1611.5 (23.2)*

Notes: Standard deviation of the three replicates is given in parentheis and * indicates those incubations that are statistically different than the control ($p<0.05$).

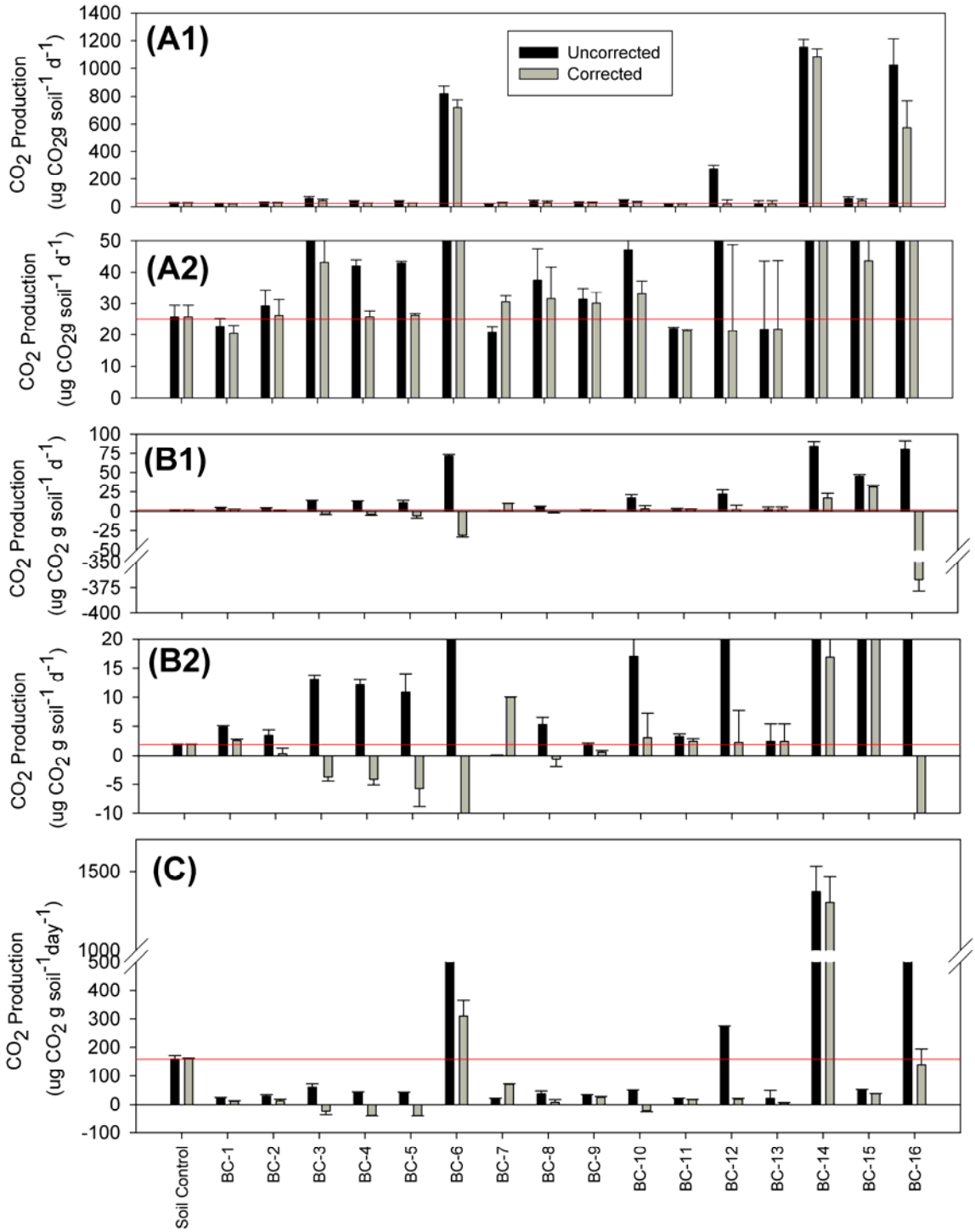

Figure 1 CO_2 production by biochar additions in (A) agricultural soil (A1 and rescaled in A2), (B) forest nursery soil (B1 and rescaled in B2) and (C) a landfill cover soil. Averages of triplicate incubations are shown along with the corresponding standard deviation. Data presented are for the uncorrected and corrected production rates, Eq. (1). The horizontal line represents production from the soil control for reference.

