The effect of bio-char on soil properties and corn grain yields in Iowa

Rachel Colleen Unger

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The effect of bio-char on selected soil properties and corn grain yields in Iowa

by

Rachel Colleen Unger

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Co-Majors: Environmental Science; Soil Science

Program of Study Committee:
Randy Killorn, Major Professor
Lee Burras
Robert Brown

Iowa State University
Ames, Iowa
2008
To:

My grandparents, who were always proud of me and my parents who have always supported me.
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Abstract

An incubation study was conducted to study the effect of three different types or “qualities” of nitrogen-enriched bio-char on total nitrogen (N), extractable phosphorus (P), extractable potassium (K), nitrate-N, ammonium-N, pH, SOM, and total organic carbon (C) in two soils. The different “qualities” represent the bio-char created with three different amounts of atmospheric air (0, 10, and 25%) present in the pyrolysis reactor when the bio-char was created. A field study was conducted to study the effect of N-enriched bio-char on corn grain yields, biomass yields, and soil ammonium (NH$_4^+$-N) and soil nitrate (NO$_3^-$-N) concentrations. The incubation study occurred in a lab for eight weeks and the field study was conducted on one site from 2007 through 2008. The incubation study used a Nicollet surface soil (fine-loamy, mixed, superactive, mesic Aquic Hapludoll) and a Storden subsoil (fine-loamy, mixed, superactive, mesic Typic Eutrudol) with 18 Mg ha$^{-1}$ of three different “qualities” of bio-char along with 0, 56, 112, or 224 kg ha$^{-1}$ of urea (46-0-0) to simulate N-enrichment. The field study used bio-char created with 10% atmospheric air present. Bio-char was applied at 0, 4.5 and 18 Mg ha$^{-1}$ along with 0, 56, 112, and 224 kg ha$^{-1}$ urea. Soil samples (0-30 cm) were taken to measure NH$_4^+$-N and NO$_3^-$-N concentrations weekly for the first eight weeks of the growing season in 2007 and post harvest. In 2008 heavy rainfall precluded collecting soil samples for the first three weeks of the growing season, but were started in week four and continued for five weeks and post harvest. Soil samples of 31-60 cm depth were also taken post harvest. Bio-char did not appear to affect NH$_4^+$-N and NO$_3^-$-N in either experiment. The properties studied tended to increase with increasing N-rates and the increases tended to have statistically significant differences due to N-rates.
General Introduction

The amount of oil remaining in the world as well as the amount that is accessible is unknown. The uncertainty in the amount of oil left and increasing fuel costs are creating a demand for alternatives. One alternative is bio-oil, which is one of three co-products produced from pyrolysis of biomass. The other products produced from pyrolysis include a gaseous material referred to as “syngas” and a carbon (C)-rich, charcoal material known as bio-char (Lehmann, 2007). Each co-product has potential as an energy source, but other possible applications are being researched.

Pyrolysis takes place in a reactor that is heated to a controlled temperature, usually between 300 and 900° C, with a controlled amount, usually between 0% and 25%, atmospheric air allowed into the reactor (Lehmann et al., 2006). Malcolm Fowles (2007) described pyrolysis as heating biomass in the absence of air, which drives off many constituent parts, such as oil tars, but leaving carbon behind in a solid form. The solid form of carbon left in the reactor is what is being referred to as bio-char.

During this process, the high temperatures present in the reactor volatilize the nitrogen (N). The volatile N is then captured in a condenser before it can be released as a greenhouse gas and returned to the bio-char in the form of ammonium-bicarbonate, creating an N enriched bio-char.

Pyrolysis has the potential to be a “carbon neutral” process by using the co-products as the energy source for the reactor. “Syngas” currently has the highest potential to be the primary energy source for the reactor. Bio-oil has the potential to be used as a fuel alternative and bio-char as a soil amendment.
Soils discovered in the Amazon River Basin, known as Terra Preta de Indio, have been determined to have higher levels of charcoal which can be up to 70 times higher than the surrounding soils, are more productive than surrounding soils and have been around for hundreds to thousands of years (Mann, 2002; Glaser et al., 2001 and 2002; Lehmann, 2007). Terra Preta soils have been measured with as much as 150 g/kg organic matter, which is higher than the surrounding soils (Petersen et al., 2001; Woods et al., 2000). These soils are also higher in essential nutrients including phosphorus, calcium, sulfur and nitrogen, cation exchange capacity (CEC) and have a more neutral pH than the typical acidic oxisol soils found around the Terra Preta soils (Mann, 2002; Lehmann et al., 2003; Lehmann, 2007). The improved chemical properties of the Terra Preta soils result in productive farm land where it typically did not exist.

Higher levels of charcoal C have been found in areas around the world that historically have been burned repeatedly (Skjemstad et al., 2002; Fowles, 2007). Research also shows that between 5 and 15% of C in Midwestern U.S. soils is charcoal and can be attributed to a long history of prairie fires (Laird, 2008). Carbon plays an important role in the soil. It has the potential to influence physical and chemical processes in the soil (DeLuca et al., 2006; Glaser et al., 2001). It has also been shown to affect soil productivity, quality and fertility and nutrient cycling, which all affect crop production (Skjemstad et al., 2002; Lal, 2004). Carbon plays an influential role in many soil properties; therefore understanding how the addition of carbon may influence the soil is essential.

