



Article

# Poultry Litter, Biochar, and Fertilizer Effect on Corn Yield, Nutrient Uptake, N<sub>2</sub>O and CO<sub>2</sub> Emissions

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Abstract: Biochar holds promise as a soil amendment with potential to sequester carbon, improve soil fertility, adsorb organic pollutants, stimulate soil microbial activities, and improve crop yield. We used a hardwood biochar to assess its impact on corn (*Zea mays*) grain, biomass yields and greenhouse gas emission in central Kentucky, USA. Six treatments included as follows: control (C) with no amendment applied; poultry litter (PL); biochar (B); biochar + poultry litter (B + PL); fertilizers N-P-K (F); and biochar + fertilizers (B + F). Biochar was applied only once to plots in 2010 followed by rototilling all plots. Only PL and fertilizer were applied annually. When applied alone, biochar did not significantly increase dry matter, grain yield, and N-P-K uptake. There was also no significant difference between the combined treatments when compared with PL or F applications alone. We observed a slight increasing trend in corn grain yield in the following 2 years compared to the first year from biochar treatment. Poultry litter treatment produced significantly greater N<sub>2</sub>O and CO<sub>2</sub> emissions, but emissions were lower from the B+PL treatment. We conclude that this biochar did not improve corn productivity in the short term but has potential to increase yield in the long term and may have some benefit when combined with PL or F in reducing N<sub>2</sub>O and CO<sub>2</sub> emissions.

Keywords: animal manure; poultry litter; biochar; corn; greenhouse gas; nutrient

#### 1. Introduction

One strategy that has been advocated for mitigating and reducing global CO<sub>2</sub> concentration is based on the pyrolysis of biomass—a process that produces a byproduct known as biochar. When biochar is produced from biomass, it represents a net withdrawal of CO<sub>2</sub> from the atmosphere [1]. Biochar is black carbon, but not all black carbon materials are biochar [2]. The C in biochar is highly resistant to microbial degradation for many years [3]. It has also been emphasized that biochar holds great promise as a soil amendment to sequester carbon, improve soil fertility, adsorb organic pollutants, and stimulate soil microbial activities. Additionally, there are other benefits of incorporating biochar into a soil such as increases in cation exchange capacity (CEC) [4], increases in nutrient retention and availability for plant uptake particularly in highly weathered soils (Ultisols), and increases in fertilizer N use efficiency [5–8]. Clough and Condron [9] reported that agronomic benefits of biochar addition are well documented for highly weathered soils; however, little information exists on biochar impact on soil properties and crop yields in moderately weathered soils (Alfisols).

Biochar adds C structures into the stable soil organic matter (SOM) pool which improves soil fertility and crop productivity. The addition of biochar to soils may produce immediate effects on soil properties such as soil nutrition, water retention, and microbial activities [10–12]. Although these effects vary depending on soil type, the impacts may be long-term on soil and environments [13,14]. The addition of biochar to soils has not proven to be consistent with increasing crop yields. Approximately 50% of

the compiled studies observed short-term positive yield or growth impact, while 30% have reported no significant differences and 20% reported negative yield or growth effects [2]. They also reported that greater positive yield impacts for biochar addition occurred when it was applied to highly weathered or degraded soils with limited fertility and productivity. Novak et al. [15,16] reported that biochar produced at higher pyrolysis temperatures increased soil pH. They also concluded that biochar produced from different feedstocks under different pyrolysis conditions affects soil physical and chemical properties in different ways. Jeffery et al. [17] and Crane-Droesch et al. [18] evaluated the impact of various biochar on crop yield. They used results from two meta-analyses of biochar studies and showed an overall average crop yield increase of 10% after applying biochar to soil. They also reported that crop yields were soil-type-dependent and growth enhancements were highly variable. Another more recent meta-analysis using data from 84 reports by Crane-Droesch et al. [18] reported that biochar increased crop yields in the highly weathered soils of humid tropics more than in nutrient-rich temperate soils. One reason for crop yield variability in these studies may be due to differences in biochar quality associated with the feedstock, pyrolysis conditions, application rates, and soil properties [19]. For example, yield improvements were often associated with biochar application to low pH, nutrient-poor soils because alkaline biochar induced a soil-liming effect [20,21]. The array of controversies regarding the benefits of biochar and the variabilities reported for similar treatments through different studies as reported in the literature warrants further and continued research with different types of biochar for specific regions and crops. Therefore, the objective of this study was to investigate the impact of hardwood biochar alone and in combination with poultry litter or with chemical fertilizer on corn growth, grain yield, and greenhouse gas emissions on a Crider silt loam near Bowling Green, Kentucky USA. We hypothesized that the hardwood biochar used in this study, whether applied alone or combined with PL, would increase corn productivity and reduce N<sub>2</sub>O and  $CO_2$  emissions.