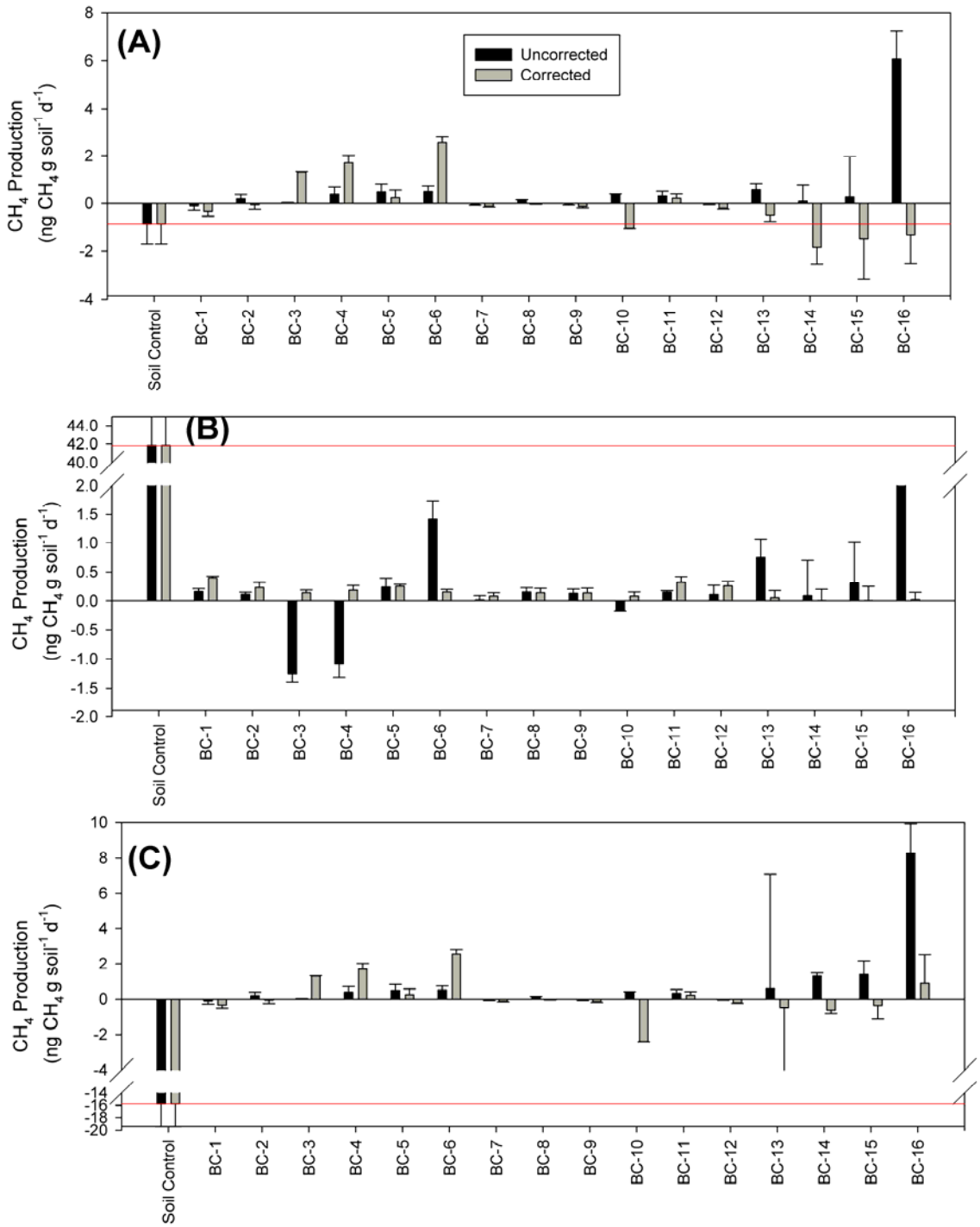

Figure 2 CH_4 production (+) or oxidation(-) by biochar additions in (A) agricultural soil, (B) forest nursery soil and (C) a landfill cover soil. Averages of triplicate incubations are shown along with the corresponding standard deviation. Data presented are for the uncorrected and corrected production rates, Eq. (1). The horizontal line represents production from the soil control for reference.