Carbon sequestration may be a partial solution to the increasing concern over global climate change. Sequestrating C implies moving atmospheric CO₂ into long-lived pools for storage so it is not immediately reemitted (Lal, 2004). It has been established that using bio-
char for sequestration represents long-term storage of the C (Lehmann et al., 2006; Glaser et al. 2001; Lehmann, 2007). Sequestering C in the soil with bio-char, using “syngas” to power the reactor and the use of bio-oil as a fuel alternative for the transportation of the biomass would take CO$_2$ out of the atmosphere and may result in a net C neutral or even net negative system.

Studies have also been conducted that have shown that bio-char application can sequester other greenhouse gases, specifically nitrous oxide and methane (Lehmann, 2007; Lehmann et al., 2006; Fowles, 2007). The mechanism behind this sequestration is poorly understood. Reducing the amount of greenhouse gases that enter the atmosphere could potentially play a vital role in global climate change.

Black C and charcoal are often used interchangeably throughout the literature. Black C or charcoal is from partial or incomplete combustion of organic materials (Glaser et al., 2001; DeLuca et al., 2006), while bio-char is created in a reactor under specific conditions. The creation of charcoal and bio-char are different, so how they react in the soil may not be the same. Research is needed to better understand how bio-char will act in the soil as well as influence important soil properties.

There were two objectives of this study. One was to determine the optimal form of bio-char to be used for a field study and to measure the effects of the bio-char on different soil properties during an incubation study. The second was to determine the effect of bio-char and N fertilizer on selected soil properties, corn grain yields and biomass yields during a two-year field study.


Thesis Organization

This thesis is organized with a literature review, two papers that will be submitted for publication and a general conclusion. Each individual paper is organized with an abstract, introduction, materials and methods, results and discussion, and a summery and conclusions.
The effect of three different qualities of bio-char on selected soil properties

A paper to be submitted to Communications in Soil Science and Plant Analysis

R. Unger and R. Killorn
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Abstract

The application of bio-char made from corn stover to soils has the potential to reduce the need for nitrogen fertilizer, as well as enhance soil chemical and physical properties. This incubation study was conducted to find how bio-char interacts with a nitrogen fertilizer, as well as how it reacts in the soil. The study also measured the impact on soil properties and how the properties differed with different bio-chars. The different bio-chars were produced with different amounts of atmospheric air present in the reactor.

One hundred grams of two different Iowa soils, Nicollet surface soil and Storden subsoil, were mixed with three different types of char. The bio-char was pyrolyzed with three different amounts of atmospheric air in the reactor while the bio-char was being formed, 0% (bio-char 1), 10% (bio-char 2), and 25% (bio-char 3), respectively at 500°C. Each of the bio-chars was applied to the different soils at a rate of 17.9 Mg ha⁻¹. Along with the bio-char, nitrogen fertilizer as urea (46-0-0) was applied at rates of 0, 56, 112, and 224 kg N ha⁻¹. Treatments were replicated three times. Soil tests for pH, total nitrogen, extractable phosphorus, potassium, ammonium, nitrate, organic matter, and total carbon were performed immediately after application, and after one, two, four, six, and eight weeks. The different bio-chars significantly affected the total N, total carbon, and pH in both soils at all rates of urea applied. In the first incubation study the total N in bio-char 1
treatment increased over time. The total N in bio-char 2 and 3 treatments decreased at
the second week of sampling and increased thereafter. A second incubation study was
done in order to check these results. The second incubation study resulted in total N
remaining constant over the course of the study. During the study, the amount of total
carbon decreased in bio-chars 1 and 2, but remained steady in char 3, which had the
lowest total carbon when the study began. The pH of the bio-char and soil mixtures
decreased over time. The conditions during pyrolysis, with respect to atmospheric air,
influence how the bio-char/fertilizer reacts with the soil.

**Introduction**

The use of charred materials (bio-char) as soil amendments is not a new concept.
There are areas in the Amazon River Basin that have become productive and have
remained that way for thousands of years due to charcoal accumulation that significantly
increased the carbon’s stability against microbial decay (Steiner et al., 2007) and
therefore Terra Preta de Indio’s sustainability (Glasser et al., 2001). Anthropologists
discovered Terra Preta de Indio, or Amazonian Dark Earth, (Glasser et al., 2004) and now
scientists are trying to determine what caused it and how to recreate it. The Terra Preta
soils can be used as a guide to create a carbon sink in soils as well as have the possibility
to reduce the amount of fertilizer farmers need to apply to fields.

The process of charring transforms labile carbon pools into stable soil organic
matter (SOM) (Glasser et al., 2001). The high levels of SOM as well as fertility have
resulted in the capability to grow crops without the use of fertilizers on previously
unproductive soils. SOM is important to soil fertility because it contains at least 95% of
the total nitrogen and sulfur along with 20 to 75% of phosphorus in the soil surface (Steiner et al., 2007). Charcoal can be as much as 35% in SOM of the Terra Preta de Indio soils and is responsible for the stability of the SOM (Glaser et al., 2001; Steiner et al., 2007). Bio-char is being used to potentially replicate charcoal found in the Terra Preta de Indio soils and can be used as a soil conditioner, improving soils’ physical and chemical properties (Lehmann et al., 2006). The addition of bio-char to soil may result in improvements in crop growth in a sustainable fashion.

Soil cation exchange capacity (CEC) has also been shown to increase with the addition of char (Lehmann et al., 2003; Fowles, 2007). The increase in the CEC results in plants taking up nutrients more easily (Fowles, 2007). The pH has been shown to change to a more neutral pH, especially in acidic soils (Fowles, 2007). The changes in CEC and pH create a suitable environment for growing crops in an area that isn’t known for agriculture.

