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Short-term CO_2 mineralization after additions of biochar and switchgrass to a Typic Kandiudult ☆

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ABSTRACT

Biochar additions to soil can increase soil organic carbon (SOC) concentrations; however, minimal information is available on relationships with soil nitrogen (N) cycle. We hypothesized that biochar additions to sandy soils should be resistant to microbial mineralization in short-term studies but may prime organic carbon (OC) mineralization of fresh residue that promotes N immobilization. A laboratory pot incubation study was conducted with a Norfolk loamy sand (Fine-loamy, kaolinitic, thermic, Typic Kandiudult) mixed with pecan-shell biochar at rates of 0, 5, 10 and 20 g kg^{-1} and with 0 and 10 g kg^{-1} dried, ground switchgrass (*Panicum virgatum* L.). On days 25 and 67 of the incubation, all pots were leached with 1.2 to 1.3 pore volumes of deionized H_2O and the leachate NO_3–N, NH_4–N, and dissolved organic (DOC) concentrations were measured. Also cumulative soil CO_2 fluxes after days 25 and 67 were determined. Biochar alone and mixed with soil and switchgrass after 67 days of incubation were characterized using Fourier transformed infrared spectroscopy (FT-IR). Mixing biochar with switchgrass after 67 days caused a significant increase in SOC content while soil total nitrogen (TN) and leachate DOC concentrations showed mixed results. Biochar mineralization by itself was found to be minimal, but by days 25 and 67, soil with biochar and switchgrass exhibited higher cumulative CO_2 fluxes implying stimulation of switchgrass mineralization. Significant NO_3–N immobilization occurred after 25 days in treatments with biochar + switchgrass; however, by day 67 the NO_3–N concentrations rebounded slightly. The FT-IR analysis revealed that switchgrass in the presence of biochar underwent some structural modifications. Biochar applications in the short-term can cause N immobilization resulting in temporary plant available NO_3–N concentration reductions.

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1. Introduction

Sandy agricultural soils of the Southeastern USA Coastal Plain region have inherently low SOC contents in the surface 0- to 15-cm depth (6.3 to 9.2 g kg^{-1}, Hunt et al., 1996; Novak et al., 2007) due to decades of row crop production using inversion tillage (Gray, 1933; Trimble, 1974). Conventional inversion tillage practices in sandy soil accelerate organic residue decomposition (Bauer et al., 2006). Due to intensive leaching of bases, agricultural soils in this region also are extensively weathered (Daniels et al., 1970; Shaw et al., 2004) and have low soil pH values (<5) and low cation exchange capacities (2 to 8 $cmol_c$ kg^{-1}, Gamble and Daniels, 1974; Daniels et al., 1978). In order to improve soil quality, conservation tillage practices are typically recommended.

Conservation tillage practices can facilitate increases in SOC contents of these soils (Hunt et al., 1996; Novak et al., 2007). However, the weakness of this practice is that increases are limited to the top few cm of soil, and to achieve a significant SOC increase, large quantities of biomass OC are typically required (Novak et al., 2009b). For example, in the 0 to 3-cm depth of sandy, South Carolina Coastal Plain soils, almost 15 Mg ha^{-1} of OC as crop residue was returned over 6 years, but only a 0.51 Mg ha^{-1} SOC increase was observed (Novak et al., 2009b). This equated to less than 3.5% (by weight) of the 6 year cumulative residue OC mass was incorporated into the SOC pool; the other 96.5% was released to the atmosphere as CO_2 or leached through the sandy soil profile. The sandy soil textures coupled with very rapid residue mineralization severely limits agricultural management options to raise SOC contents, which are a requisite for increasing crop productivity.

Similar soil characteristics, low pH, SOC and CEC values (Tiessen et al., 1994; Lehmann et al., 2003) cause fertility concerns for the Oxisols of the inter-tropical regions of the Amazonian basin (Eswaran and Tavernier, 1980). In spite of these poor soil characteristics, Pre-Columbian farmers successfully managed the Amazonian Oxisols for

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crop production by adding charcoal from hearths and produced through 'slash and char' practices along with manure, fish bones, and other organic materials (Glaser et al., 2001, 2002; Mann, 2005). Today more than 500 years after the practices ceased that led to their development; these anthrosols known as Terra Preta have much higher levels of SOC, higher CECs, higher pHs, and higher levels of fertility than the Oxisols from which they were derived. Recent investigations (Glaser et al., 2002; Lehmann et al., 2003; Lehmann and Rondon, 2006) of Terra Preta soils showed that charcoal added to the Oxisols contributed substantially to their high levels of OC and available nutrients.

Applying charcoal (or termed biochar when used as a soil amendment) to degraded agricultural soils in the USA could be beneficial for simultaneously improving soil fertility while sequestering C as a means of reducing anthropogenic emissions of CO_2 to the atmosphere (Laird, 2008). Biochar amendments enhance soil fertility by adding a highly stable form of SOC that contributes CEC and adsorbs both nutrients and less stable biogenic humic materials. Biochar additions increase fertility status and pH of soils because the biochar contains inorganic components (e.g., Ca, K, Mg, P, etc.) that act as a liming agent and supply plant available nutrients (Glaser et al., 2002; Chan et al., 2007; Novak et al., 2009a).

