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Article

Effect of biochar on soil greenhouse gas emissions at the laboratory and field scales

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Abstract: Biochar application to soil has been proposed as a means for reducing soil greenhouse gas emissions and mitigating climate change. The effects, however, of interactions between biochar, moisture and temperature on soil CO_2 and N_2O emissions, remain poorly understood. Furthermore, the applicability of lab-scale observations to field conditions in diverse agroecosystems remains uncertain. Here we investigate the impact of a mixed wood gasification biochar on CO_2 and N_2O emissions from loess-derived soils using: (1) controlled laboratory incubations at three moisture (27, 31 and 35%) and three temperature (10, 20 and 30°C) levels, and (2) a field study with four cropping systems (continuous corn, switchgrass, low diversity grass mix, and high diversity grass-forb mix). Biochar reduced N_2O emissions under specific temperatures and moistures in the laboratory and in the continuous corn cropping system in the field. However, the effect of biochar on N_2O emissions was only significant in the field, and no effect on cumulative CO_2 emissions was observed. Cropping system also had a significant effect in the field study, with soils in grass and grass-forb cropping systems emitting more CO_2 and less N_2O than corn cropping systems. Observed biochar effects were consistent with previous studies showing that biochar amendments can reduce soil N_2O emissions under specific, but not all, conditions. The disparity in N_2O emission responses at the lab and field scales suggests that laboratory incubation experiments are not reliable for predicting the impact of biochar at the field scale.

Keywords: Biochar; greenhouse gas emissions; incubation; soil; corn; switchgrass; CO2; N2O; cropping system; diversity

1. Introduction

The production and application of biochar – a carbon-rich material produced during the pyrolysis of biomass – to soil has been proposed as a means for mitigating anthropogenic greenhouse gas (GHG) emissions [1]. The Pyrolysis-Biochar Bioenergy Platform (PBBP) has the potential to mitigate GHG emissions through three primary pathways. First, bioenergy produced by PBBP will offset GHG emissions from the burning of fossil fuels and by converting photosynthetic biomass carbon (C) into recalcitrant biochar C. Indeed, pyrolysis converts 10-50% of the original biomass C into biochar C, which persists in soils for hundreds to thousands of years [1–4]. Second, biochar amendments increase soil quality, potentially increasing net primary productivity and thereby reducing economic pressure to convert native lands to agricultural production [5]. Although negative crop yield responses to biochar applications have been observed [6,7], under most circumstances biochar either increases or has no impact on crop biomass production [8,9]. Third, soil biochar applications may directly reduce GHG emissions (primarily N_2O) from soils. This direct effect, however, is highly variable and difficult to model, due to: (1) the complexity of soil biogeochemical processes and interactions involving biochar amendments with soil types and soil

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temperature and moisture, (2) lack of knowledge regarding biochar weathering or aging in the field, and (3) poor understanding of the relationship between GHG emissions measured at the lab and field scales [10–12]. In the United States, where upland agriculture dominates, CO_2 and N_2O emissions are the soil GHGs of primary concern. Thus, further examination of biochars' impacts on upland soil CO_2 and N_2O emissions – especially under variable moisture and temperature conditions found in agricultural fields – is critical for modeling the potential of the PBBP to help mitigate climate change [9,11,13].

Most studies examining CO_2 emissions from biochar-amended soils report either no significant effect or an increase in CO_2 emissions due to biochar amendments – typically equivalent to <3% of biochar C [14]. Meta analyses by Song et al. (2016), Liu et al. (2016) and He et al. (2016) all report positive average effects of biochar amendments on soil CO_2 emissions, but the magnitude of the effects differed [15–17]. Both He et al. [17] and Song et al. [15] reported significant increases in CO_2 emissions (19 and 22%, respectively); by contrast, Liu et al. found no significant impact of biochar on soil CO_2 emissions. Differences in CO_2 response likely arose from differences in the number and/or types of studies chosen. For example, Song et al., Liu et al., and He et al. [15–17] used 77, 167 and 402 total observations, respectively; of these, only 31, 69 and 17 were from field studies. All three meta-analyses report higher CO_2 emissions from biochar-amended soils in laboratory incubations than in the field. He et al. noted an interaction between fertilizer application and study type: biochar amendment significantly increased CO_2 emissions from unfertilized soil and decreased CO_2 emissions from fertilized soil in the lab, whereas in the field there was no significant effect of biochar on CO_2 emissions. In addition to study type effects, the meta-analyses found significant impacts of other variables including study duration, soil texture, soil pH, biochar pH, biochar feedstock, and biochar application rate. Short-term CO_2 emissions (< 1 yr) have been shown to be influenced by both inorganic C and labile organic C in biochar [18,19], whereas there is a lack of consensus regarding long-term (>2 yr) impacts on CO_2 emissions [20–29]. Thus, while biochars appear to pose minimal risk of exacerbating soil CO_2 emissions in the long term, more studies examining both field and lab results are needed to ascertain whether CO_2 responses to biochar amendment observed in the lab can be used to predict CO_2 responses in the field – and to accurately predict long-term CO_2 emissions of biochar amended soils at the field scale.

In general, most studies have found biochar amendments to either decrease or not significantly affect soil N_2O emissions; however, some reports have found increased N_2O emissions following biochar amendments. A meta-analysis of biochars' effect on N_2O emissions, which included both long and short-term studies, reported that biochars reduced soil N_2O emissions by 54 ±3% at the lab scale and by 28 ±16% at the field scale [30]. The higher variability of the field scale estimate likely reflects both lower biochar application rates as well as effects of variable climate and cropping systems in the field-scale studies compared with higher biochar application rates and controlled conditions in the lab studies. The lower magnitude of the effect of biochar on N_2O emissions in the field relative to the lab studies may reflect lower rates of biochar application used in the field studies. Only ten field studies reported significant reductions in N_2O emissions, five reported no significant impact, and one reported a significant increase. Furthermore, all but two of the studies reporting significant changes in N_2O emissions measured ≤12 months after biochar application, and all studies focused on only one cropping system [31–41]. Recent evidence suggests that biochars' impacts on N_2O emissions may change over time as biochar ages, highlighting the need for studies comparing fresh and aged biochar, especially at the field scale [42]. In one of the few studies incorporating parallel field and laboratory experiments, Keith et al. [43] found that fresh biochar suppressed N_2O emissions in the laboratory and also reduced N_2O emissions in the field by a similar magnitude three years following biochar amendment to a sunflower cropping system – thereby contradicting the findings of Spokas (2013) [42]. Thus, despite numerous studies, the direction and magnitude of soil N_2O emissions responses to biochar amendments remains difficult to predict at the field scale for specific cropping systems and over time.

