

**The promise of biochar:  
From lab experiment to national scale impacts**

by

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**DEDICATION**

*This was just for you mom !*

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## ABSTRACT

Biochar is a carbon rich soil amendment produced from biomass by a thermochemical process, pyrolysis or gasification. Soil biochar applications have generated a great deal of interest as a strategy for mitigating climate change by sequestering carbon in soils, and simultaneously as a strategy for enhancing global food security by increasing crop yields especially on degraded and poor quality soils.

In this study we evaluated the effect of biochars presence on soil and crop in various spatial scales ranging from lab experiments to regional scale simulations.

In the first chapter, we used an incubated experiment with 3 biochar application rates (0%, 3% and 6%), two application methods and three replications. Soil water retention curves (SWRC) were determined at three sampling times. The Van-Genuchten (VG) model was fitted to all SWRCs and then used to estimate the pore size distribution (PSD). Standard deviation (SD), skewness and mode (D) were calculated in order to interpret the geometry of PSDs. The Dexter S-index and saturated hydraulic conductivity ( $K_s$ ) were also estimated. Statistical analysis was performed for all parameters using a linear mixed model. Relative to controls, all biochar treatments increased porosity, water content at both saturation and field capacity and improved soil physical quality. Biochar applications lowered  $K_s$ , bulk density and D indicative of a shift in pore size distributions toward smaller pore sizes.

The second chapter was focused on evaluating the impacts of biochar on soil hydraulic properties at the field scale by combining a modeling approach with soil water content measurements. Soil water measurements were collected from a corn-corn cropping system over two years. The effect of biochar was expected to be the difference between the physical soil properties of the biochar and no-biochar treatments. An inverse modeling was performed after a global sensitivity analysis to estimate the parameters for the soil physical properties of the APSIM (The Agricultural Production

Systems sIMulator ) model . Results of the sensitivity analysis showed that the drainage upper limit (DUL) was the most sensitive soil property followed by saturated hydraulic conductivity (KS), saturated water content (SAT), maximum rate of plant water uptake (KL), maximum depth of surface storage (MAXPOND), lower limit volumetric water content (LL15) and lower limit for plant water uptake (LL). The difference between the posterior distributions (with and without biochar) showed an increase in DUL of approximately 10%. No considerable change was noted in LL15, MAXPOND and KS whereas SAT and LL showed a slight increase and decrease in biochar treatment, respectively, compared to no-biochar.

In the third chapter, we tried to answer the question: Where should we apply biochar? For this task, we developed an extensive informatics workflow for processing and analyzing crop yield response data as well as a large spatial-scale modeling platform. we used a probabilistic graphical model to study the relationships between soil and biochar variables and predict the probability of crop yield response to biochar application. Our Bayesian network model was trained using the data collected from 103 published studies reporting yield response to biochar. Our results showed an average 12% increase in crop yield from all the studies with a large variability ranging from -24.4% to 98%. Soil clay content, pH, cation exchange capacity and organic carbon appeared to be strong predictors of crop yield response to biochar. we also found that biochar carbon, nitrogen content and highest pyrolysis temperature significantly influenced the yield response to biochar. Our large spatial-scale modeling revealed that 8.4% to 30% of all U.S. cropland can be targeted and is expected to show a positive yield response to biochar application. It was found that biochar application to areas with high probability of crop yield response in the U.S could offset a maximum of 2% of the current global anthropogenic carbon emissions per year.

In the last chapter, we made regional scale simulations of biochar effects on crop yield and nitrate leaching using APSIM for parts of Iowa and California. Three main pieces of work were integrated in this study. The suitable areas found for biochar application in the previous chapter in both states, the biochar module in the APSIM model and a new developed algorithm for speeding up the large spatial scale simulations. This allowed us to simulate 30 years of biochar effects on



soil and crop for corn-corn cropping system in Iowa and alfalfa in California starting in 1980 until 2016. Model outputs were then aggregated at a climate division level and the effect of biochar was estimated as the percent change relative to no biochar. In this study, the APSIM model suggested an insignificant change in crop yield/biomass following biochar application with a more substantial effect on nitrate leaching depending on weather conditions. It was found that in wet years ( $PDSI \geq 3$ ) there is a reduction in nitrate leaching along with an increase in crop yield, suggesting more mineral nitrogen being available for the crop. As one of the significant findings of this study, it was found that the biochar effect lasted almost for the entire 30 years of simulation period while biochar application allowed for sustainable harvest of the crop residue without losing yield or increasing nitrate leaching. During the simulation period, biochar acted as a source of carbon which consistently helped with increasing the mineral nitrogen pool through carbon mineralization and relieving nitrogen stress.

## CHAPTER 1. GENERAL INTRODUCTION

Biochar is a carbon rich soil amendment produced from biomass by a thermochemical process, pyrolysis or gasification. Soil biochar applications have generated a great deal of interest as a strategy for mitigating climate change by sequestering carbon in soils, and simultaneously as a strategy for enhancing global food security (Crane-Droesch et al., 2013; Paustian et al., 2016; Laird, 2008b; Woolf et al., 2010) by increasing crop yields especially on degraded and poor quality soils (Lehmann and Joseph, 2015). There is evidence that the recalcitrant C in biochar has a significantly greater residence time compared to C in uncharred plant biomass (Fidel et al., 2017; Woolf et al., 2010) suggesting that biochar application is a possible avenue for drawing down carbon from atmosphere and stabilizing it in the soil (Lehmann et al., 2007; Crane-Droesch et al., 2013). The alkalinity of biochar, its high internal porosity (Dokoochaki et al., 2017b), and capacity to absorb cations (high cation exchange capacity) can increase soil nutrient and water holding capacity (Basso et al., 2013; Cheng et al., 2006) without compromising soil conservation goals (Woolf et al., 2010). This can lead to increases in crop yields in less fertile and degraded soils which often coincide with high rural poverty (Crane-Droesch et al., 2013; Woolf et al., 2010). However, the ability of biochar to sequester carbon and alleviate soil limitations depends on biochar's properties, which are influenced by properties of the feedstock used to produce the biochar and by production technology (pyrolysis/gasification technologies) (Laird et al., 2009; Fidel et al., 2017).

Biochar, due to its high internal porosity, is expected to change various soil physical properties including bulk density (Laird et al., 2010b; Lei and Zhang, 2013; Sun and Lu, 2014; Devereux et al., 2012; Jones et al., 2010), total porosity (Oguntunde et al., 2008; Abel et al., 2013), pore size distribution (Major et al., 2009; Devereux et al., 2012; Hardie et al., 2013), water retention (Rawls et al., 2003; Major et al., 2009; Tryon, 1948; Auerswald et al., 2003), water holding capacity (Jones et al., 2010; Atkinson et al., 2010; Major et al., 2009; Sohi et al., 2009; Zwieten et al., 2012; Basso

et al., 2013) and aggregate stability (Jones et al., 2010; Tejada and Gonzalez, 2007). In addition, biochar has the ability to affect soil aggregation through interactions with SOM, minerals, and microorganisms, which can also affect saturated hydraulic conductivity (Asai et al., 2009; Uzoma et al., 2011) and infiltration rate (Downie et al., 2009; Asai et al., 2009; Brockhoff et al., 2010). Changes in soil physical properties due to biochar application can alter the depth (Devereux et al., 2012) and density distribution of plant roots (Bruun et al., 2014) and consequently the ability of plants to acquire water and soluble nutrients from the soil (Devereux et al., 2012).

While there is no or little incentive for farmers to adopt most climate change mitigation practices, the potential yield increase following biochar application has made it a promising new climate mitigation strategy. However, the degree of adoption of biochar technology is closely tied to the farmer's costs and benefits (Crane-Droesch et al., 2013) hence, in the absence of a C credit market, crop yield increase is the primary factor determining the economic viability of biochar applications (Laird et al., 2017; Laird, 2008a). Thus, the ability to accurately predict crop yield response to biochar applications is critical to the development of a viable biochar industry and to the design of incentive programs to enhance biochar adoption and C sequestration.

The complex nature of biochar interactions with soils and crops and lack of clear understanding of interactions (Atkinson et al., 2010; Sohi et al., 2009) has led to reports with conflicting interpretations, even under similar conditions (Jeffery et al., 2015). In addition, the large amount of missing data in the literature (Spokas et al., 2012) including inconsistent reporting of soil and biochar properties (Jeffery et al., 2015) has made the prediction of biochar behavior in soil a very challenging modeling exercise (Crane-Droesch et al., 2013).

In theory, we think that biochar affects crop growth and development through changes in the soil physical and chemical properties. Therefore, in the first two chapters of this thesis we explored the role of biochar in changing soil water balance as a result of changes in soil physical and hydrological properties. In addition, in the last two chapters we expanded our analysis by exploring the effect of biochar on crop yield and other environmental variables such as nitrate leaching using a statistical model (chapter3) and a process-based model (APSIM) in the last chapter.

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## CHAPTER 2. ASSESSING THE BIOCHAR EFFECTS ON SELECTED PHYSICAL PROPERTIES OF A SANDY SOIL: AN ANALYTICAL APPROACH

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Biochar application to soils is a promising practice with agronomic and environmental benefits. Our analysis is based on an incubated experiment with 3 biochar application rates (0%, 3% and 6%), two application methods and three replications. Soil water retention curves (SWRC) were determined at three sampling times. The Van-Genuchten (VG) model was fitted to all SWRCs and then used to estimate the pore size distribution (PSD). Standard deviation (SD), skewness and mode (D) were calculated in order to interpret the geometry of PSDs. The Dexter S-index and saturated hydraulic conductivity ( $K_s$ ) were also estimated. Statistical analysis was performed for all parameters using a linear mixed model. Relative to controls, all biochar treatments increased porosity, water content at both saturation and field capacity and improved soil physical quality. Biochar applications lowered ,  $K_s$ , bulk density and D indicative of a shift in pore size distributions toward smaller pore sizes.

### Introduction

Biochar is a porous and low-density carbon-rich material produced through the heating of organic materials under low-oxygen conditions (Lehmann et al., 2011; Singh et al., 2010; Sun and Lu, 2014). Biochar can help poor quality soils by improving their physical and chemical properties (Liang et al., 2006; Boivin et al., 2009), which can lead to increased crop yields when soil properties are limiting crop growth (Lehmann et al., 2003; Steiner et al., 2008; Van Zwieten et al., 2010; Peng et al., 2011). To date, most biochar studies have focused on the nutrient and chemical status of the

amended soils, while complex interactions between biochar and soil physical properties need more in-depth analysis.

Biochar, due to its high internal porosity, is expected to change various soil physical properties including bulk density (Laird et al., 2010b; Lei and Zhang, 2013; Sun and Lu, 2014; Devereux et al., 2012; Jones et al., 2010), total porosity (Oguntunde et al., 2008; Abel et al., 2013), pore size distribution (Major et al., 2009; Devereux et al., 2012; Hardie et al., 2013), water retention (Rawls et al., 2003; Major et al., 2009; Tryon, 1948; Auerswald et al., 2003), water holding capacity (Jones et al., 2010; Atkinson et al., 2010; Major et al., 2009; Sohi et al., 2009; Zwieten et al., 2012; Basso et al., 2013) and aggregate stability (Jones et al., 2010; Tejada and Gonzalez, 2007). In addition, biochar has the ability to affect soil aggregation through interactions with SOM, minerals, and microorganisms, which can also affect saturated hydraulic conductivity (Asai et al., 2009; Uzoma et al., 2011) and infiltration rate (Downie et al., 2009; Asai et al., 2009; Brockhoff et al., 2010). Changes in soil physical properties due to biochar application can alter the depth (Devereux et al., 2012) and density distribution of plant roots (Bruun et al., 2014) and consequently the ability of plants to acquire water and soluble nutrients from the soil (Devereux et al., 2012).

Biochar physical properties can be characterized according to porosity (Herath et al., 2013), particle size, and specific surface area; but these characteristics are highly dependent on the feedstock and pyrolysis process (Lei and Zhang, 2013; Major et al., 2010; Ahmad et al., 2012). Lei and Zhang (2013) reported that the effect of biochar on soil physical and hydraulic properties varied for biochars produced with different feedstock materials and pyrolysis temperatures. In addition to biochar source, application method can lead to different responses. For example, Blackwell et al. (2010) used a subsurface banding method for biochar application, instead of the more common method of surface application with top soil mixing, and found positive effects on yield. They concluded that the benefits more likely resulted from improved soil physical properties like water and nutrient retention, rather than through a direct nutrient supply from biochar. Although a growing amount of research is focused on the effect of biochar on soil physical properties, there is not yet a consensus on the effects of biochar on soil porosity and hydraulic properties (Hardie et al., 2013).

This study builds on previous work by (Basso et al., 2013) by using several indicators derived either directly or indirectly from soil water retention curves (SWRC). Our approach is to assess the effects of biochar amendments on pore size distribution (PSD) and the influence of PSD on the soils hydrological properties (Dexter, 2004; Reynolds et al., 2002). This analytical approach provides insight into the underlying mechanisms, which were not explored in (Basso et al., 2013) or similar studies, and it explores biochar impacts on soil microstructure (changes in the geometry of pore size distribution). The objectives of this research are to determine whether:

- 1- Biochar applications can significantly change soil water retention curve parameters and the geometry of the pore size distribution of a sandy soil.
- 2- Different methods or application rates of biochar affect the hydraulic and physical properties of a sandy soil.

## Materials and Methods

### Soil and biochar

This study was conducted using soil taken from the top 15 cm of a sandy loam soil (68% sand, 25% silt and 7% clay) on the Iowa State University Boyd research farm in Boone County, Iowa, USA. Soil particle size distribution was determined by the hydrometer method of (Gee et al., 1986). The biochar used in this study was produced by Avello Bioenergy, Inc. (BioCentury Research Farm, 1327 U Avenue, Boone, Iowa) using red oak (*Quercus rubra*) feedstock. It was produced by fast pyrolysis (500 °C) in a 6 inch bubbling fluidized bed reactor, using N<sub>2</sub> (183 L min<sup>-1</sup>) as the fluidizing gas. The biochar was characterized using ultimate (ASTM-D3176, 2009) and proximate (ASTM-D3172, 2007) analyses conducted by Hazen Research, Inc. (4601 Indiana Street Golden, Colorado 80403, U.S.A). Further experimental design details and chemical analysis of ash are reported in (Basso et al., 2013) .

### **Soil columns incubation**

Air-dried soil was mixed with 0% (control), 3% and 6% (by volume) biochar for 10 min in a cement mixer. Six iron cylinders were placed in the cement mixer to crush soil aggregates and thoroughly mix the soil. After mixing, the soil was passed through a 6mm sieve and stored in closed plastic containers until used (Basso et al., 2013). The soil columns were constructed using 18 cm long 7.7 cm id PVC pipes that were cut longitudinally and joined together with two hose clamps and then fitted with an end cap that had a 3 mm hole for drainage. The end cap was filled with 100 g of coarse sand (4-7 mm), and each column received a total oven dry mass of 994 g of soil plus biochar or soil only (controls). Two biochar application methods were used in this study in order to simulate subsurface, deep-banding in rows (DBR), and uniform topsoil mixing (UTM) applications. The biochar mixed with soil was applied either in the top 11.4 cm or bottom 11.4 cm of the soil column. An additional 5 cm of soil without biochar was added either at the top of the DBR columns or the bottom of the UTM columns. Three application rates of biochar were tested in this study, 0% (control), 3% and 6%; here the percent application refers only to the section of the soil column where the biochar was added. All columns were packed using a similar amount of force, which resulted in initial bulk densities that varied slightly (within  $0.1 \text{ g cm}^{-3}$ ) with treatment (Basso et al., 2013). A total of 72 columns (2 biochar application methods, 3 biochar rates, 4 sampling dates, and 3 replications) were randomly distributed on two square tables and incubated at 30 °C and 80% RH in a dark room. At each of 4 sampling times (1, 15, 29 and 91 days after the start of the incubation), 18 soil columns (2 biochar application methods, 3 biochar rates and 3 replications) were split into sub-samples and analyzed for various physical and chemical properties. Soil water retention curves were determined only for columns sampled on days 15, 29, and 91.

### **Soil Water Retention Curves**

Soil water retention curves were determined on sub-samples taken from the columns. Intact sections taken from the 6.4-11.4 cm depth of each column were inserted into 5 cm tall and 7 cm

diameter cylinders, and moisture content was measured at matric potentials of -0.01, -0.025, -0.05, -0.1, -0.2, -0.33 and -0.5 bar applied using the pressure chamber method (Klute, 1986). The pressure plate method (Klute, 1986) was used for determining water contents held at -1 and -15 bar after 7 days of pressure equilibration. The oven dried weight of soil samples was determined after heating at 105 °C for 24 h. The analysis of the water retention curves was carried out using the RETC (V6.02) software. The water retention curves were modeled using the Van Genuchten (VG) equation (Van Genuchten, 1980), where:

$$\theta(\psi) = \theta_r + \frac{(\theta_s - \theta_r)}{\{1 + (n|\psi|)^n\}^{1-\frac{1}{n}}} \quad (2.1)$$

$\theta_r$  = Residual water content,  $\theta_s$  = Saturation water content,  $\alpha$  is a shape parameter related to the inverse of the air entry suction and  $n$  is a parameter related to the shape of pore-size distribution ( $n > 1$ ).

### Measurement and calculations

Bulk density was determined on days 0, 21, 63 and 90 of incubation. To do so, the volume of headspace in each column was estimated by measuring the distance from the top of the column to the soil surface. Soil volume was then determined as total column volume minus headspace volume minus coarse sand volume. Bulk density was calculated by dividing the oven dry mass of soil by the soil volume. This approach assumes no changes in soil mass during the incubation and the value obtained was the average bulk density of the column. Bulk density was used to determine total porosity ( $\phi$ ) using the following equation:  $\phi = 1 - \left(\frac{\rho_b}{\rho_s}\right)$ , where:  $\rho_s$  soil particle density taken as 2.655 g cm<sup>-3</sup>,  $\rho_b$  bulk density .

The pore size distribution was estimated from the soil water characteristic curve using the Young - Laplace equation, which assumes that the pores are perfectly cylindrical, uniform, and equally drained (Hardie et al., 2013). The Young - Laplace equation is approximated by:

$$D = \frac{30}{|\psi_m|} \quad (2.2)$$

Where:  $D$  is the pore diameter (in  $\mu\text{m}$ ) and  $|\psi_m|$  is the absolute value of the soil matric potential ( $m$ ). The pore size distribution was assumed to be log-normal, and different descriptive indices were used to investigate pore size distribution and geometry. The highest rate of change in soil water content per unit of suction corresponds to the most frequent (mode) pore size diameter. Standard deviation (SD) and skewness of the pore size distribution were determined using the following equations (Reynolds et al., 2009):

$$SD = e^{\left(\frac{\ln d_{0.84} - \ln d_{0.16}}{4} + \frac{\ln d_{0.95} - \ln d_{0.05}}{6.6}\right)} ; \quad 1 \leq SD < \infty \quad (2.3)$$

$$Skewness = \frac{1}{2} \left[ \frac{\ln d_{0.84} + \ln d_{0.16} - 2(\ln d_{0.5})}{\ln d_{0.84} - \ln d_{0.16}} + \frac{\ln d_{0.95} + \ln d_{0.05} - 2(\ln d_{0.5})}{\ln d_{0.95} - \ln d_{0.05}} \right] \quad (2.4)$$

$$Kurtosis = \frac{\ln d_{0.05} - \ln d_{0.95}}{2.44(\ln d_{0.25} + \ln d_{0.75})} \quad (2.5)$$

where  $d_{0.05}$ ,  $d_{0.95}$ , ... were determined using the following equation:

$$d_\theta = \frac{2980 \alpha}{\left(\theta^{-\frac{1}{m}} - 1\right)^{\frac{1}{n}}} ; \quad 0 \leq \theta \leq 1 \quad (2.6)$$

where  $\theta$  is water content,  $m = 1 - \frac{1}{n}$  and  $\alpha$  and  $n$  are the Van Genuchten parameters. A standard deviation (SD) equal to one, indicates no variation in pore sizes (all pores have equal size) and a large SD represent large ranges in pore sizes. Skewness values vary between -1 and +1, a skewness of 0 indicates a symmetrical distribution, negative skewness values indicate asymmetry with dominance of small pores, and positive skewness values indicate asymmetry with a dominance of large pores. Kurtosis is also a descriptor of the shape of a probability distribution and varies between 0.41 and  $\infty$ . Kurtosis indicates the sharpness of the peak or the degree of concentration of the grains relative to the average. A kurtosis value equal to 1 corresponds to a log-normal distribution, while values greater than 1 indicate that it peaks more in the center, and values less than 1 indicate that it is less tailed in the extremes than the log-normal curve (Reynolds et al., 2009). The S-index (Dexter, 2004) was calculated using soil water characteristic parameters with the following equation:

$$S = -n(\theta_s - \theta_r) \left[ \frac{2n - 1}{n - 1} \right]^{\frac{1}{n} - 2} \quad (2.7)$$

The S-index is the slope (S) of the soil water retention curve (SWRC) at its inflection point and has been used as an index of the physical quality of the soil (Dexter, 2004), where larger S values indicate a soil with better physical qualities. Saturated hydraulic conductivity ( $K_s$ ;  $\text{cm day}^{-1}$ ) was estimated using the following model (Aschonitis and Antonopoulos, 2013):

$$K_s = 1632.5|S|(3.9f)^{-30.9f} \quad (2.8)$$

Where:  $f = \alpha \phi_e$  .

