



Carbon mineralization in two ultisols amended with different sources and particle sizes of pyrolyzed biochar



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HIGHLIGHTS

- Sources and particle sizes of biochars influenced biochar mineralization and stability.
- Stability of biochar in soil is salient feature to evaluate its use as C sequestration tool.
- Biochar processed into pellets and dust-sized had significant effect on its mineralization.
- Site specific application is an effective use of biochar as a soil amendment.

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ABSTRACT

Biochar produced during pyrolysis has the potential to enhance soil fertility and reduce greenhouse gas emissions. The influence of biochar properties (e.g., particle size) on both short- and long-term carbon (C) mineralization of biochar remains unclear. There is minimal information on the potential effects of biochar particle sizes on their breakdowns by soil microorganism, so it is unknown if the particle size of biochar influences C mineralization rate and/or stability in soils. In order to evaluate the effect of different sources (**BS**) and particle sizes (**BF**) of biochar on C loss and/or stability in soils, an incubation study on C mineralization of different biochar sources and particle sizes was established using two soils (**ST**): Norfolk soil (fine loamy, kaolinitic, thermic, typic Kandiudults) and Coxville soil (fine loamy kaolinitic, thermic, Paleaquults). In separate incubation vessels, these soils were amended with one of two manure-based biochars (poultry litters, **PL**; swine solids, **SS**) or one of two lignocellulosic-based biochars (switchgrass, **SG**; pine chips, **PC**) which were processed into two particle sizes (dust, <0.42 mm; pellet, >2 mm). The amount of CO₂ evolved varied significantly between soils ($p \leq 0.0001$); particle sizes ($p \leq 0.0001$) and the interactions of biochar source ($p \leq 0.001$) and forms of biochars ($p \leq 0.0001$) with soil types. Averaged across soils and sources of biochar, CO₂-C evolved from dust-sized biochar (281 mg kg⁻¹) was significantly higher than pellet-sized biochar (226 mg kg⁻¹). Coxville soils with SS biochar produced the greatest average CO₂-C of 428 mg kg⁻¹ and Norfolk soils with PC had the lowest CO₂-C production (93 mg kg⁻¹). Measured rates of carbon mineralization also varied with soils and sources of biochar (Norfolk: PL > SS > SG ≥ PC; Coxville: PC > SG > SS > PL). The average net CO₂-C evolved from the Coxville soils (385 mg kg⁻¹) was about threefold more than the CO₂-C evolved from the Norfolk soils (123 mg kg⁻¹). Our results suggest different particle sizes and sources of biochar as well as soil type influence biochar stability.

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1. Introduction

Intensive crop production depletes nutrients and reduces organic carbon from soils. A potential solution is the use of biochar as a soil amendment to enhance soil fertility and offset expenses for fertilizer and lime (Forbes et al., 2006; Lehmann et al., 2006;

Fowles, 2007; Novak et al., 2009a,b; Busscher et al., 2010; Novak and Busscher, 2012). An increase in soil fertility is the most frequently reported benefit linked to adding biochar to soils (Manya, 2012; Novak et al., 2012). However, the relationship between biochar properties and its potential to enhance agricultural soils is still unclear and does not allow the establishment of appropriate process conditions to produce a biochar with desired characteristics (Hammes et al., 2008; Sanchez et al., 2009; Brewer et al., 2009; Keiluweit et al., 2010; Manya, 2012). Past research has shown organic residues added to soils to improve soil organic C

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content and fertility levels in the southeast Coastal Plain region have made minimal gains because materials decompose easily due to the region's sandy-textured soils, warm climate and abundant rainfall (Novak and Busscher, 2012).

There is also interest in its role as a biomass-energy sources and as a carbon (C) sinks that could be an important step toward greenhouse gas emission mitigation and soil organic matter conservation (Glasser et al., 2002; Fowles, 2007; Laird, 2008; Gaunt and Lehmann, 2008; Schahczenski, 2010; Qayyum et al., 2012). Due to its relative recalcitrance, biochar may contribute to the refractory soil organic C pool that can decrease atmospheric CO₂ concentrations, thus decreasing effects of global warming (Lehman, 2007; Mathews, 2008; Luo et al., 2011).

The stability of biochar in soil is a salient feature to evaluate the potential use of biochar as sequestration tool. The influence of biochar properties (e.g., particle size, surface chemistry) on the short- and long-term C mineralization of biochar remains unclear. Flavel and Murphy (2009) reported that C mineralization varied between various organic amendments including poultry manure, green waste compost, straw compost and vermicompost, which they attributed to differences in C quality as measured by ¹³C Nuclear Magnetic Resonance (NMR) Spectroscopy. Bruun et al. (2008) reported that CO₂ evolution from plant materials proceeds with a lag phase, followed by a period of higher evolution and finally a period of very low evolution. Evolution of CO₂ from the biochar showed no lag phase, but a period of faster evolution for the first 5–8 days, followed by a period of slow evolution. Steinbeiss and Gleixner (2009) noticed the mean residence times for biochar varied between 4 and 29 years depending on soil type and quality of biochar.

Other researchers have reported that biochar degradation rate is controlled more strongly by combustion temperature and duration than source materials (Zimmerman, 2010). Bruun et al. (2008) reported that mineralization of charcoal appeared to decrease with increasing production temperature. Baldock and Smernik (2002) found that 20%, 13%, and 2% of the C in red pine (*Pinus resinosa*) wood uncharred or charred at 150 and 350 °C, respectively, was re-mineralized after four months. They further reported that for biochar produced from red pine wood, an inversely proportional relationship between pyrolysis peak temperature and C mineralization. More recently, Nguyen et al. (2010) reported strong influences of both water regimes and temperature on mineralization of biochar; whereas Qayyum et al. (2007) observed different C mineralization rates of a wheat (*Triticum aestivum*) straw-derived biochar for three types of soils (Ferrasols, topsoil Lixisols, and subsoil Lixisols). During 60-day microbial incubations, Hamer et al. (2004) measured a 0.8%, 0.7%, and 0.3% C loss derived from maize (*Zea mays*), rye (*Secale cereal*; 350 °C, 2 h) and oak (*Quercus velutina*; 800 °C, 22 h), respectively, as recorded by CO₂ evolution.