Carbon added to the fields in the form of bio-char, could give farmers carbon credits that can be sold on a carbon credit market for additional income. Soils are considered a finite carbon sink, but it is believed that adding black carbon in the form of bio-char would increase the carbon sink in the soil (Lehmann et al., 2006). Increasing the carbon sink in soil will help reduce the amount of CO₂ and other greenhouse gasses that enter the atmosphere, such as methane and nitrous oxide. Studies conducted by Rondon et al. (2005), have found that minimal amounts of charcoal added to soils can offset net emissions of methane and nitrous oxide. There is currently no agreed upon mechanism in the literature about how the sequestration of methane and nitrous oxide occurs.
Currently, this is an important topic with the continual loss of rain forests and the increasing concern over global climate change.

The objective of this study was to determine the affect of three N-enriched biochars on selected soil chemical properties of two different soils.

**Materials and Methods**

One hundred grams of soil, either a Nicollet (fine-loamy, mixed, superactive, mesic Aquic Hapludoll) or subsoil from a Storden (fine-loamy, mixed, superactive, mesic Typic Eutrudept) soil, along with one of the three different types of bio-char at a rate of 0.8 g, equivalent to 18 Mg ha\(^{-1}\), assuming an application depth of 15 cm, were placed in 250 ml plastic containers. The initial properties of the two soils can be seen in Table 1. The bio-char was obtained from Biomass Energy Conversion (BECON) Facility in Nevada, IA. Corn stalks were removed from fields and taken to BECON where they were shredded before being charred at 500° C in the presence of three different amounts of atmospheric air (0, 10, and 25%). This process was done following methods outlined in "Enthalpy for pyrolysis for several types of biomass" (Dougard and Brown, 2003) and "The transport phase of pyrolytic oil exiting a fast fluidized bed reactor” (Dougard, 2003). The soil/bio-char was mixed by turning the container on its side and rotating it five times. After the bio-char and soil had been thoroughly mixed, a urea (46-0-0) solution of 0, 0.0025, 0.005, and 0.01 g, equivalent to 0, 56, 112, and 224 kg N ha\(^{-1}\), was added and mixed by hand to bring the soils to their water holding capacity with the correct amount of N. Each combination of soil, bio-char, and urea was replicated three times for each sampling time, which occurred immediately after treatment application,
and 1, 2, 4, 6 and 8 weeks. The samples sat for two days to let them equilibrate before the initial sampling took place.

A second, smaller, incubation study was done to check the results of total N analysis from the first study. French square bottles (125 ml) were used instead of the 250 ml plastic containers due to the smaller nature of the study. Each bottle contained 50 g of soil, either a Nicollet (fine-loamy, mixed, superactive, mesic Aquic Hapludoll) or subsoil from a Storden (fine-loamy, mixed, superactive, mesic Typic Eutru.dept) soil, along with one of the three different types of bio-char at a rate of 0.4 g, equivalent to 18 Mg N ha$^{-1}$. The soil and bio-char were mixed by rotating the container approximately 5 times. A urea solution was added to each container at the rate of 0.01 g, which is equivalent to 224 kg ha$^{-1}$. Each combination was replicated three times for each sampling time, which was the same as the first study. The samples again sat for two days to let them equilibrate before the initial sampling took place.

**Soil Analysis**

Soil samples were analyzed for total nitrogen (N), extractable phosphorus (P), extractable potassium (K), nitrate-N, ammonium-N, pH, SOM, and total organic carbon (C) immediately after application, after one, two, four, six, and eight weeks by the Iowa State Soil Testing Laboratory. Total N, total organic carbon, and SOM were determined using the method of Combs and Nathan (1998). Phosphorus and K were determined using the Bray P-1 for P and ammonium acetate for K (Frank et al., 1998). Nitrate-N and ammonium-N were determined using the method of Gelderman and Beegle (1998). Soil pH was determined according to Watson and Brown (1998).
Statistical Analysis

The experiment was a factorial combination of bio-char and N-rate replicated three times in a completely randomized experiment. The data from each sampling time were analyzed separately. The analysis of the results used the analysis of variance (ANOVA) and an LSD all-pairwise comparison in the computer program Statistix 8 (Analytical Software, 2003).

Results and Discussion

Affect of Bio-Char Quality

Total Nitrogen

There was a slight increase in the amount of total N for all three bio-chars across time (Fig. 1). The only reading where there was a statistically significant difference between the three bio-chars was in the initial sampling time in the first incubation study (Table 2). The magnitude of the increases was from about 0.13 % N to about 0.145% N. A second incubation study, total N remained essentially constant over time (Fig. 2). There were no statistically significant differences between any of the bio-chars over the eight-week period (Table 3). There was typical experimental error in both studies. It is therefore concluded from both studies that bio-char had no effect over time.

Carbon

Bio-char 3 treatments always had the lowest amount of total C until week 6. Bio-char 1 treatment had the lowest amount of total C for weeks 6 and 8, but the difference between bio-char treatments 1 and 3 in the last two sampling times was not significantly different. All other sampling times, differences among the different bio-chars were statistically significant (Table 4). There was a trend for the amount of C to decrease over
time and then to level off at week 6 (Fig. 3). This suggests that there was biologically active C in the bio-chars, which was utilized by soil microorganisms as an energy source. Bio-chars 1 and 2 had more biologically active C than bio-char 3 until sometime between weeks 4 and 6. This C was exhausted by about week 6.