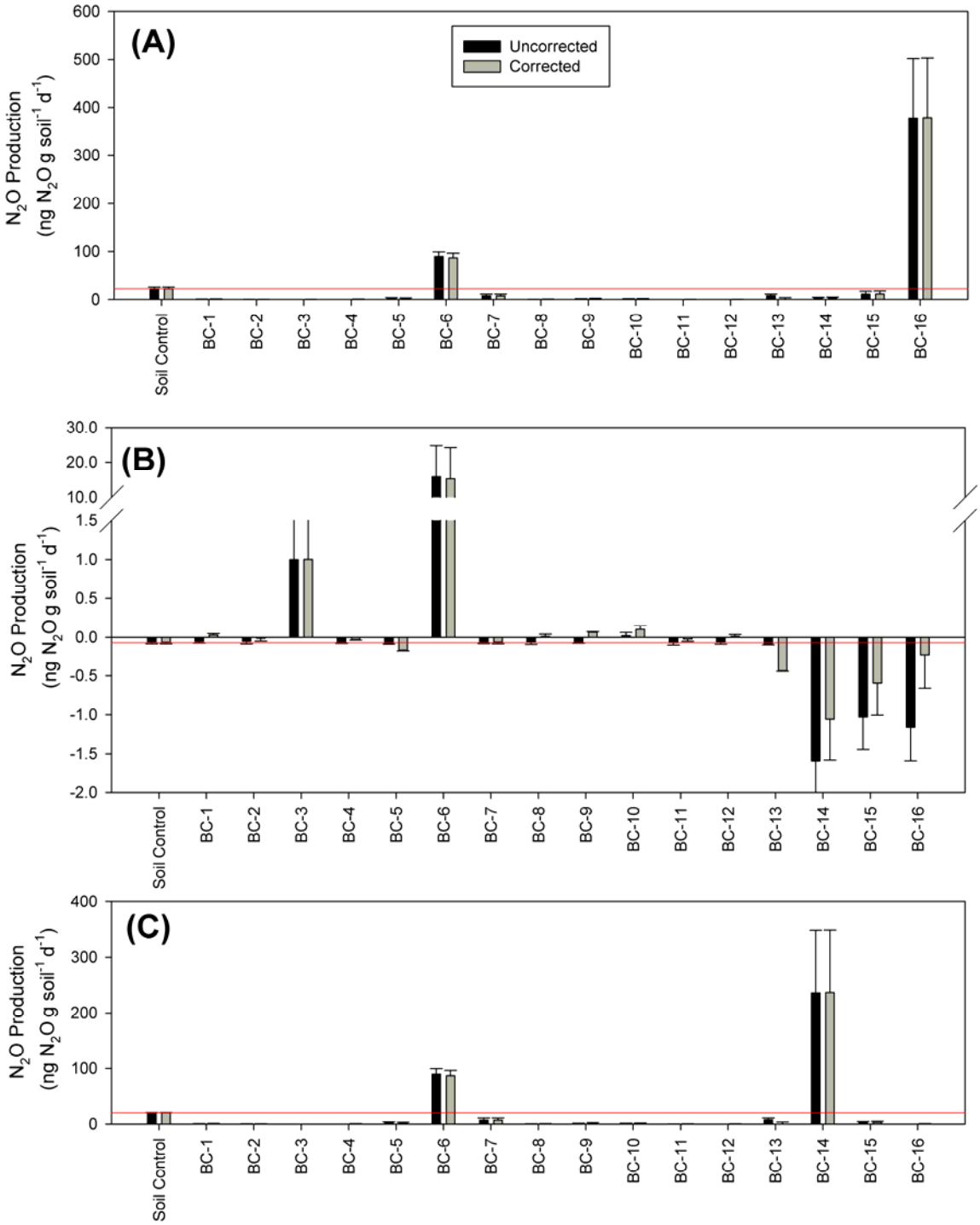

Figure 3 Observed N_2O production (+) or oxidation (-)by biochar additions in (A) agricultural soil, (B) forest nursery soil (note the break in the scale) and (C) a landfill cover soil. Averages of triplicate incubations are shown along with the corresponding standard deviation. Data presented are for the uncorrected and corrected production rates, Eq. (1). The horizontal line represents production from the soil control for reference.

4. DISCUSSION

4.1. Biochar-Alone Incubations

CO_2. Rates of CO_2 production/consumption were not correlated with specific surface area, C/N ratios, composition (C, O, N and H contents), initial moisture content or ash content of the different biochars (Table 2). Various abiotic degradation mechanisms have been suggested in the literature. Elevated temperature aerobic oxidation [23,24], reactions with chemical oxidants [25] as well as ozone oxidation [26] have been shown to cause oxidation of chars over short periods of time. Furthermore, it has been suggested that these abiotic processes are more important than biotic processes in the initial phases of oxidation of freshly produced char [20], and therefore the age of the char may be an important factor in determining CO_2 release.