Feedstocks including agricultural crop waste, manure, and wood waste materials that serve as the biochar source are often pulverized into smaller particles to improve the thermal conversion process (Laird, 2008; Lehmann and Joseph, 2009; Sohi and Lopez-Capel, 2009). The particle size of biochars is an important characteristic for its ability to react with soil particles (Laird et al., 2009) and is believed to impact its resistance to microbial mineralization (Manya, 2012). There is minimal information concerning biochar particle size on its breakdown by soil microorganisms, so it remains largely unknown if particle size significantly influences its mineralization rate and its stability in soils. In soil, biochar can be degraded by both photochemical and microbiological processes, as reported in a relatively small number of short-term incubations studies (Hamer et al., 2004; Cheng et al., 2006; Novak et al., 2009a,b; Novak and Busscher, 2012).

We hypothesize that feedstock processed into pellets will have lower rate of C mineralization in soils compared with dust-size

biochar particles from the same feedstock. To successfully evaluate the potential of using biochar in sequestration and in enhancing soil fertility for both short- and long-term benefits, it is necessary to know their decomposition rate within the soil. The objective of this study was to compare C mineralization in two Ultisols (Norfolk and Coxville) soils amended with different sources and particle sizes of biochars.

2. Materials and methods

2.1. Soil and site description

Two soil series were used in this experiment: the Norfolk (fine loamy, kaolinitic, thermic, Typic Kandudult) and Coxville (fine loamy kaolinitic, thermic, Paleaquult) soil series. Both soils series belong to the Ultisols order (US Soil Taxonomy) formed in extensively weathered Coastal Plain marine sediments with the clay fraction dominated by kaolinite. The Norfolk is a well drained soil located in upland while the Coxville is a poorly-drained soil positioned in closed depressional areas (Daniels et al., 1999). Both soil series were collected from the Clemson University, Pee Dee Research and Education Center, Darlington, South Carolina. The collection site has a long history of row crop production (>30 yrs), which in 2007, was converted to switchgrass (*Panicum virgatum*) production.

The Ap horizons of the Norfolk and Coxville soils were collected in 2011 and 2012, respectively, using a front-end loader to remove the top 15 cm of soil. The soil samples were air-dried; and then passed through a 2 mm sieve to remove plant material and large aggregates. Particle size analyses were carried out using the hydrometer method (Soil Characterization Laboratory, The Ohio State University, Columbus, Ohio). Both the Norfolk and Coxville Ap soils organic carbon (SOC) and total nitrogen (TN) contents were measured using a LECO Truspec analyzer (LECO Corp., St. Joseph, Michigan). Table 1 summarized some selected soil chemical and mineralogical properties of two soils used in the study.

2.2. Feedstock description, biochar production, and characterization

The feedstocks used in this study were collected from agricultural and forestry operations located in the southeastern USA Coastal Plain region. Switchgrass (SG; *Panicum virgatum*) and pine chips (PC; *Pinus taeda*) were collected in Florence and Berkley County, SC respectively, while poultry litter (PL) was collected in Orangeburg County, SC. The separated swine solids (SS) were obtained from a swine waste treatment system located in Sampson County, NC (Cantrell et al., 2012). Selected chemical properties of biochars used in the study are presented in Table 2.

The PC and SG samples were both mechanically processed using a hammermill into 6-mm flakes. These materials had a moisture content average of 6.3% by weight. The PL had a moisture content of 22.9% by weight. The separated SS underwent sequential air drying and heating at 60 °C until moisture content of 29.6% by weight was achieved. For both manures, large aggregates were broken using a spade until an even visual distribution of particle size. For the SS, once the large aggregates were broken, it was ready for pelletization. Biochar dimensions were determined via light microscopy using an Epson Perfection V500 flatbed scanner and ImageJ software from the National Institute of Health (<http://rsbweb.nih.gov/ij/>). Pellets samples were weighed then placed on a flat glass plate and scanned at 600 dots per inch. The dust was dropped from a height of 10 cm onto a microscope slide to get a dispersed pattern. The mass of the slide was subtracted from the mass of the empty slide and then the slide was scanned at 12,800 dots per inch. The images were smoothed using ImageJ

Table 1

Selected soil chemical and mineralogical properties of two soils used in the study.

Soil series	pH (H ₂ O)	Soil organic carbon (g kg ⁻¹)	Total nitrogen (g kg ⁻¹)	Sand (g kg ⁻¹)	Silt (g kg ⁻¹)	Clay (g kg ⁻¹)	Mineralogy of clay (<2- μ m) fraction
Coxville	5.06	26.3	1.8	421	434	145	Kaolinite, chlorite, quartz
Norfolk	5.93	3.9	bd ^a	807	167	26	Kaolinite, chlorite, quartz

^a Below detection limit of 0.1 g/100 g.**Table 2**

Selected chemical properties of biochar used in the study.

