Corn and Soil Response to Biochar Application and Stover Harvest

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Abbreviations: CEC - calcium carbonate equivalent; ECEC – effective cation exchange capacity;

SOM – soil organic matter; TC- total carbon; TN – total nitrogen;

Abstract

Soil biochar amendments are hypothesized to help mitigate potential negative soil quality effects of harvesting crop residues for bioenergy production. This study quantified effects of a onetime biochar application on crop yields and changes in soil properties at a Midwestern U.S.A. site where corn (*Zea mays*) stover is being harvested. The long-term experiment was established in Boone County, Iowa by application of 0, 9.8, and 18.4 Mg ha⁻¹ of <0.64 cm hardwood biochar, in the fall of 2007. Soil properties were measured in summer 2010, three years after the biochar application and following two stover harvests (0, ~50 and ~90% of above ground residue). Fertilization rates were adjusted to account for removal of nutrients with residue. Corn and biomass yields were measured for the 2008-2012 crop years. Biochar applications increased total carbon (TC) of soils by about 0.5% and soil pH by about 0.5 pH units but had no significant effect on total nitrogen (TN), soil test nutrient concentrations, bulk density (BD), aggregate stability or effective cation exchange capacity (ECEC). Residue removal had no significant effect on TC, TN, ECEC, or soil test nutrients except for Mehlich III extractable Zn and S concentrations. The 90% residue removal treatment significantly reduced wet aggregate mean weight diameter by 13% compared to no residue harvest. During the first five years of the study, the 50 and 90% residue removal treatments significantly increased corn grain yields by 1.4 Mg ha⁻¹, averaged across all biochar treatments. When analyzed on an annual basis, biochar had no significant effect on grain yield, but when averaged across years, the 18.4 Mg ha⁻¹ biochar application rate significantly increased yields by 0.49 Mg ha⁻¹ for the zero residue removal treatment but not for the 50% and 90% residue removal treatments. Residue removal increased yield to a greater extent during years of stress due to either excess moisture (2008 and 2010) or drought (2012). There was no yield effect in 2011, a year with favorable climatic conditions. The results suggest that during the first five years of study, residue removal in general had

positive effect on yield of continuous corn. Application of biochar at the high rate increased yield in the plots with 0% residue removal.

1. Introduction

Development of commercial-scale cellulosic industries may provide a boost to rural economies, create jobs, and reduce dependence on imported oil; but if crop residue harvest is managed in unsustainable ways soil degradation and environmental risks could be severe. Notably, soil scientists have raised concerns that continuous harvest of crop residues may negatively impact soil quality and ultimately agricultural productivity (Laird and Chang, 2013; Tolessa et al., 2014; Wilhelm et al., 2004).

Many characteristics of highly productive soils relate to the organic matter fraction, which imparts numerous positive physical, chemical and microbiological characteristics to soil (Doran et al., 1998; Jastrow, 1996). Crop residue management influences the annual inputs of above and below ground biomass to soils, and hence impacts of residue management on soil quality and crop productivity can be observed on short term (within a year) as well as longer time frames. Crop residues contribute labile forms of soil organic matter (SOM), which have a large influence on soil physical properties, such as aggregation, structure, and aggregate stability (Six et al., 1999; Stetson et al., 2012). In turn, aggregation and aggregate stability have a large influence on water infiltration, soil water-holding capacity, aeration, bulk density and penetration resistance (Carter, 2002). Crop residue management also influences soil pH, nutrient availability, nutrient cycling, ion exchange capacity, and buffering capacity. Residues contain nutrients such as K and Ca, hence the removal of residue can deplete soil of basic cations and lead to soil acidification (Laird and Chang, 2013; Tolessa et al., 2014). For example, complete removal of residues for 19 years resulted in reductions of effective cation exchange capacity (ECEC) by 7.3%, N mineralization potential by 28%, and soil organic carbon by 12% (Laird and

Chang, 2013). Despite strong evidence for the negative effect of excessive residue removal on soil physical and chemical properties, evidence of crop residue harvesting impacts on crop yields is inconsistent (Karlen et al., 2011a). Some studies show decreased yields in years following residue harvest (Linden et al., 2000; Wilhelm et al., 1986), while others have shown no detectable yield declines and even yield increases (Biau et al., 2013; Karlen et al., 2011b; Sindelar et al., 2013).

Residue management influences a complex set of interactions associated with soil microbiology and surface conditions that both directly and indirectly influence crop performance. Dense crop residue coverage has been observed to decrease yields due to poor weed control, nutrient immobilization, wet and cool soils, poor soil-seed contact during planting (Kaspar et al., 1990), and release of allelochemicals from decomposing residues - all of which have been documented to reduce plant stand and early season plant growth (Rogovska et al., 2014; Swan et al., 1994; Wilhelm et al., 2004; Yackle and Cruse, 1984). Positive effects of surface residue on crop yields have mostly been associated with retention of essential nutrients, protection from raindrop impacts and surface crusting, and soil water conservation (Saha and Ghosh, 2013). In the US Corn Belt, residue removal has generally been shown to have a positive or no effect on yields of continuous corn (Karlen et al., 2011a; Kaspar et al., 1990). Residue harvest in a no-till system increase yield of continuous corn, while no effect was observed for a chisel plow system (Pantoja et al., 2015). Seed-row residue removal was shown to increased yield of continuous corn regardless of tillage system in a 3-yr experiment in central Iowa (Kaspar et al., 1990). Thus, removal of crop residue from the field for any use must be balanced against the potential for increased soil erosion, loss of soil organic matter, and both positive and negative impacts on productivity.