## 2. Material and Methods

Field experiments were conducted in 2010, 2011, and 2013 (the experiment was lost in 2012 due to severe summer drought) in which no-till corn was grown for grain on a Crider silt loam soil (Fine-silty, mixed, active, mesic, Typic Paleudalfs) of 1-2% slope in Bowling Green, Kentucky, Kentucky, USA (36°56′19.1" N, 86°28′51.2" W), with textural analysis of 3.1% sand, 65.3% silt, and 31.6% clay and soil organic matter of 25 g kg<sup>-1</sup>. The region has a temperate climate with a typical mean temperature of 14.5 °C and rainfall of 1300 mm year<sup>-1</sup>. Precipitation data were collected from a nearby weather station (Western Kentucky University Research Farm) during the growing seasons. The experimental design was a randomized complete block with three replicated plots (4.6-m × 3.5-m). The study site was fallow under mixed grasses such as tall fescue, orchardgrass, and white clover. We purposely chose the site because it had not been fertilized for the previous 5 years. The study included six treatment controls (C) with no amendment applied, poultry litter (PL) (a mixture of poultry manure and bedding materials) applied at a rate to provide 224 kg N ha<sup>-1</sup>; biochar (B) applied alone at the rate of 21.28 Mg ha<sup>-1</sup>; biochar + poultry (B + PL); chemical fertilizers; N-P-K (F); and biochar + chemical fertilizers (B + F). Every PL (alone or combined) was surface broadcast applied at the rate to provide 224 kg N ha<sup>-1</sup> assuming 50% of the PL total N becomes plant-available during the growing season. Poultry litter application also supplied 245, 181, 187, and 376 kg P ha<sup>-1</sup>, and 599, 447, 484, and 747 kg K ha<sup>-1</sup> in 2010, 2011, 2012, and 2013, respectively. Due to the unbalanced nutrient content of the poultry litter, particularly N:P:K compared to the N:P:K requirement of corn, there was a surplus of P and K applied from litter treatment, since the poultry litter quantity was applied base on the N requirement of the corn. The chemical fertilizers consisted of a blend of urea, muriate of potash, and diammonium phosphate (46-0-0, 0-0-60, 18-46-0). The fertilizer blend was surface broadcast applied at the rate of 224 kg N ha<sup>-1</sup> plus P and K based on soil test recommendations, 67.2 kg P ha<sup>-1</sup> and 112 kg K ha<sup>-1</sup> respectively.

Soil samples (background) were taken to a depth of 15 cm before initial treatment applications. Five random cores of soil were taken with a 2.54-cm diameter soil probe from each plot, combined in a

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plastic zip seal bag, air-dried, and ground with a Dynacrush soil crusher (Custom Laboratory Inc., Holden, MO, USA) to pass a 2.0-mm mesh. The soil chemical properties were as follows: pH (4.7) measured on a 1:1 soil:CaCl<sub>2</sub> (0.05 M) solution using a combination electrode (Accuphast electrode, Fisher Scientific, Pittsburg, PA, USA), total N (1.4 g kg<sup>-1</sup>) and TC (13.05 g kg<sup>-1</sup>) in soil were measured using a Vario Max CN analyzer (Elementar Americas, Inc. Mt. Laurel, NJ, USA), and NH<sub>4</sub>-N (22.8 mg kg<sup>-1</sup>) and NO<sub>3</sub>-N (0.84 mg kg<sup>-1</sup>) were extracted from soil samples with 2 M KCl [22] and then analyzed using flow injection analysis (QuickChem FIA+, Lachat Instruments, Milwaukee, WI, USA). Soil nutrient availability was also assessed after extraction with Mehlich 3 [23], and then elements were quantified using Inductively Coupled Plasma–Optical Emissions Spectroscopy (ICP-OES; Varian, Vista Pro; Varian Analytical Instruments, Walnut Creek, CA, USA). The elements analyzed were as follows: P 4.88 mg kg<sup>-1</sup>; Ca 1334 mg kg<sup>-1</sup>; Mg 117 mg kg<sup>-1</sup>; K 152 mg kg<sup>-1</sup>; Na 79 mg kg<sup>-1</sup>; Fe 87 mg kg<sup>-1</sup>; Mn 144 mg kg<sup>-1</sup>; and Zn 1.85 mg kg<sup>-1</sup>.

Approximately 340 kg of CQuest™ biochar for this experiment was produced using sawdust generated from the wood flooring process using mixed hardwood species subject to a fast pyrolysis process at 500–600 °C by the Dynamotive Technologies Corp., (West Lorne, ON, Canada). The biochar was pulverized to fine-sized (<0.5-mm) material and stored in steel drums. Chemical and physical analysis of the hardwood biochar is presented in Table 1. The % moisture, ash content, fixed C, volatile C, and elemental (C, H, O, and N) contents were determined on an oven dry-weight basis by Hazen Research, Inc. (Golden, CO, USA) following ASTM D 3171 and 3176 standard methods (ASTM, 2006). In this method, the O content was determined by difference. These results were used to calculate a molar O/C and H/C ratio. The total K, Ca and P contents were determined using the USEPA 3052 microwave-assisted acid digestion method (USEPA, 1996) and their concentrations were quantified using an inductively-coupled plasma mass spectrometer as outlined by Ref. [24]. The hardwood biochar pH, specific surface area (SAA), and total acidity were measured as outlined by Ref. [15]. The hardwood biochar was surface broadcast applied to all B treatments and incorporated to soil to a depth of 10 cm by a rototiller to prevent potential surface transport of biochar out of the plots by wind or water. The biochar was applied only once at the start of this study in the spring of 2010.

Table 1. Characteristics of hardwood biocha	(oven dry basis, SD = standard deviation).
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Property	Mean	SD
%H <sub>2</sub> O	4.6	0.61
%ash	14.16	13.21
%Fixed C	46	8.49
%Volatile C	54	26
%C	68.29	6.86
%Н	2.67	0.65
%N	0.25	0.09
%O*	13.38	3.86
O/C	0.16	0.02
H/C	0.51	0.04
%Ca	0.49	0.06
%K	0.65	0.05
%P	0.03	na
рН (H <sub>2</sub> O)	5.59	0.61
$SSA (m^2/g)^{\dagger}$	1.29	na
Total acidity (cmol/100g)	120	na

<sup>&</sup>lt;sup>†</sup> where SAA = specific surface area, and na = not available.

