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AGRONOMY AND SOILS

Manure-Derived Biochars for Use as a Phosphorus Fertilizer in Cotton Production

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ABSTRACT

Biochars made from animal manure feedstock appear to be a potential phosphorus (P) fertilizer source. Five different manure-derived biochars, pyrolyzed at two different temperatures (350 and 700 °C) were assessed for their potential as a P fertilizer for cotton (*Gossypium hirsutum* L.). A greenhouse study was conducted using a Uchee sand soil. Biochar was applied at rates that provided 40 mg P kg^{-1} soil. Four rates of calcium phosphate (0, 20, 40, and 60 mg P kg^{-1} soil) were included in the study. Cotton plants were allowed to grow to 60 days post-emergence at which point leaves and stems were harvested for physical and chemical analysis. The experiment was conducted twice. Results demonstrated that biochar worked as a P fertilizer and that feedstock choice combined with biochar processing temperature accounted for a majority of the differences among the 10 treatments tested. When applied at standard P fertilization rates, manure-derived biochars perform equally to calcium phosphate fertilizer.

Considerable efforts have been expended to recycle phosphorus (P) from agricultural wastes (Karunanithi et al., 2015; Morse et al., 1998), with the aim of using this recovered P to support sustainable agriculture. As a P recovery technology, pyrolysis of animal manures has particular promise due to its ability to couple nutrient densification in a land-applicable char, with energy-laden gas and liquid byproducts, as well as elimination of pathogens, antibiotic resistance genes, and contaminants of environmental concern (Ro et al., 2007). Pyrolysis of manure as compared to plant material provides a more nutrient-laden product (Novak et al., 2014).

Although pyrolysis requires a relatively dry feedstock such as poultry litter or beef feedlot manure (Cantrell et al., 2008), dewatering can render wastewater solids and other manure feedstock suitable for processing (Ro et al., 2010). These condensed, solid char, pyrolysis byproducts—biochar—have elicited interest for their potential use as soil conditioners, able to alter soil physical properties to enhance soil fertility (Novak et al., 2009, 2012). Likewise, biochar has the potential to improve soil biological and chemical properties (Ducey et al., 2013; Gul et al., 2015), and although a considerable portion of biochar research focuses on C sequestration (Lehmann et al., 2006), a growing body of literature has focused on the viability of biochar as a fertilizer (Ding et al., 2016). Pyrolysis preserves the majority of the P in a bioavailable form (Wang et al., 2012).

Physical and chemical properties of biochars are affected by the characteristics of the feedstock and the pyrolysis conditions, including temperature (Antal and Gronli, 2003; Gaskin et al.,2008; Singh et al., 2010). Previously, Cantrell et al (2012a) compared the effect of pyrolysis temperature (350 and 700 °C) on the characteristics of biochars produced from five different manure feedstock: beef, chicken, dairy, swine, and turkey. Subsequently, Hunt et al. (2013) showed that these biochars can serve as P fertilizer sources for ryegrass (*Lolium multiflorum* Lam.), though ryegrass biomass and nutrient concentrations were dependent on manure feedstock source and pyrolysis temperature. This report details the findings of using these biochars as a P fertilizer source for cotton. The objective study was to determine the effect of manure feedstock source and pyrolysis temperature on cotton growth and P uptake.

MATERIALS AND METHODS

Biochar Production. A total of 10 manure biochars were created from five manure feedstock (beef, dairy, poultry, swine, and turkey). The composition of each manure feedstock is described in detail in Cantrell et al. (2012a). Briefly, dairy manure was collected from the milking parlor holding area, whereas beef (feedlot)

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manure was collected from a commercial deep-bedded facility that used shredded corn stalks as bedding material. Separated swine solids were collected using a polyacrylamide separation process. Poultry and turkey litter was obtained from facilities using soft wood shavings as bedding material, both used approximately for 12 months. Each of the five manures was converted into biochar via slow pyrolysis in a nitrogen atmosphere for 120 min. equilibrium held at either 350 or 700 °C as described (Cantrell et al., 2012a; Cantrell and Martin, 2012a, b). Phosphorus content and application rate of the manure-derived biochars are shown in Table 1, and further characterization of both feedstocks and biochars are detailed in Cantrell et al. (2012a) and Hunt et al. (2013).