Harvested plant biomass can be used in several ways (*i.e.*, as animal feed or for the biochemical/thermochemical production of bioenergy products). Processing harvested crop

residue biomass through a distributed network of fast pyrolyzers and returning the biochar co-product to the soil has been hypothesized to recycle nutrients and add stable forms of carbon, mimicking soil building effects of natural prairie fires, and thus increase the sustainability of crop residue harvesting (Laird, 2008). Biochar has been shown to adsorb nutrients and agricultural chemicals, thus reducing leaching of those chemicals to surface and ground water, and to increase CEC in acidic soils, a benefit that would further increase the soil's ability to hold nutrients (Bell and Worrall, 2011; Chintala et al., 2014; Laird et al., 2010a; Ventura et al., 2013). Biochar is also a low density, highly porous material that has been documented to reduce soil bulk density, improve aeration, increase water infiltration and water holding capacity of sandy soils (Glaser et al., 2002; Uzoma et al., 2011b). On the other hand, biochar effects on aggregate stability have not been consistent, with some studies showing significant improvements (Herath et al., 2013; Hua et al., 2014; Ouyang et al., 2013) while others report no effect on either aggregate stability or mean aggregate diameter (Liu et al., 2012).

Biochar application to soils can either increase or decrease soil pH depending on properties of the biochar and the soil (Hass et al., 2012; Novak et al., 2009; Peng et al., 2011; Uzoma et al., 2011a). Most biochars used in agriculture are alkaline and serve as liming agents potentially offsetting the acidifying effect caused by ammonium fertilizers and the removal of basic cations with crop residue harvest (Lu et al., 2012; Revell et al., 2012). Biochar typically has calcium carbonate equivalent (CCE) values of 9 to 22 %, which compares with 98 to 100% CCE values for crushed calcitic limestone (Hass et al., 2012). For Mollisols, changes in soil pH due to biochar application are generally small (<1.5 pH unit) reflecting high buffering capacity from the elevated SOC content and relatively low CCE of biochars (Novak et al., 2014; Rogovska et al., 2014; Streubel et al., 2011).

This paper summarizes findings of a 5-year field plot experiment aimed at assessing the impact of residue removal following a onetime biochar application on soil fertility and maize

grain and biomass yields. Maize residue harvesting for bioenergy production is now occurring at large scale in the US Midwest, particularly in Iowa with the opening of two new commercial cellulosic ethanol facilities that use maize cobs and stover as feedstock. Therefore, there is a need to document how residue removal along with biochar application will affect crop productivity and characteristics of highly fertile Midwestern Mollisols.

2. Materials and Methods

2.1. Establish and management of field plots

Large field plots (0.11 ha each) were established on two fields (Fields 70&71) at the Iowa State University Agronomy and Agriculture Engineering Research Farm in Boone County, Iowa in October 2007. The soils are classified as a Clarion-Nicolet-Webster soil association, (Typic Hapludolls, Aquic Hapludolls, and Typic Endoaquolls). Soil texture was predominantly loam, clay loam, and silty clay loam with total carbon content in the surface 0-15 cm averaging 2.4% (Soil sampling in 2005). The two fields had been in a long-term tillage study with moldboard plow, chisel plow, spring disk, till-plant, and slot-plant from 1975 through 2006. Initiated as a corn-soybean rotation, Field 70 was converted to “continuous corn” in 1979 while Field 71 remained in a corn-soybean rotation. Following the 2006 harvest, the entire site was deep-tilled to a depth of ~40 cm, cropped with oats which was harvested for both grain and straw in 2007, and deep tilled again to minimize residual effects from the historical tillage treatments.

The complete long-term study included six different management systems (22 treatments) involving tillage (chisel plow vs. no-tillage), rates of residue removal (0, 50, or 90%), planting density and configuration (single 76 cm rows vs. twin-rows spaced 18 cm apart on 76 cm centers), biochar applications, and use of cover crops. This paper focuses only on the effects of

1 biochar applications and corn stover removal on soil properties and corn grain yields under chisel
2 plow tillage.

3 The biochar used in this study was purchased from Streumph Charcoal (Belle, MO).

4 Lump charcoal was produced by slow pyrolysis in traditional steel kilns operated at about 450 °C
5 from mixed hardwood [primarily oak (*Quercus* spp.), elm (*Ulmus* spp.) and hickory (*Carya*
6 spp.)]. Use of corn stover biochar would have been preferable, but hardwood biochar was the
7 only material commercially available in quantities sufficient for a large scale field experiment.

8 The lump charcoal was ground before application using a hammer mill to pass through a
9 0.64 cm screen. Volatiles, fixed C, ash, and moisture content of the biochar were determined by
10 proximate analysis using ASTM standard method D1762-84 (2007). The dry biochar consisted
11 of 71.5% total C and 0.72% total N by mass and contained 63.8% fixed C, 13.9% ash, 19.7%
12 volatile matter and 2.6% moisture by proximate analysis (Laird et al., 2010b). The biochar pH
13 was 7.6 when first placed in DI water, but increased to 8.4 after 7 days (Gaskin et al., 2008).

