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ENVIRONMENTAL BENEFITS OF BIOCHAR

Extent of Pyrolysis Impacts on Fast Pyrolysis Biochar Properties

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A potential concern about the use of fast pyrolysis rather than slow pyrolysis biochars as soil amendments is that they may contain high levels of bioavailable C due to short particle residence times in the reactors, which could reduce the stability of biochar C and cause nutrient immobilization in soils. To investigate this concern, three corn (*Zea mays* L.) stover fast pyrolysis biochars prepared using different reactor conditions were chemically and physically characterized to determine their extent of pyrolysis. These biochars were also incubated in soil to assess their impact on soil CO_2 emissions, nutrient availability, microorganism population growth, and water retention capacity. Elemental analysis and quantitative solid-state ^{13}C nuclear magnetic resonance spectroscopy showed variation in O functional groups (associated primarily with carbohydrates) and aromatic C, which could be used to define extent of pyrolysis. A 24-wk incubation performed using a sandy soil amended with 0.5 wt% of corn stover biochar showed a small but significant decrease in soil CO_2 emissions and a decrease in the bacteria:fungi ratios with extent of pyrolysis. Relative to the control soil, biochar-amended soils had small increases in CO_2 emissions and extractable nutrients, but similar microorganism populations, extractable NO_3 levels, and water retention capacities. Corn stover amendments, by contrast, significantly increased soil CO_2 emissions and microbial populations, and reduced extractable NO_3. These results indicate that C in fast pyrolysis biochar is stable in soil environments and will not appreciably contribute to nutrient immobilization.

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Biochar is attracting considerable attention as a potential soil amendment for enhancing soil quality (Glaser et al., 2002) and as a means of sequestering photosynthetically fixed C in soils for hundreds or thousands of years (Woolf et al., 2010). Most of the research on the use of biochar as a soil amendment has been conducted using biochar produced by slow pyrolysis. The economic viability of slow pyrolysis is questionable, however, because only relatively low-value heat and electrical power are potential coproducts of slow pyrolysis (Brown et al., 2011). Fast pyrolysis, by contrast, is optimized for the production of bio-oil, which can be upgraded to high-value liquid transportation fuels or processed into a variety of organic chemicals. Fast pyrolysis processes typically produce 10 to 30% biochars on a feedstock weight basis; these biochars contain 15 to 40% of the C and nearly all of the mineral (ash) content of the original biomass. Use of the biochar coproduct of bioenergy production as a soil amendment has been proposed as a means of enhancing soil quality, sequestering C, and returning nutrients to soils, thereby making the harvesting of biomass for bioenergy production more sustainable (Laird, 2008). Before fast pyrolysis biochars are applied to soils, however, more information about their properties in relation to slow pyrolysis biochars is desirable.

Biochar properties and soil responses vary considerably with biochar feedstock and processing conditions. For example, in a study of the impacts of 16 different biochars on greenhouse gas emissions from three different soils, Spokas and Reicosky (2009) found that soil response was both biochar and soil dependent, although they were not able to specifically correlate greenhouse gas flux with feedstock type, pyrolysis temperature, composition, or surface area of the biochars available. Two previous studies in our lab have shown that biochars from fast pyrolysis and gasification of switchgrass (*Panicum virgatum* L.) and corn (*Zea mays* L.) stover have very different properties compared to biochars derived from slow pyrolysis of hardwoods (Brewer et al., 2009, 2011).

One biochar property of interest is C bioavailability. Biochars that contain high levels of bioavailable C could decrease crop yields due to N immobilization (Deenik et al., 2010; Gundale and DeLuca, 2007; Novak et al., 2010)

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Abbreviations: CP, cross polarization; DP, direct polarization; MAS, magic angle spinning; NMR, nuclear magnetic resonance spectroscopy.

and would be less effective for C sequestration (Baldock and Smernik, 2002; Joseph et al., 2009; Lehmann et al., 2009). For slow pyrolysis biochars, where variation in temperature within particles during pyrolysis is small due to the long particle residence times, the highest temperature reached during pyrolysis is believed to play a key role in the chemistry and bioavailability of biochar C (Keiluweit et al., 2010; Zimmerman, 2010). In a study of the bioavailability of C in red pine (*Pinus resinosa* Aiton) biochars, Baldock and Smernik (2002) found that heating the wood above 200°C in a limited oxygen environment decreased the C mineralization rate by an order of magnitude. For fast pyrolysis biochars, heat transfer rates and particle residence times may be as important as peak reactor temperature. Heat transfer limitations may cause the outer part of the particles to reach a higher temperature than the core and create biochars that are fully carbonized only on the outside (Bruun et al., 2011; Di Blasi, 2002). Hence, material in the core of fast pyrolysis biochar particles may be dominated by torrefied biopolymers rather than the condensed aromatic C structures believed to stabilize biochar C against microbial degradation in soils (Lehmann et al., 2009).

Information on the soil application effects and stability of fast pyrolysis biochars is currently very limited. A preliminary 3-yr field experiment by BlueLeaf Inc. (Drummondville, QC, Canada) found that soybean [*Glycine max* (L.) Merr.] and forage plant biomass yields were higher from a single plot amended with approximately 3.9 Mg ha^{-1} hardwood waste CQuest fast pyrolysis biochar (Dynamotive Energy Systems Corporation, West Lorne, ON, Canada) than from an adjacent unamended plot (Husk and Major, personal communication, 2011). No indicators of N immobilization were reported. A biochar characterization and soil incubation study using wheat (*Triticum aestivum* L.) straw biochars made at different temperatures by a fast pyrolysis centrifuge reactor found labile carbohydrates (unreacted cellulose and hemicellulose) in the biochars made at lower reactor temperatures (Bruun et al., 2011). Biochar C losses, as measured by soil surface CO_2 fluxes from biochar-amended soils, were relatively high (3–12%) after 115 d and were found to be inversely related to pyrolysis reactor temperature and biochar labile carbohydrate content. The authors concluded that the relative ease of degradability of the fast pyrolysis biochars compared to slow pyrolysis biochars made at similar temperatures (475–575°C) was due to the specific design of the fast pyrolyzer and the short residence times (Bruun et al., 2011).