Feedstock	pH (H ₂ O)			Compositional analyses (g kg ⁻¹)		
	Pellet	Dust	Ash	C	N	C/N
Pine chip	5.3	6.0	179	787	3.7	213:1
Poultry litter	9.4	9.9	326	511	56.1	9:1
Swine solids	6.4	7.3	333	504	65.6	8:1
Switchgrass	6.0	6.4	32.1	755	5.2	145:1

software to prevent aliasing, and analyzed using the method outlined by Pordesimo (2010) to obtain dimension statistics on each sample. For analysis, the minimum threshold for pellets was set at 0.04 mm² because any particles this small would have been rejected by the pelletization process, while the minimum size for dust was set at 0.0004 mm² because any particles smaller than silt would likely go airborne during handling. Pellet surface area was calculated assuming each particle had a shape of a lateral spheroid.

Cylindrical-shaped pellets from the four feedstocks were produced by raising their total moisture content to 30% by weight using deionized H₂O and pelletizing using a PP200 pellet mill (Pellet Pros, Inc. Davenport, Iowa) equipped with a 6-mm die and roller set. Pelletization of pine chips and switchgrass flakes required the addition of a 50:50 (w:w) mixture of deionized H₂O and commercial vegetable oil (soybean-based) during the process to act as a lubricant for pellet extraction from the mill.

Biochars were produced from each of the pelletized feedstocks using a slow pyrolysis procedure at 350 °C (Cantrell and Martin, 2012). After pyrolysis, all biochar pellets were passed through a 2-mm sieve, and the portion remaining on the sieve is referred to as pellets. A subsample of the biochar pellets was further ground to pass through a 0.42 mm sieve and is referred to a dust-sized material. Photos (magnified 1.6–1.9) of pelleted and dust-sized biochars used in the study are shown in Fig. 1.

The pH of all pelletized biochars was measured using a 1:2 (v/v) biochar:deionized H₂O mixture after a 2 h shaking at 200 rpm. The biochars ash, C and N contents were determined on an oven dry-weight basis by Hazen Research, Inc. (Golden, Colorado), following the ASTM D1372 and 3176 standard method (ASTM, 2006). The C:N ratio for each biochar sample was then calculated using the individual C and N contents.

2.3. Biochar incubation and mineralization in soils

The soil:biochar treatments were prepared by weighing 200 g of air-dried Norfolk and Coxville soil into a plastic sealable bag and then adding 2.0 g of biochar for a 1% (w/w) mixture. Each bag was then gently mixed by hand and spread out onto wax paper. To the Norfolk soil with biochar added, 20 g of degassed deionized H₂O was added, and the samples were gently mixed using a trowel to obtain a soil moisture content of 10% (w/w). A 50 g portion (corrected for H₂O) of the soil + biochar mixture was transferred into a sterile 250 mL glass incubation bottle (autoclaved) and sealed using a plastic cap equipped with a 3 mm thick Teflon lined silicon septa. After sealing, each incubation bottle was weighed. A similar technique was used for the Coxville + biochar treatments, except 30 g of deionized H₂O was used for a moisture content of 15%

(w/w). Unamended Norfolk and Coxville soils (no biochar) served as control. All soils with biochar treatments along with the controls were set up in triplicate. Additionally, triplicate bottles containing no soil or biochar were assembled for quantifying background CO₂ concentrations in the headspace. All bottles were then placed in a randomized pattern in an incubator at 25 °C and incubated for 50 days.

Periodically, each bottle was removed from the incubator for headspace gas sampling. Prior to headspace gas sample removal, the head pressure in each incubation vessel was measured and then was pressurized by injecting 5 mL of He. This procedure assured a minimal pressure vacuum was created in the vessel in response to removing a 5 mL aliquot of the headspace gas. Subsequently, headspace CO₂ concentrations were corrected for this He addition. The 5-mL headspace sample contained within the gas-tight syringe was then injected into a 10-mL headspace vial capped with 3-mm thick Teflon-lined silicon septa. The headspace vials were then placed into an automatic injector rack of a Combi-Pal auto-sampler installed on a Bruker 450 (Bruker Daltonics, Billerica, Massachusetts) gas chromatograph (GC). The GC oven was run in an isocratic mode at 40 °C. It was equipped with a model 1041 injector operating at 50 °C and 263 kPa. Five-mL of vial headspace gas was injected using a Combi-Pal autosampler equipped with a CTC Analytical headspace syringe. The gas flow proceeded through a 1.8 m long × 1.6 cm outside diameter column packed with 80/110 mesh Hay Sep Q (Varian Inc. Austin, Texas) using He at a flow rate of 55 mL min⁻¹. Carbon dioxide in the sample was detected using a thermal conductivity detector operating at 150 °C with a filament temperature of 200 °C. Headspace CO₂ peaks were corrected for background CO₂ and were then quantified relative to external standards.

After sampling the headspace gas, all incubation bottles were uncapped and remained open for 2 h to exchange their past atmosphere with new room air. The bottles were then re-weighed and adjusted back to their initial weight using deionized H₂O, ensuring that any soil moisture lost during headspace gas exchange was replaced.

2.4. Experimental design and data analyses

To determine the effect of different sources and particle sizes of biochar on C mineralization in two Ultisols soils, a three-factor experimental design (2 × 4 × 2) was followed. The two soil types (Norfolk and Coxville) was the main treatment while four sources of biochars (PC, PL, SG and SS) and two forms of biochars (pelleted and dust-sized) were the sub-treatments, respectively. The mean CO₂-C concentrations evolved were sorted and compared using a Duncan's Multiple Range Test via a SAS PROC ANOVA (v10. SAS Institute, Cary, NC). In these analyses, the sources of variation were soil types (**ST**), biochar sources (**BS**), biochar forms (**BF**), and interaction among these treatment variables. Additionally, to assess the statistical difference of biochar mineralization between the two Ultisols, means of CO₂-C were sorted by soils using PROC SORT. Finally, CO₂-C mineralization rate constants were calculated using linear regression analyses with the mean rate constants sorted by soil series. They were tested for significant differences using an ANOVA at a *P* < 0.05 level of significance.

