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The effects of walnut shell and wood feedstock biochar amendments on greenhouse gas emissions from a fertile soil

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ABSTRACT

Land application of biochar, as a strategy to enhance soil fertility and reduce greenhouse gas (GHG) emissions is receiving widespread interest. Short-term soil incubations (29 days) were used to investigate the effects of agriculturally relevant biochar applications from two contrasting feedstocks and temperatures on CO_2 and N_2O emissions from a fertile agricultural soil amended with different types of fertilizer (organic and synthetic). In addition, the effects of biochar on the denitrification process were examined using an acetylene based method to ascertain N_2O and N_2 emissions during denitrification. Complementary incubation experiments without soil (biochar and biochar with compost) examined the impact on natural or amended organic matter (compost) and biochar stability and surface chemistry were also investigated. Batch incubations (25 °C) of biochar (softwood pyrolyzed at 410 °C [WF_{410}] and 510 °C [WF_{510}] and walnut shell pyrolyzed at 900 °C [WA_{900}]) amended soils were performed to determine emissions of CO_2 and N_2O due to complete (absence of acetylene [C_2H_2]) and incomplete denitrification (presence of C_2H_2). Similarly, GHG emissions from the complementary incubations were also measured. Concurrent biochar surface compositional changes were investigated with attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy. Biochar effects on CO_2 emissions were not significantly different from controls. WA_{900} biochar (high pH) affects N cycling resulting in significantly higher emissions of N_2O under conditions of complete denitrification and of N_2 under conditions examining incomplete denitrification. WF_{410} (highest H/C ratio and lowest surface area) treatments with compost resulted in higher GHGs emissions which is attributed to a priming effect of the compost organic matter (COM). In addition, WF_{410} was most susceptible to degradation, evident from infrared spectroscopic analysis of the biochars. Although these results suggest that not all biochars provide substantial benefits as a soil amendment, the data do demonstrate potential for development of biochars with beneficial impacts on GHG emission mitigation and enhancement of soil C stocks.

1. Introduction

One potential strategy to enhance sequestration of C from plant litter and animal wastes is through production of biochar. Biochar is the product of the pyrolysis of biomass made with the intention of using it as a soil amendment, carbon storage, or filtration of percolating soil water (Lehmann and Joseph, 2009). The product is highly aromatic and has increased C stability relative to original feedstock materials. The use of biochar as a soil amendment has received increased attention since the discovery of the Terra Preta de Indio soils in the Amazon. Although not fully explained, these soils are believed to have received historical applications of anthropogenic black carbon or charcoal and today have higher organic C and improved soil fertility (Glaser et al., 2000, 2001; Lehmann and Joseph, 2009; Sombroek et al., 2003). Additionally, some research suggests that biochar application to soil may help increase N-retention and decrease N_2O emissions, while retaining native C, improving soil fertility, and increasing water retention in soil (Lehmann et al., 2006; Major et al., 2009; Rondon et al., 2007; Singh et al., 2010; Sohi et al., 2010). For these reasons, biochar is often proposed as a strategy to be used in agriculture to reduce GHG emissions and mitigate climate change (Woolf et al., 2010).

While reduced GHG emissions have been observed upon addition of biochar to soil (Case et al., 2012; Singh et al., 2010; Yanai et al., 2007), variable results regarding C and N cycling have also been noted and attributed to biochar and soil physical/chemical properties (Novak and Reicosky, 2009; Novak et al., 2010). Novak et al. (2010) showed increased CO_2 release after 25 and 67 days of incubation (pecan shell biochar with dried switchgrass in loamy sand). Another study investigating 16 biochars with three fertile soils (100 day incubation), also reported increased CO_2 and N_2O emissions in some of the treatments (Novak and Reicosky, 2009). The authors indicated

Abbreviations: GHG, greenhouse gas; WFPS, water filled pore space; COM, compost organic matter; OM, organic matter; HSD, Honest Significant Difference; ANOVA, Analysis of variance; DOC, Dissolved organic carbon; ATR–FTIR, Attenuated Fourier Transformed Infrared spectroscopy.

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that these results highlight the fact that GHG emissions from biochar amended soils are strongly dependent on the biochar feedstock, pyrolysis method, and soil properties. The diversity of biochar source material, pyrolysis methods, soils, and agricultural systems lends complexity to determining the appropriate circumstances for biochar amendments.

To date no studies have attempted to investigate the effect of biochar on the complete and incomplete denitrification. Biochar has potential to enhance net denitrification because of its effect on several soil properties considered drivers of denitrification namely: water filled pore space (WFPS); inorganic N concentrations; labile C; pH; and oxygen content. Biochar has been shown to increase soil water holding capacity (Karhu et al., 2011; Major et al., 2009); increase soil cation exchange capacity and nutrient retention (Liang et al., 2006), and raise soil pH (Glaser et al., 2002; Novak and Reicosky, 2009), all of which directly or indirectly affect denitrification (Sahrawat and Keeney, 1986).

CO_2 and N_2O emissions from denitrification may occur during the priming of native organic matter following biochar amendment, here defined as changes in the mineralization rate of soil OM (Zimmerman et al., 2011). Both increased (Novak et al., 2010; Wardle et al., 2008) and decreased (Kuzyakov et al., 2009; Spokas and Reicosky, 2009) rates of OM decomposition in the presence of biochar have been observed. Low temperature biochar (made at <450 °C) has been shown to prime OM mineralization and in turn undergo concurrent degradation (Luo et al., 2011; Zimmerman et al., 2011), however, no study has investigated the concurrent surface compositional changes in the biochar.

