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Effects of biochar and other amendments on the physical properties and greenhouse gas emissions of an artificially degraded soil

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HIGHLIGHTS

- Short-term field study conducted comparing soil quality under HA, WTR, and biochar.
- Biochar significantly increased soil-C and N_2-surface area and reduced bulk density.
- Only WTR significantly increased soil microporous surface area compared to control.
- Cumulative N_2O emission was significantly decreased in the biochar-amended soil.
- WTR and HA resulted in net soil C losses and biochar as a soil C gain.

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ABSTRACT

Short and long-term impacts of biochar on soil properties under field conditions are poorly understood. In addition, there is a lack of field reports of the impacts of biochar on soil physical properties, gaseous emissions and C stability, particularly in comparison with other amendments. Thus, three amendments – biochar produced from oak at 650 °C, humic acid (HA) and water treatment residual – (WTR) were added to a scalped silty-loam soil @ 0.5% (w/w) in triplicated plots under soybean. Over the 4-month active growing season, all amendments significantly increased soil pH, but the effect of biochar was the greatest. Biochar significantly increased soil-C by 7%, increased sub-nanopore surface area by 15% and reduced soil bulk density by 13% compared to control. However, only WTR amendment significantly increased soil nanopore surface area by 23% relative to the control. While total cumulative CH_4 and CO_2 emissions were not significantly affected by any amendment, cumulative N_2O emission was significantly decreased in the biochar-amended soil (by 92%) compared to control over the growing period. Considering both the total gas emissions and the C removed from the atmosphere as crop growth and C added to the soil, WTR and HA resulted in net soil C losses and biochar as a soil C gain. However, all amendments reduced the global warming potential (GWP) of the soil and biochar addition even produced a net negative GWP effect. The short observation period, low application rate and high intra-treatment variation resulted in fewer significant effects of the amendments on the physicochemical properties of the soils than one might expect indicating further possible experimentation altering these variables. However, there was clear evidence of amendment–soil interaction processes affecting both soil properties and gaseous emissions, particularly for biochar, that might lead to greater changes with additional field emplacement time.

1. Introduction

Soil degradation and nutrient depletion are a global concern. Soil restoration techniques to increase soil organic matter (SOM), and stability of soil carbon (C) are required to increase productivity and minimize risks of soil degradation and environmental pollution. To this end, impacts of a range of agricultural and industrial by-products (waste materials) and composts have been studied as soil amendments to enhance soil physical properties (SerraWittling et al., 1996; Sikora and Yakovchenko, 1996; Wells et al., 2000; Zebarth et al., 1999), availability

Abbreviations: AC, ash content; AWC, available water capacity; BD, bulk density; C, carbon; CEC, cation exchange capacity; EC, electrical conductivity; GHG, greenhouse gas; GMD, geometric mean diameter; GWP, global warming potential; HA, humic acid; MRT, mean residence time; MWD, mean weight diameter; OM, organic matter; P, phosphorus; PR, penetration resistance; SA, surface area; SOM, soil organic matter; VM, volatile matter; WHC, water holding capacity; WSA, water stable aggregate; WTR, water treatment residual.

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of plant nutrients (Tejada et al., 2001), increase SOM concentrations and populations of beneficial microbes (Freixo et al., 2002; Lal and Kimble, 1997; Madrid et al., 2007; Reeves, 1997; von Lutzow et al., 2002), and decrease incidences of plant pathogens (Abawi and Widmer, 2000). A range of environmentally-friendly industrial and agricultural by-products have also been tested for their ability to minimize losses of nutrients by leaching and transport of soil contaminants and nutrients such as phosphorus (P) in water runoff (Agyin-Birikorang and O'Connor, 2007; Glaser et al., 2002; Smith et al., 2004). Humic acid (HA), water treatment residual (WTR) and biochar are considered to be among the most promising soil amendment materials for serving these broad ranging purposes.

Humic substances, consisting of HA and fulvic acid, are the dark colored heterogeneous complex organic components of soil that are important to soil fertility. They are formed naturally from plant and animal residues by decomposition and re-synthesis processes (Senesi and Plaza, 2007). Application of HA may improve soil characteristics by buffering pH, chelating micronutrients (Kudeyarova, 2007; Mackowiak et al., 2001; Motojima et al., 2012), and increasing cation exchange capacity (CEC) and available water capacity (AWC) of soil (Senesi and Plaza, 2007; Sharif et al., 2002; Soler-Rovira et al., 2010; Tahir et al., 2011). Coal-derived HA substances, the type used in this study, can increase water retention, AWC and aggregate stability of degraded soils (Piccolo et al., 1996). Despite the consensus that HA could be a promising soil amendment, limited field-scale research has been carried out to understand the effects of HA on soil physical properties, greenhouse gas (GHG) emissions and stability of soil C.

The WTRs, by-products of the water clarification process, may be another effective environmental remedient. For example, application of WTR reduced P leaching from a coastal sandy soil (Ippolito et al., 2011), and water soluble P concentration in a manure-impacted soil (Agyin-Birikorang et al., 2007). Application of WTRs can have positive benefits in regard to (i) reducing heavy metal runoff (Fan et al., 2011; Mahmoud, 2011), (ii) enhancing soil physical quality (Hsu and Hseu, 2011; Park et al., 2010), and (iii) increasing crop yield (Hsu and Hseu, 2011; Mahdy et al., 2009; Oladeji et al., 2009; Park et al., 2010; Titshall and Hughes, 2009). Soil application of WTRs increased pH, aggregate stability, porosity, water holding capacity (WHC), and saturated hydraulic conductivity, and decreased bulk density (BD) in a range of soils (Hsu and Hseu, 2011; Park et al., 2010) with attendant improvements in crop growth (Hsu and Hseu, 2011; Mahdy et al., 2009; Oladeji et al., 2009). While WTR amendment might be expected to decrease SOM degradation via sorptive protection, data on GHG emissions and stability of C in WTR-amended soil are lacking.

The term 'biochar' refers to the solid carbonaceous product of pyrolyzed biomass that is intentionally produced for use as a soil amendment. Considerable progress has been made in understanding its properties, sorption ability, and effects on plant growth when applied to soils. For example, biochar amendments can increase soil pH, base saturation, available nutrient content, nutrient retention and CEC (Glaser et al., 2002; Moreira et al., 2005; Mukherjee and Zimmerman, 2013; Tiessen et al., 1994), and decrease Al toxicity (Glaser et al., 2002; Kishimoto and Sugiura, 1985; Tryon, 1948). Addition of hardwood-derived biochar to sandy and loamy soils was shown to effectively increase CEC 1.5 times and base saturation nine times, and significantly increase available K, Ca, Mg, total N and P (Glaser et al., 2002; Tryon, 1948). Seed germination, plant height and crop yield were doubled following miombo wood-derived biochar amendment (Chidumayo, 1994; Glaser et al., 2002). Several column leaching studies with biochar-amended soils have shown enhanced nutrient release after biochar addition (Laird et al., 2010a; Mukherjee and Zimmerman, 2013), though these results varied strongly with biochar and soil type. While available information shows that the use of biochar can increase soil surface area (SA) (Laird et al., 2010a; Laird et al., 2010b; Liang et al., 2006), decrease BD (Chen et al., 2011; Jones et al., 2010; Laird et al., 2010b), and increase WHC (Jones et al., 2010; Laird et al., 2010b; Uzoma et al., 2011), there is a lack of data on the effects of biochar on soil physical properties under field conditions or these parameters measured in conjunction with crop yields (Mukherjee and Lal, 2014a).