Sorption of CO_2 by the gasifier ash (BC-7) is in agreement with other studies that have seen CO_2 sorption by high-temperature ashes and is related to the microcrystalline structure and concentration of hydroxyl groups [22]. Incidentally, the pH of the BC-7 char was the highest of the chars evaluated in this study (pH 10.6).

The activated coconut shell char (BC-13) had a CO_2 production that was not statistically different than the control (Table 4), potentially indicating a higher degree of recalcitrant C in the activated charcoal than in the other biochars tested. However, this lack of increased CO_2 from the activated charcoal also could be attributed to the activation process, which removes all sorbed volatiles and contaminants from the char surface: the other biochars evaluated would possess these contaminants since they were non-activated.

CH_4. BC-16 had a significant CH_4 production rate (74 ng CH_4 g_{soil}^{-1} d^{-1}, Table 4). The exact source of this methane is not fully understood. Hydrocarbons (including methane) have also been observed in oils and syngas formed during char production [27]. Therefore, this CH_4 could be a consequence of the fresh nature of the char and resulting off-gassing from pores and/or surface desorption. Only two biochars had a significant difference between the wet and dry behaviors for CH_4 production (BC-6 and 10). In BC-6, addition of water increased observed CH_4 oxidation, likely due to the presence of methanotrophic bacteria in the high N compost + biochar (BC-6) mixture. The other noteworthy behavior was BC-10, which went from net CH_4 consumption (sorption or oxidation; -0.3 ng CH_4 g_{char}^{-1} d^{-1}) to a net methane production (+5.6 ng CH_4 g_{char}^{-1} d^{-1}) when wet. This biochar was unique since the char was stored in a pile (outside) for a year before analyses were conducted. This weathered char indicates the potential for differing behaviors based on aging of the char material and/or possible leaching and could be a critical parameter in the assessment of chars. Note that BC-10 lost over 67% of the N and gained 286-times in surface area compared to the un-weathered peanut hull char (BC-3; Table 2). However, no correlation was found between the CH_4 oxidation/production and specific surface area, C/N ratios, composition data (C, O, N and H contents), initial moisture content or ash content of the different biochars.

N_2O. The N_2O consumption rates observed (<1 ng N_2O g_{char}^{-1} d^{-1}) are lower than in other studies that have documented higher sorption rates (>1550 ug N_2O $g^{-1}hr^{-1}$ from 30 ppm N_2O mixtures) on wood charcoal [28]. Sorption behavior of N_2O on charcoal has been known for some time [29]. The difference between these findings could be related to the age of the char as well as the elevated N_2O concentrations (30 ppm or pure N_2O in the sorption studies versus 0.3 ppm for ambient levels conducted here). At least for atmospheric levels of N_2O, we did not observe significant N_2O sorption with the range of chars evaluated. However, since a majority of the chars were stored under atmospheric conditions since production, the sorptive sites for N_2O could be filled or the pores could be blocked by bio-oils that could be freed with repeated flushing, evacuation or activation of the char [29]. These uncertainties require further research.

O_2. Rates of CO_2 production and O_2 consumption were well correlated ($R^2 = 0.84$). This initially suggests that the O_2 consumption could be related to biotic activity. It is possible that biological contamination of biochar from processing, handling, air and storage conditions occurred. However, abiotic reactions cannot be ruled out, since abiotic mechanisms also can consume oxygen. If these reactions involve components of the char it would suggest that the age of the char (along with storage conditions – aerobic or anaerobic) could influence the resulting response in the soil. The reactions of labile components of char are suggested as a source of error in assessing degradation rates of biochar [30-32]. The rate of BC degradation by biotic and abiotic oxidation is highly variable due to different biomass feedstock sources and pyrolysis conditions (temperature, pressures, resident times) [20,33-35]. Oxidation of char may occur through abiotic chemisorption of oxygen [20,36,37,38], particularly on moist char surfaces [36,38], which would explain the increased O_2 consumption with moisture additions (Table 4). Furthermore, it has been observed that temperature controls whether these reactions occur on the surface (lower temperatures) or deeper layers in the

char structure (higher temperatures) [20]. However, detailed studies on the alteration in the surface chemical characteristics of the char were not conducted.

