Impact of biochar field aging on laboratory greenhouse gas production potentials

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Abstract

Recent observations of decreased greenhouse gas (GHG) production from biochar amended soils have been used to further substantiate the environmental benefit of biochar production and soil incorporation strategies. However, the mechanisms behind this biochar-mediated response have not been fully elucidated. In addition, the duration of these GHG reductions is not known and is of pivotal importance for the inclusion of biochar into future bioenergy production and climate abatement strategies. In this study, the impacts of biochar field aging on the observed GHG production/consumption were evaluated. Two different wood-derived biochars and a macadamia nut shell biochar were weathered in an agricultural field in Rosemount, MN (2008–2011) and the impacts on net soil GHG production/consumption were assessed through laboratory incubations. For the three biochars evaluated here, weathering negated the suppression of N_2O production that was originally observed from the fresh biochar in laboratory incubations. On the other hand, all three weathered biochars enhanced CO_2 production (three- to tenfold compared with the fresh biochar amendments) in laboratory soil incubations, suggesting an enhanced microbial mineralization rate of the weathered biochar. This enhanced mineralization could be aided by the chemical oxidation of the biochar surfaces during weathering. Fresh biochar reduced observed soil methane oxidation rates, whereas the weathered biochars had no significant impacts on the observed soil methanotrophic activity. This study demonstrates that for these three biochars, weathering greatly alters the GHG response of the soil systems to biochar amendments.

Keywords: black carbon, carbon dioxide, carbon sequestration, nitrous oxide, soil amendment

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Introduction

The pyrolysis of biomass, or the chemical–thermal conversion in the absence of oxygen, can be a significant source of renewable bio-energy (Özçimen & Karaosmanoglu, 2004), and at the same time providing three products: a solid, liquid, and a gas (Bridgwater *et al.*, 1999). Prior to the late 1980s, pyrolysis was solely used for the generation of energy and not as a vehicle of carbon sequestration (Goldberg, 1985; Seifritz, 1993; Kuhlbusch & Crutzen, 1995). Biochar is the name given to the solid residual, when the purpose for the biomass pyrolysis is to achieve a carbon sequestration benefit (Lehmann, 2007). Due to the fact that biochar is a chemical–thermal transformation product of the original biomass, biochar is part of the black carbon continuum (Spokas, 2010).

Initial research indicates that biochar can act as an agent for carbon sequestration (Goldberg, 1985; Lehmann, 2007; Laird, 2008). When biochar is added to soils, secondary benefits of liming acidic soils (Van

Zwieten *et al.*, 2010a), reducing aluminium availability (Steiner *et al.*, 2008), increasing cation exchange capacities (Glaser *et al.*, 2002), reducing N-nutrient leaching (Major *et al.*, 2010a), remediating heavy metal and/or chemical contaminated sites (Hale *et al.*, 2011), increasing agrochemical sorption (Uchimiya *et al.*, 2012), and reducing net soil greenhouse gas (GHG) emissions (Major *et al.*, 2010a; Singh *et al.*, 2010; Sohi *et al.*, 2010; Spokas *et al.*, 2012) have been documented. However, observations for alterations in net soil GHG production/emission have been variable, with some biochars suppressing while other biochars stimulate or have no significant effects on GHG production (Spokas & Reicosky, 2009; Clough *et al.*, 2010; Van Zwieten *et al.*, 2010b; Zimmerman *et al.*, 2011). These biochar-mediated impacts on soil GHG production appear to be a complex interaction of both biotic and abiotic processes, which are intimately linked to particular biochar and soil combinations (Shneour, 1966; Spokas & Reicosky, 2009; Atkinson *et al.*, 2010; Lehmann *et al.*, 2011). The exact mechanisms responsible for these biochar mitigation effects in soil GHG production are still unresolved (Warnock *et al.*, 2007; Lehmann *et al.*, 2011), but recent hypotheses have focused on chemical compound

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inhibitors sorbed to the biochar, particularly for the N_2O and plant pathogen suppression (Clough et al., 2010; Graber et al., 2010; Spokas et al., 2010) as well as alteration in soil microbial communities (Khodadad et al., 2011; Lehmann et al., 2011).

On the other hand, not all biochars have suppressed soil nitrous oxide (N_2O) production following incorporation. Some high nitrogen containing biochars, such as those from animal manures or food wastes, have stimulated N_2O production following soil incorporation (Spokas & Reicosky, 2009; Singh et al., 2010; Van Zwieten et al., 2010b; Bruun et al., 2011). These observations support the conclusion that biochars need to be targeted to remedy specific soil deficiencies (Novak & Busscher, 2012), which has been hypothesized for some time for biochar (charcoal) amendments (Kirwan, 1793).

The duration of these positive GHG suppression actions and soil fertility improvements are paramount to the forecasting of the net economic and environmental benefits of biochar utilization and bioenergy production (Spokas et al., 2012). Particularly, as biochar application to soils has had questionable economic value since the beginning of modern science (Kirwan, 1793; Holbrook, 1849). A majority of the existing laboratory and field studies have utilized freshly created biochars. On the other hand, the impact of aging has been hypothesized as a critical factor for the interaction of biochar with the plant and soil systems, particularly for the sorption of nitrogen containing compounds (Seredych & Bandosz, 2007; Wang et al., 2012).