The term is the effective porosity ( $\text{cm}^3 \text{cm}^{-3}$ ) and  $\alpha$  is the shape parameter of the VG equation. Effective porosity is defined as the difference between the total porosity and the water content at field capacity (Aschonitis and Antonopoulos, 2013).

### Statistical Analysis

In order to test the effects of treatment and sampling date on the changes in soil physical properties a linear mixed model was set up with biochar treatment and sampling time as the fixed terms. Due to the small number of sample points in time, no autocorrelation was found among the residuals. Pair-wise comparisons were used to test for significant differences ( $P < 0.05$ ) between means. Statistical analyses were carried out with the software package SAS 9.3 (SAS Institute, Cary NC).

## Results and Discussion

### Differences in SWRC and VanGenuchten model parameters

Soil water retention curves (SWRC) were modeled using mean VG equation coefficients for all treatments at each sampling time (Fig. 2.1). All biochar treatments had higher water content values near saturation and a steeper slope at the SWRC inflection point in comparison to the control for the 29 and 91 sampling dates, but not for the 15 sampling date. Because the shape of a SWRC is determined by the structural pores rather than the matrix pores, the observed changes in the shape of SWRCs imply that the biochar amendments caused a change in soil structure

(Fig. 2.1). Increased water content at lower tensions (Table 2.1 and Fig 2.1) indicate that biochar additions increased total porosity (Hardie et al., 2013; Sun et al., 2015). Higher water retention by soils receiving biochar amendments relative to the control is similar to the effect of an increase in soil organic matter content (Rawls et al., 2003; Basso et al., 2013), which increases specific surface area (Smith et al., 1985) and decreases soil bulk density.

All biochar treatments, except UTM6, have significantly lower  $\alpha$  values than the control treatment. The value of  $\alpha$  corresponds to the suction at the air entry point and is proportional to the radius of the openings of the largest pore (Ghanbarian-Alavijeh et al., 2010). The lower value of  $\alpha$  for biochar amended soils relative to the control indicates that the largest pore diameter was smaller for the biochar treated soils than for the control. An increase in total porosity and a smaller value for largest pore size are consistent with higher water content at low moisture tensions and lower saturated hydraulic conductivity in the biochar amended soils relative to the control. Similarly, Lei and Zhang (2013) found that loamy soils amended with woodchip biochar produced by pyrolysis at 500 and 700 °C had lower  $\alpha$  values than the control soils in their study.

No clear treatment effects were evident in the SWRCs for the samples collected on day 15 of the incubation, however, treatment effects were apparent for samples harvested on days 29 and 91 of the incubation (Fig. 2.1). Furthermore, a significant difference for  $\theta_s$  after day 29 and  $\theta_r$  for samples harvested on days 29 and 91 were found between the control and the biochar treatments. All treatments experienced a reduction in  $\theta_s$  and an increase in  $\theta_r$  over the course of the study, which can be related to soil consolidation (increasing soil bulk density) with time caused by wetting and drying cycles.

The subsurface banding biochar application caused significantly lower  $\alpha$  and  $\theta_s$  values in comparison with the uniform mixing of biochar in the topsoil. The 6% biochar applications resulted in significantly lower  $\alpha$  and  $n$ , and higher  $\theta_s$  values than the 3% biochar applications or the controls. A larger  $\theta_s$  found in the 6% than in the 3% application rate indicates larger soil porosity or pore volume that needs to be filled with water to reach saturation.



The significant influence of biochar rate and application method on water retention curves observed here is consistent with findings from other studies (Novak et al., 2009; Dumroese et al., 2011; Lei and Zhang, 2013). In contrast, Hardie et al. (2013) found no significant changes in Van Genuchten parameters for a sandy loam soil thirty months after biochar additions. The discrepancy between these results might be due to the different biochar types and application rates, or to biochar aging, which may diminish the effect of biochar on soil physical properties over time.

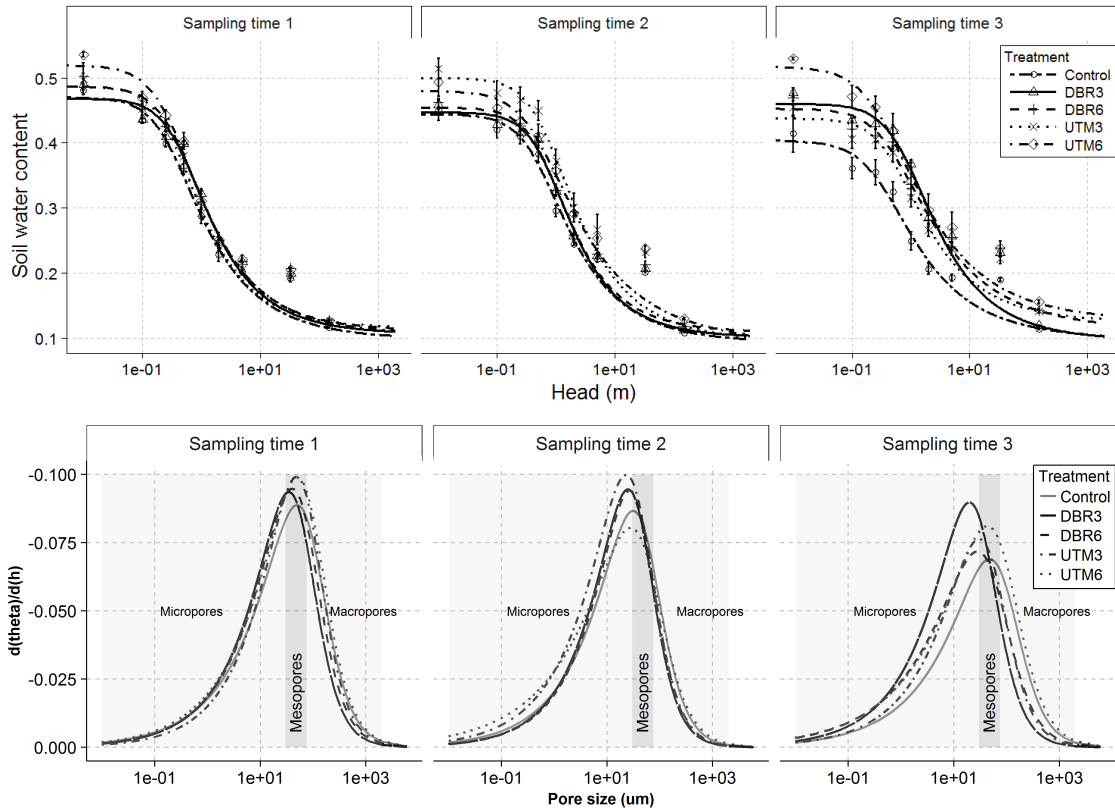


Figure 2.1: Soil water retention curve on top panel and pore size distribution on bottom panel estimated for different treatments and sampling times.

### Differences in Bulk density ( $\rho_b$ ) and Porosity ( $\phi$ )

Except for the DBR3 treatment, the biochar amended soils had significantly lower mean bulk densities and higher mean total porosities than the control (Table 2.1). A reduction in bulk density along with an increase in total porosity following biochar application have been reported by others

Table 2.1: Van-Genuchten model parameters and measured bulk density and field capacity for all treatments.

Treatment	$n$	$\theta_r$ ( $\text{cm}^3 \text{cm}^{-3}$ )	$\theta_s$ ( $\text{cm}^3 \text{cm}^{-3}$ )	$\alpha$ ( $\text{cm}^{-1}$ )	$D$ ( $\mu\text{m}$ )	$S_{index}$	$K_s$ ( $\text{cm day}^{-1}$ )	$\rho_b$ ( $\text{g cm}^{-3}$ )	$\phi$ (%)	$FC$ ( $\text{cm}^3 \text{cm}^{-3}$ )
Control	1.51	0.096	0.439	0.0312	44	0.082	238	1.43	46.1	0.31
UTM (3%)	1.55	<b>0.111</b>	<b>0.474</b>	<b>0.0217</b>	34	<b>0.092</b>	226	<b>1.37</b>	<b>48.1</b>	<b>0.35</b>
UTM (6%)	1.45	0.107	<b>0.505</b>	0.0320	42	<b>0.088</b>	258	<b>1.32</b>	<b>50.2</b>	<b>0.36</b>
DBR3 (3%)	1.57	<b>0.101</b>	0.458	<b>0.0172</b>	<b>27</b>	<b>0.092</b>	<b>204</b>	1.42	46.3	<b>0.34</b>
DBR (6%)	1.53	<b>0.111</b>	<b>0.464</b>	<b>0.0217</b>	32	0.087	218	<b>1.35</b>	<b>48.8</b>	<b>0.34</b>

tBold font indicates that significant difference ( $\alpha=0.05$ ) was found between a biochar treatment and the control treatment;  
*D*: most frequent pore size Diameter;  $K_s$ : saturated hydraulic conductivity;  $\rho_b$ : bulk density;  $\phi$ : porosity;  $FC$ : field capacity

(Downie et al., 2009; Lei and Zhang, 2013; Busscher et al., 2010; Devereux et al., 2012). In the present study, the 6% biochar application rate and the UTM application method resulted in lower bulk densities and higher porosities than the 3% application rate and DBR application method, respectively. The higher soil porosity of biochar amended soils relative to the control soils may be due to the direct contribution of the pores in biochar particles, differential packing or consolidation of biochar amended and control soils, increase in aggregate stability or increase in soil biota (Hardie et al., 2013). Our results show a minor change in bulk density with time among the biochar amended soils but a slow increase in bulk density in the control soils with time. This finding is consistent with previous reports, which showed greater consolidation of control soils than biochar amended soils over the course of a 500-day soil column incubation study (Laird et al., 2010a). These results indicate that biochar primarily acts as a soil conditioning agent similar to soil organic matter (Tisdall and Oades, 1982). Similar trends were reported by Jones et al. (2010) and Hardie et al. (2013).

### **Differences in geometry of pore size distribution (PSD)**

All biochar treatments shifted the PSD towards smaller pore sizes relative to the control. The biochar treatments also resulted in more meso and micro-pores and fewer macro-pores compared to the control (Fig. 2.1), based on the pore size classification suggested by Brewer (1964). This phenomenon is the major reason for the observed increases in water content near field capacity and saturation, both of which are strongly influenced by pore size distribution (Jones et al., 2010). The shift in pore size distribution for all biochar treatments was evident by the second sampling date (29 days), and these differences continued through the rest of the experiment (Fig. 2.1). It has been reported that increasing the pyrolysis temperature results in production of biochars with smaller diameter pores (Downie et al., 2009); hence higher temperature biochars may help coarse-textured soils to retain more plant available water.

The peak of a PSD curve represents the most frequent pore diameter, and it can provide quantitative evidence of differences in pore size distributions between biochar treated and control

Table 2.2: Comparison between physical soil parameters obtained for two application methods and two application rates. Values are probabilities (p-value)

Contrast	$n$	$\theta_r$ ( $\text{cm}^3 \text{cm}^{-3}$ )	$\theta_s$ ( $\text{cm}^3 \text{cm}^{-3}$ )	$\alpha$ ( $\text{cm}^{-1}$ )	$D$ ( $\mu\text{m}$ )	$S_{index}$	$K_s$ ( $\text{cm day}^{-1}$ )	$FC$ ( $\text{cm}^3 \text{cm}^{-3}$ )	$\phi$ (%)
DBR VS UTM	0.072	0.308	<b>0.004</b>	<b>0.0152</b>	<b>0.014</b>	0.890	<b>0.013</b>	0.087	<.001
3% VS 6%	<b>0.015</b>	0.443	<b>0.015</b>	<b>0.0150</b>	<b>0.026</b>	0.101	0.059	0.369	<.001

Bold font indicates that a significant difference ( $\alpha = 0.05$ ) was found between a biochar treatment.

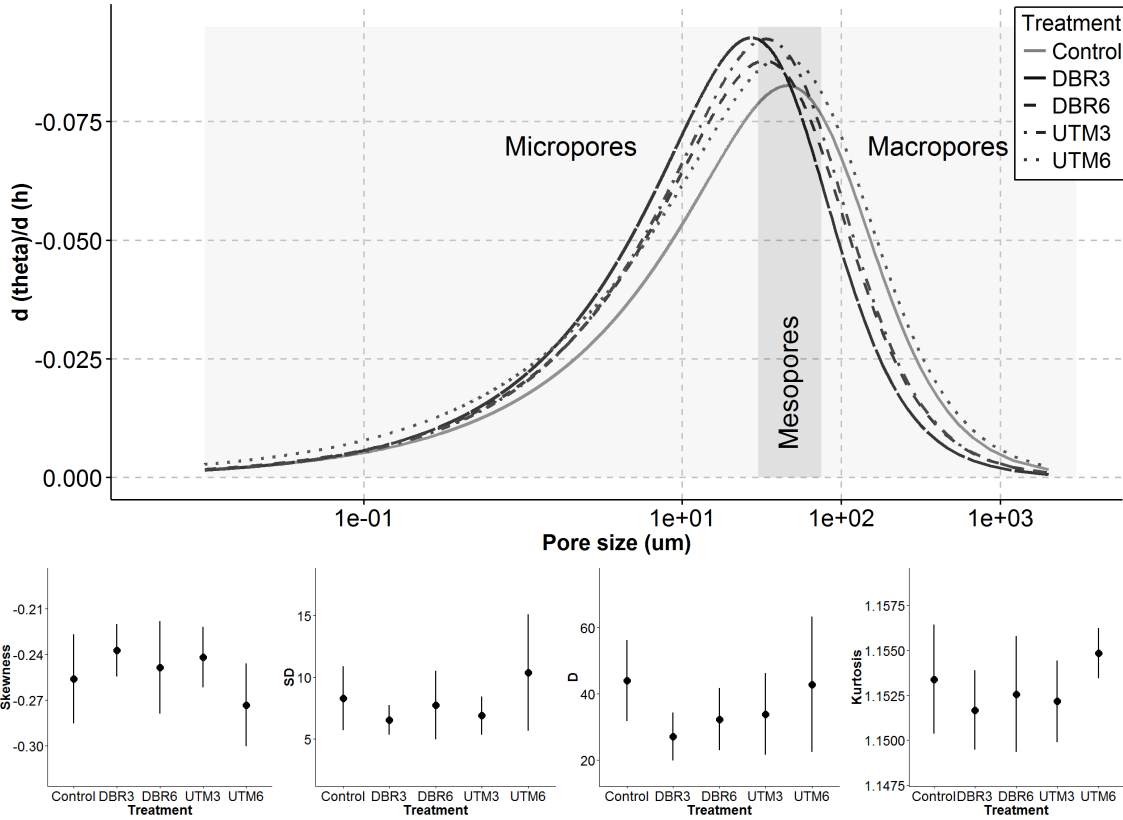


Figure 2.2: a) Pore size distribution of control and biochar amended soils b) Geometry parameters of pore size distributions. Pore size classes are suggested based on Brewer (1964).

soils. Our results show that biochar additions significantly reduced  $D$  for DBR3 (Table 2.1) relative to the control. Except for UTM6, the average  $D$  was reduced to lower than  $30 \mu\text{m}$  in biochar amended soils (equivalent diameter associated with field capacity), and it suggests a possible cause for the larger field capacity in biochar treatments compared to the control. At the end of the study (91 days incubation) all biochar treatments except UTM6 shifted  $D$  toward the micro-pores, compared to the first sampling time (day 15) when all treatments started with similar  $D$  values within the meso-pore class (Fig. 2.1). Such a shift might be more beneficial in sandy soils dominated by macropores, which have a limited capacity to retain water. Our analysis suggests that application of 3% biochar with sub-surface banding results in a significantly lower  $D$  in comparison to the 6% and the uniform top mixing method (Table 2.2).

The standard deviations indicate that soil pore size distributions for all treatments fall into the very poorly sorted category, which indicates a very large range in equivalent pore diameters. All biochar treatments except for UTM6 had smaller SD than the control, indicating that biochar amendments decreased the range of pore sizes (Fig. 2.2). Interestingly, this trend was more dominant in the 3% compared to the 6% biochar treatments.

In general, the negative skewness found for all treatments indicates a longer left tail and more total pore volume on the right side (i.e. larger pore sizes) of the peak. However, except for UTM6, the less negative skewness for the biochar amended treatments compared to the control shows that biochar shifts the PSD toward the left side (i.e. smaller pore sizes) of the distribution (Fig. 2.2). Thus, in the soils with biochar amendment there is an increase in the volume of smaller pores in comparison to the control (Fig. 2.2). This trend was more dominant in 3% biochar application treatments indicating a smaller range of pore sizes. This finding is consistent with previous reports by Jones et al. (2010) and Devereux et al. (2012) who found a reduction in the number of macropores with biochar addition for sandy and sandy loam soils, respectively.

According to Blot and Pye (2001), the kurtosis value found for all treatments falls into the Leptokurtic category, which means that the SD is influenced by extreme pore sizes or, alternatively, the PSD is centered on D. On the other hand, the kurtosis value was similar for the biochar treatments and the control, indicating that biochar affected just a specific range of pore sizes in the soil, here the micro- and meso-pores.

### **S-index (S) and saturated hydraulic conductivity (Ks)**

The S-index is a quantitative index of soil microstructure, which controls many major soil physical properties (Dexter, 2004) and has been used to discriminate among soil management practices (Tormena et al., 2008). The S-index is related to soil bulk density, organic matter content and root growth capacity. In this study, except for DBR6, the S-index increased for all biochar treatments compared to the control (Table 2.1 and 2.2). Soils with high S-index have a high root growth capacity, because the S-index is correlated with the soil compressibility (Dexter, 2004). Our

results suggest that biochar, similar to soil organic matter (OM), influences soil water content at the SWRC inflection point (Jong et al., 1983), therefore, along with changes in bulk density, this may be the major cause for higher S-index values for biochar amended soils. Although all of the S-indices found in the current study are higher than 0.035 (critical value suggested by Dexter (2004)), even higher values of this index can lead to increased plant absorption of water and nutrients.

Biochar amended soils had lower  $K_s$  values than the control soils, and this difference was significant for DBR3 (Table 2.1). A lower  $K_s$  value found for the biochar treatment indicates fewer large pores contributing to saturated water flow in the amended soils. Our results suggest that the DBR method had significantly lower  $K_s$  values in comparison to the UTM method. The 6% biochar application rate had marginally significantly higher  $K_s$  in comparison to the 3% (Table 2.2). This might be because this application rate has higher D values, as  $K_s$  is strongly influenced by soil macropores (Jirku et al., 2013). The biochar used in this study had high ash content, (Basso et al., 2013) and, according to Verheijen et al. (2009), the ash fraction can cause the soil particles to move closer together increasing the secondary macro porosity, and as a result, increase the saturated hydraulic conductivity. In similar studies, Brockhoff et al. (2010) and Uzoma et al. (2011), also found a reduction in saturated hydraulic conductivity due to biochar applications.