14 Biochar was surface applied at rates of 0, 9.9, and 18.4 Mg ha⁻¹ (Biochar treatment names
15 are Control, C1, and C2, respectively) in the fall of 2007 and incorporated to the depth of ~20 cm
16 by chisel plow tillage. In the spring of 2008, plots were planted to corn and conventionally
17 managed with fall chisel plow and spring cultivation for the next five years as outlined in Table
18 1. Starting in the fall of 2008, three stover removal treatments (nominally referred to as 0, 50,
19 and 90%) were imposed on biochar amended plots which resulted in nine biochar rate by residue
20 removal treatments, each replicated four times. The “0% residue removal” treatment indicates
21 that all biomass, with the exception of the grain, was left on the soil. The “50% residue
22 removal” treatment was imposed using a single-pass technique that removed grain and the upper
23 half of the plant by cutting just below the ear with a row-crop head attached to a commercial-
24 scale combine. The “90% residue removal” treatment was imposed using the same single-pass

equipment but cutting the corn plant at approximately 15 cm above the soil surface. With the exception of 2008, the amount of biomass harvested from each plot was recorded every year.

Fertilization practices were based on annual surface soil test (pH, P and K) results and interpretation based on Iowa State University (ISU) Extension and Outreach recommendations (ISU, 2013). Because the ISU recommendations were developed assuming the stover would be returned, K and P fertilization rates for the 50 and 90% removal treatments were increased to account for the additional nutrients removed by stover harvest (Table 2). Fertilizer P and K were applied in the Fall in the form of 7-21-7, 11-52-0 (monoammonium phosphate) or 0-0-63 (KCl). Application rates of S were the same (22.4 kg/ha) during 2008, 2011 and 2012 and varied from 16 to 27 kg/ha in 2009 and 2010 depending on the residue removal treatment (Table 2), Nitrogen fertilizer rates were also increased for the 50 and 90% residue removal treatments in 2009 and 2010 to compensate for N removed with the harvested residue but not in 2011 and 2012 (Table 2). Sidedress N was applied in the form of 28 or 32% UAN. Fall N was applied in the form of NPK as 7-21-7 or 11-52-0.

2.2. Climatic conditions

The growing season (April-August) rainfall amount for the study site was 905 mm in 2008; 515 mm in 2009; 927 mm in 2010; 554 mm in 2011; and 370 mm in 2012. The 25-year average for this location is 593 mm (st. dev. 187). Both, 2008 and 2010 had excessive rainfall during the growing season which increased the risk of nutrient leaching and loss of nutrients to surface runoff, whereas 2012 was characterized by widespread drought.

2.3. Soil and plant sampling

Annual near-surface (0 to 15-cm) soil samples were collected beginning fall of 2007 (before biochar application), analyzed for Mehlich III extractable P and K (Mehlich, 1984) and pH (1:1 soil/water suspension (Thomas, 1996)). Fifteen cores were collected from each plot with

a hand probe to a depth of 15 cm in October or November of each year and used to guide the annual fertilization and liming practices. During the 2010 growing season, an additional set of surface soil (0 to 15 cm) measurements were collected to evaluate the impact of biochar, two stover harvests and wheel traffic on soil properties. Bulk density was determined on undisturbed soil cores collected in July 2010. Six samples were collected from each plot using metal rings with an inner diameter of 7.5 cm and a height of 8.5 cm height (Grossman and Reinsch, 2002); three samples were collected from inter-rows that were subjected to compaction by wheel traffic and three were collected from non-wheel-traffic inter-rows in each plot.

Samples were also collected to determine aggregate size distribution from the same rows. For that analysis, five bulk surface (0-15 cm) soil samples were combined into one composite sample for both high and low wheel traffic inter-rows. Samples were carefully handled to avoid soil compression. Large clods were gently broken by hand into smaller aggregates before air drying at room temperature. Aggregate size distribution and mean diameter were determined by wet sieving as outlined by Nimmo and Perkins (2002).

Mehlich III extractable nutrients (Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn) were measured on the soil samples collected for bulk density determination (Mehlich, 1984). The soil samples were also analyzed for total C and N by high temperature combustion using a Carlo Erba NA1500 NSC elemental analyzer (Haake Buchler Instruments, Paterson, NJ) and effective cation exchange capacity which was determined by the method of Sumner and Miller (1996).

At the end of the 2010, 2011, and 2012 growing seasons, corn stover samples were collected from each plot (15 per plot) and analyzed for nitrate concentrations to assess the nitrogen status of the crop (Blackmer and Mallarino, 1996). Stalk nitrate concentrations below 250 mg kg⁻¹ indicate high probability of N deficiency during the growing season; 250-2000 mg kg⁻¹ stalk nitrate levels indicate that yields were unlikely to be limited by N; and >2000 mg kg⁻¹ stalk nitrate levels indicate excessive N uptake during the growing season.

2.4. Grain and biomass harvest

Corn grain and biomass were harvested with a John Deere 9750 STS dual-stream single-pass harvesting system. The modified combine collects both grain and stover and then separates them into two different harvest streams. The single-pass system, which was co-developed by Iowa State University and Deere & Company of Moline, IL, includes a modified row crop header and corn reel attached to the front of the combine and a chopper and blower attached to the back. The row-crop head cuts the corn plant off at the entry point and transfers both the ears and plant biomass into the combine. The stover is cut into 5-cm segments that are then blown into a trailing wagon equipped with load cells (resolution of ± 9 kg). The grain was unloaded into a calibrated weigh wagon after each test pass to determine the grain weight. Grain and biomass subsamples were collected for moisture content determination and subsequent nutrient analysis. Grain yields were adjusted to a moisture content of 155 g kg^{-1} , while biomass yields are presented as dry-matter (*i.e.*, 0 g kg^{-1} water content).