The overall goal of this study was to fit fast pyrolysis biochars into a larger biochar property framework using *extent of pyrolysis*, analogous to the already widely used *peak reactor temperature* for slow pyrolysis biochars. The specific objectives of this study were (i) to evaluate chemical and physical properties of corn stover fast pyrolysis biochars that had been noticeably affected by reactor conditions, and (ii) to quantify the impact of these biochars on CO_2 emissions, extractable soil nutrients, water retention, and microbial populations of an amended sandy soil. We hypothesized that (i) the extent of pyrolysis for fast pyrolysis biochars depends on reactor heating rate and particle residence times in addition to reactor temperature; (ii) fast pyrolysis biochar with a low extent of pyrolysis (as determined by chemical properties) contain bioavailable C that will, when used as a soil amendment, increase CO_2 emissions, microorganism population growth, and N immobilization relative to biochar with a high extent of pyrolysis; and (iii) amending a sandy soil with fast pyrolysis biochar will increase extractable soil nutrients and water retention capacity.

Materials and Methods

Biochar Production

Corn stover was harvested locally (Story County, IA), dried to <10% moisture, and ground using a hammer mill to pass a 6-mm (1/4-in) sieve. Three corn stover fast pyrolysis biochars were derived from this feedstock and produced on reactors at Iowa State University's Center for Sustainable Environmental Technologies. The pyrolysis reaction parameters are listed in Table 1. The reaction temperatures refer to the reactor settings rather than the temperatures reached by the particles during pyrolysis; this is especially important for Biochars 1 and 2, which were produced under conditions that did not allow for sufficient heat transfer time on a free-fall fast pyrolyzer (Ellens, 2009). Biochar 3 was produced in a fluidized-bed fast pyrolyzer with higher heat transfer rates (Pollard, 2009).

Biochar Characterization

Biochar characterization followed methods previously described (Brewer et al., 2009). Briefly, moisture, volatiles, fixed C, and ash content of the biochars were determined by a standard proximate (thermogravimetric) analysis method, ASTM D1762-84 (ASTM, 2007). Elemental analysis was performed using TRUSPEC-CHN and TRUSPEC-S analyzers (LECO Corporation, St. Joseph, MI). Oxygen content was determined by difference. Surface area (BET) was estimated by nitrogen gas sorption analysis at 77 K (NOVA 4200e, Quantachrome Instruments, Boynton Beach, FL). Particle density was measured by helium pycnometer (Pentapycnometer, Quantachrome Instruments, Boynton Beach, FL).

Solid-state ^{13}C nuclear magnetic resonance spectroscopy (NMR) experiments were performed on a Bruker DSX400 spectrometer (Bruker Biospin, Karlsruhe, Germany) at 100 MHz for ^{13}C and 400 MHz for ^{1}H. Qualitative corn stover and biochar spectra were obtained using ^{13}C cross polarization magic angle spinning with total suppression of spinning sidebands (CP/MAS/TOSS); samples were analyzed in 7-mm MAS rotors at a spinning speed of 7 kHz with 0.5-s recycle delay, 4-μs ^{1}H 90° pulse length, and 1-ms CP contact time. Quantitative biochar spectra were obtained using ^{13}C direct polarization (Bloch decay) magic angle spinning (DP/MAS)

Table 1. Fast pyrolysis reaction conditions and char properties of the corn stover biochars.

Reaction condition	Biochar no.		
	1	2	3
Reactor configuration	Free fall	Free fall	Fluidized bed
Reactor temperature (°C)†	500	600	500
Feed rate (kg h^{-1})	0.5	0.5	5
Feedstock particle size (μm)	500	500	6000

† Reactor temperature is not necessarily the temperature reached by the chars during pyrolysis; this is especially important for Biochars 1 and 2.

NMR in 4-mm MAS rotors at a spinning speed of 14 kHz with 75-s recycle delay, 4.5-μs 90° ^{13}C pulse length, and a Hahn echo to avoid baseline distortions (Mao and Schmidt-Rohr, 2004). A spectrum with a longer recycle delay (280 s) showed no meaningful intensity increase for any of the main peaks, proving that the magnetization was fully relaxed after 75 s. To acquire the spectra of the nonprotonated C fraction, DP/MAS with recoupled ^{1}H–^{13}C dipolar dephasing was used (68-μs dephasing time) (Mao and Schmidt-Rohr, 2004).

Soil Incubation

The soil used was the A horizon of a Sparta (sandy, mixed, mesic Entic Hapludoll) loamy fine sand (87.6% sand, 8.7% silt, 3.7% clay), collected on 10 Sept. 2009 from a hill (9–14% slope) near Ames, IA (41°59′39.24″ N, 93°33′28.59″ W). The soil was passed through a 2-mm sieve and visible root biomass was removed by hand. Soil moisture was 4 wt% on an oven-dry basis; soil moisture measured by pressure plate (Richards and Ogata, 1961) at −33 kPa soil water matric potential was 7 wt%.

Incubations were performed in glass, pint-size (0.47 L) canning jars with sealable lids. To each jar was added 100 g of 110°C dry-weight-equivalent soil, 0.5 g of oven-dry (110°C) corn stover or biochar amendment (approximately 11 Mg ha^{-1}). Sterile nutrient solution (6.0 mL) containing $(NH_4)_2SO_4$ (5.5×10^{-4} mol L^{-1}) and KH_2PO_4 (5.5×10^{-5} mol L^{-1}) was also added so as to achieve a soil moisture level of 10 wt% on an oven-dry basis, a maximum C-to-N ratio of 30:1 (assuming <40% C content in the amendments) and an N:P ratio of 10:1. The control received the nutrient solution but no amendment. There were nine replicates for each of the five treatments (Biochar 1, Biochar 2, Biochar 3, stover, and control) and a total of 45 jars. Samples were incubated in the dark at 23°C for 24 wk. At 8 wk, three replicate jars from each treatment were destructively sampled for microbial population and soil property analyses; the incubation was then continued with the remaining six jars for each treatment. Evolved CO_2 was trapped using a vial containing 30 mL of standardized NaOH (1 mol L^{-1}) solution in each of the sealed jars. The amount of CO_2 evolved was measured by first precipitating any dissolved CO_2 with 25 mL of $BaCl_2$ (2 mol L^{-1}), then titrating the solution to the phenolphthalein endpoint with standardized HCl (1 mol L^{-1}). Jars were left open during the titration to ensure sufficient exchange of air. Before resealing, a fresh aliquot of NaOH was added to the vial in each jar and the soil moisture readjusted to 10% by addition of distilled water.

