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Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil

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ABSTRACT

A potential abatement to increasing levels of carbon dioxide (CO_2) in the atmosphere is the use of pyrolysis to convert vegetative biomass into a more stable form of carbon (biochar) that could then be applied to the soil. However, the impacts of pyrolysis biochar on the soil system need to be assessed before initiating large scale biochar applications to agricultural fields. We compared CO_2 respiration, nitrous oxide (N_2O) production, methane (CH_4) oxidation and herbicide retention and transformation through laboratory incubations at field capacity in a Minnesota soil (Waukegan silt loam) with and without added biochar. CO_2 originating from the biochar needs to be subtracted from the soil–biochar combination in order to elucidate the impact of biochar on soil respiration. After this correction, biochar amendments reduced CO_2 production for all amendment levels tested (2, 5, 10, 20, 40 and 60% w/w; corresponding to 24–720 t ha^{-1} field application rates). In addition, biochar additions suppressed N_2O production at all levels. However, these reductions were only significant at biochar amendment levels >20% w/w. Biochar additions also significantly suppressed ambient CH_4 oxidation at all levels compared to unamended soil. The addition of biochar (5% w/w) to soil increased the sorption of atrazine and acetochlor compared to non-amended soils, resulting in decreased dissipation rates of these herbicides. The recalcitrance of the biochar suggests that it could be a viable carbon sequestration strategy, and might provide substantial net greenhouse gas benefits if the reductions in N_2O production are lasting.

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1. Introduction

From the standpoint of reducing the sources of global warming and sustainable resource management, biomass is attracting attention as a renewable energy resource to replace current fossil fuel resources. Pyrolysis has been cited as one of the renewable processes most capable of competing with non-renewable fossil fuel resources (Özçimen and Karaosmanğlu, 2004). Burning biomass in the absence of oxygen (pyrolysis) yields three products: a liquid (bio-oil), solid (biochar) and a gas (syngas) (Bridgwater, 2003). Depending on the type of process (slow, fast, flash) and the pyrolysis conditions (e.g. temperature, pressure, time, heating rate and biomass material), the yields of each phase vary dramatically (IEA, 2007). Typically, biochar production decreases with increasing pyrolysis temperature (Bridgwater et al., 1999).

If biochar is returned to soil, it has the potential of generating several positive soil quality benefits as well as a potential carbon sequestration benefit (Fowles, 2007; Lehmann, 2007). This carbon sequestration benefit results from the fact that biochar takes carbon from the atmosphere–biosphere pool and transfers it to a slower cycling form that has the potential to exist for hundreds to thousands of years (e.g. Fowles, 2007) or possibly longer (e.g. Masiello and Druffel, 1998). It has been estimated that biochar already represents 15–20% of the total C in temperate, coniferous forest mineral soils due to natural production of biochar by wildfires (DeLuca and Aplet, 2008) and up to 35% of the total C in natural prairie soils (Skjemstad et al., 2002).

Several studies have already observed that biochar additions alter soil nutrient availability by affecting soil physico-chemical properties (e.g. Tryon, 1948; DeLuca et al., 2006). Lehmann et al. (2003) observed that charcoal additions in Anthrosols had positive effects on plant growth and reduced leaching of applied N fertilizers. Soil fertility benefits have also been noted on the locations of historical charcoal hearths in the Appalachian Mountains (East Coast US) (Young et al., 1996). In addition to direct soil nutrient status and crop growth, biochar additions may aid in stabilizing existing soil organic carbon (SOC) (Amonette et al., 2003) and be linked to positive impacts on mycorrhizal associations (Warnock et al., 2007).

Initial research indicates that there are some secondary benefits to net greenhouse gas emissions resulting from biochar additions.

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Rondon et al. (2005) observed a 50% reduction in nitrous oxide (N_2O) emissions from soybean plots and almost complete suppression of methane (CH_4) emissions from biochar amended (20 mg ha^{-1}) acidic soils in the Eastern Colombian Plains. Yanai et al. (2007) observed an 85% reduction in N_2O production of rewetted soils containing 10 wt% biochar compared to soils without biochar. However, this effect was highly moisture dependent. The exact causes of these reductions in greenhouse gas production are unclear.

Carbon in soil resulting from combustion of vegetative material has been shown to affect processes controlling pesticide behavior in soils for >45 years. For instance, carbon arising from cane leaf burning was shown to affect sorption of herbicides in sugar cane soils (Hilton and Yuen, 1963). More recently, ash from burning wheat (Yang and Sheng, 2003a,b; Sheng et al., 2005), and rice (Yang and Sheng, 2003b), have been reported to increase sorption of a number of herbicides.

While pyrolysis biochars from tree wood (Pignatello et al., 2006; Wang et al., 2006) and pine needles (Chen et al., 2008) have been shown to sorb significant amounts of diverse polar and nonpolar aromatic contaminants and humic and fulvic acids, there is very limited research on the effects of biochars, added as an amendment to soil, on pesticide processes in soil. Charcoal added to soils has been reported to increase herbicide sorption (Yamane and Green, 1972; Yu et al., 2006). The purpose of this study was to document the impact of biochar application to a Minnesota agricultural soil on CO_2 and N_2O production, CH_4 oxidation potentials and alterations in sorption/degradation characteristics for two common herbicides (atrazine and acetochlor).