There is already evidence in the literature suggesting that biochar aging will have an effect on sorption (Hale et al., 2011; Jones et al., 2011a). In one of the first studies on the alteration of biochar surface chemistry, Sheldon (1920) observed a threefold increase in the N_2 sorption as a function of aging, a biochar for 3 years under laboratory storage conditions. Incidentally, an increase in N_2 sorption was also observed for a peanut shell biochar that was stored in an outdoor pile for 1 year (Spokas & Reicosky, 2009). These alterations in the sorption behavior of biochar are a function of how biochar is created, stored, treated, and conditioned (including chemical/ thermal activation) (Rideal & Wright, 1926; El-Shobaky & Youssef, 1978; Adams et al., 1988; Uchimiya et al., 2012). By the way, these production and activation processes have been optimized in activated charcoal manufacturing (Wigmans, 1989). In a recent study, Martin et al. (2012) observed reductions of 47–68% in the sorption capacity of diuron and the sorption capacity for atrazine was statistically equal to the unamended soil for two different biochar amended soils as a consequence of a 32 month aging period in Australia. These data suggest that the initial results for the increased sorption by biochar are of limited temporal extent.

In addition to sorption, weathering influences the cation exchange capacity of biochar amended soils (Steiner et al., 2007; Major et al., 2010b). Weathering results in alterations of biochar surface group chemistries due to abiotic surface reactions (Puri et al., 1958; Degroot et al., 1991; Cheng et al., 2006, 2008; Joseph et al., 2010), which even occur at ambient conditions and can be catalyzed by various enzymes and soil elements (Watts, 1958; Goldberg, 1985; Zepp et al., 1997; Mul et al., 1998; Neeft et al., 1998; Bird et al., 1999). The impact of biochar weathering/aging on GHG suppression has received limited attention in the literature, which is surprising given the critical influence that the duration of the GHG suppression benefit has in economic and carbon accounting studies (e.g., Gaunt & Lehmann, 2008; Spokas et al., 2012). Laboratory incubations are typically short term, lasting typically less than 1 year (e.g., Cayuela et al., 2010; Bruun et al., 2011; Wang et al., 2011).

Differences in the response of the biochar amendment on field GHG suppression with time have been already observed. Assessments of GHG emissions from biochar-amended field plots have measured differences shortly after application and then no significant differences between the biochar and control plots at later sample times (Castaldi et al., 2011). Studies examining the reapplication of biochar to field plots have also suggested a short-term duration of the biochar-mediated responses (Quilliam et al., 2012). In addition, Scheer et al. (2011) observed no statistical difference in the N_2O emission rate of biochar-amended plots compared with controls when assessed with high temporal intensity GHG flux measurements. These data suggest that a potential reason for these cited differences between biochar and control plot emissions measured by flux chambers could be due to temporal GHG flux differences, as biochar is known to also influence physical properties of the amended soil (e.g., bulk density, soil water holding capacities, and hydraulic conductivity) (Tryon, 1948; Laird et al., 2010; Dumroese et al., 2011; Uzoma et al., 2011). These soil physical alterations of biochar amended soil could directly affect temperature and moisture transport as well as indirectly impact the GHG flux assessments (Venterea et al., 2009). Other studies have observed significant decreases in field GHG emission rates following biochar addition of 70% from ruminant urine patches (Taghizadeh-Toosi et al., 2011) and reductions in N_2O emissions have also been observed following fertilizer application to biochar amended soils (Wang et al., 2011, 2012; Zhang et al., 2012a). The temporal duration of these reductions was not assessed.

To examine the duration of these GHG reductions from biochar amendments, the impacts of field aging on the observed soil GHG production were evaluated. This study compares the response of three fresh biochars to

their paired field-aged biochar to determine the differences in soil GHG production following biochar additions in laboratory incubations.

Materials and methods

Study location

Field strips were established at the University of Minnesota's Research and Outreach Station in Rosemount, MN (44°45′ N, 93°04′ W) in the fall of 2008. Soil at the site is a Waukegan silt loam (fine-silty over skeletal mixed, super active, mesic typic Hapludoll) containing approximately 22% sand, 55% silt, and 23% clay with a pH (1 : 1 H_2O) of 6.4, 2.6% total organic carbon, slope <2%, and a field capacity moisture content (−33 kPa) of 14.8% (w/w). Individual plots were 4 × 28 m (16 × 92 ft) each, with a 4 m buffer area between and around the plots. The field plots and boarder areas were in a continuous corn rotation during this experiment.

