

EFFECT OF LOW-TEMPERATURE PYROLYSIS CONDITIONS ON BIOCHAR FOR AGRICULTURAL USE

J. W. Gaskin, C. Steiner, K. Harris, K. C. Das, B. Bibens

ABSTRACT. *The removal of crop residues for bio-energy production reduces the formation of soil organic carbon (SOC) and therefore can have negative impacts on soil fertility. Pyrolysis (thermoconversion of biomass under anaerobic conditions) generates liquid or gaseous fuels and a char (biochar) recalcitrant against decomposition. Biochar can be used to increase SOC and cycle nutrients back into agricultural fields. In this case, crop residues can be used as a potential energy source as well as to sequester carbon (C) and improve soil quality. To evaluate the agronomic potential of biochar, we analyzed biochar produced from poultry litter, peanut hulls, and pine chips produced at 400°C and 500°C with or without steam activation. The C content of the biochar ranged from 40% in the poultry litter (PL) biochar to 78% in the pine chip (PC) biochar. The total and Mehlich I extractable nutrient concentrations in the biochar were strongly influenced by feedstock. Feedstock nutrients (P, K, Ca, Mg) were concentrated in the biochar and were significantly higher in the biochars produced at 500°C. A large proportion of N was conserved in the biochar, ranging from 27.4% in the PL biochar to 89.6% in the PC biochar. The amount of N conserved was inversely proportional to the feedstock N concentration. The cation exchange capacity was significantly higher in biochar produced at lower temperature. The results indicate that, depending on feedstock, some biochars have potential to serve as nutrient sources as well as sequester C.*

Keywords. *Agricultural residues, Biochar, Bioenergy, Black carbon, Carbon sequestration, Charcoal, Plant nutrition, Pyrolysis, Soil fertility, Soil organic carbon.*

Pyrolysis of crop residues to produce renewable energy is one option to reduce the use of fossil fuels. Pyrolysis generates biochar, oil, and gas products that can all be used as fuels (Ioannidou and Zabaniotou, 2007). Pyrolytic biochar can also potentially be used as a low-cost sorbent (Ioannidou and Zabaniotou, 2007) or as a soil amendment to improve soil fertility and sequester carbon (Lehmann et al., 2006; Steiner, 2007). Removal of crop residues for energy production can have deleterious effects on soil organic carbon (SOC) and consequently on soil fertility (Lal, 2004). Pyrolysis of crop residues with C returned to the soil in the form of biochar may help maintain or increase stable SOC pools and cycle nutrients back into agricultural fields. Pyrolysis with biochar C sequestration may offer an option to reduce the conflict between cultivating crops for different purposes, e.g., energy vs. C sequestration or food.

There are several lines of evidence that charcoal plays an important role in soil fertility. Charcoal has been identified as an important soil constituent in fertile Chernozems (Schmidt et al., 1999) and in anthropogenic enriched dark

soil (Terra Preta) found throughout the lowland portion of the Amazon Basin (Glaser et al., 2000). Research on tropical soils indicates that charcoal amendments can increase and sustain soil fertility (Steiner et al., 2007). The beneficial effects appear to be related to alterations in soil physical, chemical, and biological properties, such as reduced acidity (Topoliantz et al., 2005), increased cation exchange capacity (CEC) (Cheng et al., 2008; Liang et al., 2006), enhanced nitrogen (N) retention (Lehmann et al., 2003; Steiner et al., 2008b), increased microbiological activity (Steiner et al., 2008a), and increased mycorrhizal associations (Warnock et al., 2007). Research on the effect of wildfire charcoal in forest ecosystems indicates that it stimulates microbial activity (Pietikäinen et al., 2000) and influences nitrogen cycling (Berglund et al., 2004; DeLuca et al., 2006; Wardle et al., 1998). Research also indicates that charcoal is recalcitrant (Seiler and Crutzen, 1980), and it may persist for hundreds or thousands of years.

Charcoals produced from wildfire or traditional charcoal production may have different chemical and physical characteristics from pyrolytic biochars created under specific conditions for energy production. Both feedstock and pyrolysis conditions such as temperature and carrier gas affect the chemical and physical characteristics of biochar (Antal and Grønli, 2003; Bansal et al., 1988; Benaddi et al., 2000; Guo and Rockstraw, 2007a; Strelko et al., 2002). Most of the literature discusses high-temperature biochars that are produced at greater than 500°C or activated carbon typically produced at 800°C. As pyrolysis temperatures increase, volatile compounds in the biochar matrix are lost, surface area and ash increase, but surface functional groups that can provide exchange capacity decrease (Guo and Rockstraw, 2007a).

Submitted for review in August 2008 as manuscript number SW 7634; approved for publication by the Soil & Water Division of ASABE in November 2008.

The authors are **Julia W. Gaskin**, Sustainable Agriculture Coordinator, **Christoph Steiner**, Post-Doctoral Associate, **Keith Harris**, Technician, **K. C. Das**, Associate Professor, and **Brian Bibens**, Research Engineer, Department of Biological and Agricultural Engineering, Driftmier Engineering Center, University of Georgia, Athens, Georgia. **Corresponding author:** Julia W. Gaskin, Department of Biological and Agricultural Engineering, Driftmier Engineering Center, University of Georgia, Athens, GA 30602; phone: 706-542-1401; fax: 706-542-1886; e-mail: jgaskin@engr.uga.edu.

Pyrolysis of nutrient-rich feedstock is likely to produce nutrient-rich biochar, but nutrient conservation and availability in biochars is not well understood. Nutrients susceptible to volatilization such as N are almost completely lost after a burn (Giardina et al., 2000). Whether elements are retained during pyrolysis, the availability of nutrients for plants, and the effect of pyrolysis conditions on these characteristics are unclear. For biochar to be used in agriculture, a better understanding of its properties and how it affects soil fertility is needed. Therefore, our objectives were to determine the effect of feedstock, temperature, and carrier gas on key characteristics of biochar for agricultural use. Specifically, we wished to compare characteristics critical for agricultural use including pH, CEC, total nutrient concentrations, and potentially available nutrient concentrations in biochars from three feedstocks under two temperature regimes using two carrier gases with and without secondary steam activation.

MATERIALS AND METHODS

BIOCHAR PRODUCTION

We selected three common feedstocks to represent a range of physical properties and mineral content: raw poultry litter from broiler houses (*Gallus domesticus*, PL), pelletized peanut hulls (*Arachis hypogaea*, PN), and raw pine chips (*Pinus taeda*, PC). Biochars were produced in a batch pyrolysis unit at two peak temperatures (400°C and 500°C) with either steam or nitrogen (N₂) as a carrier gas. The biochars produced with N₂ as a carrier gas were produced with or without steam activation at the original pyrolysis temperatures (400°C and 500°C). Each of the production combinations (three feedstocks, three pyrolysis types, two temperatures = 18) was replicated three times. The conversion efficiency was calculated as the percentage of the feedstock input (dry weight, DW) and biochar output (biochar DW / feedstock DW).