Much research into biochar's effects on soil CO_2 and N_2O emissions at the lab and field scales is challenged by confounding variables. Both soil CO_2 and N_2O emissions are known to be especially

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sensitive to soil moisture and temperature [44–47], and both biochar and soil properties also influence GHG emissions [11,17]. Indeed, He et al. found that N fertilization, soil texture, biochar pH, biochar application rate, and latitude all significantly influenced CO_2 emissions response ratios [17]. Similarly, multiple meta-analyses show that N_2O emissions are sensitive to biochar feedstock, pyrolysis conditions, biochar C:N and H:C ratios, biochar application rate, soil pH, and soil texture [11,17,30]. The impact of soil texture was additionally shown to be moisture-dependent: under low moisture conditions (<80% WFPS), biochar reduced N_2O emissions from coarse to medium-textured soils, while under high moisture conditions (>80% WFPS) biochar reduced emissions from medium to fine-textured soils [11].

Published biochar literature inconsistently addresses interactions between biochar amendments and cropping systems on N_2O emissions. Of the 16 field studies examined by Cayuela et al (2015), only four examined biochar effects in multiple cropping systems [30]. Of these, three reported consistent suppression of N_2O in biochar-amended maize, rice and wheat systems, whereas one reported decreased N_2O emissions with biochar for two crops (broccoli and kabocha) and increased N_2O emissions for one crop (bok choy) [48]. More recently, Bass *et al.* (2016) observed reduced N_2O emissions with biochar amendment in a papaya cropping system - but not in a banana cropping system [49]. These observations clearly show the potential for cropping system factors to interact with biochar factors influencing GHG emissions, but do not systematically examine what environmental or management aspects of the cropping system affect biochar-by-cropping system interactions.

The aforementioned studies do not document a consistent magnitude or direction of GHG emission responses to biochar amendment. Furthermore, a clear pattern explaining differences in responses has yet to emerge. To explain why biochar induces different GHG responses in different contexts, studies must systematically compare GHG responses to biochar amendment under multiple environmental conditions using the same soils and biochars. Currently there is in particular a lack of experiments examining the effects of biochar on soil GHG emissions impacts at the laboratory and field scales, and these studies have not incorporated potentially key variables such as moisture, temperature, biochar aging, and cropping system diversity. Therefore, here we analyze the impact of a mixed wood gasification biochar on soil CO_2 and N_2O emissions from Midwestern agricultural soil in (a) a controlled laboratory incubation at three moistures and temperatures, and (b) a field study under four cropping systems. We hypothesize that (1) biochar's impact on CO_2 and N_2O emissions will depend on soil moisture, temperature and cropping system, (2) biochar suppression of N_2O emissions will be greater in cropping systems with higher average N_2O emissions, and (3) biochar amendment will have a similar effect on N_2O emissions at the laboratory and field scales.

2. Materials and Methods

2.1 Biochar

The biochar used in both the field and laboratory incubation studies was from a mixture of hardwood and soft wood feedstocks (primarily *Quercus, Ulmus* and *Carya* spp. woodchips with particle sizes 0.1-2000 mm) in an auger bed gasifier at 550-650°C (ICM, Inc., Colwich, KS, USA). The biochar had a pH of 8.8 and was comprised of 55% fixed carbon, 16% volatile matter, and 29% ash, with molar H:C and C:N ratios of 0.35 and 150, respectively [50]. Further information concerning this biochar, including soil impacts and chemical properties, can be found in Fidel et al. (2017a) [50].

2.2 Field site

The field site used for this study was located at the Iowa State University Armstrong Research and Demonstration Farm in southwest Iowa. The soils at this site were loess-derived Mollisols (Ackmore-Colo-Judson, Clarinda, Exira, and Marshall), and varied widely with respect to drainage class and slope. Four cropping systems were established by Bonin et al (2018) in 50 x 68 m plots the spring of 2012: no-till continuous corn (CC), switchgrass (SG), low-diversity grass mix (LD), and high-diversity grass and forb mix (HD). The cropping systems were chosen by Bonin et al (2018) to compare grain-based and perennial species based cellulosic bioenergy feedstocks production systems [51]. Plots were arranged in a completely randomized split plot design with four replicates for each cropping system (sixteen plots total). A split plot design was used wherein half of each plot received no biochar (control) and the other half received 9.3 Mg ha^{-1} (dry weight equivalent) biochar amendment of moist (~50% water by mass) biochar in the fall of 2011, which was incorporated to a depth of 15 cm (equivalent to 0.5% on an oven dry weight basis). Since the application of the biochar, the plots have been in perennial biomass crops or managed for continuous no-till maize production. Because 2012 was a drought year, the switchgrass plots were not properly established, and needed to be re-planted in the spring of 2013. Thus the 2014 growing season can be considered two years after the establishment of the grass mixes (LD and HD) and one year after the establishment of SG. In 2014, fertilizer was applied to corn plots (CC) at 224 kg N ha^{-1} as urea ammonium nitrate (knife application in every row) on May 4th and to grass and grass-forb plots (SG, LD and HD) at 56 kg N ha^{-1} as urea (broadcasted application) on May 2nd; corn was planted in 76 cm rows on May 8th.

2.3 Incubation study

The laboratory incubation study was conducted to examine the effects of biochar on CO_2 and N_2O emissions at three different moistures and temperatures for comparison with field study results. Soil for the incubation study was collected from the top 5 cm of the control (biochar-unamended) portion of a continuous corn (CC) plot at the Armstrong study site (Exira soil with 15% sand, 80% silt and 5% clay) prior to fertilization in the spring (2014), and frozen for 6 months. Soil was incubated with and without biochar at three soil moistures (-1, -1/3 and -1/10 bar matric potential-equivalent) and temperatures (10, 20 and 30°C) for a total of 140 days in a full factorial design with five replicates. Prior to use, soil was thawed and sieved to <4 mm. Gravimetric moisture content was determined by oven-drying (10 g of soil for 2 hrs at 105^{0}C), biochar was amended at a 0.5% (wt/wt) rate, and all samples were stirred thoroughly. Moisture contents of control and biochar-amended soil at -1, -1/3 and -1/10 bar pressure were determined using a pressure plate prior to the initiation of the study, and it was found that the biochar did not significantly affect soil moisture at these matric potentials. For the incubations, 10 g (dry weight equivalent) of sieved (<0.4 mm) field-moist soil was weighed into 150 mL glass serum vials.