A distinct property of biochar is its stability in soils relative to other forms of SOC. The mean residence time of biochar C in soils is commonly >1000 years and can be as great as 10,000 years (Swift, 2001); biogenic humic substances have much shorter residence times (between 74 and 3280 years; Stevenson, 1994). A highly condensed aromatic-core is responsible for the recalcitrant nature of biochar and hence its longevity (Schmidt and Noack, 2000; Glaser et al., 2001; Sombroek et al., 2003; Liang et al., 2008).

Biochars, however, will not last forever in soils. Structural changes in biochar, primarily surface oxidation can occur in relatively short periods of time (months) (Liang et al., 2006; Cheng et al., 2006). Although information regarding biochar turnover in field soils is scarce, laboratory incubations studies have determined that some biochar C (0.26 to 0.79% of total C) is lost during short-term (60 days) incubations (Hamer et al., 2004).

Biochars recalcitrant nature suggests that it should have limited influences on the chemical and biological processes controlling the soil C and N cycles. Liang et al. (2009) recently reported that added organic matter (sugarcane) was incorporated into aggregates more rapidly in biochar-rich Brazilian soils than biochar-poor soils resulting in less total C mineralization. On the other hand, there are reports that biochar additions to soils stimulated mineralization of indigenous soil organic matter (Comerford et al., 2008; Rogovska et al., 2008; Wardle et al., 2008). Similarly, N mineralization was stimulated in forest soils after charcoal additions from a forest fire (DeLuca et al., 2006). These contradictions suggest a need for critical evaluation of biochar use in soil quality restoration. Studies have shown that biochars may prime soil microbial communities to heighten decomposition of indigenous SOC or exogenous OC residues potentially negating the positive effects of adding biochar. Simultaneously, greater rates of indigenous SOC or exogenous OC residue mineralization could promote N immobilization and decrease N availability to plants.

Biochar C and N mineralization processes can be evaluated by monitoring CO_2 production, measuring soluble N concentrations in soils or collected leachate, and examining biochar structural modifications with FT-IR spectroscopy. Monitoring CO_2 production from mineralization of organic compounds requires CO_2 measurements using either labeled or unlabelled substrates (Anderson, 1982). Soil and leachate inorganic N concentrations can be readily measured using various methods (Mulvaney, 1996) to ascertain if N mineralization or immobilization has occurred. Potential biochar structural modifications can be examined using FT-IR spectroscopy (Rutherford et al., 2004; Reeves et al., 2007; 2008).

The aromatic backbone of biochar is highly stable in soil environments; however, many surface functional groups are subject to both abiotic and microbial mediated oxidation reactions (Cheng et al., 2006; 2008). Methyl (CH_3) functional groups may be oxidized to carboxyl (COOH) groups, or replaced by carbonyl (C O) or hydroxyl (OH) groups (Alexander, 1977). Several strains of *Mycobacterium* sp. (Semba et al., 1996) and the fungus *Beauveria sulfurescens* (Vigne et al., 1986) can hydroxylate aromatic compounds. Therefore, FT-IR spectral patterns of biochars before microbial breakdown should exhibit sorption bands at about 1600 cm^{-1} from the predominance of C C bonds in aromatic structures. After microbial mineralization, biochar structural modifications and formation of functional groups should be observable in FT-IR spectral scans between 1820 to 1660 cm^{-1} and 3400 to 2400 cm^{-1}, respectively for formation of C O, −OH groups in COOH and inserted −OH functional groups (Nguyen et al., 2008). The appearance of adsorption bands in FT-IR spectra from these structural modifications and functional groups changes can depend on biochar quality (Cheng et al., 2006), climatic conditions (Cheng et al., 2008), and soil microbial communities able to produce enzymes that mineralize biochar (Hamer et al., 2004).

Based on the literature, we hypothesized that in short-term biochar addition experiments to sandy soils, the biochar should be fairly resistant to microbial mineralization, but may promote degradation of exogenous plant residue and cause a negative N priming effect. The objectives of this investigation were to; (i) determine the degree of biochar oxidation in Norfolk soil treated with and without switchgrass by collecting CO_2 flux measurements and by FT-IR spectroscopy; (ii) quantify DOC and N species in leachate to ascertain C and N dynamics.

2. Material and methods

2.1. Production and characterization of pecan-shell biochar

Initial pecan-shell characterization and biochar pyrolysis conditions were described in Novak et al. (2009a). Briefly, pecan shells obtained from NC were ground to pass through a 2-mm sieve. Pecan shells were pyrolysized in a Lindberg programmable furnace (model 5116HR, Lindberg, Watertown, Wisconsin) equipped with a N_2 purged retort. The furnace was initially heated to 40 °C; the temperature was then ramped to 170 °C at 5 °C min^{-1} and maintained for 30 min at this temperature. Next, the temperature was increased to 700 °C under the same ramping conditions, and then held for an additional 30 min. At termination, the biochar was cooled overnight while maintaining the N_2 purge and was later ground to pass a 2-mm sieve.