CHEMICAL ANALYSES

Biochars were ground in a ball mill to pass a 300 µm sieve before nutrient analysis. Feedstock and the biochars were analyzed for total C, N, and sulfur (S) by dry combustion (CNS-2000, Leco Corp., St. Joseph, Mich.). Total minerals were extracted using a closed-vessel microwave digestion with HNO₃ (USEPA method 3050; USEPA, 1994). A Mehlich I extraction (0.05 M HCl + 0.0125 M H₂SO₄) (Mehlich, 1953) was also used on biochar samples as an index of potentially plant-available nutrients. Aluminum, Cu, Ca, Fe, Mg, Mn, P, K, Na, and Zn were measured by inductively coupled plasma spectrometry (ICP, Thermo Jarrell-Ash model 61E, Thermo Fisher Scientific, Waltham, Mass.).

Biochar pH was measured in deionized water using a 1 to 5 wt/wt ratio. Samples were thoroughly mixed and allowed to equilibrate for 1 h. The pH was measured with a digital pH meter (AR15, Thermo Fisher Scientific, Waltham, Mass.).

Cation exchange capacity of the biochar was measured by a modified ammonium-acetate compulsory displacement

(Sumner and Miller, 1996). Samples were leached with deionized water five times before starting the CEC extraction to reduce interference from soluble salts. Twenty mL of deionized water was added to a 1 g sample of biochar in a disposable nalgene 0.45 µm cellulose nitrile filter flask. The flask was placed on an orbital shaker and shaken at 180 rpm for 5 minutes. The sample was vacuum filtered, and the leachate was saved for further analysis. After the fifth wash, 10 mL of Na-acetate (pH 7) was added to the sample, and the mixture shaken for 10 min. This process was repeated three times to ensure that exchange sites were saturated with Na ions. Biochar samples were then washed three times with ethanol to remove excess Na. Sodium ions were displaced with NH₄-acetate (pH 7) three times and measured by atomic adsorption (PE 4100ZL, Perkin Elmer, Waltham, Mass.).

The reserved leachate from the five washings (CEC procedure above) was composited and analyzed for dissolved carbon (DC), dissolved inorganic carbon (DIC), ammonium-nitrogen (NH₄-N), and nitrate-nitrogen (NO₃-N). Dissolved carbon and DIC was measured by combustion (Shimadzu TOC-5050A, Shimadzu, Columbia, Md.). Dissolved organic C (DOC) was calculated by difference (DOC = DC - DIC). Nitrate-nitrogen and NH₄-N were analyzed on an autoanalyzer using cadmium reduction and phenate colorimetric methods (EnviroFlow 3000, Perstorp, Toledo, Ohio).

STATISTICAL ANALYSES

Treatment effects were analyzed by general linear model (GLM) univariate analysis of variance (ANOVA). The detection limit was used for results below the detection limit, if other results were above the limit. This allowed a conservative estimate of the elemental concentration of the biochar. If all results were below the detection limit, then no statistical analysis was performed. Significant differences (p < 0.05) between the feedstock and treatments were separated by the Tukey test. Statistical analyses and plots were performed using SPSS 12.0 and SigmaPlot 8.02 (SPSS, Inc., Chicago, Ill.).

RESULTS AND DISCUSSION

Steam pyrolysis of the peanut hull pellets in the batch reactor presented difficulties due to excessive swelling by the peanut hull feedstock that clogged the reactor. Low-temperature steam pyrolysis in a batch reactor may not be appropriate for this feedstock. Analysis of PC and PL biochars revealed no difference in total nutrients, Mehlich I extractable nutrients, CEC, or pH between steam and N₂ as carrier gas; consequently, we report on the results from pyrolysis with the N₂ carrier gas with or without subsequent steam activation.

INFLUENCE OF FEEDSTOCK

The total element concentrations in the feedstock had the strongest influence on the chemical composition of the

Table 1. Total element concentrations in the three agricultural feedstocks used for pyrolysis at 400°C and 500°C.

Feedstock	Values in g kg ⁻¹										Values in mg kg ⁻¹							
	C	N	P	K	S	Ca	Mg	Al	Fe	Na	Cd	Cr	Cu	Mn	B	Mo	Ni	Zn
Poultry litter (PL)	326	45.1	19.5	29.5	5.8	28.0	5.66	6.32	3.91	9.27	1.4	7.3	381	377.0	49.9	3.5	8.0	414
Peanut hulls (PN)	552	13.6	0.61	5.06	0.9	1.84	0.79	0.92	0.42	0.04	<1	2.0	36.5	44.0	15.2	15.6	1.5	20.2
Pine chips (PC)	571	0.9	0.08	0.59	0	0.75	0.21	0.03	0.13	0.04	<1	2.1	1.7	13.8	2.1	<1.0	<2.0	47.8

Table 2a. Means and standard errors for pH, CEC, and total macronutrient concentrations in poultry litter, peanut hull, and pine chip biochars. Feedstock and temperature columns indicate significant differences ($p < 0.05$, $n = 3$).^[a]

	Poultry Litter (PL)				Peanut Hulls (PN)				Pine Chips (PC)				Feedstock	
	400 °C		500 °C		400 °C		500 °C		400 °C		500 °C			
	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA		
pH (S.U.)	10.1 ±0.04	10.1 ±0.07	9.74 ±0.05	9.88 ±0.09	10.5 ±0.05	10.5 ±0.10	10.1 ±0.02	9.96 ±0.01	7.55 ±0.09	7.99 ±0.09	8.30 ±0.15	8.10 ±0.60	PC<PL<PN	Temp.
CEC (cmol kg ⁻¹)	61.1 ±0.73	57.4 ±1.4	38.3 ±1.7	37.0 ±1.6	14.2 ±0.46	11.7 ±2.04	4.63 ±0.10	4.46 ±0.13	7.27 ±0.54	6.00 ±0.11	5.03 ±0.85	6.02 ±3.12	PC<PN<PL	500<400
C (g kg ⁻¹)	392 ±3.8	399 ±7.4	392 ±8.6	421 ±23	732 ±14	762 ±3.4	804 ±1.7	806 ±5.8	739 ±17	761 ±3.6	817 ±1.9	820 ±17	PL<PN, PC	400<500
N (g kg ⁻¹)	34.7 ±0.79	34.7 ±0.77	30.9 ±0.89	32.3 ±1.6	24.3 ±0.18	24.0 ±0.37	24.8 ±0.89	24.8 ±0.34	2.55 ±0.40	1.95 ±0.06	2.23 ±0.09	2.20 ±0.12	PC<PN<PL	500<400
P (g kg ⁻¹)	30.1 ±0.16	32.2 ±2.3	35.9 ±1.6	34.8 ±2.6	1.83 ±0.11	1.70 ±0.12	1.97 ±0.03	2.06 ±0.11	0.15 ±0.004	0.14 ±0.004	0.14 ±0.02	0.20 ±0.02	PC<PN<PL	400<500
K (g kg ⁻¹)	51.1 ±1.3	52.6 ±4.9	58.6 ±2.9	54.7 ±1.5	15.2 ±0.58	14.40 ±1.40	16.4 ±0.19	16.5 ±0.79	1.45 ±0.06	1.51 ±0.07	1.45 ±0.18	2.25 ±0.25	PC<PN<PL	400<500
Ca (g kg ⁻¹)	42.7 ±0.30	45.7 ±3.0	50.4 ±2.2	49.1 ±3.7	4.62 ±0.06	4.46 ±0.29	5.12 ±0.12	5.21 ±0.20	1.71 ±0.11	1.69 ±0.02	1.85 ±0.14	2.17 ±0.04	PC<PN<PL	400<500
Mg (g kg ⁻¹)	10.7 ±0.23	11.4 ±0.91	12.9 ±0.50	12.4 ±1.0	2.19 ±0.06	2.17 ±0.16	2.50 ±0.05	2.59 ±0.11	0.60 ±0.04	0.58 ±0.03	0.59 ±0.06	0.76 ±0.01	PC<PN<PL	400<500
S (g kg ⁻¹)	13.67 ±0.39	12.3 ±0.09	13.93 ±1.1	13.9 ±0.37	0.56 ±0.02	0.51 ±0.03	0.55 ±0.09	0.37 ±0.09	0.01 ±0.04	0.16 ±0.05	0.06 ±0.01	0.08 ±0.04	PC, PN<PL	