Table 1. Phosphorus characteristics of the 10 manure biochars utilized in this study[z]

Feedstock	Pyrolysis Temperature °C	P_2O_5 (%)	Application Rate[y] (% w/w)
Beef	**350**	**2.6**	**0.1533**
Chicken	**350**	**4.8**	**0.0841**
Dairy	**350**	**2.3**	**0.1736**
Swine	**350**	**8.9**	**0.0449**
Turkey	**350**	**6.0**	**0.0667**
Beef	**700**	**3.9**	**0.0993**
Chicken	**700**	**7.2**	**0.0559**
Dairy	**700**	**3.9**	**0.1034**
Swine	**700**	**13.5**	**0.0297**
Turkey	**700**	**8.4**	**0.0477**

[z] Full analysis previously reported in Cantrell et al., 2012.

[y] Biochar added based on a rate of 40 mg P_2O_5 per kg of soil.

Experimental Setup. Soil used was an Uchee sand (loamy, kaolinitic, thermic Arenic Kanhapludults), collected from a wooded area that recently had been harvested. Foreign material was removed using a 5-mm sieve. Due to low soil pH (4.5), lime was added to achieve a target pH of 6.0 prior to biochar amendment (1.99 g lime kg^{-1} soil). A total of 6.1 kg of soil was added to a 7.6-L pot (20-cm diameter; 24-cm height), and biochar was added at a rate of 40 mg of P_2O_5 kg^{-1} soil and mixed thoroughly into the entire profile. Biochar addition was calculated based on previous total P concentrations determined by Cantrell et al. (2012a). Four treatments of calcium phosphate (0, 20, 40, and 60 mg kg^{-1} P), which received no biochar additions, were included in the experiment. Both N (added as NH_4Cl at day 33 post-emergence) and K (added as KCl at day 0) were added to pots at a rate of 50 mg kg^{-1}. Experimental design was randomized complete block and there were four replicates. The entire experiment was conducted twice, with the start of each spaced 3 wks apart.

Cotton cultivar FM 1740 B2F (*Gossypium hirsutum* L.) was used in this study. A total of 10 seeds per pot were planted to a depth of 25.4 mm, and thinned to 3 plants per pot at 1 wk post-emergence. Each pot received a total of 0.64 cm of water per day using an automated drip irrigation system (Netafim USA, Fresno, CA). Plants were grown in a greenhouse with heater, cooling fans, and evaporative cooling systems set to activate at 18, 26, and 32 °C respectively. Plants received no supplemental lighting.

Soil and Plant Analysis. Plants were harvested at 60 d post-emergence and separated into leaf and stem fractions. Fresh leaf surfaces were measured using a LI-3100 Area Meter (LI-COR, Lincoln, NE), and all leaves were included in the study. Plant material was then dried at 60 °C for 72 h in an oven. To determine biomass, dry leaf and stem weights were recorded using an analytical balance (SI-4002, Denver Instruments, Bohemia, NY). Prior to further analysis, samples were ground using a cyclone mill. Leaf and stem samples were analyzed for P by digesting them as previously described (Peters et al., 2003) and then determining P concentration with an inductively coupled plasma-atomic emission spectrometer (ICP-AES; VistaPro, Varian, Inc., Walnut Creek, CA).

For soil P analysis, a 2.5-cm diameter soil core was collected from the entire profile of each pot. Each core was air dried for 1 wk, ground, and then sieved using a 2-mm sieve. After Mehlich 3 extraction (Mehlich, 1984), P in the extract was determined using ICP-AES.

Statistical Analysis. The data were analyzed in three ways. First, to determine the response of cotton to P rate on this soil, the calcium phosphate rates were analyzed separately using an analysis of variance using the GLM procedure of SAS (SAS Institute, Cary, NC). Sources of variation were experiment and P rate. Linear, quadratic, and cubic single degree of freedom contrasts were calculated to describe response curves. Second, to determine main and interaction effects of manure feedstock source and pyrolysis temperature, the remaining data were analyzed using analysis of variance using the GLM procedure of SAS with sources of variation being experiment, blocks within experiment, feedstock source, pyrolysis temperature, and interactions. When sources of variation from this analysis were significant ($p \leq 0.05$), means were separated using a protected least significant difference ($LSD_{0.05}$). Third, as stated earlier, the biochars were applied at a rate of 40 mg P kg^{-1} soil. To evaluate the efficacy of the biochar feedstock manures as fertilizer sources, a second analysis using the GLM procedure was conducted using all of the data. Each feedstock x pyrolysis temperature combination was considered as a treatment and sources of variation for this analysis were experiment, blocks within experiments, treatment, and the experiment x treatment interaction. Single degree-of-freedom contrast comparisons were made to determine whether each manure feedstock source at each pyrolysis temperature differed from the 40 mg P kg^{-1} soil calcium phosphate treatment.