2.5. Statistical analyses

The main experiment was set up as a randomized complete block design to account for some of the spatial variability in soil quality. All statistical analyses were conducted using SAS 9.2 for Windows (SAS Institute). Statistical differences between treatments were determined using a mixed linear model (Proc MIX), $P \leq 0.05$. A two-way ANOVA was used to test for main effect and interactions between factors. Univariate test was used to check for normal distribution of variables. Block was treated as random variable. Multiple comparisons between treatments were performed using Tukey test.

3. Results

3.1. Soil carbon and nitrogen

Extensive soil sampling for physical and chemical properties was performed during the summer of 2010; three years post-biochar application and after two years of residue removal. Biochar application significantly increased TC content from 2.4% in Control plots to 2.9% in the high (C2) biochar treatment plots, but had no significant effect on TN (Table 3). By contrast, neither residue removal nor wheel traffic intensity had significant effects on TC or TN content of the soil three years after the experiment initiation. Soil C:N ratios were significantly higher for samples from the biochar treated plots than samples from the Control plots (11.6, 13.2, and 14.3 for the Control, C1, and C2 treatments, respectively).

3.2. Soil nutrient status

Biochar application did not significantly impact nutrient status of the soil (Table 3). Averaged across biochar treatments, residue harvest had significant impacts only on soil test S and Zn (Table 3). Concentrations of soil test S were slightly higher for plots with 90% residue removed (6.6 mg kg^{-1}) relative to the 0% residue removal plots (5.2 mg kg^{-1}) and significantly higher than soil test S (4.6 mg kg^{-1}) for plots receiving the 50% residue removal treatment. This difference can be explained by increased application rate of S to the plots with 90% residue removal (16 vs. 27 kg S ha^{-1}). Soil test Zn concentrations for plots with 90% residue removal (2.05 mg kg^{-1}) were significantly greater than for plots with the 0% and 50% residue removal treatments (1.62 and 1.56 mg kg^{-1} , respectively). It is not clear why residue removal increased Mehlich III extractable Zn as no Zn fertilizer was applied.

3.3. Soil pH and bulk density

Soil pH variability was observed between plots before initiation of the experiment and those differences remained after biochar and residue removal treatments (Figure 1). The pH values for all but the Control-0% residue removed plots increased about 0.5 pH units from 2007 to 2008, after which soil pH gradually declined until 2011 when 2.2 Mg ha^{-1} lime was applied to

all plots. The greatest decline in pH was observed for Control plots with 50 or 90% residue removal; pH declined from 6.5 and 6.1 to 5.5 and 5.3, respectively (Figure 1).

Averaged across residue removal treatments, the biochar C1 and C2 treatments significantly increased soil pH from 6.2 (Control) to 6.7 and 6.6, respectively, in 2008, a year after biochar application ($P < 0.001$). In 2009 and 2010 average pH values slightly declined for all treatments but remained significantly higher for the C1 and C2 treatments (6.2) relative to the Control plots (5.8). In 2011 all three biochar treatments had significantly different pH values ($P < 0.001$): Control - 5.4; C1 – 5.8; C2 – 6.0. Lime was applied in the fall of 2011 after which significant differences remained between Control (pH 5.3) and C1 and C2 (pH 5.7) plots.

Additional sampling in the summer of 2010 revealed that residue removal had a significant impact on changes in pH; plots with 90% residue removed had significantly lower pH values than plots with 50% residue removed (Table 3).

Soil bulk density samples were collected from trafficked and untrafficked interrows during the growing season of 2010. Neither biochar nor residue removal had a significant impact on soil bulk density. A significant difference was observed only between trafficked and untrafficked interrows (Figure 2).

3.4. Aggregate size

The onetime biochar application did not significantly affect aggregate stability and mean aggregate diameter three years post biochar application. However, when averaged across biochar (0, 9.8, and 18.4 Mg ha⁻¹) and traffic (traffic, no traffic) treatments, 90% residue removal significantly reduced mean aggregate diameter compared to 0% residue removal treatment; 0.28 vs 0.32 mm, respectively (Figure 3). Mean aggregate diameter measured for plots with 50% residue removal (0.29 mm) was not significantly different from that of plots with 0 or 90%

1 residue removal treatments. No difference in mean aggregate size was observed between
2 samples collected from high and low traffic interrows, 0.30 mm for both groups.

3.5. End-of-season cornstalk nitrate concentrations

4 The end-of-season corn stalk nitrate concentrations were measured for the 2010-2012
5 growing seasons to assess N status of corn plants (Figure 4). In 2010, residue removal had a
6 significant impact on stalk nitrate concentrations ($P<0.001$), whereas the main effect of biochar
7 did not ($P=0.44$). However, there was significant interaction between biochar and residue
8 removal rates ($P<0.001$), with lower stalk nitrate levels apparent for the C2 biochar treatment
9 relative to the Control for the 90% residue removal plots. Despite total N application of 212 to
10 258 kg N ha⁻¹ (Table 2), which is within or beyond recommended rates (202 to 226 kg N ha⁻¹;
11 Iowa State University recommendations), fall stalk nitrate analysis indicated N deficiency on
12 half of the plots independent of the residue removal or biochar application treatments for the
13 2010 growing season. N deficiency in 2010 was probably caused by excessive April through
14 August rainfall amounts (923 mm vs 25-year average of 593 mm), which probably resulted in
15 loss of NO₃-N to leaching (Balkcom et al., 2003; Lawlor et al., 2008; Yang et al., 2015).