^[a] SA = steam activation.

Table 2b. Means and standard errors for total micronutrient and selected element concentrations in poultry litter, peanut hull, and pine chip biochars. Feedstock and temperature columns indicate significant differences ($p < 0.05$, $n = 3$).^[a]

	Nutrient and pH concentrations in feedstock and temperature columns indicate significant differences (p < 0.05, n = 3).												Feedstock	Temp.
	Poultry Litter (PL)				Peanut Hulls (PN)				Pine Chips (PC)					
	400 °C		500 °C		400 °C		500 °C		400 °C		500 °C			
	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA		
Al (g kg ⁻¹)	9.87 ±1.36	8.12 ±1.59	13.02 ±0.36	14.25 ±1.97	2.40 ±0.07	2.33 ±0.16	2.73 ±0.05	2.81 ±0.13	0.07 ±0.01	0.05 ±0.005	0.07 ±0.01	0.06 ±0.008	PC, PN<PL	400<500
Fe (g kg ⁻¹)	6.06 ±0.52	5.55 ±0.42	8.03 ±0.55	8.89 ±1.27	1.00 ±0.02	0.97 ±0.07	1.15 ±0.02	1.20 ±0.06	0.15 ±0.11	0.04 ±0.007	0.05 ±0.01	0.20 ±0.07	PC, PN<PL	400<500
Na (g kg ⁻¹)	15.1 ±0.31	15.8 ±1.37	17.2 ±1.02	16.6 ±1.12	0.026 ±0.001	0.028 ±0.006	0.035 ±0.004	0.044 ±0.005	<0.014 ±0.004	0.053 ±0.032	0.013 ±0.002	0.075 ±0.054	PN, PC<PL	
B (mg kg ⁻¹)	91.5 ±3.16	96.0 ±8.25	100 ±0.31	93.0 ±3.98	32.5 ±1.57	29.9 ±2.87	33.7 ±0.27	34.1 ±1.15	5.69 ±0.30	6.69 ±0.21	4.21 ±0.62	6.94 ±1.33	PC<PN<PL	
Cd (mg kg ⁻¹)	2.75 ±0.73	<2.65 ±0.83	<1 ±0.10	<1.10 ±0.10	<1.35 ±0.35	<1.35 ±0.35	<1 ±0.35	<1 ±0.35	<1 ±0.35	<1 ±0.35	<1 ±0.35	<1 ±0.35		
Cr (mg kg ⁻¹)	28.0 ±4.1	28.8 ±5.2	59.4 ±3.3	56.1 ±4.5	3.95 ±0.31	3.00 ±0.57	3.63 ±0.31	3.94 ±0.16	<1 ±0.09	1.23 ±0.09	3.43 ±0.88	17.7 ±5.9	PN, PC<PL	400<500
Cu (mg kg ⁻¹)	805 ±23	880 ±49	1034 ±68	943 ±81	16 ±0.60	13 ±1.27	19 ±0.50	19 ±1.84	25 ±7.03	10 ±6.18	9 ±2.34	13 ±5.57	PC, PN<PL	400<500
Mn (mg kg ⁻¹)	596 ±5.6	637 ±37	725 ±29	697 ±46	116 ±2.3	116 ±8.0	131 ±2.3	136 ±5.7	274 ±9.3	269 ±7.8	258 ±30	350 ±4.0	PN<PC<PL	400<500
Mo (mg kg ⁻¹)	17.1 ±5.3	12.1 ±0.41	14.2 ±1.1	13.8 ±1.2	4.78 ±3.6	<1 ±0.35	<1 ±0.35	<1 ±0.35	<1 ±0.35	<1 ±0.35	<1 ±0.35	<4.11 ±3.11	PC, PN<PL	
Ni (mg kg ⁻¹)	13.6 ±0.00	19.5 ±3.7	20.3 ±1.1	29.1 ±8.4	<2.29 ±0.29	<2 ±0	<2 ±0	<10.4 ±8.0	<2 ±0	<2 ±0	<2.91 ±0.55	17.5 ±14.7	PC, PN<PL	
Zn (mg kg ⁻¹)	628 ±12	680 ±41	752 ±28	728 ±50	35 ±2.2	31 ±2.9	37 ±2.1	36 ±0.00	15 ±1.1	16 ±0.7	18 ±0.6	20 ±2.4	PC, PN<PL	400<500

^[a] SA = steam activation; < indicates mean contains results below the detection limit; ±0.00 indicates all results were near instrument detection limit.

biochar. Concentrations of plant nutrients in the feedstocks generally followed the pattern of PC < PN < PL. Feedstock carbon concentrations had the opposite pattern, with PL < PN < PC (table 1).