Among the three amendments, HA, WTR and biochar, only biochar has been studied widely for its effects on GHG emissions and these have mainly been laboratory incubation studies that do not necessarily replicate native processes including rhizosphere processes, bioturbation and aggregation and effects of weathering (Kuzyakov et al., 2009). In general, biochar CO_2 emissions have been found to increase with heating temperature and duration (Zimmerman, 2010), but also varied with biomass and climate (Jones et al., 2011; Mukherjee and Lal, 2014a; Scheer et al., 2011; Zimmerman et al., 2011). Some studies have also reported reduction in N_2O emissions from biochar-amended soils, perhaps due to increases in soil aeration (Castaldi et al., 2011; Rogovska et al., 2011; Zhang et al., 2012a). However, both increased (Rondon et al., 2005; Spokas et al., 2009; Spokas and Reicosky, 2009) and decreased CO_2 emissions (Liu et al., 2011) have been reported from biochar-amended soils. Similarly, CH_4 emission from soil may be either enhanced or suppressed by biochar addition (Liu et al., 2011; Rondon et al., 2006; Rondon et al., 2005).

It is difficult to compare the relative benefits of different amendment types because few studies have simultaneously examined a wide range of soil and plant responses to a number of materials. In addition, only a few field studies have monitored changes in soil physical properties with biochar amendment (Mukherjee and Lal, 2014a) and several drawbacks of biochar in this context are recently reported (Mukherjee and Lal, 2014a). Thus, a field study was conducted over 16 weeks, comparing the effects of biochar with two other non-traditional amendments (WTR and HA) on the characteristics of a simulated degraded soil, and GHG emissions under soybean (*Glycine max*). The biochar chosen for this study, oak (*Quercus lobata*) charred at 650 °C (oak-650), has the potential to improve soil conditions based on previous studies (Mukherjee and Zimmerman, 2013; Mukherjee et al., 2011). It is hypothesized that HA (with a high complexation ability) and WTR (with high pH and SA) will improve soil characteristics, and positively impact C stability and soil fertility. Specific objectives of the study were to: (i) assess changes in soil properties over a short time horizon, (ii) understand the relationship between the evolved physicochemical characteristics of the amended soil and GHG emission, and (iii) evaluate the relative short-term effects of these amendments on global warming potential (GWP).

2. Materials and methods

2.1. Materials and field measurements

A field experiment was conducted at the Waterman Farm of The Ohio State University, Columbus, Ohio (40°02′00″N, 83°02′30″W) from June 25th to October 8th, 2012 under a Crosby (fine, mixed, mesic, Aeric Ochraqualf) silt loam soil (Abid and Lal, 2009). Previous studies conducted at this research site found that on average, about half of the annual CO_2 efflux occurs, during the experimental period of time, a single summer growing season (Datta et al., 2013; Shrestha et al., 2009; Shrestha et al., 2013; Ussiri and Lal, 2009; Ussiri et al., 2009), as the ground is frozen or covered by snow during much of the rest of the year.

Commercial coal-derived HA was obtained from Sigma Aldrich, MO, USA and aluminium WTR was collected from a water treatment plant located in Columbus, Ohio. Biochar was produced from oak wood ($5 \times 5 \times 30$ cm pieces), collected in Gainesville, Florida, by combustion for 3 h at the peak temperature of 650 °C in a lidded container sealed loosely to allow smoke to exit. Detailed information on biochar preparation and chemical and physical characteristics of the freshly prepared oak-650 biochar have been presented elsewhere (Kasozi et al., 2010; Mukherjee et al., 2011; Zimmerman, 2010). The coarse size fraction

(0.25–2 mm) of each amendment was used in the field experiment. Some properties of the three amendments are presented in Table 1.

To simulate a degraded soil, the top 5 cm of the soil was mechanically scalped, i.e. removed. The remaining soil contained 2.2 wt.% C. Twelve 2 × 2 m plots, including triplicated treatments and control plots with no amendments, were randomly positioned in the 5 × 30 m scalped portion of the field at Waterman Farm, Columbus, Ohio. Amendments were applied randomly at the rate of 3 kg per plot (dry weight, equivalent to 7.5 Mg ha^{-1} or 0.5% by weight), and mechanically worked into the upper 10 cm of the scalped soil. It was necessary to add equivalent weights of amendments rather than equivalent C amounts because one of the amendments (WTR) was not thought of as carbonaceous compared to others (HA and biochar). The amendment rate used was in the lower end of the range generally considered to be effective for biochar (Biofuelwatch, 2011; Jeffery et al., 2011; Jones et al., 2012; Kammann et al., 2011; Zhang et al., 2013), but in the upper end of the range of the amount of WTR that might be considered affordable for growers to apply. Soil samples were collected by soil core method after four months (i.e., the end of the active growing season) from the 0 to 10 cm depth interval, air-dried, ground and passed through 2 mm sieve prior to laboratory analyses.

Soybean was seeded on each plot at the rate of 56 kg ha^{-1} by a broadcasting method three days after the amendment applications in the plots while plots did not receive any fertilizer or irrigation. Upon harvest, all the plant materials were oven dried at 60 °C, ground and sieved through 500 μm mesh to prepare for vegetative-C and N analyses (Nelson and Sommers, 1996).

At the start of the experiment, high density polyvinyl chloride gas chambers (25 cm high and 15 cm diameter) were installed in the middle of each plot, 8 cm deep into the soil, on average. While there was no plant inside the chambers though root growth inside the chambers was possible. Gaseous samples were withdrawn on a weekly basis until six weeks, and bi-weekly thereafter, using a 20 mL syringe inserted through a sampling port at 5-minute interval (Castaldi et al., 2011; Shrestha et al., 2009). Gaseous samples were always collected at the same time of the day, 11 am–2 pm, the period assumed to be most active for soil respiration. No significant differences in soil respiration were observed within this time frame. Gas samples were stored in 20 mL air tight previously-evacuated glass vials and concentrations of CO_2, CH_4, and N_2O were determined using a gas chromatograph (GC-2014, Shimadzu Corp., Japan). The flux of a gas (F, in m^{-2} day^{-1}) was computed by Eq. (1) (Shrestha et al., 2009):

$$F = \left(\delta G \times 10^{-6}/\delta t\right)(V_C/A)(M/V)1440\ \text{min day}^{-1} \quad (1)$$

where, G is the gas concentration (ppm), t is the time (minute), V_C is the volume of the chamber (m^3), A is the soil surface area within the chamber (m^2), V is the ideal gas molar volume at 25 °C (24.5 L = 0.0245 m^3 mol^{-1}), and M is the molecular weight of the gas (g).