3. Results

3.1. Soil cumulative carbon dioxide–carbon evolution

The cumulative amount of CO₂-C evolution from the Norfolk and Coxville soils were generally higher in biochar-amended soils (especially in the Coxville soil with dust-sized biochars) than in control soils (Table 3). The cumulative CO₂-C evolutions from the Norfolk and Coxville soil amended with dust-sized biochars were significantly higher than the amount of CO₂-C evolution from both soils amended with pelleted biochars. By the end of day 50, total CO₂-C evolution (mg kg⁻¹) from the Norfolk and Coxville soils with dust-sized biochars were in the order: PL (422) > SS (312) > SG (271) > PC (195) and SS (953) > PC (884) > SG (787) > PL (681), respectively. The order for the Norfolk and Coxville soils with pelleted biochars were: PL (301) > SG (245) > SS (222) > PC (207) and PC (749) > SG (744) > SS (718) > PL (489), respectively (Table 3). Table 4 showed the significant interaction effects of soil types with the different sources and forms of biochars on CO₂-C evolutions. However, the interaction effects among ST, BS and BF on CO₂-C

evolutions failed to reach any level of statistical significance (Table 4).

A comparison between soil types shows the Coxville soil had greater CO₂-C evolution (dust, 826 mg kg⁻¹; pellet, 675 mg kg⁻¹) than the Norfolk soil (dust, 300 mg kg⁻¹; pellet, 244 mg kg⁻¹). The average cumulative CO₂-C evolution from the Coxville was about 781 mg kg⁻¹ or about 176.2% more than the average amount CO₂-C that evolved from Norfolk soil (272 mg kg⁻¹). Application of dust-sized biochars in both soils had an increase of about 25% in the cumulative CO₂-C evolution over the application of pelleted biochars (Table 3).

3.2. Soil net carbon dioxide–carbon evolution

Net CO₂-C evolution was significantly affected by the interaction effects ($p \leq 0.0001$) of biochars source (BS) and particle size (BF) with soil type (ST). Net CO₂-C evolution also varied widely with ST ($p \leq 0.0001$) and BF ($p \leq 0.0001$), but was not significantly affected by the different BS (Table 4). Zimmerman (2010) reported that the degradation of biochar was controlled more strongly by

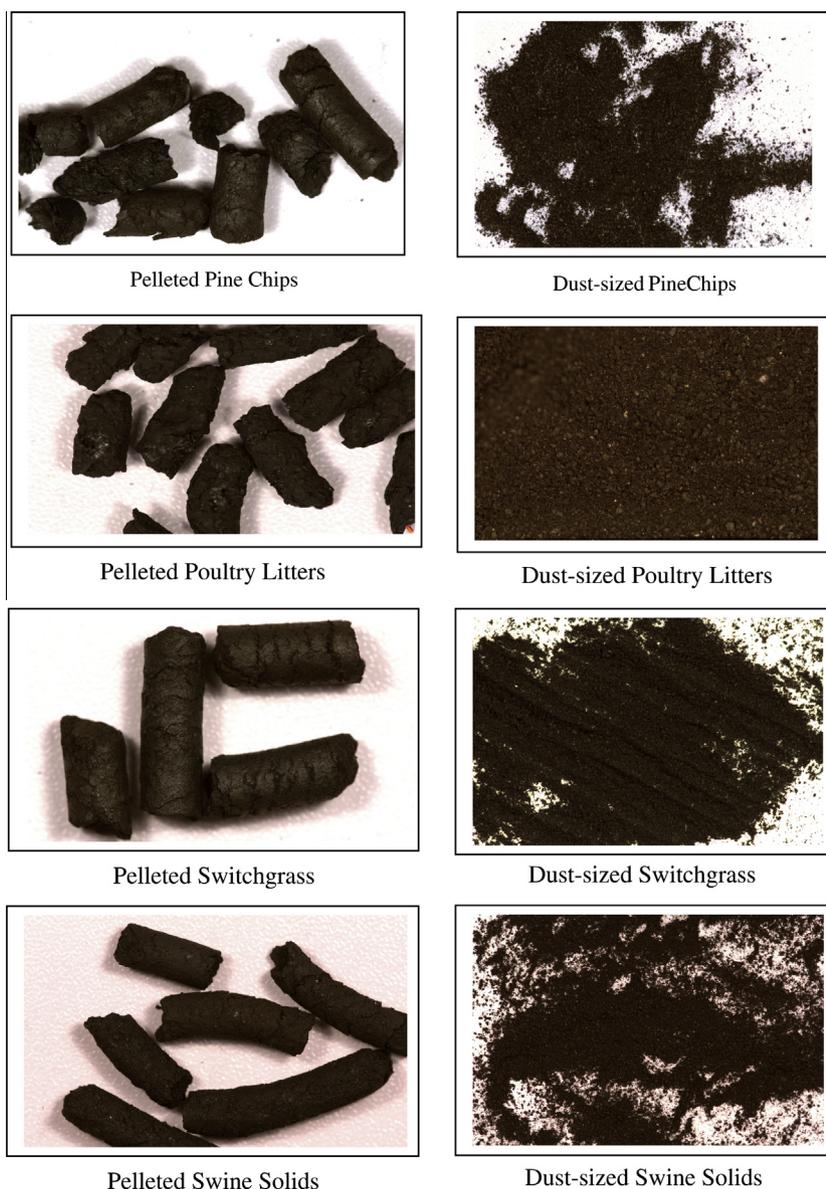


Fig. 1. Photos (magnified 1.6–1.9×) of pelleted and dust-sized biochars used in the study.

Table 3
Cumulative CO₂-C evolved from the mineralization of pelleted and dust-sized biochars in two soils.