**pH**

The soil pH of all treatments initially increased after application of the bio-char, but then decreased with time in both soils ending at approximately the original pH. The decrease was probably due to nitrification of the N added as urea. Bio-char 3 treatments always had a slightly higher pH in the Nicollet soil, as shown in Figure 4. There was a statistically significant difference among the bio-chars at each sampling time (Table 5). The pH in the Storden subsoil remained close between the three chars over time with the exception of week 6 (Fig. 5). There was no statistically significant difference between any of the bio-chars at any of the sampling times in the Storden subsoil (Table 6). The free calcium carbonate present in the Storden subsoil buffered the soil pH.

**Affect of N-Rates**

**Phosphorus**

The concentration of extractable P decreased until sometime between week 2 and week 4 (Fig. 6). From week 4 to the end of the study, there was an increase in the amount of extractable P. This could be explained by the increase in microbial numbers due to bio-available C causing microbial immobilization of N and P. As the system returned to equilibrium and there was microbial decomposition of the bio-char over time, P was mineralized. This is supported by the nitrate-N (NO$_3^-$-N) results (Fig. 7). Week 4 was the only sampling time where the differences in extractable P due to N rates were
significant (Table 7). Treatments were averaged across all bio-char treatments because the interaction of bio-char and nitrogen fertilizer the differences were not statistically significant.

**Potassium**

The concentration of extractable K decreased at first, but between week 2 and week 4 there was an increase. That increase continued to the end of the study, as shown in Figure 8. One possible explanation for this occurrence is the K was physically sequestered. As the bio-char was broken down, K was released. Each week, except week 6, there was a significant difference between each of the different rates of N (Table 8). Treatments were averaged across all bio-char treatments because the interaction of bio-char and nitrogen fertilizer the differences were not statistically significant.

**pH**

The soil pH initially increases in both soils before decreasing over time to approximately the original pH. The pH of the soils that had 0 kg N ha\(^{-1}\) treatments changed the least amount over the study, while the pH of the soils that had the 224 kg N ha\(^{-1}\) treatment added resulted in the greatest change in the Nicollet soil (Fig. 9). There are changes across each nitrogen fertilizer treatment in the Storden subsoil (Fig. 10). Each sampling time had a statistically significant difference between the different levels of N with the exception of week 8 in the Nicollet soil (Tables 9 and 10). Immediately after the application of fertilizer and the first week of sampling in the Nicollet soil, there was a statistically significant difference between each of the amounts of fertilizer applied to the soil. The differences lessened over the course of the study. This is probably due to
hydrolysis, the more urea that was applied to the soil, the larger the effect on the soil.
The variability in the Storden soil was probably due to random variability in the study.

Summary and Conclusions

The amount of urea used influenced potassium and pH. The first incubation study raised questions concerning total N in the soil that were unable to be answered. A second incubation study was run to check the outcome of the first study. The second study resulted in the total N remaining constant over the course of the study. The difference between the two studies may be attributed to typical experimental error. Both studies show that bio-char has no effect on total N over time.

The amount of atmospheric air in the reactor at the time the bio-char was created influenced how the bio-char reacted in the soil. Total C and pH of the Nicollet soils were influenced by the different bio-chars and therefore by the different amounts of atmospheric air present while creating the bio-char.

The different soils influenced the results due to the pH of the soil. The Storden sub-soil, unlike the Nicollet surface soil, had free calcium carbonate, which buffered the pH of the soil.

In this study, as the bio-char decomposed over time extractable P and K were released. The conditions in the reactor influenced the amount of biologically active C in the bio-chars. With the carbon being more bio-available, some of the carbon was lost.
Acknowledgements

I would like to acknowledge Justinus Satrio for furnishing the bio-chars for this experiment.

References


Figure 1. Change in the concentration of total N in the three different qualities of bio-char over time and averaged across the different N-rates.

Figure 2. Change in the concentration of total N in the three different qualities of bio-char over time in the second incubation study and averaged across the different N-rates.
Figure 3. Change in the concentration of total carbon in the three bio-char-soil treatments over time and averaged across the different N-rates.

Figure 4. Change in pH of the three different qualities of bio-char over time in the Nicollet surface soil averaged across the different N-rates.
Figure 5. Change in pH of the three different qualities of bio-char over time in the Storden subsoil averaged across the different N-rates.

Figure 6. Mehlich-3 extractable phosphorus compared by four different nitrogen fertilizer rates and averaged by the three bio-char qualities over time.
Figure 7. Nitrate-N compared across four different rates of nitrogen fertilizer and averaged by the three bio-char qualities over time.

Figure 8. Mehlich-3 extractable potassium compared across four different rates of nitrogen fertilizer and averaged by the three bio-char qualities over time.
Figure 9. pH compared by four different rates of nitrogen fertilizer rates in the Nicollet soil and averaged by the three bio-char qualities over time.

Figure 10. pH compared by four different rates of nitrogen fertilizer rates in the Storden subsoil and averaged by the three bio-char qualities over time.
Table 1. Initial soil properties of the Nicollet surface soil and the Storden subsoil.

<table>
<thead>
<tr>
<th>Soil Properties</th>
<th>TN</th>
<th>TC</th>
<th>OM</th>
<th>pH</th>
<th>P</th>
<th>K</th>
<th>NO3-N</th>
<th>NH4-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nicollet</td>
<td>1.678</td>
<td>17.14</td>
<td>31.31</td>
<td>5.9</td>
<td>34</td>
<td>135</td>
<td>14</td>
<td>18</td>
</tr>
<tr>
<td>Storden</td>
<td>0.726</td>
<td>18.06</td>
<td>32.99</td>
<td>8.05</td>
<td>9</td>
<td>71</td>
<td>8</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 2. The concentration of total N in three different qualities of bio-char in the initial study averaged across N-rates over time.