2. Materials and methods

Soil for the laboratory studies was collected at the University of Minnesota's Research and Outreach Station in Rosemount, MN (44°45′N, 93°04′W). 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 6.3–6.6, 2.6% organic carbon and a slope <2%. This site was farmed in a conventionally tilled (moldboard plow) corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] rotation. The soil was sampled following corn harvest. Surface soil (0–5 cm) was collected, sieved to <2 mm and homogenized for the incubation study. Soil was collected within 1 month of initiating the soil incubations to reduce the impacts of storage on the microbial assessments (Zelles et al., 1991).

The biochar tested here was CQuest™ biochar produced by Dynamotive Energy Systems[1] (Vancouver, BC, Canada) from a fast pyrolysis process (500 °C) of mixed sawdust optimized for the production of liquid biofuel, with yields of 60–75 wt% oil, 15–20 wt% biochar and 10–20 wt% gases (Dynamotive, 2008). The biochar had a surface area of 1.6 m^2 g^{-1}, bulk density of 225 kg m^{-3} and a volatile solids content of 21% (Dynamotive, 2008). This surface area is a bit lower than other produced chars and could be due to sorbed oil clogging pores. Biochar was used as received from the supplier in sealed drums. The biochar contained 69% carbon (C), 0.3% nitrogen (N), 2.7% hydrogen, 14.6% oxygen, 0.02% sulfur and 5% moisture by air dry weight basis (Novak, personal communication). Biochar was transferred from the sealed drum to an airtight container which was then stored at 4 °C until the incubations were prepared. The total storage time for the biochar after removal from the drum was less than 5 d.

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

2.1. CO_2 and N_2O production and CH_4 oxidation potentials

Incubations of the following combinations of biochar, soil and deionized water were conducted:

1. 0.10 g biochar + 5 g soil + 0.74 mL water (2% w/w),
2. 0.25 g biochar + 5 g soil + 0.74 mL water (5% w/w),
3. 0.5 g biochar + 5 g soil + 0.74 mL water (10% w/w),
4. 1.0 g biochar + 5 g soil + 0.74 mL water (20% w/w),
5. 2.0 g biochar + 5 g soil + 0.74 mL water (40% w/w),
6. 3.0 g biochar + 5 g soil + 0.74 mL water (60% w/w),
7. 0.74 mL water (Control).

The above incubations were carried out at field capacity (−33 kPa). Yanai et al. (2007) used rates of 10% w/w. However, in actual field application rates these ranges would span from approximately 24 t ha^{-1} to 720 t ha^{-1} assuming a 10 cm incorporation depth. Despite the fact that the high rates are impractical for field application, the impacts of biochar at these high application rates were still assessed. In addition, triplicate incubations were established with differing amounts of biochar (0.1, 0.25, 0.5, 1.0, 2.0 and 3.0 g) with three different moisture additions (0, 1.0 and 3.0 mL of deionized water) to evaluate the production/consumption of CH_4, CO_2 and N_2O solely from the biochar. These biochar + water incubations did not receive any inoculum.

Triplicate sub-samples were placed in sterilized 125 mL serum vials (Wheaton Glass, Millville, NJ) and sealed with red butyl rubber septa (Grace, Deerfield, IL). Periodic samples were withdrawn from the incubations for analysis on a gas chromatographic–mass spectrometer (GC–MS) system to quantify gas production over the 100-d incubation period. The control incubations were run as the incubation blanks to ensure no sorption or reaction of the analyzed gases with the serum vial or septa occurred. No detectable sorption or loss of CO_2, CH_4 or N_2O was observed.

2.2. Gas sampling and analysis

To sample the incubations, initially 5 mL of air (known composition) was injected into the sealed incubation. The syringe was flushed repeatedly three times to allow for adequate mixing of the serum bottle headspace. Five milli liters of gas was then pulled back into the syringe and then injected into an autosampler vial that was previously helium flushed for analysis. Concentrations from the GC were corrected for dilution from the 5 mL of air.

The GC system consisted of a headspace sampler (Agilent, Foster City, CA, model 7694) that was modified with the addition of a 10-port diaphragm sample valve (Valco, Houston, TX, model DV22-2116) to avoid trace air contamination from rotor valves. For the gas analysis, the sample vial (10 mL) was initially pressurized within the sampler using He (138 kPa). After 0.4 min, 60 μL, 120 μL and 500 μL sample loops were filled during venting of the pressurized vial (on interconnected 10 port and 6 port valves). After equilibration (0.4 min), the sample loops were injected onto three different columns that are contained in a single gas chromatograph oven (Perkin Elmer, Waltham, MA, Clarus 600).

The first column (60 μL loop) was a RT-Molesieve 5A (0.32 mm × 30 m, Restek, Bellefonte, PA) with a 2.0 mL min^{-1} He flow rate. The second column (120 μL loop) was a RT-QSPLOT (0.32 mm × 30 m, Restek, Bellefonte, PA), also with a 2 mL min^{-1} He flow rate. These two columns are connected to the mass spectrometer (Perkin Elmer, Waltham, MA, model 600T) through a diaphragm valve (Valco, Houston, TX, DV22-2116) that permitted the selection of which effluent stream was sent to the detector. The use of the timed control on the column effluents allow the oxygen, nitrogen and water peaks to be safely vented away from the mass spectrometer (MS). CO_2 and N_2O peaks were detected on the MS

from the RT-QSPLOT column at 3.5 and 4.1 min, respectively. Single ion monitoring (SIM) was used at 44 *m/z* for CO_2 and 30 + 44 *m/z* for N_2O quantification. CH_4 peak (16 *m/z*) was quantified from the RT-Molesieve 5A column at 6.4 min. Internal gas standards (SF_6 and Ar) are injected through an independent sample valve (50 μL) to enable internal standardization of the mass spectrometer response.