2.2. Analytical methods

The volatile matter (VM) content of each material was determined as weight lost after combustion in a ceramic crucible loosely covered with a ceramic cap at 850–900 °C for 6 min and ash content (AC) as weight lost after combustion at 750 °C for 6 h with no cover (ASTM, 1990; Mukherjee et al., 2011). The pH and electrical conductivity (EC) of soil and amendments were determined using a 1:2 soil:water ratio slurry and a Thermo-scientific Orion Star Series pH/Conductivity Meter. Field BD of soils (wet and dry) from the 0 to 10 cm depth interval was determined by the core method (Grossman and Reinsch, 2002). Bulk densities of the amendments were measured in the laboratory using a graduated cylinder method (ASTM, 2009). Concentrations of total C and N in the soil were determined on samples ground and sieved to 250 μm using an 'Elemntar' (Vario Max, Elemntar Americas, Inc., Germany) by dry combustion (900 °C).

The aggregate size distributions and quantity of water stable aggregate (WSA) in each soil were determined by the wet sieving method (Yoder, 1936). The data were used to compute weight percent WSA, mean weight diameter (MWD), and geometric mean diameter (GMD) of soil aggregates (Youker and McGuinness, 1957). Soil water retention at matrix potentials of −0.033 and −1.5 MPa was measured using a pressure plate apparatus (Dane and Hopmans, 2002). Undisturbed soil cores were used to determine the water retention at field capacity (−0.033 MPa), while loose sieved samples (<2-mm size) were used to determine the permanent wilting point (−1.5 MPa). The AWC of the soil was calculated as the difference in volumetric water content at −0.033 and −1.5 MPa moisture potentials. Three penetration resistance (PR) measurements were made for the 0–10 cm depth from each plot using an Eijkelkamp-type hand penetrometer (Herrick and Jones, 2002). The values were adjusted using the individual moisture content of each plot.

The SA was measured on a Quantachrome Autosorb1 instrument using N_2 and CO_2 sorptometry (N_2-SA and CO_2-SA, respectively) (Mukherjee et al., 2011). Nanopore (>1.5 nm diameter) surface areas (N_2-SA) were calculated using multi-point adsorption data from the 0.01 to 0.3 P/P_o linear segment of the N_2 adsorption isotherms made at 77 K on the basis of the Brunauer, Emmet, and Teller (BET) theory (Brunauer et al., 1938). The SA, including those of the nanopores and micropores (<1.5 nm diameter), was determined on CO_2 adsorption isotherms measured at 273 K generated in the partial pressure range 0.001–0.15 using grand canonical Monte Carlo simulations of the non-local density functional theory (CO_2-SA) (Jagiello and Thommes, 2004). All biochar samples were de-gassed under vacuum at least 24 h at 180 °C prior to analysis.

3. Data modeling

3.1. C-budget

To understand the broader effects of each treatment, the gas emission data was used to model soil C stability and GWP using three approaches. The C-budget for the control and each amended soil was calculated by using the following equation and the assumptions that: (i) all harvested plant biomass was part of potential C-gains, (ii) all root exudates became a portion of the measured CO_2–C emitted, and (iii) negligible C was lost from the soil by leaching of dissolved-C:

$$\begin{aligned}\text{Net C-Sequestered} &= \text{C gains–C losses}\\ &= (\text{biomass-C grown} + \text{added amendment-C}) - \\ &(\text{cumulative emitted } CH_4\text{–C} + \text{cumulative emitted } CO_2\text{–C}).\end{aligned} \quad (2)$$

Table 1
Characteristics of the amendments used in the study, means followed by letters indicating those treatments that are significantly different at $p < 0.1$.

Sample	pH	EC	VM	AC	N_2-SA	CO_2-SA	BD	C	N
		(dS m^{-1})	(%)		(m^2 g^{-1})		(Mg m^{-3})	(g 100 g^{-1}, %)	
HA	5.0c ± 0.0	7.2a ± 1.1	31a ± 0.4	33c ± 0.3	0.1c ± 0.2	58c ± 26.8	0.8b ± 0.0	27b ± 0.1	0.7a ± 0.0
WTR	9.5a ± 0.3	0.9bc ± 0.1	9.8b ± 0.7	45b ± 3.2	16b ± 0.8	84b ± 3.4	0.6b ± 0.0	16c ± 0.3	0.1b ± 0.0
Biochar	9.4a ± 0.1	1.5b ± 0.0	11b ± 1.4	4.3d ± 1.4	214a ± 17	604a ± 6.4	0.3c ± 0.0	90a ± 1.0	0.3b ± 0.0

Abbreviations: HA = humic acid, WTR = water treatment residual, EC = electrical conductivity, VM = volatile matter, AC = ash content, SA = surface area, BD = bulk density.

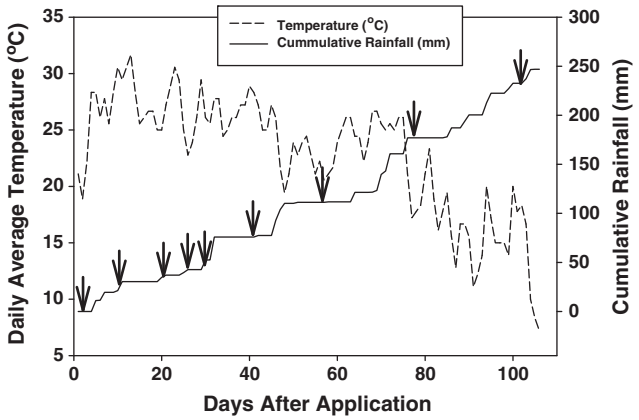

Fig. 1. Average daytime temperature and rainfall recorded during the field trial period (June 25–October 8) following amendment application. Arrows indicate the day of sampling.

3.2. Mean residence time (MRT)

The MRT of soil-C was calculated by fitting a first-order decay model to the gas emission data. Thus, it was assumed that C loss from soil occurred only by gaseous pathways such that:

$$\delta A/\delta t = -kA_o \quad (3)$$

where, $\delta A/\delta t$ is the rate of change of C concentration over time t, and k is the apparent decomposition rate constant (solved graphically), and A_o is the initial C concentration. The MRT of C was then calculated as:

$$MRT = 1/k. \quad (4)$$

Though this model treats soil C and amendment C as a single component, degrading at a single rate, which is certainly not the case, this model was used because other more complex models (double decay or power) fit the data less well. Furthermore, the mono-exponential decay model can be considered a conservative approach, i.e. is less likely to overestimate the amount of C mineralized over the longer term.

3.3. Global warming potential (GWP)

Cumulative gas emission was calculated by summing the weighted daily fluxes in each soil column by numerical integration of the area underlying the gas flux curve using the trapezoid rule over the active growing season (Dendooven et al., 2012). The GWP of each treatment was calculated as the sum of cumulative gas emissions of CO_2, CH_4 and N_2O, multiplied by the radiative forcing factor of each gas 1, 23 and 296, respectively, for a time horizon of 100 years (USEPA, 2007).

3.4. Statistical analyses

All values are presented as means ± standard deviations of single measurements made in the triplicated field treatment. Significance of differences between treatments was analyzed using Tukey's test in PROC GLM in SAS version 9.2 (SAS, 2012). Because of the high natural variability expected within each treatment due to intra-field soil variations, relationships with p values <0.1 were judged to be significant rather than the more commonly used significance level of $p < 0.05$ in order to allow greater chance to detect differences between treatments (Kammann et al., 2012).