The biochar moisture content and ash content were determined by oven drying and dry combustion at 80 and 760 °C, respectively (Novak et al., 2009a). The pH was determined using the method of Ahmedna et al. (1998) and the abrasion resistance/hardness was determined using the wet attrition method (Toles et al., 2000). The biochar moisture content was 14 g kg^{-1}, ash content was 38 g kg^{-1} and its abrasion resistance was low (2.8% indicating a high degree of mechanical strength). The biochar OC and TN content were determined using American Society Testing Materials (ASTM) method D 3176 (American Society Testing Materials, ASTM, 2006) and were expressed on a dry, (w w^{-1}) ash-free basis. A solid-state cross-polarization magic angle-spinning total-sideband suppression ^{13}C NMR spectral pattern of the biochar was obtained using a Bruker DSX-300 spectrometer (Karlsruhe, Germany) with operating conditions and spectral pattern assignments as described by Wang et al. (2007). The NMR spectral pattern revealed that the majority of C (58%) was aromatic, with lesser amounts of aliphatic (29%) and carboxyl (13%). A Diffuse Reflectance Infrared Fourier Transformed (DRIFT) spectral scan of the biochar was obtained in the absorbance mode by mixing 3 mg into 97 mg of KBr using a pestle and mortar and scanning the powder using a Perkin Elmer Spectrum One FT-IR spectrometer (Kang and Xing, 2007). The KBr powder was used as the background. The

spectrophotometer was equipped with a lithium tantalite ($LiTaO_3$) detector and DRIFT accessory (Shelton, CT). A DRIFT spectrum was obtained by collecting 500 scans with a spectral resolution of 1 cm^{-1} between 450 and 4000 cm^{-1} at a scan speed of 0.5 cm s^{-1}.

2.2. Site and soil description

A Norfolk Ap horizon (0 to 15-cm deep) soil sample from a field currently under conservation tillage and row crop production was sampled using a shovel near the USDA-Coastal Plains Research Center, Florence, South Carolina, USA. The soil was collected in April approximately 1 week after fertilization with 49 kg N ha^{-1} of UAN (urea-ammonium nitrate, 28–0–0) for an impending corn crop. After air-drying and 2-mm sieving, particle size analysis using the sedimentation method (Soil Characterization Lab, The Ohio State University, Columbus, Ohio) revealed that the soil was a loamy sand comprised of 730, 250 and 20 g kg^{-1}, respectively, sand, silt, and clay. The pH of the Norfolk Ap was 4.8 using a 1:1 soil to deionized water mixture (Novak et al., 2007). A LECO TruSpec CN analyzer (LECO Corp., St. Joseph, Michigan) was used to measure total carbon and TN (except NH_4). Because the Norfolk soil pH was acidic, the total carbon content was assumed to equal OC content.

2.3. Biochar incubation in Norfolk Ap soil

Twenty-four, open-top PVC columns (10-cm diameters × 17-cm tall) were used for the soil incubation; the bottoms were sealed using a nylon mesh fabric. Biochar that was 0.25-mm sieved was mixed into 750 g of air-dried, 2-mm sieved soil to create 0, 5, 10, and 20 g kg^{-1} treatments equating to a field application rate of 0, 10, 20 and 40 tons ha^{-1}. Each treatment was set up in triplicate. To 12 of the PVC columns, 10 g kg^{-1} switchgrass (air-dried, 0.25-mm sieved) was mixed into the soil to observe potential biochar simulation of switchgrass oxidation (a positive C priming effect). Remaining treated and untreated dry-Norfolk Ap soil was retained and regarded as day 0 samples.

All dry-soil treatments were then wetted with sufficient deionized water to obtain a 100 g kg^{-1} soil moisture content representing the Norfolk Ap horizon upper field capacity range. The moist soil treatments were then placed into the column, and were gently tapped to obtain a 1.2 g cm^{-3} bulk density. The columns were incubated for 67 days under laboratory temperature and relative humidity conditions of between 17 to 27 °C and 23 to 61%, respectively. The soils were allowed to dry to between 30 and 50 g kg^{-1} moisture contents then were brought back to 100 g kg^{-1} moisture on a weekly basis to simulate wet/dry cycles.

The CO_2 flux from each soil treatment was measured twice per week (total $n = 16$) using a LiCor 6000-09 (LiCor Biosciences, Lincoln, Nebraska) soil respiration chamber (1038 cm^3 volume, 71.6 cm^2 soil-exposed area) connected to a LiCor 6250 CO_2 analyzer. The headspace in each soil column was measured periodically ($n = 4$) during the 67 day experiment, and this headspace value (mean = 748.4 cm^3, $n = 24$ columns) was added to the chamber volume for a total head space volume (mean = 1786.4 cm^3, $n = 24$). Air in the chamber was at ambient CO_2 concentration before placing the chamber onto the soil column for each measurement. Each measurement was initiated when CO_2 concentrations increased at a constant rate, usually between 30 and 60 s of the chamber being placed onto the soil column. All CO_2 flux values were measured before re-wetting the soil back to 100 g kg^{-1} moisture because prior soil laboratory incubation studies involving organic substrate mineralization revealed that CO_2 flux readings after wetting were artificially high because the added water flushed CO_2 from pore spaces. To estimate switchgrass mineralization alone, the cumulative CO_2 flux values from Norfolk + biochar + switchgrass treatments were corrected by subtracting the cumulative CO_2 flux values from similar treatments that lacked switchgrass. This procedure implies that biochar mineralization alone in the Norfolk soil was minimal; results shown in Table 3 supports this contention. A similar CO_2 correction procedure was used by Spokas et al. (2009).