The third sample loop (500 μL) is connected to a CTR-1 column (Grace, Deerfield, IL) with a 45 mL min^{-1} He flow rate which is connected to a thermal conductivity detector (TCD). The output from the TCD detector was used for the quantification of oxygen (2.5 min) and nitrogen (4.5 min).

The column temperature program started at 35 °C for 5 min, followed by heating to 120 °C at 20 °C min^{-1} with a 0 min hold time for all columns. The total runtime was 15 min, which included the column conditioning ramp between samples to drive off water vapor from the columns. The system (MS and TCD) was calibrated using multiple traceable gas standards (Scott Specialty Gases; Troy, MI and Minnesota Oxygen Supply; Minneapolis, MN). The GC system remained within 10% for all calibration check samples that were run (one every 15 samples). Random blank He flushed vials were also analyzed to validate the quality control of the He vial flushing (five random vials per 100 flushed) and all blanks showed no detectable contamination.

2.3. Herbicide degradation

Soil samples (50 g oven-dried equivalent) of Waukegan silt loam soil (58.1 g wet weight) were weighed into thirty 250-mL Teflon bottles. Biochar (2.5 g) was added to half of the bottles, and the soil and biochar were thoroughly mixed. Each soil sample was treated with 3 mL of an aqueous solution containing 17.3 μg mL^{-1} atrazine and 17.7 μg mL^{-1} acetochlor. The solution was added drop wise, and the soil was thoroughly mixed. The final soil concentrations were 1.04 μg g^{-1} atrazine and 1.06 μg g^{-1} acetochlor. The soil moisture was adjusted to −33 kPa by adding 4.38 g of water drop wise. The soil was again thoroughly mixed. Samples were incubated in the dark at 20 °C until analyzed at 0, 3, 7, 11 and 21 d after herbicide treatment.

For analysis, at each sampling time, 75 mL of a 4:1 methanol–water solution (v:v) was added to the triplicate bottles of treated soil with and without biochar, and the bottles were shaken overnight. The bottles were then centrifuged at 1000 rpm for 15 min and the supernatants were decanted into evaporation flasks. This process was repeated, and the supernatants were added to the previous supernatants. For a finishing wash, 75 mL methanol was shaken with the soil, centrifuged, and then added to the previously combined supernatants. The methanol was then evaporated using a Turbo-Vap II at 40 °C.

The herbicides were extracted from the remaining water using solid phase extraction (SPE) cartridges (Varian C18 200 mg). The cartridges were conditioned with 9 mL methanol, followed by 9 mL water, after which the aqueous samples were passed through the SPE cartridge. The herbicides were eluted from the cartridge into a GC vial using 1 mL of methanol. The cartridges were then eluted a second time with 1 mL methanol into a second vial. Vials were stored at 4 °C until analyzed. The remaining water was then extracted twice by liquid–liquid extraction (LLE) using dichloromethane (DCM) (4:1 v:v, water:DCM). The extraction DCM solutions were combined, and the DCM was dried by passing through phase separator paper (Whatman 1PS, 15 cm). The DCM was evaporated just to dryness using a Turbo-Vap II at 40 °C. The herbicides were then dissolved in 1 mL methanol, which was transferred into a GC vial. The vials were stored at 4 °C until analyzed.

2.4. Herbicide sorption

Soil samples (7.5 g) of air-dried Waukegan silt loam soil were weighed into thirty 35-mL glass centrifuge tubes. Biochar (0.4 g) was added to half of the tubes, and the soil and biochar were thoroughly mixed. Triplicate soil samples with and without biochar were treated with 10 mL of an aqueous solution (0.17, 0.5, 1.7, 5.0 or 17 μg mL^{-1} atrazine and acetochlor). After the solution was added, the soil was thoroughly mixed with a vortex mixer and then shaken overnight. The samples were centrifuged at 1500 rpm for 20 min. The supernatants were decanted into 7 mL vials. The vials were stored at 4 °C until analyzed. For analysis, 3 mL of the solutions were passed through pre-conditioned SPE cartridges (see above). Atrazine and acetochlor were eluted from the cartridge with 1 mL of methanol containing 1 μg mL^{-1} metazachlor as an internal standard into GC vials for analysis.

2.5. Herbicide GC–MS analysis

The samples were analyzed by GC–MS using an Agilent 5973 mass selective detector coupled to a 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA) fitted with a split-splitless injector and a HP-5MS capillary column (30 m × 0.32 mm ID, 0.25 μm film thickness). The injection volume was 2 μL The column was held at 40 °C for 3 min and then the oven temperature was increased to 250 °C at 20 °C min^{-1}, then the temperature was held for 5 min. The column was directly connected to the ion source of the mass spectrometer through a heated transfer line maintained at 280 °C. Electron impact (EI) mass spectra were obtained at 70 eV with the instrument scanning from 100 to 300 amu and the source maintained at 230 °C.

