

Designing relevant biochars as soil amendments using lignocellulosic-based and manure-based feedstocks

Jeffrey M. Novak · Keri B. Cantrell · Donald W. Watts ·
Warren J. Busscher · Mark G. Johnson

Received: 27 November 2012 / Accepted: 28 February 2013
© Springer-Verlag Berlin Heidelberg© (outside the USA) 2013

Abstract

Purpose Biochars are a by-product of the biofuel processing of lignocellulosic and manure feedstocks. Because biochars contain an assemblage of organic and inorganic compounds, they can be used as an amendment for C sequestration and soil quality improvement. However, not all biochars are viable soil amendments; this is because their physical and chemical properties vary due to feedstock elemental composition, biofuel processing, and particle size differences. Biochar could deliver a more effective service as a soil amendment if its chemistry was designed *ex ante* with characteristics that target specific soil quality issues. In this study, we demonstrate how biochars can be designed with relevant properties as successful soil amendments through feedstock selection, pyrolysis conditions, and particle size choices.

Materials and methods Biochars were produced by pyrolysis of parent lignocellulosic feedstock sources—peanut hull (PH; *Arachis hypogaea*), pecan shell (PS; *Carya illinoensis*), switchgrass (SG; *Panicum virgatum*), pine chips (PC; *Pinus taeda*), hardwood wastes (wood), and poultry litter manure (PL; *Gallus domesticus*), as well as blends of these feedstocks at temperatures ranging from 250 to 700 °C. Additionally, blended feedstocks were made into pellets (>2 mm) prior to pyrolysis at 350 °C. Dust-sized (<0.42 mm) biochar

was obtained through grinding of pelletized biochars. After chemical characterization, the biochars were evaluated as fertility amendments in a Norfolk soil (fine-loamy, kaolinitic, thermic, Typic Kandiodult) during two different pot incubation experiments.

Results and discussion PL biochars were alkaline and enriched in N and P, whereas biochar from lignocellulosic feedstocks exhibited mixed pH and nutrient contents. Blending PL with PC resulted in lower biochar pH values and nutrient contents. In pot experiment 1, most biochars significantly ($P<0.05$) raised soil pH, soil organic carbon, cation exchange capacity, and Mehlich 1 extractable P and K. PL biochar added at 20 gkg⁻¹ resulted in excessive soil P concentrations (393 to 714 mgkg⁻¹) and leachate enriched with dissolved phosphorus (DP, 22 to 70 mgL⁻¹). In pot experiment 2, blended and pelletized PL with PC feedstock reduced soil pH and extractable soil P and K concentrations compared to pot experiment 1. Water leachate DP concentrations were significantly ($P<0.05$) reduced by pelletized biochar blends.

Conclusions Short-term laboratory pot experiments revealed that biochars can have different impacts at modifying soil quality characteristics. Keying on these results allowed for creating designer biochars to address specific soil quality limitations. In the process of manufacturing designer biochars, first, it is important to know what soil quality characteristics are in need of change. Second, choices between feedstocks, blends of these feedstocks, and their accompanying particle sizes can be made prior to pyrolysis to create biochars tailored for addressing specific soil quality improvements. Utilization of these principles should allow for effective service of the designed biochar as a soil amendment while minimizing unwanted *ex facto* soil quality changes and environmental effects.

Keywords Carbon sequestration · Designer biochar · Feedstocks · Leaching · Nutrients · Pyrolysis

Responsible editor: Caixian Tang

J. M. Novak (✉) · K. B. Cantrell · D. W. Watts · W. J. Busscher
Coastal Plains, Soil, Water, and Plant Research Center,
US Department of Agriculture, Agricultural Research Service,
2611 West Lucas Street,
Florence, SC 29501, USA
e-mail: jeff.novak@ars.usda.gov

M. G. Johnson
Western Ecology Division, National Health and Environmental
Effects Research Laboratory, US Environmental Protection
Agency, 200 Southwest 35th Street,
Corvallis, OR 97333, USA

1 Introduction

During pyrolysis of lignocellulosic (Antal and Grønli 2003; Laird et al. 2009; McHenry 2009) and poultry litter (PL) (Bridgewater et al. 1999; Koutcheiko et al. 2007; Kim et al. 2009), a solid by-product called biochar is produced. Biochar has attracted tremendous global attention for its use as a soil amendment for C sequestration purposes as well as improving soil chemical and physical conditions (Lehmann 2007; Laird 2008; Sohi et al. 2009; Singh et al. 2010; Spokas et al. 2012). Biochars contain a diversity of volatile and aromatic organic structures (Keiluweit et al. 2010; Brewer et al. 2011) along with a myriad of inorganic elements (Spokas et al. 2012; Novak et al. 2012b; Cantrell et al. 2012). The literature has shown that biochar can (1) serve as a mechanism to increase C sequestration (Glaser et al. 2002; Laird et al. 2009), (2) enhance plant nutrient levels (Chan et al. 2007, 2008; Novak et al. 2009; Van Zwieten et al. 2010), (3) improve soil water retention (Novak et al. 2012a; Liu et al. 2012), and (4) enhance microbial activity (Steiner et al. 2008; Lehmann et al. 2011).

Biochars can have a positive impact on soil quality; however, this improvement does not always translate into higher crop yields (Grundale and DeLuca 2007; Lentz and Ippolito 2012; Jones et al. 2012). Van Zwieten et al. (2010) reported that biochar pyrolyzed from paper mill waste increased biomass in soybeans (*Glycine max* (L.) and radish (*Raphanus sativus*) in a Ferrosol, but reduced wheat (*Triticum aestivum*) biomass when biochar was added to a Calcarosol. Deenik et al. (2011) reported that a biochar composed of relatively high content of volatile compounds when added to an acidic Ultisol temporarily suppressed maize (*Hordeum vulgare*) growth. Jones et al. (2012) reported no effect on maize yields, in spite of significant improvements in soil fertility characteristics after hardwood biochar additions to a highly fertile soil (Eutric Cambisol).

To further understand the variability of biochar as a soil amendment, both Jeffrey et al. (2011) and Spokas et al. (2012) conducted meta-analyses among published reports that evaluated crop yield responses from biochar application. Among the 17 studies examined, Jeffrey et al. (2011) detailed that the mean crop productivity was improved by only 10 % in soils receiving biochar. In the meta-analyses conducted by Spokas et al. (2012), they reported mixed results as to the “effectiveness” of biochars applications. Approximately 50 % of the published reports ($n=45$) showed a short-term positive yield or growth impacts, 30 % reported no significant difference with controls, and 20 % reported negative yields or growth impacts (Spokas et al. 2012).

If some biochars have a benign influence on soil fertility and crop yield improvements, they may be most appropriately used if the goal of biochar application is carbon sequestration.

However, when the goal is improving soil productivity, it may be more important to apply a biochar with definitive chemical characteristics, elemental composition, and structural properties that are known in advance to change soil properties. In this way, applying a biochar that has no effect or one that leaves an unwanted soil fertility legacy is avoided. This approach was first reported by Day et al. (2005) who crafted their production process so that the resultant biochar had pore structures capable of entrapping N for its use as a slow release fertilizer. Novak et al. (2008a) theorized that biochars could be furthered engineered through feedstock and pyrolysis choices to produce materials possessing different chemical and physical properties to resolve specific soil physical and chemical deficiencies. The concept was termed “designer biochar” (Novak et al. 2008b), and the theory was quickly supported by others (Steinbeiss et al. 2009; Atkinson et al. 2010; Singh et al. 2010; Ippolito et al. 2012).

Novak and Busscher (2012) furthered advanced the theory of how the properties could be engineered for designer biochars; this could be accomplished through choices of feedstock selection, blending, and pyrolysis conditions. Missing from their list of biochar properties was the influence of biochar particle size on soil properties. A literature review revealed only a few reports that investigated the effects of biochar particle size on soil chemical and physical conditions. Lehmann et al. (2003) reported that biochar particle size (20 vs. 2 mm) did influence soil fertility levels, but it had only a minor impact on nutrient uptake or crop biomass production. Dumroese et al. (2011) reported that pelleted biochars added to peat mixtures improved their hydraulic conductivity and base saturation levels. We propose that a further understanding of biochar particle size on nutrient turnover and availability is important to refine protocols for designer biochars manufacture, amendment selection, and soil application. We hypothesize that pelletizing designer biochars will influence soil nutrient availability and its ability to modify soil chemical properties. Two different soil pot incubation experiments were conducted to determine the effects of feedstock choice, blending feedstocks, particle size (pellets vs. dust), application rates (10 vs. 20 gkg⁻¹), and pyrolysis temperature on extractable soil nutrient levels and leaching of elements. The specific objectives were the following: (1) to chemically characterize designer biochars produced from different feedstocks, blends, particle sizes, and pyrolysis temperatures; (2) to evaluate soil fertility and nutrient leaching impacts of these biochars after incubation in a sandy soil; and (3) to provide a road map outlining protocol development for designer biochar manufacture and use.