4. Results

4.1. Weather

Over the experimental period, average temperature was 25 °C with highs averaging 30 °C and lows averaging 21 °C, not including the last day of sampling in which temperature dropped to ~8 °C (Fig. 1). The total rainfall during the experimental time was 247 mm, considerably lower than the local average of 446 mm for the same period.

4.2. Physicochemical characteristics of amendments

The physical and chemical properties of the amendments differed greatly. Most notably, WTR and biochar had significantly higher pH than HA, but the latter had significantly higher EC and N contents and VM (Table 1). On the other hand, biochar had significantly greater N_2 and CO_2-SA and C concentration and lower AC than the other amendments.

4.3. Effects of amendments on physicochemical characteristics of soils

After the 16 weeks of field emplacement, some soil characteristics were influenced by the amendments while others were not (Table 2). For example, while application of HA significantly increased pH, GMD and MWD, by 0.3 unit, 8% and 41%, respectively, WTR only significantly enhanced pH and N_2-SA (by 0.3 unit and 23%, respectively). Application of biochar also significantly increased pH of the amended soil by 0.4 unit, reduced BD by 24%, and increased CO_2-SA by 15% (Table 2). Relative to the control, while soil-C was significantly increased with biochar addition (by 26%), soil-N was not changed for the duration of the experiment. However, no significant shifts in EC, AWC, WSA and PR were observed for any of the amendments.

4.4. Effects of amendments on crop growth

Soybean growth and other physiological parameters were generally and non-significantly improved by all three amendments. The soybean (stem, root, fruit etc.) biomass and yield were generally low because it was one of the driest years (Lal et al., 2012). Detailed soybean yield data is not included in this manuscript because it was a preliminary experiment (only one growing season of a dry year) with low amendment application rate and no fertilizer or irrigation was supplied.

Table 2
Soil quality indicators after 16 weeks of amendment field application; all data are based on surface soil (0–10 cm); means followed by letters indicating those treatments that are significantly different at $p < 0.1$.

Treatments	pH	EC	AWC	BD	N_2-SA	CO_2-SA	PR	WSA	GMD	MWD	Soil C	Soil N
		(dS m^{-1})	(%)	(Mg m^{-3})	(m^2 g^{-1})		(MPa)	(%)	($m \times 10^{-3}$)		(g 100 g^{-1}, %)	
Eroded soil	6.8b ± 0.2	0.15a ± 0.0	41a ± 15	1.7a ± 0.1	22b ± 3	27b ± 2	3.8a ± 1.6	70ab ± 7	1.2b ± 0.1	1.7b ± 0.1	2.3bc ± 0.3	0.20a ± 0.02
Soil + HA	7.1a ± 0.0	0.15a ± 0.0	40a ± 12	1.5ab ± 0.2	22b ± 3	28ab ± 1	4.3a ± 0.8	77a ± 9	1.3a ± 0.1	2.3a ± 0.7	2.6ab ± 0.1	0.21a ± 0.00
Soil + WTR	7.1a ± 0.0	0.13a ± 0.0	37a ± 16	1.5ab ± 0.2	27a ± 2	30ab ± 2	3.7a ± 0.2	71ab + 6	1.2b ± 0.0	1.6b ± 0.2	2.0c ± 0.4	0.16a ± 0.02
Soil + biochar	7.2a ± 0.0	0.13a ± 0.0	35a ± 2	1.3b ± 0.1	23b ± 1	31a ± 3	3.1a ± 0.1	63b ± 3	1.2b ± 0.0	1.4b ± 0.3	2.9a ± 0.4	0.20a ± 0.02

Abbreviations: Same as given in Table 1 as well as: AWC = available water capacity, PR = penetration resistance, WSA = water stable aggregate, GMD = geometric mean diameter, MWD = mean weight diameter.

4.5. Greenhouse gas emissions from amended soils

In general, application of biochar and WTR reduced GHG emissions (CH_4, CO_2, and N_2O) and HA increased CO_2 and CH_4 emissions (Fig. 2). However, differences in daily measured emissions among treatments were usually not statistically significant due to the high variability among the replicates. Generally, fluxes of all three gases were the lowest soon after seeding regardless of the treatments including the control, and the highest GHG emissions were observed during the later sampling dates. By the end of the growing season, cumulative emissions of CH_4, CO_2, and N_2O from biochar amended soils were reduced by 56, 43, and 92%, respectively, compared to those of the control (Fig. 3). Cumulative CH_4, CO_2, and N_2O emissions from HA-amended soils were altered by −28, −17, and 61%, respectively (negative sign indicates an increase). Emissions were reduced by 7, 70 and 58%, respectively, from WTR-amended soil compared to those of the control. However, the observed differences in cumulative fluxes from treatments compared with the control were not statistically significant except in the case of a significant decrease in the cumulative N_2O flux for the biochar treated soil (Fig. 3).

5. Discussion

5.1. Impacts of amendments on soil physicochemical characteristics

Clearly, application of biochar and other amendments can alter some soil properties. The expected properties of this amended soil can be calculated as a weighted additive value of the properties of the two materials combined (original soil and amendment). But a critical question is whether aging in the field, either through soil/amendment chemical interaction or microbial/plant processes, the field soil/amendment combinations developed properties different from the weighted additive calculations.