Corn (*Zea mays*) (DeKalb DKC61-69 RR/BT) was planted (76 cm row spacing) in  $4.6 \,\mathrm{m} \times 3.5 \,\mathrm{m}$  sized plots (total of six rows per plot) on 12 May 2010; 9 May 2011, and 2 May 2013. Total aboveground plant biomass was determined at physiological maturity (R6 growth stage) on 17 August 2010, 4 August 2011, and 14 August 2013. For biomass measurement, six plants were randomly selected per plot from

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a non-border row, cut above the soil surface, weighed, and shredded with a wood chipper (Modern Tool and Die Company, Cleveland, OH, USA) to allow homogenous mixed subsamples to be taken. Samples were then oven-dried at 65 °C for a minimum of 72 h and ground into composite samples with a grinder mill (Thomas Wiley Mill Model 4; Thomas Scientific, Swedesboro, NJ, USA) to pass a 1-mm mesh. Corn was harvested as grain on 9 September 2010, 23 August 2011, and 25 September 2013, by hand-picking the two center rows of each plot for a harvest area of 1.5 m  $\times$  3.5 m. Grain subsamples from each plot were taken for analyzing moisture content. Samples were oven-dried at 65 °C and ground with a grinder mill to pass a 1-mm mesh for chemical analysis. Plant tissue samples were analyzed for total N and C using a CN analyzer, and a dry ash/acid extraction procedure [25] was used to analyze samples for total P and K using ICP-OES.

Gaseous emissions (N<sub>2</sub>O and CO<sub>2</sub>) were measured during the growing seasons using static, vented chambers [26] and a gas chromatograph analyzer. Measurements of the N<sub>2</sub>O and CO<sub>2</sub> fluxes were taken from May (planting) to September (harvest) for only 2 years (2010 and 2011) following the procedures reported by Mosier et al. [27]. Measurements were generally taken two to three times per week midmorning of each sampling day. The chambers used were made of aluminum and measured 10 cm tall. After treatment applications, anchors were forced into the ground to a depth of 15 cm in each plot such that they were flush with the soil surface. Anchors were installed each year, 1 to 3 days prior to beginning measurements and were not removed until the fall after harvest. At each flux measurement time, the chambers were placed on fixed anchors (38 cm wide and 102 cm long). The anchors were placed such that the 102 cm length was parallel to the corn rows. Plants emerging inside the measurement area were removed. Flux measurements sites were included within each replicate of each treatment plot. Air samples (40 mL) were collected from inside the chambers by syringe at 0, 15, and 30 min intervals after the chambers were seated on the anchors. The air samples were injected into 20 ml evacuated vials that were sealed with grey butyl rubber septa. Samples were analyzed with a gas chromatograph (CP-3800, Varian, Inc., Palo Alto, CA, USA) equipped with a thermoconductivity detector and an electron capture detector for quantification of CO<sub>2</sub> and N<sub>2</sub>O. A quality control standard sample (known concentration) was also analyzed after every 25 unknown samples' analysis. Fluxes were calculated for each gas from the linear or non-linear [28] increase in concentration (selected according to the emission pattern) in the chamber headspace with time as suggested by Livingston and Hutchinson [26]. To calculate the cumulative growing season fluxes, estimates of daily N2O and CO<sub>2</sub> emissions between sampling days were calculated using a linear interpolation between adjacent sampling dates.

The experimental design was a randomized complete block with three replicated plots (4.6-m  $\times$  3.5-m). Differences among treatments and years were determined by analysis of variance (ANOVA) using PROC GLM procedure (SAS Institute, 2001). Blocks were considered as random factor and year as repeated measurement. All statistical comparisons were made at  $\alpha$  = 0.05 probability level using Fisher's protected LSD to separate treatment means.

## 3. Results and Discussion

# 3.1. Environmental Condition

The 3-year experiment was established in 2010 with a corn planting date of 20 May. In 2012, the experiment was completely lost due to severe drought particularly during the critical growing season months of June, July, and August; hence, we continued the study for 1 more year in 2013. The total precipitation for the three critical months of June, July, and August were 309 mm, 286 mm, and 473 mm for 2010, 2011, and 2013, respectively (Figure 1). However, the distribution of the rainfall among the critical growing season months was better in 2013 followed by 2011 and 2010.

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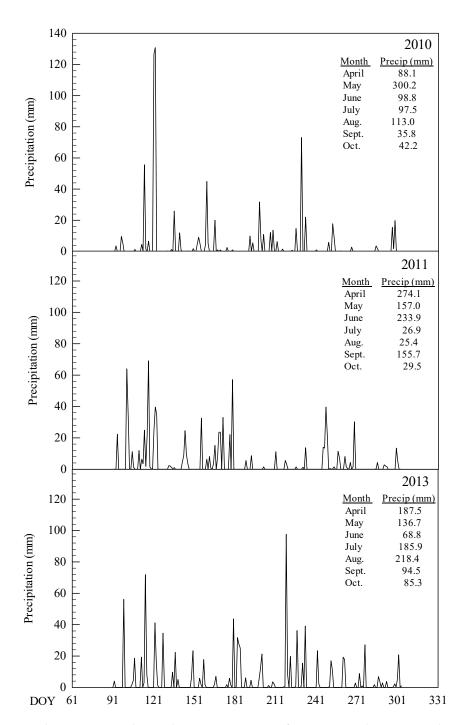


Figure 1. Daily precipitation during the growing seasons of 2010, 2011 and 2013. DOY, day of year.