4.2. Soil + Biochar Incubations

CO_2. Only one char (BC-14) stimulated CO_2 respiration across all soil types evaluated. The stimulation varied across soils (agricultural soil 4124%; forest soil 773%; landfill soil 721%). The reason for this is uncertain, but it could be related to the fact that this biochar is produced in a limited aerobic environment instead of a strictly anaerobic environment. This is important, since the behavior of BC-14 could be different because this char was produced in a partially aerobic environment. The rest of the chars are produced in a strict anaerobic environment (typically flushed with N_2) and thereby have lower total oxygen contents (Table 2). Furthermore, the activity of the biochars is significantly different than activated charcoal BC-13, which did not significantly affect the CO_2 respiration across all soil types evaluated.

Structural differences have been noted between chars of historical origin (e.g. Terra Preta) and pyrolysis chars, which have no proteins and fatty acids [39]. There are large differences in the time since production and these differences could be the result of multiple causes (e.g. decomposition, weathering, microbial activity, etc.). The effect of structural and composition differences in chars on the behavior in soils warrants further investigation.

Reductions in CO_2 respiration from char-amended soils has been observed in other studies. A lower C mineralization rate, which indicates lower microbial activity, has been observed in BC-rich Anthrosols compared to BC-poor adjacent soils [40]. In another study [41], lower or no significant impacts on basal respiration were observed with addition of charcoal powder and freshly burned litter when these amendments are applied to Xanthic Ferralsols. These studies suggest that the biochar is not supplying micronutrients, since the biochar amendments did not stimulate basal CO_2 respiration [41]. However, it should be noted that significant increases in basal and substrate-induced respiration were observed following mineral fertilizer coupled with biochar additions [41]. This effect was also observed in our study with the high N compost + biochar (BC-6).

CH_4. Our current hypothesis is that the net soil methanotrophic activity was reduced by the char additions. However, the overall contributions of lower CH_4 oxidation and higher CH_4 production are difficult to separate unequivocally with the data collected here. Our hypothesis is that this reduction was due to a reduced CH_4 oxidation activity in the landfill and agricultural soils based on the following observations. First, there were minimal interactions of the chars with CH_4 observed in the char-alone incubations (Table 4), indicating that sorption/desorption of CH_4 was not a significant factor with the majority of char materials. Second, since these incubations were conducted under aerobic conditions, the production of CH_4 would not be favored under these conditions. Lastly, there was no stimulation of CH_4 production seen in the forest nursery soil, which was a net CH_4 producer. One would expect if increased CH_4 production was the cause of the decreased CH_4 oxidation activity observed in the other soils, the rate of CH_4 production should have been enhanced in the forest nursery soil (Figure 2B).

These results for CH_4 are in agreement with other laboratory assessments of the initial impacts of char on agricultural soil [13]. However, these results do not appear to support the conclusions of Rondon et al. [10,11] on the reduction observed in methane emissions from field plots, which was interpreted as an increase CH_4 oxidation activity. This effect also could be explained by a decrease in methanogen activity (CH_4 producing bacteria) and thereby have the same net effect on reducing the observed CH_4 emissions. Our laboratory data would support the hypothesis of a decrease in overall microbial activity (e.g. CO_2 respiration, CH_4 oxidation, CH_4 production and N_2O production) within the first 100 d following biochar application. This decreased activity of the methanogens would be consistent with the field observations [10,11]. The exact cause for the decreased CH_4 emissions in the field plots was not elucidated and is still unknown. However, since all the evaluated biochars reduced observed greenhouse gas production rates, it would be improbable that biochar amendments increased CH_4 oxidation rates in the short term. However, no data were collected here on the long-term impacts of the biochar amendment.

N_2O. For N_2O, a majority of the chars suppressed N_2O production, which has been seen in the field [10,11] and unsaturated laboratory incubations [13,16]. However, this was not universally true. BC-6 (high N compost + pine wood chip) char increased N_2O production across all three soil types. This is hypothesized to be a consequence of the added nutrients and labile organic matter, since the addition of organic material to soils typically increases N_2O production rates, especially with low C/N residues [42]. Net N_2O production is a balance between production and N_2O consumption [43]. Thereby, lower N_2O production in our study might be explained by a greater rate of N_2O reduction (to N_2) or a lower rate of N_2O production.

Given the results of the previous greenhouse gases generally illustrating decreased activity, our hypothesis is that the rate of N_2O production is lowered, particularly since there was a negative impact on CO_2 respiration in some of the chars.

