

AN ABSTRACT OF THE THESIS OF

Matt Rovero for the degree of Master of Science in Environmental Sciences presented on June 12, 2019.

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Abstract approved:

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Biochar has shown promise as a soil amendment for improvement of agricultural and forest productivity, remediation of heavy metals, and sequestration of carbon, but has not yet been adopted for widespread use in any of these applications. By assessing the production potential as a carbon sequestration tool, and the stability of biochar products, it is hoped to foster greater interest in research and large-scale application of these products. Previous studies have observed differences between the effects of freshly produced and aged biochar on soil, but the nature of these differences has not been explored. Here, the chemical and thermal changes of biochar under storage were measured using Fourier-transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry / Thermogravimetric Analysis (DSC/TGA) on several distinct biochars stored in glass under air, in glass under nitrogen, or in plastic under air, to assess the influence these storage conditions have on thermal and chemical properties over time. An

understanding of these changes is vital to scaling up biochar implementation so that delivered products will perform reliably. Results indicate that biochar produced at 700°C is minimally impacted by a storage time of 7 months, but that biochar produced at 300°C does exhibit greater changes both in chemical and thermal properties which appear to correlate with a loss of cellulose and hemicellulose structures over the storage duration. Storage of biochar within air-permeable plastic was associated with greater adsorption of water and volatile compounds, although no benefit from storing samples under nitrogen was observed.

The production and application of biochar to soil as part of a carbon sequestration strategy has been advocated by several researchers to mitigate the effects of climate change. This study estimates the quantity of biochar that could be produced annually in the United States from crop residues, forestry residues, and municipal waste, without requiring changes to land use. Annually, an estimated 836 Mt of these materials are available, composed of 77% crop residue, 19% forestry residue, and 4% municipal waste. Conversion of this into biochar would prevent approximately 224 Mt of carbon (819 Mt CO₂) from entering the atmosphere as a result of natural decomposition, which would offset 12.6% of annual U.S. greenhouse gas emissions. Beneficial rates of biochar application to agricultural and forest soils found in literature were used to determine the soil biochar capacity, which is estimated at over 70 times the feasible annual production, therefore even high production of biochar will result in secondary benefits to soils. Modeling of feedstock decomposition was conducted at various decomposition rates and harvest

frequencies to estimate the time required for conversion to biochar to enhance carbon storage under different scenarios. The results of this model suggests that the use of crop residues is favorable in less than five years, while conversion of forest residues may require anywhere from 4 to 200 years for decomposition to equal the carbon lost during the biochar production process. Selection of forest residues to avoid ecosystems or residue fractions with low decomposition rates would decrease the total available mass and maximum carbon sequestration capacity but also ensure that benefits are realized within the appropriate time scale. The quantity of material that would fall into this range is unable to be determined with the current research available, and would likely need to be determined on a site-by-site basis.

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Stability of Biochar Under Storage Conditions and Evaluating its Potential as a
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CONTRIBUTION OF AUTHORS

Dr. Mark G. Johnson contributed to “Effect of Storage Conditions on Thermal and Chemical Properties of Biochar” on experimental design, method selection, and revision of drafts.

Dr. Mark E. Harmon contributed to “Biochar as a Carbon Sequestration Tool in the United States” to the creation of a carbon stores model and recommendations for its use.

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Chapter 1: Introduction

Charcoal has always been a component of soil, from naturally produced wildfire residue to anthropogenic *terra preta de Indio* found in the Amazon basin (Lehmann et al., 2006). A sampling of five distinct soils collected from four different areas of the United States found a significant fraction of the soil organic carbon present, from 10-35%, was due to the presence of charcoal, whether that soil was from a farm plot or an undisturbed prairie (Skjemstad et al., 2002). The carbon present in these charcoals is stable for long periods of time, and charcoal components in soil have been radiocarbon dated at thousands of years old (Glaser, 2006).

The modern rendition of mixing charcoal with soil has taken the name of biochar, which has been steadily gaining popularity among home gardeners, farmers, foresters, and researchers since the early 2000s. The market for biochar as of 2017 showed a demand of 353.4 thousand metric tons globally, worth \$737 million USD, with an anticipated compound annual growth rate of 12% through 2025 (Grand View Research, 2017). Researchers have identified numerous benefits from biochar application to agricultural and forest systems such as decreased nutrient leaching, improved water holding capacity, and greater crop yields (Laird et al., 2010; Zhu et al., 2014; Pandit et al., 2018b). Additionally, biochar has found applications in remediation projects for heavy metals and other contaminants due to its high surface area and ability to immobilize compounds of interest (Kumar et al., 2018; Tang et al., 2013). Biochar has also been evaluated as a method to sequester carbon to combat climate change and has proven a promising technology (Gaunt and Lehmann, 2008; Laird, 2008; Lehmann et al., 2006;

McElligott et al., 2011). Despite the range of applications, within the United States biochar is still largely a niche product rather than a common component in conventional agricultural and forest systems to enhance productivity and maintain or enhance soil quality. The lack of large-scale applications has been connected in part with the absence of government programs supporting construction of biochar production facilities and compensation or subsidies to encourage biochar application, and the existence of programs favoring alternative technologies such as bioenergy production (Pourhashem et al., 2018).