RESULTS AND DISCUSSION

The soil used in the experiment provided a good evaluation of the biochars as P fertilizer sources because of its low P concentration (Table 2). The influence of calcium phosphate on cotton growth, P status, and soil P at the end of the experiments is shown in Table 2. Leaf area, leaf biomass, total biomass, leaf P, and stem P all increased with increasing rates of calcium phosphate. Leaf area and leaf and stem P all increased linearly with calcium phosphate rate. Both the linear and the quadratic contrasts were significant for leaf and total biomass. For the two biomass variables, the difference between applied rates grew larger as the application rate increased (Table 2). Soil P concentration at the end of the experiment also increased linearly.

Significance levels for sources of variation from the ANOVA are shown in Table 3. The two experiments of the study yielded similar results on the effect of manure feedstock and pyrolysis temperature for all data collected on the cotton plants; however, the experiment x feedstock interaction was significant for soil P. Averaged over temperatures, soil P at the end of the first experiment ranged from 25.1 mg kg^{-1} for the swine manure feedstock to 28.3 mg kg^{-1} for the chicken manure feedstock. In the second experiment, the soil P range was much larger with values ranging from 20.5 mg kg^{-1} for the beef manure biochar to 29.6 mg kg^{-1} for the swine manure biochar. The reason for this is not clear, but because neither experiment nor any interaction that included experiment were significant for any of the parameters measured on the cotton plants, it does not appear to have had a significant influence on plant uptake.

Table 2. Rate of calcium phosphate influence on cotton growth and nutrient concentration and on extractable P at the end of the experiment

Treatment	Leaf Area	Leaf Biomass	Total Biomass	Leaf P	Stem P	Soil P
mg P kg^{-1}	cm^2	g	g	ug g^{-1}	ug g^{-1}	mg g^{-1}
P-0	109.3 ± 12.2	0.89 ± 0.10	1.78 ± 0.14	977 ± 64	649 ± 23	18.2 ± 0.94
P-20	121.6 ± 10.1	1.01 ± 0.08	1.98 ± 0.17	961 ± 29	676 ± 24	20.0 ± 0.64
P-40	164.0 ± 7.7	1.27 ± 0.04	2.40 ± 0.08	1080 ± 98	750 ± 48	22.9 ± 0.98
P-60	202.3 ± 14.5	1.65 ± 0.07	3.01 ± 0.09	1080 ± 33	789 ± 32	26.0 ± 2.10
Contrast^z	L**	L**, Q*	L**, Q*	L*	L**	L**

^{z} Letters indicate significant contrasts of calcium phosphate application rate: L = linear, Q = quadratic. *, ** indicate contrasts were significant at $p \leq 0.05$ and $p \leq 0.01$ respectively.

Table 3. Results from analysis of variance of cotton fertilized with 40 mg P_2O_5 from five manure feedstock sources and two pyrolysis temperatures

Source	Leaf Area	Leaf Biomass	Total Biomass	Leaf P	Stem P	Soil P
Experiment	ns	ns	ns	ns	ns	**
Feedstock	ns	ns	ns	**	**	ns
Temperature	ns	ns	ns	ns	ns	ns
Exp * Feedstock	ns	ns	ns	ns	ns	**
Exp * Temperature	ns	ns	ns	ns	ns	ns
Feedstock * Temperature	**	**	*	*	*	ns
Exp * Feedstock * Temperature	ns	ns	ns	ns	ns	ns

*, ** indicate sources of variation were significant at $p \leq 0.05$, $p \leq 0.01$, respectively.