A similar conclusion of decreased nitrification/-denitrification activity has been reached from studies of the impacts of agrochemicals on N_2O production rates [44] even without decreases in observed CO_2 respiration [45]. Therefore, there appears to be an advantage to converting the biomass to char prior to soil incorporation for reducing N_2O emissions. However, additional research on this reduction and the temporal duration of the reduction is needed.

The effects of biochar amendments on soil were both biochar and soil-specific. This is not surprising since the make-up of the microbial community drives the net production of greenhouse gases in the soil system [46]. This is seen in the variety of biochars that increase gas production in one soil and then correspondingly decrease the production in another soil (Figures 1-3). Two chars had some universal impacts. BC-6 (high N compost + biochar) stimulated N_2O production in all soils, despite the fact that the stimulation was different in various soils. This is in agreement with other studies that have observed an initial spike in N_2O production following a non-activated green waste char and N_2O suppression was observed with the addition of activated chars [17]. BC-14 stimulated CO_2 production in all soils, which could be related to the high oxygen content of this char. Research has indicated that the high oxygen content of biomass feed stocks favors cross-linking of carbon chains during pyrolysis versus the formation of higher degrees of carbon ordering (graphitization) [47]. This reduced ordering in biomass chars increases their reactivity [47]. The lack of CO_2 release/sorption from steam activated charcoal alone compared to the other biochars (Table 4) could be a consequence of the activation of the coconut char. Sorbed materials (gases, oils, etc.) on non-activated chars could impact the initial effects of biochar amendments on soils. Furthermore, it is important to note that the results of these short term incubations may not be indicative of the long-term (>1 yr) impacts of biochar amendments.

Our current results suggest there is some microbial inhibition as a consequence of the char amendments. This needs further work to elucidate the mechanism and duration of the effect. The fact that it was observed across various soils and for a majority of the chars evaluated here, particularly for CH_4 and N_2O production, support this conclusion. Furthermore, these laboratory incubations were conducted in the absence of plants, worms, rainfall, variability in temperature and soil moisture and the many effects these factors may have on greenhouse gas production and oxidation in the field.

5. CONCLUSIONS

This is one of the first studies comparing the impacts of several biochar amendments of various types on greenhouse gas production potentials across multiple soil-types. The results suggest that the impacts of biochar additions are both biochar and soil type specific. However, feedstock type, pyrolysis temperature, elemental composition and surface area were found to be uncorrelated to any of the observed impacts on greenhouse gas production/consumption. Most chars evaluated here reduced the rate of net CH_4 oxidation in soil, decreased CH_4 production in an initial CH_4 producing soil, and all decreased N_2O production activity in these incubations. However, when one examines the total data set for all three gases (CO_2, CH_4, and N_2O), there is some evidence that the char amendments initially decrease soil microbial activity. However, this is based on laboratory incubations and additional research is needed to elucidate the mechanisms of these observed suppressions. These preliminary laboratory incubation results confirm the complexity of biochar impacts on soil properties and processes that need to be examined before initiating large scale char applications. They lead to the conclusion that all chars are not created equal. The specific nature of these properties and processes await further research.

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REFERENCES

[1] Demirbas A. Biomass resources for energy and chemical industry. *Energy Edu. Sci. Technol.*, 2000, 5: 21-45.

[2] Aygün A, Yenisoy-Karakas S, Duman I. Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical, and adsorption properties. *Microp. Mesop. Materials*, 2003, 66: 189-195.

[3] El-Hendawy ANA, Samra SE, Girgis BS. Adsorption characteristics of activated carbons obtained from corncobs. *Coll. Surf. A: Physicochem. Eng. Aspects*, 2001, 180: 209-221.

[4] Sensöz S. Slow pyrolysis of wood barks from *Pinus brutia Ten.* and product compositions. *Biores. Technol.*, 2003, 89: 307-311.

[5] Pütün AE, Özbay N, Önal EP, Pütün E. Fixed-bed pyrolysis of cotton stalk for liquid and solid products. *Fuel Process. Technol.*, 2005, 86: 1207-1219.

[6] Bridgwater AV, Bridge SA. A review of biomass pyrolysis and pyrolysis technologies. In: Bridgwater AV, Grassi G eds. *Biomass Pyrolysis Liquids Upgrading and Utilization*. London: Elsevier Science, 1991, 11-92.

[7] Baldock J, Smernik R. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. *Org. Geochem.*, 2002, 33: 1093-1109.