On incubation days 25 and 67, each column was leached with 1.2 to 1.4 pore volumes of deionized water; the leachate was collected and weighted. The leachates were filtered (0.45-μm) and analyzed for DOC using a Shimadzu TOC-Vcs analyzer (Shimadzu Corp., Columbia, Maryland). An unfiltered leachate sample representing the TOC fraction was also analyzed, but the DOC concentrations were reported because TOC:DOC ratios samples were similar (1:0.98, data not presented). Leachate dissolved NO_3–N and NH_4–N concentrations were measured using a TRACCS 800 Auto-Analyzer following EPA method 353.1 and 350.1, respectively (U.S. Environmental Protection Agency, USEPA, 1983). EPA-certified quality control samples were routinely analyzed to verify results.

Soil samples from the treatments were also analyzed using DRIFT spectroscopic techniques as described previously. The spectra were corrected by subtracting the spectral pattern obtained from untreated soil controls (Kang and Xing, 2007).

2.4. Statistics

The mean values for %SOC and TN on day 0 and 67 were compared to determine their overall modifications between treatments. The means of cumulative CO_2 fluxes, leachate DOC, NO_3–N and NH_4–N concentrations between treatments were evaluated on day 25 and 67 because they correspond to the day of water leaching. For these measurements, a two-way ANOVA was used for significant differences between factors as the biochar, switchgrass, and their interaction. In addition, a Holms–Sidek multiple pair-wise comparison procedure was used to determine significance of increasing %biochar additions on measured variables. All statistical tests were performed using SigmaStat v. 3.5 software (SPSS Corp., Chicago, Illinois) at a $P < 0.05$ level of significance.

3. Results

3.1. Initial amendment characterization

Pecan-shell biochar was mildly alkaline, was enriched in OC but had a low level of TN, which resulted in a wide C:N ratio (Table 1). The OC content of the switchgrass was less than half that of the biochar. The Norfolk Ap soil had a strongly acidic pH value. Compared to other analyses of the Norfolk Ap soil, the sample used in this study had a high OC content because the field has been under conservation tillage management. Norfolk Ap soils with a long history of row crop and disk tillage typically have OC contents of <10 mg kg^{-1} (Hunt et al., 1996; Novak et al, 2009b) because of rapid mineralization of plant residue (Bauer et al., 2006).

3.2. Effects of biochar and switchgrass mineralization on soil and leachate characteristics

Additions of biochar caused a systematic increase in SOC for both day 0 and day 67 samplings (Table 2). The largest SOC increase happened when mixing in 20 g kg^{-1} biochar; the mean Norfolk Ap SOC content

Table 1
Organic carbon (OC), total combustible nitrogen (TCN) content, carbon to nitrogen (C:N) ratio and pH value of a Norfolk Ap soil, pecan-shell biochar, and switchgrass.

Material	OC	TCN	C:N	pH[a]
	g kg^{-1}			
Norfolk Ap	18	1.2	15	4.8
Biochar	834	3.4	245	7.5
Switchgrass	485	6.6	73	–

[a] Measured in a 1:1 soil:water (v v^{-1}) ratio.

Table 2
Soil organic carbon (SOC) and total nitrogen (TN) contents in a Norfolk Ap soil amended with biochar and switchgrass before and after 67 days of incubation.

Biochar ($g\,kg^{-1}$)	Incubation (days)	SOC ($g\,kg^{-1}$)		TN ($g\,kg^{-1}$)	
		Switchgrass ($g\,kg^{-1}$)*			
		0	10	0	10
0	0	17.0a,a**	17.2a,a	1.26a,a	1.24a,a
5	0	18.1a,a	19.4a,a	1.14a,a	1.15a,a
10	0	22.2a,b	23.3a,b	1.25a,a	1.28a,a
20	0	31.2a,c	29.7a,c	1.48b,b	1.14a,a
Mean		22.2a	22.4a	1.28b	1.20a
0	67	17.5a,a	18.4a,a	1.23a,a	1.27a,a
5	67	18.3b,b	21.4a,a	1.30a,a	1.40a,a
10	67	22.0b,c	24.3a,b	1.07a,a	1.37a,a
20	67	29.2a,d	30.0a,c	1.20a,b	1.30a,b
Mean		22.0b	23.3a	1.20b	1.33a

* Soil supplemented with 10 $g\,kg^{-1}$ air-dried, 2-mm sieved switchgrass.
** A two-way ANOVA was used to examine for significance of biochar and switchgrass additions and their interaction at $P<0.05$. The first letter shows differences between switchgrass rates in rows and the second letter indicates differences among biochar rates in columns.

increased almost two-fold. Mixing 10 $g\,kg^{-1}$ switchgrass with the soil did not result in significant SOC increases on day 0, but there were mixed effects on day 67. For SOC, there was no significant interaction on day 0 between biochar and switchgrass, but a significant interaction occurred on day 67. Soil TN contents on day 0 and day 67 were, for the most part, similar between biochar treatments with and without switchgrass. There was a significant interaction between biochar and switchgrass for TN on day 0, probably as a result of the higher mean value in soil treated with 20 $g\,kg^{-1}$ biochar. By day 67, there was also a significant interaction in soil TN contents probably in response to results found between soils treated with switchgrass and 10 $g\,kg^{-1}$ biochar. After incubation, the most apparent modification in the Norfolk Ap soil following biochar and switchgrass addition was its SOC, while changes in its TN content were variable.