For confirmation and quantification, the GC–MS was operated in SIM mode. For confirmation, retention time (RT) and two characteristic ions (*m/z*) were used for each herbicide: atrazine RT = 11.8 min, *m/z* 215, 200; acetochlor RT = 12.6 min, *m/z* 223, 162; propachlor RT = 11.0 min, *m/z* 176, 120; and metazachlor RT = 13.4 min, *m/z* 209, 133. Propachlor was used as a surrogate and metazachlor was used as an internal standard. For quantification, the peak areas of the two ions were converted to concentrations by external standard calibration. Blanks and standards were analyzed before, during and after each set of samples.

2.6. Statistical analysis

Results for the CO_2 and N_2O production and CH_4 oxidation activities were arithmetic means of triplicate samples. CH_4 oxidation rate was determined from the linear decrease in headspace CH_4 concentration (typically within 20 d). Linear regression analysis for CH_4 oxidation rates (zero-order kinetics) has been performed in other studies (e.g. Reay et al., 2001; Spokas et al., 2007), and is justified based on observed linear decreasing concentrations over the incubation periods (data not shown). CO_2 and N_2O production rates were also determined from the linear increase in headspace concentrations over the incubation period.

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

3. Results and discussion

3.1. CO_2, N_2O and CH_4 evolution from biochar

There was observable CO_2 accumulation in the biochar + water incubations (Fig. 1A). It is important to note that these incubations did not receive any inocula. The amount of CO_2 evolved was correlated with the amount of biochar (R^2 = 0.98), and less dependent on moisture additions. Overall, there was increased production of CO_2 from the biochar with the addition of moisture (Fig. 1A). However, the amount of CO_2 produced was statistically equal at the two different moisture additions evaluated (Fig. 1A), except for the 3 g biochar additions. The exact source of the CO_2 is still unknown. However, placing the biochar under a vacuum (−68 cm Hg) for 4 h prior to initiating the incubations reduced the observed CO_2 production by 7% (Table 1). Rinsing the biochar with hexane prior to initiating the incubations reduced the amount of CO_2 production by 24% (Table 1). Therefore, the observed CO_2 is hypothesized to result from reactions involving water and O_2, since headspace O_2 concentrations decreased during the biochar incubations (data not shown). It is not known if these reactions are biotic or abiotic. Furthermore, since the hexane rinsed biochar reduced CO_2 production, the potential exists that this CO_2 was produced by liable or reactive components sorbed to the biochar that were partially removed by the hexane. However, the hexane also could have diminished any microbial population on the char. Due to the low difference with the vacuum pretreatment, an unlikely source

Table 1
Comparisons of production rates for CO_2, N_2O, and CH_4 in laboratory incubations with pretreatments of 0.5 g of biochar and 1.0 mL water addition (50-d incubation). Negative production rates represent oxidation.

Pretreatment	CO_2 production ($\mu g\ CO_2\ g^{-1}_{biochar}\ d^{-1}$)	N_2O production ($ng\ N_2O\ g^{-1}_{biochar}\ d^{-1}$)	CH_4 production ($ng\ CH_4\ g^{-1}_{biochar}\ d^{-1}$)
Control (no biochar)	0.1 ± 0.1	−0.05 ± 0.06	−0.01 ± 0.1
No pretreatment	162.8 ± 2.1	−0.6 ± 0.7	−0.3 ± 0.4
Vacuum (4 h)	149.9 ± 3.0	−0.7 ± 0.7	−0.4 ± 0.4
Hexane rinsed	123.6 ± 3.5	−0.6 ± 0.6	−0.3 ± 0.5