16 In both 2011 and 2012 a uniform rate of N fertilizer (224 kg N ha⁻¹) was applied to all
17 plots regardless of residue removal treatments. In 2011 neither residue removal nor biochar
18 treatments significantly affected fall stalk nitrate levels and all plots had fall stalk nitrate test
19 values within the optimum range, reflecting favorable climatic conditions with near average
20 April through August rainfall amounts (554 mm in 2011, 25-year average for this location is 593
21 mm, st. dev. 187mm). In 2012 both biochar and residue removal had a significant impact on the
22 end-of-season stalk nitrate concentrations ($P=0.04$ and $P<0.01$, respectively). Severe drought
23 impacted N uptake by corn plants during the 2012 growing season resulting in significantly
24 lower cornstalk nitrate concentrations compared to the previous year with the same rates and

time of N applied. Plots with 50 and 90% residue removed had end-of-season stalk nitrate levels within the optimal range, while some plots with no residue removed had low stalk nitrate levels indicating a shortage of N during growing season. Averaged across biochar treatments, plots with 90% residue removal treatment had significantly higher stalk nitrate concentrations than the 0% residue removal plots; 934 vs. 422 mg NO₃-N kg⁻¹, respectively. As in 2010 the biochar effect was only significant for the 90% residue removal plots in 2012; with plots receiving C1 biochar treatment having lower stalk nitrate levels than the control plots. The cause of the biochar effect in 2010 and 2012 on the 90% residue removal plots is not yet clear.

3.6. Biomass and grain yields

Total amount of biomass harvested is reported in Table 4. Averaged across biochar treatments, amount of biomass removed from plots with 50% residue removal treatment ranged from 3.2 to 4.1 Mg ha⁻¹ depending on the year; whereas for plots with the 90% residue removal treatment it ranged from 4.6 to 7.2 Mg ha⁻¹ – a 38 to 76% increase in biomass harvest compared to 50% removal treatment. With the exception of 2012, biochar did not have an effect on the amount of biomass removed. In 2012, the high biochar rate (C2) significantly increased biomass yield in plots with the 90% residue removal treatment compared to Control plots (Table 4). Averaged across biochar treatments, the amount of residue harvested from the 50% and 90% residue removal treatment plots was significantly greater in 2009 and 2011 than in 2010 and 2012. On average, 4.1 and 7.2 Mg ha⁻¹ of residue was harvested in 2009 from plots receiving the 50% and 90% residue removal treatments, which is 21 and 58% greater than the amount of residue harvested in 2010 and 26 and 54% greater than the amount of residue harvested in 2012, respectively. Biomass harvest was not recorded in 2008 – the first year of study.

There were no significant grain yield differences between biochar treatments in 2008 – the first year after biochar application. Residue removal treatment was implemented during the

harvest of 2008 and yield differences were observed the next growing season; the 50 and 90% residue removal treatments resulted in 2 to 3.7 Mg ha⁻¹ significant yield increases over the no residue removal treatment ($P < 0.001$; Figure 5). There was also a significant interaction between residue removal and biochar application ($P = 0.01$). In 2010 the yield difference between plots with no residue removed and 50 and 90% residue removal was 0.15 – 1.7 Mg ha⁻¹ ($P < 0.001$) and in 2011 there were no significant differences between any of the residue removal or biochar treatments. In 2012 significant yield differences between residue removal treatments reappeared for Control (no biochar) plots ($P = 0.03$), which may be partly explained by the drought conditions in 2012.

Pooled over a four year period (2009-2012), residue removal had the greatest effect on grain corn yield ($P < 0.001$), followed by biochar applications ($P = 0.055$); with significant interactions observed between residue removal rates and biochar application ($P < 0.001$).

4. Discussion

4.1. Soil characteristics

In general, biochar application to highly fertile Mollisols did not have an effect on soil nutrient concentrations. By contrast Laird et al. (2010a) reported significant increases in soil test K, P, Ca, and Mn following biochar and biochar plus manure applications in a laboratory soil column study using the same biochar and soil collected from the same field as used in this study. The fact that biochar effects on soil nutrients were not detected in the field study is not surprising given regular fertilization of the fields, high spatial variability of soils within the fields, and the limited content of soluble nutrients in the applied biochar.

The biochar used in this study had a C:N ratio of 99:1 and was 60% fixed C by mass as measured by proximate analysis. The increased TC and C:N ratios measured three years after

biochar application support the interpretation that the fixed C in biochar was recalcitrant to microbial mineralization even under field conditions.