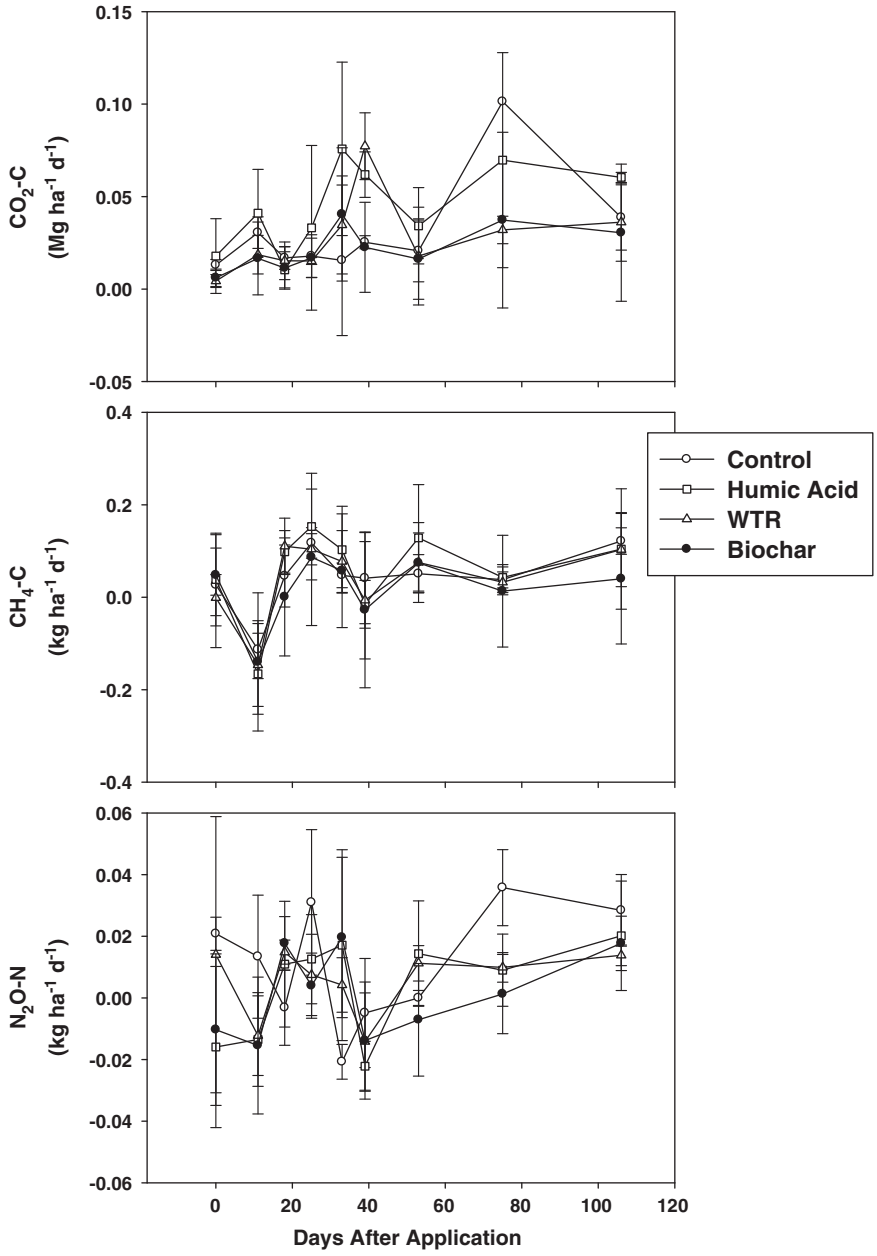

Fig. 2. GHG emissions from control and amended soil plots during the field trial period (note different scales in the y-axis).

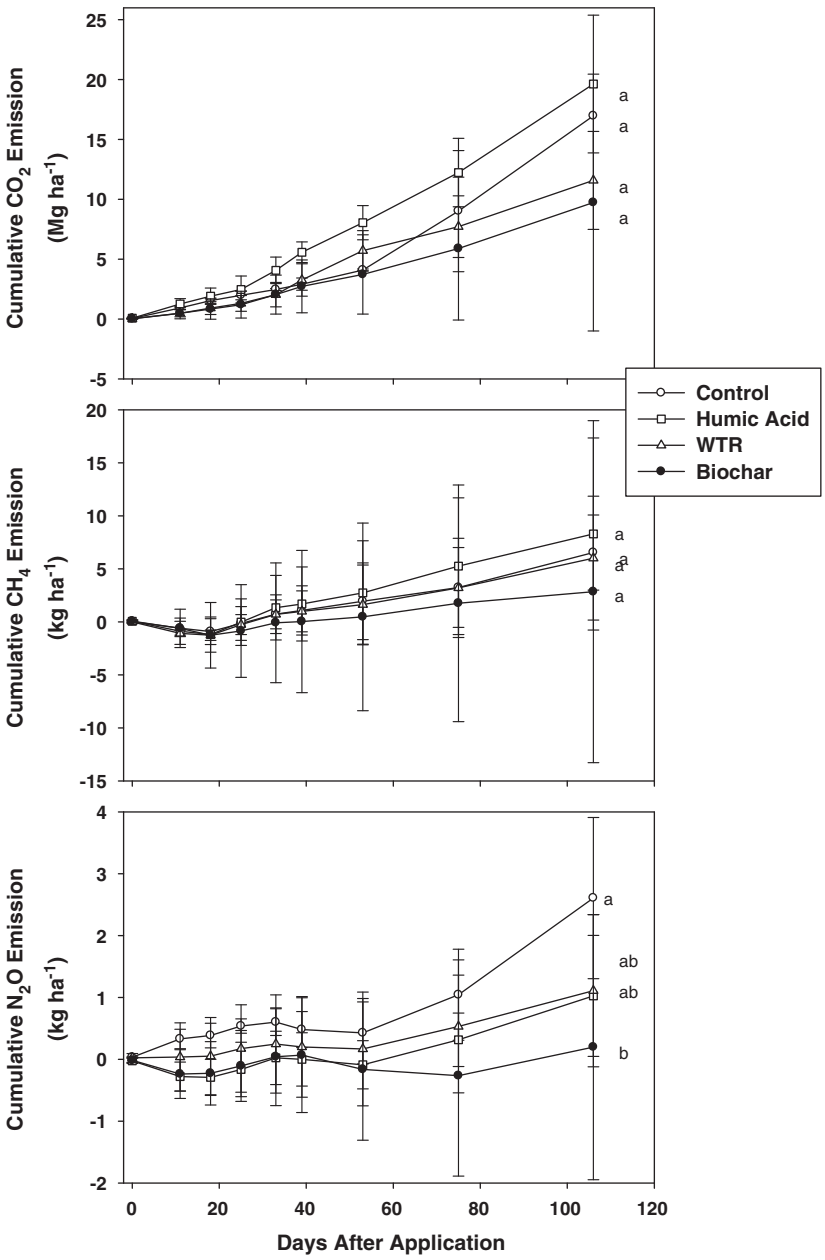

Fig. 3. Cumulative emissions of GHGs from control and amended soil plots during the field trial period (note different scales in the y-axis); letters indicate those treatments that are significantly different at $p < 0.1$.

For example, a pH increase in amended field–soil is in accordance with other studies with WTR (Bugbee and Frink, 1985; Hsu and Hseu, 2011) and biochar (Case et al., 2012; Jones et al., 2011; Laird et al., 2010b; Liu et al., 2011; Rogovska et al., 2011; Scheer et al., 2011; Zhang et al., 2010). But all the amended soil had a pH higher than would be expected from simple addition of each of the amendments and the soil indicating a positive interaction between 4.4 and 6.2% (Table 3). However, the weighted additive concept should be interpreted carefully in the case of pH because both soil (Brady and Weil, 1984) and biochar (Mukherjee et al., 2011) may have buffering capacity towards pH changes. Possible mechanisms for the amendment–soil interaction which produced even higher pH than expected include: (i) loss via leaching of volatile matter (VM) which may carry acid organic functional groups (Mukherjee et al., 2011), (ii) precipitation of basic components, such as carbonate minerals, on amendment surfaces, or (iii) release base cations (Ca, Mg, Na) during enhanced OM mineralization. However, Castaldi et al. (2011) observed that biochar derived from coppiced woodlands and pyrolyzed at 500 °C, when incubated with a silty-loam soil, increased pH up to 0.5 unit after 3 months, but pH returned back to that of the initial control soil after 14 months.

As expected, HA addition, and to some even greater extent biochar addition, added to soil C. But after the emplacement period, there was even more C and N in the HA and biochar–amended soils than predicted (Table 3). This positive priming effect suggests either reduced soil OM mineralization through sorptive protection or increased microbial biomass and OM production by both of these amendments (Zimmerman et al., 2011). The opposite effect occurred with WTR amendment and may be caused by increased microbial activity without an increase in sorptive preservation. This may be because of the more polar nature of WTR (Punamiya et al., 2013) which is reflected in its higher AC (Table 1).