Incubation time (day)	Control	Pine chips		Poultry litter		Switchgrass		Switchgrass	
		Pelleted	Dust	Pelleted	Dust	Pelleted	Dust	Pelleted	Dust
(mg kg ⁻¹)									
<i>Norfolk soil</i>									
0	6 ± 1	4 ± 0	3 ± 0	5 ± 0	7 ± 1	2 ± 1	3 ± 1	5 ± 0	6 ± 1
1	19 ± 2	16 ± 1	13 ± 0	18 ± 1	35 ± 6	11 ± 1	10 ± 2	18 ± 1	21 ± 6
2	42 ± 6	42 ± 1	37 ± 3	50 ± 5	101 ± 12	34 ± 5	41 ± 6	41 ± 2	44 ± 9
3	49 ± 5	46 ± 0	49 ± 9	75 ± 8	141 ± 25	39 ± 7	56 ± 14	58 ± 8	64 ± 9
4	55 ± 5	52 ± 1	55 ± 10	85 ± 9	154 ± 25	44 ± 7	64 ± 15	66 ± 9	72 ± 10
7	74 ± 8	67 ± 3	69 ± 13	118 ± 12	193 ± 28	57 ± 9	78 ± 12	86 ± 8	97 ± 17
9	81 ± 8	85 ± 5	85 ± 14	137 ± 15	216 ± 25	74 ± 5	100 ± 15	102 ± 9	111 ± 20
11	91 ± 8	94 ± 7	93 ± 15	152 ± 15	238 ± 27	82 ± 6	110 ± 21	109 ± 13	123 ± 20
14	101 ± 9	105 ± 7	101 ± 15	167 ± 17	260 ± 29	92 ± 5	119 ± 23	116 ± 14	133 ± 19
16	110 ± 7	111 ± 12	111 ± 16	179 ± 21	276 ± 27	101 ± 8	126 ± 23	124 ± 16	146 ± 19
18	117 ± 6	119 ± 14	118 ± 17	192 ± 21	289 ± 28	112 ± 9	135 ± 24	133 ± 16	159 ± 22
21	127 ± 5	128 ± 14	128 ± 16	203 ± 23	305 ± 30	125 ± 15	143 ± 26	145 ± 15	175 ± 24
24	133 ± 6	137 ± 16	135 ± 16	214 ± 23	316 ± 32	137 ± 19	152 ± 28	154 ± 14	189 ± 27
28	145 ± 6	153 ± 19	146 ± 17	230 ± 23	336 ± 36	159 ± 26	172 ± 31	167 ± 14	210 ± 33
31	160 ± 5	172 ± 23	160 ± 17	251 ± 25	360 ± 40	181 ± 38	192 ± 33	186 ± 10	238 ± 39
35	174 ± 7	185 ± 24	174 ± 20	267 ± 25	379 ± 39	201 ± 45	211 ± 34	201 ± 7	259 ± 43
50	203 ± 11	207 ± 38	195 ± 26	301 ± 23	422 ± 40	245 ± 65	271 ± 58	222 ± 3	312 ± 69
Total	1759	1793	1740	2744	4218	1753	2052	2011	2445
<i>Coxville soil</i>									
0	4 ± 1	5 ± 1	5 ± 1	4 ± 0	6 ± 1	7 ± 1	7 ± 0	4 ± 0	6 ± 0
1	27 ± 1	37 ± 9	57 ± 3	32 ± 3	52 ± 3	55 ± 5	66 ± 3	44 ± 4	57 ± 2
2	63 ± 5	92 ± 9	114 ± 6	71 ± 5	135 ± 11	102 ± 3	113 ± 1	99 ± 5	125 ± 12
3	102 ± 6	147 ± 14	181 ± 9	1106	219 ± 17	151 ± 10	16 ± 62	154 ± 6	209 ± 25
4	123 ± 3	195 ± 18	233 ± 9	142 ± 9	270 ± 19	191 ± 9	212 ± 3	202 ± 9	279 ± 29
7	175 ± 9	291 ± 24	327 ± 19	199 ± 24	352 ± 22	259 ± 15	306 ± 11	285 ± 19	387 ± 38
9	211 ± 12	363 ± 17	412 ± 17	246 ± 29	405 ± 19	328 ± 14	388 ± 19	359 ± 23	477 ± 60
11	250 ± 17	420 ± 11	479 ± 30	293 ± 49	456 ± 18	384 ± 18	437 ± 27	425 ± 27	541 ± 83
14	267 ± 17	459 ± 11	519 ± 33	320 ± 54	483 ± 20	421 ± 21	479 ± 29	460 ± 29	590 ± 84
16	284 ± 17	506 ± 11	566 ± 28	345 ± 59	508 ± 20	467 ± 20	517 ± 29	499 ± 28	637 ± 83
18	299 ± 19	535 ± 12	606 ± 40	365 ± 62	526 ± 20	496 ± 18	545 ± 34	523 ± 31	675 ± 92
21	318 ± 20	555 ± 29	649 ± 47	384 ± 62	550 ± 22	524 ± 12	586 ± 31	557 ± 36	714 ± 94
24	336 ± 21	589 ± 30	691 ± 51	406 ± 65	572 ± 25	561 ± 12	622 ± 33	591 ± 39	753 ± 104
28	356 ± 22	626 ± 35	735 ± 62	428 ± 66	595 ± 26	603 ± 14	665 ± 36	626 ± 42	800 ± 112
31	374 ± 21	662 ± 38	778 ± 66	450 ± 66	617 ± 32	642 ± 13	695 ± 27	655 ± 50	846 ± 120
35	385 ± 25	688 ± 34	810 ± 66	462 ± 69	632 ± 34	673 ± 15	723 ± 24	675 ± 53	876 ± 128
50	420 ± 29	749 ± 37	884 ± 86	490 ± 77	681 ± 44	744 ± 26	787 ± 30	718 ± 61	953 ± 156
Total	4125	7095	8271	4886	7326	6806	7532	7069	9174

combustion temperature and duration than the source materials. This is probably related to the biochar retaining easily degradable organic substances when pyrolyzed at lower temperature (<350 °C). On the other hand, pyrolysis at higher temperature results in the formation of more aromatic structures causing biochar to resist microbial oxidation (Lehmann et al., 2006).