There were significant differences in C concentrations in the biochar, with PL containing less C than the PN or PC biochar (table 2a). The nutrient-rich poultry litter contains relatively more minerals than the other feedstocks, which

decreases the C content. Nitrogen, P, K, Ca, and Mg concentrations in the biochar were significantly different, with PC < PN < PL (table 2a). The concentration of the micronutrients B, Cu, Fe, Mn, Na, and Zn were significantly higher in PL biochar ($p < 0.05$), but there were no differences detected between the PN and PC biochars except for Mn (table 2b). Concentrations of metals such as Al, Cr, Ni, and Mo were low. The PL biochar contained the highest

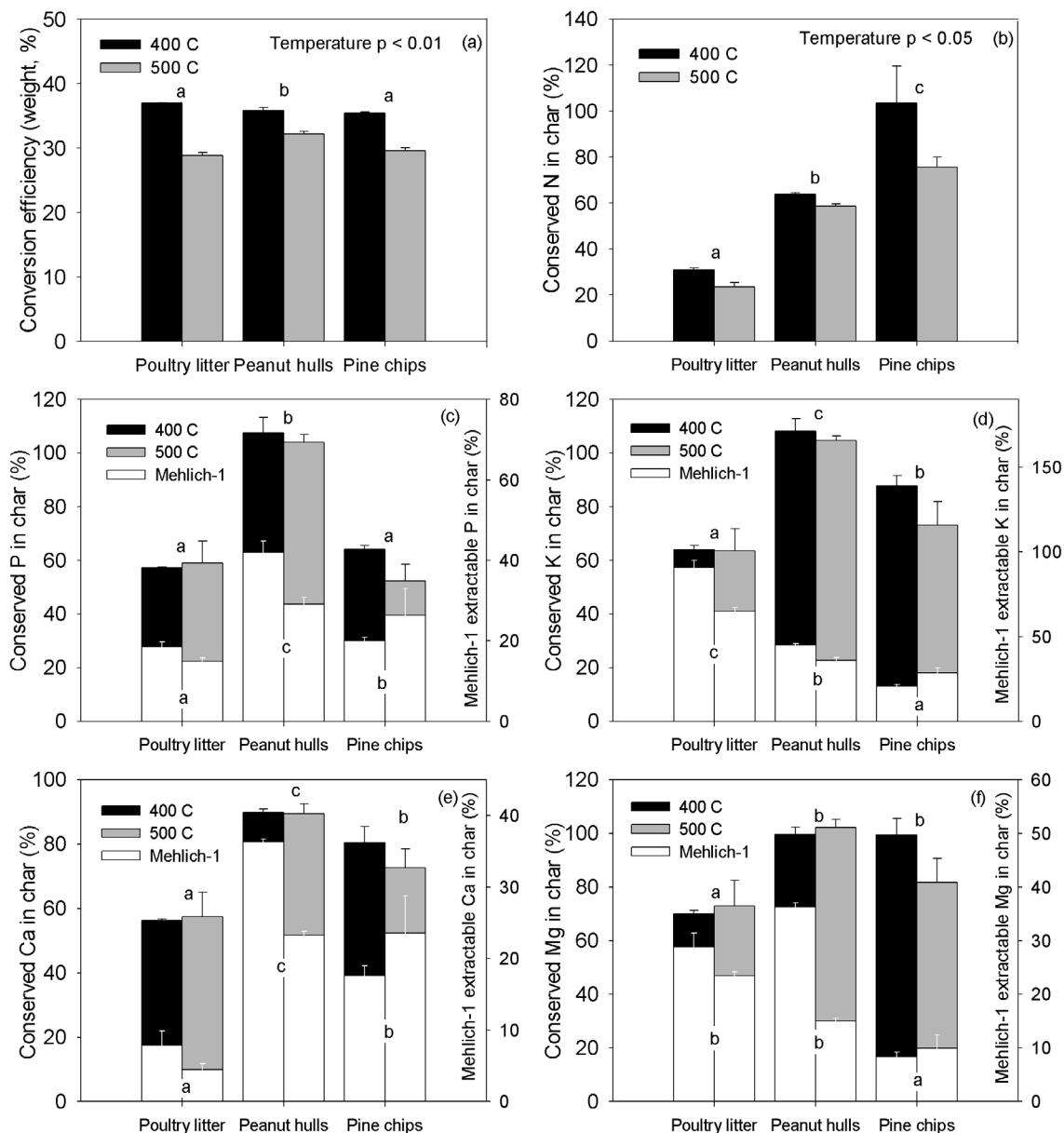


Figure 1. Percentages with standard errors of feedstock nutrients conserved in the biochar and percentages of total nutrients that were Mehlich I extractable at two pyrolysis temperatures and in three biochars. Letters above the columns indicate significant difference of nutrients conserved between biochar types ($p < 0.05$, $n = 3$). Letters within columns indicate significant difference in the percentage of total nutrients that were Mehlich I extractable ($p < 0.05$, $n = 3$).

concentrations of these metals, as would be expected from the higher feedstock concentrations. Cadmium was below the detection limit in PC biochars and near or at the detection limits in PL and PN biochars (table 2b).

The amount of N conserved ranged from 27.4% in the PL biochar to 89.6% in the PC biochar and was inversely proportional to the feedstock N concentration (fig. 1b and table 1). The higher N losses seen from the PL were likely due to the volatilization of the poultry manure $\text{NH}_4\text{-N}$ and easily decomposable N-containing organic compounds in the manure, such as uric acid. In contrast, the low concentration of N in the PC feedstock is likely to be incorporated into complex structures that are not easily volatilized.

About 60% of the P in the PL and PC feedstock was retained in the PL and PC biochar, while nearly 100% of the P in the PN feedstock was retained in the PN biochar (fig. 1c).

In general, the PL biochar had a lower proportion of nutrients retained than the PN or the PC biochar (figs. 1c through 1f). This may be due to a higher proportion of some of these elements retained in the aqueous/bio-oil fraction in PL biochar (K. C. Das, 2007, unpublished data, University of Georgia, Athens, Ga.).

The pattern of Mehlich I extractable concentrations was similar to that of the total nutrient concentrations (tables 3a and 3b). There were significant differences in Mehlich I extractable P, K, Ca, and Mg concentrations, with $\text{PC} < \text{PN} < \text{PL}$. There were differences by feedstock in the percentage of the total nutrients that were Mehlich I extractable (figs. 1a through 1f). Only 19% of the PL biochar P was Mehlich I extractable compared to over 40% in the PN biochar (400°C, fig. 1c). About 90% of the PL biochar K was Mehlich I extractable compared to only 45% in the PN biochar (400°C,

Table 3a. Means and standard errors of the Mehlich I macronutrient concentrations in poultry litter, peanut hull, and pine chip biochars. Feedstock and temperature columns indicate significant differences ($p < 0.05$, $n = 3$).^[a]

and pine chip biochar size feedstock and temperature columns indicate significant differences (p < 0.05; n = 3).														Feedstock	Temp.
Poultry Litter (PL)				Peanut Hulls (PN)				Pine Chips (PC)							
400 °C		500 °C		400 °C		500 °C		400 °C		500 °C					
Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA				
P (g kg ⁻¹)	5.58 ±0.31	4.09 ±1.22	5.33 ±0.18	4.66 ±0.20	0.76 ±0.02	0.67 ±0.06	0.57 ±0.04	0.59 ±0.03	0.03 ±0.002	0.034 ±0.004	0.04 ±0.008	0.06 ±0.03	PC<PN<PL		
K (g kg ⁻¹)	46.2 ±0.96	34.1 ±8.40	38.1 ±2.68	40.0 ±2.81	6.84 ±0.16	6.28 ±0.67	5.91 ±0.28	6.76 ±0.30	0.30 ±0.009	0.38 ±0.02	0.41 ±0.06	0.97 ±0.32	PC<PN<PL		
Ca (g kg ⁻¹)	3.34 ±0.84	1.95 ±0.82	2.21 ±0.36	1.63 ±0.13	1.68 ±0.02	1.48 ±0.15	1.19 ±0.06	1.22 ±0.06	0.30 ±0.04	0.31 ±0.05	0.43 ±0.10	0.39 ±0.16	PC<PN<PL		
Mg (g kg ⁻¹)	3.09 ±0.28	2.19 ±0.68	3.03 ±0.13	2.92 ±0.05	0.80 ±0.03	0.62 ±0.09	0.37 ±0.02	0.39 ±0.01	0.05 ±0.008	0.06 ±0.009	0.06 ±0.01	0.08 ±0.04	PC<PN<PL		

^[a] SA = steam activation.