## Conclusion

In summary, we have extended the findings of Basso et al. (2013) by showing that biochar amended soils had a change in pore size distribution with smaller most frequent pore diameters and Van Genuchten alpha parameters and larger S-index, total porosity and higher saturated, field capacity and residual water contents compared to control soils without biochar. A key novel finding is that differences in soil pore geometry parameters obtained by fitting measured SWRCs to the Van Genuchten equation provided quantitative evidence of the shift in pore size distribution to smaller average pore sizes, reducing macro- in favor of meso- and microporosity and hence enhancing soil water retention. This improvement can help biochar amended sandy soils to retain

more plant available water for crop use and reduce leaching losses of water and nutrients compared to non-amended sandy soils.

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## CHAPTER 3. INTEGRATING MODELS AND DATA TO INVESTIGATE THE EFFECT OF BIOCHAR ON SOIL HYDROLOGICAL PROPERTIES

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Biochar has been shown to improve soil hydraulic properties, but most of the research has been limited to laboratory studies. Our objective was to evaluate the impact of biochar on soil hydraulic properties at the field scale by combining a modeling approach with soil water content measurements from a corn-corn cropping system over two years. The effect of biochar was expected to be the difference between the physical soil properties of the biochar and no-biochar treatments. An inverse modeling was performed after a global sensitivity analysis to estimate the parameters for the soil physical properties of the APSIM model. The drainage upper limit (DUL) was the most sensitive soil property followed by saturated hydraulic conductivity ( $K_s$ ). The difference between the posterior distributions showed an increase in DUL of approximately 10% in the biochar treatment and no considerable change was noted in  $K_s$  compared to no-biochar. No considerable change was noted in LL15, MAXPOND and KS whereas SAT and LL showed a slight increase and decrease in biochar treatment, respectively, compared to no-biochar.

### Introduction

Biochar has recently gained considerable attention due to its agronomic benefits and carbon sequestration potential. Among its many properties, biochar high surface area (Laird et al., 2010a), small particle size (Hardie et al., 2013; Reynolds et al., 2009; Basso et al., 2013), low bulk density (Downie et al., 2009; Devereux et al., 2012) and high organic carbon content (Herath et al., 2013; Jones et al., 2010) can effectively decrease soil bulk density, increase porosity and help coarse texture soils by increasing their capacity for holding water (Basso et al., 2013). However, despite

the increased attention there is not yet a consensus on the effects of biochar on soil hydraulic properties (Hardie et al., 2013).

Short-term changes in physical and hydrological properties of amended soils with biochar have been observed in numerous lab and incubation studies (Streubel et al., 2011; Liu et al., 2012). However, laboratory-scale measurements of soil physical properties are mainly based on static steady flow assumption (Vrugt and Dane, 2005) and may produce large errors (Abbaspour et al., 1999). In addition, Mallants et al. (1997) and Reynolds et al. (2002) found that different lab techniques may result in different estimates for soil physical properties. Sensitivity to the geometry of the flow, sample size and sample collection procedure are among the reasons why dissimilar measurement of soil physical properties are observed (Reynolds et al., 2002). Although these studies allow for convenient implementation and measurements, they lack the dynamic interactions of soil properties with crop and management practices. For example, an increase in porosity and water holding capacity of amended soils with biochar can potentially promote root penetration, aeration and lead to higher water and nutrient acquisition. However, increase in crop water and nutrient uptake cannot be fully investigated in lab studies and requires a dynamic method that is capable of directly and indirectly capturing the interaction among soil, biochar and crop.

One approach for indirectly estimating field-relevant soil physical properties of amended soils with biochar is by using inverse modeling. This method, searches the input parameters space of a model for the most plausible combination of inputs that yield the best fit between model predictions and observations. Numerous studies have been conducted that use inverse methods with the aim of estimating soil physical properties, model verification or uncertainty analysis (e.g. (Abbaspour et al., 1999)). For example, Wöhling et al. (2008), suggested that inverse modeling of process-oriented crop models like APSIM is a promising technique for obtaining effective hydraulic properties of soils. Application of this technique for estimation of hydrological parameters accounts for more dynamic interaction of soil properties compared to lab measurements.

This study used the APSIM model (Holzworth et al., 2014) along with a unique dataset of continuous soil water content measurements in two cropping systems (biochar vs. no-biochar treat-



ment) for two years. We propose an optimization framework to inversely estimate hydraulic parameters for the APSIM model. This optimization framework uses measurements of soil moisture for two years as input data. We hypothesize that the analysis of this dataset with a process-oriented crop model will allow us to derive reasonable estimates of the effect of biochar on soil hydrological properties. Therefore, the main objective of this study is to derive posterior distributions for soil physical parameters using the APSIM model for biochar and no-biochar treatments. We expect that the difference between estimated posterior distributions (i.e. with and without biochar) will indicate the effect of biochar on soil physical properties in the field.

## Materials and methods

### Field experiment and measurements

The research site is located at the Armstrong Memorial Research and Demonstration Farm near Lewis, IA (41°18' N, 95°10' W). In 2011 biochar was applied at a rate of 10 Mg ha<sup>-1</sup> in 3 out of 6 plots and paired plots were left as controls. Maize was planted on May 17 in 2013 and on May 8 in 2014; it was harvested on Oct 28 in both years. Soil water content, soil temperature, and EC were measured at 30 min intervals at 4 depths (10 cm, 25 cm, 42 cm and 60 cm) for both years in all plots. We used Decagon 5TE soil moisture sensors which have an estimated accuracy of about 0.03 cm<sup>3</sup> cm<sup>-3</sup> after calibration. Sensors were installed May 2012 and they were in place until the end of the experiment. Calibration was performed using Topp's equation (Topp et al., 1980) according to the sensor's manual, which converts the bulk dielectric constants to bulk volumetric soil water content. Soil moisture measured in the time interval from Nov 20 in 2013 until the end of May in 2014 was not included in this study because the soil was frozen and the sensors were not working properly.

During early 2014 there were more extreme cold days compared to 2013, and the total precipitation was 882 mm for the first year and 1123 mm for the second year. The experimental site received an average of 15.8 (MJ m<sup>-2</sup>) solar radiation per day and 5778 (MJ m<sup>-2</sup>) in total over the course of 2013 and 15.6 (MJ m<sup>-2</sup>) per day and 5694 (MJ m<sup>-2</sup>) in total in 2014. The highest

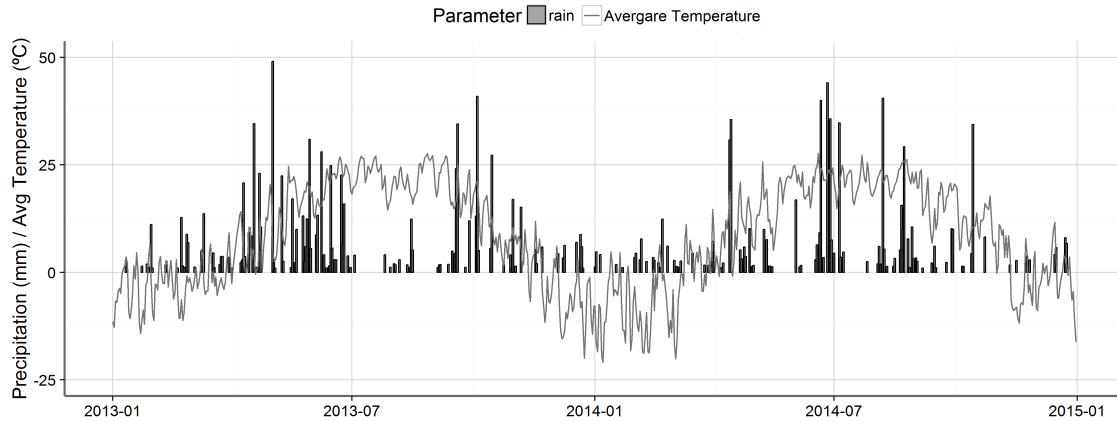


Figure 3.1: Daily precipitation and mean temperature for 2013 and 2014 in Lewis, IA.

temperature recorded in 2013 was 36 °C whereas -26 °C was the lowest air temperature. Likewise, maximum air temperature in 2014 was 34 °C and the minimum was -25 °C.

### APSIM model

The APSIM model has been designed in a modular fashion, allowing users to perform their own simulations using numerous soil, crop, climate and management components. The APSIM model can simulate soil water content, soil temperature and nutrient cycling as well as their interaction with different crop and management practices (e.g. irrigation, fertilization) on a daily time step. Specifically, for the U.S Midwest, APSIM has been used as a way to examine the indirect effects of new management practices on different soil and crop properties (Basche et al., 2016; Archontoulis et al., 2014). The SOILWAT module in APSIM (Probert et al., 1998) estimates daily changes in soil water content for different soil layers due to infiltration of irrigation and rainfall, vertical drainage, unsaturated and saturated flow, soil evaporation, and root water uptake processes. The model uses a 'tipping bucket' approach for computing soil water drainage. In this method, the excess water above the field capacity of a layer is passed directly to the layer below. Upward unsaturated flow is also computed using a conservative estimate of the soil water diffusivity and differences in volumetric soil water content of adjacent layers.

## Sensitivity analysis and optimization

The following framework was developed and employed to inversely estimate the soil hydrological parameters (see Table 3.1 for definitions) in the APSIM model

1. A Global Sensitivity Analysis was performed (GSA) on the most relevant hydrological parameters. The output variable of primary interest for this task is the soil water content. GSA was performed as a screening tool for eliminating non-influential parameters and identifying the most sensitive (those to be optimized).
2. The most sensitive parameters were inversely estimated using an Approximate Bayesian Computation framework (ABC). A set of rules were adopted to ensure that samples generated from hydrological parameters are valid (i.e., soil water content parameters must be in the 0 - 1 range) and have meaningful relationship (e.g., LL15 should be smaller than DUL and DUL should be smaller than SAT. LL15 represents the lowest soil moisture that plant can take up water from in the APSIM model whereas DUL is a proxy for field capacity and SAT represents saturated water content).
3. A diagnostic test was performed to ensure the convergence of the algorithm.
4. Soil water content simulated from accepted samples were used to display the uncertainty range of soil water contents for the simulation period.

### Sensitivity analysis

In the current study, the analysis of variance method was used for sensitivity analysis. In this method, we decompose the variability of the output (soil water content) and determine the contribution of each input parameter (Wallach et al., 2014). This method estimates the main effect for each parameter as well as its linear interactions. Main effects and total sensitivity indices can be calculated using the sums of squares (SSQ) as follows (Wallach et al., 2014):

$$S_1 = \frac{SS_1}{SS_T}; \quad S_2 = \frac{SS_2}{SS_T} \quad (3.1)$$

$$SS_{12} = \frac{SS_{12}}{SS_T} \quad (3.2)$$

$$TS_1 = \frac{SS_1 + SS_{12}}{SS_T}; \quad TS_2 = \frac{SS_2 + SS_{12}}{SS_T} \quad (3.3)$$

Where  $SS_1$  is the SSQ for the first parameter,  $SS_{12}$  is the SSQ of the interaction between first and second parameter, and  $SS_T$  is the total SSQ. A set of 26 parameters were selected to measure the sensitivity of simulated soil water content in APSIM model to soil hydrological inputs (Table 3.1). Using random samples taken from a proposed distribution for each parameter, the APSIM model was run 12,000 times and the resulting mean soil water content was stored after each simulation. Then an analysis of variance of the mean considering each parameter as a factor was performed and the contribution of each factor with its first interactions were assessed.

### Bayesian parameter estimation

We used an Approximate Bayesian Computation framework (ABC) to estimate the posterior distribution of the parameters. The main outcome of the Bayesian inference is the posterior distribution which is the conditional distribution of a vector of parameters  $\theta$  (soil hydrological inputs of the APSIM) for a given observed dataset  $D_{obs}$  (measured soil water content) given by

$$p(\theta|D_{obs}) \approx c \times p(D_{obs}|M(\theta)) \times p(\theta) \quad (3.4)$$

Where  $c$  is a constant,  $p(\theta)$  is the prior distribution, and  $p(D_{obs}|M(\theta))$  is the likelihood. The prior distribution generally reflects our prior understanding about  $\theta$ , while the likelihood is a function which returns the probability of finding observed data given  $\theta$ . Analytically deriving the posterior distribution is possible but not practical for most real-world problems; therefore, numerical estimation based on random sampling techniques is preferred. Within the ABC framework, the idea of evaluating the likelihood is replaced with a difference measure such as the sums of squares (Hartig et al., 2014; Toni et al., 2009).

The Metropolis - Hastings algorithm was used to estimate the posterior distribution of parameters. This algorithm builds a Markov chain Monte Carlo (MCMC), in which new samples are

Table 3.1: List of hydrological parameters with their lower and upper bound used for sensitivity analysis

#	Parameter	Definition	Unit	Lower	Upper
1	CN2Bare	Curve number for bare soil	-	60	89
2	CNCov	The extent of the effect of surface residue on CN	-	1	100
3	DiffusConst	Diffusivity coefficients for unsaturated flow	-	1	300
4	DiffusSlope	Diffusivity coefficients for unsaturated flow	-	1	100
5	DUL (1)	Drained upper limit volumetric water contents-Layer1	cm <sup>3</sup> cm <sup>-3</sup>	0.12	0.39
6	LL15 (1)	Lower limit volumetric water contents for-Layer1	cm <sup>3</sup> cm <sup>-3</sup>	0.05	0.11
7	SAT (1)	Saturated volumetric water contents-Layer1	cm <sup>3</sup> cm <sup>-3</sup>	0.4	0.55
8	DUL (2)	Drained upper limit volumetric water contents-Layer2	cm <sup>3</sup> cm <sup>-3</sup>	0.12	0.39
9	LL15 (2)	Lower limit volumetric water contents for-Layer2	cm <sup>3</sup> cm <sup>-3</sup>	0.05	0.11
10	SAT (2)	Saturated volumetric water contents-Layer2	cm <sup>3</sup> cm <sup>-3</sup>	0.4	0.55
11	Salb	Soil albedo	-	0.1	0.7
12	Sini	Initial soil moisture (based on total soil fraction)	-	0.1	1
13	SummerCona	Second stage evaporation coefficient	-	1	50
14	SummerU	Potential amount of cumulative evaporation	-	1	50
15	SWCON (1)	Drainage coefficient-Layer1	-	0.01	0.99
16	SWCON (2)	Drainage coefficient-Layer2	-	0.01	0.99
17	XF	Exploration Factor	-	0.01	0.99
18	KL	Maximum rate a plant can extract water from	day <sup>-1</sup>	0	0.5
19	LL	crop LL	cm <sup>3</sup> cm <sup>-3</sup>	LL15	DUL
20	BD (1)	Bulk density-Layer1	g cm <sup>-3</sup>	1.0	1.8
21	BD (2)	Bulk density-Layer2	g cm <sup>-3</sup>	1.0	1.8
22	K <sub>s</sub> (1)	Saturated hydraulic conductivity-Layer1	m day <sup>-1</sup>	0.01	10
23	K <sub>s</sub> (2)	Saturated hydraulic conductivity-Layer2	m day <sup>-1</sup>	0.01	10
24	MWCON (1)	Controls the water flow in soil saturation condition-Layer1	-	0.1	0.9
25	MWCON (2)	Controls the water flow in soil saturation condition-Layer2	-	0.1	0.9
26	MaxPond	Maximum depth of surface storage	-	1	10

proposed according to a distribution designated as a proposal distribution, and evaluated using the Bayes rule. The algorithm is guaranteed to converge to an approximate distribution of parameters given (Toni et al., 2009) the prior and likelihood. Choices of prior and proposal distributions and how the likelihood is set up can have a significant effect on the efficiency of the algorithm. The following generic algorithm was implemented:

1. Initialize  $\theta_i$  as the starting point
2. Propose  $\theta^*$  according to the proposal distribution  $q(\theta^*|\theta_i)$
3. Simulate a dataset  $D_{sim}$  from  $M(D_{obs}|\theta^*)$
4. Estimate the  $L(X|\theta^*)$  given data  $D_{obs}$
5. If  $U \sim \text{uniform}(0, 1) \leq \frac{p(\theta^*) \times L(X|\theta^*)}{p(\theta_i) \times L(X|\theta_i)}$  accept the move
6. Repeat (go to step 2)

where the likelihood, adapted from Hartig et al. (2014) was defined as  $L(D_{obs}|M(\theta)) \approx c \times \exp\left[-\frac{1}{2} \times \frac{(D_{obs} - D_{sim})^2}{\sigma^2(\theta)}\right]$ . Prior distributions were set as normal with mean and variances estimated based on the soil type and it was set to be identical for the two treatments. The proposal distribution was also assumed to be normal and an appropriate variance (step size) was found by trial and error. Samples of hydrological soil parameters were required to be physically meaningful. For some of the parameters, samples were checked to be less than one and greater than zero. LL15, DUL and SAT were also required to obey the following rule:  $SAT > DUL > LL15$ . Using accepted samples, soil water content was simulated and compared to the corresponding observed soil moisture; the Root Mean Square Error (RMSE) was used as the statistic of merit,

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (O_i - S_i)^2}{N}} \quad (3.5)$$

where  $O_i$  is the observed soil moisture and  $S_i$  is the corresponding simulated soil moisture.

## Diagnostic test

The MCMC algorithm was implemented in R and a modified version of the `apsimr` package was used to interact with the APSIM model. We ran three chains to ensure the convergence of the algorithm and that the generated samples could be assumed to be taken from the same posterior distributions. Convergence was evaluated visually and also using the Gelman-Rubin diagnostics from the `coda` package in R (Gelman and Rubin, 1992; Plummer et al., 2006).

## APSIM setup

The APSIM model version 7.7 (r3632) was used in the current study. The soil profile was divided into 7 layers to a depth of 110 cm and the initial soil moisture was set to saturation at the beginning of the simulation. Simulations in 2013 were initialized on February 15 and ended on November 29. Planting dates were set to May 17 in 2013 and May 8 in 2014, and harvesting date was set to October 28 for both years.

## Results and discussion

In 2013 the average yield for all plots was  $11.3 \text{ Mg ha}^{-1}$  with a  $1.4 \text{ Mg ha}^{-1}$  standard deviation while in 2014 these values were 9.3 and  $1.6 \text{ Mg ha}^{-1}$  respectively for both treatments. Measured daily mean soil moisture for the biochar treatment was 0.19 and  $0.24 \text{ cm}^3 \text{ cm}^{-3}$  in 2013 and 2014 respectively which is greater compared to the no-biochar treatment with a mean of 0.17 and  $0.19 \text{ cm}^3 \text{ cm}^{-3}$  for the same years (Fig. 3.2). Interestingly, in both years, the biochar treatment hit a lower minimum soil water content ( $0.07$  and  $0.13 \text{ cm}^3 \text{ cm}^{-3}$ ) compared to no-biochar treatment ( $0.1$  and  $0.15 \text{ cm}^3 \text{ cm}^{-3}$ ) during the growing season suggesting higher water uptake by the crop.