## 3.2. Corn Dry Matter Yield

Since the interaction between year and all the agronomic measurements (dry matter yield, grain yield, and nutrient uptake) were significant, the results are reported on a yearly basis. No significant corn dry matter yield differences occurred among treatments in 2010 (dry year). In 2011, PL treatment produced the greatest dry matter yield and was significantly different than control, biochar, and fertilizer (N-P-K) treatments. The combination of PL and biochar resulted in significantly higher dry matter yield compared to biochar alone in the 2011 growing season (Table 2, Figure 2). In 2013, fertilizer, PL, and their combinations with biochar treatments produced significantly greater dry matter yields than control and biochar alone treatments. Similar to 2011, the addition of nutrients by way of fertilizer or PL enhanced the impact of biochar on corn dry matter production particularly under more favorable

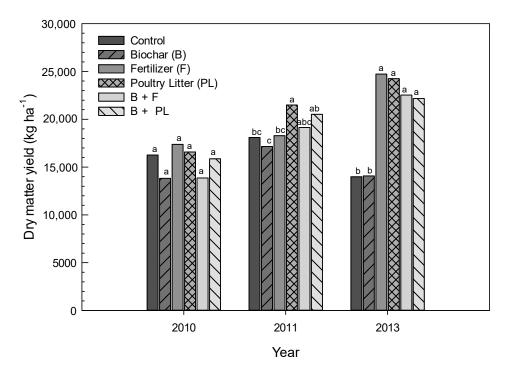
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soil moisture conditions. We believe the level of impact of these treatments on corn dry matter yield was mostly related to the precipitation and soil moisture availability in each year. Results suggest that biochar alone did not contain the quantity and specific forms of required plant nutrients for optimum corn growth in this study. However, above ground dry matter yield increased when biochar was supplemented with nutrients from poultry litter and fertilizer under optimum soil moisture content compared to biochar alone treatment (Table 2, Figure 2). This is indicative of the synergistic effect of biochar when applied with fertilizer sources. Such a synergistic effect has been reported in various studies such as for the increased production of maize by Yamato et al. [29] through combined biochar and fertilizer; Yamato et al. reported a 4–12 times higher yield of rice and sorghum when combined with fertilizer and compost [14,30] and reported increases in corn yield through increased P availability and uptake when biochar combined with arbuscular mycorrhiza (AM) fungal spores [31,32].

**Table 2.** Whole plant dry matter and grain yield influenced by different treatment and growing season year.

	Whole l		Grain Yield			
Treatment (T)	2010	2011	2013	2010	2011	2013
			kg l	na <sup>-1</sup>		
Control	16,262a <sup>†</sup>	18,100bc	13,995b	6480a	7201a	8952bc
Biochar (B)	13,828a	17,168c	14,090b	5619ab	6629a	8042c
Fertilizer (F)	17,379a	18,291bc	24,721a	5382ab	6036a	12,632a
Poultry Litter (PL)	16,581a	21,495a	24,245a	5037b	7062a	13,163a
B + F	13,875a	19,145abc	22,526a	4706b	5430a	11,723ab
B + PL	15,874a	20,524ab	22,170a	4721b	6281a	13,114a
$LSD_{(0.05)}$	4454	2920	6276	1232	1825	3557

<sup>&</sup>lt;sup>†</sup> Values within columns followed by the same letters are not significantly different according to Fisher's LSD (0.05) level.

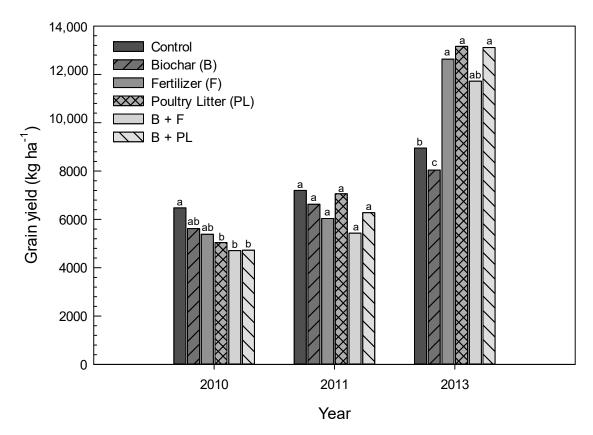


**Figure 2.** Effect of biochar, poultry litter, chemical fertilizer, and the combined treatments tested on corn dry matter yield in 2010, 2011, and 2013 growing seasons. Within each year, values followed by the same letters are not significantly different according to Fisher's LSD (0.05) level.

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#### 3.3. Corn Grain Yield

Significant differences in corn grain yield occurred among treatments in 2010 and 2013 growing seasons with 2013 producing the greatest, followed by 2011 and 2010 (Table 2, Figure 3). All treatments produced a similar grain yield in 2011 while biochar alone and control treatments had the lowest grain yield in 2013. When applied alone, biochar treatment did not increase corn grain yield in the three growing seasons compared to other treatments; however, the results indicate that over time, biochar positively impacted grain yield (Table 2), with a significant increase each consecutive year compared to the first year, which seems to indicate that biochar has potential to positively impact yield in the long term. This result is indicative of the carrying over effect of biochar also reported in a study by Adejumo et al. [33]. We also believe that the low soil pH may have influenced nutrient availability and uptake by corn. We also speculate that the low soil pH may have created a situation for Al toxicity for corn. Besides, organic matter is known to release nutrients slowly over time with only a small fraction of nutrients available the first year of application [34,35]. Biochar is also known to have a long-term effect on nutrient availability which is due to its potential to increase cation exchange capacity [6], consequently leading to increased yield over time. The control treatment was the same or higher than other treatments under limited moisture availability in 2010 and 2011. It seems to indicate that the addition of more nutrients through fertilizer and PL application exerted more stress and had a slightly negative impact on corn plants under drought conditions of 2010 and 2011 growing seasons (Table 2, Figure 3).



**Figure 3.** Effect of biochar, poultry litter, chemical fertilizer, and the combined treatments tested on corn dry matter yield in 2010, 2011, and 2013 growing seasons. Within each year, values followed by the same letters are not significantly different according to Fisher's LSD (0.05) level.