The N_2-SA was only increased significantly by WTR addition and, surprisingly, not with biochar which had highest SA compared to all the amendments (Table 1). A possible reason for this is that microbes

Table 3
Calculation of physico-chemical characteristics predicted by the arithmetic weighted combination of amendment and original soil (Add.), those measured in amended soil, and the percent difference between the measured and predicted parameters.

Soil/amendment	Soil	Amendment	Add.	Meas.	%Difference (Add. vs. Meas.)
pH					
Soil/HA	6.8	5.0	6.7	7.1	6.2
Soil/WTR	6.8	9.5	6.8	7.1	4.4
Soil/biochar	6.8	9.4	6.8	7.2	5.8
BD (Mg m^{-3})					
Soil/HA	1.7	0.8	1.7	1.5	−9.9
Soil/WTR	1.7	0.6	1.7	1.5	−13.2
Soil/biochar	1.7	0.3	1.7	1.3	−20.4
N_2-SA (m^2 g^{-1})					
Soil/HA	22.3	0.1	22.2	21.7	−2.2
Soil/WTR	22.3	16.0	22.2	27.4	23.2
Soil/biochar	22.3	213.9	23.2	23.3	0.2
CO_2-SA (m^2 g^{-1})					
Soil/HA	27.5	58.2	27.7	28.3	2.2
Soil/WTR	27.5	83.7	27.8	29.7	6.9
Soil/biochar	27.5	603.7	30.4	30.8	1.3
Soil-C (g 100 g^{-1}, %)					
Soil/HA	2.3	27.0	2.4	2.6	5.9
Soil/WTR	2.3	16.0	2.4	2.0	−15.2
Soil/biochar	2.3	90.0	2.7	2.9	6.5
Soil-N (g 100 g^{-1}, %)					
Soil/HA	0.2	0.7	0.2	0.2	4.9
Soil/WTR	0.2	0.1	0.2	0.2	−17.2
Soil/biochar	0.2	0.3	0.2	0.2	3.5

Abbreviations: Same as given in Table 1.
Add. = predicted by weighted addition of soil and amendment properties, Meas. = measured values after field sampling, %Difference (Add. vs. Meas.) = difference between predicted (additive) and measured value.

stimulated by biochar or HA addition clogged nanometer-sized soil mineral pore openings resulting in a lowering of the SA (N_2-SA) of the amended soils. Alternatively, the pores on biochar and HA surfaces may have been blocked by SOM sorption (Kasozi et al., 2010; Lin et al., 2012). However, the majority of biochar surface area has been found to occur in the micropore (<1.5 nm, Kasozi et al., 2010), thus biochar increased CO_2-SA significantly relative to control (Table 2), and apparently remained largely unblocked by microbial growth or SOM sorption.

A number of studies have also reported biochar addition to reduce soil BD (Case et al., 2012; Jones et al., 2011; Zhang et al., 2010). While, in this study, soil BD was reduced to the greatest extent by biochar addition (Table 2), it was also found to interact with the soil to the greatest extent such that bulk density was even lower (20.4%) than that expected by the simple additive approach (Table 3). Increased production of SOM may have been responsible for this BD-lowering interaction, and the high correlation between BD and CO_2-SA (Table 4) suggests that surface-specific processes may also be involved such OM sorption. Creation of aggregates was apparently not responsible for the increase in BD as only HA addition resulted in a change (increase) in parameters associated with aggregate stability such as GMD and MWD (Table 2). While this supports the hypothesis that the many active functional groups of HA enhance complexation of soil minerals, one should expect the same from biochar as it possesses a wide range of surface functional groups as well (Baldock and Smernik, 2002; Cheng et al., 2008; Mukherjee, 2011; Mukherjee and Zimmerman, 2013; Rutherford et al., 2004; Rutherford et al., 2008). The low biochar application rate (0.05%, w/w) and short interaction time between amendments and soil might explain these observations. A low application rate of biochar was not successful in increasing soil aggregation in at least two previous cases. Application of pecan shell (*Carya illinoinensis*) biochar produced at 700 °C reduced aggregate stability by up to 23% with application rate of up to 2.1% (w/w) but mixing soils with switchgrass increased aggregation (Busscher et al., 2011; Busscher et al., 2010). Another greenhouse study indicated that application of rice-straw (*Oryza sativa*) biochar to an Ultisol at the rate of 1% had no effect on aggregate stability (Peng et al., 2011). On the other hand, it was proposed that aggregation may increase only over time after biochar application as biochar may go through a 2-phase (fast and slow) interaction mechanism in soil to create stable soil aggregates via complexation involving labile (aliphatic-C) and refractory (aromatic-C) parts of biochar and soil/biochar mineral phases (Mukherjee and Lal, 2014a). The second phase is proposed to be slow to form specific chemical bonding to ultimately create soil stable aggregates (Mukherjee and Lal, 2014a), and thus, 16 weeks (and possibly dry conditions which was not conducive to arbuscular mycorrhizal fungi growth) of this study may not have been sufficient to develop biochar–soil aggregates.

Previous studies have indicated both increases (Briggs et al., 2012; Jones et al., 2010; Karhu et al., 2011; Novak et al., 2012) and decreases (Tryon, 1948) in soil AWC following biochar addition. For example, pine and oak biochars increased AWC of a sandy soil slightly, but had no effect on a loam and decreased that of a clayey soil (Tryon, 1948). In another case, pecan shell biochar had no significant effect on AWC when added to a loamy sand, however, a significant increase in AWC was observed when biochar was mixed with switchgrass (Busscher et al., 2010). The lack of effect of biochar, or any of the three amendments, on AWC may also be due to the short time period, low application rate, or dry weather conditions of this study.

There are a few previous reports of biochar's effect on soil PR in field or laboratory settings and perhaps none with HA and WTR. Soil factors which influence soil PR include BD, soil moisture content (MC), soil compressibility, soil structure, soil texture, and organic matter content (Landsberg et al., 2003; Page-Dumroese et al., 2006). Thus, while not significant due to the high variability in the PR of the control soil, the 18% average reduction in the PR of the biochar-amended soil is in line

Table 4
Correlation matrix (linear correlation coefficients, r) relating various properties of all control and amended soils (n = 12) after 16 weeks field application; negative signs indicate inverse correlations and bold numbers indicate significant correlation ($p < 0.1$).

r	pH	EC	N_2-SA	CO_2-SA	BD	WSA	AWC	PR	GMD	MWD	CH_4	CO_2
EC	−0.57											
N_2-SA	0.30	−0.30										
CO_2-SA	−0.15	0.23	0.02									
BD	−0.45	−0.06	−0.05	**−0.86**								
WSA	−0.07	0.00	−0.06	−0.13	0.20							
AWC	−0.22	0.20	−0.18	−0.41	0.69	0.12						
PR	−0.58	0.38	−0.11	−0.09	0.12	0.11	0.23					
GMD	−0.13	−0.05	−0.38	0.03	−0.12	0.52	−0.13	0.58				
MWD	−0.06	−0.15	−0.31	−0.07	0.02	**0.80**	−0.03	0.36	**0.90**			
CH_4	0.02	0.18	0.03	−0.01	0.34	0.37	0.42	−0.10	0.09	0.19		
CO_2	−0.02	−0.18	0.02	−0.34	0.51	0.59	0.43	0.03	0.31	0.49	**0.77**	
N_2O	−0.32	0.05	0.08	−0.31	0.58	0.49	0.40	−0.12	−0.01	0.22	**0.77**	**0.80**