Table 3b. Means and standard errors of the Mehlich I micronutrient and selected element concentrations in poultry litter, peanut hull, and pine chip biochars. Feedstock and temperature columns indicate significant differences ($p < 0.05$, $n = 3$).^[a]

	Poultry Litter (PL)				Peanut Hulls (PN)				Pine Hips (PC)				Feedstock	Temp.
	400 °C		500 °C		400 °C		500 °C		400 °C		500 °C			
	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA		
Al (g kg ⁻¹)	0.47 ±0.11	11.3 ±2.24	1.43 ±0.31	1.52 ±0.24	330 ±24	585 ±213	1129 ±32	1360 ±51	6.17 ±0.59	6.35 ±0.53	7.53 ±1.12	12.12 ±4.76	PL, PC<PN	400<500
Fe (g kg ⁻¹)	0.66 ±0.21	3.16 ±0.08	0.06 ±0.007	0.19 <i>n</i> = 1	140 ±2.2	142 ±18	197 ±3.8	221 ±11	3.72 ±0.26	4.58 ±0.19	14.6 ±2.89	33.3 ±8.39	PL, PC<PN	400<500
Na (g kg ⁻¹)	9.57 ±0.19	7.08 ±1.61	6.98 ±0.43	7.24 ±0.07	0.02 ±0.001	0.02 ±0.002	0.02 ±0.58	0.03 ±0.002	0.03 ±0.002	0.03 ±0.002	0.03 ±0.005	0.08 ±0.037	PN, PC<PL	
B (mg kg ⁻¹)	16.7 ±1.59	18.8 ±2.05	18.67 ±0.85	20.4 ±0.59	4.20 ±0.12	4.96 ±1.08	3.97 ±0.22	5.84 ±0.66	0.45 ±0.04	0.41 ±0.07	0.52 ±0.07	1.15 ±0.49	PC<PN<PL	
Cr (mg kg ⁻¹)	0.19 ±0.03	0.19 ±0.02	0.14 ±0.01	0.11 ±0.01	<0.04	<0.04	0.41 ±0.04	0.52 ±0.03	<0.06	<0.06	<0.06	<0.06		
Cu (mg kg ⁻¹)	0.40 ±0.06	0.29 ±0.08	<0.08 ±0.02	<0.05 ±0.005	0.67 ±0.04	<0.59 ±0.32	<0.04 ±0.001	<0.04	6.55 ±2.18	2.48 ±0.68	2.70 ±0.89	3.82 ±3.34	PL, PN<PC	
Mn (mg kg ⁻¹)	7.69 ±1.23	8.64 ±1.28	6.75 ±1.03	5.17 ±0.43	24.7 ±0.70	21.2 ±2.33	14.4 ±0.45	16.3 ±0.71	22.6 ±2.61	25.2 ±3.79	24.1 ±6.67	36.2 ±12.5	PL<PN<PC	
Mo (mg kg ⁻¹)	0.87 ±0.19	1.11 ±0.22	1.42 ±0.14	1.94 ±0.19	<0.04	<0.04	<0.04	<0.04	0.15 ±0.002	0.25 ±0.06	0.11 ±0.03	0.65 ±0.35		
Ni (mg kg ⁻¹)	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.2	<0.2	<0.2	<0.2		
Zn (mg kg ⁻¹)	0.06 ±0.01	0.30 ±0.02	0.05 ±0.07	<0.04	10.51 ±1.22	7.36 ±0.59	5.58 ±0.26	6.30 ±0.45	2.20 ±0.17	2.31 ±0.21	1.36 ±0.26	3.66 ±1.17	PL<PC<PN	

^[a] SA = steam activation; < indicates mean contains results below the detection limit.

fig. 1d). Manganese and Zn concentrations were significantly lower in the PL biochar than the PC or PN biochars. Copper, Al, and Fe was also lower in the PL biochar compared to the PN biochar. These patterns are the reverse of that seen in the feedstock or the total element concentrations in the biochars. If pyrolysis can reduce P and other metal availability in poultry litter, it may reduce some of the environmental concerns associated with land application of poultry litter. These results should be interpreted with caution. The Mehlich I extraction, which is a weak double acid extraction, may not have been strong enough to remove these acid-soluble cations under the high pH conditions found in the PL biochar.

The Mehlich I extraction was developed for acidic soils in the southeastern U.S. with low CEC or base saturation (Kuo, 1996), and it is the standard extraction used for plant-available nutrients and fertilizer recommendations in Alabama, Georgia, Florida, South Carolina, Tennessee, and Virginia. In this study, Mehlich I extractable element concentrations were used as an index to compare the

potential for different biomass sources and production techniques to supply plant-available nutrients. The extraction has not been calibrated for biochar and may not reflect actual plant-available nutrient concentrations. However, data from a greenhouse trial using pine chip and peanut hull biochar amendment of three different Ultisols (Speir, 2008) and from a field trial with the same biochars (Gaskin et al., 2007) indicate an increase in Mehlich I K and Mg in soils amended with peanut hull biochar. The increased Mehlich I K in the soil was reflected in an increase of these nutrients in corn tissue (*Zea mays*) in the field trial.

The pH and CEC of the biochars were also significantly influenced by feedstock (table 2a). All the biochars were basic, with the highest pH seen in the PN biochar. Tryon (1948) reported increased soil pH with the addition of pine and hardwood charcoal. He attributed the greater pH increase seen in the hardwood charcoal treatment to the higher ash content, in particular to the hydrolysis of salts of Ca, K, and Mg in the presence of water. In this study, PC biochar had both the lowest total concentrations of these cations and the

Table 4. Means and standard errors of dissolved carbon (DC), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), ammonium-nitrogen (NH₄-N), and nitrate-nitrogen (NO₃-N) in leachate from poultry litter, peanut hull, and pine chip biochars. Feedstock and temperature columns indicate significant differences ($p < 0.05$, $n = 3$).^[a]