2 Materials and methods

2.1 Feedstock selection, blending, and pelletization processing

The feedstocks used in this study were collected from locations in the southeastern USA and Pacific Northwest (Table 1). These feedstocks included the following: peanut hull (PH, *Archis hypogaea*), pecan shell (PS, *Carya illinoensis*), switchgrass (SG, *Panicum virgatum*), pine chips (PC, *Pinus taeda*), hardwood wastes (wood), and PL (*Gallus domesticus*). They required a number of preprocessing steps that included air-drying and a reduction in their initial particle size by either hammer milling (PPH1000D; Pellet Pro, Davenport, IA, USA) or passage through a Wiley mill (Thomas Scientific, Swedesboro, NJ, USA) to approximately 6 mm. Specifically, PC and SG feedstocks were hammer-milled, whereas PL and SS feedstocks were ran through a Wiley mill. The processed feedstocks were then transferred to separate storage bins.

For pot incubation experiment 1, four lignocellulosic and PL feedstock were chosen (see Table 1). For pot incubation experiment 2, PL and PC were chosen as the parent feedstocks for the blends based on their respective high and low P contents (Table 2). The blending ratios of PC+PL were determined based on the theoretical amount of Mehlich 1 P (M1-P) supplied to a Norfolk soil after applying 10 t ha⁻¹ of biochar. For a Norfolk sandy loam with a low background M1-P concentration (10 to 15 mg kg⁻¹), adding biochar should bolster the soil M1-P concentration to between 15 and 30 mg M1-P kg⁻¹ soil; this amount is needed to produce a 6,271-kgha⁻¹ corn yield (North Carolina State University 1994). Preliminary calculations revealed that a gross PC+PL blending ratio of 90:10 (w/w) delivered at 10 g kg⁻¹ soil would supply sufficient P, as indicated by the M1-P extraction to achieve the 15 to 30 mg M1-P kg⁻¹ soil. Narrower PC+PL blending ratios (e.g., 80:20 and 50:50) were included in incubation experiment 2 to ensure that the soil

contained sufficient M1-P if the preliminary estimates of potential P supply were low. In addition to the blends, a 100:0 and 0:100 PC+PL treatment was included that represents the pure feedstocks alone. The blends were then produced by physically mixing appropriate masses of PL and PC.

Cylindrical pellets were made of the respective PC+PL treatments by bringing the pure components and blends up to 30 % total moisture content using deionized H₂O and pelletizing using a PP220 pellet mill (Pellet Pros, Inc., Davenport, IA, USA) equipped with a 6-mm die and roller set. The flaky texture of the 100:0 PC+PL treatment blend caused the pellets to break apart when just deionized H₂O was used. Satisfactory pellets were achieved after a 30 % moisture content was obtained using a 50:50 (w/w) mixture of deionized H₂O and generic vegetable (soybean) oil as lubrication in the pelletizing process.

2.2 Pyrolysis procedures

The pyrolysis procedures for conversion of the five raw feedstocks used in pot experiment 1 varied according to their respective processes as outlined in Novak et al. (2012b). Biochars were made using both fast and slow pyrolysis methods at temperatures ranging from 250 to 700 °C (see Table 1). This wide range of pyrolysis temperature was chosen to provide the biochars with different structural and chemical characteristics (Novak et al. 2009). All biochars for soil pot experiment 1 were ground and sieved to <0.25 mm.

For pot incubation experiment 2, biochars were made by slowly pyrolyzing the pellets at 350 °C as outlined in Cantrell and Martin (2012). This lower pyrolysis temperature was chosen so that the biochars would contain cellulose-type and hemicellulose-type structures that are suggested to contribute to both soil nutrient and water retention improvements (Novak and Busscher 2012). After pyrolysis, all biochar pellets were passed through a 2-mm

Table 1 Description of feedstocks and pyrolysis conditions for biochars used in pot incubation experiments 1 and 2

Biochars for	Collection location	Pyrolysis (°C)	Pyrolyzer	Residence time at pyrolysis temperature (h)
Incubation experiment 1				
PH (<i>Archis hypogaea</i>)	Tifton, GA	400 and 500	Heated rotary drum	1 to 2
PS (<i>Carya illinoensis</i>)	Lumberton, NC	350 and 700	Electric box+retort	1 to 2
PL (<i>Gallus domesticus</i>)	Starkville, MS	350 and 700	Electric box+retort	1 to 2
SG (<i>Panicum virgatum</i>)	Darlington, SC	250 and 500	Electric box+retort	1 to 8
Hardwood wastes (wood)	Vancouver, BC	500	Fast	5 s
Incubation experiment 2				
PC (<i>Pinus taeda</i>)	Cordesville, SC	350	Electric box+retort	2
PL (<i>Gallus domesticus</i>)	Orangeburg, SC	350	Electric box+retort	1 to 2

Table 2 Chemical properties of biochars used in pot incubation experiments 1 and 2 (means with standard deviations in parentheses were run in triplicate, other results were from a single measurement)

Biochar (°C)	Size ^a	pH (H ₂ O)	Ash and elemental composition (% w/w _{dry basis}) ^b				P	
			Ash	C	K	N		
Incubation experiment 1								
PH400	<0.25 mm	7.9	8.2	74.8	1.86	2.7	0.26	
PH500	<0.25 mm	8.6	9.3	81.8	1.9	2.7	0.26	
PS350	<0.25 mm	5.9	2.4	64.5	0.23	0.26	0.03	
PS700	<0.25 mm	7.2	5.2	91.2	0.46	0.51	0.05	
PL350	<0.25 mm	8.7	35.9	46.1	5.89	4.9	2.94	
PL700	<0.25 mm	10.3	52.4	44.0	8.66	2.69	4.28	
SG250	<0.25 mm	5.4	2.6	55.3	0.48	0.43	0.10	
SG500	<0.25 mm	8.0	7.8	84.4	1.16	1.07	0.24	
Wood500	<0.25 mm	5.7	8.9	71.4	0.62	3.0	0.03	
Incubation experiment 2								
Blending ratios (w/w)	pH (H ₂ O)		Group ^c	Ash and elemental composition (% w/w _{dry basis})				P
	Pellet ^d	Dust		Ash ^e	C ^e	K	N ^e	
PC+PL (100:0)	5.3 (1.7)	6.0 (0.7)	5.69a	1.8 (0.08)a	78.7 (0.1)a	0.15	0.4 (0.02)a	0.02
PC+PL (0:100)	9.4 (0.2)	9.9 (0.0)	9.62 b	32.1 (0.2)b	51.5 (0.6)b	5.9	5.1 (0.03)b	2.4
PC+PL (50:50)	9.2 (0.3)	9.0 (0.1)	9.1b	18.5 (0.04)c	63.7 (0.06)c	4.1	3.4 (0.01)c	1.4
PC+PL (80:20)	7.0 (0.4)	8.4 (0.3)	7.69c	7.3 (0.03)d	75.8 (0.3)d	0.9	1.3 (0.02)d	0.5
PC+PL (90:10)	6.7 (0.7)	8.0 (0.1)	7.30c	4.4 (0.01)e	78.1 (0.6)a	0.6	0.9 (0.02)e	0.3
Source of variation			P value					
Blending ratio			<0.001					
Particle size			0.007					
Blending ratio × particle size			0.237					

^a These biochars were ground to <0.25 mm prior to ash and elemental analysis

^b Some biochar chemical characteristics were previously published in Novak et al. (2009, 2012a)

^c A two-way ANOVA was used to determine significant differences and interaction between factors with means within a column followed by a different letter indicating significant differences at $P=0.05$

^d Pelletized (>2 mm) and dust-sized (<0.42 mm) blended feedstocks were made prior to pyrolysis at 350 °C

^e A one-way ANOVA was used to determine significant differences between biochar means within a column with means followed by a different letter indicating significant differences at $P=0.05$

sieve, and material remaining on the sieve was referred to as “pellets.” A portion of the pellets was then ground to pass through a 0.42-mm sieve; this particle size was referred to as “dust.” For characterization, biochars were ground to <0.25 mm.