## Sensitivity analysis

DUL2 followed by  $K_s1$  explained a large proportion of the variability of the SWC; in other words, these two parameters showed the highest sensitivity. Moreover, MaxPond, along with DUL1, SAT1, KL2, and LL15-2 showed high sensitivity over the two years of analysis. Each of the most sensitive

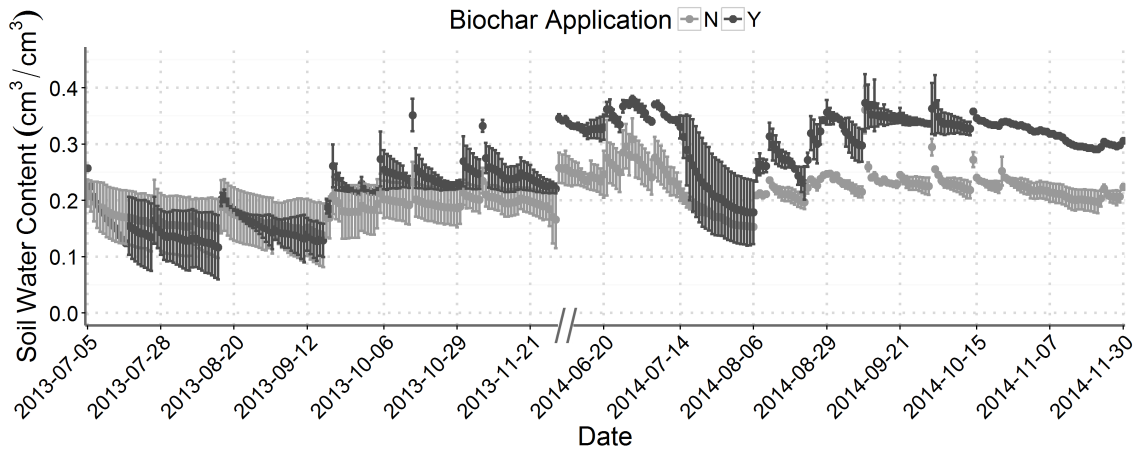


Figure 3.2: Daily mean soil water content of 10cm depth for 2013 and 2014 in corn plots. The light line indicates no biochar and the dark line indicates the biochar treatment.

parameters explains a different aspect of the soil water cycle. Within the tipping bucket framework used for simulation of SWC in APSIM, DUL, LL15 and SAT are the most important parameters for defining the bucket size (the capacity of the soil for storing water) while MaxPond is used in infiltration calculations and subsequent calculation of the amount of runoff. In addition,  $K_s$  is the main driver of saturated water flow and soil seepage; LL15-2, LL and KL2 directly affect crop water uptake (transpiration) and indirectly affect soil evaporation. Residuals containing the leftover interactions of higher than second order interactions among all the parameters resulted in less than approximately 10% of the total variance (Fig. 3.3).

The number of parameters chosen for the optimization process highly depends on the number of target variables as well as the total number of independent measurements corresponding to the target variable (SWC in our case). Even though a total of 296 SWC measurements were made, the autocorrelation (correlation in time among the measurements) among the observations reduces the total number of independent measurements to about 20-25. Considering this number of independent measurements, we decided to use no more than 10 parameters (half the measurements) and by trial and error found that 8 was the most appropriate number of parameters. Therefore, only the top 8 most sensitive parameters were used for optimization. The ranking for parameters found as a



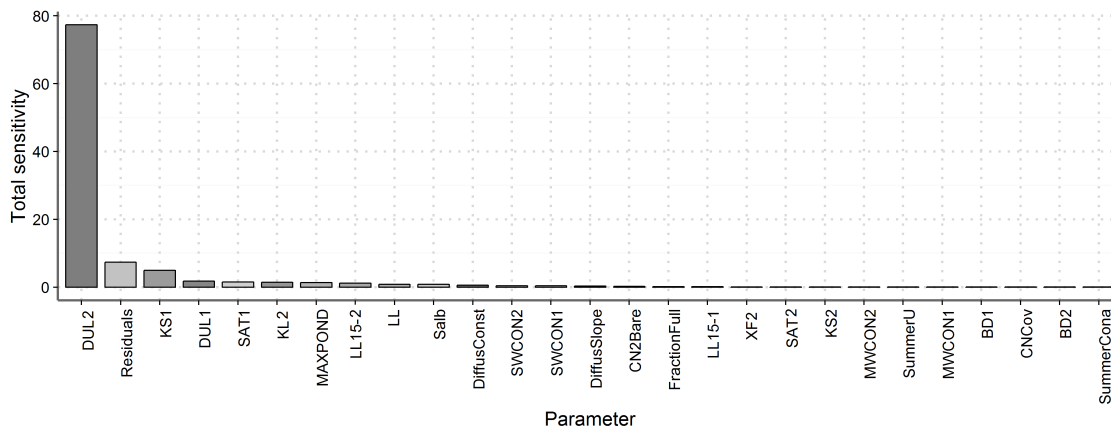


Figure 3.3: Result of sensitivity analysis on the mean of soil water content. Numbers next to the variables represent the soil layer for the tested parameter.

result of the sensitivity analysis is only valid for this study; hence no inference should be extended to other soils, crops, or weather environments. However, it is highly likely that, for example, any simulation that involves soil water content will find DUL as a very sensitive parameter.

## Optimization

The Bayesian approach enabled us not only to use prior information and different sources of data for parameter estimation, but also supported quantification of the model output uncertainty (Wallach et al., 2014). Thus, using the optimization process in this study, both the marginal posterior distribution of selected parameters and the uncertainty of the simulated soil moisture due to parameter uncertainty were estimated. Uncertainty of the model inputs may arise from several sources of uncertainty, including temporal and spatial variability in the nature of the process, measurement error, or model deficiencies.

Given that marginal densities do not reveal correlations among parameters and make the uncertainties appear larger compared to when joint distributions are investigated; the posterior densities need to be carefully interpreted. In this study, the marginal density of all parameters exhibited low to moderate uncertainty (about 5-40%) around their medians, confirming that all contributed to the model fit. Some level of association was also observed among  $K_s1$ , SAT1, and MaxPond in both

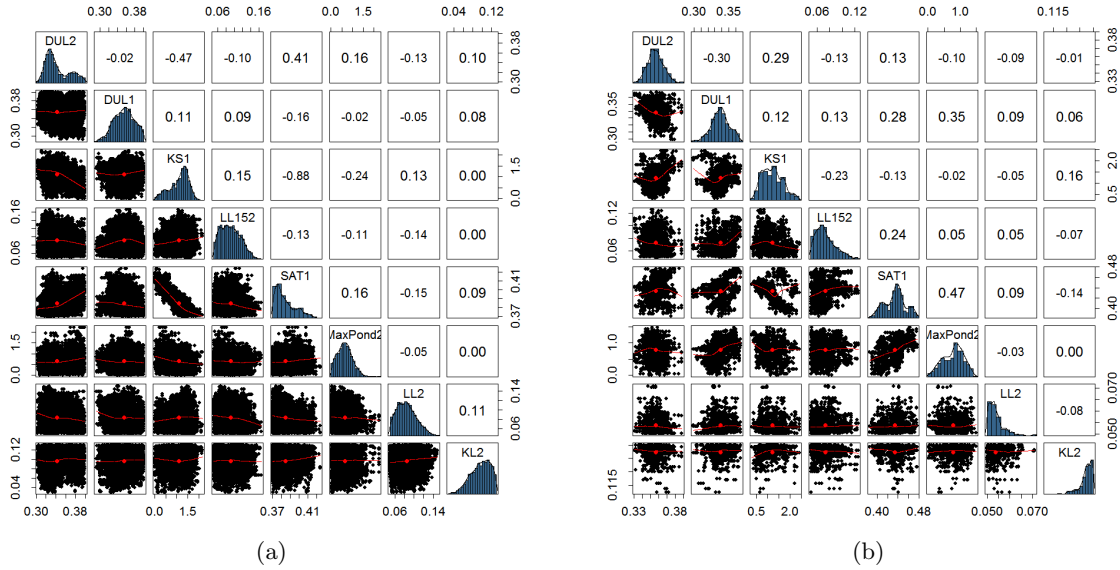


Figure 3.4: Scatterplot matrices of the posterior distribution of parameters for no-biochar (on the left) and biochar treatment (on the right). In this plot the diagonal shows the histogram for each parameter while in the upper diagonal the paired correlations are presented. In the lower diagonal, a bi-variate plot is shown for each of the parameter combinations.

treatments resulting in larger variability compared to other parameters. The medians of DUL2 and DUL1 for the biochar treatment were found to be approximately  $0.35$  and  $0.34 \text{ m}^3 \text{ m}^{-3}$  respectively, while these values were  $0.32$  and  $0.35$  for the no-biochar control (Fig. 3.4). This suggests that, in the current study, biochar application resulted, on average, in about 10% increase in water-holding capacity assuming no change in lower limit (PWP) for water uptake. The estimated increase in water holding capacity in this study is lower than 27 to 35 % increase found by Abel et al. (2013) and 20 to 50% increase found by Liu et al. (2012). Those experiments were conducted in the field on a sandy soil and loamy-sand texture respectively with biochar application ranging from 5 to 30  $\text{Mg ha}^{-1}$ . Streubel et al. (2011) also found a range of 5-35% increase in water holding capacity for combinations of five different soil types with 4 different biochar sources in an incubation study. This increase is possibly linked to a change in the total number of pores, pore size distribution (PSD), or changes in soil surface area (Dokoohaki et al., 2017).

Predicted saturated hydraulic conductivity ( $K_s1$ ) was insensitive to the biochar/no-biochar treatments. The first quantile (Q1) of  $K_s1$  for no-biochar controls is 0.6 and the third quantile (Q3) is 1.3 ( $\text{m day}^{-1}$ ). For the biochar treatment, Q1 is also 0.6 while Q3 is 1.2 ( $\text{m day}^{-1}$ ), which is not a highly meaningful difference between treatments. The biochar treatment exhibited greater SAT1 with a median of  $0.42 \text{ m}^3 \text{ m}^{-3}$  compared to the no-biochar treatment with a median of  $0.39 \text{ m}^3 \text{ m}^{-3}$ . The lower SAT found in the no-biochar treatment could be associated with a reduction in soil porosity due to settlement after a long series of intensive wetting and drying cycles (Dokoohaki et al., 2017). In contrast, we speculate that, the biochar treatment reduced the number of macro pores and increased aggregate stability because of higher organic carbon content and that this resulted in less soil settling and compaction and less reduction in total porosity and hence higher SAT. Since the saturated water content is highly related to the soil porosity and given the greater SAT in the biochar treatment, we can speculate that biochar application resulted in a slight increase in porosity which could lead to significant improvements in root growth and water uptake (Laird et al., 2010b; Lei and Zhang, 2013; Sun and Lu, 2014; Devereux et al., 2012; Jones et al., 2010).

The maximum rate of water uptake by plants (KL) usually happens when there is a maximum demand (high VPD) from the atmosphere but it is also limited by the capacity of the soil to supply this demand. Therefore, KL as well as LL incorporate both plant and soil factors to define the water uptake capacity in the APSIM model. The KL and LL values found in this study indicated a higher capacity of the crop for water uptake in the biochar treatments relative to the controls. Higher KL and lower LL found for the biochar treatment is consistent with an increase in the soil water-holding capacity (capacity to supply the water demand) and our speculation about an increase in total porosity and root growth. Not including these parameters in the simulation of soil water content would not allow us to capture the different rates of water uptake by the biochar and no-biochar treatments. In addition, given the fact that the APSIM model was able to estimate the yield for both years within a plausible range of observed values ( $12.5 \pm 0.65 \text{ Mg ha}^{-1}$  in 2013 and  $8.6 \pm 0.4 \text{ Mg ha}^{-1}$  in 2014), we expect that transpiration/water uptake by the crop was also

estimated (it was not measured) in a reasonable range because the approach in APSIM typically results in tightly linked yield, biomass and transpiration simulated values.

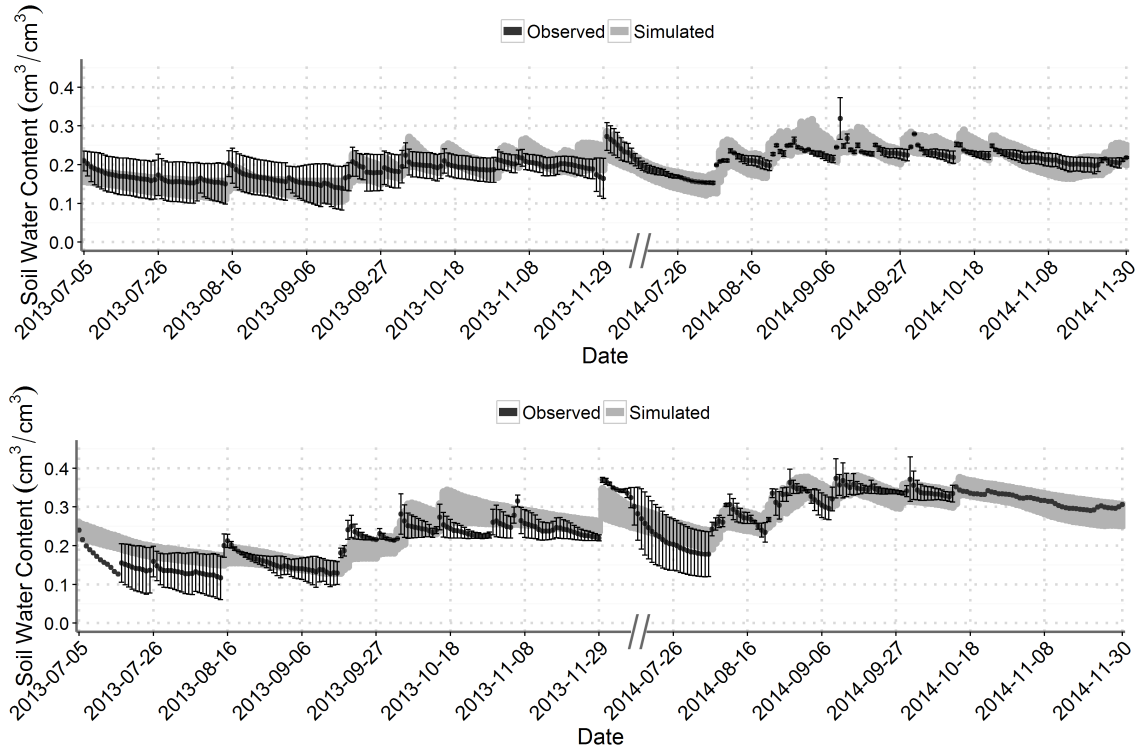


Figure 3.5: Mean and standard error estimated for soil water content observed and simulated for both biochar (bottom) and no-biochar (top) treatments.

The uncertainty band estimated for soil moisture using the posterior distribution of parameters falls within the error bars of the observations for both treatments. This shows that the samples generated from the posterior distributions produced plausible values for soil moisture. The mean RMSE between simulated and observed soil moisture was  $0.025 \text{ (cm}^3 \text{ cm}^{-3}\text{)}$  for the no-biochar treatment and  $0.032 \text{ (cm}^3 \text{ cm}^{-3}\text{)}$  for the biochar treatment. In a similar study, Scharnagl et al. (2011) used inverse modeling for estimation of soil hydraulic parameters using the HYDRUS-1D model. Simulations of soil moisture in a bare soil, resulted in a RMSE of  $0.009 \text{ (cm}^3 \text{ cm}^{-3}\text{)}$ . In another study, Houska et al. (2014) used a Monte Carlo-based GLUE method for optimization of their new coupled catchment model. In their study, simulations of top 30 cm soil moisture resulted in a RMSE of approximately  $0.024 \text{ (cm}^3 \text{ cm}^{-3}\text{)}$ .

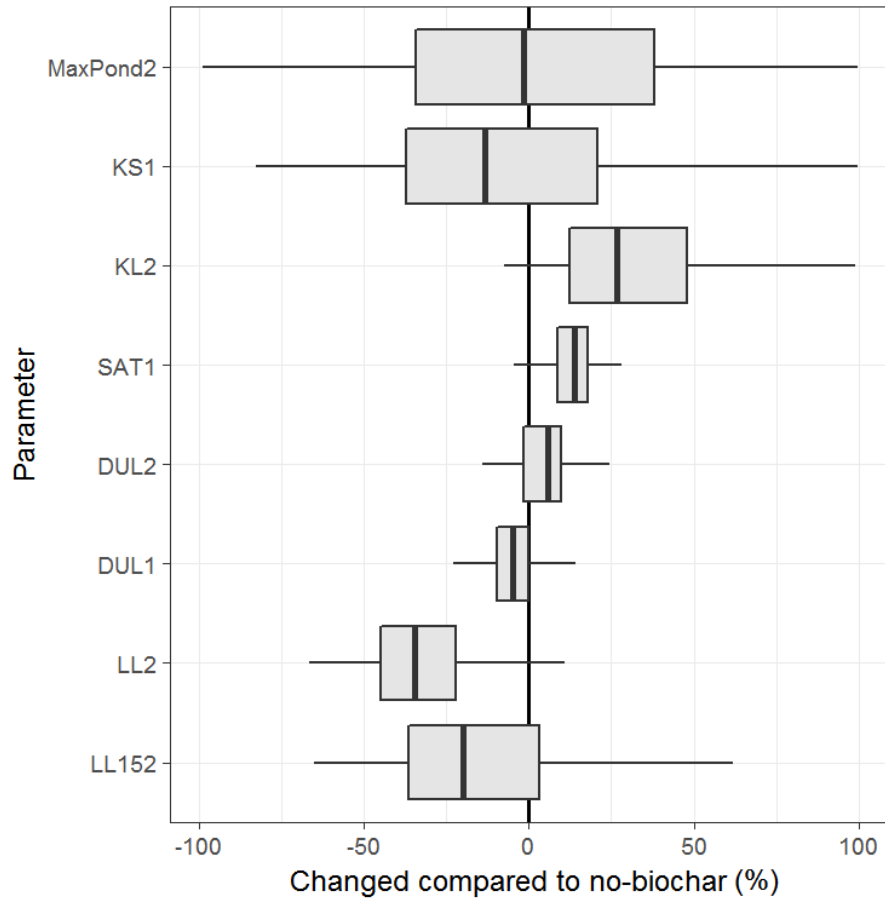


Figure 3.6: Comparison between the posterior distribution of soil hydrological parameters for biochar and no-biochar treatments. The Y-axis shows the different parameters and the X-axis indicates the corresponding distribution (boxplot) for that parameter.

Overall, results of the parameter estimation for both years show trends in agreement with expected effects on soil physical properties of application of biochar (Fig. 3.6). The biochar treated plots showed an increase in DUL (field capacity) and SAT in the amended soil layer compared to the no biochar treatment. On the other hand, no significant change to slight decrease (compared to margin of error of the parameter estimate) was found on the median value of LL15-2,  $K_s$  and MaxPond. Furthermore, the higher water uptake capacity observed in the soil moisture measurements (Fig. 2.2) was also reflected in the higher KL and lower LL values for the biochar treatment relative to the control. Direct field measurements of complex variables such as plant water uptake requires

an expensive and usually time-consuming approach such as lysimeters or frequent destructive plant sampling. However, inverse modeling using APSIM offered a more convenient approach and helped us to convert soil water content measurements into a set of hydrological parameters, which show the effect of the biochar treatment. These types of modeling exercises enabled us to extend our understanding of new management practices like biochar application beyond lab and incubation studies. The accuracy of estimated soil properties obtained using inverse modeling is highly dependent on the accuracy of the measurements and the spatial variation of soil water content within the field.

## Conclusion

We provided evidence that biochar application resulted in improved soil physical properties in continuous maize plots under field conditions for over two years. An increase was found in DUL and KL along with a slight increase in SAT which can be attributed to the biochar treatment while no significant change in LL15,  $K_s$  and MAXPOND was observed. Increase in the capacity of the soil for holding water resulted in higher water uptake with lower LL for the biochar treatment. A key novel component in this study was the integration of field-level measurements with a modeling component for estimation of more realistic soil properties as a result of biochar application.

## Acknowledgment

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## CHAPTER 4. WHERE SHOULD WE APPLY BIOCHAR?

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This manuscript is under review in environmental research letters journal.

Biochar is a low-density organic by-product of thermochemical conversion of biomass that is being evaluated as a soil amendment. Biochar can be used to sequester carbon in soil and also has the potential to boost crop yields when it is used to improve yield-limiting soil properties. However, because of the complex interactions among biochars, soils, crops and climate there is no clear understanding of its agronomic potential. These complex interactions have made it challenging to answer the question of where biochar should be applied for the maximum agronomic and economic benefit. We addressed this challenge by developing an extensive informatics workflow for processing and analyzing crop yield response data as well as a large spatial-scale modeling platform. We used a probabilistic graphical model to study the relationships between soil and biochar variables and predict the probability of crop yield response to biochar application. Our Bayesian network model was trained using the data collected from 103 published studies reporting yield response to biochar. Our results showed an average 12% increase in crop yield from all the studies with a large variability ranging from -24.4% to 98%. Soil clay content, pH, cation exchange capacity and organic carbon appeared to be strong predictors of crop yield response to biochar. We also found that biochar carbon, nitrogen content and highest pyrolysis temperature significantly influence the yield response to biochar. Our large spatial-scale modeling revealed that 8.4% to 30% of all U.S. cropland can be targeted and is expected to show a positive yield response to biochar application. It was found that biochar application to areas with high probability of crop yield response in the U.S could offset a maximum of 2% of the current global anthropogenic carbon emissions per year.