	Poultry Litter (PL)				Peanut Hulls (PN)				Pine Chips (PC)				Feedstock	Temp.
	400 °C		500 °C		400 °C		500 °C		400 °C		500 °C			
	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA	Biochar	SA		
DC (g kg ⁻¹)	2.20 ±0.31	1.85 ±0.25	0.85 ±0.01	0.75 ±0.02	0.51 ±0.09	0.40 ±0.02	0.52 ±0.02	0.41 ±0.10	0.13 ±0.10	0.13 ±0.10	0.12 ±0.05	0.19 ±0.07	PC<PN<PL	500<400
DIC (g kg ⁻¹)	0.39 ±0.04	0.44 ±0.04	0.57 ±0.03	0.54 ±0.03	0.32 ±0.03	0.31 ±0.03	0.38 ±0.03	0.37 ±0.04	0.014 ±0.003	0.025 ±0.003	0.034 ±0.005	0.055 ±0.012	PC<PN<PL	400<500
DOC (g kg ⁻¹)	1.81 ±0.34	1.46 ±0.29	0.28 ±0.04	0.21 ±0.04	0.20 ±0.06	0.10 ±0.03	0.14 ±0.03	0.10 ±0.03	0.12 ±0.01	0.10 ±0.01	0.09 ±0.003	0.10 ±0.01	PC, PN<PL	500<400
NH ₄ -N (mg kg ⁻¹)	8.5 ±0.39	6.69 ±0.69	11.3 ±6.41	3.49 ±0.15	2.86 ±0.27	1.94 ±0.01	2.12 ±0.12	2.28 ±0.44	1.75 ±0.29	7.93 ±6.16	2.41 ±0.16	2.37 ±0.08	PN<PL	
NO ₃ -N (mg kg ⁻¹)	<0.4	<0.4	<0.4	<0.4	1.02 ±0.01	1.07 ±0.02	1.27 ±0.06	1.11 ±0.02	<0.4	<0.4	<0.4	<0.4		

^[a] SA = steam activation; < indicates mean contains results below the detection limit.

lowest pH, which would support Tyron's hypothesis; however, the pH of PL biochar was similar to the PN biochar although it contained higher concentrations of total Ca, K, and Mg than PN biochar (table 2).

Higher CEC was associated with higher concentrations of minerals in the feedstock. Mészáros et al. (2007) hypothesized that K, Mg, Na, and P in the biomass may catalyze the formation of oxygen groups on the biochar surface at low pyrolysis temperatures. Oxygen groups such as carboxyls, lactones, and phenols could contribute to the presence of negative surface charges (Boehm, 1994).

Dissolved C concentrations were very low (table 4). Feedstock had a significant effect on DC in the biochar leachate, with PC < PN < PL. Dissolved inorganic C was also affected by feedstock, with PC < PN < PL. The PL biochar had a higher proportion of DOC than PC or PN biochars. The PL feedstock is a combination of wood chip (typically pine) bedding and poultry manure. The manure may contribute to higher DOC leached from the PL biochar.

DOC plays an important role in many soil processes, including serving as an energy source for the microbial community and reacting with other soil solution components (Sposito, 1989). Biochars are known to contain condensed volatile compounds. These compounds are either lost to the gaseous or liquid phase or undergo further reactions to form secondary char at high temperatures (Antal and Grønli, 2003). Garcia-Perez et al. (2007) identified water-soluble compounds from pyrolysis of lignin materials to contain mono- and oligo-sugars, formic and acetic acids, as well as methanol, hydroxyl-acetaldehyde, and 1-hydroxyl-2-propanone. Schnitzer et al. (2007) identified numerous organic compounds in the light and heavy fractions of poultry litter pyrolyzed at 330°C, including N-heterocyclics, substituted furans, phenol and substituted phenols, benzenes and substituted benzenes, as well as aliphatic C chains. It is likely that some of these compounds remain trapped in the biochar pore structure, but few of these compounds appear to be immediately water soluble.

Ammonium-nitrogen in the biochar leachate was also found in very low concentrations (table 4). No NO₃-N was detected in any of the leachates. The NH₄-N concentrations were highest in the leachate from the PL biochar. Fresh poultry litter typically contains about 2.8 g NH₄-N kg⁻¹ (University of Georgia Agricultural and Environmental

Services Laboratory, unpublished data). Small amounts of this NH₄-N may remain trapped, or microbes may have mineralized nitrogen-containing organic compounds in the biochar. Das et al. (2008) found that the liquid products obtained from poultry litter pyrolysis enhanced microbial growth in well water and concluded that N-heterocyclic compounds derived from proteins were responsible for that increase. A small fraction of these compounds may be present in the biochars.

INFLUENCE OF PYROLYSIS TEMPERATURE

The average conversion ratio (biochar weight / feedstock weight) was 33.2%. Biochar yield decreased with increased pyrolysis temperature, and except for N, nutrient concentrations were higher in the biochar produced at 500°C (tables 2a and b). Due to the wide range of initial nutrient concentrations in the feedstock, there were significant interactions between feedstock and temperature for total N, P, Mg, Mn, Cu, Fe, Zn, and Al ($p < 0.05$).

As noted earlier, N was conserved in the biochar (fig. 1b). After forest fires, on average, only 3% of the N in the biomass is found in ash, which contains black carbon or biochar (Giardina et al., 2000). Almendros et al. (2003) found C and N enrichment in charred residues during thermal transformation of peat organic matter. Nitrogen was incorporated into structures resistant to heating at moderate thermal oxidation by aromatization and formation of heterocyclic N (Almendros et al., 2003). Studies of wildfire effects on biomass composition indicate that N begins to volatilize at 200°C, and above 500°C half of the N in organic matter is lost to the atmosphere. Our study indicated that a relatively high proportion of the feedstock N was conserved at low pyrolysis temperatures, and as expected more N was retained in the biochar at 400°C compared to 500°C (fig. 1b).

Knicker et al. (2005) has shown that fire and carbonization can increase the N content of SOC, but the alterations in chemical structure have long-term consequences for N availability (Knicker and Skjemstad, 2000). Field trials of PN and PC biochar as a soil amendment with corn (*Zea mays*) indicate that PN biochar N is not plant available (Gaskin et al., 2007). However, Tagoe et al. (2008) studied N recovery of ¹⁵N-labeled chicken manure and did not find differences in N availability between carbonized and dried chicken manure.

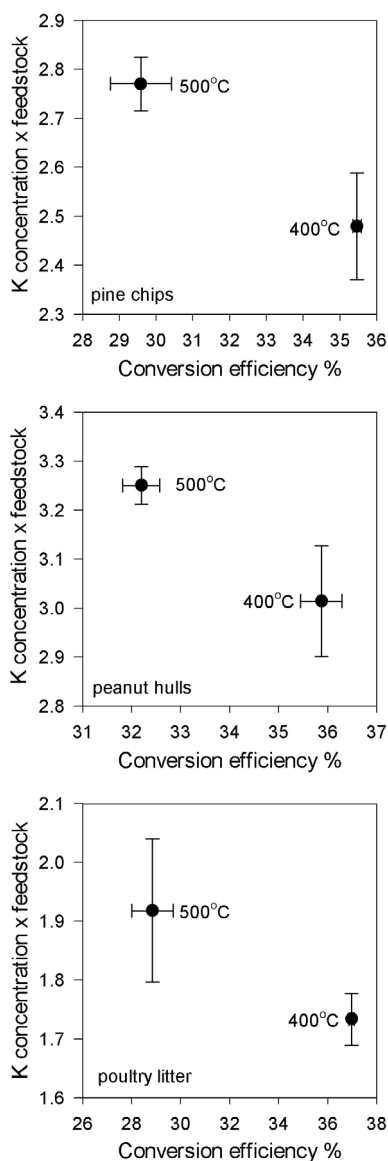


Figure 2. Representative relationship of the ratio of nutrient (K) in the biochar to feedstock and conversion efficiency for pine chip, peanut hull, and poultry litter biochars. Solid circles represent means, and bars indicate standard errors.