2.3 Biochar characterization

For each ground biochar sample, the pH was measured using a 1:2 (v/v) biochar/deionized H₂O mixture after shaking for 200 rpm for 2 h. The biochars ash, C, and N contents were determined on an oven dry weight basis by Hazen Research, Inc. (Golden, CO, USA), following the American Society for Testing and Materials (ASTM) D1372 and 3176 standard combustion methods (ASTM 2006). Their P and K contents were determined on an oven dry weight basis using the Environmental Protection Agency (EPA) method 3052, a microwave-assisted acid digestion procedure (US EPA 1996, SW-846); and these contents were quantified using

an inductively coupled plasma mass spectrometer as outlined in Novak et al. (2009).

2.4 Norfolk soil characterization and biochar incubations

The Norfolk soils used in pot incubation experiments 1 and 2 were collected from two locations in a field with a long history (>30 years) of row crop production at the Clemson University Pee Dee Research and Education Center, Florence, SC, USA. Row crop production in the field was terminated in 2007 and, thereafter, was planted with SG. After 1 year of SG production, Norfolk Ap horizon (0 to 15 cm depth) was collected for pot incubation 1 from a slightly rolling (2 to 3 % slope) area of the field. The Ap horizon was determined to be a loamy sand with a particle size distribution of 740, 250, and 10 gkg⁻¹, respectively, of sand, silt, and clay. After 4 years of SG production, Norfolk soil was recollected from the Ap horizon in a more level area of the field (<1 % slope). This soil was used in pot

incubation experiment 2 and was also loamy sand with a particle size distribution of 800, 170, and 30 g kg^{-1} , respectively, of sand, silt, and clay. Both Norfolk soil samples were analyzed for textural analyses using the sedimentation method (Soil Characterization Laboratory, The Ohio State University, Columbus, OH, USA). They were also characterized for pH, cation exchange capacity (CEC), and background M1-P and M1-K concentrations by the Clemson University Soil Testing Laboratory (Clemson, SC, USA).

2.5 Soil leaching

Both incubation experiments were conducted in open-top flower pots that contained drainage holes. For incubation experiment 1, 9 g of <0.25 mm biochar was mixed into 450 g of air-dried soil for a 20 g kg^{-1} mixture ($\approx 40 \text{ t ha}^{-1}$). Pots consisting of Norfolk Ap without biochar served as a control. Each treatment was set up in four replicates. Deionized H_2O was then mixed into each replicate treatment to obtain a soil moisture content of 10 % (w/w), which represented the upper range of field capacity values for a typical Norfolk Ap soil horizon. Each pot was gently tamped down to obtain a bulk density of 1.3 to 1.4 g cm^{-3} (the field-measured bulk density of the Norfolk soil). The pots were then laboratory-incubated for 127 days, and their gravimetric moisture contents were adjusted twice per week to maintain the 10 % moisture content. A similar procedure was followed for incubation experiment 2, except 10 g kg^{-1} of biochar pellets or dust were mixed separately into triplicate pots containing the Norfolk soil; Norfolk Ap soil without biochar served as the control. This incubation experiment was reduced to 78 days. The reasoning for both the decrease in elapsed time and reduced leaching events was based on the findings from Novak et al. (2012a), which showed that minimal improvements in soil moisture retention occurred after more than two leaching events.

All pots in incubation experiments 1 and 2 were leached periodically with 1.2 to 1.3 pore volumes of deionized H_2O . After free drainage had ceased, the collected H_2O leachates were weighed for their mass. Four leaching events occurred for incubation experiment 1 on days 28, 63, 90, and 118; in incubation experiment 2, only two leaching events occurred on days 30 and 75. All leachates were filtered through a Supor 450-type 0.45- μm membrane filter (Pall Corp., Ann Arbor, MI, USA) and were analyzed for dissolved phosphorus (DP) with a Varian ICP-OES (Varian Inc., Palo Alto, CA, USA).

At the end of both incubation experiments, soils were removed from the pots and allowed to air-dry for several days. Soil samples from incubation experiment 1 were sent to the Clemson University Soil Test Laboratory and analyzed for their pH and CEC, along with M1-P and M1-K concentrations (<http://www.clemson.edu/public/regulatory/>

[ag_svc/index/html](http://www.clemson.edu/public/regulatory/ag_svc/index/html)). Soil samples from incubation experiment 2 were analyzed in-house for soil pH and M1-P and M1-K concentrations. These procedures were performed in-house to ensure that the analyzed subsamples included pellets. Both soil-extracted M1-P and M1-K concentrations were determined using previously described ICP methods. Soil organic carbon (SOC) contents in samples from the two incubation experiments were assessed using two different techniques. This was performed to maintain as much analysis on the subsamples “as is” as well as to address concerns with subsample mass and even distribution of biochar. During the mixing of the soil and biochar mixtures, it was quickly noted that the occurrence of dust biochar (<0.25 mm) was evenly distributed throughout the soil matrix, even at small mass quantities. Because pellets concentrate the biochar particles in “pockets” throughout the soil matrix, a larger subsample of pelleted biochar/soil subsample (compared to the dust) was desired to aid in addressing the issue of homogeneity of the pelleted biochar/soil matrix. Taking all this into consideration, soil subsamples at the end of incubation in experiment 1 were analyzed using a LECO TruSpec CN analyzer (LECO Corp., St. Joseph, MI, USA). SOC contents in samples from incubation experiment 2 were determined using the loss on ignition (LOI) method; this method required a slightly larger sample size, which was prohibitive with the TruSpec CN analyzer. The LOI method used oven-dried samples placed into a muffle furnace for dry oxidation at 575 °C for 16 h following ASTM E1755 (ASTM 2002). The difference between the oven dry weight of a sample and the weight after oxidation was used to calculate the quantity of SOC as grams per kilogram.

2.6 Statistical analyses

Both one-way and two-way analyses of variance (ANOVA) were used to test for significant differences on measured parameters. The two-way ANOVA was employed to determine if there were significant differences between results obtained by PC+PL blending ratios, differences between results from pellet vs. dust, and for the interaction between pellets and dust. When the degree of interaction was non-significant, a group mean for the particular variable was reported. All statistical tests were performed using SigmaStat v.3.5 software (SPSS Corp., Chicago, IL, USA).

3 Results

3.1 Chemical properties of biochars

For the biochars used in pot incubation experiment 1, increasing the pyrolysis temperature to ≥ 500 °C generated biochars with alkaline pH values and higher ash contents (compared to their lower-temperature counterparts). For the

plant-based biochars in experiment 1, increasing the pyrolysis temperature to >500 °C intensified concentrations of C, K, N, and P (see Table 2); one exception was the consistent P concentration in PH at both 400 and 500 °C. PL exhibited a different trend to increased pyrolysis temperature with respect to C and N; both C and N decreased with pyrolysis temperature increases. Largely due to the nature of the PL feedstock compared to the lignocellulosic-based feedstocks, PL biochar had the highest pH values along with the greatest ash, N, K, and P contents. In contrast, biochar produced from PS had among the lowest pH values and ash, N, K, and P contents. In fact, the P content of PS biochar was between 0.03 and 0.05 %, which is several-fold lower than the P contents in both the PL biochars (PL350 and PL700).

Characterization of biochars and blends used in pot incubation experiment 2 showed that the high pH and nutrient concentrations in the PL biochar were reduced through blending with the PC feedstock. There was, however, no significant effect of particle size on their pH values (see Table 2). Hence, grouped pH means were reported that showed blending with PC feedstock at the wider ratios (i.e., 80:20 and 90:10) significantly reduced the pH of the blends. The ash and elemental compositions of the pelleted and dust biochars were considered the same since the dust was formed from ground pellets. However, the ash and N contents in the biochar-blended materials were significantly reduced compared to the pure PL biochar by blending PC and PL feedstocks. As to be expected when diluting the PL concentration in the biochar, the 90:10 PC+PL blends, among all the blends, yielded the lowest ash, K, and P contents. Concomitantly, the C contents increased in the biochars when initial feedstock blends contained greater amounts of the C-dense PC feedstock (see Table 2). Interestingly, the 90:10 PC+PL biochar was similar to the 100:0 PC+PL with respect to C.