Both residue removal and biochar application had a significant impact on changes in soil pH (Figure 1). The pH and calcium carbonate equivalent (CEC) of the biochar, determined in the previous study (Laird et al., 2010b), was 8.4, and 8.8%, respectively. Application of 18.4 Mg ha⁻¹ (C2) is equivalent to supplying of about 1.6 Mg ha⁻¹ of lime; therefore, only small liming effect was anticipated. Similar results were observed in the previous column study which utilized the same biochar and one of the soil types comprising Clarion-Nicolet-Webster soil association of the experimental area (Laird et al., 2010b). In this study application rate of 10 g kg⁻¹ (1%) biochar closely corresponds to 18.4 Mg ha⁻¹ (~0.7%) in the field study and resulted in about the same pH increase of 0.5 pH units. The general decline in soil pH with time reflects the acidifying effects of N-fertilizer and removal of basic cations through biomass harvesting. The slight (not significant) increase in pH observed in 2008 for plots that did not receive biochar might reflect seasonal pH variation due to different sampling times during those years; in 2007 plots were sampled on Aug 1st, whereas in 2007 and other years plots were sampled in mid to late November. It is not uncommon to observe seasonal variation of pH of up to 2 pH units (Lehr, 1950; Slattery and Ronnfeldt, 1992).

Neither biochar nor residue removal had a significant impact on soil bulk density three years after a onetime biochar application and two years of continued residue removal. We anticipate that the effects of continuous residue removal will ultimately be evident by an increase in soil bulk density, but it is not clear how many years may be required before the effect will be observable in this type of soil. Biochar has been shown to significantly decrease bulk density in laboratory and greenhouse experiments (Albuquerque et al., 2014; Kelly et al., 2014; Laird et al., 2010b). Indeed we reported bulk densities that averaged about 0.1 g cm⁻³ lower for biochar

1 treatments in the laboratory soil column study using the same biochar and soil from the same
 2 field as the present study (Laird et al., 2010b). Under field conditions results are mixed;
 3 significant differences in bulk density were observed in no-till experiments with much greater
 4 rates of biochar application (Hardie et al., 2014; Rogovska et al., 2014; Zhang et al., 2012),
 5 whereas no consistent effect of biochar on bulk density was observed in experiments that utilized
 6 tillage and biochar rates lower than 20 Mg ha⁻¹ (Nelissen et al., 2015).

7 Excessive residue removal can lead to rapid reduction of labile SOM and thus lower
 8 aggregate stability and increased bulk density, as SOM dynamics strongly influence soil
 9 structure (Carter, 2002). Biochar, however, supplies mostly recalcitrant C which may not have
 10 the same effect on soil bulk density as labile biogenic forms of C. The time needed to observe
 11 significant changes in physical and chemical characteristics of soil due to residue removal varies
 12 depending on soil type and other management practices involved. For example, Blanco-Canqui
 13 et al. (2006) reported an inverse relationship between bulk density and SOM as a result of
 14 residue harvest after only one year under no-till management. Moebius-Clune et al. (2008)
 15 documented an increase in bulk density from 1.39 to 1.51 Mg m⁻³ under plow tillage after 32
 16 years of continuous corn residue removal on an Aeric Epiaquept, but no changes under no
 17 tillage.

18 Residue removal negatively impacted mean aggregate size measured by wet sieving,
 19 whereas biochar application had no effect. Soil structure, aggregation and, thus, mean aggregate
 20 diameter is affected by labile organic matter, which comes from decomposing plant residues
 21 (Christensen, 2001; Oades, 1984). Due to the labile nature of macro aggregate binding agents,
 22 residue management influences aggregation on relatively short time scales, such as the two years
 23 observed in current study. Even though biochar increased SOC by almost 0.5%, most of the
 24 biochar C was recalcitrant and did not contribute labile organic matter, therefore biochar
 25 amendments had no measurable effect on mean aggregate diameter.

4.2. End-of-season cornstalk nitrate concentrations, grain and biomass yield

The yearly variation in the amount of crop residue harvested, the end-of-season cornstalk nitrate concentrations and corn yield strongly reflected climatic conditions and residue removal rates. The lowest biomass yields for the 90% residue removal rate were observed in 2010 – a year with excessive growing season rainfall, and 2012 – a year characterized by widespread drought (April-August rainfall was 927 and 370 mm in 2010 and 2012, respectively). Similar pattern was observed for the grain yields. The observed higher grain yields for plots that had partial or full residue removal rates reflects a greater supply of soil N and other nutrients to the corn plants due to increased SOM mineralization and/or decreased nutrient immobilization as evident by the results of the end-of season stalk nitrate tests (Figure 4). Averaged across biochar treatments, plots with 50 or 90% biomass removal had higher stalk nitrate concentrations in 2010 and 2012 than plots with no residue removed. Higher stalk nitrate concentrations in 2010 may be influenced by increased N fertilization on those plots; however, a uniform rate of N fertilizer was applied to all plots in 2011 and 2012, hence the higher stalk nitrate levels in 2012 are not a fertilizer effect. Another explanation for the higher grain yields in plots with residue removal is the absence of negative effects due to allelopathy. Decomposing residue releases phytotoxic compounds capable of reducing yields of the next year's crop, thus, removing residues can significantly improve corn yields in continuous corn cropping systems in the upper Midwest where over winter residue decomposition is limited (Martin et al., 1990; Singh et al., 2010; Yackle and Cruse, 1984). The presence of biochar in soil may mitigate the negative effects of allelopathy by adsorbing allelopathic compounds. Rogovska et al. (2014) reported a significant yield increase in biochar amended plots that received excessive amounts of corn residue (4.5 times greater than normally left after corn harvest) the first year after biochar application. In the present study, this hypothesis is further supported by a significant yield increase due to 18.4 Mg

1 ha⁻¹ biochar application (C2) when averaged across four years (2009-2012) relative to the Control plots for the 0% residue removal plots. By contrast, no effect of biochar on yields averaged over the four years was observed for plots with 50 or 90% residue removed treatments (Figure 5). Biochar has limited fertilization effect therefore significant yield increases were not expected in the fertile Midwestern Mollisols.