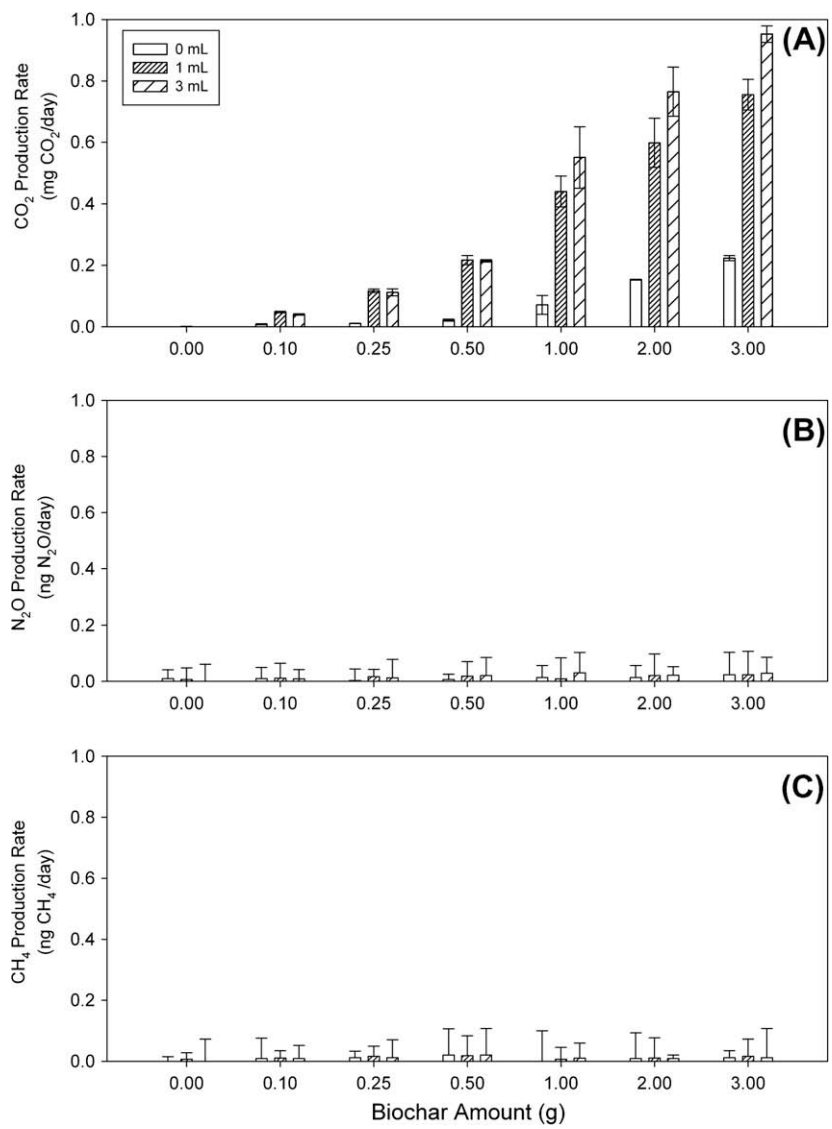

Fig. 1. Observed cumulative production of (A) CO_2, (B) N_2O and (C) CH_4 versus added biochar amounts and varying moisture additions (0, 1 and 3 mL) over the 100-d incubation. Standard deviations of the replicates are shown. Negative production rates represent net oxidation.

would be trapped CO_2 within the pores of the biochar or reactions with extremely volatile species. There was no observable production or consumption of N_2O or CH_4 in any of the biochar incubations (Fig. 1B and C; Table 1), indicating that the char did not sorb any detectable quantities of N_2O or CH_4 during the incubations.

3.2. Production

At first inspection, it would appear that the biochar amendments increased CO_2 production (Fig. 2A). However, an important factor that needs to be accounted when analyzing the CO_2 production of biochar + soil combinations is to account for the CO_2 production from the biochar alone (Fig. 1A). This production was detailed in Section 3.1 (~0.30 mg CO_2 d^{-1} $g^{-1}_{biochar}$), and the average production at the two different moisture contents (1 and 3 mL) was used for the correction. Assuming that the behavior of the char in the soil + char system is similar, the biochar amendments suppressed CO_2 production compared to the control soil (Fig. 2B) after the char production is subtracted. The magnitude of this suppression was related to the amount of biochar addition to soil (R^2 = 0.98; Fig. 2B). For this particular wood chip biochar and the Minnesota soil, the addition of biochar resulted in suppression of soil CO_2 production at all levels evaluated. With higher biochar amendment rates, the magnitude of this suppression increased. The exact cause of this reduction is not known. One potential explanation is related to the fact that moisture availability in the soil + biochar mixture will be different than the sole biochar + water incubations used for the correction. Thereby, the production of the CO_2 released by the biochar could be overestimated. However, this is unlikely due to the lack of significant differences between the CO_2 releases from the biochar at different moisture additions (Fig. 1A). It is important to note that without this correction it would appear that the biochar stimulated CO_2 production (Fig. 2A), masking the fact that biochar overall suppressed CO_2 production (Fig. 2B). Our results do agree with the hypothesis of Amonette et al. (2003), in that biochar additions might aid in stabilizing SOC by reducing the rates of mineralization.