### 3.4. Corn Biomass N, P, and K Concentration and Uptake

The whole plant biomass N, P, and K concentrations were measured yearly at plant maturity followed by total N, P, and K uptake determination for each treatment. Since year by treatment

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interactions were mostly significant for N, P, and K biomass concentration and N, P, and K uptake, the results are shown separately by year in Tables 3 and 4. The biomass N concentration was significantly different among treatments in each year (Table 3). In more favorable soil moisture conditions (2011 and 2013), biochar treatment (alone) had lower biomass N concentration than other treatments except for control treatment; however, in 2010, a dry year, biochar alone had higher N concentration than when biochar alone was applied in the other years. In all three growing seasons, the biomass N content increased significantly when biochar was combined with nutrients by way of fertilizer or poultry litter compared to the biochar (alone) application (Table 3). The 2013 biomass N concentration was lower for all treatments compared to 2011 and 2010, probably due to greater biomass yield because of optimum soil moisture condition and better N use efficiency in 2013. The biomass P and K concentrations were significantly different among treatments except for PL and B + PL treatments, which had numerically higher P and K concentrations (Table 3). Table 4 shows N, P, and K uptake by corn for each growing season. No significant differences regarding N uptake among treatments were noted in the 2010 growing season. However, all treatments had significantly greater N uptake than biochar alone and control treatments in 2011 and 2013 growing seasons. In general, no specific trend regarding P and K uptake occurred in any of the growing seasons except for the B+PL treatment which had significantly greater P and K uptake than biochar alone treatment, indicating the low level of available nutrients of the biochar (Table 4). We speculate that precipitation and soil moisture availability may have had a big impact on corn nutrient uptake. Biochar in combination with fertilizer or poultry litter treatments positively influenced the N, P, K uptake more than biochar treatment alone, indicating a synergistic effect of the combined treatments [14,29,30]. Corn plants which were grown on poultry litter alone as a source of nutrients utilized N, P, and K more efficiently than other treatments (Table 4). It should be noted that even though the amount of P and K applications for the fertilizer treatment were based on the standard soil test recommendations, the poultry litter treatment provided more P and K because the quantity of poultry litter application was calculated based on the N requirement of the corn.

**Table 3.** Whole plants nutrients (N, P, and K) concentrations influenced by different treatments and growing season year.

Whole Plant N, P, and K Concentration									
	N			P			K		
Treatment (T)	2010	2011	2013	2010	2011	2013	2010	2011	2013
					g kg <sup>-1</sup>				
Control	11.1c <sup>†</sup>	7.9d	6.8b	1.3c	1.0d	1.3c	8.9b	13.8b	8.2b
Biochar (B)	12.9b	8.5d	7.3b	1.5bc	1.2cd	1.4c	10.6b	14.1b	8.7b
Fertilizer (F)	13.2ab	12.5ab	9.6a	1.5bc	1.4bc	1.6b	9.7b	15.5ab	8.6b
Poultry Litter (PL)	13.9ab	11.6bc	9.9a	2.0a	1.8ab	2.0a	11.8ab	18.5a	12.7a
B + F	14.0a	13.3a	9.2a	1.7b	1.5b	1.6b	11.4ab	17.6a	8.7b
B + PL	14.2a	10.7c	9.7a	2.1a	1.9a	2.0a	13.8a	18.9a	13.3a
$LSD_{(0.05)}$	1.09	1.35	0.99	0.26	0.35	0.21	2.99	3.40	3.29

<sup>&</sup>lt;sup>†</sup> Values within columns followed by the same letters are not significantly different according to Fisher's LSD (0.05) level.

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<b>Table 4.</b> Whole plants nutrients (N, P, and K) uptake influenced by different treatment and	growing
season year.	

Whole Plant N, P, and K Uptake										
	N				P			K		
Treatment (T)	2010	2011	2013	2010	2011	2013	2010	2011	2013	
					kg ha <sup>-1</sup>					
Control	182a <sup>†</sup>	144b	95b	21.0b	16.5d	17.6b	150b	250c	116c	
Biochar (B)	178a	146b	103b	20.6b	20.2cd	19.1b	145b	243c	123c	
Fertilizer (F)	230a	228a	239a	26.5ab	25.8bc	40.1a	170ab	283bc	212b	
Poultry Litter (PL)	231a	249a	240a	33.9a	37.8a	48.5a	195ab	398a	306a	
B + F	194a	254a	207a	23.0b	29.5b	36.0a	159ab	337ab	195b	
B + PL	225a	220a	215a	32.5a	39.0a	44.8a	217a	390a	287a	
$LSD_{(0.05)}$	62.6	37.5	68.0	9.40	6.86	14.08	66.7	75.0	53.9	

<sup>&</sup>lt;sup>†</sup> Values within columns followed by the same letters are not significantly different according to Fisher's LSD (0.05) level.

## 3.5. Quantification of $N_2O$ and $CO_2$

The impact of biochar and poultry litter alone and in combined treatments on the loss of N and C by way of greenhouse gas emission (N2O and CO2) were measured during 2010 and 2011 growing seasons (Table 5 and Figure 4). Poultry litter treatment produced significantly greater N<sub>2</sub>O emission in both years; however, the N<sub>2</sub>O emission decreased significantly when PL was combined with biochar in 2010. The decrease in N<sub>2</sub>O emission was most likely due to the conversion of different N forms from PL by microorganism activities which occur with biochar presence. This is due to the ability for biochar to provide a habitat for microorganisms, thus increasing microbial activities. Biochar has been shown to both increase and lower nitrous oxide  $(N_2O)$  emissions [9] which seem to be related to the type of biochar used and the soil properties. In this study, the latter occurred. The N<sub>2</sub>O emission from biochar was the same as the control. The  $N_2O$  fluxes did not increase significantly when biochar was combined with PL or fertilizer, except in 2010 (Table 5). Fertilizer treatment resulted in significantly greater  $N_2O$ emission than when it was combined with biochar. The N<sub>2</sub>O emission factors (emission per total N applied for each treatment) and emission based on yield scale followed the same trend as N2O emission for each treatment (Table 5). Similar to N<sub>2</sub>O, CO<sub>2</sub> emission was greatest with PL treatment. In general, biochar slightly lowered the emission of N<sub>2</sub>O and CO<sub>2</sub> when combined with PL or fertilizer in both years (Table 5). Cumulative N<sub>2</sub>O and CO<sub>2</sub> fluxes were lower for the first 2 weeks after application (DOY 135, mid-May) and then increased drastically for the following 2 weeks until mid-June (DOY 165) (Figure 4). Poultry litter treatment produced greater (mostly significant) cumulative N<sub>2</sub>O and CO<sub>2</sub> fluxes than other treatments. The cumulative fluxes were higher in 2010 than in 2011. The higher fluxes may be due to the fresh application of litter, biochar, and fertilizer in 2010 (Figure 4), along with air and soil moisture content differences in each year (Figure 5). We also speculate that the disturbance of the experimental plots from no-till grass covered plots (in order to apply biochar and planting corn) may have caused a temporary aerobic condition and increased microbial activities resulting in influxes of more  $N_2O$  and  $CO_2$  in 2010 compared to 2011 (Figure 4, Table 5).