3.2 Soil and leachate characteristics from both incubation experiments

The Norfolk control soil used in pot incubation experiment 1 was acidic and had moderate background soil fertility characteristics (Table 3); background P was within recommended P levels. Most biochars added at 20 g kg^{-1} to the Norfolk soil resulted in significant soil fertility improvements; there were a few exceptions. Among all the treatments, additions of both PL biochars resulted in the most significant soil fertility enhancements by increasing pH, SOC, P, and K contents. However, after additions of both the PL biochars, the Norfolk M1-P and M1-K contents were raised many-fold relative to the Norfolk control. Among these two PL biochars, higher M1-P and M1-K soil concentrations were obtained after applying biochar pyrolyzed at 700 °C. The M1-K concentrations were also

significantly increased, especially after additions of the PH and PL biochars. Significant soil fertility improvements also occurred after additions of PS, SG, and wood biochar; however, the magnitude of the increases were far less when compared to changes after using PL biochars.

In pot incubation experiment 1, DP was measured in all leachates from the Norfolk control, but the concentrations were $<1 \text{ mg L}^{-1}$ (Table 4). For the most part, additions of these biochars at 20 g kg^{-1} resulted in the leachates containing elevated DP concentrations. Among the leachates from the biochar treatments, the DP concentration increases varied widely. Additions of both PL biochars caused the largest relative increase in leachate DP concentrations; the highest concentrations were measured in leachates from Norfolk soil treated with the PL350 biochar. Even though the P content was greater for the PL700 biochar, the highest leachate DP concentration measured was 70 mg L^{-1} from Norfolk soil treated with PL350 biochar. Biochars produced from SG after incubation in the Norfolk soil resulted in moderate increases in leachate DP concentrations. Smaller leachate DP increase occurred after the addition of PS and wood biochars. Using the higher pyrolysis temperatures regime, biochars produced from the PL and SG feedstocks resulted in higher amounts of DP solubilized than their counterpart material produced at the lower pyrolysis temperature. Additionally, there were nearly similar DP concentrations among the multiple leachates, implying persistent solubilization of DP even after 127 days of incubation. These results illustrate that repeated di- H_2O leaching of soil treated with biochars at the 20-g kg^{-1} rate resulted in recurrent releases of DP into solution.

In pot incubation experiment 2, the Norfolk Ap control soil was acidic, and it had low background P and K contents (Table 5). This Norfolk soil had a higher SOC content than the Norfolk soil used in pot incubation experiment 1. The soil fertility properties of the Norfolk soil used in experiment 2 were improved after mixing in the designer biochar blends, but the degree of improvement varied among treatments. For instance, gains in soil fertility improvements were influenced differently by the biochars delivered as either pellets or dust and through blending of PL with PC (see Table 5). Biochars (blends or pure feedstock) delivered as a pellet had no significant impact at improving SOC contents. But when biochar was delivered as dust, the Norfolk's SOC contents almost doubled relative to the control. When the biochar dust blends contained equal amounts of PL and PC (50:50) or more PL than PC (0:100), there was less SOC content enhancement. The SOC results support the finding of a significant interaction ($P < 0.003$) between blending ratio and materials particle size.

Norfolk soil pH values, in general, increased when biochar was delivered either as dust, pellet, or blend. Except for the pure PC biochar pellet treatment, biochar pellets significantly increased soil pH values. Biochars added as

Table 3 Mean Norfolk soil fertility characteristics at termination of pot incubation experiment 1 ($n=4$; standard deviations are in parentheses; 20 g kg^{-1} of <0.25 mm sieved biochar mixed into soil and incubated for 127 days; SOC soil organic carbon, CEC cation exchange capacity)

Treatments ($^{\circ}\text{C}$)	pH (H_2O) ^a	SOC gkg^{-1}	CEC (cmol kg^{-1})	Mehlich 1 extractable nutrients (mgkg^{-1})	
				Phosphorus	Potassium
Norfolk control	5.6 (0.0)a	3.1 (0.1)a	2.1 (0.1)a	27 (2)a	19 (1)a
PH400	7.6 (0.1)b	18.1 (1.7)b	2.4 (0.3)a	36 (1)b	155 (18)b
PH500	7.8 (0.1)c	19.5 (2.7)bd	2.1 (0.0)a	28 (2)a	174 (9)b
PS350	6.3 (0.1)d	15.5 (0.9)c	3.1 (0.3)b	24 (1)c	60 (1)c
PS700	7.8 (0.0)c	21.2 (0.5)d	2.9 (0.1)b	31 (0)d	41 (1)d
PL350	8.4 (0.1)e	10.7 (0.8)e	8.5 (0.6)c	393 (29)e	209 (26)e
PL700	9.0 (0.0)f	11.6 (1.4)e	13.6 (0.5)d	714 (31)f	277 (9)f
SG250	6.2 (0.0)g	12.5 (1.9)e	2.5 (0.2)a	29 (2)a	60 (4)c
SG500	7.0 (0.1)h	19.6 (1.2)b	2.3 (0.1)a	32 (1)d	85 (4)g
Wood500	6.6 (0.1)i	17.2 (1.1)b	2.3 (0.3)a	22 (2)c	62 (3)c

^a Means within a column tested for significant differences using a one-way ANOVA with means followed by a different letter being significantly different at $P=0.05$

dust, regardless of blending ratio, also significantly increased soil pH values. The greatest increase in soil pH occurred when the treatments contained more equal amounts of PL and PC (50:50) or more PL than PC (0:100). These results support the significant interaction ($P<0.001$) between blending ratio and particle size with their impact on Norfolk soil pH values (see Table 5).

M1-P and M1-K extracted from the Norfolk soil in pot incubation experiment 2 were impacted when biochars were delivered as pellets or dust and by blending (see Table 5). When added as a pellet, soil M1-P concentrations increased by a factor of up to 2.4 relative to the control using the pure PL (0:100) and blended with PC (50:50) biochars. Much higher M1-P concentrations were extracted from Norfolk soils when biochars were delivered as dust and at the 0:100 and the 50:50 PC+PL blending ratios. Even when the biochar application rate was reduced to 10 gkg^{-1} , biochars delivered as dust at a 0:100 or 50:50 PC/PL blend still greatly exceeded the target M1-P concentration goal of 15 to 30 mgkg^{-1} . However, reducing the amount of PL by blending with PC at 80:20 and 90:10 ratios as both pellet and dust resulted in M1-P concentrations closer to the target range of 15 to 30 mgkg^{-1} . In only two of the five treatments, biochar as a pellet caused significant M1-P concentration differences as opposed to biochar pellets. This effect was adequate to influence the degree of interaction between the particle size and blending ratio ($P<0.001$; Table 5). For the most part, M1-K concentrations were influenced by blending ratio, with the 0:100 and 50:50 PC/PL treatments having the highest extractable concentrations. By reducing the mass of PL in the blending ratio, the group mean M1-K concentrations declined as the ratio became wider (80:20 and 90:10). There was no significant interaction between blending ratio and particle size, indicating that particle size did not impact Mehlich 1 extractable levels of K.

In pot incubation experiment 2, DP concentrations were especially low ($<0.2 \text{ mgL}^{-1}$) in both leaching of the Norfolk control soil and soil treated with 100:0 (PC+PL) biochar (Table 6). The DP concentrations increased in both leachates from soils treated with biochars as a function of both blending ratio and particle size. The leachates from the 0:100 PC+PL treatment as dust contained between 16 and 24 mgL^{-1} of DP. Similarly, biochar delivered as dust for the 50:50 and 80:20 PC+PL treatments also had relatively high DP concentrations that ranged from 2.5 to 14.5 mgL^{-1} . For all biochars delivered as dust or pellets, in general, DP concentrations significantly declined in leachates collected from soil treated with wider PC+PL ratios. In some cases, biochars incubated as pellets in the Norfolk soil did influence leachate DP concentrations compared to soils treated with dust-sized biochars. The impact of blending ratio and particle size was sufficient to produce a significant interaction ($P<0.001$) with DP concentrations in both leachates.