Abbreviations: Same as given in Tables 1 and 2 and CH_4, CO_2 and N_2O = cumulative amounts of each gas emitted during active growing season.

with the observed significant reduction of BD compared to those in control. This study contrasts with previous observations of increased PR with biochar addition of 7% and 24% in a Norfolk loamy sand E and Bt horizon, respectively (Busscher et al., 2011). However, PR was significantly reduced when the same biochar was mixed with Norfolk loamy sand Ap (Busscher et al., 2010). In the present study, PR's weak correlation with BD ($r = 0.12$), and moderate correlation with MC ($r = 0.59$, data not shown) indicate that PR in the degraded silty clay loam soil was probably influenced more by other soil factors such as soil structure, texture or compressibility than by BD.

5.2. Impacts of amendments on GHG emissions and soil C stability

Total CO_2 emissions from the control soil measured during the growing season were 4.6 Mg ha^{-1} (Table 5) which corresponds to an estimated annual emission rate of about 9.2 Mg ha^{-1} $year^{-1}$ given the previous finding that half the annual CO_2 efflux occurs during a growing season in this soil (Datta et al., 2013; Shrestha and Lal, 2011; Shrestha et al., 2009; Shrestha et al., 2013; Ussiri and Lal, 2009; Ussiri et al., 2009). This figure is comparable to the annual CO_2 efflux from the same soil under long-term tillage and continuous corn (6.6 Mg ha^{-1} $year^{-1}$, Ussiri and Lal, 2009), and from other fertilized and residue-amended soils of central Ohio [3.8–6.6 Mg ha^{-1} $year^{-1}$ (Duiker and Lal, 2000), and 4.4–7.7 Mg ha^{-1} $year^{-1}$ (Jacinthe et al., 2002)] and other mid-latitude locations (Drury et al., 2006; Duiker and Lal, 2000; Fortin et al., 1996; Jacinthe et al., 2002; Jarecki and Lal, 2006; Kammann et al., 2011; Scheer et al., 2011; Zhang et al., 2012a). Thus, the measured respiration rates, though of an intentionally degraded soil, are not atypical.

This study, like the other few field measurements of gaseous emissions by biochar-amended soils published to date (Castaldi et al., 2011; Karhu et al., 2011; Scheer et al., 2011; Zhang et al., 2012b), found no significant or only minor effect of biochar amendment on CO_2 efflux. As with the measurements of soil physical properties, this is likely due to the high variability found within the control and treatment plots and, perhaps, because of the short experiment period. All the GHG emissions were significantly correlated to each other as soil respiration is primarily controlled by microbes but were not related to any of the measured soil properties (Table 4), suggesting lesser extent of effects of soil physical parameters on gaseous emissions.

While none of the amendments significantly reduced cumulative GHG emissions except in the case of N_2O under biochar treatment (Fig. 3), the same trends in average GHG emissions for each treatment were observed at each sampling period and, thus, warrant consideration. For example, HA treatment resulted in greater CO_2 and CH_4 emissions compared to the control or the other treatments throughout the 4-month period (Figs. 2, 3). The significantly higher labile VM content of HA compared to those of WTR and biochar (Table 1) suggests a greater labile OM content for HA and several laboratory experiments indicated HA to be highly biodegradable (Dehorter and Blondeau, 1992; Grinhut et al., 2007; Grinhut et al., 2011; Qualls, 2004). For example, three isolates of fungi effectively mineralized up to 30% of HA isolated from forest soil within six weeks (Mishra and Srivastava, 1986). Similarly, when incubated under laboratory condition, up to 50% of HA isolated from forest litter and synthetic HA prepared from catechol was degraded by basidiomycete fungi in the presence of Mn^{2+}, which acted as catalyst (Steffen et al., 2002). These findings are in line with the results of the current field study showing 31% of the C in the HA-amended soil to have been mineralized during the 16 week study period, corresponding to a C half-life of 0.5 y.

In contrast to HA, the 0.5% (w/w) application rate of oak-650 biochar consistently reduced GHG emissions and resulted in cumulative CH_4, CO_2, and N_2O emissions 56, 43, and 92% lower than the control soil, by the end of the growing season (Fig. 3). Spokas et al. (2009) also observed reduced emission of CO_2 from a silt loam soil amended with wood chips biochar, but the decreased emission of N_2O was only observed with application rates >20% (w/w). The large reduction in N_2O emission due to biochar amendment could be driven by both abiotic and biotic processes including: (i) enhanced soil aeration (van Zwieten et al., 2010; Yanai et al., 2007), (ii) sorption of NH_4^+ or NO_3^- on biochar surfaces (Singh et al., 2010; van Zwieten et al., 2010; van Zwieten et al., 2009) or (iii) presence of inhibitory or toxic organic compounds that could suppress N_2O emission from biochar-amended soil abiotically (Spokas et al., 2010). The first mechanism is suggested here by the significantly lower BD in biochar-amended soils. On the other hand, the significantly higher pH of biochar amended soils might have increased activity of denitrifiers (Cavigelli and Robertson, 2000; Cavigelli and Robertson, 2001) or denitrifying enzymes which can also reduce N_2O by converting it to N_2 (Taghizadeh-Toosi et al., 2011).

Soil C budgets for the growth season calculated using the assumptions given in the method section show that biochar was the only amendment that resulted in a net soil C gain (sequestration) during the growing season (Table 5). However, both HA and WTR addition resulted in a reduction of C loss from the soil (by 28 and 89%, respectively) compared to the control. These calculations show that both soil C losses and C gains must be considered when evaluating the effectiveness of a soil amendment as a climate mitigation tool. For example, the increased soil C mineral due to HA addition was offset by the C added resulting in the decrease in soil C loss in this case. And biochar resulted in the greatest C gain because it both added large amounts of C and reduced soil C losses via gas emission.

Total C MRT calculated using field emission data ranged from 0.9 y for HA-amended soil to 2.4 y for biochar-amended soil and bracketed the control soil, 1.7 y (Table 5). There might be reason to suspect these residence times to be lowered by the fact that gas sampling was carried out during highest emission period of the day and only during the active growing season when there may have been input from root exudates. The MRT calculated is much lower than those of laboratory incubations of biochar alone [3–658 y MRT (Zimmerman and Gao, 2013)] or biochar C when mixed with soil where biochar C and soil C degradation could be distinguished [3–170 y MRT (Zimmerman and Gao, 2013)]. However, laboratory studies do not account for losses of biochar C via leaching which can be significant (Mukherjee and Zimmerman, 2013; Mukherjee et al., 2014b). Also, as discussed above, the gas emission rates recorded are similar to those measured previously of other

Table 5
Soil carbon budget (flux) and mean residence time (MRT) of C in control and amended soils calculated using first order kinetics modeling of 16 week CO_2 and CH_4 emission data.