Biochars

Three different biochars were used in these experiments: (1) a slow pyrolysis hardwood biochar [BC1; oxygen exclusion kiln; approximately 1 day residence time; Cowboy Charcoal, Brentwood, TN, USA], (2) a slow pyrolysis wood pellet biochar [BC2; updraft gasifer; limited but not excluded O_2 entry; residence time approximately 10–15 min; Chip Energy, Goodfield, IL, USA], and (3) a fast-pyrolysis macadamia nut shell biochar [BC3; inert (N_2) gas purge in reactor (no O_2 presence); 30 s residence time; Biochar Brokers; Denver, CO, USA]. All three biochars were created at similar temperatures (500–550 °C), although different residency times, pyrolysis units, and feedstocks were used. Biochars (BC1 to BC3) were manually applied as received (no grinding, sieving, or milling; Fig. 1). As seen in Fig. 1, biochars possessed different initial average particle sizes of 4 cm for BC1, 0.8 cm for BC2, and 2 cm for BC3. Even though particle size influences weathering processes (i.e., Jackson *et al.*, 1947), biochars were used as received to mimic the likely application technique for larger field scale applications. Biochars were applied in the fall of 2008 at a rate of 22 000 kg ha^{-1} and incorporated to a depth of 15 cm (average bulk density = 1.2 g/cc; resulting rate approximately 1% w/w) by rototilling. Following incorporation, these biochar strips were managed as continuous corn plots with annual rototilling in the spring prior to planting (15 cm depth). In Fall 2011 (~3 years after application), random soil samples were collected from 0–15 cm depth interval from these field strips following harvest. Due to the particle sizes of these biochars (Fig. 1), the biochar could be manually separated from the soil through sieving and hand picking with tweezers. This process was continued until ~50 g of biochar was
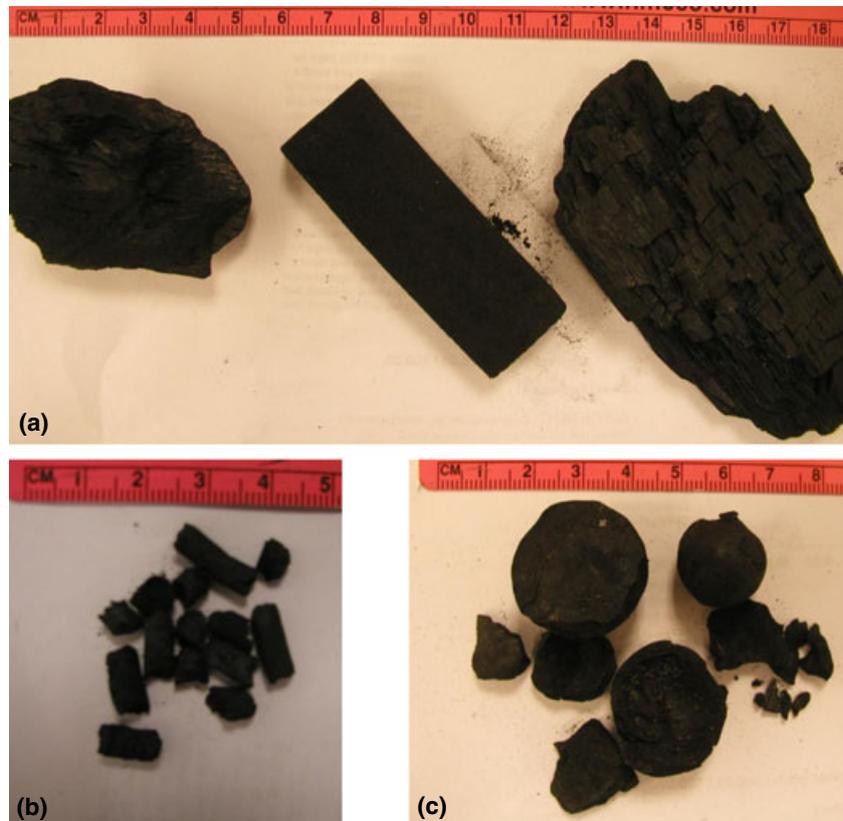
Fig. 1 Illustrations of the three fresh biochars: (a) hardwood slow pyrolysis biochar (BC1), (b) slow pyrolysis wood pellet biochar (BC2), and (c) macadamia nut shell biochar (BC3).

recovered. The biochars did experience particle size reduction as a consequence of the field tillage operations (≈50%). The recovered biochar was further separated from the soil by rinsing with deionized water (≈50 g biochar: 1 L deionized water) and allowing the biochar to air dry. Following air drying, the biochar was placed in a sealed container until establishment of the laboratory incubations.

This resulted in three weathered samples for BC1 through BC3, corresponding to WBC1 to WBC3. The rinsing with deionized water to remove the soil was not seen as a significant contribution to weathering, as the biochar would have experienced various infiltration/precipitation events in the field (Table 1). In addition, there were no statistically significant differences observed in GHG production potentials between water-rinsed and non-rinsed weathered biochars (data not shown). Water rinsing did visually remove a portion of the incorporated soil, which is the reason the rinsed weathered biochars were used. The fresh biochars were not rinsed and used as received.

Biochar analyses (SEM-EDX, ultimate, and proximate analyses)

Biochars were analyzed using scanning electron microscope-electron diffraction analysis (SEM-EDX) for elemental analysis pre and postweathering. EDX analysis allows the estimation of chemical composition as well as visual inspection of the biochar specimens (Nuspl et al., 2004). Analyses were conducted using ASPEX Corporation (Delmont, PA, USA). Proximate and ultimate analyses, following ASTM methodology for coal were performed by Hazen Research (Golden, CO, USA). The pH of

the biochar was determined in 1 : 5 biochar : deoinzed water slurries.

Soil for laboratory GHG incubations

Surface soil (0–5 cm) that was located outside of the biochar-applied field strips was collected, sieved to <2 mm, and homogenized for the incubation study. Soil was collected within 30 days of initiating the soil incubations to reduce the impacts of storage on the microbial assessments (Zelles et al., 1991). Soil was collected following corn harvest in 2011.

GHG incubations

The biochars were then utilized in triplicate greenhouse gas incubation studies, which were similar in design to those performed by Spokas et al. (2009) as given below:

1 5 g soil + 0.75 mL deionized (DI) water (soil control),
2 0.5 g biochar + 0.75 mL DI water (biochar control), and
3 0.5 g biochar + 5 g soil + 0.75 mL DI water.