Synthesizing the results from the biochar characterization, impact on soil nutrient concentrations, and P leaching experiments, a model was developed consisting of different pathways for producing relevant designer biochars capable of improving specific soil issues (Table 7). This model considered only soil fertility (i.e., pH, CEC, and soil nutrient concentrations) and soil C sequestration issues in a highly weathered, sandy-textured agricultural soil. Both lignocellulose and manure feedstocks alone, in blends, or as dust and pellets were considered in these pathways. To increase soil-sequestered C, an appropriate feedstock choice could be wood and nutshell lignocellulose that are pyrolyzed at a high temperature and delivered to soil as a pellet. Soil pH issues could be improved using either

Table 4 Mean concentrations of DP in four deionized water leachates from Norfolk soil collected during pot incubation experiment 1 ($n=4$; standard deviations are in parentheses; 20 gkg^{-1} of <0.25 mm sieved biochar mixed into soil and incubated for 127 days)

Treatment ($^{\circ}\text{C}$)	DP concentration (mgL^{-1}) in leachate on incubation day			
	Leachate 1 on day 28 ^a	Leachate 2 on day 63	Leachate 3 on day 90	Leachate 4 on day 118
Norfolk control	0.5 (0.0)a	0.7 (0.0)a	0.7 (0.0)a	0.6 (0.0)a
PH400	4.5 (0.4)b	5.4 (0.2)b	4.0 (0.8)b	6.0 (0.1)b
PH500	4.0 (0.3)b	4.6 (0.7)b	5.6 (0.9)c	5.3 (0.5)c
PS350	0.6 (0.1)a	0.9 (0.2)a	1.2 (0.0)d	1.2 (0.0)d
PS700	1.3 (0.1)c	1.4 (0.1)d	1.3 (0.1)d	1.1 (0.1)d
PL350	34.5 (2.1)d	61.5 (6.5)e	70.0 (13)e	55.0 (1.7)e
PL700	24.8 (0.6)e	27.7 (3.1)f	28.2 (1)f	22.2 (1.3)f
SG250	0.9 (0.0)f	1.3 (0.2)d	1.6 (0.2)d	1.6 (0.1)g
SG500	3.7 (0.1)g	5.1 (0.5)b	6.4 (0.2)c	4.9 (0.1)c
Wood500	0.8 (0.0)f	0.9 (0.1)a	1.0 (0.1)d	0.9 (0.1)d

^a Means within a column tested for significant differences using a one-way ANOVA with means followed by a different letter being significantly different at $P=0.05$

lignocellulose or manure feedstocks that are pyrolyzed under a high or low temperature regime and as either a pellet or dust particle size. Depending on the level of nutrients (depleted or excessive) to be modified, soil nutrient concentration issues can also be managed using combinations of manure alone or through lignocellulose blends with pyrolysis temperature and biochar particle size selected based on the modification direction (i.e., raising or lowering) for soil nutrient contents.

4 Discussion

Designing relevant biochars with characteristics tailored for improving specific soil limitations requires an understanding of how feedstock selection, pyrolysis conditions, and material sizes influence their chemical properties, elemental composition, and nutrient release behavior. Therefore, several biochars reported in this study were created using a combination of feedstocks alone and in blends, at different pyrolysis temperatures, and finally, in different particle sizes (see Table 1). The characterization of these biochars and blends revealed some prominent chemical as well as passive features that could serve as a predictor for their ability to modify issues in a sandy coastal plain agricultural soil. Biochars made from PL distinguished themselves as having both high ash contents and pH values, as well as containing some of the highest K, N, and P contents. Others have reported similar elemental analyses of biochars made from PL (Chan et al. 2008; Gaskin et al. 2008; Cantrell et al. 2012; Revell et al. 2012). Biochars made from PH and SG had medium quantities of elements, while biochars from PS and wood contained lower quantities of nutrients. The

biochars' pH and ash values were influenced by pyrolysis temperatures because of the concentration of inorganic elements as the volatile compounds were removed as bio-oxid and noncondensable gases (Antal and Grønli 2003).

The biochars' nutrient release behavior and impact on Norfolk fertility were assessed through two laboratory incubation experiments involving a high (20 gkg^{-1}) and a low (10 gkg^{-1}) application rate. In both of these experiments, DP solubilization into soil and its subsequent translocation with water leaching were deemed important properties to ascertain especially from soil treated with the PL biochars (see Table 2). Both Norfolk control soils used in these experiments had a low buffer capacity due to the acidic pH and low quantity of SOC. In pot incubation experiment 1, the Norfolk soil was chemically shocked by the application of 20 gkg^{-1} of biochar due to the huge shift in pH; the largest increase occurred after incubation of both PL biochars. In fact, soil pH values were >8 after both PL biochars were incorporated. Additions of the other biochars also raised soil pH values to range between 6.2 and 7.8. There is a serious soil fertility consequence of raising soil pH values >6.5 because the availability of important plant macronutrient and micronutrient will become limited (Troeh and Thompson 2005). Therefore, biochar application rates are a concern.

The most promising feedstock for raising soil C contents that should resist oxidation in the Norfolk soil was PS biochar pyrolyzed at 700 $^{\circ}\text{C}$. This was expected because this biochar had the highest C content (91.2 %; Table 1) and was composed of mostly aromatic C compounds (Novak et al. 2009), a structural property known to influence its recalcitrance (Glaser et al. 2002). Incubation experiment 2 revealed that biochars delivered as pellets did not significantly

Table 5 Mean Norfolk soil fertility characteristics at termination of pot experiment 2 that were incubated with pelletized and dust-sized biochar blends of PC and PL feedstocks ($n=3$; standard deviations are

in parentheses; 10 g kg^{-1} of biochars were mixed into soil and incubated for 78 days; SOC soil organic carbon)

Biochar blends	Blending ratio (w/w)	SOC (g kg^{-1}) ^a		pH (H_2O)		Mehlich 1 extractable nutrients (mg kg^{-1})				
		Pellet ^b	Dust ^b	Pellet	Dust	Phosphorus		Potassium		Group
						Pellet	Dust	Pellet	Dust	
Control	na	12.6 (0.6)a		6.00 (0.15)a		11 (2)a		31 (10)a		
PC+PL	100:0	13.0 (0.6)a,a	22.5 (0.6)b,b	6.19 (0.05)a,a	6.32 (0.03)b,a	11 (1)a,a	11 (2)a,a	26 (8)	25 (3)	26a
PC+PL	0:100	12.4 (0.3)a,a	17.7 (2.5)c,b	7.11 (0.08)b,a	7.91 (0.19)c,b	52 (16)b,a	237 (7)b,b	199 (51)	245 (39)	222b
PC+PL	50:50	13.6 (0.5)a,a	20.2 (0.3)d,b	7.25 (0.14)b,a	7.69 (0.08)c,b	73 (15)b,a	113 (3)c,b	146 (14)	148 (3)	147c
PC+PL	80:20	12.5 (0.1)a,a	22.8 (0.3)b,b	6.83 (0.06)c,a	7.03 (0.13)e,a	22 (4)a,a	29 (2)d,a	68 (4)	65 (3)	68de
PC+PL	90:10	13.9 (1.4)a,a	22.4 (0.6)b,b	6.49 (0.02)d,a	6.62 (0.13)f,a	19 (3)a,a	23 (2)e,a	43 (2)	56 (7)	49ae
Source of variation		<i>P</i> values								
Blending ratio		<0.001		<0.001		<0.001		<0.001		
Particle size		<0.001		<0.001		<0.001		0.161		
Blending ratio × particle size		0.003		<0.001		<0.001		0.286		

^a A two-way ANOVA was used to determine significance and the degree of interaction, with the first letter after the mean indicating significant differences between treatments within a column and the second letter indicating differences between pellets and dust sorted by biochar blending ratio at $P=0.05$

^b Pelletized ($>2 \text{ mm}$) and dust-sized ($<0.42 \text{ mm}$) blended biochars were made by pyrolyzing blended, pelletized feedstock at $350 \text{ }^\circ\text{C}$

improve soil C sequestration. There are a few explanations for this, including: (1) the soil samples containing the pellets were heterogeneous due to soil to pellet weight ratios that did not contain sufficient pellet mass to show SOC improvements and (2) the sample size (5 g) was not large enough to obtain quantitative results from the LOI technique. The noted significant improvements in SOC with biochar blended with more PC were simply C-enriched (see Table 2) and were more homogeneously mixed with the soil due to their finer particle size. We were able to discern that biochars delivered as dust caused significant improvements in the SOC contents, although biochar delivered as a pellet may also have a significant impact, but our sampling and/or analytical methods were insufficient to measure a difference.