	Mg ha^{-1} $season^{-1}$							MRT of C	
	Potential C addition (input flux)			Measured C loss (output flux)					
	Amended-C	Biomass-C[a]	Total-C	CH_4–C	CO_2–C	Total emitted-C	C gain	Years	Model R^2
Eroded soil	0.0 ± 0.0	1.1 ± 0.2	1.1 ± 0.2	0.00 ± 0.00	4.6 ± 3.3	4.6 ± 3.3	−3.6 ± 3.5	1.7 ± 1.3	0.91
Soil + HA	2.0 ± 0.0	1.4 ± 0.2	3.4 ± 1.2	0.01 ± 0.01	5.4 ± 1.6	5.4 ± 1.6	−2.6 ± 2.7	0.9 ± 0.2	0.97
Soil + WTR	1.2 ± 0.0	2.0 ± 0.1	3.1 ± 0.6	0.00 ± 0.00	3.2 ± 1.1	3.2 ± 1.1	−0.4 ± 1.5	1.6 ± 0.7	0.97
Soil + biochar	6.8 ± 0.1	1.3 ± 0.2	8.0 ± 0.1	0.00 ± 0.01	2.7 ± 2.9	2.7 ± 2.9	4.2 ± 2.8	2.4 ± 1.8	0.97

Abbreviations: CH_4–C and CO_2–C = cumulative amounts of C in each gas emitted during active growing season, C gain = (total C addition − total emitted-C), MRT = mean residence time.

[a] These figures are tentative since they include only one season of data on soybean plant.

regional soils using other sampling regimes, it seems likely that the calculated MRT reflects the stability of native soil C, as affected by interaction with the soil amendment (see below) as much as the stability of the C in the amendment itself.

The MRT of C in soils amended with biochar and WTR was 2.2 and 1.2-fold greater, and that of HA amended soil was 47% less, than that of the control. These calculations showing the C in HA-amended soil to be more easily remineralized than the native soil C and the C in biochar and WTR-amended soil to be more refractory may be attributed to either or all of (i) the inherent chemical lability of the OM in each of the materials, (ii) the effects of each amendment on the soil environment which influence microbial activity, and (iii) the interaction between soil OM and the amended material. Interactions that have a stimulatory effect on soil C mineralization, termed 'positive priming', include the addition of a labile substrate that may act as a co-metabolite to the mineralization of more refractory OM. Interactions that have an inhibitory effect on soil C mineralization, termed 'negative priming', include the protection of soil OM from mineralization by occlusion with biochars pores or, vice versa, sorption of labile OM released by biochar onto soil mineral surfaces. Both positive priming and negative priming have been observed in biochar-amended soil and likely depend upon the biochar and soil type and time period observed (Zimmerman et al., 2011). From the MRT calculations, it appears likely that, even at the short time scale of these experiments, the HA caused positive priming while WTR and biochar, with their greater surface area and porosity, may have produced negative priming.

The effect of each amendment type on GWP during the growing season was compared using the data shown in Table 5. Though differences among each treatment's GWP associated with GHG emissions were not statistically significant due to the high intra-treatment variability, examination of the trends is instructive. It is clear from these calculations that, in all soils, CO_2 emissions, rather than that of CH_4 or N_2O, played the dominant role by far in GWP effect (Fig. 4). Also, while all the amendments reduced the net GWP effect of the soil (shown as arrows in Fig. 4), only biochar addition resulted in net negative GWP effect. For example, HA amendment lowered the GWP of the control soil to about half whereas biochar made the soil a net climate ameliorator. It should be understood, however, that the full effect of each amendment on GWP can only be determined through a full life cycle analysis (LCA) of each material that considers the emissions associated with the production, transport and application and long term stability of each material and its long term effects on soil chemistry and fertility. It should be noted, for example, that biochar can be produced by a variety of technologies, each with trade-offs between the production of biochar, bio-oil and gas and GHG emissions. Estimation of full LCA is of future scientific interest and requires collection of long-term data of different amendments on this aspect, which is under consideration at this point. The true effect of the amendments on GWP should include more information linked to the balance of gases. This may include the amount of GHG emitted during the production of the amendments (for example, there was an emission of 43.3% of the parent biomass C (Zimmerman, 2010) during the production of oak-650 biochar) in order to estimate the full extent of GWP, which is beyond the scope of this research. In addition to the C emission by the parent biomass used for biochar production, the energy costs involved with production, transport and application of amendment in the soil should be taken into account. However, thinking in a 'global' budget, the application of biochar in one determined area is made in detriment of the exportation of biomass from other area where the biomass was produced. This does not happen for WTR, but is crucial for the calculation of GWP in the soil amended with biochar. Thus, the estimated GWP may actually reflect 'partial' GWP as other energy balance was not considered in this calculation.

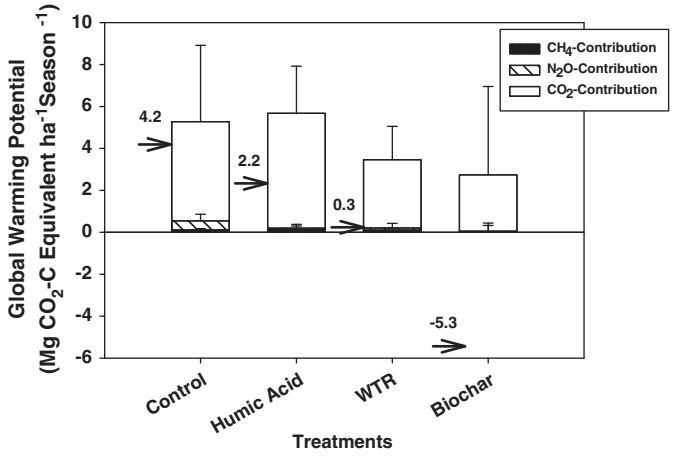

Fig. 4. Contribution of control and amended soils to global warming potential (GWP) during the field trial period. Columns represent contribution from average GHG emitted by each treatment (with error bars as standard deviation). Arrows with numbers represent the net effect on GWP when C gain by soil (amendment C added to soil and biomass growth) is included as removals from the atmosphere.

6. Summary and future research

This field-based study, which evaluated the effects of three soil amendments on a wide range of soil physicochemical properties along with MRT and GWP, produced a number of valuable insights. First, only a few soil properties were significantly altered by the application of HA, WTR or biochar at the rate of 0.5% (w/w) due to the high intra-treatment variability. Field studies often times show high intra-treatment variability because the conditions cannot be controlled as in the cases of laboratory or greenhouse settings. The sensitivity of the measurements of the current experiment appeared to be even higher than expected probably due to the soil being artificially and manually degraded. While GHG emissions were greatest and soil C stability the lowest for the HA-amended soil, and GHG emissions were the lowest and soil C stability the greatest for biochar-amended soil, all the amendments had a lower GWP than the control soil, with that of only biochar being net negative. However, given the interactions shown to occur between the soil and the amendments over the growing period, the physicochemical properties of the amended soil will likely continue to change over time. Thus, the effects of each amendment type on crop growth, C-sequestration and GWP require consideration of the time scale of interest as well as a careful interpretation in the context of soil, crop and management variables.

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