When biochar was not present, soils with 0 and 10 $g\,kg^{-1}$ switchgrass on days 25 and 67 had similar CO_2 flux measurements implying that switchgrass was not readily mineralized relative to indigenous SOC compounds (Table 3). This would imply that CO_2 production in these treatments was from mineralization of indigenous SOC. Biochar mineralization by itself was probably also very minimal because there were no significant differences between biochar treated and untreated soil. In treatments with switchgrass, however, biochar additions showed increased CO_2 fluxes, but not all increases were significant. In fact, when averaged across soil with 10 $g\,kg^{-1}$ switchgrass, adding biochar stimulated about a 1.5-fold increase in mean CO_2 fluxes. Because biochar mineralization was found to be minimal, cumulative CO_2 flux values were corrected for indigenous SOC mineralization to estimate cumulative CO_2 flux values from switchgrass mineralization itself (Table 3). The corrected cumulative CO_2 values on days 25 and 67 ranged between +0.18 to +19.91 $\mu mol\,m^{-2}s^{-1}$. Although, biochar presence in soil with switchgrass had a significant influence on CO_2 fluxes, adding more biochar did not correspondingly stimulate higher cumulative or corrected CO_2 fluxes.

Mineralized OC compounds not assimilated by microbial communities should increase soluble OC concentrations in soil pore water (Alexander, 1977) that can be flushed and measured in water leachates. Only two treatments on day 25 had significantly greater DOC concentrations; while on day 67 there were no differences between treatments. Adding more biochar (except for 1 treatment), did not result in a corresponding increase in leachate DOC concentrations. It appears that there is no strong relationship between leachate DOC concentrations vs. the biochar amount.

The Norfolk Ap soil was collected approximately 1 week after N fertilization for corn production, and hence the control soil (0 biochar + 0 switchgrass) contains appreciable NO_3–N and NH_4–N concentrations (Table 4). When switchgrass was added to the Norfolk Ap soil, irrespective of biochar amount, however, there was a significant concentration decline in both N species. On day 25, all water leachates collected from soil treated with switchgrass irrespective of biochar additions were devoid of NO_3–N. Averaging among switchgrass treatments corroborated that biochars presences significantly promoted N immobilization. The immobilization was short-term because by day 67, NO_3–N was measurable. By day 25, after switchgrass was added with no biochar, soil microbes were scavenging NH_4–N in response to mineralization. Mixing in more biochar showed a mean NH_4–N concentration decline in soils with 0 switchgrass, but not in soils with switchgrass. By day 67, all leachates were devoid of measurable NH_4–N concentrations.

Leachate NO_3–N concentration on day 25 declined in soils treated solely with biochar. More biochar added to the Norfolk Ap soil with 0 switchgrass correspondingly resulted in significant mean NO_3–N concentrations declines. Nitrogen was increasingly immobilized by increasing addition of biochar in the absence of switchgrass on day 25 of the incubation. On day 67, however, there was a positive relationship between biochar addition and NO_3–N leaching at a lower concentration level than on day 25.

3.3. DRIFT scans of biochar alone and with Norfolk soil

The DRIFT scans of the pecan-shell biochar (before incubation) revealed that it was composed of a variety of broad bands; assignments for these bands were identified in Fig. 1. The relatively broad

Table 3
Cumulative and corrected CO_2 flux values from a Norfolk Ap amended with biochar and switchgrass on days 25 and 67 of incubation.

Biochar ($g\,kg^{-1}$)	Incubation (days)	Cumulative CO_2 fluxes ($\mu mol\,m^{-2}s^{-1}$)		Corrected cumulative CO_2 fluxes ($\mu mol\,m^{-2}s^{-1}$)**
		Switchgrass ($g\,kg^{-1}$)*		
		0	10	
0	25	15.96a,a***	16.16a,a	+0.20
5	25	13.55a,a	24.76a,a	+11.21
10	25	14.94a,a	22.17b,a	+7.77
20	25	9.30a,a	21.71b,a	+8.26
Mean		13.45a	21.33b	+7.88
0	67	22.78a,a	22.96a,a	+0.18
5	67	20.84a,a	32.83b,a	+11.99
10	67	20.92a,a	30.68b,a	+9.76
20	67	14.49a,a	27.4b,a	+12.91
Mean		19.76a	28.47b	+8.71

* Soil supplemented with 10 $g\,kg^{-1}$ air-dried, 2-mm sieved switchgrass.
** Fluxes corrected by subtraction of [cumulative $CO_{2\ 1\%switchgrass,\ X\%\ biochar}$] minus [cumulative $CO_{2\ 0\%\ switchgrass,\ X\%\ biochar}$].
*** A two-way ANOVA was used to examine for significance of biochar and switchgrass additions and their interaction at $P<0.05$. The first letter shows differences between switchgrass rates in rows and the second letter indicates differences among biochar rates in columns.

Table 4
Leachate dissolved organic carbon (DOC), nitrate (NO_3–N), and ammonium (NH_4–N) concentrations collected from Norfolk Ap soil amended with biochar and switchgrass on days 25 and 67 of incubation (nd = not detected).