Control and biochar-amended samples were equilibrated during a pre-fertilization period for 60 days, followed by the addition of corn stover and fertilizer, and then incubated for an additional 80 days. During the first two weeks of the pre-fertilization period, soil moistures were gradually adjusted from field moisture levels to the target -1, -1/3 and -1/10 bar matric potential levels (equivalent to 27, 31 and 35% wt/wt moisture). During this pre-fertilization period, CO_2 and N_2O emissions were quantified on days 0, 2, 6, 9, 20, 23, 30, 36, and 56. After 60 days, corn stover was mixed in at 0.5% (wt/wt), and fertilizer was added as NH_4NO_3 and K_2HPO_4 at a rate equivalent to 72, 42 and 54 mg/kg of N, P and K, respectively. Soils were incubated for an additional 80 days following fertilization, during which time emissions were quantified on days 0, 1, 2, 3, 7, 10, 16, 38, 52, 62 and 80. For each gas flux rate measurement, serum vials containing soil and biochar were sealed with grey butyl septa and crimp caps, and 11.5 mL gas samples were collected from these serum vials using a syringe three times over the course of 16 to 48 hours, with longer gas accumulation times used when flux rates were low. Serum vials were left uncapped for 15-20 min prior to each flux rate measurement to allow for gas circulation; vials were capped at all other times to minimize moisture loss.

2.4 Field study

Emission rates of CO_2 and N_2O from soil under four cropping systems with and without biochar were quantified during the 2014 growing season at the Armstrong field site. Prior to fertilization and corn planting, two stainless steel pans (49 x 29 cm) were installed in each split plot (4 per plot). Pans within each split plot were 17 m apart, and pans in opposite split plots were 26.4 m apart (each was 13.2 m from the boundary between split plots). Pans in CC plots were removed

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prior to fertilization and planting and re-installed afterwards; care was taken to avoid installing pans in disturbed soil. Following fertilizer application, all pans in CC plots were placed along the fertilized band, such that the longer edge of each pan was parallel to the strip of fertilized soil located within the pan. This orientation allowed each pan to have the same number of corn stalk stumps from the previous growing season. To minimize the effect of root respiration and root exudates, soil within each pan and in a 50 cm radius around each pan was kept free of plants using a combination of gentle hand-weeding and hand-spraying with both pre-and post-emergent herbicides. Care was taken not to disturb soil within the pans. Following pan installation, greenhouse gas emissions were measured regularly from April 21st to September 16th (days 0, 14, 22, 29, 38, 45, 50, 60, 72, 79, 86, 93, 109, 120, and 148). These dates reflect more frequent measurements during periods of expected high GHG emission rates directly following fertilizer application and rainfall. Gas sampling dates were chosen so as to capture post-rainfall fluxes while avoiding saturated soil conditions. Plots – arranged spatially at random – were organized into four temporal blocks, with one plot of each cropping system in each block, and gas samples from every plot within a block were taken within one hour of each other to minimize diurnal temperature variability within each block. Soil moisture (% by volume) and temperature (°C) were measured at each pan location at 5 cm depth concurrently with gas sampling. To quantify emission rates, pans were covered with an insulated pan lid and clamped down to form an airtight seal, then gas samples were collected at four times with a syringe through a grey butyl septa installed in the lid of the pan, and average gas accumulation time was 30-90 minutes (longer times were used on days with lower expected emission rates). Gas samples were stored and analyzed in the same manner as in the incubation study (see above). At the conclusion of the field study, soil was destructively harvested from within the GHG sampling pans (0-5 cm depth) and analyzed for total C and N (Vario Microcube).

2.5 Gas sample analysis

All gas samples collected in the lab and field were stored in helium-flushed and evacuated airtight 6 mL Exetainer vials, and then analyzed for CO_2 and N_2O using a gas chromatograph equipped with a Methanizer flame ionization detector and an electron capture detector (SRI Instruments, Torrance, CA 90503; Model 8610C). Concentrations were measured in volume ppm units and converted to mass ppm units using the ideal gas law. Following termination of the incubation, soil samples were oven dried and analyzed for total C and total N using a combustion analyzer (Vario Microcube, Elementar).

2.6 Calculations and statistical analyses

Gas fluxes were calculated from the slope of the linear increase in gas concentrations over time, and any slopes with r^2 <0.5 were assumed to be zero [52]. Cumulative emissions were calculated by interpolating linearly between daily fluxes (“trapezoidal interpolation”). All statistical analyses were conducted using SAS (v. 9.2). Daily gas fluxes (field and laboratory), soil moistures (field only), and soil temperatures (field only) were compared using repeated measures (ante-dependence and compound symmetry models, as appropriate). For the statistical analysis, plots were divided into four blocks (one of each crop treatment per block) based on in-field sampling times to reduce variance due to diurnal temperature fluctuations. Accumulated gas fluxes measured over the entire season or incubation period were compared using ANOVA. Significance was evaluated at $p = 0.05$.

3. Results

3.1 Soil laboratory incubation

Emission rates for CO_2 during the 60 day pre-fertilization period varied over time and did not consistently correspond to biochar and moisture treatments, but CO_2 emissions did exhibit a significant increase with increasing temperature (Figure S1a). Over the course of the 80-day post-fertilization incubation, daily CO_2 emissions increased significantly with increasing temperature (10°C < 20°C < 30°C), and this effect was consistent over time and among different moisture and biochar treatments (Table 1, Figure 1). By contrast, the effects of soil moisture treatments on CO_2 emissions were variable: on some days emissions increased with increasing moisture while on other days they decreased, and the response to moisture was inconsistent across temperature and biochar treatments. The lack of a consistent moisture response may have been in part due to the small difference in percent moisture (8%) between the highest and lowest moisture treatments. In spite of the variability in daily emissions, both temperature and moisture had positive effects on cumulative CO_2 emissions, and the temperature*moisture interaction was significant (Table S2). The main effect of biochar and interaction effects including biochar (biochar*moisture, biochar*temperature, etc), however, had no significant effect on cumulative CO_2 emissions. These data support previous research showing that long-term soil CO_2 emissions are often unaffected by biochar amendments [10,18,53].

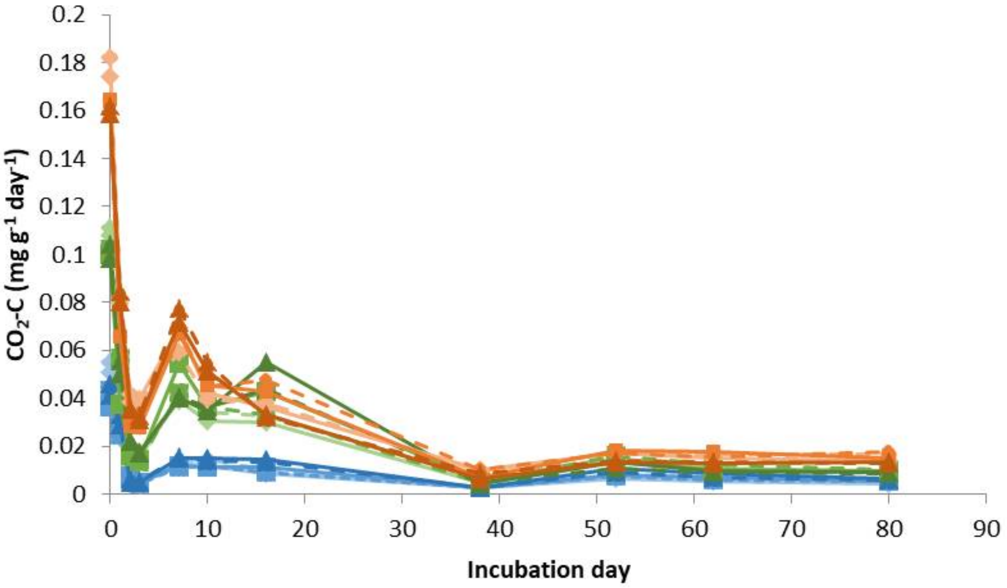

Figure. 1 Daily post-fertilization CO_2-C emissions, in mg of CO_2-C per gram of soil per day (5 replicates) (blue = 10°C, green = 20°C, orange = 30°C; diamonds = 27%, squares = 31%, and triangles = 35% moisture; dashes = controls, solid lines = biochar)