Soil Testing

Soil pH was measured at a 1:5 soil-to-water ratio. Soil water retention was measured at −33 kPa and −500 kPa soil water matric potentials using the pressure plate method to estimate plant-available water. All other soil analyses were performed using standard soil methods (Bray P, ammonium acetate, and Mehlich III extractable cations, total N and total C by combustion, and inorganic N by colorimetry) by the Soil and Plant Analysis Laboratory (Iowa State University, Ames).

Enumeration of Microbial Populations

Microbial populations were estimated by a pour plate method following generally accepted recovery and enumeration practices (Zuberer, 1994). Soil dilutions were made using sterile physiological saline solution (0.85% NaCl) and manual shaking (20 repetitions) for dispersion. Fungi were cultured at three dilutions (10^{-3}, 10^{-4}, and 10^{-5}) with two replicates each on Martin's medium, a peptone dextrose agar containing rose bengal (30 mg L^{-1}) and streptomycin (30 μg L^{-1}) to limit bacterial growth (Johnson et al., 1959). Bacteria (including actinomycetes) were cultured at three dilutions (10^{-4}, 10^{-5}, 10^{-6}) with two replicates each on a 1/10-strength tryptic soy agar (Difco, BD, Sparks, MD). Plates containing 20 to 200 colonies were counted after 9 d of incubation at 23°C.

Statistics

The experimental setup followed a completely randomized design. Statistical significance was determined at a 95% confidence level ($p < 0.05$) using single-factor ANOVA and Tukey's honest significant difference test.

Results

Biochar Physical and Chemical Properties

The results of the corn stover biochar characterizations are shown in Table 2. Note the low C content and high ash content of the biochars; this is due to the high mineral (especially relatively inert silica) content of corn stover and the partitioning of most of the C from the feedstock into the liquid bio-oil fraction during fast pyrolysis. Molar H/C and O/C ratios of the amendments decreased (see Fig. 1) and fixed C/volatiles ratios (see Table 2) increased in the order of stover, Biochar 1, Biochar 2, and Biochar 3. This order was used as the amendments' relative extent of pyrolysis, from least pyrolyzed to most pyrolyzed. All BET surface areas were very low, <9 m^2 g^{-1} (Table 2).

The qualitative CP/TOSS NMR spectra in Fig. 2 clearly show the transition from C associated with cellulose and lignin present in the biomass to aromatic C associated with biochar as the extent of pyrolysis increases. Biochar 1 in particular has a large ~75-ppm peak indicative of O-alkyl-C; its small width and the other sharp peaks near 106, 88, 85, and 65 ppm show that residual cellulose is present. This indicates that a part of Biochar 1, probably at the core of the particles, had not undergone sufficient thermal transformation.

The quantitative DP/MAS NMR spectra for all C (thick lines) and nonprotonated C (thin lines) in the biochars are shown in Fig. 3. All three biochars contained measurable amounts of nonprotonated aromatic C as part of the overall aromatic C fraction, indicating the presence of condensed aromatic ring structures (peak at ~127 ppm in the thin-line DP/MAS with recoupled ^{1}H–^{13}C dipolar dephasing spectra). Carbon composition and aromaticity of the biochars by spectral integration are detailed in Table 3. The composition and aromaticities of the biochars were consistent with their relative extents of pyrolysis: Biochar 1 contained the most aliphatic and oxygenated C functional groups while Biochar 3 contained the most aromatic C and highest fraction of nonprotonated C. The composition of Biochar 2 was intermediate.

Table 2. Composition and physical properties of corn stover and corn stover fast pyrolysis biochars (n = 3 for proximate and CHNS analyses; surface area and particle density were single measurements). Proximate analysis data reported on a wet basis; CHNOS data are on a dry basis.

Property	Corn stover	Biochar no.		
		1	2	3
Moisture (g kg^{-1})	37	25	18	17
Volatiles (g kg^{-1})	726	262	171	138
Fixed C (g kg^{-1})	102	249	254	252
Ash (g kg^{-1})	135	464	557	593
Dry ash (g kg^{-1})	140	476	567	603
C (g kg^{-1})	405	349	314	295
H (g kg^{-1})	61	29	20	16
N (g kg^{-1})	7	7	6	6
S (g kg^{-1})	ND†	0.6	0.3	0.2
O (g kg^{-1} by difference)	387	139	92	79
H/C molar ratio	1.81	0.99	0.77	0.63
O/C molar ratio	0.72	0.30	0.22	0.20
C/N molar ratio	68	51	54	46
Fixed C/volatiles	0.14	0.95	1.49	1.83
BET surface area (m^2 g^{-1})	ND	4.5	3.3	8.5
Particle density (g cm^{-3})	ND	1.78	1.88	2.06

† ND, not determined.

Carbon Dioxide Evolution from Amended Soils

The rates of CO_2 evolution (in mg CO_2–C per 100 g soil per day) from the soils are shown in Fig. 4. For all treatments, the amount of microbial respiration was greatest in the first week and decreased thereafter. Evolution rate differences between all of the treatments were statistically significant in the first week. Rates of CO_2 evolution decreased with extent of pyrolysis as defined by amendment C characteristics: stover > Biochar 1 > Biochar 2 > Biochar 3 > control. This relationship continued in the weeks that followed (with various degrees of statistical significance). An analytic error when measuring trapped CO_2 for Biochar 2–amended soils on Day 56 resulted in that data point being excluded.