Residue removal can improve early season growing conditions by allowing faster warming of soils, better seed germination and less favorable habitat for plant pathogens. As our data (Figure 4, year 2012) indicates residue removal can enhance nutrient availability due to enhanced soil organic matter mineralization and/or decreased nutrient immobilization. Other advantages of residue removal on plant growth have been attributed to better root system development, which increases access to nutrients and water from deeper soil horizons. Significant yield increase in Control (no biochar) plots due to residue removal in 2012 (drought year) can be explained by better soil conditions during early stages of plant development, which facilitated early root development and allowed the plants to better access stored soil moisture. The lack of a residue removal effect during 2012 for biochar amended plots (C1 and C2), can be explained by the ability of biochar to hold and supply more water to the plants. Numerous reports indicated that biochar amended soils have greater moisture holding capacity than non-amended soils (Bruun et al., 2014; Rogovska et al., 2014; Uzoma et al., 2011b) and this can be a distinct advantage during drought conditions. When left undisturbed, residue cover can have similar effect on soil moisture retention, however in this study, residues were incorporated with chisel plow and were not expected to significantly influence soil moisture retention.

5. Conclusion

One time biochar application followed by two years of continuous corn residue removal at 50 and 90% rate had minimal or no effect on Mehlich III extractable nutrients, ECEC, and soil

bulk density. Biochar applications, however, significantly increased soil organic C levels and soil pH. Residue harvest negatively impacted aggregate stability, while biochar applications had no effect on this soil parameter. Residue removal at both rates significantly boosted yields during the first two years of the study during which N deficiencies due in part to excess rainfall occurred. These yield boosts can be attributed to greater nutrient availability from enhanced fertilizer inputs, greater soil organic matter mineralization/decreased N immobilization rates and possibly due to absence of negative effects of allelopathy on early season growth. No yield boost associated with residue removal or biochar applications was observed in 2011, a year with near optimum weather conditions. Yield differences between residue removal treatments reappeared in 2012, a drought year, only for the Control (no biochar) treatment as biochar amended soils most likely held more plant available water.

During the first five years of the experiment, residue removal had generally positive effects on corn yields. Soil quality parameters measured two years after continuous residue removal did not show significant changes mostly due to short period of time and the ability of Mollisols to buffer against changes in physico-chemical characteristics. The magnitude of yield increase due to residue removal, up to 3.7 Mg ha^{-1} , may be an attractive option for farmers who considering selling agricultural residue to local biorefineries. However, this short term economic gain may lead to long term loss if residue harvest results in depletion of SOM. Biochar application can potentially mitigate this degradation by increasing SOC content, however; biochar C, is qualitatively different from the biogenic C supplied by crop residues and is not expected to be as effective as residue in stabilizing soil structure and will not protect soils from erosion. Thus some residue should be left on the surface even for soils that receive high doses of biochar.

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Figure 5. Corn grain yield (Mg Ha^{-1}) differences among treatments. Different letters define significant differences in yield between treatments within a year based on Tukey test for multiple comparisons. Error bars represent standard deviations.

Table 1. Management practices including tillage, planting and harvesting dates that were used in the long-term experiment from 2008 to 2012.

		Tillage		Planting	
	date	method, depth in cm	date	rate, plants ha-1	Harvest date
2008	4/16/2008	Field Cultivator, 7.62	5/6/2008	74,100	10/16/2008
	4/30/2008	Field Cultivator, 7.62			
	11/24/2008	Chisel plow, 20.32			
2009	3/31/2009	Field Cultivator, 7.62	5/5/2009	80,275	10/19/2009
2010	4/1/2010	Chisel plow, 20.32	4/28/2010	74,100	9/28/2010
	4/10/2010	Field Cultivator, 7.62			
	10/11/2010	Chisel plow, 20.32			
2011	5/1/2011	Field Cultivator, 7.62	5/3/2011	86,450	11/4/2011
	11/16/2011	Chisel plow, 20.32			
2012	4/24/2012	Field Cultivator, 7.62	4/25/2012	79,040	9/20/2012
	11/9/2012	Chisel plow, 20.32			

Table 2. Annual fertilization rates and timing of fertilizer applications. Fertilization rates were based on soil test values and adjusted to compensate for nutrients removed with corn stover harvest.

Year	Fertilization	Residue removal, %								
		0	50	90	0	50	90	0	50	90
		N, kg ha ⁻¹			P, kg ha ⁻¹			K, kg ha ⁻¹		
2008	Pre-plant*	66	66	66	56	56	56	56	56	56
	Sidedress	147	147	147	0	0	0	0	0	0
	Total	212.8	212.8	212.8	56	56	56	56	56	56
2009	Pre-plant	40	85	92	84	89.6	92.96	67.2	164.64	181
		134	134	134	0	0	0	0	0	0
	Total	174	219	226	84	89.6	92.96	67.2	164.64	181
2010	Pre-plant	31	35	37	76	88	98	55	139	210
	Sidedress	181	206	220	0	0	0	0	0	0
	Total	212	241	257	76	88	98	55	139	210
2011	Pre-plant	41	45	47	76	88	98	55	139	210
	Sidedress	183	179	177	0	0	0	0	0	0
	Total	224	224	224	76	88	98	55	139	210
2012	Pre-plant	44	47	49	81	95	104	57	101	123
	Sidedress	180	177	175	0	0	0	0	0	0
	Total	224	224	224	81	95	104	57	101	123

*Pre-plant includes fall application and spring starte

Table 3. Total soil C and N (TC and TN, respectively), effective cation exchange capacity (ECEC), pH, and Mehlich III extractable nutrients (Ca, Cu, K, Mg, Mn, P, S, and Zn) measured three years post-biochar application and after two years of continuous residue removal. Numbers in parenthesis indicate standard deviations.