The majority of soil sample N_2O emissions were not significantly different from zero during the pre-equilibration period (Figure S1; Table S1), then became greater than zero during the first 10 days of the incubation after fertilization; however, N_2O emissions fell below the pre-fertilization emission rates after day 10. Hence, only emissions during the first 10 days following fertilization are presented in Figure 2 and considered in the statistical analysis of N_2O emissions. Temperature, moisture, and day significantly affected daily N_2O emissions following fertilization, but biochar amendment did not have a significant impact. Similar to daily emissions, the main effects of temperature and moisture as well as the temperature*moisture interaction on N_2O accumulated over the first 10 days were all significant, and the main effect of biochar was not significant ($p > 0.05$; Table 1, Table S2). The biochar*temperature*moisture, biochar*temperature, and biochar*moisture interactions were also not significant. Although the biochar effect wasn't significant, biochar amendment did reduce total N_2O emissions by 50% at 20°C and 31% moisture, a result consistent with a previous study using the same biochar and soil [50]. Thus, both moisture and temperature significantly affected CO_2 and N_2O emissions; overall results suggest that biochar amendment presents a minimum potential for increasing CO_2 and N_2O emissions, and may reduce N_2O emissions under specific contexts including moderate temperatures and moistures.

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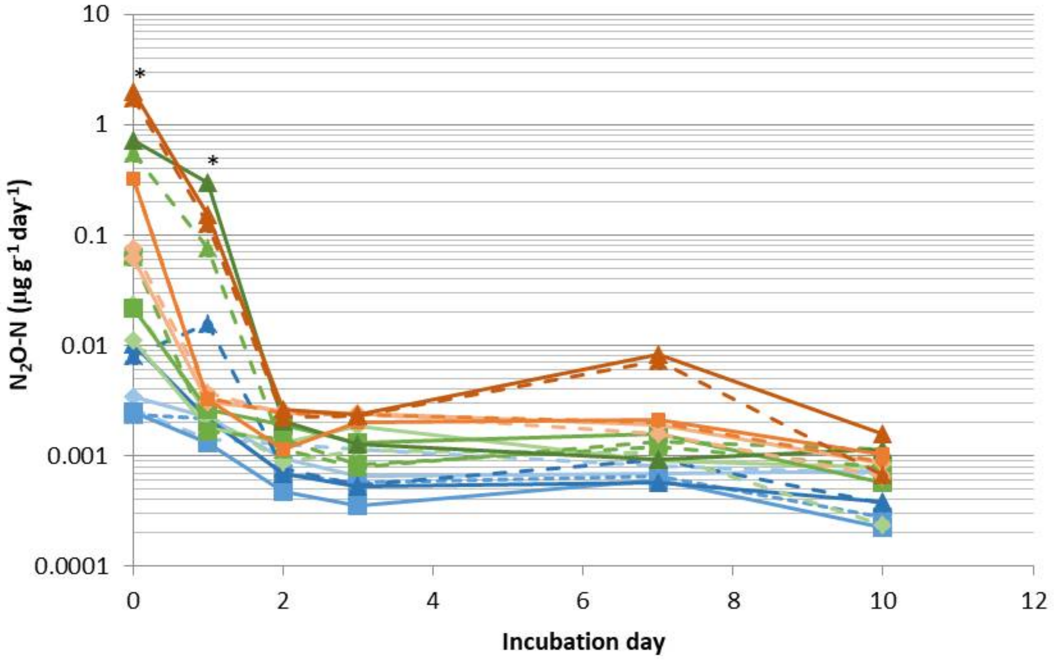

Figure. 2 Daily N_2O-N emissions during the first 10 days of the post-fertilization period, in µg of N_2O-N per gram of soil per day *(emissions below detection limit after day 10)* (5 replicates) (blue = 10°C, green = 20°C, orange = 30°C; diamonds = 27%, squares = 31%, and triangles = 35% moisture; dashes = controls, solid lines = biochar)

*interaction of biochar*moisture*temperature*day significant ($p < 0.05$)

Table 1. Cumulative total CO_2 and N_2O emissions from biochar-amended and control soil measured over 80 days and 10 days, respectively, following fertilization during the laboratory incubation (± se). *No significant effects of biochar amendment were observed.*

Temperature	**Moisture (%)**	**CO_2** (mg CO_2 g^{-1})		**N_2O** (µg N_2O g^{-1})	
		control	biochar	control	biochar
10°C	**27**	2.33 ±0.05	2.1 ±0.1	0.043 ±0.003	0.047 ±0.002
	31	2.21 ±0.09	2.4 ±0.1	0.041 ±0.006	0.029 ±0.006
	35	2.6 ±0.1	2.9 ±0.1	0.1 ±0.05	0.10 ±0.07
20°C	**27**	5.7 ±0.4	5.4 ±0.4	0.15 ±0.02	0.09 ±0.01
	31	5.8 ±0.5	6.2 ±0.5	0.34 ±0.1	0.15 ±0.02
	35	5.9 ±0.2	6.6 ±0.6	3.2 ±0.4	4.3 ±0.9
30°C	**27**	8.0 ±0.5	7.9 ±0.4	0.4 ±0.05	0.4 ±0.07
	31	8.4 ±0.5	8.2 ±0.6	1.6 ±0.5	1.6 ±0.5
	35	7.5 ±0.1	7.2 ±0.3	7 ±2	10 ±2

Field study: total C and N, precipitation, temperature and moisture

Average total C and N of soil collected from within the GHG sampling pans (5 cm depth) are shown in Table 2. Biochar consistently increased total C but did not affect total N. Cropping system also had a minimal impact on total C and N, although the soil from switchgrass (SG) plots did have slightly higher total C than soil from continuous corn (CC) plots.

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Total rainfall for the study period was 726 mm (Figure 3). Total rainfall from April through September was 949 mm, higher than the 624 mm 30-year average rainfall of the field site for this period. Major rainfall events (>40 mm) occurred on days 21, 44, 129 and 142.