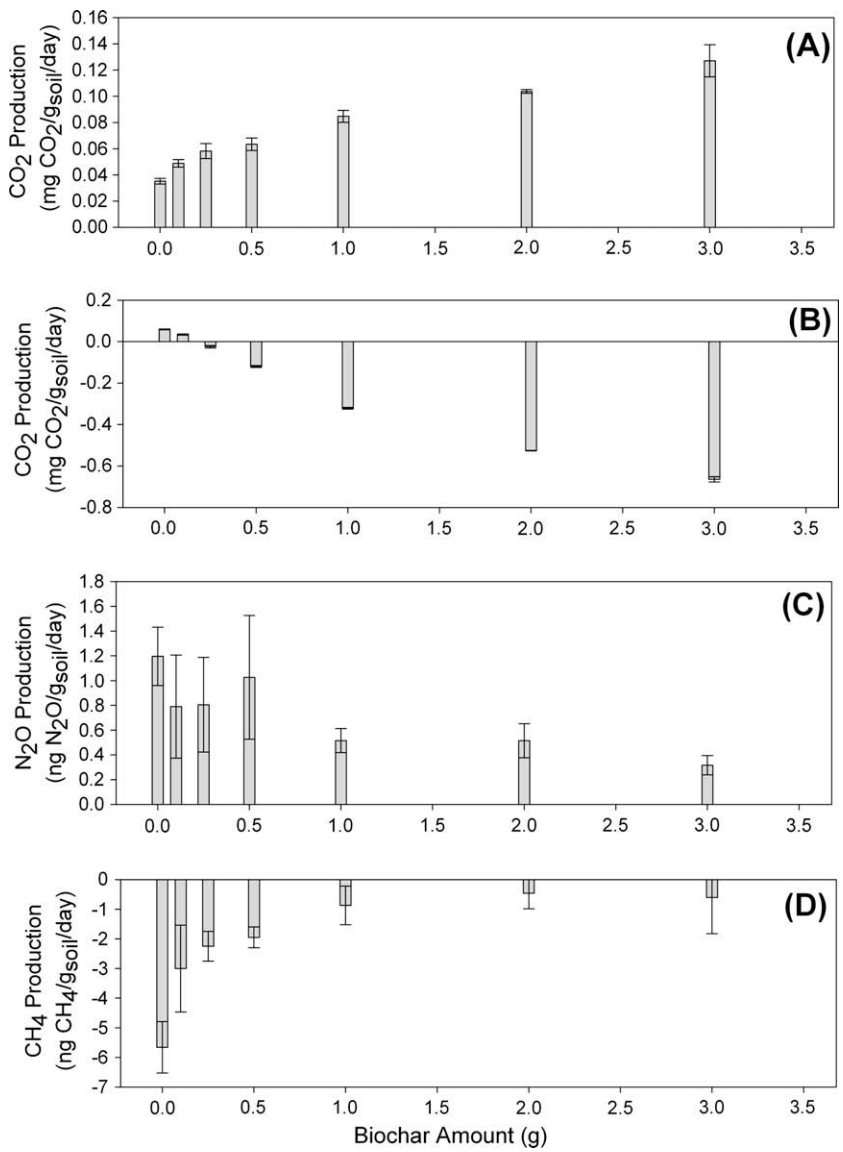

Fig. 2. Observed cumulative production rates of (A) CO_2, (B) corrected CO_2 production after biochar production is subtracted, (C) N_2O and (D) CH_4 versus added biochar amounts with 5 g of Waukegan silt loam soil over a 100-d incubation period. Standard deviations of the replicates are shown. A negative production rate represents oxidation.

3.3. Biochar stability in soil

The fact that biochar amendments suppressed CO_2 production suggests that the biochar is recalcitrant within the 100-d incubation. Indeed, there was no observable CO_2 production attributable to biochar degradation. This confirms the recalcitrant nature of the biochar as already observed by others (e.g. Fowles, 2007). There are studies that show no detectable increase in CO_2 respiration after 40 week for biochar mixed with a volcanic soil (Shindo, 1991), which is in agreement with our results. There is a need for explicit quantification of chemical and physical properties of biochar based on some benchmark materials (Goldberg, 1985; Schmidt and Novack, 2000; Lehmann et al., 2003). Depending on the feedstock and pyrolysis parameters, biochar tends to be alkaline (typical range pH = 6–9.6), but can be produced over a wide pH range (pH = 4–12) (Lehmann, 2007). When added to the soil, this may be detrimental to plant and microbial growth without some modification. In addition, high pH (10–12) can dissolve existing SOC (Stevenson, 1994). The effect of charcoal on native soil carbon needs to be explicitly considered to better understand the potential of biochar as an ecosystem sink and an agent for carbon sequestration.

3.4. N_2O production/consumption

There was no observable production or consumption of N_2O in the solely biochar incubations (Fig. 1B). In addition, no sorption of N_2O by the biochar was observed (Fig. 1B). Due to this lack of N_2O production/consumption, the impact of the biochar can be directly determined by the difference between the soil and soil + biochar incubations. There was no statistically significant difference in the observed net N_2O production at field capacity moisture with biochar addition of 2–10% w/w. However, at higher rates a significant decrease in net N_2O production rates were observed with 57%, 57% and 74% reduction at the 20, 40 and 60% w/w additions, respectively (Fig. 2B). This is in general agreement with the results of Yanai et al. (2007), except that our reductions were significant at field capacity.

The exact cause of this reduction in N_2O production potential is still unknown. However, potential explanations would include altering of the soil moisture potential within the soil and biochar system (Tryon, 1948), increased potential for anaerobic or aerobic microsites within the char (Warnock et al., 2007), increased oxygen diffusion into the soil due to the char particles reducing the bulk density, abiotic reactions of the organic species with N_2O and O_2 (Avdeev et al., 2005) or metal oxides (Oviedo and Sanz, 2005) or even sorbed organics being toxic to the microbial community.

3.5. Oxidation

It is important to recognize that what was measured in this experiment was the net result of CH_4 oxidation and CH_4 production. Overall, the net CH_4 oxidation activity observed in the Rosemount soil (5.58 ng CH_4 d^{-1}) was low relative to forest or landfill cover soils (e.g. Mosier et al., 1997; Spokas et al., 2007). Others have also observed that agricultural soils tend to have lower methanotrophic activity (Mosier et al., 1997; Boeckx et al., 1998; Spokas et al., 2007). Curiously, the addition of biochar to soil reduced net CH_4 oxidation at all levels evaluated (Fig. 2C). Tillage (Mosier et al., 1997), mineral fertilizers (Seghers et al., 2003) and soil fumigants (Spokas et al., 2007) have also been shown to decrease soil CH_4 oxidation capacities.