The total concentration of other elements (P, K, Ca, and Mg) significantly increased with increasing volatilization losses of C, H, O, and N (tables 2a and 2b). Potassium is representative of the nutrient concentration seen (fig. 2). Potassium and P vaporize at temperatures above 760°C, S and Na need temperatures above 800°C, and Mg and Ca are lost only at temperatures above 1107°C and 1240°C, respectively (Lide, 2004, reviewed by Knicker, 2007). There was a significant interaction between temperature and feedstock for Mehlich I extractable concentrations of these elements ($p = 0.05$). At the low nutrient concentrations seen in the PC biochar, temperature appeared to have little effect. In the PN and PL biochars, Mehlich I extractable nutrients tended to decrease with increasing temperature. Mehlich I extractable Al and Fe were significantly increased in the 500°C biochar (table 3b).

The CEC of biochar produced at 500°C was significantly less than that produced at 400°C (table 2a, $p < 0.01$). There was a significant interaction between feedstock and temperature. In general, the literature indicates the loss of surface functional groups with the increase in pyrolysis temperature. Guo and Rockstraw (2007b) showed that the number of acidic functional groups decreased with increasing temperature. The highest decrease occurred between 300°C and 400°C, and the loss of these acidic groups slowed after 400°C. This process may have contributed to the lower CEC seen at higher temperatures. Iyobe et al. (2004) indicated that lignin and cellulose undergo thermolysis at 400°C to 500°C, which creates acidic functional groups such as carboxyls and phenolic hydroxyls. Chun et al. (2004) found decreasing acidity and increasing basicity with increasing pyrolysis temperature.

Temperature influenced DC (table 4). The higher temperature reduced the concentration of organic C but increased inorganic C significantly.

INFLUENCE OF STEAM ACTIVATION

Steam activation had little effect on the studied parameters (tables 2a, 2b, 3a, 3b, and 4). Production technology is known to influence physical parameters, and steam can improve the yield and surface characteristics at elevated pressures and temperatures (Antal and Grønli, 2003). At the relatively low pyrolysis temperatures used in this study, we only found significantly higher C and Mehlich I extractable B concentrations in steam-activated biochar ($p < 0.05$).

CONCLUSIONS

Pyrolytic biochar has the potential to be used in agricultural production to sequester carbon and serve as a fertilizer. Although pyrolysis conditions are known to affect the chemical and physical characteristics of biochar, at the relatively low pyrolysis temperatures used in this study, feedstock characteristics had the greatest influence on key agricultural characteristics. Carbon concentrations in the biochars decreased with increasing mineral content of the feedstock. Little DC was leachable from the fresh biochar. A high proportion of the feedstock N was conserved in the biochar; however, the N may not be plant available. Nutrients such as P, K, and Ca are extractable with a weak double acid extractant and may be plant available.

The higher pyrolysis temperature increased nutrient concentrations, except for N, but decreased CEC. Recent literature has shown that natural long-term oxidation of biochar in the soil increases the amount of negative charges on the biochar surface (Cheng et al., 2008). Development and optimization of pyrolysis and post-production treatments to increase CEC or available nutrients is important in order to increase the immediate benefits of biochar applications in agriculture.

ACKNOWLEDGEMENTS

This work was conducted with funding from the State of Georgia and the U.S. Department of Energy. We wish to thank Dr. Jim Kastner for his helpful comments on various ideas in the manuscript, and Mr. Roger Hilten for assistance with this project.