The above incubations were carried out at field capacity (-33 kPa) and on each of the six different biochars (Table 2). Biochar was not mechanically ground prior to the incubations, as this would expose new surfaces during the grinding and might not be reflective of the weathered surfaces. Instead, individual fragments of <12 mm (to fit into the serum bottle opening) were selected for the incubation study. However, this would not guarantee equivalent weathering for all the biochar fragments. Soil and biochar were manually mixed in the serum bottle prior to the moisture addition. Triplicate sub-samples were placed in clean and sterilized 125 mL serum vials (Wheaton Glass, Millville, NJ, USA) and sealed with red butyl rubber septa (Grace, Deerfield, IL, USA). The incubations were preincubated for 7 days to allow reestablishment of steady-state conditions, as the production of GHG after moisture and amendment addition is highly variable (i.e., Cabrera, 1993; Franzluebbers et al., 1996; Lamparter et al., 2009). Following the preincubation, periodic headspace gas samples were withdrawn from the incubations for analysis on a gas chromatographic system (GC-FID/TCD/ECD) that was previously described in Spokas & Bogner (2011) to quantify gas production over the 100 day incubation period. The individual gases analyzed were oxygen, nitrogen,

Table 1 Annual climatic data for the Rosemount, MN site

| Year | Air temperature (°C) | | | Precipitation mm total |
	Maximum	Average	Minimum	
2008	38.9	7.25	−23.9	446
2009	32.0	7.74	−30	511
2010	35.0	9.03	−25.6	537
2011	35.0	8.58	−27.2	513
1820–2011 (average)		7.02		703

Table 2 Ultimate and proximate analysis of biochar samples. Averages of the analyses are shown along with the standard deviation in parentheses. Percentages are given in reference to the dry sample basis

Biochar ID	C (%)	H (%)	N (%)	O (%)	Ash (%)	Volatile matter (%)	Fixed C (%)	pH
BC1	90.1 (0.1)	1.5 (0.1)	0.2 (0.1)	8.2 (0.3)	2.5 (0.1)	12.5 (0.2)	85.0 (0.6)	7.4 (0.1)
WBC1	89.0 (5.4)	2.5 (0.9)	0.2 (0.1)	8.3 (0.8)	3.0 (1.2)	14.8 (3.2)	82.2 (4.1)	6.4 (0.4)
BC2	73.4 (1.0)	1.3 (0.4)	0.2 (0.1)	25.1 (0.3)	6.4 (0.1)	12.3 (0.3)	81.3 (0.5)	10.1 (0.1)
WBC2	76.9 (3.2)	2.1 (1.1)	0.2 (0.1)	20.8 (1.4)	8.8 (1.5)	23.6 (2.0)	67.6 (5.9)	5.7 (0.5)
BC3	93.2 (1.0)	2.6 (0.4)	0.6 (0.4)	3.6 (0.3)	1.9 (0.1)	16.9 (0.3)	81.2 (0.5)	7.5 (0.1)
WBC3	84.3 (4.2)	2.8 (1.0)	0.7 (0.2)	12.2 (1.5)	4.8 (1.8)	21.0 (2.3)	74.2 (8.2)	5.4 (0.5)

carbon dioxide, nitrous oxide, and methane. The GC system was calibrated for the above gases using multiple traceable gas tank mixtures (Minneapolis Oxygen, Minneapolis, MN, USA). If the O_2 level dropped below 15% during the incubation, the incubation was stopped and the rates of production were calculated up to that point to maintain comparison of aerobic conditions across all incubations. This aeration limit does not impact the rate calculation as the observed production rates were linear ($R^2 > 0.85$) for the 100 day incubation period. The linearity of the GHG production was further ensured due to the preincubation period (7 days), which does not account for the variable pulse of CO_2 resulting from rewetting soil samples (i.e., Fierer & Schimel, 2003) and initial biochar degassing/production (Jones *et al.*, 2011b; Zimmerman *et al.*, 2011). Total GHG production/consumption for the soil and the soil + biochar incubations was calculated as shown below:

$$\text{Total GHG Production Rate} = \frac{[(\text{GHG}_{\text{Soil+Biochar}}) - (\text{GHG}_{\text{BiocharControl}})]}{5\text{g soil}}, \quad (1)$$

where $\text{GHG}_{\text{Soil+Biochar}}$ is the total production/consumption rate of the particular GHG in the soil + biochar treatment (see Eqn 2), and $\text{GHG}_{\text{BiocharControl}}$ is the total production rate of the gas in the biochar control treatment (if applicable). In this fashion, the production/consumption of the biochar is accounted for in the estimated net impact on the GHG production (Spokas *et al.*, 2009; Zimmerman, 2010). The total production rate of a particular GHG from the incubations can be estimated by the following formula (assuming 25 °C and 1 atm):

$$\text{GHG Production Rate (mg d}^{-1})= \frac{\text{slope(ppmv d}^{-1})}{V_{molar}}(MW)(\chi)\left(\frac{120\text{mL}}{1000000\text{mL m}^{-3}}\right), \quad (2)$$

where the slope is the change in GHG concentration in the headspace per day (fitted with a linear regression on the periodic headspace gas concentrations), MW is the molecular weight of the gas of interest, and χ is the ratio of the molar mass of C or N to molecular weight of the gas (i.e., 12/44 for CO_2, 28/44 for N in N_2O; 12/16 for CH_4), V_{molar} is the molar volume of a gas (2.447×10^{-2} m^3 mol L^{-1}), and finally the last term is the conversion of volume units and accounting for the headspace volume of the serum bottle (120 mL).