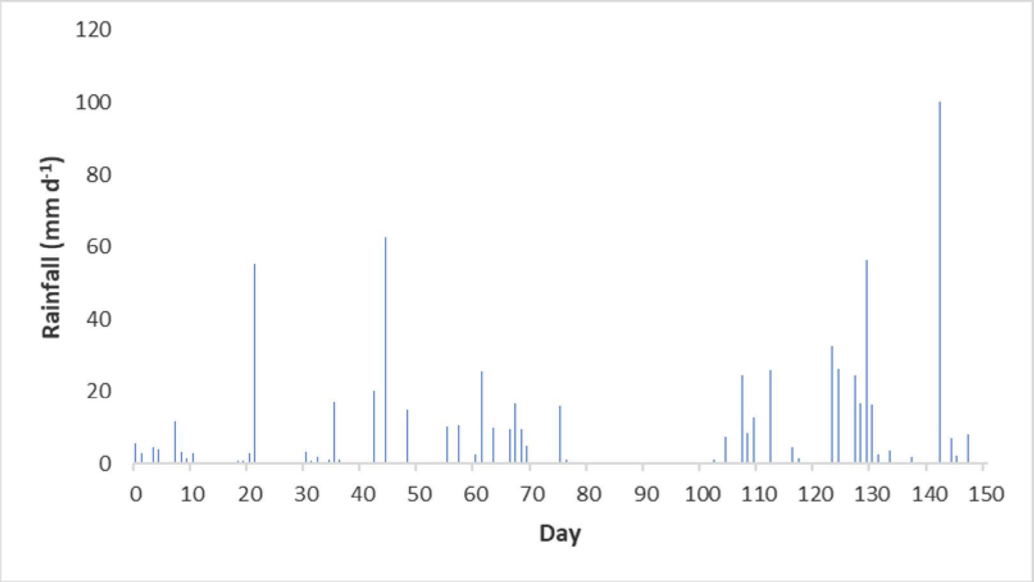

Figure. 3 Daily precipitation in mm of rainfall per day during the 148 day field experiment (April 21st – September 16th), where the beginning of the experiment (April 21st) is defined as day 0.

The main effects of crop, day, and block (representing plot location and sampling time group) on 5 cm soil temperatures were all significant (5 cm depth), but the effect of biochar was not significant (Figure 4; Table S3). Average soil temperatures were highest in the high diversity (HD) plots, followed by low diversity (LD), SG and CC plots. The differences in soil temperatures among cropping systems likely resulted from differences in canopy cover. Grass and grass-forb plots had less average canopy cover over the growing season because grasses were slower-growing than corn, and the LD and HD plots contained weedy areas with less canopy cover near the gas sampling pans (visual observation). In addition, the HD plots were mowed on day 120 to minimize weed proliferation, which further decreased canopy cover. By contrast, the average difference in temperature between the biochar-amended and unamended soils was negligible (<0.1°C). Thus cropping system had a dominant effect on soil temperature, which likely plays a role in cropping systems' influence on soil GHG emissions.

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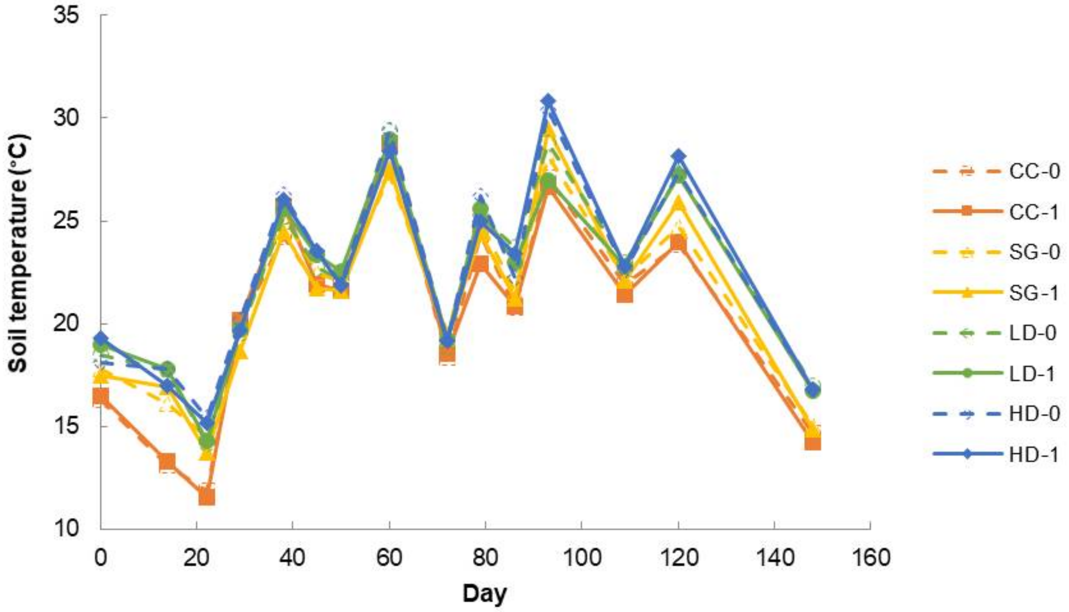

Figure. 4 Average soil temperatures measured for each cropping system with biochar and without biochar on each day that GHG emissions were measured (CC = continuous corn, SG = switchgrass, LD = low diversity grass mix, HD = high diversity grass and forb mix; 0 = control, 1 = biochar-amended).

The main effects of crop, biochar, day, and block on moisture were all significant (5 cm depth; p <0.05, Figure 5). The crop*biochar*day interaction was significant on eight out of 15 measurement days. Soil moisture tended to be highest in SG plots and lowest in HD plots, but the effect of cropping system was somewhat variable over time. The LD plots exhibited the greatest increase in moisture with biochar amendment, followed by SG, CC and HD; when moistures were averaged over all measurement dates, biochar increased average moisture by 1-3% within each cropping system. Differences in soil moisture between biochar-amended and control soils within each cropping system were generally greater on days with lower average soil moisture; biochar increased soil moisture for at least three out of four cropping systems when control soils had ≤30% moisture on average. Biochar was especially effective at increasing soil moisture during a dry period occurring from mid-July through mid-August (days 72-93). Thus, the results show that biochar consistently increased average soil moisture (at 5 cm depth), and was generally most effective at increasing soil moisture in plots with higher grass density (LD and SG) and during soil drying cycles.