Table 5. Cumulative growing-season CO <sub>2</sub> -C and N <sub>2</sub> O-N emissions, N <sub>2</sub> O-N emission factor, are	ıd
yield-scaled N <sub>2</sub> O emissions for each treatment in 2010 and 2011.	

Treatment	CO <sub>2</sub> -C Emissions		N <sub>2</sub> O-N Emissions		N <sub>2</sub> O-N Emission Factor ‡		Yield Scaled N <sub>2</sub> O-N Emissions	
	2010	2011	2010	2011	2010	2011	2010	2011
	Mg l	Mg ha <sup>-1</sup> kg l		kg ha <sup>-1</sup>		6	kg N <sub>2</sub> O-N Mg	grain yield <sup>-1</sup>
Control	4.04ab †	2.80ab	4.72d	1.09c	-	-	0.73e	0.15c
Biochar (B)	3.94ab	2.61bc	5.01cd	1.36c	-	-	0.91de	0.21c
Fertilizer (F)	3.92ab	2.16cd	8.53b	3.92ab	1.70a	1.26a	1.82b	0.63b
Poultry litter (PL)	4.73a	3.19a	11.95a	4.76a	1.61a	0.82a	2.54a	0.88a
B + F	3.52b	1.89d	6.16c	3.43b	0.64b	1.05a	1.22c	0.51b
B + PL	4.04ab	2.94ab	5.83cd	4.24ab	0.25b	0.70a	1.09cd	0.71ab

<sup>&</sup>lt;sup>†</sup> Values for each year (column) followed by the same letters are not significantly different according to Fisher's LSD (0.05) level. <sup>‡</sup> Calculated based on the TN application rate for each treatment.

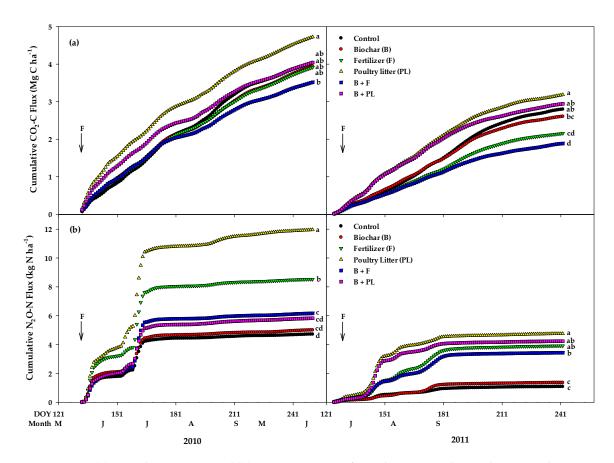
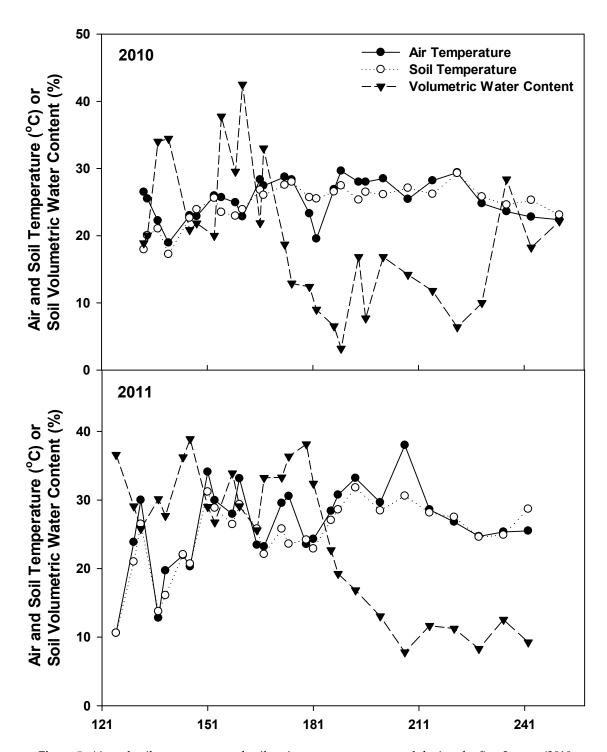


Figure 4. (a) Cumulative  $CO_2$ -C and (b)  $N_2O$ -N emissions for each treatment during the 2010 and 2011 growing seasons as a function of day of year (DOY). Cumulative values within each year for same effect followed by the same letters are not significantly different according to Fisher's LSD (0.05) level. B, biochar; F, fertilizer; PL, poultry litter.



**Figure 5.** Air and soil temperature and soil moisture content measured during the first 2 years (2010 and 2011) of the study.