Statistics

Results for the GHG production/consumption activities were arithmetic means of triplicate samples. Linear regression analysis was conducted over the 100 day period to calculate the rate of change in headspace concentration per day (Eqn 2). This linear extrapolation has been performed in other studies (Spokas *et al.*, 2009), and is justified based on observed linear changes in the concentrations over the 100 day incubation period ($R^2 > 0.85$). 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, USA) between the paired fresh and weathered biochars as well as between biochar amended and control incubations. 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.
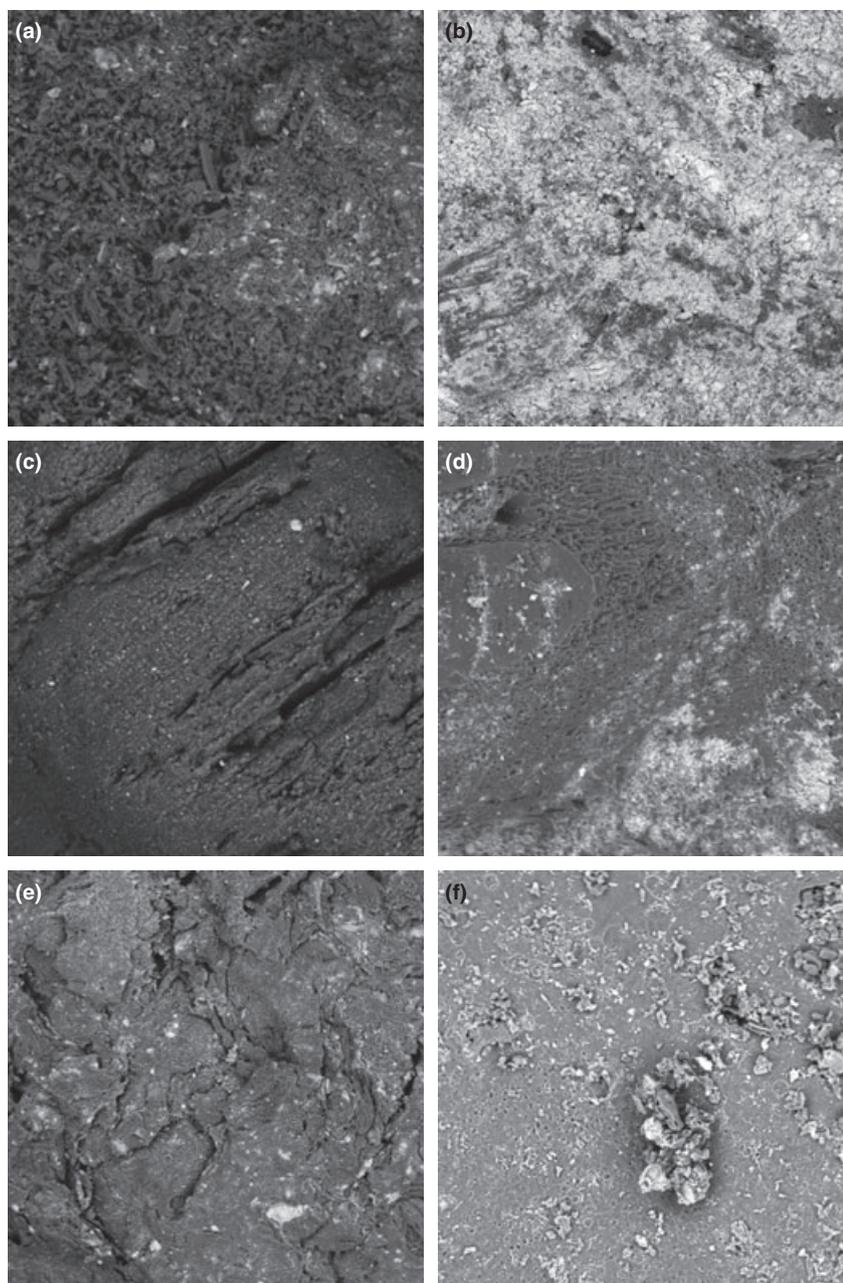
Results

Climate data

The maximum, average, and minimum air temperatures along with the annual total precipitation for 2008 through 2011 for the Rosemount, MN field site are given in Table 1. The last 190 year average weather record reflects an average air temperature of 7.7 °C and 70 cm of precipitation. The average air temperature for 2008, 2009, 2010, and 2011 were 7.3, 7.7, 9.0, and 8.6 °C, respectively. The total annual precipitation ranged from 446 to 537 mm over this same period.

Biochar analyses

The ultimate and proximate analyses showed increases in ash and volatile matter content with corresponding decreases in fixed carbon of the weathered biochars (Table 2). The magnitudes of the differences were a function of the individual biochars. Incidentally, the pH values of the three biochars also decreased (Table 2). As mentioned above, the soil at the Rosemount, MN, USA site has a pH of 6.4. The most significant pH decrease was observed in BC2, which is a slow pyrolysis wood pellet biochar, which decreased from 10.1 to 5.7 as a consequence of the weathering. BC1 dropped one pH unit from 7.4 to 6.4 for WBC1 and BC2 dropped almost two units, from 7.5 to 5.4 for WBC2 as a consequence of the field weathering.

Also noteworthy is the observation that all weathered biochar samples possessed higher analytical variability (increase in standard deviations; Table 2). One of the causes of this can be deduced from the EDX data. The EDX analyses indicated the presence of entrapped soil into the biochar pores (Fig. 2). This can be seen by the increase in Al, O, K, and Si presumably from soil minerals (Table 3) and this soil was visualized in the SEM images by the coloration change (whiter reflections in the weathered samples are mineral soil; Fig. 2). If during the EDX measurement, the analysis region was limited manually to the carbon skeletal portion of the biochar, virtually equivalent composition was achieved in the pre and postweathered samples of BC1 and BC3, and there was a ~16% loss of C in the BC2 skeletal component, dropping from 78.3 to 62.5% carbon (Table 3). However, this difference in C content could be related to actual biochar particle differences and not solely due to weathering losses.