Overall, Coxville soil with SS biochar had the greatest average amount of CO₂-C evolved (428 mg kg⁻¹) while Norfolk soil with PC biochar had the least average amount of CO₂-C evolved (93 mg kg⁻¹). Averaged across soil types and biochar sources, significantly ($p \leq 0.05$) higher net CO₂-C had evolved from dust-sized biochars (281 mg kg⁻¹) than pellet biochars (226 mg kg⁻¹). For Coxville soils amended with <0.42 mm biochars (dust-sized) and >2 mm biochars (pellet), the net amount of CO₂-C evolved ranged from 386 to 483 mg kg⁻¹ and 257–394 mg kg⁻¹, respectively. On the other hand, the net amount of CO₂-C respired from Norfolk soils that were amended with <0.42 mm biochars and >2 mm biochars ranged from 94 to 222 mg kg⁻¹ and 92–144 mg kg⁻¹, respectively (Table 4; Fig. 2).

The net amount of CO₂-C evolved varied significantly with incubation time (Fig. 2). Overall, net amount of CO₂-C evolved was linearly increasing with time, except for the pelleted biochars (PL, SG, SS, and PC) in Norfolk soils. These pelleted biochars had negative net amount of CO₂-C evolved between day 1 and day 5. However, we did not observe any negative net amount of CO₂-C evolution in Coxville soil. Again, the amount of CO₂-C evolved in Coxville soil

with dust-sized and pelleted biochars had both a positive and linear increasing trend with incubation time (Fig. 2).

By day 50, the average net amount (mg kg⁻¹) of CO₂-C evolved from each biochar source in the Coxville soil was in the order: SS (428) > PC (415) = SG (377) > PL (321) and PL (183) > SS (117) > SG (100) = PC (93) for the Norfolk soil. In total, the average net amount of CO₂-C evolved in the Coxville soil of 385 mg kg⁻¹ was threefold greater than the average amount of CO₂-C evolved in the Norfolk soil of 123 mg kg⁻¹ (Table 4).

3.3. Biochar mineralization rates in soils

The mineralization rate constants determined by regression analysis of results in Table 5 substantiate that in the Norfolk and Coxville soils, dust-sized biochars, in general, will decompose more readily than the pelleted size biochars. Mineralization rates varied widely ($p \leq 0.05$) between two Ultisols soils (Table 5). The rate constants (mg CO₂ day⁻¹) in the Coxville soil of 17.9 ± 0.9 for dust-sized biochars and 14.9 ± 0.9 for pelleted biochars were significantly ($p \leq 0.05$) higher than the rate constants in Norfolk soils of 5.8 ± 0.5 for dust-sized biochars and 4.9 ± 0.2 for pellet size biochars, respectively. The overall biochar mineralization rates in the Coxville soil was about 15.7 ± 1.3 mg CO₂ day⁻¹ and 5.3 ± 0.3 mg CO₂ day⁻¹ for the Norfolk soil, suggesting remarkable differences between biochar mineralization between these two Ultisols (Table 5).

Table 4
Net average CO₂ evolutions in two soils amended with different forms and sources of pyrolyzed feedstocks.

Soil Series	Sources	Forms	n	CO ₂ evolved (mg kg ⁻¹)	Average CO ₂	
Coxville	Pine chips	Dust	19	435	415ab ^a	
		Pellet	19	394		
	Poultry Litter	Dust	19	386	321b	
		Pellet	19	257		
	Switchgrass	Dust	19	396	377ab	
		Pellet	19	358		
	Swine Solids	Dust	19	483	427.5a	
		Pellet	19	372		
	Average				385	LSD (0.05) = 82.9
	Norfolk	Pine Chips	Dust	19	94	93b
Pellet			19	92		
Poultry Litter		Dust	19	222	183a	
		Pellet	19	144		
Switchgrass		Dust	19	108	100b	
		Pellet	19	92		
Swine Solids		Dust	19	129	117b	
		Pellet	19	106		
Average					123	LSD (0.05) = 27.5
Sources of variations					F-values	
Soils (ST)					207.91 ^{***b}	
Sources (BS)					0.95 ns	
Forms (BF)					24.2 ^{***}	
ST × BS					4.01 ^{**}	
ST × BF					7.19 ^{***}	

^a Means within a column followed by a different letter(s) are significantly different from each other at $p \leq 0.05$ level of significance.

^b ns – Not significant.

^{**} Significant at $p \leq 0.001$.

^{***} Significant at $p \leq 0.0001$.

We observed different mineralization rates between manure-based biochars and lignocellulosic-based biochars in the Coxville soil and Norfolk soil. The average mineralization rate of manure-based biochars in the Coxville soil was about 14.2 ± 1.5 mg CO₂ day⁻¹ and 6.2 ± 0.5 mg CO₂ day⁻¹ in the Norfolk soil. The average mineralization rates of lignocellulosic-based biochars in the Coxville and Norfolk soils were 17.2 ± 1.1 mg CO₂ day⁻¹ and 4.4 ± 0.2 mg CO₂ day⁻¹, respectively (Table 5).