The aims of this study are to determine 1) how biochar soil amendments (at agriculturally relevant rates of N fertilization) to fertile soils affect C and N cycling; 2) how biochar additions affect the ratio of N_2O and N_2 emissions during denitrification; 3) how these biochar affect the decomposition of compost organic matter (COM); and 4) how the incubations impact the structural stability of biochar and alter their composition of surface functional groups. Due to the fact that denitrification is often considered the predominant process responsible for N_2O emissions in agricultural systems (Opdyke et al., 2009; Senbayram et al., 2009), particular emphasis has been given to this process.

2. Materials and methods

2.1. Soil and biochar

Soil was collected from the Ap horizon in a walnut orchard (Winters, CA). The soil series is Yolo (fine-silty, mixed, nonacid, thermic Typic Xerorthent) and contains approximately 7% sand, 62% silt and 31% clay (silt loam). The compost used was a composite sample from the composting facility at the Agricultural Sustainability Institute Student Farm in Davis, CA. Subsamples were collected for moisture content determination by oven drying at 105 °C and the remainder of the soil and compost were air dried and passed through a 2 mm sieve. The untreated soil was analyzed for total C and N with a C/N Analyzer (ECS 4010 Costech Analyzer), pH and moisture content (Table 1).

Two commercially available biochars, namely low temperature (410 °C) wood feedstock (WF_{410}); high temperature (510 °C) wood feedstock (WF_{510}), and a third, high temperature (900 °C) walnut shell (WA_{900}) biochar, were obtained from suppliers (see supporting information of Mukome et al., 2013). The wood biochars were made from a feedstock mixture of primarily Douglas fir (*Pseudotsuga menziesii*) and additional White fir (*Abies concolor*) by slow pyrolysis with 25 min residence time and 50 psi of steam at the end of the process. The walnut shell (*Juglans californica*) biochar was made using a Biomax 50 downdraft gasifier. Details regarding biochar characterization are provided in Mukome et al. (2013). Briefly, samples were sieved to pass through a 2 mm mesh and analyzed for pH (1:2 w/v in water), and surface area analysis (BET N_2 sorption, Quantachrome Autosorb-1). Surface area was determined on ball ground samples and after 16 h outgassing at 120 °C. The ash content was determined by dry oxidation of the biochar at a temperature of 575 ± 25 °C (ASTME1755-95, 1995). The total surface basicity of the biochars was determined by the conventional back titration method (Jindarom et al., 2007). For this, about 0.20 g of biochar was soaked in 25 mL of 0.025 M HCl solution in a centrifuge tube and agitated for 48 h at room temperature. The suspension was centrifuged and the filtered supernatant titrated with 0.025 M NaOH solution to determine the remaining HCl in solution.

Table 1
Properties of soil (Yolo silt loam) and compost used in incubation experiments.

	Soil	Compost
pH_w (1:2)	7.8	9.1
Moisture (wt.%)	3.3	4.6
C (wt.%)	1.94	7.4
N (wt.%)	0.18	0.79
C/N	10.8	9.4

2.2. Incubations

Biochar (0.5 g) was mixed into 50 g of soil for a 1% mixture (w/w), which equates to a field-application rate of approximately 12 metric ton ha^{-1} assuming a 10 cm incorporation depth, as the soil bulk density was 1.2 g/cm^3. Treatments consisted of soil + biochar + compost. Compost was augmented to the different biochar treatments in order to achieve total application rate of 100 mg N kg^{-1} soil or 120 kg N ha^{-1}. A comparative treatment of soil with inorganic fertilizer (Surea) and controls of soil only (S only), and soil with compost (SC) were also setup. N application rates for the urea and compost treatments were 100 mg N kg^{-1} soil or 120 kg N ha^{-1}. Breakdowns of the components of each treatment are shown in the supplementary data, Table S1.

Short term CO_2 and N_2O evolution were determined by placing the soils in 1 L gas tight jars and incubating at 25 °C in the dark for 29 days. The jars were placed in a randomized block design with an initial moisture content of 90% WFPS and allowed to dry down and maintained at a moisture content of 55 to 60% WFPS. Headspace gas samples (20 mL) were withdrawn from the enclosed headspace using gas tight syringes, with two way stopcocks, and immediately injected into pre-evacuated 12 mL gas exetainer tubes (Labco, Buckinghamshire, UK). From the same samples, N_2O and CO_2 were measured via gas chromatography (Shimadzu GC 2014) equipped with an electron capture detector (ECD) for N_2O and a flame ionization detector (FID) for CO_2 detection. The difference in syringe and exetainer volumes ensured the exetainers were over pressured thus minimizing external air diffusion. The incubations were performed in triplicate with daily samplings for the first week and then on days 7, 10, 14, 18, 21, 24 and 29.

The acetylene inhibition method, used to determine the emissions of N_2O to N_2 gases, were set up with 10% v/v of C_2H_2 added after removing an equivalent amount of air from the headspace. C_2H_2 was generated by reacting CaC_2 with distilled water prior to use. After each sampling, the jars were vented to ensure no residual gas was retained. Headspace samples of ambient air similarly capped were used to correct sample gas concentration. For all the incubations, extractable DOC (dissolved organic carbon), NH_4–N (ammonium), NO_3–N (nitrate) and pH were measured before and after incubation. Soil (4 g) was extracted with 40 mL of 0.5 M K_2SO_4 (Jones and Willett, 2006) by shaking for 1 h on a reciprocating shaker, filtering using Whatman no. 42 paper, and then analyzing the filtrates within 48 h. DOC concentrations were determined with a Shimadzu TOC–TN analyzer (Shimadzu Corp., Kyoto, Japan) and NH_4–N (Forster, 1995) and NO_3–N (Doane and Horwath, 2003) concentrations were determined colorimetrically via UV–Vis (Genesys 10S UV–Vis, Thermo Scientific) at a wavelength of 540 nm (NH_4–N) and 650 nm (NO_3–N).