<table>
<thead>
<tr>
<th>Time of Sampling</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-char 1</td>
<td>1.30</td>
<td>1.32</td>
<td>1.39</td>
<td>1.41</td>
<td>1.46</td>
<td>1.44</td>
</tr>
<tr>
<td>Bio-char 2</td>
<td>1.39</td>
<td>1.35</td>
<td>1.34</td>
<td>1.42</td>
<td>1.47</td>
<td>1.41</td>
</tr>
<tr>
<td>Bio-char 3</td>
<td>1.30</td>
<td>1.32</td>
<td>1.29</td>
<td>1.35</td>
<td>1.43</td>
<td>1.45</td>
</tr>
<tr>
<td>Prob &gt; F</td>
<td>&lt; 0.01</td>
<td>0.79</td>
<td>0.16</td>
<td>0.08</td>
<td>0.31</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Table 3. The concentration of total N in three different qualities of bio-char in the second study averaged across N-rates over time.

<table>
<thead>
<tr>
<th>Time of Sampling</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-char 1</td>
<td>1.34</td>
<td>1.44</td>
<td>1.33</td>
<td>1.29</td>
<td>1.27</td>
<td>1.33</td>
</tr>
<tr>
<td>Bio-char 2</td>
<td>1.39</td>
<td>1.50</td>
<td>1.37</td>
<td>1.40</td>
<td>1.35</td>
<td>1.34</td>
</tr>
<tr>
<td>Bio-char 3</td>
<td>1.34</td>
<td>1.45</td>
<td>1.30</td>
<td>1.38</td>
<td>1.32</td>
<td>1.30</td>
</tr>
<tr>
<td>Prob &gt; F</td>
<td>0.33</td>
<td>0.52</td>
<td>0.54</td>
<td>0.09</td>
<td>0.22</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Table 4. The concentration of total C in three different qualities of bio-char averaged across N-rates over time.

<table>
<thead>
<tr>
<th>Time of Sampling</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
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<tbody>
<tr>
<td>Bio-char 1</td>
<td>21.31</td>
<td>22.15</td>
<td>21.36</td>
<td>21.74</td>
<td>20.60</td>
<td>19.80</td>
</tr>
<tr>
<td>Bio-char 3</td>
<td>20.08</td>
<td>20.29</td>
<td>20.05</td>
<td>20.69</td>
<td>20.67</td>
<td>20.33</td>
</tr>
<tr>
<td>Prob &gt; F</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.04</td>
<td>0.65</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 5. pH of the Nicollet surface soil averaged across N-rates over time in three qualities of bio-char.

<table>
<thead>
<tr>
<th>Time of Sampling</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prob &gt; F</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>
Table 6. pH of the Storden subsoil averaged across N-rates over time in three qualities of bio-char.

<table>
<thead>
<tr>
<th>Time of Sampling</th>
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<th>4</th>
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<td>8.375</td>
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<td>0.33</td>
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</table>

Table 7. Melich-3 extractable P compared by four N-rates and averaged across bio-char quality over time.

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<thead>
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<th>2 kg ha⁻¹</th>
<th>4 kg ha⁻¹</th>
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<td>0</td>
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<td>28.833 mg kg⁻¹</td>
<td>32.111 mg kg⁻¹</td>
<td>33.889 mg kg⁻¹</td>
<td>34.500 mg kg⁻¹</td>
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<td>56</td>
<td>30.167 mg kg⁻¹</td>
<td>29.222 mg kg⁻¹</td>
<td>28.389 mg kg⁻¹</td>
<td>30.111 mg kg⁻¹</td>
<td>34.611 mg kg⁻¹</td>
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<tr>
<td>112</td>
<td>31.556 mg kg⁻¹</td>
<td>30.389 mg kg⁻¹</td>
<td>30.278 mg kg⁻¹</td>
<td>32.667 mg kg⁻¹</td>
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<td>224</td>
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Table 8. Melich-3 extractable K compared by four N-rates and averaged across bio-char quality over time.

<table>
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<th>2 kg ha⁻¹</th>
<th>4 kg ha⁻¹</th>
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</thead>
<tbody>
<tr>
<td>0</td>
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<td>217.89 mg kg⁻¹</td>
<td>201.39 mg kg⁻¹</td>
<td>213.17 mg kg⁻¹</td>
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<td>240.06 mg kg⁻¹</td>
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<tr>
<td>56</td>
<td>231.72 mg kg⁻¹</td>
<td>231.39 mg kg⁻¹</td>
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<td>246.44 mg kg⁻¹</td>
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<tr>
<td>112</td>
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<td>224.50 mg kg⁻¹</td>
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<td>237.67 mg kg⁻¹</td>
<td>248.44 mg kg⁻¹</td>
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<tr>
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<td>239.44 mg kg⁻¹</td>
<td>242.06 mg kg⁻¹</td>
<td>237.11 mg kg⁻¹</td>
<td>232.00 mg kg⁻¹</td>
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</tr>
<tr>
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<td>&lt;0.01</td>
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<td>&lt;0.01</td>
<td>0.24</td>
<td>&lt;0.01</td>
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Table 9. pH of the Nicollet surface soil compared by four N-rates and averaged across bio-char quality over time.

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<th>2 kg ha⁻¹</th>
<th>4 kg ha⁻¹</th>
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<tr>
<td>56</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
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Table 10. pH of the Storden subsoil compared by four N-rates and averaged across bio-char quality over time.