Some of the hypothesized causes for the reduced N_2O potential could be explanations for the reduced CH_4 oxidation potential. However, typically reduced bulk density and increased oxygen diffusion would increase the soil CH_4 oxidation capacities. However, as seen above the biochar incubations reduced rates of CH_4 oxidation. This does suggest that there is a potential inhibitor for the methanotrophs present on the char (e.g. organics, pH alterations or metal toxicity). However, the potential also exists that the methanotrophs are utilizing sorbed organic compounds versus CH_4, since methanotrophs can utilize a variety of substrates (e.g. Scheutz et al., 2009). CH_4 oxidation rates would be suppressed until these sorbed organics are consumed. The fact that the CO_2 production, N_2O production and CH_4 oxidation were all negatively impacted also suggests that the biochar amendment might suppress microbial activities initially, but the long term impacts are unknown.

3.6. Atrazine and acetochlor

As expected, sorption of both atrazine and acetochlor increased in soil after the addition of biochar (Figs. 3 and 4), presumably as a result of the increase in organic carbon in the soil. However, it is difficult to quantify the effects of biochar on atrazine sorption. Although the Freundlich K_f value (3.12 $\mu g^{1-1/n}\,mL^{1/n}\,g^{-1}$) in amended soil was greater than K_f (2.25 $\mu g^{1-1/n}\,mL^{1/n}\,g^{-1}$) for unamended soils, K_f values cannot be statistically compared because the corresponding $1/n$ values were not equal. The effect of biochar

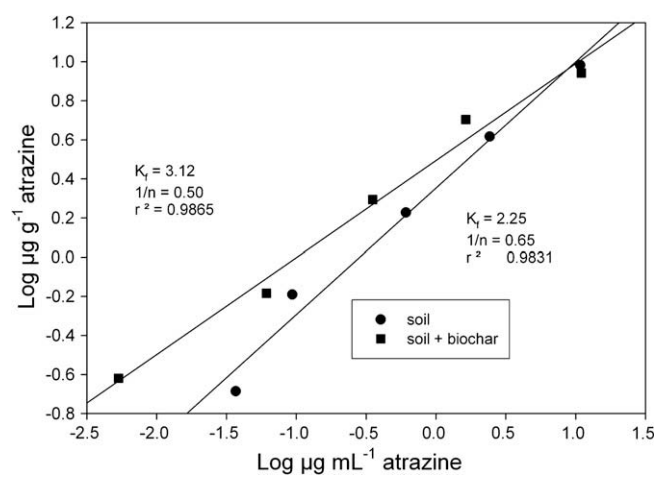

Fig. 3. Freundlich isotherms for atrazine sorption on unamended and biochar amended (5% w/w) Waukegan silt loam soil.

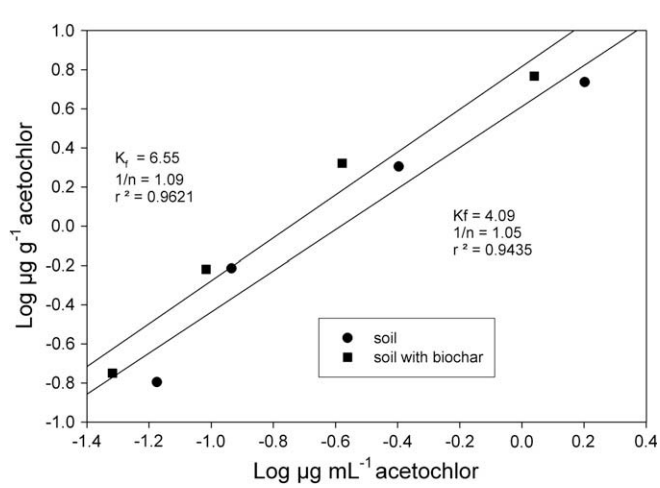

Fig. 4. Freundlich isotherms for acetochlor sorption on unamended and biochar amended (5% w/w) Waukegan silt loam soil.

on atrazine sorption was greater at lower atrazine concentrations (Fig. 3). At the highest initial atrazine concentration, 17 $\mu g\ mL^{-1}$, there was no effect of biochar addition. In contrast, sorption of acetochlor in unamended and amended soil can be compared using Freundlich parameters; $1/n$ values were equal. Acetochlor sorption was greater in amended soil, $K_f = 6.6\ \mu g^{1-1/n}\ mL^{1/n}\ g^{-1}$, as compared to unamended soil, $K_f = 4.1\ \mu g^{1-1/n}\ mL^{1/n}\ g^{-1}$.

Sorption of herbicides in soils with differing organic carbon contents is often normalized to the organic carbon content of the soils to obtain K_{oc} values for modeling of herbicide behavior in dissimilar soils. However, it appears that this approach will not work in characterizing sorption in biochar-amended soils versus unamended soils, as K_{oc} values exhibited a trend opposite to that using K_f values. Atrazine and acetochlor K_{oc} values were greater in unamended soils (atrazine = 75 $\mu g^{1-1/n}\ mL^{1/n}\ g^{-1}$, acetochlor = 136 $\mu g^{1-1/n}\ mL^{1/n}\ g^{-1}$) than in amended soils (atrazine = 51 $\mu g^{1-1/n}\ mL^{1/n}\ g^{-1}$, acetochlor = 107 $\mu g^{1-1/n}\ mL^{1/n}\ g^{-1}$).