Fig. 2 Paired SEM pictures of biochar particles for: (a) fresh BC-1, (b) weathered BC-1 (WBC1), (c) fresh BC2, (d) weathered BC2, (e) fresh BC3, and (f) weathered BC-4 (WBC4). All images were collected at identical magnification, and the corresponding EDX results are shown in Table 3. Images were provided by Aspex Corporation (Delmont, PA).

From the EDX analysis, the weathered biochar samples also lost a majority of the Ca (50–93% loss) and P (50–100% loss) during weathering (Table 3). However, the selected analysis region for the postweathering biochar influences the EDX chemical composition results, as biochar is not a homogeneous substance, which is further hampered by the trapped soil in the pores of postweathering samples increasing sample heterogeneity.

GHG impacts

There was a significant reduction in the impact of the biochar on soil GHG production observed as a function of environmental weathering across all three biochars analyzed here. Figure 3 shows the results comparing the fresh and weathered biochar impacts on GHG production in the laboratory incubations. Fresh biochar amendments did reduce observed N_2O production by

Table 3 Elemental data from SEM-EDX analysis of biochar particles. Values are given in percentages

Biochar	C	O	Al	Si	P	S	K	Ca
Hardwood (slow pyrolysis) biochar								
BC1	78.6	11.0	0.5	0.5	0.2	0.1	2.3	4.4
WBC1	84.3	10.0	0.9	1.9	0	0	1.7	0.4
WBC1 (char-no pore)	75.5	12.5	0	0	0	0	0.2	0.1
Wood pellet (slow pyrolysis) biochar								
BC2	78.3	4.0	0	0	0.2	0	1.8	13.5
WBC2	26.5	51.0	0.2	10.0	0	0	3.8	0.9
WBC2 (char-no pore)	62.5	9.5	0	0	0	0	0.2	0.3
Macadamia nut shell (fast pyrolysis)								
BC3	60.2	36.0	0.0	0.1	0.4	0.1	1.9	0.8
WBC3	22.6	58.0	3.9	6.9	0.2	0.2	3.2	0.4
WBC3 (char-no pore)	60.5	35.4	0	0.0	0	0	1.0	0.1

23–34%. These suppressions were variable for the different biochars, with BC1 suppressing 34%, BC2 reducing 27%, and BC3 suppressing 23% compared with the control soil N_2O production (Fig. 3a).

Originally, all fresh biochars did suppress N_2O production. However, the weathered biochars resulted in no statistically significant decreases in the N_2O production compared with the control soil. In fact, WBC3 actually resulted in a statistically significant increase in the N_2O production rate of 21% from 29 to 34 ng $N-N_2O$ g_{soil}^{-1} d^{-1} (Fig. 3a).

For methane oxidation, the fresh biochar amendments suppressed the methane oxidation potential for all the biochars studied here (Fig. 3b). The initial biochars suppressed methane oxidation, even causing the soil + biochar mixture to become a net methane producer for BC1 (2 ± 10 ng $C-CH_4$ g_{soil}^{-1} d^{-1}) and BC2 (13 ± 4 ng $C-CH_4$ g_{soil}^{-1} d^{-1}), and the rate of observed methane oxidation was reduced ~60% with the addition of BC3 compared with the control soil (-24 to -10 ng $C-CH_4$ g_{soil}^{-1} d^{-1}) (Fig. 3b). However, after amending the soil with weathered biochar, the methane oxidation capacities were not impacted. Two of the weathered biochars (WBC1 and WBC3) resulted in statistically non-significant increases in methane oxidation capacities and WBC2 resulted in no detectable alteration (Fig. 3b).

There were also significant differences in the response of fresh and weathered biochar as seen in the CO_2 production data (Fig. 3c). BC1 did not impact the CO_2 production rate, but BC2 slightly increased the CO_2 production by 14% and addition of BC3 resulted in a 14% reduction in CO_2 production rates compared with the soil control. There was a larger impact observed as a result of amending the soil with weathered biochars.

WBC1 and WBC2 both doubled the observed CO_2 production to 57 ± 11 and 69.7 ± 13 μg $C-CO_2$ g_{soil}^{-1} d^{-1}, respectively. On the other hand, WBC3 caused an increase to 263 ± 26 μg $C-CO_2$ g_{soil}^{-1} d^{-1} from 28.3 ± 1 μg $C-CO_2$ g_{soil}^{-1} d^{-1} for the soil control. However, the source (soil organic matter, biochar, or sorbed organic compounds) of the CO_2 was not directly determined.

Discussion

Climate

Minnesota is characterized by a continental climate, with cold, often frigid winters (October–May) and warm summers (June–September). As seen in Table 1, recent climates reflect a warmer average air temperature and slightly dryer annual precipitation patterns than the historical averages. However, the annual temperature extremes still bracket an approximate 60 °C span, characteristic of Minnesota's annual seasonal dynamics (-27 °C winter to $+35$ °C summer).