## Introduction

Biochar is a carbon rich soil amendment produced from biomass by a thermochemical process, pyrolysis or gasification. Soil biochar applications have generated a great deal of interest as a strategy for mitigating climate change by sequestering carbon in soils, and simultaneously as a strategy for enhancing global food security (Crane-Droesch et al., 2013; Paustian et al., 2016; Laird, 2008b; Woolf et al., 2010) by increasing crop yields especially on degraded and poor quality soils (Lehmann and Joseph, 2015). There is evidence that the recalcitrant C in biochar has a significantly greater residence time compared to C in uncharred plant biomass (Fidel et al., 2017; Woolf et al., 2010) suggesting that biochar application is a possible avenue for drawing down carbon from atmosphere and stabilizing it in the soil (Lehmann et al., 2007; Crane-Droesch et al., 2013). The alkalinity of biochar, its high internal porosity (Dokoohaki et al., 2017b), and capacity to absorb cations (high cation exchange capacity) can increase soil nutrient and water holding capacity (Basso et al., 2013; Cheng et al., 2006) without compromising soil conservation goals (Woolf et al., 2010). This can lead to increases in crop yields in less fertile and degraded soils which often coincidence with high rural poverty (Crane-Droesch et al., 2013; Woolf et al., 2010). However, the ability of biochar to sequester carbon and alleviate soil limitations depends on biochar's properties, which are influenced by properties of the feedstock used to produce the biochar and by production technology (pyrolysis/gasification technologies) (Laird et al., 2009; Fidel et al., 2017).

While there is no or little incentive for farmers to adopt most climate change mitigation practices, the potential yield increase following biochar application has made it a promising new climate mitigation strategy. However, the degree of adoption of biochar technology is closely tied to the farmer's costs and benefits (Crane-Droesch et al., 2013) hence, in the absence of a C credit market, crop yield increase is the primary factor determining the economic viability of biochar applications (Laird et al., 2017; Laird, 2008a). Thus, the ability to accurately predict crop yield response to biochar applications is critical to the development of a viable biochar industry and to the design of incentive programs to enhance biochar adoption and C sequestration.

**Why is the estimation of yield response to biochar a challenging task?** Crop yield responses to soil biochar applications is highly variable (Fidel et al., 2017; Verheijen et al., 2010; Rajkovich, 2010; Van Zwieten et al., 2010) and the yield responses in quantitative reviews have ranged from negative to positive due, in part, to variations in soil properties, biochar properties, and complex soil  $\times$  crop  $\times$  biochar  $\times$  climate  $\times$  management interactions (Fidel et al., 2017; Biederman and Harpole, 2013; Jeffery et al., 2015). Based on 507 field study yield differences, only 25% showed a significantly negative or positive biochar effect (21.6% positive and 3.5% negative) and the rest were not significant (Fidel et al., 2017). Biederman and Harpole (2013) also reported a minor increase in crop productivity and yield with considerable variability. Jeffery et al. (2015) found that, overall, there was a small but statistically significant increase in crop productivity (either grain or biomass) from both pot and field experiments. The key finding of their study was the large variability (from -28% to 39%) found in response to biochar. This large range varied from killing the crop to cases where the crop would fail to grow without biochar applications.

The complex nature of biochar interactions with soils and crops and lack of clear understanding of interactions (Atkinson et al., 2010; Sohi et al., 2009) has led to reports with conflicting interpretations, even under similar conditions (Jeffery et al., 2015). In addition, the large amount of missing data in the literature (Spokas et al., 2012) including inconsistent reporting of soil and biochar properties (Jeffery et al., 2015) has made the prediction of crop yield response to biochar a very challenging modeling exercise (Crane-Droesch et al., 2013).

In this study, we addressed the challenge of predicting crop yield responses to biochar applications by developing an extensive informatics platform for collecting, preprocessing and analyzing data and large-scale spatial modeling. Several statistical procedures and informatics technologies were integrated to facilitate the interpretation and modeling of crop yield responses to biochar. We used probabilistic graphical models in our platform to study the causal relationships among different soil and biochar variables and model the yield response at a large spatial scale. These models are inherently capable of handling missing data (Chawla et al., 2016) and accounting for uncertainty associated with observations (Chen and Pollino, 2012; Zhu et al., 2013). In this plat-

form, we combined expert knowledge (for better defining the relationship among the variables) and data (for estimating the parameters of the model) to deal with the complexity of our problem.

Probabilistic graphical models are commonly used in cases with incomplete datasets (Bressan et al., 2009) and high uncertainty (Aguilera et al., 2011) which makes them a suitable candidate for the current status of biochar science. Building this platform using most of the peer-reviewed data available today will allow us to refine our understanding of biochar interactions with crops and soils. Furthermore, our platform can help us make large scale predictions of regional average crop response to different types of biochar. Our main goal was to identify areas with high probability of crop yield response to biochar applications in the United States. We believe our results can significantly advance the science of biochar use in agriculture by identifying highly responsive areas and the reasons these regions are responsive and the practice of using biochar by lowering uncertainty around crop yield response to biochar applications. Our output also allows us to identify the regions in the United States where farmers are most likely to benefit economically from applying biochar. Therefore, our main objectives were:

- First, we want to understand the relationships between soil and biochar properties associated with crop yield increase following biochar application.
- Second, we identify regions with the highest probability of positive crop yield response following biochar application in the United States.

## Methods

### Data collection

We built our database on top of the raw data previously collected from a meta-analysis study conducted by Crane-Droesch et al. (2013). The original dataset which has more than 40 studies (published up to 2013) was filtered and 17 relevant variables and 685 observations were selected. New peer-reviewed studies were found using academic search engines (Google Scholar, Web of Science) and the same variables were extracted and added to the database. Among all studies,

publications which examined the effect of biochar application on crop production (grain/biomass) were selected. We did not include studies or observations in the database if either biochar application rate or grain/biomass yield data were missing. In total, from the 63 new studies which met our criteria, 575 more observations were added to the database.

Given that absolute yield is not readily comparable among studies, Crane-Droesch et al. (2013) used the Response Ratio (RR) as the target variable. The RR is defined as:

$$RR = \ln \left( \frac{Yield_{Biochar}}{Yield_{control}} \right) \quad (4.1)$$

A positive RR indicates a positive yield response to biochar application, whereas a RR of 0 shows no change from control treatment. This variable also can be easily transformed back to Relative Increase (RI) using:

$$RI = (e^{RR-1}) \times 100 \quad (4.2)$$

Soil Organic Carbon (SOC), sand, silt, clay content, CEC and soil pH were extracted from all studies to describe both chemical and physical properties of soil. Biochar carbon, nitrogen, ash content, pH, C:N ratio, highest pyrolysis temperature, feedstock and thermochemical process were also variables extracted to account for both the feedstock properties and pyrolysis process in assessing biochar type. Biochar feedstock was classified into woody, non-woody and manure, while pyrolysis type was characterized as fast and slow.

Along with soil and biochar properties, latitude, N content and biochar application rates were incorporated into our model in order to predict the RR, the target variable. As stated in Crane-Droesch et al. (2013), many key drivers of crop yields (e.g. soil N) particularly soil nutrient levels are not included in the database, because nutrient availability does not perfectly correlate with total nutrient content in the soil given spatially heterogeneous soil chemistry. Therefore, we expect to observe a smaller variability in the model estimates of RR compared to the observed RR.

## Model Development

A Bayesian belief Network (BN) was used for modeling the yield response to biochar applications. BN models usually are made of qualitative and quantitative components. The qualitative component is a graphical model which represents how the variables are statistically dependent on each other; nodes indicate variables and arcs show dependencies. The quantitative component is the conditional probability distribution of a node  $x_i$  (specified in the graphical model) on its parents  $pa(x_i)$ . Taking into account the conditional independence assumption (Markov condition), the joint distribution over all the variables  $x_i, i = 1, \dots, n$  is equal to (Zhu et al., 2013):

$$p(x_1, \dots, x_n) = \prod_{i=1}^n p(x_i | pa(x_i)) \quad (4.3)$$

Which is the product of conditional distributions defined for each variable.

When new evidence is introduced, it propagates through the BN and the posterior probabilities are computed. This is called an inference and it allows for detecting the change in the probabilities of some variables given a value for other variables (Aguilera et al., 2011).

In the current study, a hybrid BN model (a model that includes both discrete and continuous variables) was developed within the R environment (R Core Team, 2017) and by using the Bayes Server software (Bayes Server, 2017). The final design of the model's structure resulted in 84 parameters. The heterogeneity among crop species and other key drivers of yield that are not included in the model, convinced us to use the probability of yield increase  $P(RR > 0)$  instead of directly using estimated mean of RR; this inherently accounts for the variability around the average estimate of RR. Thereby, the estimated mean and variance were used to estimate  $P(RR > 0)$  and identify places with high probability of yield increase.

We setup a repeated cross validation procedure with 250 iterations for training and testing our BN. In each iteration, the model was trained with 80% of the observations in the dataset and tested against the remaining 20% of observations. Predictions made by the BN were then compared with the statistical model developed by Crane-Droesch et al. (2013). Model Efficiency (EF) and Mean Absolute Difference (MAD) were used to compare the performance of these models as follows:



$$EF = 1 - \frac{\sum(Y_m - Y_O)^2}{\sum(Y_O - \bar{Y}_O)^2} \quad (4.4)$$

$$MAD = \frac{|Y_m - Y_O|}{n} \quad (4.5)$$

Where,  $Y_m$  is modeled,  $Y_O$  is observed,  $\bar{Y}_O$  is the mean of the observed and  $n$  is the number of the observations. EF varies between  $-\infty$  to 1; EF=1 represent the perfect match between modeled and observed data, whereas EF<0 indicates an unsatisfactory model performance.

The final BN model was then projected onto all cultivated lands in the U.S. (based on Cropland Data Layer (CDL) 2016 with 30m×30m resolution (Boryan et al., 2011)) using the gSSURGO soil database for 5 predefined biochar types and 2 application rates (5 and 15 Mg ha<sup>-1</sup>). The gSSURGO database provides a wide range of soil properties in 10m×10m resolution including all the variables required for our model (Chaney et al., 2014). A pixel in the map is considered cultivated if it is identified as cultivated in at least two out of the five years of CDL data. The gSSURGO database includes the heterogeneity of soil properties (as different compartments) for each pixel. In the current study, the most representative soil type was used to extract the basic soil properties. Biochar properties were produced from common biomass feedstock materials such as corn (C), soybean (S), switchgrass (G) and hardwood (W) using both fast (F) and slow (S) pyrolysis engineering (hereafter designated as CS, CF, GS, SF and WS). Details on biochars properties can be found in Table 4.1.

Table 4.1: Chemical properties of biochars as well as pyrolysis engineering used for suitability analysis in this study. HPT: Highest Pyrolysis Temperature

#	pH	C (%)	N (%)	HPT (°C)	Ash (%)	CN (Molar)
GS	9.9	71	0.88	500	15.2	94.1
CS	9.9	69.8	1.25	500	9.1	65.4
CF	8.4	52.4	0.46	500	37	134.4
SF	9.3	53.1	0.63	500	56.9	98.3
WS	7	77.6	0.53	500	7	169.2

## Results

### Analyzing the literature data

The estimated average Response Ratio (RR) to biochar showed a 12% increase for all studies in our database. A large variability in RR was also observed, ranging from -24.4% to 98%, with the Inter Quartile Range (IQR) ranging from 0 to 21% (Fig 4.1). Among all soil properties, clay content, soil organic carbon, pH and CEC showed a significant negative correlation with RR, while sand and silt content were positively correlated with RR.

Yield response was not affected by with nitrogen application rate, biochar ash content and biochar pH. The highest pyrolysis temperature, biochar N and C:N showed a significant negative correlation to RR, and higher biochar C content was significantly correlated with higher RR (Fig. 4.1). A linear model analysis revealed a minor (not significant) association between feedstock and crop type with RR while no direct association was found between thermochemical technology and RR.

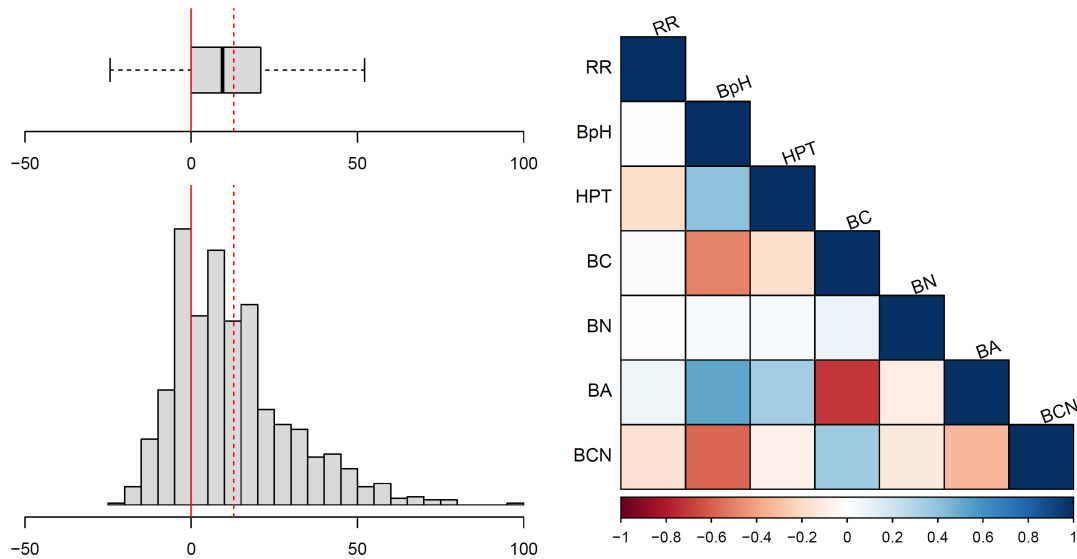


Figure 4.1: Estimated histogram of RR (on the left); the dotted red line is the mean and the solid red line is the threshold for no yield response to biochar application. Correlation matrix plot for RR with biochar properties (on the right); BpH: Biochar pH, HPT: Highest pyrolysis temperature, BC: Biochar Carbon, BN: Biochar Nitrogen, BA: Biochar Ash, BCN: Biochar C:N

## Large-spatial scale modeling

We compared our Bayesian Network (BN) model and the only available statistical model for explaining the heterogeneity in yield response to soil and biochar properties. Crane-Droesch et al., (2013) used a generalized additive model (GAM) with 162 parameters to develop smooth functions mapping of independent variables to RR. In more than 250 iterations, only based on predictions the BN model consistently outperformed the GAM; as the BN model average Model Efficiency (EF) and Mean Absolute Difference (MAD) values were 0.23 and 0.10, respectively, compared to -1.96 and 0.18 for the GAM. Negative EF implies that the observed mean is a better predictor than the model; and the positive average EF proves the merit of the BN and indicates that it can be used to explore different scenarios of soil and biochar properties within the scope of the training dataset. Given the proficiency of the BN model, spatially explicit analysis of response to biochar was explored for cropland in the U.S. under different biochar scenarios. Fig 4.2 shows the estimated probability of yield increase for hardwood biochar and 15 Mg ha<sup>-1</sup> application rate scenarios.

Regions known to have a high soil quality (e.g. Des Moines lobe in north central Iowa) showed a low probability of having a yield increase under all biochar scenarios. Our model indicates a high chance of a positive RR in areas with highly weathered soils (e.g. Eastern half of San Joaquin valley). Yield response was predicted to be most negative in areas with very high SOC, CEC or soil pH such as those found in north Texas and Minnesota (Fig. 4.2).

We estimated the total area where a 75% (or higher) probability of yield increase is expected for each scenario as well as areas where this is expected to be lower than 25% (Fig. .1). This helped us identify the most and least responsive regions to biochar applications across the U.S. Total high probability areas for biochar application range from 8.4% to 30% of total cropland in the U.S. The WS15 was the scenario with the largest high probability area with 39.7 Mha, whereas SF5 (SF5 represent 5 Mg ha<sup>-1</sup> application of SF biochar) resulted in the lowest high probability area with 11.2 Mha. In general, for similar application rates, biochar produced from hardwood and corn stover resulted in larger responsive areas than switchgrass, while fast pyrolysis soybean biochar showed the lowest response. In low quality soils, the higher application rate (15 Mg ha<sup>-1</sup>)

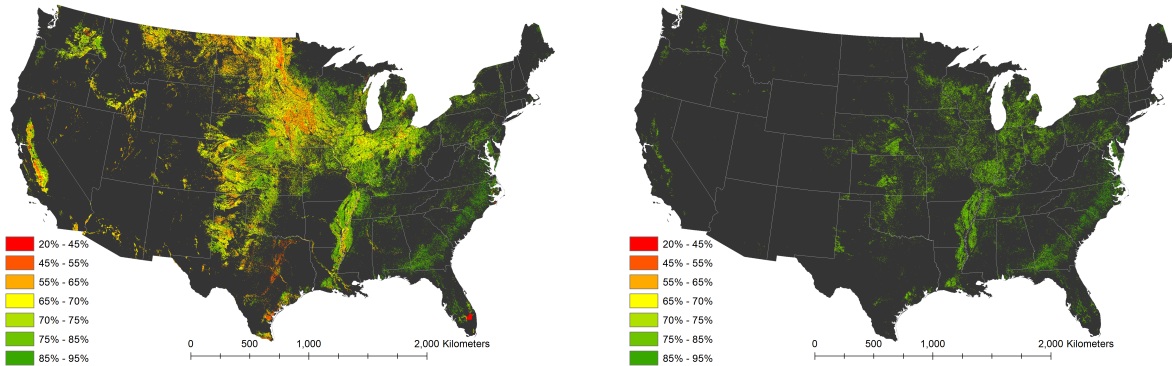


Figure 4.2: Estimated probability of yield increase for WS15 (left). Areas with more than 75% chance of yield increase for WS15 (right). WS15 represent the 15 Mg ha<sup>-1</sup> application of WS biochar.

resulted in a higher probability of a yield increase, whereas high quality soils showed no response to application rate.

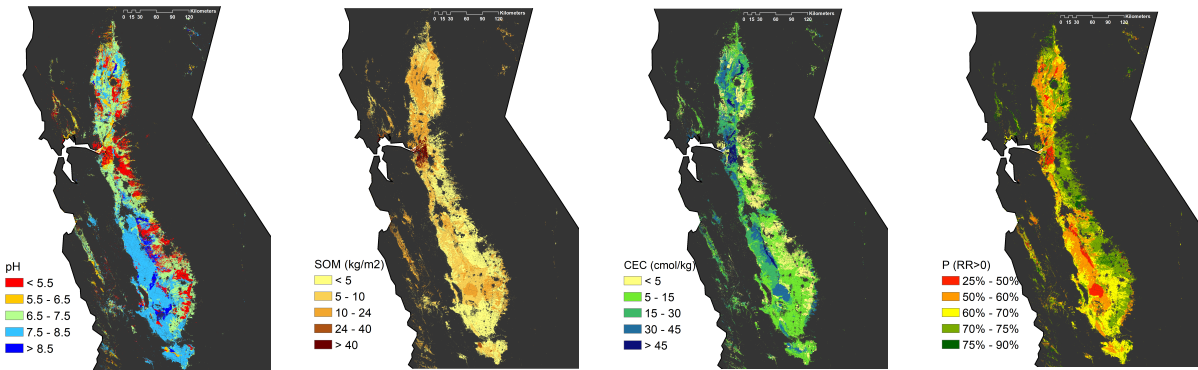


Figure 4.3: Spatial variation of soil properties and probability of a yield increase for WS15 scenario in the Central valley of California. SOM: Soil Organic Matter; CEC: Cation Exchange Capacity; P(RR>0):Probability of finding positive yield response to biochar application.