Table 2. Total %C and %N (weight basis) of soil within greenhouse gas monitoring pans (±se) (CC = continuous corn, SG = switchgrass, LD = low diversity grass mix, HD = high diversity grass and forb mix)

	%C		%N	
crop	control	biochar	control	biochar
CC	2.5 ± 0.3	2.9 ± 0.2	0.26 ± 0.01	0.26 ± 0.02
SG	2.5 ± 0.1	3.2 ± 0.3	0.26 ± 0.01	0.26 ± 0.01
LD	2.2 ± 0.1	3.4 ± 0.2	0.24 ± 0.01	0.27 ± 0.01
HD	2.9 ± 0.3	3.2 ± 0.3	0.27 ± 0.01	0.27 ± 0.02

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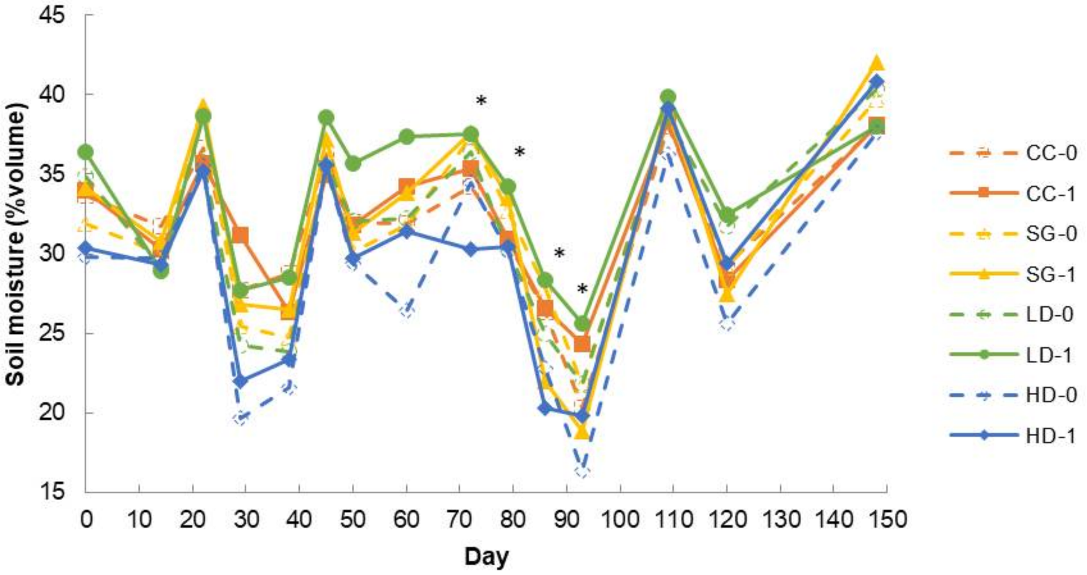

Fig. 5 Average soil moistures measured from each cropping system, with biochar and without biochar (n=8) on each day that GHG emissions were measured.
*significant effect of biochar within at least one cropping system ($p < 0.05$)

3.2 Field study: CO_2 emissions

Daily soil CO_2 emissions were significantly affected by day, crop and block (spatial and diurnal variability), but not by biochar (Figure 6; Table S3). Transient significant differences were observed between biochar-amended and control soils within the SG and LD cropping systems, but these effects were inconsistent. Compared with controls, significantly higher CO_2 emissions were measured from biochar-amended soils on some days, and on other days emissions from biochar-amended soils were lower than controls. On average, daily CO_2 emissions increased in the order CC<HD~LD<SG (Figure 6), and this trend was reflected in the cumulative total CO_2 emissions (Figure 7).

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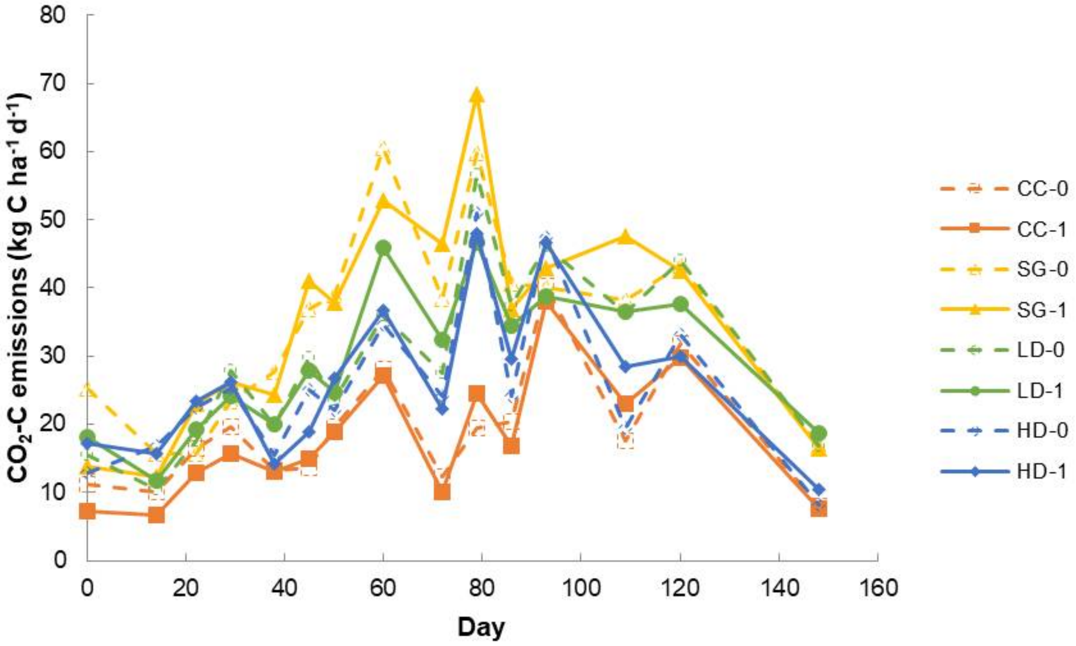

Fig. 6 Average daily soil CO_2-C emissions measured for each treatment.

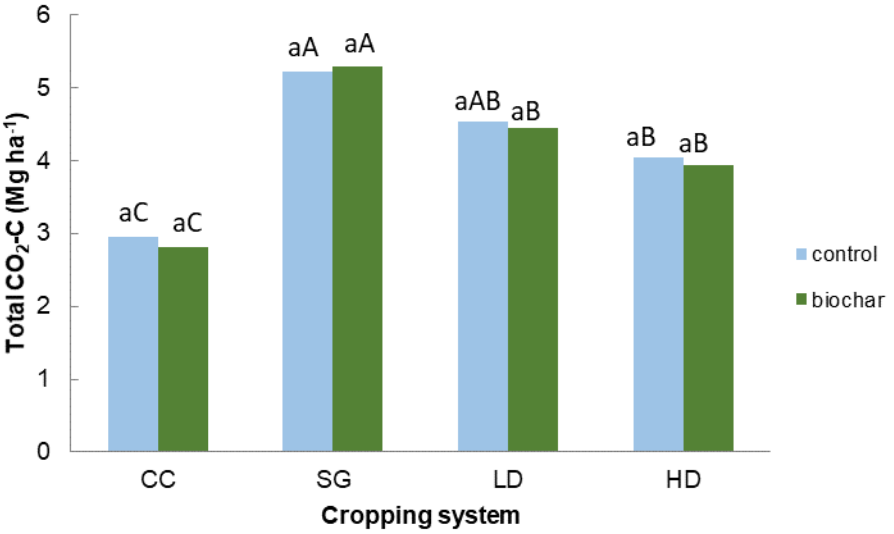

Fig. 7 Accumulated total soil CO_2-C emissions from the four cropping systems, with and without biochar. Lowercase letters indicate significant differences within each cropping system; uppercase letters indicate significant differences between cropping systems (effect of biochar not significant).