Comparison of the K_{oc} values to K_f values for atrazine and acetochlor indicates that, on a mass basis, this biochar is a less effective organic sorbent than other forms of SOC. In contrast, wheat and rice char were 400–2500 times more effective than other forms of SOC in sorbing diuron (Yang and Sheng, 2003b). In a related study, Sheng et al. (2005) found that 1% wheat char contributed 80–86% to the sorption of diuron and bromoxynil by char-amended soil, and 70% of ametryne by char-amended soil. It is not known whether this is a transient effect, observed only in freshly amended soil. Delgado-Moreno et al. (2007) observed an increase in K_f values for four triazine herbicides in soil freshly amended with olive-mill waste as compared to unamended soil. However, if the soil was preincubated with the organic amendment for 1–3 months, there was no difference in sorption for amended and unamended soils.

If biochar affects herbicide sorption in soil, it may in turn affect herbicide persistence. Addition of biochar to soil affected the dissipation of both atrazine and acetochlor. Although biochar did not affect atrazine dissipation during the first 11 d of incubation, >2*X* times more atrazine remained after 20 d in biochar-amended soil as compared to unamended soil (Fig. 5). In contrast to atrazine dissipation, there was no lag phase prior to the start of acetochlor dissipation. Biochar decreased the rate of acetochlor dissipation in soil (Fig. 6). Extrapolated times for 50% dissipation (DT_{50}) were 9.7 d in unamended soil and 34.5 d in amended soil.

Few studies have examined the influence of other soil-applied organic amendments on herbicide bioavailability. Wheat straw-derived char has been reported to affect degradation of organic chemicals in soil, presumably through effects on sorption (Yang et al., 2006; Zhang et al., 2006). Results of Yang et al. (2006) suggest that increased sorption of diuron in wheat char-amended soil as compared to unamended soil decreased bioavailability of diuron as evidenced by decreased microbial degradation and herbicidal efficacy in soil. However, as mentioned previously, any effect of added organic amendments on herbicide processes in soil including degradation may disappear after a period of incubation of the organic amendment in soil (Delgado-Moreno et al., 2007). More research on the effects of aged biochar residues on herbicide dissipation and weed control is needed.

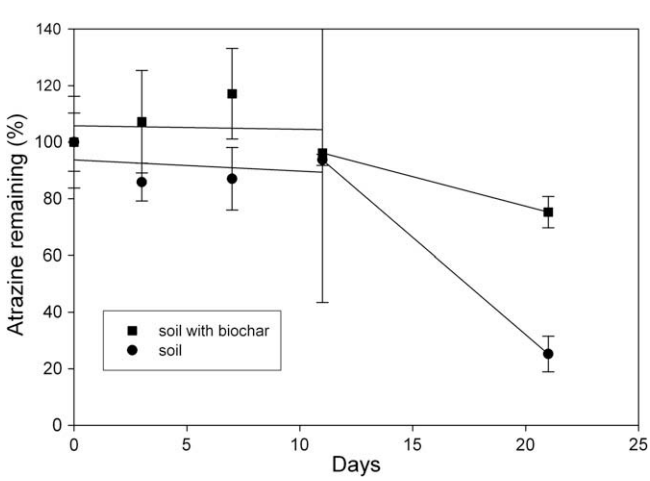

Fig. 5. Atrazine dissipation in unamended and biochar amended (5% w/w) Waukegan silt loam soil.

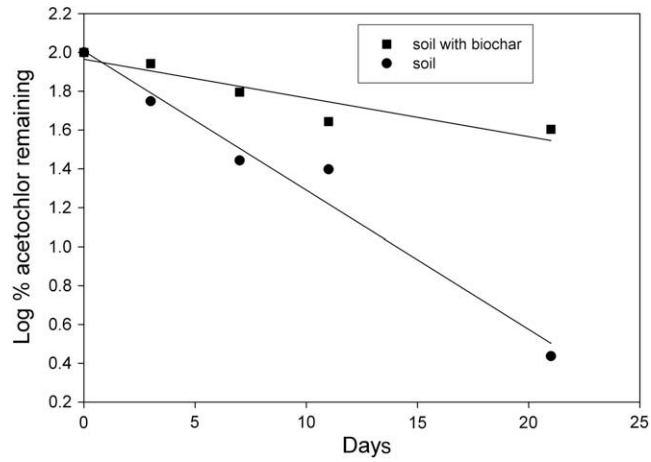

Fig. 6. Acetochlor dissipation in unamended and biochar amended (5% w/w) Waukegan silt loam soil.

4. Conclusions

These results confirm that biochar is resistant to microbial degradation, and hence may be an effective mode of carbon sequestration. Furthermore, there appears to be a positive greenhouse gas benefit, primarily due to the reduction in N_2O production as a consequence of the sawdust biochar addition. This reduction in observed N_2O production could easily offset the 60% reduction in CH_4 oxidation activity with10% w/w biochar additions in the net greenhouse gas balance. Biochar also increased the sorption of two common herbicides, reducing the likelihood of leaching and runoff losses, but also reducing bioavailability, perhaps necessitating higher application rates. However, additional field scale trials are necessary to further investigate the impacts of biochar amendments. In addition, it is important to note that the impacts observed in these laboratory incubations were the initial effects and the long term impacts of the biochar amendments still need to be assessed. These initial observations could be influenced by sorbed organics that will dissipate with time. Therefore, aged biochar could cause entirely different impacts than those observed here with freshly produced biochar.

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