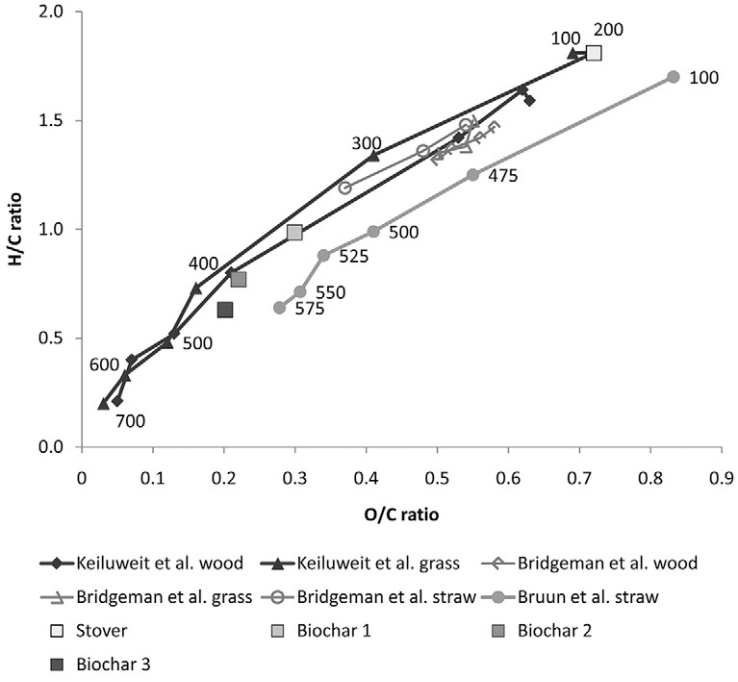

Fig. 1. Van Krevelen plot of corn stover and corn stover fast pyrolysis biochars used in this study, as well as pine wood and fescue grass slow pyrolysis biochars made at different temperatures (Keiluweit et al., 2010), willow wood, reed canary grass, and wheat straw torrefaction biochars made over 230 to 290°C temperature range (Bridgeman et al., 2008), and wheat straw centrifuge reactor fast pyrolysis biochars made at different temperatures (Bruun et al., 2011). Numbers listed are reactor temperatures (°C).

Soil Chemical Properties

Soil chemical properties of replicates destructively sampled on Day 56 are shown in Table 4. No significant differences in organic matter, total N, Na, Mg, or Ca contents were observed in the amended soils. All amendments slightly increased soil pH and decreased plant-available NO_3–N and NH_4–N, though only the decreases in NO_3–N in the stover, and the NH_4–N in the Biochar 1 and Biochar 2 were statistically significant. Bray P increased with all three biochar amendments. Available K increased significantly for all amendments but more with the biochars than with the corn stover. Finally, Mehlich III–extractable Al increased with stover and Biochar 3, extractable Fe increased for all biochars, and extractable Mn increased for all amendments relative to the controls.

Soil Water Retention Capacity

Water retention capacities of the control and amended soils are shown in Fig. 5. At the low tension (−33 kPa), none of the amendments significantly increased the soil water retention. Under drier conditions (−500-kPa tension), most of the amended soils had slightly higher soil moisture levels than the control; however, only the stover-amended soil was significantly higher than the control (8% relatively).

Enumeration of Soil Microbial Populations

The estimates of soil microbial populations based on dilution plate counts are listed in Table 5. The soil amended with the corn stover had the highest populations of both fungi and bacteria. Fungi populations in the biochar-amended soils tended to increase with extent of pyrolysis

but were not significantly different from those in the control. Populations of bacteria tended to decrease with extent of pyrolysis; however, only the population in the Biochar 3–amended soil was significantly lower from the control soil. Population ratios of bacteria to fungi were high in the control, low in the corn stover–amended soil, and decreased with extent of pyrolysis in the biochar-amended soils.

Discussion

Extent of Pyrolysis and Apparent Pyrolysis Temperature

Fast pyrolysis biochars can best be compared to other biochars based on their properties and effects when amended to soils. For practical discussions, however, it may be beneficial to define apparent slow pyrolysis temperatures for fast pyrolysis biochars such that their extent of pyrolysis might be more quickly conveyed. Such apparent slow pyrolysis temperatures can be estimated for the biochars in this study using several temperature–property relationships described in the literature. McBeath and Smernik (2009) related the degree of aromatic condensation with increasing pyrolysis temperatures for a set of phalaris grass (*Phalaris aquatica* L.) straw biochars using ^{13}C NMR spectra. The straw biochar made at 250°C has larger alkyl and oxygenated C peaks than those of Biochar 1, suggesting that Biochar 1 achieved a temperature higher than 250°C. The spectrum of the straw char made at 450°C closely resembles that of Biochar 3. Using these spectra, the temperatures reached by the biochars in this study are estimated to be between 250 and 450°C. A nonspectroscopic method for estimating the extent of pyrolysis compares the relative amounts of volatile and fixed C as determined by proximate or thermogravimetric analysis. Biochars with higher fixed C/volatiles (FC/V) ratios reached higher slow pyrolysis temperatures and are considered more completely pyrolyzed (Deenik et al., 2010; Zimmerman et al., 2011). The FC/V values from pine (*Pinus ponderosa* Douglas) wood and fescue grass (*Festuca arundinacea* Schreb.) slow pyrolysis biochars used by Keiluweit et al. (2010) range from 0.28 to 14.6 for slow pyrolysis reaction temperatures ranging from 100 to 700°C, respectively. Using the fescue grass biochar data, the analogous slow pyrolysis temperatures for Biochars 1, 2, and 3 are estimated to be 350, 375, and 400°C, respectively. Another nonspectroscopic method for estimating the extent of pyrolysis is evaluation of biochar O/C and H/C molar ratios, most often plotted as a van Krevelen diagram. As the pyrolysis reaction progresses, the removal of H_2O, CO_2, and other small O- and H-containing molecules shifts the composition of biochars toward the origin on a van Krevelen plot. Data for slow pyrolysis/torrefaction biochars produced by pyrolysis of fescue grass and pine wood (Keiluweit et al., 2010) and reed canary grass (*Phalaris arundinacea* L.), wheat straw, and willow (*Salix viminalis* L.) (Bridgeman et al., 2008) are shown in Fig. 1. Biochars 1, 2, and 3 closely follow the pattern of the Keiluweit et al. (2010) data and have apparent slow pyrolysis temperatures of 350, 400, and 450°C.