4. Discussion

It has been observed in several studies that biochar additions improve soil fertility and thus increased crop yields (Marris, 2006; Chan et al., 2007). However, an important aspect in biochar as an amendment that is recently attracting more attention is on how biochar addition could contribute to longer term carbon storage and its effect on mitigating the increasing atmospheric CO₂ concentrations (Steinbeiss and Gleixner, 2009; Lehman, 2007). Steinbeiss and Gleixner (2009) noted that little is known about turnover times and decomposition rates of biochars in soils and long-term storage function contradicts the fertility function of biochars. In our present study, we investigated the CO₂-C mineralization in two Ultisols (Norfolk and Coxville) soils amended with different feedstock sources and sizes of biochars.

Results indicated that main treatment and the interaction effects of soil type and sources and forms of biochars significantly affected both the net CO₂-C evolution and biochar mineralization rates. We speculate that differences in soil profile development between Norfolk and Coxville soils caused some of the impacts on biochar mineralization. For instance, differences in the SOC, TN and clay contents between Coxville and Norfolk soils are due to differences in soil formation (Daniels et al., 1999). Biochars may be

more stable in well-drained sandy soils with inherently lower SOC and TN contents (e.g., the Norfolk series) than a poorly drained organic matter enriched sandy soil (e.g., the Coxville series). The relatively higher stability of pellet-sized biochar added to Norfolk soil implies higher amount of soil C sequestration should occur compared with the Coxville soil. In this study, additions of biochars have contributed in a positive way of sequestering C in soils. Applications of biochars have lead to either a build-up of soil C over time or a reduction in the rate at which organic carbon is depleted from soils, thereby contributing to the build-up in the stable C fraction in soils.

A number of factors could have affected the C mineralization of biochars in our study. The rapidity and stability with which given biochars are oxidized in the soil will depend on biochars' physical and chemical composition and the physical and chemical conditions of the surrounding soil environment (Stevenson, 1999). In addition, the C:N ratio of the biochars, age of the feedstocks and the degree of disintegration or particle size of the biochars govern the rate of their decomposition. It is well known that biochars produced from manure-based feedstocks (SS and PL) have higher pH values and greater ash and N contents than lignocellulosic-based (PC and SG) biochars (Novak et al., 2009a,b; Cantrell et al., 2012; Spokas et al., 2012). Biochars produced from lignocellulosic feedstocks have higher C:N ratio than manure-based biochars (Table 2). Interesting to notice is that the cumulative CO₂-C evolved was two to threefold higher in the Coxville soil than the Norfolk soil (Table 3). This may be related to the Coxville soil probably containing a different microbial community composition since it has higher indigenous SOC contents as well as higher TN contents than the Norfolk soil.

We observed that Coxville soil with SS biochar had the greatest average amount of CO₂-C evolved while Norfolk soil with PC biochar had the least average amount of CO₂-C evolved and these results could be related to the C:N ratio of the biochars. The C:N ratio of SS biochar was about 8:1 while the C:N ratio of PC biochar was about 213:1 (Table 2). The profound difference in the C:N ratio of these biochars explain the striking difference in the decomposition rates of SS biochar in the Coxville soil and PC biochar in the Norfolk soil. Pine chip biochar with high C:N ratio and low nitrogen content is associated with slow decay while SS biochar with low C:N ratio and containing high nitrogen content may undergo rapid mineralization (Table 2). Our results from Norfolk soils have demonstrated that manure-based biochars (PL and SS) with low C:N ratio had greater mineralization rates than lignocellulosic-based biochars with high C:N ratio (145:1 for SG biochar and 213:1 for PC biochar).

As a rule, the small particulate materials are more readily degraded than are the large particle (Sims and Frederick, 1970). Undoubtedly, the rate of decomposition of biochars is also governed by size of the particles subject to microbial attack. Our results have shown that additions of dust-sized (<0.42 mm) biochars to Coxville and Norfolk soils resulted in greater net amount of CO₂-C evolution and faster mineralization rates when compared with coarser (pellet, >2 mm) biochar materials. Earlier results of studies have shown that large charcoal particles originated from forest wildfires remained in soils for thousands of years (Pessenda et al., 2001; Gavin et al., 2003). For smaller particles as derived from grassland burning can hardly be detected in steppe ecosystems (Forbes et al., 2006). As noted previously, the particle size of biochars is an important characteristic for its ability to react with soil particles (Laird et al., 2009) and is believed to impact its resistance to microbial mineralization (Manya, 2012). In the case of dust-sized biochars, they have more finely divided or powdered solids that will normally produce a faster reaction than if the same mass is present as pelleted biochars. The powdered solid has a greater surface area than the pelleted biochar (see Table 6 for