Biochar analyses

Weathering typically results in the increased abundance of carbonyl, carboxylic, and phenolic functional groups on the biochar surface (Shneour, 1966; Joseph & Oberlin, 1983; Degroot et al., 1991; Cheng et al., 2008; Yao et al., 2010; Lin et al., 2012), which coincides with a decrease in biochar pH (Yao et al., 2010). Similar trends were also observed in other studies of field weathered biochar in Australia (Joseph et al., 2010), UK (Jones et al., 2012), as well as laboratory-aged biochars (Yao et al., 2010). Joseph et al. (2010) observed a decrease in the total C of the biochar samples (poultry waste and a green waste biochar) and an increase in the oxygen content leading to an alteration in the O : C ratio from <0.2 to ≈0.75 after 2 years of field weathering. In this study, assuming that the ultimate analyses are representative of the bulk biochar, the only biochar that had a significant alteration in the O : C ratio was BC-3, which increased from 0.02 to 0.11 as a result of the weathering. The other two biochars had no change (BC1; 0.07) and a slight decrease in the O : C ratio of the weathered biochar occurred for BC2 (0.25–0.20). This increase in the O : C ratio for BC3 was not as high as the alteration documented in Joseph et al. (2010). Nevertheless, this increase in the O : C ratio could have implications on the stability of the biochar, as the O : C ratio has been cited as a critical characteristic controlling biochar's resistance to microbial mineralization (Spokas, 2010; Harvey et al., 2012). In addition, the surface chemistry has been cited as the dominant factor determining biochar's interaction with N-containing species (Seredych & Bandosz, 2007).
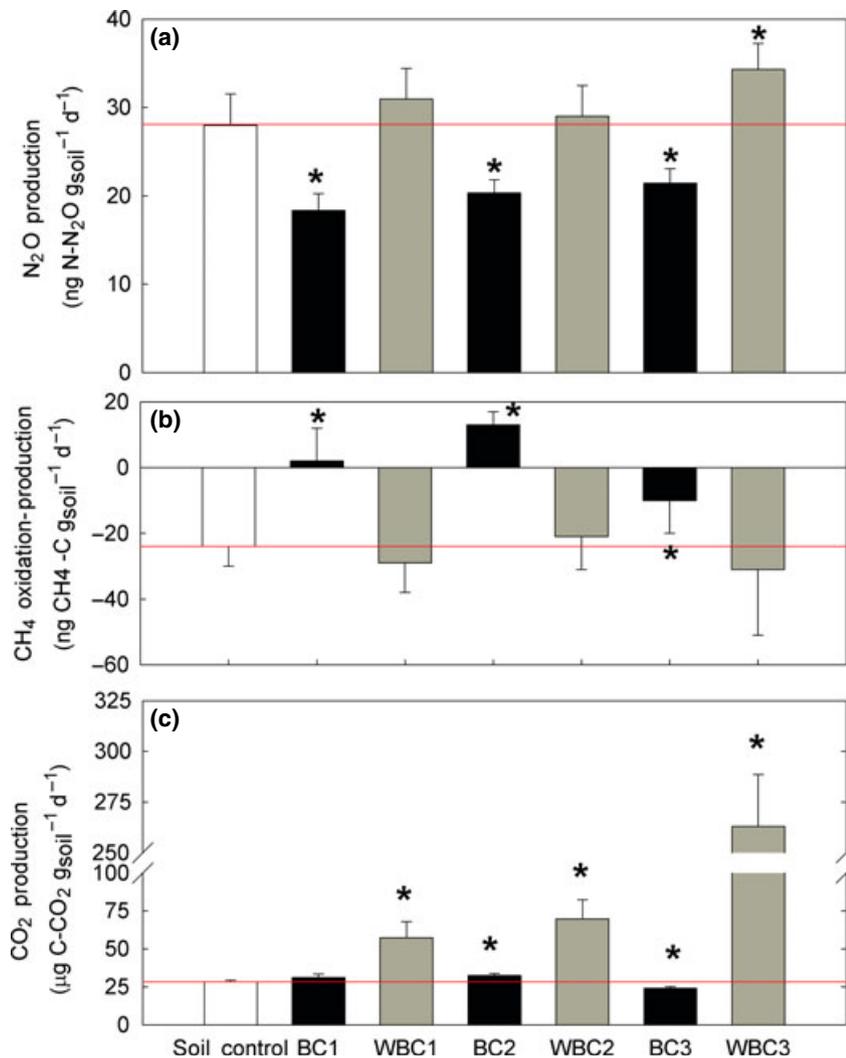
Fig. 3 Illustration of the observed alteration in the greenhouse gas production for (a) nitrous oxide, (b) methane, and (c) carbon dioxide as a function of the fresh and weathered biochars. The solid horizontal line in each graph represents the control soil production. The fresh biochar is given in the black fill and the weathered is in gray-filled bars. The asterisks indicate production rates that are statistically different than the soil control ($P < 0.05$).

We observed a loss of some biochar nutrients during weathering, which is similar to other studies. Yao *et al.* (2010) observed a similar disappearance of Ca, Mg, and K nutrients in weathered biochars. However, this was with a modified laboratory Soxhlet reactor setup and not in the natural environment. Hollister (2011) observed leaching of Ca (7–46% removed solely by laboratory DI water rinsing) and was attributed to the mineralogical alteration of calcium oxalate (present in biomass) to the more soluble calcite (precipitated on biochar) following pyrolysis. In Hollister (2011), 24–64% of the P in biochars was observed to be removed by water rinsing. Novak *et al.* (2009) also observed the increased leaching of P in biochar-amended soils. On the other hand, less than 1% of the P was observed in

the weathering solution in the Yao *et al.* (2010) study. Although not fully understood, this variability in biochar nutrient leaching is dependent on the biochar and soil combination.

Even though the magnitudes of the decrease in pH were variable, all the biochars went from an alkaline to an acidic material as a consequence of the weathering. This drop in the biochar pH has been observed in other studies (Van Zwieten *et al.*, 2010a,b; Yao *et al.*, 2010; Rivera-Utrilla *et al.*, 2011; Seredych *et al.*, 2011). The main implication of this pH alteration is on the use of biochar as a liming agent. Weathering results in acidifying the biochar through surface oxidation reactions, forming carboxylic acids (Sheldon, 1920; Boehm *et al.*, 1964; Carrasco-Marín *et al.*, 1996; Chen *et al.*, 2009).