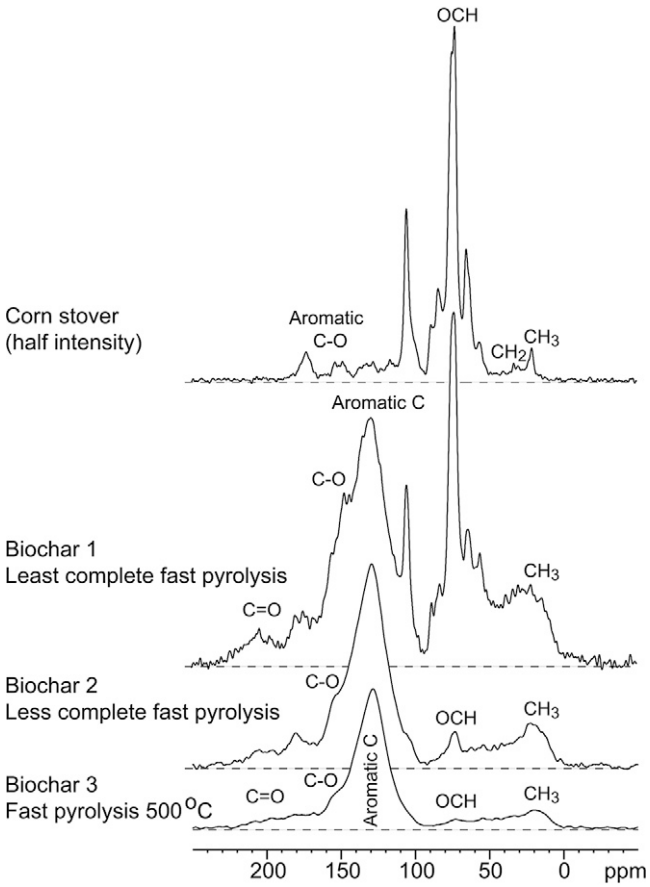

Fig. 2. Qualitative carbon spectra of corn stover and corn stover biochars by solid-state ^{13}C cross-polarization magic angle spinning with total suppression of spinning sidebands nuclear magnetic resonance spectroscopy. OCH = alcohol and ether moieties.

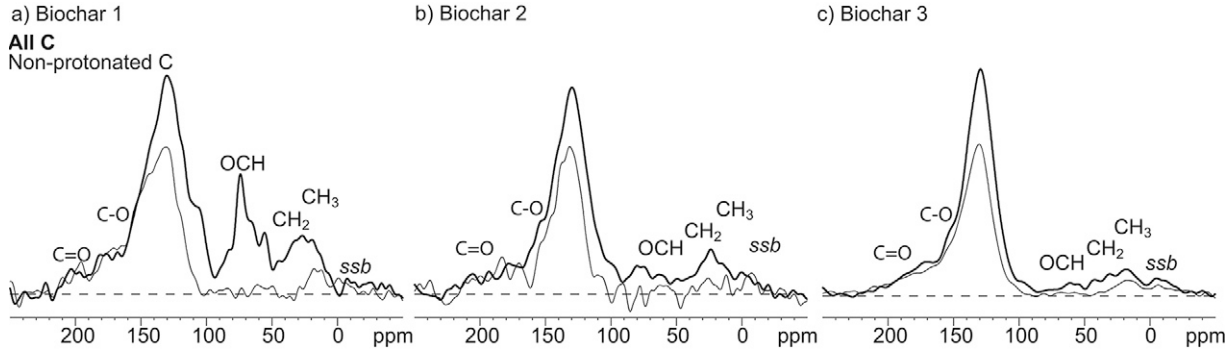

Fig. 3. Quantitative solid-state ^{13}C nuclear magnetic resonance spectra of corn stover biochars, obtained with direct polarization under 14-kHz magic angle spinning: (a) Biochar 1 (lowest extent of pyrolysis), (b) Biochar 2 (intermediate extent of pyrolysis), (c) Biochar 3, fast pyrolysis at 500°C (highest extent of pyrolysis). Thick-line spectra: all C; corresponding thin-line spectra: nonprotonated C and CH_3. *ssb* = spinning side band.

Table 3. Composition and aromaticity of C fraction in biochars by quantitative solid-state ^{13}C direct polarization magic angle spinning\nuclear magnetic resonance spectroscopy. Values are percentage of total ^{13}C signal. C_{nonpro} = nonprotonated aromatic C. Integration included primary and secondary aromatic spinning side bands.

Moiety	Carbonyl		Aromatic			Alkyl			Aromaticity
	C=O	COO	$CO_{0.75}H_{0.5}$	C_{nonpro}	C-H	$HCO_{0.75}H_{0.5}$	$CH_{1.5}$	CH_3	
Range (ppm)	210–183	183–165	165–145	145–90		90–50	50–25	25–6	
Corn stover†	0	5	5	5	10	68	5	4	20
Biochar 1	4	5	11	30	18	19	7	6	59
Biochar 2	4	4	11	39	24	8	5	5	74
Biochar 3	3	5	12	44	25	3	4	4	81

† Fang et al. (2010).

A series of wheat straw fast pyrolysis biochars from Bruun et al. (2011) is also plotted in Fig. 1 (dry wheat straw data are represented as biochar made at a reactor temperature of 100°C). Compared to the Keiluweit et al. (2010) data, the apparent slow pyrolysis temperatures for these biochars are estimated to be 300 to 500°C, well below the actual reactor temperatures of 475 to 575°C. In general, fast pyrolysis biochars' apparent slow pyrolysis temperatures will be lower than their reactor temperatures, but the magnitude of this difference is dependent on the reactor's specific heat transfer rates and particle residence times.

Carbon Sequestration and Soil Respiration Rates

Differences in soil CO_2 emissions between the control and amended soils are commonly used to estimate C mineralization rates and the potential of amendments to enhance soil C sequestration. With respect to biochar, such studies can provide valuable insight into biochar's relative stability but have several drawbacks. Unless isotope labeling (Kuzyakov et al., 2009) or stable C isotopic analysis (i.e., using a succession of C_3–C_4 plants) are used (Smith et al., 2010; Zimmerman et al., 2011), it is generally not possible to distinguish CO_2 produced by the mineralization of biochar from CO_2 that comes from the mineralization of soil organic matter or organic residues in the soil. Furthermore, biochar has been reported to accelerate mineralization of soil organic matter (Wardle et al., 2008) and enhance stabilization of organic residues (Rogovska et al., 2011; Zimmerman et al., 2011). In this study, use of soil as the inoculation media meant that soil organic matter and mineral interactions were able to occur during the incubation but also that the source of the CO_2 could not be definitively identified. Even so, the increases in CO_2 emissions for biochar-amended soils relative to the control soil were much smaller than the increase in CO_2 emissions from the stover-amended soil, suggesting that even a low extent of pyrolysis is still highly effective for stabilizing corn stover C.