[8] Whitman T, Lehmann J. Biochar – one way forward for soil carbon in offset mechanisms in Africa? *Environ. Sci. Policy*, 2009, in press.

[9] Pessenda LCR, Gouveia SEM, Aravena R. Radiocarbon dating of total soil organic matter and humin fraction and its comparison with ^{14}C ages of fossil charcoal. *Radiocarbon,* 2001, 43: 595-601.

[10] Laird DA. The charcoal vision: A win–win–win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. *Agronomy J.*, 2008, 100: 178-181.

[11] Rondon MA, Molina D, Hurtado M, Ramirez J, Lehmann J, Major J, Amezquita E. Enhancing the productivity of crops and grasses while reducing greenhouse gas emissions through bio-char amendments to unfertile tropical soils. Presentation at the 18th World Congress of Soil Science, Philadelphia, PA, July 9-15, 2006, Presentation #138-68.

[12] Rondon M, Ramirez JA, Lehmann J. Charcoal additions reduce net emissions of greenhouse gases to the atmosphere. In: *Proceedings of the 3rd USDA Symposium on Greenhouse Gases and Carbon Sequestration in Agriculture and Forestry*, 2005 Mar 21–24; Baltimore, MD: University of Delaware Press, 208.

[13] Spokas KA, Koskinen WC, Baker JM, Reicosky DC. Impacts of woodchip biochar additions on greenhouse gas production and sorption/ degradation of two herbicides in a Minnesota soil. *Chemosphere*, 2009, 77: 574-581.

[14] Guerro M, Ruzi MP, Alzuet MU, Bilbao R, Miller A. Pyrolysis of eucalyptus at different heating rates: studies of char characterization and oxidative reactivity. *J. Anal. Appl. Pyrolysis*, 2005, 74: 307-314.

[15] Venterea RT, Baker JM. Effects of soil physical nonuniformity on chamber-based gas flux estimates. *Soil Sci. Soc. Amer. J.*, 2008, 72: 1410-1417.

[16] Yanai Y, Toyota K, Okazani M. Effects of charcoal addition on N_2O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. *Soil Sci. Plant Nutri.*, 2007, 53: 181-188.

[17] Van Zweiten L, Singh B, Joseph S, Kimber S, Cowie A, Chan KY. Biochar and emissions of non-CO_2 greenhouse gases from soil. In: Lehmann J, Joseph S eds. *Biochar for Environmental Management: Science and Technology*. London: EarthScan, 2009, 227-249.

[18] Gee GW, Bauder JW. Particle-size analysis. In: A. Klute (ed.) *Methods of soil analysis. Part 1. 2nd edition.* Agron. Monogr. 9. Madison, WI: ASA and SSSA, 1986, 383-411.

[19] Nelson DW, Sommers LE. 1996. Total carbon, organic carbon, and organic matter. In: Sparks DL ed. *Methods of soil analysis. Part 3*. SSSA Book Ser. 5. Madison, WI: SSSA, 1996, 961-1610.

[20] Cheng CH, Lehmann J, Thies JE, Burton SD, Engelhard MH. Oxidation of black carbon by biotic and abiotic processes. *Org. Geochem.*, 2006, 37: 1477-1488.

[21] Zimmerman A. Physical and chemical controls on biochar stability in the environment. Presentation at the 2009 North American Biochar Conference, Aug. 9-12, 2009. Boulder, CO.

[22] Fisher GL, Chang DPY, Brummer M. Fly ash collected from electrostatic precipitators: Microcrystalline structures and the mystery of the spheres. *Science*, 1976, 192: 553-556.

[23] Morterra C, Low MJD, Severdia AG. IR studies of carbon. 3. The oxidation of cellulose chars. *Carbon*, 1984, 22: 5-12.