We selected the Central Valley of California to assess the model’s response to different soil properties under the CS15 scenario. The Central Valley is an agricultural region drained by the Sacramento and San Joaquin rivers, about 82 km wide, and it extends 600 km northwest from the Tehachapi Mountains to Redding. The southern part of the valley, also known as San Joaquin valley, is well-known for having highly variable alluvial soils ranging from very acidic-low organic

matter soils to very alkaline-high organic matter soils. The BN model successfully captured the essence of our general understanding of crop yield response to biochar on high and low-quality soils. Yield response was the weakest in west side of the San Joaquin valley, which is dominated by soils with high clay, pH, CEC and organic matter (Fig. 4.3). On the other hand, the old, highly weathered soils on the east side of the valley, which have low organic matter, CEC and pH, showed the greatest response to biochar applications. The model's response was not attributed to just one variable, as all soil properties contributed to the estimation of yield response (Fig. 4.3). The total area with high probability of yield response to biochar application varied from 0.01 Mg ha<sup>-1</sup> for SF5 to 0.6 Mg ha<sup>-1</sup> for WS15, which is approximately 1% and 15% of total cropland in the Central Valley, respectively.

## Discussion

In contrast to other researchers (Jeffery et al., 2015; Sohi et al., 2009), who found the greatest effect of biochar on coarse texture soils with an average 10% increase in yield, we did not find significant correlation between RR and sand content, hence our results are similar to those in the original database (Crane-Droesch et al., 2013). Our results indicate a negative correlation with clay, SOC, soil pH and CEC, meaning that the soils with lower the value of any of these soil properties, the higher the probability of yield increase after biochar application. This is expected, for example, as the pH of an acidic soil will rise following biochar application likely resulting in increased microbial activity (Warnock et al., 2007; Spokas et al., 2012), increased nutrient availability (Major et al., 2010; Biederman and Harpole, 2013) and reduced mobility of toxic elements (Hass et al., 2012). As another example, biochar has a high capacity to retain nutrients and water and therefore there is a higher probability that biochar will help increase nutrient and water availability to crops grown in soils with low activity clays.

In contrast to the findings of Biederman and Harpole (2013) and Crane-Droesch et al. (2013), we found evidence suggesting that RR is influenced by biochar properties such as C, N content, and C:N. Highest pyrolysis temperature (HPT) was closely associated with biochar C and C:N

showing a negative correlation with RR, meaning that the lower the HPT the higher the C content in biochar and the higher the probability of a yield increase.

It was found that SF resulted in less suitable area with a high probability of a positive response to biochar regardless of application rate, compared to other types of biochar. The reason for this difference in performance of biochars lies either in feedstock material or thermochemical process. Given that the model is only weakly sensitive to biochar ash content, the lower C content of the SF may have been the dominant factor influencing the small crop yield response to the SF biochar. The large portion of carbon content in GS, CS and WS, which is in more labile form, may have induced more C mineralization, which should also result in an increase in the size of the inorganic nitrogen pool. Given that no additional N fertilizer was assumed to accompany biochar applications in our simulations, the relative sizes of the labile C pool in the biochar and the inorganic N pool in the soil are critical factors influencing N availability to crops and may cause large differences in crop yields for different types of biochar. The large variation in measured crop yield responses (Fidel et al., 2017; Biederman and Harpole, 2013; Jeffery et al., 2015) and the probability of crop yield responses predicted by our model for different scenarios shows the importance of optimizing the selection of specific biochar types, application rates and management for achieving high probability of a positive crop yield increase.

Examining the model's behavior revealed that crop yield response to biochar was dominated by soil properties and that increases in biochar application rate resulted in higher probability of crop yield increases for soils with lower quality. The increase in probability is not sufficient to compensate for the additional cost of the higher application rate. In soils with  $PP < 0.25$  (mostly high quality soils) there was no direct association between biochar application rate and crop yield response. Biederman and Harpole (2013) and Jeffery et al. (2015) also found no clear relationship between productivity and application rate although they did not differentiate based on soil quality.

Crop yields are strongly influenced by weather during the growing season and yield responses to biochar applications are expected to be strongly influenced by complex weather  $\times$  biochar  $\times$  soil  $\times$  crop  $\times$  management interactions. Therefore, the estimated yield increases, as a result of biochar

application, predicted by our model are long-term (5-10 years) averages, which are attributed to improvements in soil physical and chemical properties.

The BN developed in this study is computationally fast and accurate enough to be used for large scale modeling, nonetheless, our results have several caveats. For example, our understanding suggests that various management practices (such as residue removal, increases in N fertilization rates, etc.), soil properties (such as inorganic N available in the soil) and biochar properties (such as the size of labile C and N pools) are potential drivers of crop yield responses that are not specifically defined in the model. Adequate data is currently unavailable in the literature to cover all possible soil-biochar interactions, and therefore the model focuses on available information. Therefore, the inference domain of the model's output is limited to the extent of the training dataset however, our model paves the way for the use more computationally intensive process-based crop models by identifying regions, soil types, and biochar types with high and low probability of crop yield response.

The average technical potential of biochar for removing greenhouse gas (GHG) from the atmosphere is estimated between 0.2 to 0.8  $\text{CO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$  depending on soil and biochar properties (Paustian et al., 2016). Therefore, we estimate that the net reduction in GHG emissions due to biochar applications on soils with a high probability of a crop yield response in the U.S to vary between 0.002 to 0.3  $\text{Pg CO}_2 \text{ (eq) yr}^{-1}$  depending on type of biochar. This results in an estimated 2% reduction in the current global anthropogenic  $\text{CO}_2\text{-C}$  (16  $\text{Pg CO}_2 \text{ (eq) yr}^{-1}$ ) emissions, attainable with the corresponding synergistic crop yield benefits in the U.S. By contrast, Woolf et al. (2010) estimated 12% to be the maximum potential of biochar to offset anthropogenic  $\text{CO}_2\text{-C}$  by applying biochar to all crop lands in the world. Policies that incentivize biochar applications will be necessary for biochar to achieve its full potential as a strategy to reduce GHG emissions.

## Acknowledgments

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## CHAPTER 5. LONG TERM IMPACT OF BIOCHAR ON CROP YIELD, SOIL ORGANIC CARBON AND NITRATE LEACHING: FOCUS ON LEAST PRODUCTIVE SOILS AND LARGE SPATIAL SCALE

Hamze Dokoohaki, Fernando E Miguez, Sotirios Archontoulis, David Laird

This manuscript is in preparation.

We developed regional scale simulations of biochar effects on crop yield and nitrate leaching using APSIM model for parts of Iowa and California. Three main pieces of work were integrated in this study. The suitable areas found for biochar application in the previous chapter in both states, the biochar module in the APSIM model and a new developed algorithm for speeding up large spatial scale simulations. This allowed us to simulate 30 years of biochar effects on soil and crop for corn-corn cropping system in Iowa and alfalfa in California starting in 1980 to 2016. Model outputs were aggregated at a climate division level and the effect of biochar was estimated as the percent change relative to no biochar. In this study the APSIM model suggested an insignificant change in crop productivity (yield/biomass) following biochar application with a more substantial effect on nitrate leaching depending on weather conditions. It was found that in wet years (where palmer drought index is less than 3) there is a reduction in nitrate leaching along with an increase in crop yield suggesting more mineral nitrogen being available for the crop. It was found that the biochar effect lasted almost for the entire 30 years of simulation period while biochar application allowed sustainable harvest of the crop residue without losing yield or increasing nitrate leaching. During the simulation period biochar acted as a source of carbon which consistently helped to increase the mineral nitrogen pool through mineralization and relieving nitrogen stress.

### Introduction

Biochar is a low-density organic matter product recently used as a soil amendment, and its application has been adopted as a new management practice with the aim of enhancing both soil

quality and crop production (Lehmann et al., 2003; Steiner et al., 2008). Biochar offers benefits with respect to soil/water quality and it can last longer in the soil compared to organic matter. Moreover, given the high surface area, small particle size, and charge density on the biochar surface, it can enable increase retention of water and nutrients in the soil, resulting in additional agronomic benefits (Lehmann et al., 2011; Dokoohaki et al., 2017a). However, the capacity of biochar to improve physical and chemical properties of soil highly depends on biochar's properties, which are influenced by parent material (known as feedstock) and pyrolysis.

The variability of biochar due to different production engineering techniques and feedstock, soil types and crops, raises concerns and questions for both farmers and policy makers (Major et al., 2010; Ahmad et al., 2012). How long does the effect of biochar last? What regions are more likely to receive the highest agronomic return from biochar application? And, in what years or weather conditions does biochar provide the most benefit? Thus, understanding the implications of large scale biochar application on crop yield and environmental outcomes can greatly advance the efficiency of biochar use and its financial return due to improved resource management.

The knowledge gained from past studies about biochar has been mainly restricted to short-term lab and field experiments. However, short-term experiments are limited in identifying key underlying mechanisms that cause long-term variability in response to biochar due to variability in climate. Moreover, these studies are limited by the scale of experimentation and they are not well suited to explore the impacts of biochar application for large spatial extents.

Process-based crop models are currently recognized as effective tools for assessing different management strategies (Dokoohaki et al., 2017b; Basche et al., 2016) at both the field and regional scales. They not only help researchers to refine their understanding of different agro-ecosystem components, but also help policy makers and farmers explore management options at both the farm-level and regional scales. Such models capture the effects of different practices on soil dynamics and the interactions with crop physiological processes (Holzworth et al., 2014). APSIM (Agricultural Production Systems sIMulator) is a model that provides a fully-tested framework with a flexible

structure that is capable of simulating interactions among weather, soils, crops, and previously known management systems (Keating et al., 2003).

In one of the first efforts at modeling the effects of biochar on soils, Lychuk et al. (2015) incorporated the effects of biochar in the EPIC model (Environmental Policy Integrated Climate) by developing an algorithm which accounted for biochar impacts on soil properties. In that algorithm, biochar directly impacts soil CEC, pH, bulk density, and organic carbon (SOC) and the dynamic interaction between SOC and biochar as well as the change in soil water dynamic and mineral nitrogen in soil. Assessment of model performance, showed a satisfactory result in reproducing field observations of biochar impacts on short-term crop yields and soil properties (Lychuk et al., 2015).

A biochar sub-model has been developed for the APSIM model with the aim of providing a dynamic process-based framework for modeling the effect of biochar on soil and crop processes (Archontoulis et al., 2016). This sub-model can simulate the decomposition of carbon in biochar and mechanistically estimate changes in soil water, bulk density, pH, CEC, and organic and mineral nitrogen. Results of the model calibration showed that it can predict soil (pH, bulk density, total carbon, and water content) and crop-related variables (corn grain yield and corn stover) with a mean relative error ranging from -0.4% to 13.1% (Archontoulis et al., 2016). The authors concluded that the model provided a clear understanding of the impact of biochar on soil physical and chemical properties.

Following recent tests of the APSIM biochar module for Central Iowa (Aller et al., 2017), here we propose applying it at a larger spatial scale and investigate the stability of biochar effects on crop productivity (yield/biomass) and nitrate leaching for different soils and climates. So far, no study has been published with focus on large-scale evaluation of biochar effects on crop yield and environmental factors using process-based simulation models. We believe that application of a sophisticated process-based crop model like APSIM would help to explain the complexity of biochar interactions with soil and climate. Therefore, the objective of this study is to estimate the long-

term impacts of biochar application on poor quality soils regarding crop yield, soil organic carbon and  $\text{NO}_3$  leaching.

## Methods

### APSIM and biochar module

The APSIM cropping systems model is a collection of sub-models (modules), with each module independently simulating one or multiple soil, crop, or management processes. This model can simulate soil processes such as water dynamics, soil temperature, and nutrient cycling (i.e. nitrogen and phosphorus cycle and availability in soils), as well as their interaction with different crops and management practices (e.g. irrigation, fertilization) (Holzworth et al., 2014). The flexible structure of the APSIM framework allows for developing complex simulations and new modules. The biochar module is a sub-model developed for the APSIM framework (Archontoulis et al., 2016) with the aim of providing dynamic processed-based simulation of the effects of biochar on soil and crop processes. This module was adopted by the APSIM committee and integrated into the official APSIM 7.9 release. The biochar module uses a two-pool exponential decay function model for estimation of daily carbon decomposition as a result of microbial activity. The first pool, the labile pool, represents the more susceptible fraction of total carbon in biochar for mineralization, while the second pool is assumed to be composed of more recalcitrant carbon (Archontoulis et al., 2016). Water, nitrogen, and temperature modifiers are also used to mediate biochar decomposition under limiting conditions. APSIM's water and temperature modifiers on the rate of Soil Organic Carbon (SOC) decomposition were used to directly limit biochar decomposition, while a new function was developed to account for the effect of nitrogen (N) limitation on biochar decomposition rate (Archontoulis et al., 2016). In this module, the net nitrogen mineralization/immobilization was estimated by making comparisons between the total amount of N required for biochar decomposition and N released during biochar decomposition, and both quantities were estimated as a function of the C:N of different soil and biochar pools.

The general idea underlying the estimation of changes in soil CEC is that, given the biochar mass fraction, this variable can be estimated by the weighted average of the biochar CEC and soil CEC. Soil CEC can also be estimated based on the percentage of clay in soil, SOC, and soil order. In addition, the buffering capacity of the soil and change in soil pH were estimated using a user-defined liming value for biochar as well as the soil CEC.

### **Large-scale simulations**

Running the APSIM model with the biochar module at a large spatial scale can be very time demanding and computationally intensive. Therefore, the results of suitability analysis previously performed on all U.S. farmlands (Chapter4) were integrated into the newly developed algorithm for large spatial scale crop modeling. This narrowed down simulation areas to the regions that the statistical model identified as likely to show a positive response to biochar. Model outputs were aggregated at a climate division level and the effect of biochar was estimated as the percent change relative to no biochar simulations for all output variables.

A new algorithm was developed for large spatial scale modeling which takes advantage of different inherent levels of heterogeneity in soil, management and weather. This algorithm tries to adapt the mesh size according to heterogeneity of the input domain. The Redundancy-Eliminating Algorithm for Large-scale Modeling (REALM) is a python-based geoprocessing framework that consolidates all the redundant simulation points within a given input domain. The main product of REALM is identical simulation points with unique combination of soil and weather information resulting in spatially optimized simulation grid and minimum redundant simulation. Considering that soil properties may change every few meters, weather domains may change every few km, and some management practices may vary every tens of km, one can use this property to adapt the mesh size and consolidate points with the same information.



## Model setup and management

Simulation regions were generated from the suitability analysis and by taking advantage of the REALM algorithm. Long-term impacts of biochar application on two cropping systems were studied for the states of Iowa and California.

Both of these states are major producers of agricultural products in the U.S. where, they differ mainly in their cropping system as well as their irrigation regimes. In California, irrigated alfalfa is the most planted row crop with more than  $270 \times 10^3$  ha (Johnson et al., 2010), whereas rain-fed continuous corn cropping systems are common in Iowa. The wide range of soil and climate conditions in these states allows for capturing a broad range of responses to biochar.

Our simulation regions fell into all the 9 climate divisions in Iowa whereas only two divisions in California are represented in this study. Climate divisions in Iowa are mostly of the same size whereas division 5 in California is approximately double in size compared to division 2. Suitable regions identified in chapter 4 for California fell into division 2 and 5, which have experienced two different climates in the past 30 years. Division 2 has recorded higher rainfall and lower mean temperature compared to Division 5.

In Iowa, as a general trend, there is a gradient in temperature from north to south, with the south showing higher average temperatures. Rainfall changes from south east to north west with the southeast experiencing more rainfall. Division 9 has the highest rainfall, while D1 has the lowest.

REALM allowed us to develop simulation units with  $30 \text{ m} \times 30 \text{ m}$  resolution with the assumption that every 15 ( $\text{km}^2$ ) share the same weather environment. For Iowa, regions found suitable for application of biochar produced from corn stover feedstock and under fast pyrolysis were used in the current study for investigating the stability of biochar effects. Whereas, suitable areas under biochar produced from woodchip feedstock and slow pyrolysis were selected for the state of California.

The gSSURGO (SSURGO, NRCS, 2016) and Daymet (Thornton et al., 2016) databases were used as the primary source for creating soil and weather files for the APSIM model. Simulations

were performed for corn-corn cropping system in Iowa and alfalfa in California starting in 1980 until 2016 with a one-time biochar application of  $15 \text{ Mg ha}^{-1}$  in spring of 1981 (Details about the properties of biochar can be found in Table 5.1).

For setting up the management practices, automatic irrigation was defined in APSIM for alfalfa in California in order to keep the soil moisture at field capacity. While, 50% residue removal with  $200 \text{ kg N ha}^{-1}$  application at planting was considered for corn-corn cropping system in Iowa. The harvested residue was assumed to be locally used for biochar production, however further investigation is needed to calculate more accurate estimates of required residue removal to meet the biochar production demand.

Table 5.1: Basic biochar properties used for large scale simulations

State	Feedstock	Pyrolysis	C (%)	N (%)	Ash (%)	CN
Iowa	Corn stover	Fast	52.4	0.4	37	134
California	Woodchip	Slow	77.6	0.5	7	169

The generated soil profiles were as deep as 1.2 m and  $\text{NO}_3$  leaching was estimated as the amount of  $\text{NO}_3$  ( $\text{NO}_3$  concentration  $\times$  volume of leached water) moving below the bottom of the soil profile on a daily basis. A dynamic planting strategy in APSIM was used for corn-corn cropping system and corn was harvested in early Nov.

A comparison was made between a county level yield reported and yield estimated by the model to test the adequacy of the REALM algorithm and the model setup used in our simulations. Carroll county in Iowa was selected for this comparison due its diverse range of soil types and climate environments. The Des Moines lobe splits this county into two very different soil types in terms of quality and there is approximately 100 mm difference in total annual rainfall between different parts of the county.

This comparison helps us to develop an understanding of the APSIM model and REALMs potential for representing natural processes in soil and crop at a large scale before the addition of biochar as a new layer of complexity. The model has been able to capture the overall effect of soil and climate at this scale on crop yield compared to the reported county-level yields (Fig. 5.1).

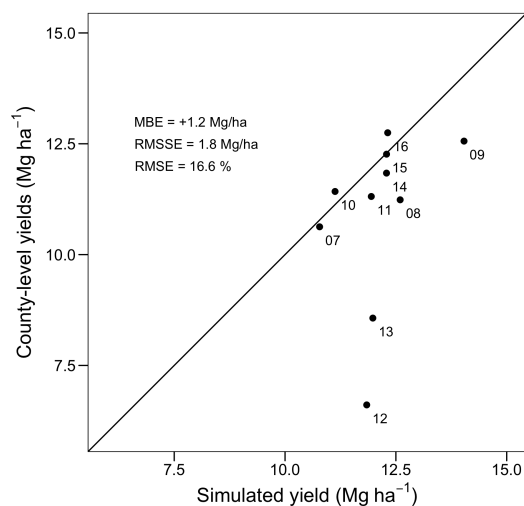


Figure 5.1: Simulated corn yield for Carrol county, IA versus reported yield by NASS (2015)

Yield estimates by the model aligns well with the 1:1 line, except for 2012 and 2013 where the county experienced a severe drought.

We used the Palmer Drought Severity Index (PDSI) and Corn Suitability Rating (CSR V1.0) as two proxies for soil water availability and soil quality respectively to explore the main drivers of the biochar effect. The PDSI (National ClimaticData Center, 2013) is sensitive to meteorological and hydrological drought conditions and an approximate measure of the cumulative effect of atmospheric moisture supply and demand (Alley, 1984). This method uses precipitation, estimated evapotranspiration and soil moisture conditions to calculate the drought severity index. The PDSI is negative if the soil is dry and positive when there is ample or surplus water. The CSR segregates soils in Iowa based on their taxonomy group, family particle size class, water holding capacity, field condition, soil depth and expert judgment. The CSR ranges from 5 to 100, with 5 for the least productive and 100 for the most.

## Results and Discussion

### Case study of Iowa

Our results showed that the estimated average yield increase following one-time biochar application for  $16 \times 10^3$  ha crop land in Iowa was approximately 0.45% ranging from -0.2% to 2.6% in different years. Although, the degree of biochar impact on yield was not practically significant, the change in  $\text{NO}_3$  leaching was substantial and varied between approximately +4% to -5% for different years. We expected to see the positive effects of biochar just in the next few years of application, however, the APSIM model suggested that the effect of one time biochar application did not diminish over the next 30 years of its application.