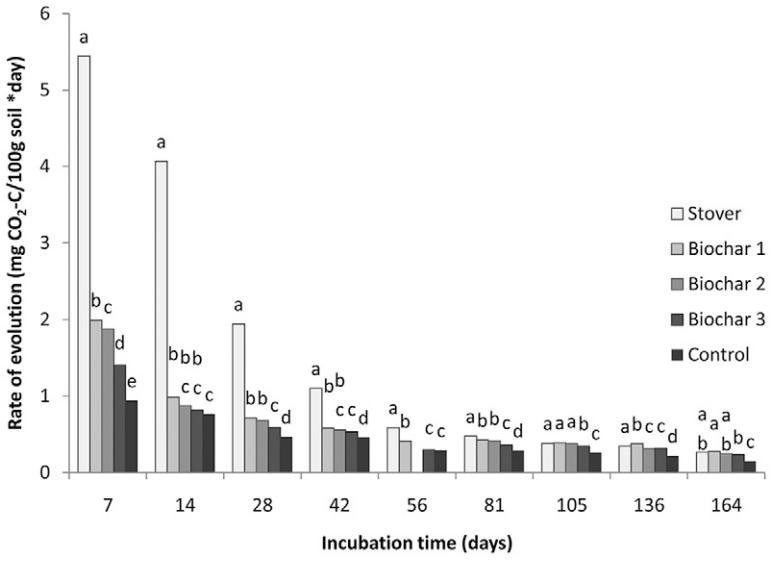

Fig. 4. Rate of CO_2 evolution from control and amended soils over 24-wk incubation. Rates measured on the same day that are marked with a different letter are significantly different ($p < 0.05$).

Changes in Extractable Plant Nutrients with Soil Amendments

The harvesting of agricultural residues for bioenergy production may deplete plant nutrients from soils. During pyrolysis, nearly all of the mineral nutrients in the biomass feedstock and about half of the N and S are concentrated in the biochar fraction (Laird et al., 2010). Use of biochar as a soil amendment returns those nutrients to the soil. Key questions, however, are whether the added nutrients are bioavailable and whether fast pyrolysis biochars bind or immobilize plant nutrients that are already in the soil. Here, extractable P, K, Fe, and Mn levels were higher for the biochar-amended soils than the control or stover-amended soils (Table 4), and no differences were observed for extractable bases (Ca, Mg, and Na). Nitrate levels were significantly lower in the stover-amended soils than any of the other soils, suggesting that the stover amendments induced N immobilization. Although the control soils had the highest NO_3 levels, they were not significantly different from the NO_3 levels in any of the three biochar-amended soils. Hence, we find evidence that at least some of the nutrients added with the biochar were bioavailable and no evidence of nutrient immobilization resulting from the fast pyrolysis biochar amendments. Most biochars are mild to moderate liming agents due to ash that is admixed with the condensed C in biochars. Here the soil pH increased by only 0.2 pH units for the biochar-amended soils relative to the control soil, so effects of pH on bioavailability of nutrients would be minimal.

Soil Water Retention Capacity

Stover amendments increase soil water retention relative to the control at −500 kPa matric potential but no effects of the biochar amendments on moisture retention were observed at either −33- or −500-kPa tension (Fig. 5). Laird et al. (2010) observed that biochar additions to a typical midwestern agricultural

Table 4. Soil properties of corn stover and biochar-amended soils after 8 wk of incubation. pH was measured in water (1:5 ratio). Base (K, Na, Mg, Ca) content was determined by ammonium acetate extraction; trace metal (Al, Fe, Mn) content was determined by Mehlich III extraction.

Soil treatment	Soil pH	Organic matter	Total N	NO_3–N	NH_4–N	Bray P	K	Na	Mg	Ca	Al	Fe	Mn
		g kg^{-1}		mg kg^{-1}									
Control	5.9 c†	17 a	1.268 a	84 a	3.7 a	37 b	96 d	20 a	119 a	1146 a	178 b	58 b	36 b
Stover	6.1 ab	19 a	1.087 a	62 b	3.3 a	34 b	117 c	23 a	127 a	1184 a	224 ab	60 b	39 a
Biochar 1	6.1 ab	18 a	1.205 a	81 a	2.7 b	45 a	160 a	21 a	137 a	1162 a	209 b	70 a	40 a
Biochar 2	6.0 bc	20 a	1.242 a	78 a	2.0 c	42 a	154 ab	21 a	132 a	1164 a	187 b	69 a	39 a
Biochar 3	6.1 a	19 a	1.145 a	76 a	3.3 a	41 a	140 b	22 a	138 a	1229 a	295 a	67 a	40 a

† Entries in a column followed by different letters are significantly different ($n = 3$, $p < 0.05$).

soil did not significantly affect water retention at −33 kPa or −1500 kPa, but significantly increased soil water retention for midrange matric potentials (−100- and −500-kPa tension). The observed increases in soil water retention, however, were generally for soils amended with higher surface area chars and at higher rates of 10 or 20 g biochar kg^{-1} soil. In this study, the amount of biochar amended may not have been high enough to produce a statistically significant effect on soil water retention.

Enumeration of Microbial Populations

Enumeration of microorganism populations by the dilution pour plate technique is widely used, but the technique is not without disadvantages. For example, not all microorganisms can be cultured, not all organisms survive or are detached from other organisms in the dilution process, use of a pour plate is inherently aerobic and automatically excludes obligate anaerobic organisms, and having enough organisms on a plate to achieve a statistically significant count can lead to competition between colonies for energy and nutrients (Zuberer, 1994). Furthermore, the high variability among replicate plate counts makes it difficult to detect significant differences in microbial populations. Here, the soils amended with corn stover contained significantly more organisms than the control soils while the biochar-amended soils had comparable microbial populations to those of the control soils (Table 5). We speculate that this was because corn stover supplied readily metabolized C whereas the C in the biochars was recalcitrant.