Similar to daily emissions, the effect of crop on cumulative total CO_2 emissions over the 148-day gas monitoring period was significant, but the effect of biochar and the crop*biochar interaction were not significant (Table S4). Differences in CO_2 emissions among cropping systems were likely due to differences in root or biomass density and resultant differences in labile soil organic carbon. Additionally, differences in fertilizer application rates and canopy cover might also have influenced CO_2 emissions. Thus, overall, CO_2 emissions were significantly affected by cropping system as well as spatial (block) and temporal (block and day) variables, but not by biochar.

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3.3 Field study: N_2O emissions

While the main effect of biochar on daily soil N_2O emissions was not significant, the crop*block*day and block*biochar*day interactions were significant (Figure 8, Table S3). The main effects of day, crop, and block were also significant ("block" encompasses spatial and diurnal variability; see methods). Emission rates from CC soils were highest directly following fertilizer application (day 22) and decreased rapidly thereafter, whereas emissions from grass system soils were elevated for a longer period (days 38-60). Differences in observed fertilizer response time are likely due to respective differences in fertilizer type (UAN vs. urea) and/or application rate (224 vs. 50 kg N ha^{-1}). For select measurements made during the first six weeks following fertilization (days 22, 29 and 60), biochar-amended CC soils had significantly lower N_2O emissions (0.04-0.06 kg N_2O ha^{-1}) than control CC soils (0.06-0.1 kg N_2O ha^{-1}). Similarly, biochar-amended SG soils had significantly lower N_2O emissions than control SG soils on days when emissions from SG plots were elevated (0.04-0.06 kg N_2O ha^{-1}). The ~40% suppression of N_2O emissions from biochar-amended CC soils observed when emissions were elevated often occurred despite higher soil moistures in biochar-amended soils relative to control soils (days 22-38 and 60). Daily N_2O emissions also tended to increase in the order HD<LD<SG<CC prior to day 80, but after day 100, SG soils tended to emit more N_2O than CC soils. Overall, biochar amendment consistently suppressed short-term N_2O emissions from CC cropping systems, and less consistently suppressed emissions from SG cropping systems.

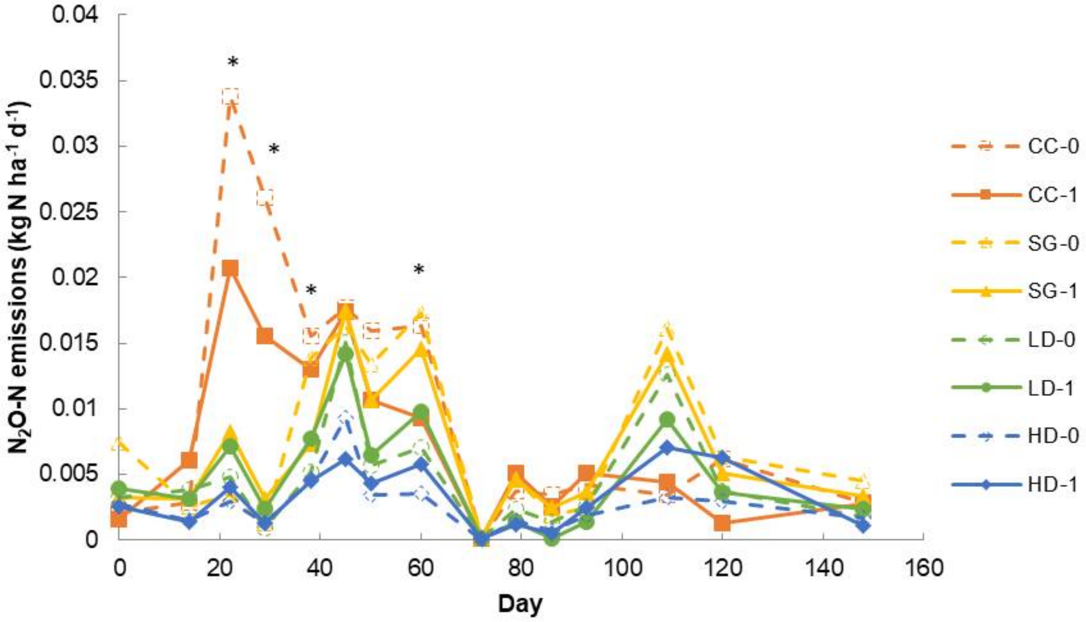

Fig. 8 Average daily soil N_2O-N emissions measured for each treatment.
*significant effect of biochar within at least one cropping system ($p < 0.05$)

With regards to total N_2O emissions accumulated over the 148-day emission monitoring period, the main effects of crop and block were significant (Figure 9, Table S4). Total N_2O emissions increased with increasing biomass production and increasing fertilizer application rate (HD≤LD<SG≤CC). Biochar reduced N_2O emissions from CC soils by 27%, a reduction of nearly the same magnitude as the field study literature average of 28% [30]. Thus, overall the N_2O results suggest that biochar did not impact total N_2O emissions but was effective at temporarily reducing emissions from the continuous corn systems directly after fertilizer application – probably because the CC systems received the highest N fertilization rates.

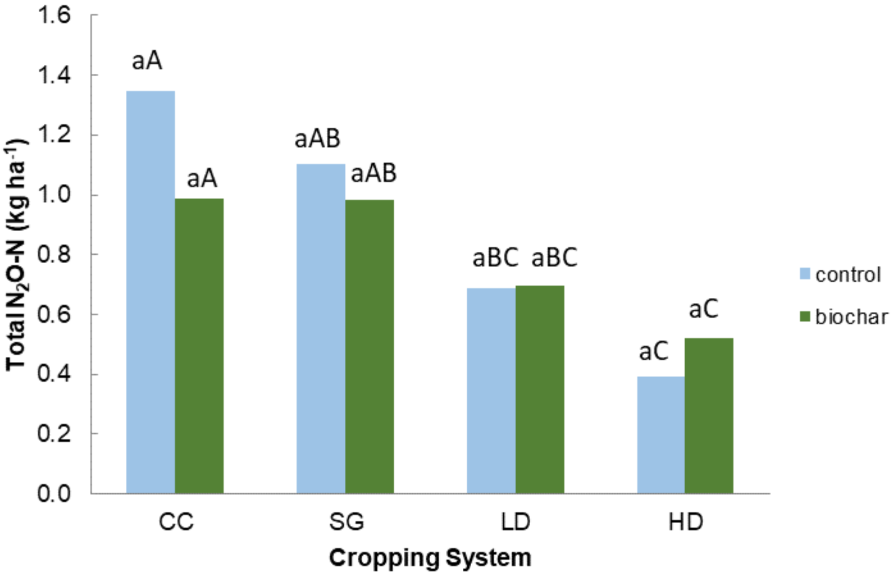

Fig. 9 Accumulated total soil N_2O-N emissions from the four cropping systems, with and without biochar. Lowercase letters indicate significant effects of biochar within each cropping system; uppercase letters indicate significant differences between cropping systems within biochar treatments (effect of biochar not significant).