[24] Toles, CA, Marshall WE, Johns MM. Surface functional groups on acid-activated nutshell carbon. *Carbon*, 1999, 38: 1207-1214.
[25] Moreno-Castilla C, Lopez-Ramon MV, Carrasco-Marin F. Changes in surface chemistry of activated carbons by wet oxidation. *Carbon*, 2000, 38: 1995-2001.
[26] Sergides CA, Jassim JA, Chughtai AR, Smith DM. The structure of hexane soot. Part III: Ozonation studies. *Appl. Spectroscopy*, 2000, 41: 482-492.
[27] Karagoz S, Bhaskar T, Muto A, Sakata Y. Comparative studies of oil compositions produced from sawdust, rice husk, lignin and cellulose by hydrothermal treatment. *Fuel*, 2005, 84: 875-884.
[28] Hitoshi T, Ai F, Haruo H. Development of advanced utilization technologies for organic waste. (Part 1). Greenhouse gas and nutrient salt adsorption properties of wood-based charcoal. *Denryoku Chuo Kenkyujo Abiko Kenkyujo Hokoku*, 2002, U02010, 17 pp.
[29] McBaim JW. Theories of adsorption and the technique of its measurement. *Nature*, 1926, 117: 550-551.
[30] Bird M I, Moyo C, Veenedaal EM, Lloyd J, Frost P. Stability of elemental carbon in a savanna soil. *Global Biogeochem. Cycles*, 1999, 13: 923-993.
[31] Murage E W, Voroney P, Beyaert RP. Turnover of carbon in the free light fraction with and without charcoal as determined using the ^{13}C natural abundance method. *Geoderma*, 2007, 138: 133-143.
[32] Glaser B, Haumaier L, Guggenberger G, Zech W., The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics. *Naturwiss.*, 2001, 88: 37-41.
[33] Nishimiya K, Hata T, Imamura Y. Analyses of chemical structure of wood charcoal by X-ray photoelectron spectroscopy. *J. Wood Sci.*, 1998, 44: 56-61.
[34] Schmidt MWI, Noack AG. Black carbon in soils and sediments: analysis, distribution, implications, and current challenges. *Global Biogeochem. Cycles*, 2000, 14: 777-793.
[35] Kawamoto K, Ishimaru K, Imamura Y. Reactivity of wood charcoal with ozone. *J. Wood Sci.*, 2005, 51: 66-72.
[36] Puri, BR. Chemistry and physics of carbon. In: Walker PL Jr ed. *Chemistry and Physics of Carbon*. New York: Dekker, 1970, 191-282.
[37] Billinge BHM, Evans MG. The growth of surface oxygen complexes on the surface of activated carbon exposed to moist air and their effect on methyl iodide-131 retention. *J. Chim. Physique et Physico-Chimie Biologique*, 1984, 81: 779-784.
[38] Adams LB, Hall CR, Holmes RJ, Newton RA. An examination of how exposure to humid air can result in changes in the adsorption properties of activated carbons. *Carbon,* 1988, 26: 451-459.
[39] Magrini-Bair K. Biomass-derived, carbon sequestering, designer fertilizers. Presentation at the 2009 North American Biochar Conference, Aug. 9-12, 2009. Boulder, CO.
[40] Liang B, Lehmann J, Solomon D, Sohi S, Thies JE, Skjemstad JO, Luizão FJ, Engelhard MH, Neves EG, Wirick S. Stability of biomass-derived black carbon in soils. *Geochim. Cosmochim. Acta*, 2008, 72: 6096-6078.
[41] Steiner C, Teixeira WG, Lehmann J, Zech W. Microbial response to charcoal amendments of highly weathered soils and Amazonian Dark Earths in Central Amazonia – preliminary results. In: Glaser B and Woods WI eds. *Amazonian Dark Earths: Explorations in Time and Space*, Berlin: Springer, 2004, 195-212.
[42] Huang Y, Zou J, Zheng X, Wang Y, Xu X. Nitrous oxide emission as influenced by amendment of plant residues with different C:N ratios. *Soil Biol. Biochem.*, 2004, 36: 973-981.
[43] Firestone MK, Firestone RB, Tiedje JM. Nitrous oxide from soil denitrification: Factors controlling its biological production. *Science*, 1980, 208: 749-751.
[44] Kinney CA, Mandernack KW, Mosier AR. Laboratory investigations into the effects of the pesticides mancozeb, chlorothalonil, and prosulfuron on nitrous oxide and nitric oxide production in fertilized soil. *Soil Biol. Biochem.*, 2005, 37: 837-850.
[45] Khin KM, Toyota K. Suppression of nitrous oxide production by the herbicides glyphosate and propanil in soils supplied with organic matter. *Soil Sci. Plant Nutrit.*, 2007, 53: 441-447.
[46] Mosier AR. Soil processes and global change. *Biol. Fertil. Soils*, 1998, 27: 221-229.
[47] Wornat MJ, Hurt RH, Yang NYC, Headley TH. Structural and compositional transformations of biomass chars during combustion. *Combustion and Flame*, 1995, 100: 131-14

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