## 4. Conclusions

We conducted a field plot study to investigate the impact of biochar and poultry litter alone or in combination on corn biomass, grain yield, nutrient uptake, and greenhouse gas emission ( $N_2O$  and  $CO_2$ ) for three growing seasons. Results indicate that biochar alone application to soil did not increase corn grain yield or N, P, and K uptake when compared to other treatments. This finding is in line with other research reports [36,37]. However, grain yield increased slightly over time from biochar application. These mixed results of delayed positive responses and even initial negative responses

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observed from the biochar in this study have also been reported by other research [2]. Soil pH for biochar treatment increased slightly from 4.7 (background) to 4.81 at the end of the study. Similar trends of slight increases in total C (22.4 g kg<sup>-1</sup>) and total N (1.7 g kg<sup>-1</sup>) observed for biochar treatments compared to background. However, we observed greater concentrations of P (7.95 mg kg<sup>-1</sup>) and K (157 mg kg<sup>-1</sup>) at the end of the study for biochar and biochar plus poultry litter treatments compared to soil background concentrations. Poultry litter application alone produced a significantly greater corn yield than biochar but was similar to chemical fertilizer. The N, P, and K uptake by corn grown on biochar alone applications were significantly lower than PL and fertilizer treatments. Results indicated that the addition of fertilizer or poultry litter to biochar had a positive effect on reducing  $N_2O$  and CO<sub>2</sub> fluxes compared to fertilizer or poultry litter application alone. In general, biochar application did not show a significant improvement in corn production parameters measured when compared to other treatments under the specific soil and environmental conditions of the study site within the three growing seasons. However, positive results were observed, such as a slight increase in grain yield in each year following biochar application and also when biochar was mixed with poultry litter or fertilizers. Therefore, more research is warranted to include different types of biochar and different rates of application under different environmental and management conditions and for longer term periods (long-term studies) to understand the impact of biochar as a soil amendment.

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#### References

- 1. Lehmann, J. Bio-Energy in the black. Front. Ecol. Environ. 2007, 5, 381–387. [CrossRef]
- 2. Spokas, K.A.; Cantrell, K.B.; Novak, J.M.; Archer, D.A.; Ippolito, J.A.; Collins, H.P.; Boateng, A.A.; Lima, I.M.; Lamb, M.C.; McAloon, A.J.; et al. Biochar: A synthesis of its agronomic impact beyond carbon sequestration. *J. Environ. Qual.* **2012**, *41*, 973–989. [CrossRef]
- 3. Lehmann, J.; Abiven, S.; Kleber, M.; Pan, G.; Singh, B.P.; Sohi, S.P.; Zimmerman, A.R. Persistence of biochar in soil. In *Biochar for Environmental Management: Science, Technology and Implementation*, 2nd ed.; Lehmann, J.L., Joseph, S., Eds.; Earthscan: London, UK, 2015; pp. 235–282.
- 4. Fowles, M. Black carbon sequestration as an alternative to bioenergy. *Biomass Bioenergy* **2007**, 31, 426–432. [CrossRef]
- 5. Glaser, B.; Lehmann, J.; Zech, W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal-a review. *Biol. Fertil. Soils* **2002**, *35*, 219–230. [CrossRef]
- 6. Liang, B.; Lehmann, J.; Solomon, D.; Kinyangi, J.; Grossman, J.; O'Neill, B.; Skjemstad, J.O.; Theis, J.; Luizao, R.J.; Peterson, J.; et al. Black carbon increases cation exchange capacity in soils. *Soil Sci. Soc. Am. J.* **2006**, *70*, 1719–1730. [CrossRef]
- 7. Chan, K.Y.; Van Zwieten, L.; Meszaros, I.; Downie, A.; Joseph, S. Agronomic values of green-waste biochar as soil amendment. *Aust. J. Soil Res.* **2007**, *45*, 629–634. [CrossRef]
- 8. Biederman, L.A.; Harpole, W.S. Biochar and its effects on plant productivity and nutrient cycling: A meta-analysis. *GCB Bioenergy* **2013**, *5*, 202–214. [CrossRef]
- 9. Clough, T.J.; Condron, L.M. Biochar and the nitrogen cycle: Introduction. *J. Environ. Qual.* **2010**, 39, 1218–1223. [CrossRef] [PubMed]
- 10. Atkinson, C.J.; Fitzgerald, J.D.; Hipps, N.A. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. *Plant Soil* **2010**, *337*, 1–18. [CrossRef]
- 11. Lehmann, J.; Rilling, M.; Thies, J.; Masiello, C.A.; Hockaday, W.C.; Crowley, D. Biochar effects on soil biota: A review. *Soil Biol. Biochem.* **2011**, *43*, 1812–1836. [CrossRef]
- 12. Novak, J.M.; Spokas, K.A.; Cantrell, K.B.; Ro, K.S.; Watts, D.W.; Glaz, B.; Busscher, W.J.; Hunt, P.G. Effects of biochar and hydrochars produced from lignocellulosic and animal manure on fertility of a Mollisol and Entisol. *Soil Use Manag.* **2014**, *30*, 175–181. [CrossRef]