The apparent shift in microbial populations from bacteria to fungi with increasing extent of pyrolysis (see bacteria:fungi ratios in Table 5) could be the result of several factors and warrants further research. The fungi may be better adapted to survive on recalcitrant aromatic C in biochar. This possibility is supported by Warnock et al. (2007) who reported increases in mycorrhizal fungi activity with the addition of biochar to soil. Shifts in soil microbial population from biochar application need to be understood, as they may influence soil fertility due to changes in the availability of nutrients, rates of nutrient cycling, soil respiration, and plant health due to differences in populations of beneficial and/or pathogenic organisms (Khodadad et al., 2011).

Conclusions

Determination of the extent of pyrolysis by more than reactor temperature is needed to make meaningful comparisons between fast pyrolysis and slow pyrolysis biochars derived from a given feedstock. In this study, several biochar chemical properties were observed to describe the extent of pyrolysis for three fast pyrolysis biochars that are consistent with reactor heat transfer rates, particle residence times, and temperatures. Proximate analysis, elemental analysis, and NMR spectroscopy showed that aromatic C content increased with extent of pyrolysis while O, H, and C in functional groups associated with unreacted biomass (alcohols, ethers, carbonyls, and carboxyls) decreased. These trends in C composition were used to estimate an apparent slow pyrolysis temperature for fast pyrolysis biochars so that these biochars might more easily be compared to other biochars in the literature. Carbon dioxide evolution rates from amended soil increased for all amendments and were inversely related to extent of pyrolysis. Rates of CO_2 evolution and microorganism population growth of the biochar-amended soils, however, were much lower than those of the stover-amended soils and addition of biochars did not significantly decrease N availability at 8 wk. These results demonstrate that C in fast pyrolysis biochar is substantially more stable than C in fresh biomass and that any nutrient immobilization resulting from the use of fast pyrolysis biochars should be minimal. Finally, amending a sandy soil with fast pyrolysis biochar under the conditions used in this study does increase the availability of some soil nutrients, including K and P, but does not affect soil water holding capacity. Overall, the properties of fast pyrolysis biochars reaching a certain extent of pyrolysis show that, from a C stability perspective, these biochars should be safe for soil application, even if their short-term positive impacts on soil may be limited.

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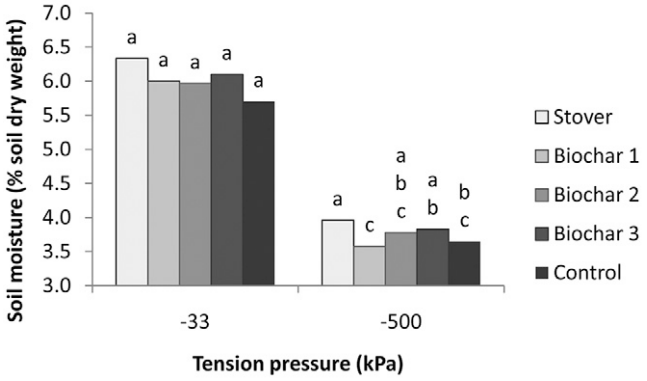

Fig. 5. Soil water retention of control and amended soils measured over matric potentials representing plant-available water. Columns labeled with different letters are significantly different ($p < 0.05$).

Table 5. Populations of microorganisms in control and amended soils based on pour plate counts (means ± SD, $n = 6$). Bacteria colony counts include actinomycetes colonies.

Soil treatment	Fungi	Bacteria	Bacteria:fungi ratio
	colonies g^{-1} soil		colonies $colony^{-1}$
Control	$(6.8 \pm 1.0) \times 10^4$ b†	$(9.9 \pm 1.9) \times 10^6$ b	148 ± 36 a
Stover	$(31.3 \pm 8.8) \times 10^4$ a	$(14.0 \pm 2.6) \times 10^6$ a	47 ± 16 c
Biochar 1	$(6.8 \pm 1.0) \times 10^4$ b	$(9.8 \pm 1.3) \times 10^6$ b	145 ± 30 a
Biochar 2	$(7.0 \pm 0.9) \times 10^4$ b	$(9.1 \pm 1.0) \times 10^6$ bc	130 ± 10 ab
Biochar 3	$(7.7 \pm 1.2) \times 10^4$ b	$(8.1 \pm 0.6) \times 10^6$ c	107 ± 11 b

† Data within a column followed by a different letter are significantly different ($p < 0.05$).

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References

ASTM. 2007. ASTM D1762-84 standard test method for chemical analysis of wood charcoal. ASTM Int., West Conshohocken, PA.

Baldock, J.A., and R.J. Smernik. 2002. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. Org. Geochem. 33:1093–1109. doi:10.1016/S0146-6380(02)00062-1

Brewer, C., R. Unger, K. Schmidt-Rohr, and R. Brown. 2011. Criteria to select biochars for field studies based on biochar chemical properties. BioEnergy Res. (in press). doi:10.1007/s12155-011-9133-7

Brewer, C.E., K. Schmidt-Rohr, J.A. Satrio, and R.C. Brown. 2009. Characterization of biochar from fast pyrolysis and gasification systems. Environ. Prog. Sustainable Energy 28:386–396. doi:10.1002/ep.10378

Bridgeman, T.G., J.M. Jones, I. Shield, and P.T. Williams. 2008. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. Fuel 87:844–856. doi:10.1016/j.fuel.2007.05.041

Brown, T.R., M.M. Wright, and R.C. Brown. 2011. Estimating profitability of two biochar production scenarios: Slow pyrolysis vs fast pyrolysis. Biofuels Bioprod. Biorefin. 5:54–68. doi:10.1002/bbb.254

Bruun, E.W., H. Hauggaard-Nielsen, N. Ibrahim, H. Egsgaard, P. Ambus, P.A. Jensen, and K. Dam-Johansen. 2011. Influence of fast pyrolysis temperature on biochar labile fraction and short-term carbon loss in a loamy soil. Biomass Bioenergy 35:1182–1189. doi:10.1016/j.biombioe.2010.12.008

Deenik, J.L., T. McClellan, U. Goro, M.J. Antal, and S. Campbell. 2010. Charcoal volatile matter content influences plant growth and soil nitrogen transformations. Soil Sci. Soc. Am. J. 74:1259–1270. doi:10.2136/sssaj2009.0115

Di Blasi, C. 2002. Modeling intra- and extra-particle processes of wood fast pyrolysis. AIChE J. 48:2386–2397. doi:10.1002/aic.690481028

Ellens, C.J. 2009. Design, optimization and evaluation of a free-fall biomass fast pyrolysis reactor and its products. M.S. thesis. Iowa State Univ., Ames. AAT 1473200.