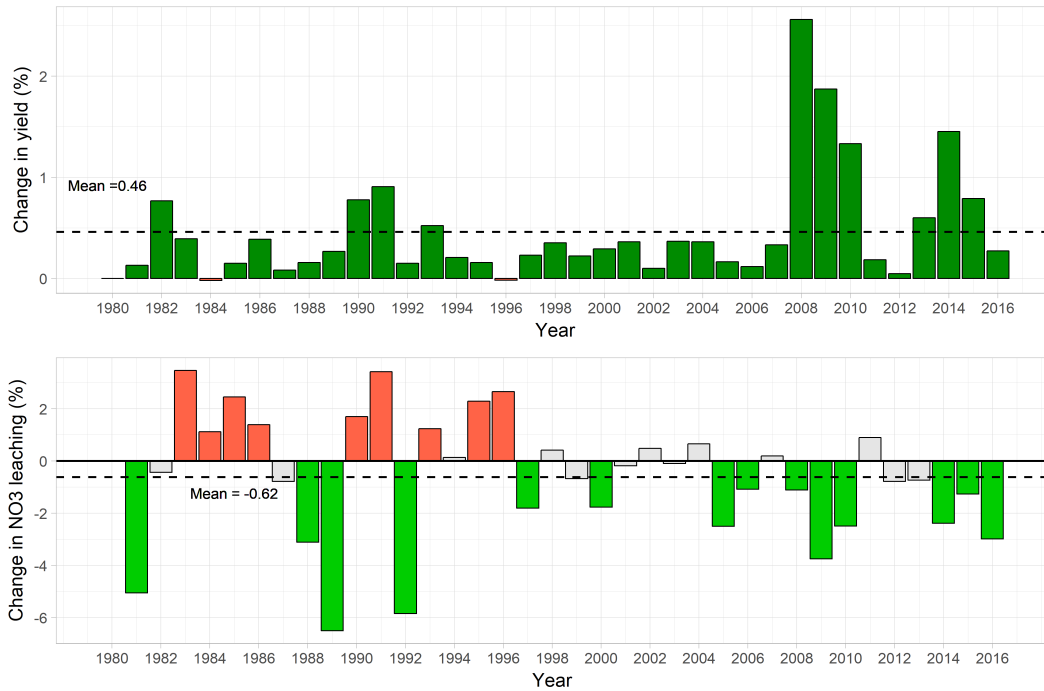


Figure 5.2: Change in crop yield (top) and  $\text{NO}_3$  leaching (bottom) following biochar application relative to no biochar for Iowa

On average, a significant  $\text{NO}_3$  leaching reduction was simulated in the first year biochar application (1981), possibly due to addition of large amounts of labile carbon to the soil which caused

an enhanced nitrogen immobilization (Fig. 5.2). After that, for approximately 10 to 15 years,  $\text{NO}_3$  leaching was slightly increased, possibly due to the recycling of previously immobilized nitrogen to the mineral form and the decomposition of more carbon from biochar (Except for 1988, 1989 and 1992 when most of Iowa experienced a severe drought) (Fig. 5.2). A slight increase in yield in biochar relative to no biochar was also found in years when water was limiting, possibly due to saving more  $\text{NO}_3$  (from mineralized biochar carbon) in the soil profile in drought years and making it available in following years.

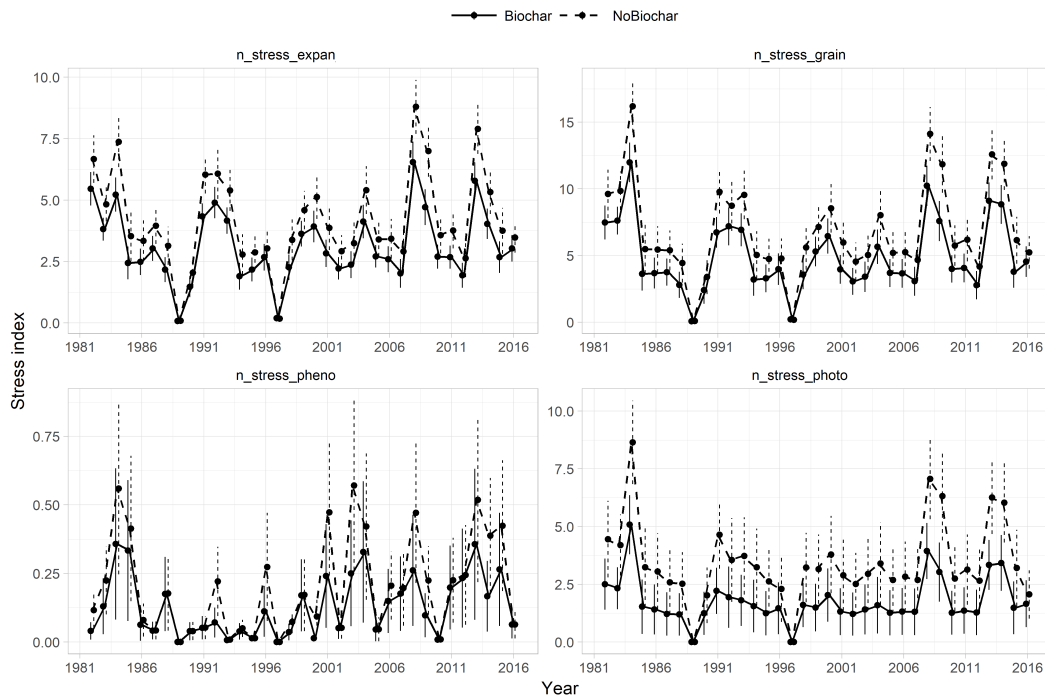


Figure 5.3: Different nitrogen stress indices simulated over the state of Iowa affecting leaf expansion (top left), grain filling (top right), phenology (bottom left) and photosynthesis (bottom right) for biochar and no biochar. The interval shows the mean  $\pm$  one standard deviation estimated around the mean for each year.

For almost the entire simulation period biochar application helped the crop by relieving nitrogen stress through increasing nitrogen mineralization. This is significant especially when no substantial increase in  $\text{NO}_3$  leaching was found (Fig. 5.4). The model did not produce a significant change

in soil physical properties following biochar application resulting in almost no change in estimated water stress index between biochar and no biochar simulations (Fig. 5).

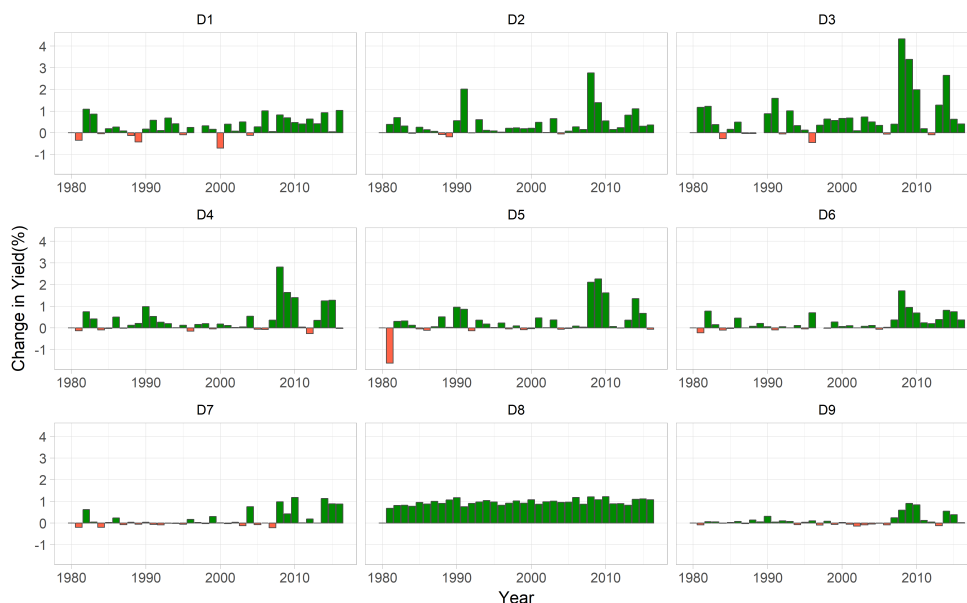


Figure 5.4: Change in crop yield following biochar application relative to no biochar for all climate districts in the state of Iowa

Interestingly, different climate divisions responded differently to biochar application as a result of the interaction of soil and climate with biochar. Our results suggested that division 8 and 3 showed the highest average yield response of 1.2% and 0.72% whereas, division 7 and 9 are the lowest with less than 0.2%. On the other hand, divisions 1 and 5 showed the greatest reduction in  $\text{NO}_3$  leaching with more than +1% reduction on average and division 8 showed the highest increase with 0.2%. The fact that division 1 and 5 showed a similar behavior in  $\text{NO}_3$  leaching reduction given the vast difference in their climate (Division 1 is the driest and 5 is among the most wet divisions in the state) reveals the important role of soil regarding  $\text{NO}_3$  leaching (Fig. 5.4).

Division 8 shows the highest and most stable (least variability) response compared to the rest of the divisions (Fig. 5.6). Interestingly, this region is known for the lowest CSR among all the divisions in Iowa, and a potential improvement in this region can be expected by restoring marginal

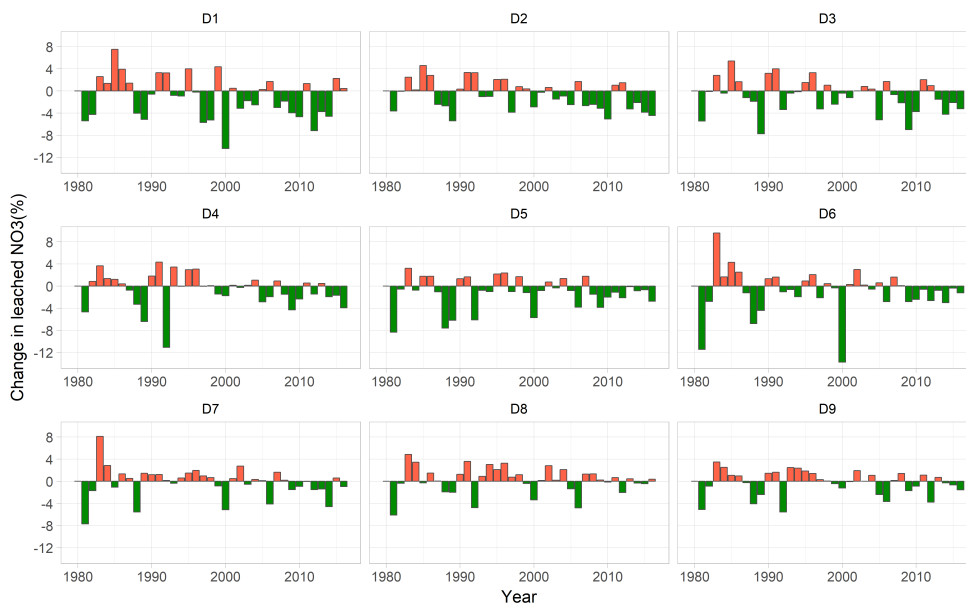


Figure 5.5: Change in  $\text{NO}_3$  leaching following biochar application relative to no biochar for all climate districts in the state of Iowa

lands and/or farms with poor soil quality. On the other hand, divisions with the highest average CSRs (5, 2 and 1) responded very closely to the average change yield and showed a substantial reduction in  $\text{NO}_3$  leaching (except division2) (Fig. 5.6).

We studied the statistical significance of the relationship between PDSI against the change in yield and  $\text{NO}_3$  leaching following biochar application. This helped us to simplify the analysis of the effect of weather on the crop and soil response to biochar. Except in division 8, the biochar effects show a positive correlation with increase in availability of soil moisture (PDSI) implying an increase in yield following biochar application with higher soil moisture values (Fig. 5.7). This increase is possibly due to increased availability of soil moisture which promotes nitrogen mineralization. No statistically significant correlation was found between change in  $\text{NO}_3$  leaching against PDSI in all divisions (except in D1 and D5) suggesting that addition of biochar did not increase  $\text{NO}_3$  leaching in wet years (Fig. 5.7).

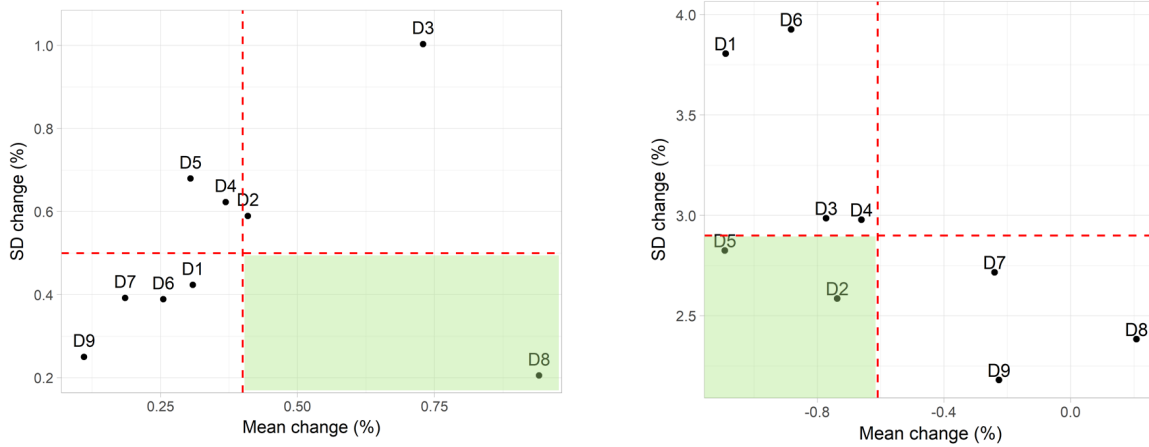


Figure 5.6: Stability of change in yield and nitrogen leaching for different climate districts in Iowa.

To support this claim, change in crop yield vs change in  $\text{NO}_3$  leaching was investigated and it was found that in wet years ( $\text{PDSI} \geq 3$ ), the reduction in  $\text{NO}_3$  leaching is associated with an increase in crop yield suggesting that  $\text{NO}_3$  is possibly taken up by the crop. This trend was in division 3 which had the highest amount of sand content among all the divisions. This suggests that biochar improved the capacity of sandy soils to retain more  $\text{NO}_3$  and in turn made it available for the crop (Fig. 5.8).

We estimated that application of biochar on Iowa's poorest soils over the whole simulation region can result in a yield increase of  $21.6 \times 10^3$  Mg on average while estimating a  $576 \times 10^3$  kg reduction in  $\text{NO}_3$  leaching and more than 4.1% increase in organic carbon over the course of 30 years of simulation.

### Case study for California

Trends found for 30 years of simulation of biochar effect on alfalfa biomass and  $\text{NO}_3$  leaching were similar to what was found for Iowa and in corn-corn cropping systems. Average change in crop biomass and  $\text{NO}_3$  leaching were practically insignificant for  $618 \times 10^3$  ha alfalfa crop land in California (Fig. 4) however, variability in  $\text{NO}_3$  leaching was more substantial compared to change



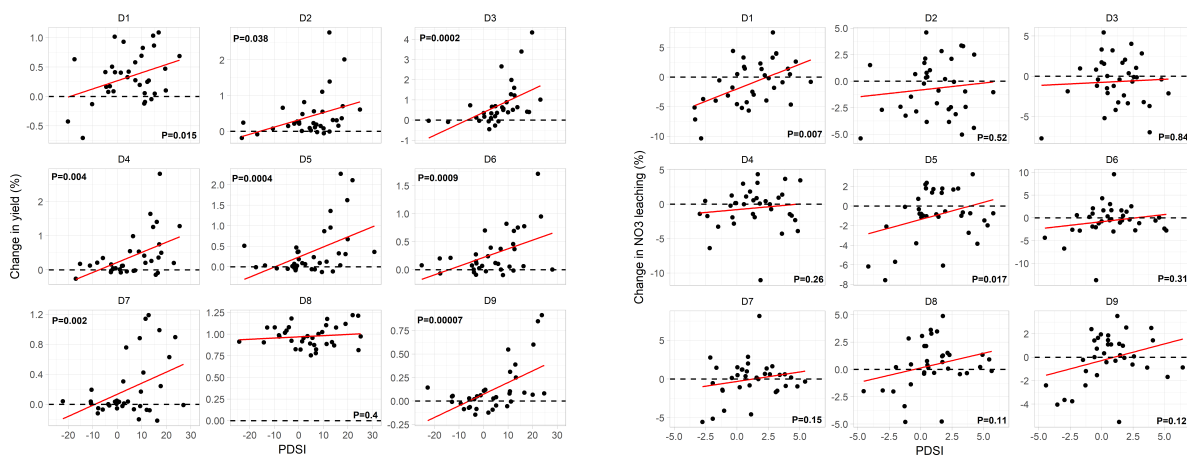


Figure 5.7: Palmer Drought Severity Index (PDSI) versus change in yield (left) and change in  $\text{NO}_3$  leaching (right) following biochar application for all climate district in Iowa. The null hypothesis for the p-value presented in the graphs is if the slope is equal to zero.

in biomass. The effects of biochar on both biomass and  $\text{NO}_3$  leaching did not diminish over time and the drier climate showed (Division 5) much lower in yield change compared to the division 2.

It was found that the change in  $\text{NO}_3$  leaching as well as biomass in Division 5 was closely linked to the PDSI in different years. In years with higher PDSI, the higher  $\text{NO}_3$  leaching and biomass increase was found. Division 2 which is also known as Sacramento valley consistently showed an increase in  $\text{NO}_3$  leaching over the course of simulations compared to Division 5 (San Joaquin drainage) possibly due to higher organic matter compared to San Joaquin drainage (Fig. 5.7). This may induce higher  $\text{NO}_3$  mineralization, crop uptake and  $\text{NO}_3$  leaching given the higher precipitation in Sacramento valley.

Similar to our findings in Iowa simulations, no substantial change in soil physical properties was simulated in California resulting in no significant influence of biochar application on soil water balance or water use.

We learned that the implemented algorithm in the biochar module mainly affects crop growth and development either through influencing soil water cycle or by affecting soil mineral nitrogen. Biochar interaction with soil mineral nitrogen pools was found to be critical primarily in presents of crops which are more dependent on nitrogen application relative to legumes that they fix nitrogen

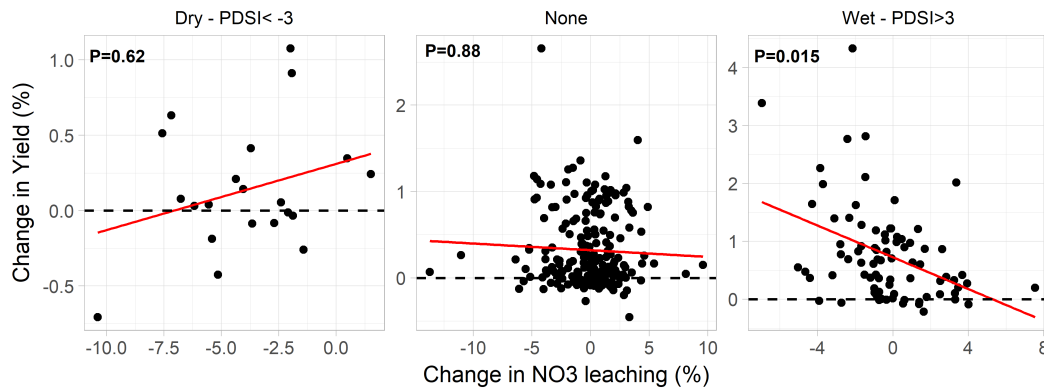


Figure 5.8: Change in yield versus change in NO<sub>3</sub> leaching following biochar application relative to no biochar for different levels of Palmer Drought Index (PDSI). The null hypothesis for the p-value presented in the graph is if the slope is equal to zero.

like alfalfa. From the soil water balance aspect also there is still not a consensus in the biochar community and literature about the magnitude of biochar effect on soil hydrological properties. Even though there is a large body of literature suggesting a significant improvement in soil physical and hydrological properties following biochar application in lab studies (Basso et al., 2013; Dokoohaki et al., 2017b; Rawls et al., 2003; Major et al., 2009), no concrete evidence has been put forward from field experiments in the literature (Hardie et al., 2014). So the estimated biochar effect on soil hydrological properties is set to be minimal. We think there is a need for more long-term and large-scale field experiments assessing the role of biochar on crop water use and soil water balance. The biochar module then can be modified accordingly and possibly increase the benefits of biochar use in large-scale simulations.