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

- 14. Van Zwieten, L.; Kimber, S.; Morris, S.; Chan, K.Y.; Downie, A.; Rust, J.; Joesph, S.; Cowie, A. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant Soil* **2010**, 327, 235–246. [CrossRef]
- 15. Novak, J.M.; Lima, I.M.; Xing, B.; Gaskin, J.W.; Steiner, C.; Das, K.C.; Ahmedna, M.; Rehrah, D.; Watts, D.W.; Busscher, W.J.; et al. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. *Soil Sci.* **2009**, *3*, 195–206.
- 16. Novak, J.M.; Ro, K.; Ok, Y.S.; Sigua, G.; Spokas, K.; Uchimiya, S.; Bolan, N. Biochars multifunctional role as a novel technology in the agricultural, environmental, and industrial sectors. *Chemosphere* **2016**, *142*, 1–3. [CrossRef] [PubMed]
- 17. Jeffery, S.; Verheijen, F.G.; Van der Velde, M.; Bastos, A.C. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. *Agric. Ecosyst. Environ.* **2011**, 144, 175–187. [CrossRef]
- 18. Crane-Droesch, A.; Abiven, S.; Jeffery, S.; Torn, M.S. Heterogeneous global crop yield response to biochar: A meta-regression analysis. *Environ. Res. Lett.* **2013**, *8*, 1–8. [CrossRef]
- 19. Ronsee, F.; Van Hecke, S.; Dickinson, D.; Prins, W. Production and characterization of slow pyrolysis biochar: Influence of feedstock type and pyrolysis conditions. *GCB Bioenergy* **2013**, *5*, 104–115. [CrossRef]
- 20. Hass, A.; Gonzalez, J.M.; Lima, I.M.; Godwin, H.W.; Halvorson, J.J.; Boyer, D.G. Chicken manure biochar as liming and nutrient source for acid Appalachian soil. *J. Environ. Qual.* **2012**, *41*, 1096–1106. [CrossRef]
- 21. Wang, L.; Butterly, C.R.; Wang, Y.; Herath, H.M.; Xi, Y.G.; Xiao, X.J. Effect of crop residue biochar on soil acidity amelioration in strongly acidic tea garden soils. *Soil Use Manag.* **2014**, *40*, 119–128. [CrossRef]
- 22. Keeney, D.R.; Nelson, D.W. Nitrogen-inorganic forms. In *Methods of Soil Analysis, Part* 2, 2nd ed.; Page, A.L., Miller, R.H., Keeney, D.R., Eds.; ASA and SSSA: Madison, WI, USA, 1982; pp. 643–698.
- 23. Mehlich, A. Mehlich 3 soil extractant: A modification of Mehlich-2 extractant. *Commun. Soil Sci. Plant Anal.* **1984**, *15*, 1409–1416. [CrossRef]
- 24. Novak, J.M.; Busscher, W.J.; Laird, D.L.; Ahmedna, M.; Watts, D.W.; Niandou, M.A. Impact of biochar on fertility of a southeastern Coastal Plain soil. *Soil Sci.* **2009**, *74*, 105–112. [CrossRef]
- 25. Miller, R.O. High-temperature oxidation: Dry ashing. In *Referenced Methods for Plant Analysis*; Kalra, V.P., Ed.; Handbook of. CRC Press: Boca Raton, FL, USA, 1998; pp. 53–56.
- 26. Livingston, G.P.; Hutchinson, G.L. Enclosure-based measurement of trace gas exchange: Applications and sources of error. In *Biogenic Trace Gases: Measuring Emissions from Soil and Water*; Matson, P.A., Harriss, R.C., Eds.; Blackwell Sci. Ltd.: London, UK, 1995.
- 27. Mosier, A.R.; Halvorson, A.D.; Reule, C.A.; Liu, X.J. Net global warming potential and greenhouse gas intensity in irrigated cropping systems in northeastern Colorado. *J. Environ. Qual.* **2006**, *35*, 1584–1598. [CrossRef] [PubMed]
- 28. Hutchinson, G.L.; Mosier, A.R. Improved soil cover method for field measurements of nitrous oxide fluxes. *Soil Sci. Soc. Am. J.* **1981**, *45*, 311–316. [CrossRef]
- 29. Yamato, M.; Okimori, Y.; Wibowo, I.F.; Anshori, S.; Ogawa, M. Effects of the application of charred bark of Acaciamangium on the yield of maize, cowpea and peanut and soil chemical properties in south Sumatra, Indonesia. *Soil Sci. Plant Nut.* **2006**, *52*, 489–495. [CrossRef]
- 30. Steiner, C.; Teixeira, W.G.; Lehmann, J.; Nehls, T.; Macedo, J.; Blum, W.H.; Zech, W. Long term effect of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. *Plant Soil* **2007**, *291*, 275–290. [CrossRef]
- 31. Mau, A.E.; Utami, S.R. Effects of biochar amendment and arbuscular mycorrhizal fungi inoculation on availability of soil phosphorus and growth of maize. *J. Degr. Min. Lands Manag.* **2014**, *1*, 69–74.
- 32. Ahmad, M.A.; Asghar, H.N.; Saleem, M.; Khan, M.Y.; Zahir, Z.A. Synergistic effect of rhizobia and biochar on growth and physiology of maize. *Agron. J.* **2015**, 107, 2327–2334. [CrossRef]
- 33. Adejumo, S.A.; Owolabi, M.O.; Odesola, I.F. Agro-physiologic effects of compost and biochar produced at different temperatures on growth, photosynthetic pigment and micronutrients uptake of maize crop. *Afr. J. Agric. Res.* **2015**, *11*, 661–673. [CrossRef]
- 34. Eghball, B.; Wienhold, B.J.; Gilley, J.E.; Eigenberg, R.A. Mineralization of manure nutrients. *J. Soil Water Conserv.* **2002**, *57*, 470–478.

35. Motavalli, P.P.; Kelling, K.A.; Converse, J.C. First-year nutrient availability from injected dairy manure. *J. Environ. Qual.* **1998**, *18*, 180–185. [CrossRef]

- 36. Lentz, R.D.; Ippolito, J.A.; Spokas, K.A. Biochar and Manure Effects on Net Nitrogen Mineralization and Greenhouse Gas Emissions from Calcareous Soil under Corn. *Soil Sci. Soc. Am. J.* **2014**, *78*, 1641–1655. [CrossRef]
- 37. Laird, D.A.; Novak, J.M.; Collins, H.P.; Ippolito, J.A.; Karlen, D.L.; Lentz, R.D.; Sistani, K.R.; Spokas, K.; van Pelt, R.S. Multi-year and multi-location soil quality and crop biomass yield responses to hardwood fast pyrolysis biochar. *Geoderma* **2017**, *289*, 46–53. [CrossRef]



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