Fang, X., T. Chua, K. Schmidt-Rohr, and M.L. Thompson. 2010. Quantitative ^{13}C NMR of whole and fractionated Iowa Mollisols for assessment of organic matter composition. Geochim. Cosmochim. Acta 74:584–598. doi:10.1016/j.gca.2009.10.008

Glaser, B., J. Lehmann, and W. Zech. 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal: A review. Biol. Fertil. Soils 35:219–230. doi:10.1007/s00374-002-0466-4

Gundale, M., and T. DeLuca. 2007. Charcoal effects on soil solution chemistry and growth of *Koeleria macrantha* in the ponderosa pine/Douglas-fir ecosystem. Biol. Fertil. Soils 43:303–311. doi:10.1007/s00374-006-0106-5

Johnson, L.F., E.A. Curl, J.H. Bond, and H.A. Fribourg. 1959. Methods for studying soil microfauna–plant disease relationships. Burgress, Minneapolis, MN.

Joseph, S., C. Peacocke, J. Lehmann, and P. Munroe. 2009. Developing a biochar classification and test methods. p. 107–126. *In* J. Lehmann and S. Joseph (ed.) Biochar for environmental management science and technology. Earthscan, London.

Keiluweit, M., P.S. Nico, M.G. Johnson, and M. Kleber. 2010. Dynamic molecular structure of plant biomass-derived black carbon (biochar). Environ. Sci. Technol. 44:1247–1253. doi:10.1021/es9031419

Khodadad, C.L.M., A.R. Zimmerman, S.J. Green, S. Uthandi, and J.S. Foster. 2011. Taxa-specific changes in soil microbial community composition induced by pyrogenic carbon amendments. Soil Biol. Biochem. 43:385–392. doi:10.1016/j.soilbio.2010.11.005

Kuzyakov, Y., I. Subbotina, H. Chen, I. Bogomolova, and X. Xu. 2009. Black carbon decomposition and incorporation into soil microbial biomass estimated by ^{14}C labeling. Soil Biol. Biochem. 41:210–219. doi:10.1016/j.soilbio.2008.10.016

Laird, D.A. 2008. The charcoal vision: A win–win–win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. Agron. J. 100:178–181.

Laird, D.A., P. Fleming, D.D. Davis, R. Horton, B. Wang, and D.L. Karlen. 2010. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. Geoderma 158:443–449. doi:10.1016/j.geoderma.2010.05.013

Lehmann, J., C.I. Czimczik, D.A. Laird, and S. Sohi. 2009. Stability of biochar in the soil. p. 183–206. *In* J. Lehmann and S. Joseph (ed.) Biochar for environmental management science and technology. Earthscan, London.

Mao, J.D., and K. Schmidt-Rohr. 2004. Accurate quantification of aromaticity and nonprotonated aromatic carbon fraction in natural organic matter by ^{13}C solid-state nuclear magnetic resonance. Environ. Sci. Technol. 38:2680–2684. doi:10.1021/es034770x

McBeath, A.V., and R.J. Smernik. 2009. Variation in the degree of aromatic condensation of chars. Org. Geochem. 40:1161–1168. doi:10.1016/j.orggeochem.2009.09.006

Novak, J.M., W.J. Busscher, D.W. Watts, D.A. Laird, M.A. Ahmedna, and M.A.S. Niandou. 2010. Short-term CO_2 mineralization after additions of biochar and switchgrass to a Typic Kandiudult. Geoderma 154:281–288. doi:10.1016/j.geoderma.2009.10.014

Pollard, A.J.S. 2009. Comparison of bio-oil produced in a fractionated bio-oil collection system. M.S. thesis. Iowa State Univ., Ames. AAT 1474690.

Richards, L.A., and G. Ogata. 1961. Psychrometric measurements of soil samples equilibrated on pressure membranes. Soil Sci. Soc. Am. J. 25:456–459. doi:10.2136/sssaj1961.03615995002500060012x

Rogovska, N.P., D.A. Laird, R.M. Cruse, P. Fleming, T. Parkin, and D. Meek. 2011. Impact of biochar on manure carbon stabilization and greenhouse gas emissions. Soil Sci. Soc. Am. J. 75:871–879. doi:10.2136/sssaj2010.0270

Smith, J.L., H.P. Collins, and V.L. Bailey. 2010. The effect of young biochar on soil respiration. Soil Biol. Biochem. 42:2345–2347. doi:10.1016/j.soilbio.2010.09.013

Spokas, K.A., and D.C. Reicosky. 2009. Impacts of sixteen different biochars on soil greenhouse gas production. Ann. Environ. Sci. 3:179–193.

Wardle, D.A., M.-C. Nilsson, and O. Zackrisson. 2008. Fire-derived charcoal causes loss of forest humus. Science 320:629. doi:10.1126/science.1154960

Warnock, D., J. Lehmann, T. Kuyper, and M. Rillig. 2007. Mycorrhizal responses to biochar in soil—Concepts and mechanisms. Plant Soil 300:9–20. doi:10.1007/s11104-007-9391-5

Woolf, D., J.E. Amonette, F.A. Street-Perrot, J. Lehmann, and S. Joseph. 2010. Sustainable biochar to mitigate global climate change. Nat. Commun. 1:56.

Zimmerman, A.R. 2010. Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). Environ. Sci. Technol. 44:1295–1301. doi:10.1021/es903140c

Zimmerman, A.R., B. Gao, and M.-Y. Ahn. 2011. Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. Soil Biol. Biochem. 43:1169–1179. doi:10.1016/j.soilbio.2011.02.005

Zuberer, D.A. 1994. Recovery and enumeration of viable bacteria. p. 119–142. *In* R.W. Weaver et al. (ed.) Methods of soil analysis. Part 2. Microbiological and biochemical properties. SSSA, Madison, WI.