Modifications in the soil CEC and M1-P and M1-K contents were most apparent after applying both PL biochars. While increases in CEC and M1-K are important for improving soil fertility, the M1-P concentrations of 393 and 714 mg kg^{-1} are grossly in excess of soil P concentrations ($15 \text{ to } 30 \text{ mg kg}^{-1}$) recommended for corn production in Carolina Coastal Plain sands (North Carolina State University 1994) and for corn production in sandy soils in Delaware ($20 \text{ to } 35 \text{ mg kg}^{-1}$; Sims 1998; Sims et al. 2002). Medium increases in soil CEC occurred after incubation

with both PS biochars, which is consistent with Novak et al. (2009). Both PH biochars were sufficient at increasing soil K concentrations with biochars produced from PS, PL, SG, and wood, causing significant increases in M1-K levels. In some ways, all of these biochars did raise the fertility of the Norfolk soil; however, some biochars applied at 20 g kg^{-1} induced soil fertility concerns because of the high pH and out-of-balance soil P concentrations.

A likely consequence of having P contents in excess of agronomic crop nutrient levels in sandy-textured soil is the high incidence of P leaching to shallow groundwater (Reddy et al. 1980; Novak et al. 2000; Brock et al. 2007). While some P release from biochars is necessary to supply P for crop nutritional requirements, it would be environmentally prudent to reduce excessive soluble P releases, thus minimizing potential incidence of surface water and groundwater quality degradation. Examination of the literature showed that very few studies have examined soluble P releases from biochars or biochar-treated soils. In one study, Revell et al. (2012) produced PL biochar at $450 \text{ }^\circ\text{C}$ using a fluidized bed reactor to examine P movement from pots containing sand and silt soil. They reported very little P translocation from both soils, indicating that P was most likely in insoluble forms. In contrast, Silber et al. (2010) examined the nutrient

Table 6 Mean concentrations of DP in two water leachates collected during pot incubation experiment 2 from a Norfolk soil treated with pelletized and dust-sized biochar blends of PC and PL feedstocks ($n=3$; standard deviations are in parentheses; 10 g kg^{-1} of biochars were mixed into soil and incubated for 75 days)

Biochar blends	Blending ratios (w/w)	DP concentrations (mg L^{-1}) ^a			
		Leachate 1 on day 30		Leachate 2 on day 75	
		Pellet ^b	Dust ^b	Pellet	Dust
Control (no biochar)	na	0.15 (0.01)a		0.13 (0.01)a	
PC+PL	100:0	0.13 (0.02)a,a	0.17 (0.00)a,a	0.13 (0.00)a,a	0.15 (0.01)a,a
PC+PL	0:100	0.77 (0.15)b,a	16.0 (1.20)b,b	2.80 (0.4)b,a	24.1 (6.0)b,b
PC+PL	50:50	1.66 (0.23)c,a	9.87 (1.00)c,b	7.0 (1.8)c,a	14.5 (1.3)c,b
PC+PL	80:20	0.66 (0.06)b,a	9.04 (0.67)c,b	1.3 (0.3)d,a	2.5 (0.3)d,a
PC+PL	90:10	0.20 (0.02)a,a	0.65 (0.18)d,a	0.5 (0.1)e,a	0.9 (0.0)e,a
Source of variation		<i>P</i> values			
Blending ratio		<0.001		<0.001	
Particle size		<0.001		<0.001	
Blending ratio \times particle size		<0.001		<0.001	

^a A two-way ANOVA was used to determine significance and the degree of interaction, with the first letter after the mean indicating significant differences between treatments within a column and the second letter indicating differences between pellets and dust sorted by biochar blending ratio at $P=0.05$

^b Pelletized ($>2 \text{ mm}$) and dust-sized ($<0.42 \text{ mm}$) blended biochars were made by pyrolyzing blended, pelletized feedstock at $350 \text{ }^\circ\text{C}$

release dynamics of corn straw biochar produced at $500 \text{ }^\circ\text{C}$ using a fluidized fast pyrolyzer. They reported that P was initially released rapidly, and later, it was continually solubilized over the experimental time course (600 h). For our study, biochars were produced using different pyrolysis systems (heated rotary drums and furnace with a retort; Table 1), and P release from these biochars was ascertained through multiple H_2O leaching events during the course of incubation experiment 1 (118 days). Dissolved P was released, in most cases, in concentrations higher than the control, with the DP releases being among the highest from soils treated with PL biochar. Another noticeable result was the greater DP concentrations measured in leachates collected from soils treated with the lower-temperature biochar ($350 \text{ }^\circ\text{C}$). This suggests that the P was complexed with water-soluble salts contained in this biochar. In contrast, lower DP concentrations measured in leachates from Norfolk soils treated with higher-temperature PL biochar ($700 \text{ }^\circ\text{C}$) were probably due to P bound by Ca, Mg, or Fe cations (Novak et al. 2012b) or by binding to carbonates formed at the high pyrolysis temperatures (Yuan et al. 2011). Binding to these cations would reduce P solubility due to precipitation as Ca-phosphates, Mg-phosphates, or carbonates or due to crystal formation as a result of the high pyrolysis temperatures. This was expected because high pyrolysis temperatures ($>500 \text{ }^\circ\text{C}$) are well-known to have dramatic impacts on the structural and elemental composition of biochars (Libra et al. 2011; Sun et al. 2012).

Comparison of the P release dynamics reported in our biochar experiments with the results of Revell et al. (2012) and Silber et al. (2010) may be inappropriate considering that biochars were produced from different PL sources and were made using different pyrolysis systems. However, if P solubilization from biochar is a major agronomic and environmental issue, then additional research should focus on the influence of pyrolysis systems on P contents, associated composition of potential binding phases, and P release kinetics.

In our work, results from incubation experiment 1 illustrate that fertility levels and leachate P concentrates were influenced by biochar type through choice of feedstock selection, pyrolysis temperature, and application rate. Now, the key was to synthesize results from incubation experiment 1 to retool the paradigm of biochars use as a soil amendment. A new model was created consisting of pathways that produced designer biochars with characteristics that could selectively improve Norfolk soil fertility and C sequestration issues without unbalancing soil agronomic P contents and increasing pH levels. This was accomplished by designing biochars through blending the nutrient-rich PL biochars with the more C-enriched PC feedstock, pyrolyzing at a lower temperature ($350 \text{ }^\circ\text{C}$), and reducing biochar application rates (10 g kg^{-1}). The biochars were pelletized to improve future mechanical field applications while avoiding the health and incendiary concerns of dust-sized biochar particles (Laird et al. 2009). Furthermore, this study

Table 7 Suggested matrix for matching designer biochar production to modify specific properties of a sandy soil

Soil property	Soil carbon levels	Soil pH levels		Depleted soil nutrients (P and K)	Excessive soil nutrients (P and K)	Soil CEC
Biochar action	Increase C sequestration	Maintain at <7.0	Increase to >7.0	Increase soil nutrients	Maintain soil nutrients concentrations	Increase soil CEC
Feedstock	Wood and nutshell lignocellulose	Lignocellulose ^a	Manure or lignocellulose ^a	Manure or blend of manure/lignocellulose (>50:50)	Blend of manure/lignocellulose (<50:50)	Nutshell lignocellulose or manure
Pyrolysis (°C)	500 to 700	250 to 350 (wood—500)	>350	700	350	350 to 700
Particle size	Pellet	Pellet or dust	Dust	Dust	Pellet	Not determined

^a Unless specified, lignocellulose includes the following general categories: nutshells, agricultural residues, bioenergy crops, and wood products

utilized both PL and PC as feedstocks because they are particularly plentiful in the coastal plain region of South Carolina (Novak et al. 2012b).

For incubation experiment 2, the PC+PL blending ratios were determined using a priori knowledge of the P content in a PL biochar and its associate feedstock (Cantrell et al. 2012) to assess the quantity of M1-P that would be supplied to the Norfolk soil after 10 gkg⁻¹ biochar application to achieve the recommended M1-P contents needed for a corn crop. A 90:10 PC+PL blend was calculated to deliver approximately 15 mg M1-Pkg⁻¹ soil. So if this M1-P source is combined with the background M1-P levels, the sum of both sources should cause the soil to contain the 15- to 30-mgkg⁻¹ range sufficient for the 6,271-kg/ha⁻¹ corn yields.