Biochar ($g\,kg^{-1}$)	Incubation (days)	DOC ($mg\,L^{-1}$)		NO_3–N ($mg\,L^{-1}$) Switchgrass ($g\,kg^{-1}$)*		NH_4–N ($mg\,L^{-1}$)	
		0	10	0	10	0	10
0	25	70.78a,a**	75.65a,a	256.85a,a	0b,a	4.74a,a	1.43b,a
5	25	57.81a,a	76.31b,a	158.61a,a	0b,a	1.34a,b	1.84a,a
10	25	61.28a,a	45.61b,b	135.99a,b	0b,a	1.75a,b	1.83a,a
20	25	75.91a,a	87a,a	78.67a,c	0b,a	2.25a,b	1.66a,a
Mean		66.45a	71.15a	157.51a	0b	2.52a	1.69b
0	67	45.38a,a	32.03a,a	28.25a,a	12.05a,a	nd	nd
5	67	36.74a,a	36.77a,a	30.1a,a	9.76b,a	nd	nd
10	67	45.61a,a	52.05a,a	32.96a,a	5.79b,a	nd	nd
20	67	57.95a,a	62.23a,a	43.98a,a	2.52b,a	nd	nd
Mean		46.42a	45.77a	33.83a	7.6b	–	–

* Soil supplemented with $10\,g\,kg^{-1}$ air-dried, 2-mm sieved switchgrass.
** A two-way ANOVA was used to examine for significance of biochar and switchgrass additions and their interaction at $P<0.05$. The first letter shows differences between switchgrass rates in rows and the second letter indicates differences among biochar rates in columns.

bands occur in the 3695 to 3300 cm^{-1} region were due to O–H stretching in —OH groups. More numerous bands occurred between 1595 cm^{-1} (—H stretching of C O), 1527 cm^{-1} (aromatic C C) 1461 cm^{-1} (C–H deformation of CH_3 groups), 1436 cm^{-1} (stretching of C in hetero-aromatic structures), 1368 cm^{-1} (C O stretching in COOH), and 1288 cm^{-1} (C–O stretching and OH deformation of COOH and phenolic groups).

To ascertain DRIFT peaks after biochar was mixed with soil and switchgrass, the DRIFT scans were corrected for spectral bands from indigenous OC and exogenous OC compounds added as switchgrass. Assessment was then made for OC structural changes and formation of intermediates compounds after 67 incubation days. The biochars in Norfolk Ap with 0 switchgrass showed a sharp spectral peak due to —OH groups (3695 and 3620 cm^{-1}) and a weak peak due to carbonyl (C O) stretching of carboxylate (Fig. 2a, 1368 cm^{-1}). With increasing biochar concentrations to these treatments, there were peaks at 1368 and 1288 cm^{-1} suggesting formation C–O stretching and OH deformation of carboxylate and phenolic groups (Fig. 2b, c, and d). The three biochar mixtures in Norfolk Ap (with 0 switchgrass) in this short-term experiment showed relatively minimal evidence for structural modification and formation of oxygen containing functional groups. There were pronounced peaks at 1950 and 1800 cm^{-1} in the Norfolk Ap + 10 $g\,kg^{-1}$ biochar that are of an unknown assignment.

Switchgrass incubated for 67 days in the Norfolk Ap with biochar exhibited an assortment of spectral peaks (Fig. 3). There is a small adsorption peak at 3616 cm^{-1} due to —OH stretching in the Norfolk soil + switchgrass + 0 biochar (Fig. 3a). The peaks between 2000 and 1800 cm^{-1} suggests that carbonyl groups were present; however, these peaks commonly occur between 1590 and 1720 cm^{-1} (Stevenson, 1994). Shifting of the carbonyl signal up field to a higher wave number suggests that these peaks were probably caused by cyclic ketonic structures conjugated to C O groups (Pavia et al., 1979). There are a series of peaks at 1612, and 1463 cm^{-1}, respectively, suggesting the presence of amide and methyl functional groups (Fig 3a).

When biochar was added to Norfolk Ap soil treated with 10 $g\,kg^{-1}$ switchgrass (Fig. 3b, c and d), there is evidence that biochar stimulated switchgrass mineralization as evident by the formation of a large intensity —OH peak (3616 cm^{-1}), carboxylate peaks (1612 and 1322 cm^{-1}) and loss of cyclic ketone character (2000 to 1800 cm^{-1}). Their peaks intensities' were fairly similar among the three spectral patterns. The adsorption peak at 1612 cm^{-1} may also be due N–H deformation and C N stretching from sorbed NH4–N.

4. Discussion

The biochar employed in this study has a wide C:N ratio, was mostly (58%) composed of highly condensed aromatic structures and was physically resistant to degradation (a low attrition percent). These properties influenced how the pecan biochar reacted with the Norfolk Ap soil. Mixing in 10 $g\,kg^{-1}$ or greater biochar significantly raised the Norfolk SOC content a desirable property for restoring fertility in chemically degraded soils (Thompson and Troeh, 1978). The SOC contents in the Norfolk Ap after treatment with biochar were similar between day 0 and 67 implying some recalcitrance to microbial mineralization. Others have reported similar recalcitrance

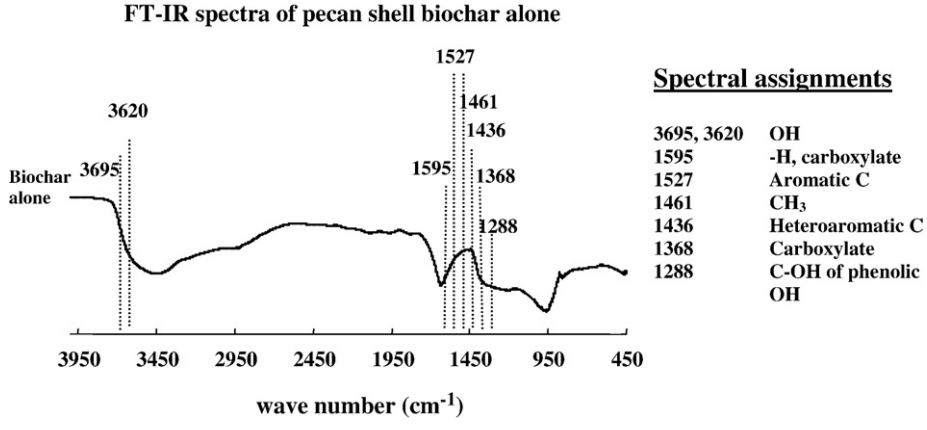

Fig. 1. FT-IR spectral scan of pecan-shell biochar (alone).