4. Discussion

Among the laboratory-incubated soils and field-scale cropping system soils investigated here, biochar had no significant effect on cumulative soil CO_2 emissions, but did reduce N_2O emissions for a no-till continuous corn cropping system. The lack of effect of biochar on soil CO_2 emissions here measured 3 years after the biochar amendment supports previous observations that the impact of biochar on CO_2 emissions is predominately restricted to the short term (<1 month) [50,54]. Also consistent with previous laboratory results, biochar reduced N_2O emissions at 20°C with 27% and 31% moisture. Although non-significant, the magnitude of reduction (38-56%) was in agreement with literature values [30]. In the field study, biochar reduced N_2O emissions from soils under continuous corn by an average of 27%; this magnitude of suppression was consistent with average reduction of 28% reported for field studies by Cayuela *et al.*, (2015) [30].

Despite 27% suppression of N_2O emissions in biochar-amended CC soil at the field scale, the emissions measured at the laboratory scale were not consistently suppressed for the three temperature and moisture levels studied. Apparent differences in N_2O emissions results between lab-scale and field-scale studies may have arisen from slight differences in study design between the lab and field, such as (a) environmental factors present in the field only, including temperature and moisture fluctuations and biological inputs, (b) differences in fertilizer type and distribution in the soil between the lab and field experiments, (c) differences in physical or biochemical properties between the soil stored and sieved in the lab for incubation and the field soils, and (d) differences in properties between the fresh biochar added in the incubation compared with the aged biochar present in the field study (since plant roots were excluded from field study pans, and no plants were grown in the incubation, the influence of plants on result differences should have been minimal). The third factor (soil properties) encompasses natural variability in soil properties present at the field scale – namely, that emissions results at the field scale were averaged across four plots per crop, whereas soil for the incubation was collected from a single plot. Furthermore, due to the inherent variability of N_2O emissions, the possibility that type II statistical errors obscured significant differences in the incubation study cannot be excluded. Moreover, Cayuela et al. (2013) found that, in studies using biochar application rates of <1% and NH_4NO_3 fertilizer, biochar was less likely to significantly suppress N_2O emissions compared with studies using other fertilizers and/or higher biochar application rates (here NH_4NO_3 was used in the lab, and UAN was used in the field corn plots) [12]. Lastly but perhaps most importantly, the biochar in the field study had been weathering in the soil for 2.5 years before the study began. Generally, biochar aging in soils or other aqueous environments is associated with an increase in oxygen functional groups, and a decrease in soluble biochar components such as salts, carbonates, and low molecular weight organic compounds. Moreover, Spokas (2013) found that fresh biochar reduced soil N_2O emissions, whereas field-aged biochar did not [42]. Thus, apparent scaling effects on emissions may be attributed to spatial variability, environmental factors, experimental design differences, and/or aging of biochar.

Cumulative cropping system N_2O emissions were, as expected, highest for continuous corn and tended to decrease with increasing plant species diversity and decreasing fertilizer application rate (HD≤LD<SG≤CC). Grass-based cropping systems tended to have lower N_2O emissions than continuous corn cropping systems, most likely due to the lower fertilizer application rate (56 kg N ha^{-1}) for the grass and grass-forb plots (SG, HD and LD) compared with the corn plots (224 kg N ha^{-1}). Lower emissions in the grass mix plots (LD and HD) compared with switchgrass may have been a result of mixed grasses and forbs taking up N over a broader range of the growing season than switchgrass alone. Alternatively, lower labile organic carbon inputs to the soil (due to lower crop biomass production) in the LD and HD plots may have decreased the supply of carbon to N_2O-producing microbes [55]. Lastly, lower N_2O emissions from grass system soils might have been influenced by lateral movement of inorganic nitrogen from within the gas measurement pans to the roots of plants growing >50 cm away from the pans, but this possibility cannot be confirmed with the available data.

Biochar either reduced or did not affect soil N_2O emissions at the field scale in spite of the increased soil moisture of biochar-amended soils. Compared with controls, soil moisture averaged over the whole growing season was consistently 1-3% higher in biochar-amended soils for all cropping systems, and this finding supported previous laboratory and field-scale evidence for biochar increasing soil moisture [56–58]. Increased soil moisture is known to contribute to elevated soil N_2O emissions [47,59], and increased N_2O emissions with increasing soil moisture was also observed in the laboratory incubation conducted here. Biochar may have reduced N_2O emissions in part by reducing the moisture sensitivity of soil N_2O production – the degree to which emissions increase with increasing moisture. Indeed, Deng et al (2015) observed that biochar amendment reduced the moisture sensitivity of soil N_2O emissions and posited that reduced moisture sensitivity arises from the synergistic impact of multiple soil properties influenced by biochar. For example, biochar may have decreased soil bulk density and increased the absorption capacity for organic molecules and nutrients, thereby simultaneously increasing oxygen availability and decreasing the availability of substrates to nitrate and nitrite-reducing microbes – two conditions that could reduce the sensitivity of N_2O emissions to changes in soil moisture.

In summation, while the results did not indicate an effect of biochar on soil CO_2 emissions, they did support our hypotheses that biochar would affect N_2O emissions, and that biochar's suppression of N_2O emissions would be greatest in continuous corn cropping systems. Results also supported the hypothesis that soil moisture and temperature would influence CO_2 and N_2O emissions. However, the results did not support the hypothesis that laboratory studies using fresh biochar could predict the impact of aged biochar on field-scale soil N_2O emissions. Furthermore, although substantial in magnitude (27%) for the entire growing season, N_2O emissions suppression in the field was only significant in the short term following fertilization. These findings also support previous observations of reduced moisture sensitivity of N_2O emissions in biochar-amended soil, and of differing effects of aged versus fresh biochars [42,60]. More research is needed to determine the mechanism(s) by which biochar reduced N_2O emissions under field and laboratory conditions, and how or if emissions impacts depend on additional contextual factors not examined here.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: Daily soil emissions from laboratory incubation, Figure S2: Cumulative N_2O emissions from laboratory incubation; Figure S3: Final NH_4^+ and NO_3^- concentrations; Table S1: Repeated measures statistical results from soil incubation; ANOVA statistical results from soil incubation; Table S3: Repeated measures statistical results from daily field emissions data; Table S4: ANOVA statistical results from cumulative field emissions data.

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