Designing the PL biochars through blending with PC and delivering it to soil as a pellet significantly reduced the concerns of raising soil pH to values >8 and lowering both soil M1-P and leachate concentrations. The 90:10 and 80:20 PC+PL blended pellets applied at 10 gkg⁻¹ resulted in soil M1-P concentrations to be within the target range of 15 to 30 mgkg⁻¹. The PC+PL blends at narrow ratios raised soil M1-P values much higher than recommended, so the 90:10 or 80:20 were optimum ratios for balancing plant-available soil P contents for a corn crop. Delivering biochar blends as pellets, therefore, is a viable production management strategy for rebalancing soil-available and plant-available P levels. As shown with the leachate results from incubation experiment 2, pelletized biochars reduced the water-soluble P probably through internal P binding sites being inaccessible to water.

While biochars as pellets reduced P releases, dust-sized biochar material facilitated more extractable P in both soils and soluble P concentrations in the leachates (see Tables 5 and 6). This is probably due to water and the acidic Mehlich extraction solution's ability to access and solubilize P held in salts and/or carbonates and not hindered by structural obstructions or blocked pores. If the soil needs to be rapidly

improved for SOC, pH, and M1-P contents, then both unblended PL biochars and their blended products should be delivered to the soil as a dust-sized material. This exemplifies the utility of designing biochars, in this case as dust-sized material, where the action of modifying soil properties can be rapidly achieved.

A goal of this study was to provide pathways for the creation of designer biochars tailored for the resolution of specific soil properties (see Table 7). The first step in the use of this convention was to decide what soil property needed modification. Selection of a soil property to modify is the most important criteria of using designer biochars. For example, the Norfolk soil series exhibits low SOC contents, acidic pH, and low to moderate plant-available P concentrations for a corn crop. The next step in the proposed procedure is to determine what feedstock, pyrolysis temperature, and particle size will deliver a biochar with tailored properties to modify the target soil properties (i.e., SOC, pH, CEC, M1-P, etc.).

Because PC is low in nutrients and are not particularly effective at increasing soil fertility levels, this feedstock is acceptable for C sequestration if pyrolyzed at high temperatures (500 to 700 °C) and delivered to the soil as a pellet. The PC biochar as a pellet would have less reactive surfaces that should hinder its oxidation through biotic and abiotic reactions. While the PC biochar is C-dense, blending it with low amounts of manure (i.e., 90:10) prior to pyrolysis maintains the potential C sequestration ability of the biochar while also providing the additional benefits of the added nutrients.

Additions of PS and PL biochar caused significant improvement in the soil CEC (see Table 3). In fact, the soil CEC increases by a factor of 1.4 to 6.5 after their additions relative to the control. Therefore, among the biochars examined in this study, biochar produced from nutshells or manure probably will also improve sandy soils' ability to retain nutrients (see Table 7).

More careful attention is needed when rebalancing or improving soil nutrient levels, especially when plant-available soil P concentrations are the target of modification. In soils with low plant-available nutrient levels, such as P and K, PL as a feedstock pyrolyzed at 700 °C could be selected and delivered as dust at the lower application rate (<10 g kg⁻¹). Application rates of PL biochars pyrolyzed under these suggested conditions should be chosen wisely so that soils are not made excessively alkaline. Finer-scale rebalancing of soil–plant nutrient levels is possible by either blending PL with PC feedstocks or delivering the biochar as dust or pellets. Additionally, the pyrolysis temperature will need to be chosen adroitly due to the concentration of certain nutrients such as P and K. For soils containing excess plant nutrients, low application (<10 g kg⁻¹) rates of a wide (<50:50) PL+PC pelletized blend is suggested because pyrolysis at low temperatures (350 °C) should not fortify the biochars elemental composition, less biochar is applied to soil, and plant nutrient solubilization is reduced.

5 Conclusions

Biochar used as an amendment to improve soil quality and achieve higher crop yields has achieved a global focus. With biochar usage around the globe, however, it has been shown that not all biochars are created equal. This means that some biochars are not capable of delivering their intended service as a soil fertility enhancer for increasing crop productivity. Herein, an alternate paradigm for more effective use of biochar as a soil amendment was presented. Two different short-term laboratory pot experiments showed that biochars have diversified impacts with improving soil quality characteristics; some biochars caused acceptable improvements, while others caused nutrient and chemical imbalances. Accepting that not all biochars are created equal prompted an alternate model whereby the selection of certain feedstocks, pyrolysis conditions, and particle sizes was conceived to create designer biochars that can be used to target specific soil characteristics. In this model, it is important to know first what soil quality limitations need to be addressed. Then, selection of feedstocks, blends of these feedstocks, and their accompanying particle sizes can be chosen before feedstock pyrolysis is used to create designer biochars. Pathways to operate this model under different conditions were provided that outlined and clarified these choices with respect to local abundant feedstocks and soil quality issues in a sandy, nutrient-poor South Carolina agricultural soil. Naturally, this model would require further evaluation of biochar performance from different feedstocks and in other agricultural soils formed in different parent materials possessing diverse fertility characteristics.

Utilization of this model offers nutrient management experts and soil fertility specialists potentially more successful use of biochars as an amendment by simply matching their soil needs with an appropriate designer biochar. The goal of following these pathways is that designer biochars offer a more effective employment of an expensive amendment while minimizing unwanted ex facto soil quality changes.

Acknowledgments The information in this article has been funded through an Interagency Agreement between the US Department of Agriculture—Agricultural Research Service (60-6657-1-204) and the US Environmental Protection Agency (EPA; DE-12-92342301-1). It has been subject to review by scientists of the USDA-ARS Coastal Plain Research Laboratory and by the National Health and Environment Effects Research Laboratory's Western Ecology Division and approved for journal submission. Approval does not signify that the contents reflect the views of the US EPA, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. We thank Ms. Sheeneka Green, Brittany Wallace, Cierra Buckman, Takeyah Powell, and Mr. Jerry Martin II for the laboratory assistance. We also thank Drs. Kurt Spokas, Jim Ippolito, and Saran Sohi for the lively conversation and for the scientific refinement of the designer biochar concept.

References

- Antal MJ, Grønli M (2003) The art, science, and technology of charcoal production. *Ind Eng Chem Res* 49:1619–1640
- Atkinson C, Fitzgerald J, Hipps N (2010) Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. *Plant Soil* 337:1–18
- ASTM (American Society for Testing and Materials) (2002) Standard test method for ash in biomass. ASTM International, West Conshohocken
- ASTM (American Society for Testing and Materials) (2006) Petroleum products, lubricants and fossil fuels; coal and coke. ASTM International, West Conshohocken
- Brewer CE, Unger R, Schmidt-Rohr K, Brown RC (2011) Criteria to select biochars for field studies based on biochar chemical properties. *Bioenergy Res* 4:312–323
- Bridgewater AV, Meier D, Peacock C, Czernik S, Piskorz J, Oasmaa A (1999) Handbook on fast pyrolysis of biomass. CPL, Newbury
- Brock EH, Kettering QM, Kleinman PJ (2007) Phosphorus leaching through intact soil cores as influenced by type and duration of manure application. *Nutr Cycl Agroecosyst* 77:269–281
- Cantrell KB, Martin JH (2012) Stochastic state–space temperature regulation of biochar production. *J Sci Food Agric* 92:481–489
- Cantrell KB, Hunt PG, Uchimiya M, Novak JM, Ro KS (2012) Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Biores Technol* 107:419–428
- Chan KY, Van Zwieten L, Meszaros IA, Downie A, Joseph S (2007) Agronomic values of green waste as a soil amendment. *Aust J Soil Res* 45:629–634
- Chan KY, Van Zwieten L, Meszaros IA, Downie A, Joseph S (2008) Using poultry litter biochars as soil amendments. *Aust J Soil Res* 46:437–444
- Day D, Evans RJ, Lee JW, Reicosky D (2005) Economical CO₂, SO_x and NO_x capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration. *Energy* 30:2558–2579