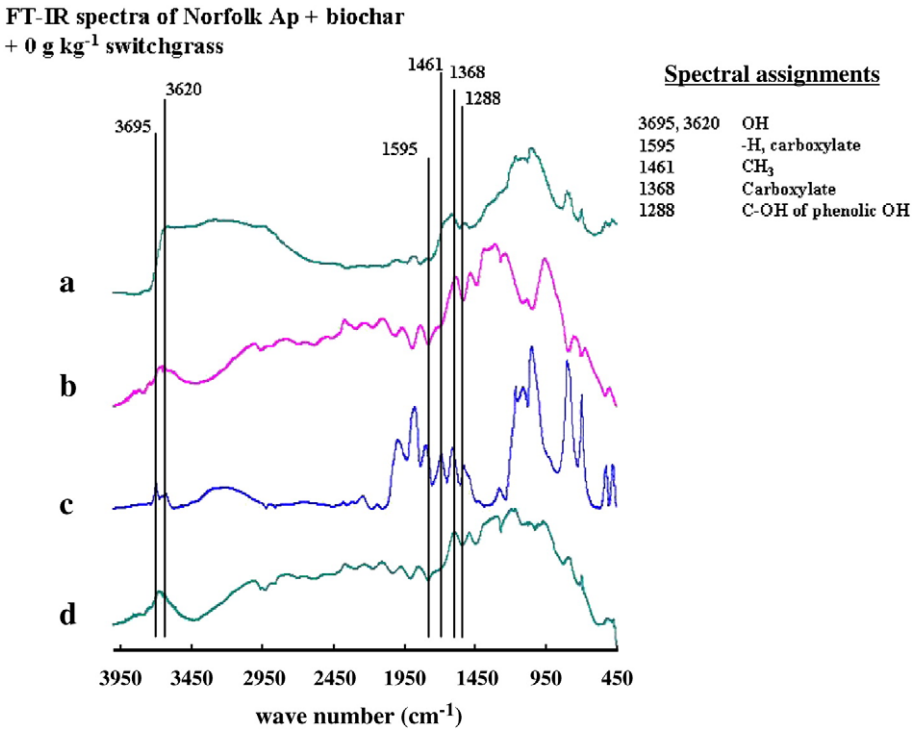

Fig. 2. FT-IR spectral scan of Norfolk Ap soil after 67 days of incubation with 0 mg kg^{-1} switchgrass and biochar at: a) 0 g kg^{-1}, b) 5 g kg^{-1}, c) 10 g kg^{-1}, and d) 20 g kg^{-1}.

characteristics for biochar in soil (Sombroek et al., 2003; Liang et al., 2006).

Biochar application to the Norfolk Ap had mixed effects on the TN contents probably due to its inherently low TN content (Table 2). High temperature pyrolysis (700 to 950 °C) will produce biochars with low total N contents (<10 g kg^{-1}; Antal and Grønli, 2003; Bourke et al., 2007) because N in amines, amino acids, and amino-sugars are volatilized and any remaining N will occur in recalcitrant heterocyclic compounds (Koutcheiko et al., 2007).

Relationships were complex between mineralization of indigenous and exogenous OC compounds in this short-term experiment. Mineralization of indigenous OC compounds was preferred because there were no significant differences in cumulative CO_2 production with and without switchgrass (in 0 biochar treatments) on incubation days 25 and 67 (Table 3). This is a puzzling situation because others have noted a positive priming effect of indigenous SOC compounds after incorporation of plant residues (Liang et al., 1999; Kuzyakov et al., 2000). It may be possible that the microbes initially mineralized