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<td>8.05</td>
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<tr>
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<td>&lt;0.01</td>
<td>0.05</td>
<td>&lt;0.01</td>
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<td>0.02</td>
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The effect of the application of bio-char on soil properties, corn grain and biomass yields in Iowa

A paper to be submitted to Communications in Soil Science and Plant Analysis

R. Unger\textsuperscript{a} and R. Killorn\textsuperscript{a}
\textsuperscript{a}Iowa State University, Ames, IA

Abstract

Bio-char is a co-product of pyrolysis of plant biomass. Its qualities vary according to reactor conditions but it contains phosphorus (P) and potassium (K). The carbon (C) in bio-char is stable, so it can be applied to soils enlarging the C sink. A field study was conducted in 2007 and 2008 to find the effects of bio-char on crop production. Treatments were arranged in a split-plot design. The main plot treatments were bio-char at rates of 0, 4.5, 18 Mg ha\textsuperscript{-1}. Sub-plot treatments were nitrogen (N) rates of 0, 56, 112, 224 kg N ha\textsuperscript{-1} as urea (46-0-0). These treatments were applied to a continuous corn cropping system. Soil samples were taken to measure ammonium-N and nitrate-N during the first eight weeks of the growing season and after harvest in 2007. Soil samples in 2008 were not taken the first three weeks of the growing season due to rain. Soil samples started in the fourth week of the growing season and were taken the following five weeks and post harvest. The K and P in the soil were also measured after harvest in 2007. The N in the plant and grain was measured along with yield of grain and plant biomass. Grain yield increased from 4.5 to 5.9 Mg ha\textsuperscript{-1} with the addition of N averaged across bio-char treatments in 2007 and from 4.9 to 11.5 Mg ha\textsuperscript{-1} in 2008. There was no difference in the yield due to the addition of char in either year.
Introduction

A recent increase in oil costs has created an increase in fuel and nitrogen fertilizer costs. The increase in fuel costs have resulted in a demand for alternative energy sources. One alternative being investigated is the production of three co-products from pyrolysis of corn biomass: bio-oil, “syngas” and bio-char. Bio-oil and “syngas” are considered potential energy alternatives. Bio-char is being studied as a potential fertilizer and soil amendment.

Pyrolysis partially burns organic matter at temperatures ranging usually from 450 to 550° C in the presence of little to no atmospheric air (Lehmann, 2007). Conditions within the reactor are specific and held constant because different conditions result in different properties of the co-products (Lehmann et al., 2006; Lehmann, 2007). Different feed stocks, such as corn stover and peanut shells have been and are being studied for use in the pyrolysis reactor.

The bio-oil is thought to be a possible fuel alternative. “Syngas” may also be used as a fuel alternative, but it is being considered as the energy source for the pyrolitic reactor. The solid material left behind, bio-char, is primarily carbon (C) and can be enriched with nitrogen (N), phosphorus (P) and potassium (K).

Charred organic materials have been added to soils for hundreds to thousands of years dating back to the indigenous peoples in the Amazon River Basin. These productive soils are called Terra Preta de Indio soils and have been shown to have beneficial properties for growing crops. These properties include increased cation exchange capacity (CEC), improved nutrient holding capacity, especially for phosphorus, calcium, sulfur and nitrogen, and a more neutral pH when compared to surrounding,
highly weathered oxisols (Mann, 2002; Lehmann et al., 2003; Lehmann, 2007; Fowles, 2007; Laird, 2008). Charcoal is also believed to be responsible for the prolonged high levels of soil organic matter in the Terra Preta soils (Glaser et al., 2001; Glaser et al., 2002; Steiner et al., 2007). There is evidence of similar sites found all over the world (Skjemstad et al., 2002; Fowles, 2007). Bio-char is hypothesized to have similar properties to the charcoal found in the Amazon River Basin and around the world.

Carbon impacts soils’ ability to sustain crop growth. The loss of C from soils can affect soil productivity, quality, fertility and nutrient cycling (Skjemstad et al., 2002; Lal, 2004). Bio-char is primarily C and therefore the addition of bio-char to soils could increase C storage in soils.

The creation of the charcoal and bio-char are different, therefore how the two materials react in the soil may also be different. Research is needed in order to understand how bio-char will impact soils.

The objective of the study was to determine the effect of N-enriched bio-char on soil ammonium-N ($\text{NH}_4^+$-N), nitrate-N ($\text{NO}_3^-$-N), and corn grain and biomass yields.

**Materials and Methods**

2007

The study was conducted in 2007 and 2008 near Ames, IA on a Nicollet soil (fine-loamy, mixed, superactive, mesic Aquic Hapludoll). A Nicollet soil is a typical soil found in much of north central Iowa and southern Minnesota. Table 1 lists baseline soil data for the plot site and cultural practices of the area are listed in Table 2.
Treatments were arranged in a split-plot design, with the main plot treatments of bio-char and sub-plot treatments of nitrogen (N) fertilizer (urea). The experimental sub-plots were 3.05 m by 9.14 m with 4 rows of corn in each sub-plot. The experimental area was in a corn-soybean rotation and the previous year had been corn.

The bio-char was created with 10% atmospheric air present in the reactor at 500°C and was applied at rates of 0, 4.5 and 18 Mg ha\(^{-1}\). The nitrogen fertilizer was applied at rates of 0, 56, 112 and 224 kg N ha\(^{-1}\) in order to replicate the effects of N-enriched bio-char. The bio-char and urea were incorporated into the soil the same day as application in order to reduce the amount of bio-char lost due to wind and N lost to volatilization.