Previous statistical models (chapter 4) estimated a very high probability of yield increase for all the simulated regions in this study (given their basic soil properties) however, APSIM model suggested that not all of those can consistently show positive yield response to biochar. Application of a more sophisticated process-based model helped explain the complexity of interaction between variable weather environments (year to year variability) and soil with biochar. One plausible reason

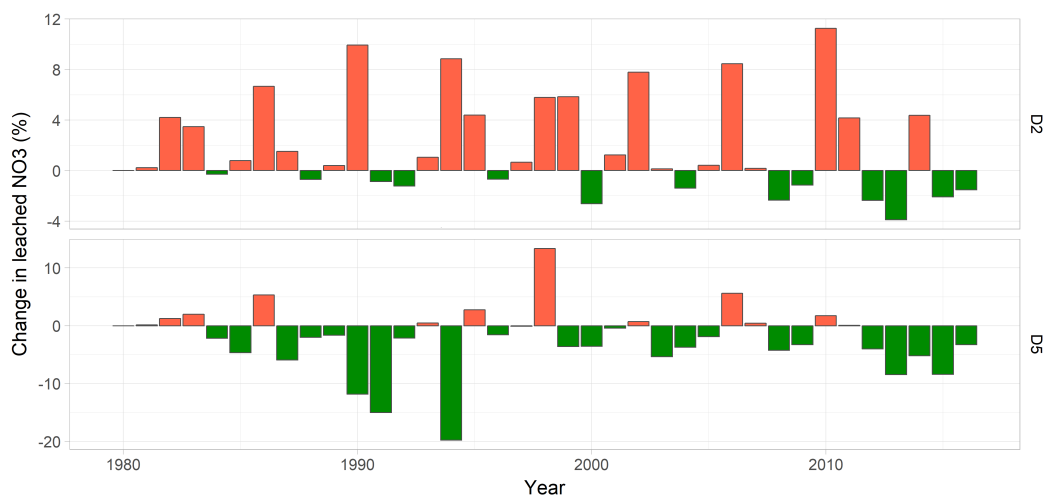


Figure 5.9: Change in NO<sub>3</sub> leaching following biochar application relative to no biochar for two climate districts in California.

for this inconsistency in response to biochar could be some stress mechanisms on crop which biochar is not designed to alleviate, such as heat stress.

Although the biochar module in APSIM is the latest advancement in the science of modeling the impacts of biochar, its full capabilities and caveats are still unknown. Modeling the biochar behavior is a difficult task because of the inconsistent reporting of results in literature (reports with conflicting interpretations, even under similar application) due to the complex nature of biochar interactions with soil and crops. Thereby even results presented in the current study needs to be cautiously interpreted.

## Conclusion

In this study the APSIM model suggested an insignificant change in crop productivity (yield/biomass) following biochar application with a more substantial effect on NO<sub>3</sub> leaching depending on weather conditions. It was found that in wet years ( $PDSI \geq 3$ ) there is a reduction in NO<sub>3</sub> leaching along with an increase in crop yield suggesting more mineral nitrogen being available for the crop.

It was found that the biochar effects lasted almost for the entire 30 years of simulation period while biochar application allowed for sustainable harvest the crop residue without losing yield or increasing NO<sub>3</sub> leaching. During the simulation period biochar acted as a source of carbon which consistently helped with increasing mineral nitrogen pool through carbon mineralization and relieving nitrogen stress.

Our general understanding of biochar interaction suggests that there should not be a persistent effect of biochar on crop yield except for very infertile and poor soils. Trends found in division 8 in Iowa brings up the idea of feedback loops between models and experiments and suggest more extensive experiments in this region for better understanding of the mechanisms involved in generating such a behavior.

### Acknowledgments

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## CHAPTER 6. SUMMARY AND DISCUSSION

In summary, in our first chapter We extended the findings of previous researchers by showing that biochar amended soils had a change in pore size distribution with smaller most frequent pore diameters and Van Genuchten alpha parameters and larger S-index, total porosity and higher saturated water content, field capacity and residual water content compared to control soils without biochar. A key novel finding is that differences in soil pore geometry parameters obtained by fitting measured SWRCs to the Van Genuchten equation provided quantitative evidence of the shift in pore size distribution to smaller average pore sizes, reducing macro- in favor of meso- and microporosity and hence enhancing soil water retention. This improvement can help biochar amended sandy soils to retain more plant available water for crop use and reduce leaching losses of water and nutrients compared to non-amended sandy soils.

We provided evidence in the second chapter that biochar application resulted in improved soil physical properties in corn plots under field conditions over two years. An increase was found in DUL and KL along with a slight increase in SAT which can be attributed to the biochar treatment while no significant change in LL15, KS and MAXPOND was observed. Increase in the capacity of the soil for holding water resulted in higher water uptake with lower LL for the biochar treatment. A key novel component in this study was the integration of field-level measurements with a modeling component for estimation of more realistic soil properties as a result of biochar application.

In our suitability analysis study, we found a negative correlation with clay, SOC, soil pH and CEC, meaning that the soils with lower the value of any of these soil properties, the higher the probability of yield increase after biochar application. Examining the model's behavior revealed that crop yield response to biochar was dominated by soil properties and that increases in biochar application rate resulted in higher probability of crop yield increases for soils with lower quality. The model developed in this study is computationally fast and accurate enough to be used for

large scale modeling, nonetheless, our results have several caveats. For example, our understanding suggests that various management practices (such as residue removal, increases in N fertilization rates, etc.), soil properties (such as inorganic N available in the soil) and biochar properties (such as the size of labile C and N pools) are potential drivers of crop yield responses that are not specifically defined in the model. Adequate data is currently unavailable in the literature to cover all possible soil-biochar interactions, and therefore the model focuses on available information. Therefore, the inference domain of the model's output is limited to the extent of the training dataset, however our model paves the way for the use more computationally intensive process-based crop models by identifying regions, soil types, and biochar types with high and low probability of crop yield response.

Results from chapter 4 estimated a very high probability of yield increase for all the simulated regions in Iowa and California (given their basic soil properties) whereas, APSIM model suggested that not all of those suitable areas can consistently show positive yield response to biochar. One plausible reason for this inconsistency in response to biochar could be some stress mechanisms on crop which biochar is not designed to alleviate, such as heat stress. Application of APSIM model helped to explain the complexity of interactions between variable weather environment (year to year variability) and soil with biochar. Furthermore, our statistical model might capture chemical processes (such as pH) and APSIM is more focused on water and nitrogen.



## APPENDIX. ADDITIONAL MATERIAL

## CHAPTER 4

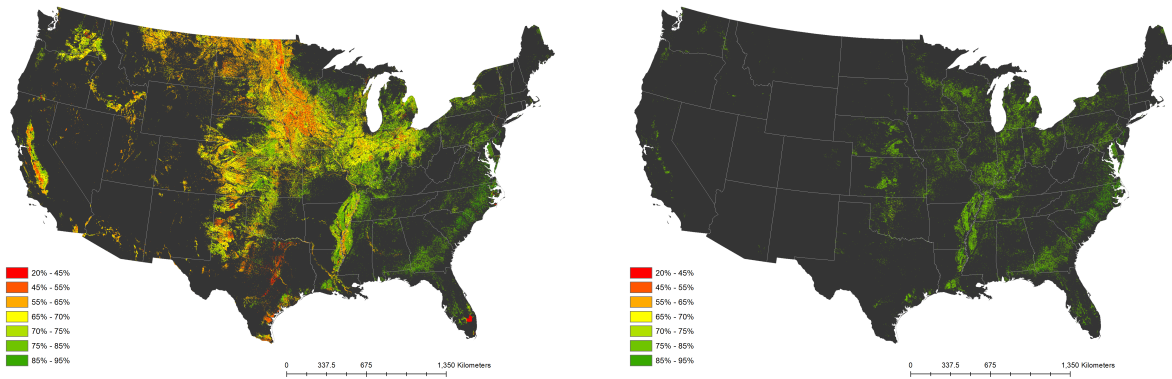


Figure .1: Estimated probability of yield increase for CS15 (left). Areas with more than 75% chance of yield increase for CS15 (right). CS15 represent the  $15 \text{ Mg ha}^{-1}$  application of CS biochar.

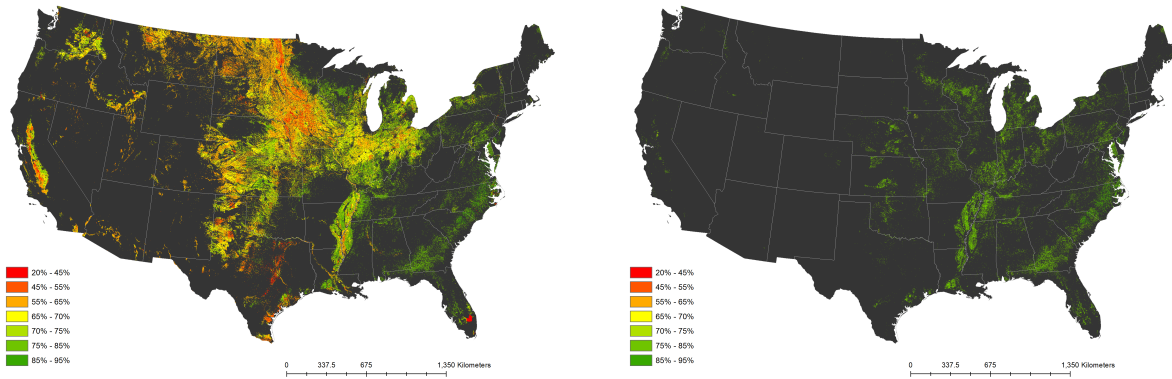


Figure .2: Estimated probability of yield increase for GS15 (left). Areas with more than 75% chance of yield increase for GS15 (right). GS15 represent the  $15 \text{ Mg ha}^{-1}$  application of GS biochar.

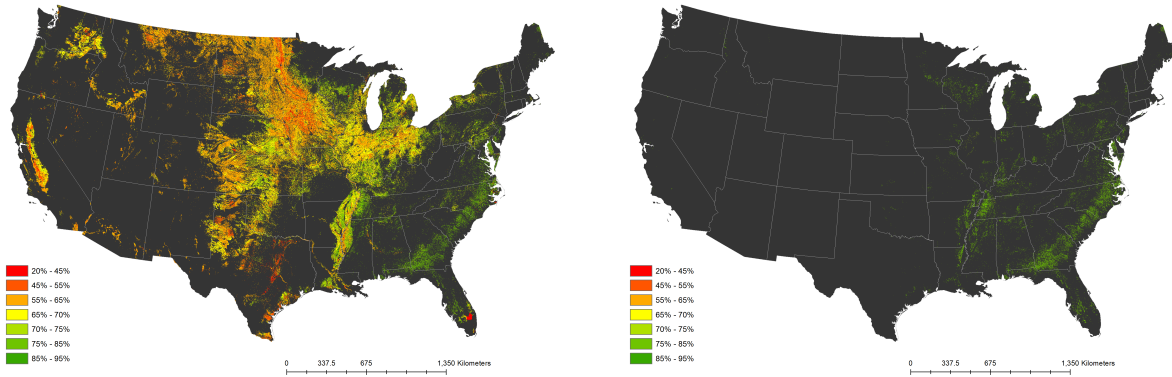


Figure .3: Estimated probability of yield increase for SF15 (left). Areas with more than 75% chance of yield increase for SF15 (right). SF15 represent the 15 Mg ha<sup>-1</sup> application of SF biochar.

### CHAPTER 5

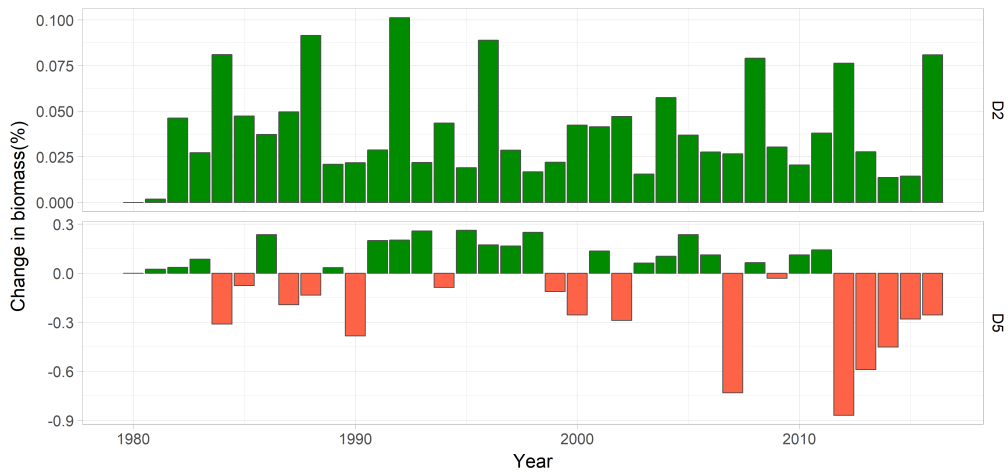


Figure .4: Change in biomass following biochar application relative to no biochar for two climate districts in California.

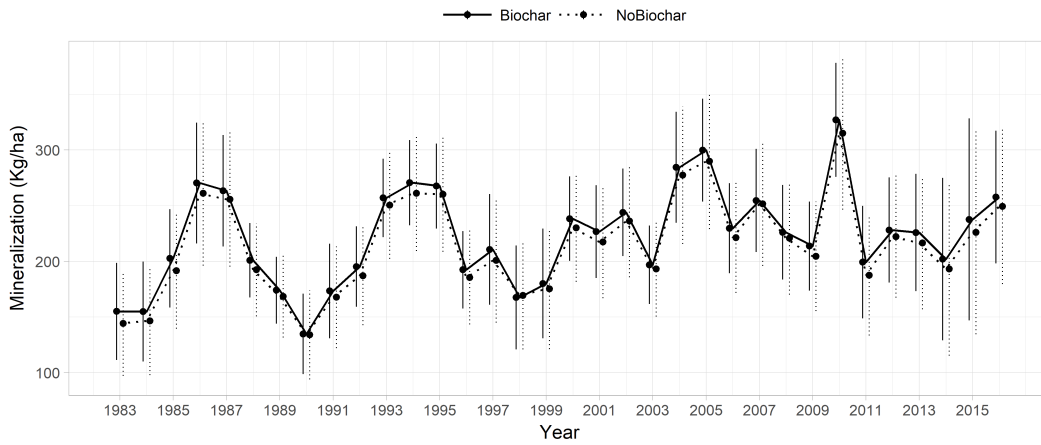


Figure .5: Average mineralization rate (Kg/ha) for the top 20 cm of soil profile simulated for biochar and no biochar in Iowa. The interval shows the mean +/- one standard deviation estimated around the mean for each year.

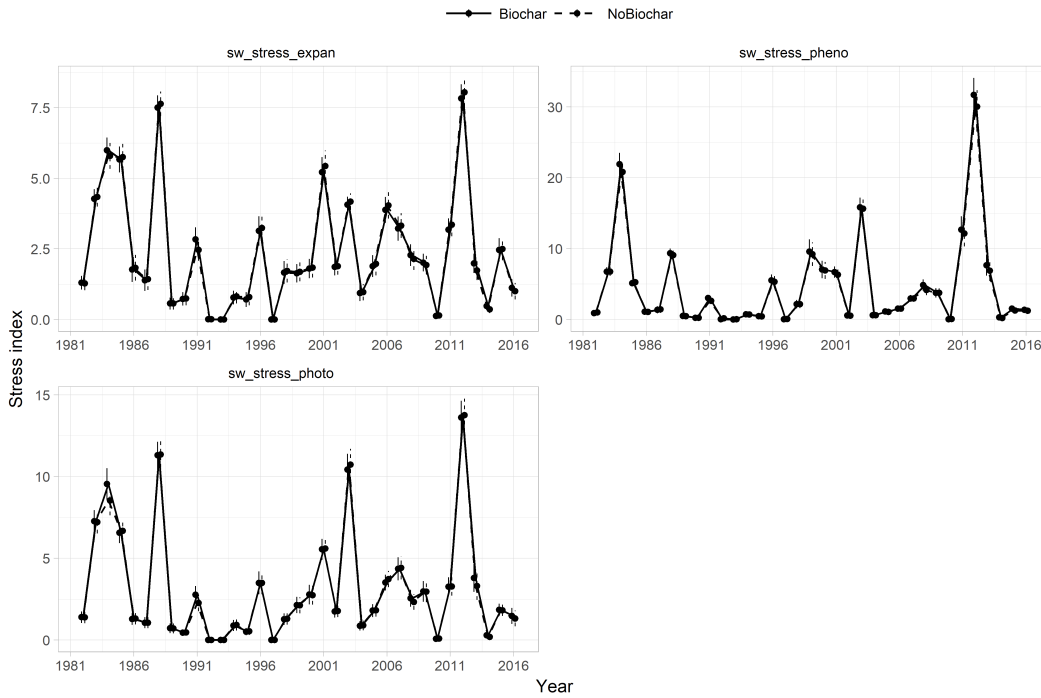


Figure .6: Different water stress indices simulated in Iowa affecting leaf expansion (top left), phenology (top right) and photosynthesis (bottom left) for biochar and no biochar. The interval shows the mean +/- one standard deviation estimated around the mean for each year. The mean cumulative water stress is estimated from all the regions in the simulation for every year.

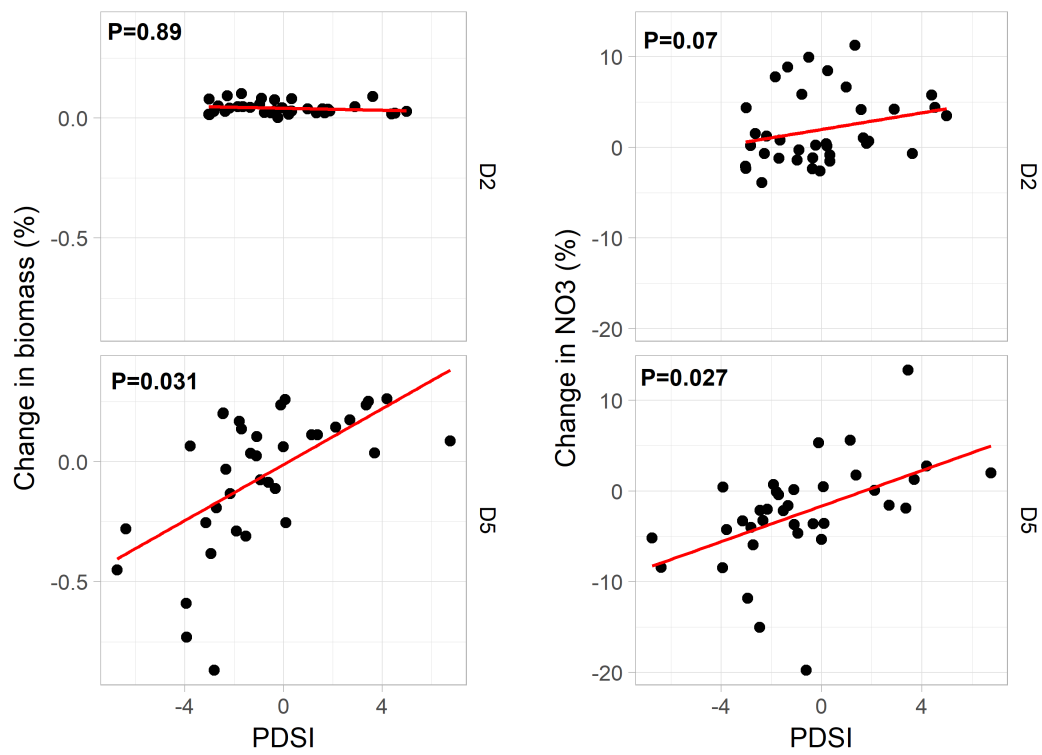


Figure .7: Palmer Drought Severity Index (PDSI) versus change in yield (left) and change in NO<sub>3</sub> leaching (right) following biochar application for D2 and D5 in California. The null hypothesis for the p-value presented in the graphs is if the slope is equal to zero.