- Deenik JL, Diarra A, Uehara G, Campbell S, Sumiyoshi Y, Antal MJ (2011) Charcoal ash and volatile matter effects on soil properties and plant growth in an acid Ultisol. *Soil Sci* 176:336–345
- Dumroese RK, Heiskanen J, Englund K, Tervahauta A (2011) Pelleted biochar: chemical and physical properties show potential use as a substrate in container nurseries. *Biomass Bioenergy* 35:2018–2027
- Gaskin JW, Steiner C, Harris K, Das KC, Bibens B (2008) Effect of low-temperature pyrolysis conditions on biochar for agricultural use. *Trans ASABE* 51:2061–2069
- Glaser B, Lehmann J, Zech W (2002) Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—a review. *Biol Fertil Soils* 35:219–230
- Grundale M, DeLuca T (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
- Ippolito JA, Laird DA, Busscher WJ (2012) Environmental benefits of biochar. *J Environ Qual* 41:967–972
- Jeffrey S, Verheijen FA, van der Velde M, Bastos AC (2011) A quantitative review of the effects of biochar application to soils on crop productivity using meta-analyses. *Agric Ecosyst Environ* 144:175–187
- Jones DL, Rousk J, Edwards-Jones G, DeLuca TH, Murphy DV (2012) Biochar-mediated changes in soil quality and plant growth in a three year field trial. *Soil Biol Biochem* 45:113–124
- Keiluweit M, Nico PS, Johnson MG, Kleber M (2010) Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environ Sci Technol* 44:1247–1253
- Kim S, Agblevor FA, Lim J (2009) Fast pyrolysis of chicken litter and turkey litter in a fluidized bed reactor. *J Ind Eng Chem* 15:247–252
- Koutcheiko S, Monreal CM, Kodama H, McCracken T, Kotlyar L (2007) Preparation and characterization of activated carbon derived from the thermo-chemical conversion of chicken manure. *Bioresour Technol* 98:2459–2464
- Laird DA (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 DA, Brown RC, Amonette JE, Lehmann J (2009) Review of the pyrolysis platform for coproducing bio-oil and biochar. *Biofuels Bioprod Bioref* 3:547–562
- Lentz RD, Ippolito JA (2012) Biochar and manure affect calcareous soil and corn silage nutrient concentrations and uptake. *J Environ Qual* 41:1033–1043
- Lehmann J (2007) Bio-energy in the black. *Front Ecol Environ* 5:381–387
- Lehmann J, da Silva JP, Steiner C, Nehls T, Zech W, Glaser B (2003) Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the central Amazon basin: fertilizer, manure and charcoal amendments. *Plant Soil* 249:343–357
- Lehmann J, Rillig M, Theis J, Masiello CA, Hockaday WC, Crowley D (2011) Biochar effects on soil biota: a review. *Soil Biol Biochem* 43:1812–1836
- Libra JA, Ro KS, Kammann C, Funke A, Berge NB, Neubauer Y, Titirici M-M, Fuhner C, Bens O, Kern J, Emmerich K-H (2011) Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes, and applications of wet and dry pyrolysis. *Biofuels* 2:89–124
- Liu J, Schulz H, Brandl S, Miehtke H, Huwe B, Glaser B (2012) Short-term effect of biochar and compost on soil fertility and water status of a Dystric Cambisol in NE Germany under field conditions. *J Plant Nutr Soil Sci*. doi:10.1002/jpln.200100172
- McHenry M (2009) Agricultural bio-char production, renewable energy generation and farm carbon sequestration in Western Australia: certainty, uncertainty and risk. *Agric Ecosyst Environ* 129:1–7
- North Carolina State University (1994) North Carolina agricultural chemical manual. The College of Agriculture and Life Sciences, North Carolina State University, Raleigh
- Novak JM, Watts DW, Hunt PG, Stone KC (2000) Phosphorus movement through a coastal plain soil after a decade of intensive swine manure application. *J Environ Qual* 29:1310–1315
- Novak JM, Busscher WJ, Watts DW, Laird DA, Niandou MAS, Ahmedna MA (2008a) Influence of pecan-derived biochar on chemical properties of a Norfolk loamy sand soil. American Society of Agronomy–Crop Science Society of America–Soil Science Society of America Annual Meeting, Houston, 5–9 Oct. 2009. Available at <http://www.biochar-international.org/>. Accessed 27 September 2012
- Novak JM, Busscher WJ, Ahmedna M (2008b) Development of designer biochar to remediate degraded coastal plain soils. Abstract for a non-funded cooperative agreement project number 6657-12000-005-03. Available at http://www.ars.usda.gov/research/projects/projects/htm?ACCN_NO=414939. Accessed 26 September 2012
- Novak JM, Busscher WJ, Laird DL, Ahmedna M, Watts DW, Niandou MAS (2009) Impact of biochar amendment on fertility of a southeastern coastal plain soil. *Soil Sci* 174:105–112
- Novak JM, Busscher WJ (2012) Selection and use of designer biochars to improve characteristics of southeastern USA coastal plain degraded soils. In: Lee JW et al (eds) *Advanced biofuels and bioproducts*. Springer, Berlin, pp 69–96. doi:10.1007/978-1-4614-3348-4_7
- Novak JM, Busscher WJ, Watts DW et al (2012a) Biochars impact on soil-moisture storage in an Ultisol and two Aridisols. *Soil Sci* 177:310–320
- Novak JM, Cantrell KB, Watts DW (2012b) Compositional and thermal evaluations of lignocellulosic and poultry litter chars via high and low temperature pyrolysis. *Bioenerg Res*. doi:10.1007/s12155-012-9228-9
- Reddy KR, Overcash MR, Khaleel R, Westerman PW (1980) Phosphorus adsorption–desorption of two soils utilized for disposal of animal wastes. *J Environ Qual* 9:86–92
- Revell KT, Maguire RO, Agblevor FA (2012) Influence of poultry litter biochar on soil properties and plant growth. *Soil Sci* 177:402–408
- Silber A, Levkovitch I, Graber ER (2010) pH-dependent mineral release and surface properties of cornstraw biochar: agronomic implications. *Environ Sci Technol* 44:9318–9323
- Sims JT (1998) Phosphorus soil testing: innovations for water quality protection. *Commun Soil Sci Plant Anal* 29:1471–1489
- Sims JT, Maguire RO, Leytem AB, Gartley KL, Paulter MC (2002) Evaluation of Mehlich 3 as an agri-environmental soil phosphorus test for the Mid-Atlantic United States of America. *Soil Sci Soc Am J* 66:2016–2032
- Singh B, Singh BP, Cowie AL (2010) Characterization and evaluation of biochars for their application as a soil amendment. *Aust J Soil Res* 48:516–525
- Sohi S, Lopez-Capel E, Krull E, Bol R (2009) Biochar, climate change and soil: a review to guide future research. CSIRO, Glen Osmond, Australia. Available at <http://www.csiro.au/files/files/poei.pdf>. Accessed 21 August 2012
- Spokas KA, Cantrell KB, Novak JM, Archer DW, Ippolito JA, Collins HP, Boateng AA, Lima AA, Lamb MC, McAloon AJ, Lentz RD, Nichols KA (2012) Biochar: a synthesis of its agronomic impact beyond carbon sequestration. *J Environ Qual* 41:973–989
- Steinbeiss S, Gleixner G, Antonietti M (2009) Effect of biochar amendment on soil carbon balance and soil microbial activity. *Soil Biol Biochem* 41:1301–1310
- Steiner C, Das KC, Garcia B, Förster ZW (2008) Charcoal and smoke extract stimulate the soil microbial community in a highly weathered Xanthic Ferralsol. *Pedobiologia* 51:359–366

- Sun H, Hockaday WC, Masiello CA, Zygourakis K (2012) Multiple controls on the chemical and physical structures of biochars. *Ind Eng Chem Res* 51:3587–3597
- Troeh FR, Thompson LM (2005) *Soils and soil fertility*, 6th edn. Blackwell, Ames
- US EPA United States Environmental Protection Agency (1996) Microwave assisted acid digestion of siliceous and organically based matrices. In: *Test methods for evaluating solid waste, physical/chemical methods*. SW-846, US EPA, Washington. Available at <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/3052.pdf>. Accessed 18 September 2012
- Van Zwieten L, Kimber S, Morris S, Chan KY, Downie A, Rust J, Joseph S, Cowie A (2010) Effects of biochar from slow pyrolysis of paper mill waste on agronomic performance and soil fertility. *Plant Soil* 327:235–246
- Yuan J-H, Xu R-K, Zhang H (2011) The forms of alkalis in the biochar produced from crop residues at different temperatures. *Biores Tech* 102:3488–3497