**Corn Yield**

Yields were measured by hand harvesting ears from 6.1 m of the center two rows of each plot. The corn was shelled, weighed and a sub-sample was retained. The sub-sample was dried at 60°C in order to determine moisture content and was ground and analyzed for total N. Reported grain yields were adjusted to a moisture content of 155 g kg\(^{-1}\).

To analyze the ground sub-sample, 0.25 g was dried, weighed and digested using the Hach Digesdahl\(^{\circledR}\) Digestion Apparatus and the Hach Plan Tissue and Tissue Analysis System (Hach Company, 1988). This was done using concentrated sulfuric acid (18 M H\(_2\)SO\(_4\)) and 50% hydrogen peroxide (H\(_2\)O\(_2\)). The digested product was used to determine total N by using a modified Nessler Method test and a Hach DR/3000 Spectrophotometer (D/R 3000 Procedure Code N.10) as described for Nitrogen Analysis in Total Plant Tissue (Hach Company, 1988). Nitrogen uptake in the grain was determined by multiplying the grain yield (dry weight) by the percent N in the grain. The
digest was then sent to the Iowa State University Soil Testing Lab to determine P and K in the grain.

**Biomass Yield**

Biomass was measured by harvesting 6 stalks of corn, 3 from each of the center 2 rows, from each plot at physiological maturity after the ear was removed. Stalks were chopped, weighed and a sub-sample retained. The sub-sample was dried at 60° C and weighed again in order to determine moisture content. The sub-sample was then ground in preparation for chemical analysis. Total N content and N uptake of the biomass were determined using the same procedures used for the grain. N uptake was determined by multiplying the biomass dry weight by the percent N in the biomass sample. The digest was sent to the Iowa State University Soil Testing Lab to determine P and K in the biomass.

**Soil Analysis**

Three random cores, 0-30 cm, were taken between the center two rows of each plot weekly for 8 weeks following planting (May 11, 2007). Three random soil samples were taken 0-30 cm and 31-60 cm between the center two rows as well as five random cores 0-15 cm post-harvest.

All soil samples were dried at 60° C and ground to pass a 2 mm sieve. A 10 g sub-sample was then weighed and extracted using 50 ml of 2 M KCl solution before being filtered. The 0-30 cm and 31-60 cm extracts were analyzed for nitrate-N (NO$_3^-$-N) using a QuickChem 8000 Automated Ion Analyzer by the QuickChem Method 12-107-06-2-A (Lachat Instruments, 1992) and ammonium-N (NH$_4^+$-N) and QuickChem Method
12-107-04-1-B (Lachat Instruments, 1993). The 0-15 cm extracts were analyzed for Bray P-1 and ammonium acetate extractable K (Frank et al., 1998).

Soil tests were run by the Iowa State University Soil Testing Laboratory.

**Statistical Analysis**

Statistix 9 (Analytical Software, 2008) was used to analyze the data. The data from each soil sampling time were analyzed separately. The analysis of the results used the analysis of variance (ANOVA) and an LSD all-pairwise comparison.

**2008**

The study was repeated in 2008 on the same site without reapplying the bio-char. This was the second year for corn on the field. Weekly soil samples could only be collected for 5 weeks instead of 8 due to rain in the area the first 3 weeks after planting (Table 10). Everything else remained consistent from 2007.

**Results and Discussion**

**Grain Yield**

Corn grain yields were higher in 2008 than 2007 (Table 3). Lower yields in 2007 may be due to heavy rainfall in August (Table 10). Increased yields in 2008 may be attributed to heavier rainfall in the key months of April through July. Yields increased with N-rate in both years. In 2007, plots with no bio-char yields were higher than plots with bio-char (Fig. 1). In 2008 there was a trend for plots with bio-char to have higher yields than plots that had no bio-char application (Fig. 2). Bio-char application had no influence.
Biomass Yield

Biomass yields were higher in 2008 than 2007. Higher biomass yields in 2008 may be due to the heavier rainfall early in the growing season, April through July (Table 10). Bio-char application did not affect biomass yield. Application of N increased biomass yields in 2008 only (Table 4). Biomass yield in 2007 remained constant across the different N-rates, but in 2008 an increasing trend with increasing N-rates (Fig. 3 and 4).

Soil Analysis

The first set of soil samples in 2008 start at approximately the fourth set of soil samples in 2007. The sampling ends at approximately the same time pre-harvest in 2007 and 2008.

The application of bio-char resulted in no statistically significant differences in soil NH$_4^+$-N in either year (Table 5 and 6). The amount of NH$_4^+$-N in 2007 and 2008 was constant and close across each rate of bio-char at each sampling time, with the exceptions of the first and fourth sampling time in 2007 (Fig. 5 and 6).

In 2007, the amount of N applied resulted in statistically significant differences due to N-rate in the first four sampling times for NH$_4^+$-N, but in none of the other sampling times. There was a trend for NH$_4^+$-N to increase as N-rates increased. The only two sampling times that did not show a statistically significant difference due to N-rate occurred in the seventh and ninth sampling time. The first and fourth sampling times, 0 Mg ha$^{-1}$ was different from the 4.5 and 18 Mg ha$^{-1}$, while all other sampling times resulted in similar results from all three bio-char rates.
In 2008, N-rates affected soil NH$_4^+$-N in only the fifth and sixth sampling times. There was a trend for NH$_4^+$-N to increase as N-rates increased. Ammonium-N in all bio-char rates at all sampling times was similar, but the 4.5 Mg ha$^{-1}$ rate tended to be lowest.