These observations suggest that biochar might not be an effective agent for long-term soil liming. Similar short-term liming effects have been observed for wood ash additions (Núñez-Delgado et al., 2011). However, the duration of the liming potential of biochar still requires further investigations.

The images in Fig. 2 demonstrate that despite the efforts of separating the soil from the biochar (water rinsing), there was still a variable amount of soil contained within the biochar pores. This trapped soil has a direct impact on the weathered biochar chemical analyses (Tables 2 and 3), and it has been postulated that these clogged pores essentially deactivate the biochar (Joseph et al., 2010). In addition, these clogged pores could provide physical protection for soil microbes (Warnock et al., 2007) or soil organic carbon.

GHG impacts

There was a significant reduction in the impact of the biochar on soil GHG production observed as a function of environmental weathering across all three biochars analyzed here. As seen in Fig. 3, the weathering of biochar did have some universal effects of (1) reducing the impact of the N_2O suppression of the biochar (Fig. 3a), (2) resulting in no significant impact on soil CH_4 oxidation activities after weathering (Fig. 3b), and (3) increasing the magnitude of the CO_2 stimulation (Fig. 3c).

One of the main findings in this study was that weathering significantly reduced the observed N_2O suppression resulting from biochar additions. For these three biochars, the 3 year weathering process eliminated the inhibition of soil N_2O production following incorporation. The exact cause of the loss of biochar's mitigation potential for soil N_2O production is uncertain. This decrease could be related to the lack of sorption potential of the weathered chars due to the clogged biochar pores (Van Zwieten et al., 2010a), if the mechanism for the decreased N_2O is direct sorption of inorganic N forms by the biochar (Taghizadeh-Toosi et al., 2011). However, activated charcoal, with even higher surface areas than biochars, has not had the same impact as biochar in suppressing N_2O production (Spokas & Reicosky, 2009).

Another potential explanation for the decrease in N_2O mitigation potential could be due to the loss (i.e., degradation or desorption) of biochar sorbed nitrification/denitrification inhibitors through weathering. Observations have suggested that organic compounds in biomass (or correspondingly degradation products of biomass) may have a direct suppression (toxicity effect) on the soil microbial biomass (Augustin, 1991; Tian et al., 1992; Capasso et al., 1995; Brown & Morra, 1997,

2009). Numerous compounds have been observed to be inhibitors of microbial nitrification/denitrification enzymatic processes, which include alcohols (Kelly et al., 2004), furans (Sahrawat et al., 1977; Datta et al., 2001), furfurals (Datta et al., 2001), pyradines (Bundy & Bremner, 2004), as well as other compound classes (Sahrawat & Mukerjee, 1977; Slangen & Kerkhoff, 1984). Biochars have been observed to possess a variety of compounds sorbed to the surface, including some microbial inhibitors (Spokas et al., 2011). Weathered biochar does possess a significantly lower quantity of the original sorbed organic compounds (e.g., furans, furfurals, and alcohols) than fresh biochar, despite the higher volatile matter percentage in weathered biochar (Table 2). However, the mechanisms responsible for these alterations in GHG responses require additional research.

There was a shift in the response of the soil system in regards to CH_4 oxidation as a consequence of weathering. The fresh biochar samples suppressed soil methanotrophic activity, which is in contrast to the cited reports of increased CH_4 oxidation inferred from field flux sampling after biochar additions (e.g., Karhu et al., 2011; Feng et al., 2012; Yu et al., 2012; Zhang et al., 2012b) and the assessment of methanotrophic activities using qPCR techniques (Feng et al., 2012). However, some of these studies have been in flooded soils. Similar to the N_2O production above, the exact mechanisms are not fully understood for the variable response in the methanotrophic activity following biochar additions (Spokas & Reicosky, 2009). However, organic compounds that inhibit nitrifier/dentrifier microbes also impact methanotrophs (Bédard & Knowles, 1989; Neufeld & Knowles, 1999). Therefore, it is plausible that the decrease in the presence of microbial chemical inhibitors on the weathered biochar could be partially responsible for the disappearance of the suppressive methanotrophic activity for the weather biochars. However, as we are solely measuring the net effects, we also would not be able to distinguish between a reduced soil methanotrophic (CH_4 oxidation) and increased methanogen (CH_4 production) activity in this study.

In all of the weathered biochars, the observed CO_2 production was enhanced, possibly suggesting that the weathered biochar was more easily decomposed by soil microbes. However, the source of this increase CO_2 emission was not directly elucidated in this study. The other potential is that the biochar itself sorbed more mineralizable C sources during the 3 years in the field (Table 2). The fact that there was not a major alteration in the O : C ratio and lack of major deterioration in the physical appearance of the biochar confirms that the biochar was recalcitrant during the 3 years of field exposure, which also validates the purpose of the material as a C sequestration tool.

Biochar is not a homogenous material and the behavior of weathering is not universal across all biochar types. In the results presented here, field weathering in Minnesota induced significant changes in the soil GHG production following biochar additions. In particular, the reduction in the N_2O suppression capability of the biochar is critical, as suppressed soil N_2O production was initially observed for all three types of fresh biochars evaluated here (Fig. 3a). These results cast doubt on the long-term duration of the mitigation of soil N_2O emissions by biochar additions. Due to the fact that these incubations were laboratory microcosms, there is a need that these observations be confirmed in the field.

Acknowledgements

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