REFERENCES

- Almendros, G., H. Knicker, and F. J. González-Vila. 2003. Rearrangement of carbon and nitrogen forms in peat after thermal oxidation as determined by solid-state ^{13}C and ^{15}N NMR spectroscopy. *Org. Geochem.* 34(11): 1559-1568.
- Antal, M. J., and M. Grønli. 2003. The art, science, and technology of charcoal production. *Ind. Eng. Chem. Res.* 42(8): 1619-1640.
- Bansal, R. C., J. Donnet, and F. Stoeckli. 1988. *Active Carbon*. New York, N.Y.: Marcel Dekker.
- Benaddi, H., T. J. Bandosz, J. Jagiello, J. A. Schwarz, J. N. Rouzaud, D. Legras, and F. Beguin. 2000. Surface functionality and porosity of activated carbons obtained from chemical activation of wood. *Carbon* 38(5): 669-674.
- Berglund, L. M., T. H. DeLucca, and O. Zackrisson. 2004. Activated carbon amendments to soil alters nitrification rates in Scots pine forests. *Soil Biol. Biochem.* 36(12): 2067-2073.
- Boehm, H. P. 1994. Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon* 32(5): 759-769.
- Cheng, C.-H., J. Lehmann, and M. H. Engelhard. 2008. Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. *Geochim. Cosmochim. Acta* 72(6): 1598-1610.
- Chun, Y., G. Sheng, C. T. Chiou, and B. Xing. 2004. Compositions and sorptive properties of crop residue-derived chars. *Environ. Sci. Tech.* 38(17): 4649-4655.
- Das, K. C., M. Garcia-Perez, B. Bibens, and N. Melear. 2008. Slow pyrolysis of poultry litter and pine woody biomass: Impact of chars and bio-oils on microbial growth. *J. Environ. Sci. Health A* 43(7): 714-724.
- DeLuca, T. H., M. D. M. Kenzie, M. J. Gundale, and W. E. Holben. 2006. Wildfire-produced charcoal directly influences nitrogen cycling in ponderosa pine forests. *SSSA J.* 70(2): 448-453.
- Garcia-Perez, M. A., H. Chaala, H. Pakdel, D. Kretschmer, and C. Roy. 2007. Characterization of bio-oils in chemical families. *Biomass Bioenergy* 31(4): 222-242.
- Gaskin, J. W., R. A. Speir, K. R. Harris, R. D. Lee, L. M. Morris, and K. C. Das. 2007. Effect of two types of pyrolysis chars on corn yield, soil nutrient status, and soil C in loamy sand soil of the southeastern United States. Madison, Wisc.: ASA-CSSA-SSSA International Meetings.
- Giardina, C. P., R. L. Sanford, I. C. Dockersmith, and V. J. Jaramillo. 2000. The effects of slash burning on ecosystem nutrients during the land preparation phase of shifting cultivation. *Plant Soil* 220(1-2): 247-260.
- Glaser, B., E. Balashov, L. Haumaier, G. Guggenberger, and W. Zech. 2000. Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region. *Org. Geochem.* 31(7-8): 669-678.
- Guo, Y., and A. D. Rockstraw. 2007a. Physicochemical properties of carbons prepared from pecan shell by phosphoric acid activation. *Bioresource Tech.* 98(8): 1513-1521.
- Guo, Y., and D. A. Rockstraw. 2007b. Activated carbons prepared from rice hull by one-step phosphoric acid activation. *Microporous Mesoporous Mat.* 100: 12-19.
- Ioannidou, O., and A. Zabaniotou. 2007. Agricultural residues as precursors for activated carbon production: A review. *Renew. Sustain. Energy Rev.* 11(9): 1966-2005.
- Iyobe, T., T. Asada, K. Kawata, and K. Oikawa. 2004. Comparison of removal efficiencies for ammonia and amine gases between woody charcoal and activated carbon. *J. Health Sci.* 50(2): 148-153.
- Knicker, H. 2007. How does fire affect the nature and stability of soil organic nitrogen and carbon? A review. *Biogeochem.* 85(1): 91-118.
- Knicker, H., and J. O. Skjemstad. 2000. Nature of organic carbon and nitrogen in physically protected organic matter of some Australian soils as revealed by solid-state ^{13}C and ^{15}N NMR spectroscopy. *Australian J. Soil Res.* 38(1): 113-127.
- Knicker, H., F. J. Conzález-Vila, O. Polvillo, J. A. González, and G. Almendros. 2005. Fire-induced transformation of C- and N-forms in different organic soil fractions from a dystric cambisol under a Mediterranean pine forest (*Pinus pinaster*). *Soil Biol. Biochem.* 37(4): 701-718.
- Kuo, S. 1996. Phosphorus: Part 3. Chemical methods. In *Methods of Soil Analysis*, 869-919. Madison, Wisc.: SSSA and ASA.
- Lal, R. 2004. Soil carbon sequestration impacts on global climate change and food security. *Science* 304(5677): 1623-1627.
- Lehmann, J., J. P. da Silva Jr., C. Steiner, T. Nehls, W. Zech, and B. Glaser. 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(2): 343-357.
- Lehmann, J., J. Gaunt, and M. Rondon. 2006. Bio-char sequestration in terrestrial ecosystems: A review. *Mit. Adapt. Strat. Global Change* 11(2): 403-427.
- Liang, B., J. Lehmann, D. Solomon, J. Kinyangi, J. Grossman, B. O'Neill, J. O. Skjemstad, J. Thies, F. J. Luizão, J. Petersen, and E. G. Neves. 2006. Black carbon increases cation exchange capacity in soils. *SSSA J.* 70(5): 1719-1730.
- Mehlich, A. 1953. Determination of P, Ca, Mg, K, Na, and NH_4 . Mimeo 1953. Raleigh, N.C.: North Carolina Department of Agriculture, North Carolina Soil Test Division.
- Mészáros, E., E. Jakab, G. Varhegyi, J. Bourke, M. Manly-Harris, T. Nunoura, and M. J. Antal. 2007. Do all carbonized charcoals have the same chemical structure? 1. Implications of thermogravimetry: Mass spectrometry measurements. *Ind. Eng. Chem. Res.* 46(18): 5943-5953.
- Pietikäinen, J., O. Kiikkilä, and H. Fritze. 2000. Charcoal as a habitat for microbes and its effect on the microbial community of the underlying humus. *Oikos* 89(2): 231-242.
- Schmidt, M. W. I., J. O. Skjemstad, E. Gehrt, and I. Kögel-Knabner. 1999. Charred organic carbon in German chernozemic soils. *European J. Soil Sci.* 50(2): 351-365.
- Schnitzer, M. I., C. Monreal, G. Jandl, P. Leinweber, and P. B. Fransham. 2007. The conversion of chicken manure to biooil by fast pyrolysis: II. Analysis of chicken manure, biooils, and char by curie-point pyrolysis-gas chromatography/mass spectrometry. *J. Environ. Sci. Health B* 42(1): 79-95.
- Seiler, W., and P. J. Crutzen. 1980. Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning. *Climatic Change* 2(3): 207-247.
- Speir, R. A. 2008. Use of pyrolysis char in southeastern soils. MS thesis. Athens, Ga.: University of Georgia, Warnell School of Forestry and Natural Resources.
- Sposito, G. 1989. *The Chemistry of Soils*. New York, N.Y.: Oxford University Press.
- Steiner, C. 2007. Slash and char as alternative to slash and burn: Soil charcoal amendments maintain soil fertility and establish a carbon sink. PhD diss. Bayreuth, Germany, University of Bayreuth, Faculty of Biology, Chemistry and Geosciences.
- Steiner, C., W. G. Teixeira, J. Lehmann, T. Nehls, J. L. V. d. Macêdo, W. E. H. Blum, and W. Zech. 2007. Long-term effects of manure, charcoal, and mineral fertilization on crop production and fertility on a highly weathered central Amazonian upland soil. *Plant Soil* 291(1-2): 275-290.
- Steiner, C., K. C. Das, M. Garcia, B. Förster, and W. Zech. 2008a. Charcoal and smoke extract stimulate the soil microbial community in a highly weathered xanthic ferralsol. *Pedobiologia* 51(5-6): 359-366.
- Steiner, C., B. Glaser, W. G. Teixeira, J. Lehmann, W. E. H. Blum, and W. Zech. 2008b. Nitrogen retention and plant uptake on a highly weathered central Amazonian ferralsol amended with compost and charcoal. *J. Plant Nutrition Soil Sci.* (in press).
- Strelko, V., D. J. Malik, and M. Streat. 2002. Characterisation of the surface of oxidized carbon adsorbents. *Carbon* 40(1): 95-104.
- Sumner, M. E., and W. P. Miller. 1996. Cation exchange capacity and exchange coefficients. In *Methods of Soil Analysis*, 1201-1230. Madison, Wisc.: SSSA and ASA.

- Tagoe, S. O., T. Horiuchi, and T. Matsui. 2008. Effects of carbonized and dried chicken manures on the growth, yield, and N content of soybean. *Plant Soil* 306: 211-220.
- Topoliantz, S., J.-F. Ponge, and S. Ballof. 2005. Manioc peel and charcoal: A potential organic amendment for sustainable soil fertility in the tropics. *Biol. Fert. Soils* 41(1): 15-21.
- Tryon, E. H. 1948. Effect of charcoal on certain physical, chemical, and biological properties of forest soils. *Ecol. Mono.* 18(1): 81-115.
- USEPA. 1994. Methods for the determination of metals in environmental samples. Supplement I EPA-600/R-94/111/May 1994. Cincinnati, Ohio: U.S. EPA, Environmental Monitoring Systems Laboratory.
- Wardle, D. A., O. Zackrisson, and M. C. Nilsson. 1998. The charcoal effect in boreal forests: Mechanisms and ecological consequences. *Oecologia* 115(3): 419-426.
- Warnock, D. D., J. Lehmann, T. W. Kuyper, and M. C. Rillig. 2007. Mycorrhizal responses to biochar in soil: Concepts and mechanisms. *Plant Soil* 300: 9-20.