	Residue removal	Control	C1	C2		Residue removal	Control	C1	C2
TC, %	0%	2.19 (0.40)	2.53 (0.42)	3.04 (0.59)	TN, %	0%	0.19 (0.03)	0.19 (0.03)	0.21 (0.5)
	50%	2.68 (0.45)	2.45 (0.34)	2.71 (0.24)		50%	0.22 (0.03)	0.19 (0.02)	0.18 (0.02)
	90%	2.33 (0.47)	2.70 (0.54)	2.83 (0.60)		90%	0.20 (0.03)	0.20 (0.03)	0.21 (0.03)
Ca, mg kg⁻¹	0%	2978 (437)	3446 (560)	3333 (244)	Mn, mg kg⁻¹	0%	104 (11)	107 (12)	101 (16)
	50%	3303 (501)	3505 (502)	3425 (905)		50%	103 (8)	88 (15)	97 (6)
	90%	3320 (808)	3352 (923)	3265 (768)		90%	99 (19)	102 (21)	100 (19)
Cu, mg kg⁻¹	0%	2.27 (0.19)	2.71 (0.64)	2.47 (0.59)	P, mg kg⁻¹	0%	67.6 (25.7)	74.0 (37.7)	62.5 (17.9)
	50%	2.59 (0.45)	2.85 (0.25)	2.55 (0.58)		50%	62.7 (23.8)	65.8 (31.6)	62.9 (25.3)
	90%	4.16 (1.99)	3.79 (2.01)	2.57 (0.62)		90%	85.2 (23.4)	72.4 (27.1)	67.3 (30.6)
Mg, mg kg⁻¹	0%	304 (47)	415 (89)	377 (137)	S, mg kg⁻¹	0%	5.06 (1.59)	5.89 (1.99)	4.74 (1.15)
	50%	365 (62)	400 (55)	377 (87)		50%	3.97 (0.76)	5.65 (1.62)	4.20 (0.93)
	90%	394 (155)	361 (93)	389 (124)		90%	6.71 (3.01)	6.15 (1.71)	7.01 (3.33)
K, mg kg⁻¹	0%	117 (40)	149 (21)	135 (1.4)	Zn, mg kg⁻¹	0%	1.49 (0.38)	1.72 (0.72)	1.64 (0.43)
	50%	134 (17)	143 (36)	156 (36)		50%	1.45 (0.53)	1.68 (0.63)	1.57 (0.49)
	90%	150 (15)	152 (20)	162 (24)		90%	2.42 (0.63)	2.08 (0.42)	1.67 (0.67)
ECEC, cmol kg⁻¹	0%	13.8 (1.9)	16.8 (2.5)	16.6 (4.1)	Soil pH	0%	4.9 (0.2)	5.6 (0.2)	5.2 (0.1)
	50%	18.9 (2.1)	15.8 (3.2)	16.4 (2.6)		50%	5.3 (0.1)	5.2 (0.3)	5.4 (0.1)
	90%	14.8 (4.0)	16.9 (2.6)	17.0 (5.4)		90%	4.6 (0.2)	5.2 (0.2)	5.4 (0.6)

Table 4. Amount of residue removed each year (Mg ha^{-1}) averaged across 4 replications. Numbers in parenthesis denote standard deviations. Biomass harvested was not recorded in 2008.

Year	Biochar trt	Residue removed*, Mg ha^{-1}	
		50%	90%
2009	Control	3.9 (0.4) ^{NS}	7.7 (1.3) ^{NS}
	C1	4.3 (1.1)	6.8 (0.5)
	C2	4.1 (1.2)	7.1 (0.2)
2010	Control	2.8 (1.0) ^{NS}	4.2 (0.7) ^{NS}
	C1	3.4 (0.9)	5.2 (0.8)
	C2	3.9 (1.5)	4.3 (1.1)
2011	Control	3.9 (0.5) ^{NS}	6.3 (0.9) ^{NS}
	C1	4.0 (0.4)	6.2 (1.0)
	C2	3.8 (0.31)	6.4 (0.6)
2012	Control	3.4 (0.7) ^{NS}	4.1 (0.5) ^B
	C1	3.0 (0.5)	4.3 (0.75) ^{AB}
	C2	3.3 (0.4)	5.7 (1.0) ^A

*Means followed by standard deviation in parenthesis.

Figure 1. Temporal change in soil pH as influenced by biochar amendment and residue removal. Error bars represent standard deviations.

Figure 2. Effect of biochar application (Control, C1, and C2 are 0, 9.9, and 18.4 Mg ha⁻¹, respectively), residue removal (0, 50, and 90%) and repeated traffic on soil bulk density measured three years after biochar application. Error bars represent standard deviations.

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