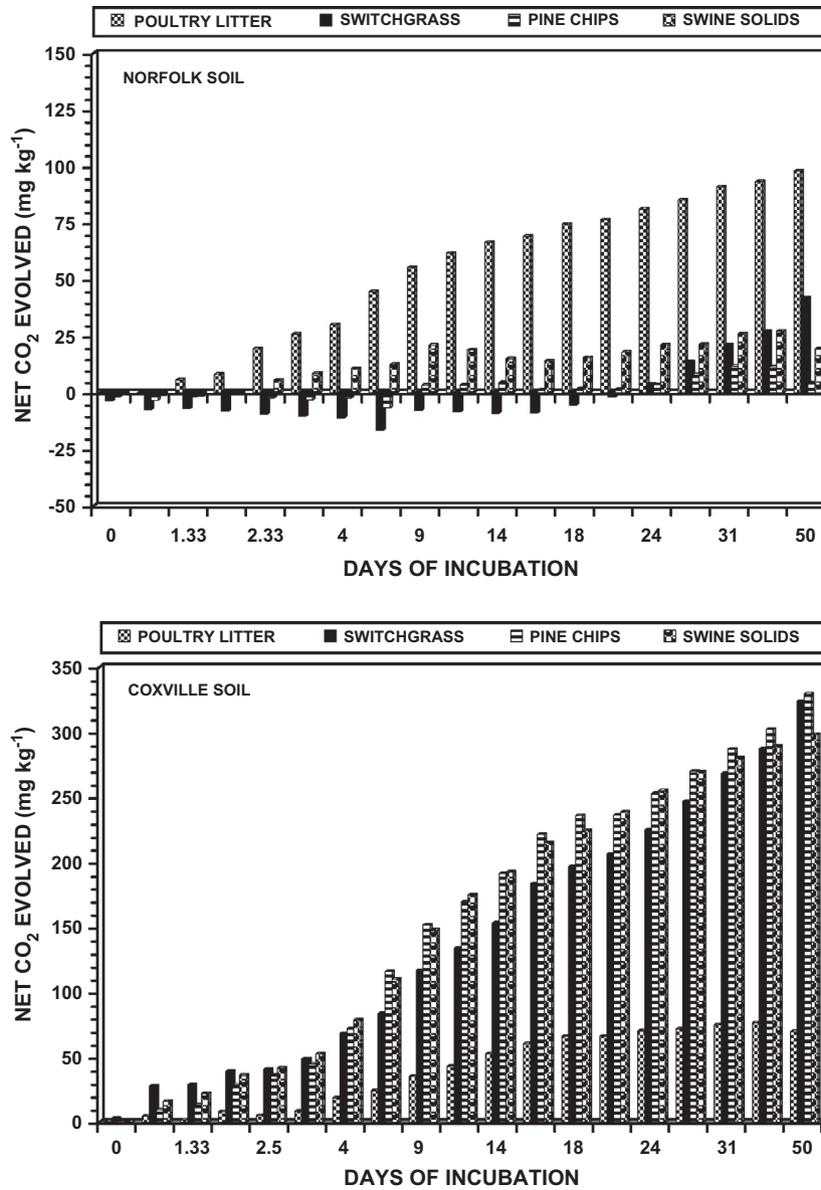


Fig. 2. Net CO₂-C evolved from the mineralization of different sources of biochars in the Norfolk and Coxville soils.

Table 5

Estimated rate constants for CO₂ evolution in two soils amended with different forms and sources of pyrolyzed biochar.

Biochar Parameters	Coxville soil		Norfolk soil	
	CO ₂ evolution rate (mg CO ₂ /day)	Adjusted, R ²	CO ₂ evolution rate (mg CO ₂ /day)	Adjusted, R ²
<i>Forms</i>				
a. Dust	17.9 ± 0.9	0.82 ^{***}	5.8 ± 0.5	0.63 ^{***}
b. Pellet	14.9 ± 0.9	0.80 ^{***}	4.9 ± 0.3	0.83 ^{***}
<i>Sources</i>				
a. Pine chips	17.8 ± 1.2	0.85 ^{***}	4.0 ± 0.2	0.93 ^{***}
b. Poultry litter	12.5 ± 1.3	0.71 ^{***}	7.1 ± 0.7	0.74 ^{***}
c. Switchgrass	16.7 ± 1.0	0.88 ^{***}	4.9 ± 0.2	0.95 ^{***}
d. Swine solids	15.9 ± 1.6	0.66 ^{***}	5.2 ± 0.3	0.90 ^{***}
Average	15.7 ± 1.3		5.3 ± 0.3	

^{***} Significant at $p \leq 0.0001$.

comparison). When large, coarse organic materials are chopped or shredded, the decomposition process accelerates. Microbial accessibility to the finer organic materials is increased causing the mate-

rials to be quickly decomposed. The huge variability in physical structures and chemical composition of the different biochar materials may lead to quite different turnover times.

Table 6
Estimated surface area of the different biochars used in the study.

Biochar sources/forms	Number particles per mass (1 g ⁻¹)	Expected surface area per particle (mm ²)	Total expected surface area per mass (mm ² g ⁻¹)
PC [*]	Pellet	19	327.4
	Dust	151,389	0.6
PL	Pellet	5	5138.8
	Dust	605,625	0.3
SS	Pellet	16	374.7
	Dust	225,177	0.4
SG	Pellet	14	327.3
	Dust	362,917	0.5

^{*} PC – pine chips, PL – poultry litters, SS – swine solids, SG – switchgrass.

5. Conclusions

Estimates of net carbon mineralized or converted to CO₂ from biochars decomposition are needed to improve our understanding on both the efficacies of biochars in enhancing soil quality, carbon sequestration, and biochar stability in soils. Results of this study strongly support our hypothesis that feedstock processed into pellets will have lower rate of C mineralization in soils compared with smaller-size (dust) biochar particles produced from similar feedstock. Hence, biochar processing into pellets and dust-sized materials had significant effect on its mineralization under laboratory conditions in two Ultisols. Application of biochars is likely to reverse the decline in soil C storage, thereby contributing to the build-up in the stable C fraction in soils. Our results further suggest that different sizes and forms of biochar as well as soil type influence biochar stabilization.

Biochar stability vary by soil types and conditions suggesting that uniform applications rates across agricultural landscapes in the southeast USA Coastal Plain may not be the best application strategy. Biochars may need to be designed to match soil conditions to enhance and/or improve soil fertility while increasing soil C sequestration. For the purposes of enhancing soil fertility, dust-sized manure-based biochars (PL and SS) could be the ideal choice, whereas pelleted lignocellulosic-based biochars like PC or SG would be beneficial for a long-term stability of carbon source in the soil. Our study represents an initial step, but further efforts are needed to perform soil test in order to establish some appropriate formulations of desired biochar properties based on sources and particle size. A quantification of net N mineralization from different sources of biochars using the estimates of CO₂ evolution similar to our study is needed because both decomposability (CO₂ mineralization) and net N mineralization are usually related to substrate N content or the C:N ratio.

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