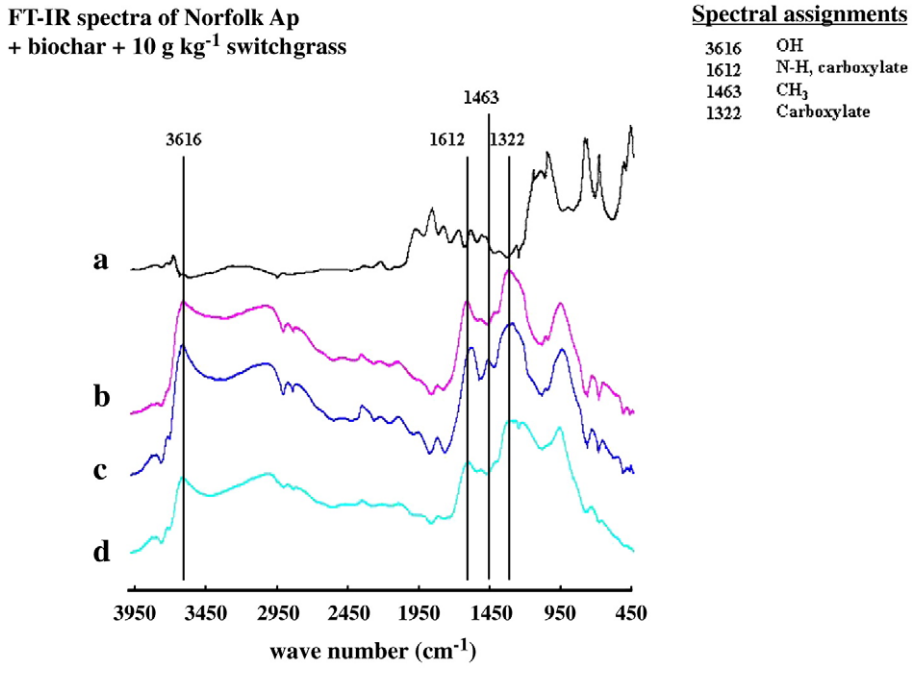

Fig. 3. FT-IR spectral scan of Norfolk Ap soil after 67 days of incubation with 10 mg kg^{-1} switchgrass and biochar at: a) 0 g kg^{-1}, b) 5 g kg^{-1}, c) 10 g kg^{-1}, and d) 20 g kg^{-1}.

the easily decomposable substrates in the switchgrass. After 25 days of incubation, however, the C mineralization fluxes were similar between soils with and without switchgrass resulting in comparable cumulative CO_2 fluxes totals.

Once biochar was added to soil with switchgrass, however, there was a significant increase in mean CO_2 flux measurements implying that biochar stimulated switchgrass mineralization. Similarly, accelerated decomposition of forest humus by charcoal addition was also reported by Wardle et al. (2008). Biochar appears to have shifted the microbe's mineralization preferences from indigenous SOC to the exogenous switchgrass. This is apparent because adding biochar to soil without switchgrass did not increase cumulative CO_2 flux values.

The FT-IR spectral analysis corroborated that biochar stimulated switchgrass mineralization and modification to its structures because peaks at 1612 and 1322 cm^{-1} due to carboxylate groups (Fig. 3). Although biochar in the presence of switchgrass stimulated its decomposition, more biochar additions did not correspondingly increase cumulative CO_2 flux values (Table 3). Using FT-IR showed that biochar mineralization was weakly distinguishable; some of the carboxylate and phenolic peak signals could just as well have been due to the biochar adsorption of soluble DOC compounds containing these functional groups.

The actual amount of OC mineralization in this study was not quantified; however, the similar SOC contents measured in treatments between 0 and 67 incubation days corroborates that this pecan biochar was resistant to mineralization. This biochars recalcitrant nature was related to its high aromatic C content (58%, Novak et al., 2009a), and its low attrition character. These characteristics may also explain the nearly similar leachate DOC concentrations from all treatments measured on day 67 (Table 3). When biochars are used to increase soils C sequestration capacity, they probably should have these two characteristics. Possession of these characteristics will probably also influence the longevity of biochars.

Besides stimulating CO_2 production, this biochar had an interesting influence on the soil N cycle. No NO_3–N was present in leachate on day 25 for the Norfolk Ap soil treated with biochar and switchgrass. This concentration decline may be the result of microbes assimilating N as NO_3–N in return for switchgrass mineralization and/or by N attraction to the biochar. Nitrogen immobilization occurred because the switchgrass had a wide C:N ratio that will cause soil microbes to scavenge N to offset OC assimilation into their tissue. The C:N ratio of the switchgrass was 73:1, microbes will immobilize N into their tissue when the residue has a C:N ratio of greater than 32:1 (Thompson and Troeh, 1978; Kuzyakov et al., 2000). Both NO_3–N and NH_4–N can be immobilized by soil microorganism; there must have been a preference for NO_3–N immobilization because NH_4–N was still measureable by day 25. On the other hand N sorption by biochar is plausible through electrostatic attraction of $NH4^+$ to the biochars negatively charged functional groups. Sorption of $NO3^-$ by biochar, on the other hand, should be minimal because of electrostatic repellency. It appears, however, there is some unexplained mechanism was causing NO_3–N concentrations declines with increasing biochar application. By day 67, however, some of the immobilized N was later mineralized resulting in a small amount of NO_3–N leaching (Table 4). By this same time, all NH_4–N was nitrified, immobilized, leached, or adsorbed to soil surfaces.

Biochar application to the Norfolk Ap soil (without switchgrass) also caused N immobilization. Lower soil N availability after biochar applications has been reported in a Brazilian Anthrosol (Lehmann et al., 2003) and a Xanthic Ferralsol (Steiner et al., 2007). These researchers viewed N immobilized after biochar application as a benefit because soil N leaching was reduced. Similarly, this may also be a soil and water quality benefit in the USA Southeastern Coastal Plain region where high rainfall and well-drained, coarse-textured soils favors N leaching (Zotarelli et al., 2007).

Our study revealed several interesting facts about the interactive effects of biochar on the C and N cycles. This pecan biochar did increase the Norfolk Ap SOC content and was resistant to microbial breakdown. A positive consequence of biochar application is a C sequestration increase in sandy soils that should last for awhile. On the negative side, this biochar stimulated mineralization of switchgrass and short-term N immobilization. Sequestered N in sandy soils may cause temporary plant available N issues; however, the N will eventually be plant available after mineralization has occurred. Biochars can restore fertility of degraded soils; however, to avoid N availability problems, it should probably not be applied when organic residues with wide C:N ratios are readily available for microbial mineralization.

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