The application of bio-char, again, resulted in no statistically significant differences in NO$_3^-$-N in either year (Tables 5 and 6). The amount of NO$_3^-$-N remained close across each bio-char at each sampling time with the exception of the first sampling time in both 2007 and 2008.

There was a trend for NO$_3^-$-N to decrease across all sampling times and bio-char rates in 2007 (Fig. 7). It is believed that plant uptake is the reason for the decrease in NO$_3^-$-N. Each sampling time with the exceptions of the seventh and ninth sampling time had statistically significant differences due to N-rates in 2007. Soil NO$_3^-$-N was significantly different due to N-rates except the first sampling time (Fig. 8).

**Grain N-Uptake**

There was an increase in N-uptake with increasing N-rates in 2007 and 2008 (Fig. 9 and 10). Generally uptake was higher in 2008 (Table 7). Bio-char did not affect N uptake.

**Biomass N-Uptake**

There was no obvious trend for biomass N-uptake in 2007 (Fig. 11). Dryer weather is believed to be the reason for the variation in 2007 (Table 9). In 2008 the low N-rates remained similar, while the high N-rates increased (Fig. 12). There was an overall increase in N-uptake from 2007 to 2008 (Table 8). The bio-char did not have an effect on uptake either year. N-rates were shown to have an effect in 2008 only.
Overall, there was no positive or negative response to the application of bio-char. There was a response to the application of the different rates of N; however, the interaction of the bio-char and N-rates did not have an effect on grain yields, biomass yields, soil properties, grain N-uptake or biomass N-uptake.

**Summary and Conclusion**

In this study, the application of bio-char did not affect grain yields, biomass yields, N-uptake in grain and biomass, or soil properties. However, there was not a negative effect. Since there was neither a positive or negative response due to the bio-char, land application of bio-char is reasonable.

The application and amount of N in the form of urea increased grain yields, biomass yields, N-uptake in grain and biomass along with the NH$_4^+$-N and NO$_3^-$-N. The amount of N in the N-enriched bio-char will influenced grain yields, biomass yields and NH$_4^+$-N and NO$_3^-$-N when applied to agricultural fields.

N-enriched bio-char will increase soil NH$_4^+$-N and NO$_3^-$-N. There will also be a positive effect on corn grain yields and biomass yields with the addition of N-enriched bio-char.

**Acknowledgements**

I would like to acknowledge Justinus Satrio for furnishing the bio-char for this experiment. His effort to get the amount of bio-char required for the field experiment was remarkable.
Works Cited


Figure 1. Effect of N-rate on corn grain yields for 2007.

Figure 2. Effect of N-rate on corn grain yields for 2008.
Figure 3. Effect of N-rate on biomass yields for 2007.

Figure 4. Effect of N-rate on biomass yields for 2008.
Figure 5. Concentration of ammonium-N in soil across all sampling times by bio-char in 2007.

Figure 6. Concentration of ammonium-N in soil across all sampling times by bio-char in 2008.
Figure 7. Concentration of nitrate-N in soil across all sampling times by bio-char in 2007.

Figure 8. Concentration of nitrate-N in soil across all sampling times by bio-char in 2008.
Figure 9. The amount of N uptake by grain in 2007.

Figure 10. The amount of N uptake by grain in 2008.
Figure 11. The amount of N uptake in biomass in 2007.

Figure 12. The amount of N uptake in biomass in 2008.
Table 1. Baseline soil properties at the 0 – 15 cm depth for 2007 and 2008.

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<td>------</td>
<td>------</td>
<td>------</td>
</tr>
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<td>785 - 890</td>
<td>6.15 - 6.8</td>
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Table 2. Cultural practices for the Curtiss farm in 2007 and 2008.

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Table 3. Corn grain yields for 2007 and 2008.

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Table 9. Growing season air temperatures (°C).

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Table 10. Growing season precipitation (cm).

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Overall Conclusions and Implications

The objectives of these studies were to determine the effect of N-enriched bio-char on selected soil properties, corn grain yields and biomass yields. The incubation study showed that how the bio-char was created influenced how it acted in the soil. Field studies showed that the bio-char alone had no effect, positive or negative, on soil NH$_4^+$-N or NO$_3^-$-N, corn grain yields and biomass yields. N-enriched bio-char simulated by the addition of urea (46-0-0) to the soils resulted in an increase of soil NH$_4^+$-N and NO$_3^-$-N with increasing rates of urea. There was an increasing trend with the higher amounts of N added.

The use of corn stover as the feedstock for bio-char will result in a large amount of stover being removed from fields. The stover is left on the fields to reduce erosion. The stover also cycles nutrients back into the field as it decomposes. It is unclear how the removal of stover will impact the soil as well as how much stover can be removed before it is detrimental to soils. Research is needed in order to better understand how the removal of the corn stover will impact soils before it becomes a common practice.

A better understanding of the chemical composition of the bio-char is also needed. This will result in a better understanding of how the bio-char will react in and influence soils.

There are many issues that are directly linked to the application and use of bio-char on agricultural fields. There is a need to better understand these issues if bio-char application is to become widespread practice.
Acknowledgments

I would like to thank Dr. Randy Killorn for all of his help, support, guidance and encouragement through my time at Iowa State. I want to thank him for believing in me and giving me this wonderful opportunity.

I would also like to thank my family and friends for all of their support and challenging me to do better than I thought I could. Without them I would have never made it this far. I would especially like to thank my parents for their love and support.

A special thank you goes to my committee members, Dr. Killorn, Dr. Burras, and Dr. Brown. Their help and encouragement throughout my time at Iowa State University has made it possible for me to have made it this far and to continue on in whatever life brings.

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