The feedstock x temperature interaction was significant for all parameters measured on the cotton plants (Table 3). Pyrolysis temperature had no effect on any cotton plant parameter when grown with biochars from beef and chicken. The pyrolysis temperature did have an impact, though, when cotton was grown with biochars made from dairy, swine, and turkey manure feedstock. For biochar from dairy manure, leaf area, leaf biomass, plant biomass, leaf P, and stem P were all greater when the manure was pyrolyzed at 350 than at 700 °C. Conversely, application of biochar from swine manure resulted in greater leaf area, leaf biomass, and total biomass when it was prepared at 700°C than when prepared at 350°C and turkey manure biochar resulted in cotton with higher leaf and stem P when it was prepared at 700 than 350 °C (Table 4). Although the difference in plant growth and P concentration due to pyrolysis temperature appears that they might be due to the small differences (though not significant) in concentrations of P in the soil for dairy manure, concentrations of soil P as affected by pyrolysis temperature for both the swine and turkey manure biochars were similar to that for dairy (Table 4). Properties of the biochars also do not appear to explain the differing responses in cotton plant growth and P concentration of the manure feedstock to temperature. All of the feedstock had higher pH, higher electrical conductivity (except swine), and greater surface area when pyrolyzed at 700 than at 350°C (Cantrell et al., 2012a). Phosphorus concentrations were 40 to 70% higher (Table 1) in biochars pyrolyzed at 700 than at 350°C, but this difference was accounted for in the application amount. More in-depth study on the behavior of these 10 biochars in soils seems appropriate.

Because the goal of this study was to evaluate these 10 biochars as P fertilizer sources and a significant feedstock source x pyrolysis temperature occurred for all of the cotton plant variables, single degree of freedom contrasts were made to compare each biochar to the 40 mg P_2O_5 kg^{-1} soil rate of calcium phosphate. Results from this analysis are shown in Table 4, with asterisks (*, **) indicating when a variable's mean differed from the calcium phosphate mean for that biochar. Significant contrasts occurred with the dairy, swine, and turkey feedstock. For the dairy feedstock biochar, differences only occurred for biochar produced at 350°C. Leaf area, leaf and total biomass, and leaf P were greater for plants grown with that biochar than from plants grown with calcium phosphate. For the swine feedstock, leaf area, leaf and total biomass, and leaf and stem P were all greater for the 700°C biochar than plants grown with calcium phosphate and leaf and stem P for plants fertilized with 350°C biochar were also greater. Cotton fertilized with turkey biochar produced at 700°C had greater stem P concentrations than plants fertilized with calcium phosphate. Soil P at the end of the experiment was also greater than the calcium phosphate soil P concentrations for one or both of the dairy, swine, and turkey biochars. None of the 10 biochars resulted in plants that had lower growth or nutrient concentrations than plants fertilized with calcium phosphate. These results indicate that cotton plants respond to P fertilization with the manure-based feedstock biochars in a manner similar to fertilization with calcium phosphate.

Table 4. Effect of biochar feedstock source and pyrolysis temperature on cotton growth, P concentration, and soil P at the end of the experiment. All biochars were applied at a rate of 40 mg P kg^{-1} soil rate. *, indicates that the value for that feedstock source and temperature differs from the 40 mg P kg^{-1} calcium phosphate rate in Table 2**

Variable	Feedstock Source										$LSD_{0.05}$^{z}
	Beef		Chicken		Dairy		Swine		Turkey		
	Pyrolysis Temperature (°C)										
	350	700	350	700	350	700	350	700	350	700	
Leaf Area (cm^2)	176	163	191	168	219**	151	173	227**	161	171	40
Leaf Biomass (g)	1.34	1.26	1.45	1.34	1.66**	1.19	1.34	1.67**	1.25	1.30	0.26
Plant biomass (g)	2.69	2.39	2.71	2.50	2.95**	2.30	2.59	3.04**	2.48	2.38	0.47
Leaf P (mg kg^{-1})	996	1027	1000	1002	1293*	937	1271*	1353**	1007	1223	194
Stem P (mg kg^{-1})	726	704	732	720	838	660	948**	958**	711	888**	112
Soil P (mg kg^{-1})	24.9	23.5	24.4	25.3	26.9*	23.8	28.3**	26.5*	27.0*	24.8	ns

^{z} LSD is for comparing pyrolysis temperature within a feedstock source.

One or more of the manures used in this study typically are endemic to areas with substantial levels of cotton production. For example, in the southeastern U.S., swine and poultry production are commonplace and would provide an ample stream of animal waste for the production of biochar (Cantrell et al., 2012b). Although the economics for the use of biochar as a method of C sequestration are still circumspect (Galinato et al., 2011), the ability to produce a fertilizer-based biochar and energy from pyrolysis might favorably shift the costs of converting manure (Ro et al., 2010). Should economics become more favorable for converting animal manures into biochars, the results from this study on cotton, along with those of Hunt et al. (2013) on ryegrass, suggest that application of any of these biochars appear suitable as a phosphorus fertilizer source for cotton on sandy soils. Further evaluations in different soils under field conditions appear warranted.

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DISCLAIMER

Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

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