For biochar to become a successful component of industrial-scale agriculture, forestry, and remediation, there needs to be a production network in place to supply the needs of end users. While studies have been conducted on the stability and fate of biochar within soil (Rechberger et al, 2016; Singh et al, 2016; Kumar et al, 2018; Ren et al, 2018; Dong et al, 2017), there appears to be a gap in current research regarding the changes that take place within biochar as it is stored. These changes would dictate to producers the amount of time between biochar production and delivery before it is no longer suitable for specific uses, or suggest additional measures be taken to extend the shelf life of these products in order to provide customers with a product with known properties. To fill this gap, a portion of this research examines changes in six biochars produced from three disparate feedstocks at both high (700°C) and low (300°C) temperature to capture a wide range of possible responses to storage conditions. Three different storage conditions were tested on each of these biochars to determine which, if any, may be beneficial in maintaining biochar close to its fresh state.

The value of biochar stems not only from its effects on soil, but also its impact on atmospheric greenhouse gas concentrations. As a stable form of carbon, biochar production provides a route to prevent biomass carbon from returning to the atmosphere as carbon dioxide and contributing to global warming while resulting in the co-production of bioenergy fuels, simultaneously reducing the long-term load of atmospheric CO₂ and substituting the release of additional fossil carbon. Assessments of economic viability of biochar production often do not account for this benefit, or express it as purely hypothetical, because the current state and federal programs are unable to adequately compensate for these effects (Pourhashem et al., 2018; Pandit et al., 2018a; Sahoo et al., 2019; Meyer et al., 2011). By promoting the potential of biochar to contribute to climate change mitigation, it is hoped that future state or federal programs would be crafted that take into account the unique mechanisms by which biochar production and application tackle this issue. An examination of the biochar production capacity of the United States was conducted, coupled with the capacity of the soils therein to make use of the produced material, to provide an understanding of its potential should current emissions reductions programs be insufficient to meet future climate goals and additional strategies be required. A simple model was created to estimate the difference in carbon storage over time in unmodified biomass (slash) versus the biochar which could be produced from it under a variety of conditions including the rate of decomposition of both materials, the frequency biomass is introduced, and impact of production efficiency, to determine the time necessary to improve carbon stores and the sensitivity of the system to each variable.

Chapter 2: Effect of Storage Conditions on Thermal and Chemical Properties of Biochar

Abstract

Biochar has gained interest as a soil amendment and remediation tool, and while some studies have explored the changes that occur after addition to the soil, none have examined effects of biochar aging during storage conditions prior to application. This study seeks to explain differences observed between fresh and aged biochars through monitoring changes that occur in biochar produced from three feedstocks, at both high (700°C) and low (300°C) pyrolysis treatment temperature, over the course of seven months when stored in either glass jars under air or nitrogen, or in plastic bags under air. Chemical changes were identified via attenuated total reflectance Fourier-transform infrared spectroscopy and changes to thermal properties and stability assessed using simultaneous differential scanning calorimetry and thermogravimetric analysis. Prominent chemical changes consisted of increasing fraction of C-O bonds among biochars produced at the low pyrolysis temperatures, but no changes were observed for high-temperature biochars. Thermal characterization found a decrease in cellulose and hemicellulose content in low-temperature biochar over the duration of storage, but no such change for high-temperature biochar. An increase in water and volatile content was observed in all material associated with storage within plastic, however no differences in volatile or total mass loss was observed between storage under air or nitrogen in glass containers.

2.1 Introduction

Biochar is the solid product formed by heating biological material, such as grasses, wood, or animal waste, in the absence of oxygen. This process, known as pyrolysis, also produces carbon-rich gases and oils that can be used for energy production or as feedstocks for organic synthesis. Biochar (a.k.a. char) has been shown to have numerous benefits associated with soil fertility, such as improved water retention, decreased nutrient leaching, and moderating soil pH (Laird, 2010). Biochar has also found a role in soil remediation, particularly for metals-contaminated sites, due to its capacity to adsorb metal ions from solutions and retain them within the char structure (Uchimiya et al, 2011; Ramola et al, 2014). The feedstock from which a biochar is produced, as well as the temperature of production, impact and influence the properties of the final biochar product, and a thorough understanding of the behavior of the selected material under pyrolysis and how that behavior translates into beneficial uses is necessary for selecting the best feedstock and pyrolysis conditions for contaminated soil remediation or rejuvenating degraded soils (Kloss et al., 2012; Ramola et al., 2014).

The ability of biochar to sorb contaminants from solution or volatile organic compounds from gases has been established (Uchimiya et al, 2011; Zhang et al, 2017), but it is unclear whether typical storage conditions biochar is exposed to between production and introduction to soil can result in significant changes in the biochar that might affect its utility as a soil amendment. Several studies have sought to understand and quantify the changes that occur within biochar after introduction to soil, including alteration of surface roughness,

hydrophobicity, aromaticity and stability of carbon compounds (Rechberger et al, 2016; Singh et al, 2016; Kumar et al, 2018; Ren et al, 2018; Dong et al, 2017). However, no studies have been found that attempt to do the same to understand the changes biochar undergoes following production and storage prior to introduction to soil, despite evidence that aged biochars perform differently within soil than fresh ones (Zhao et al, 2014; Abiven et al, 2011).

The goal of this study is to begin to understand the changes that occur as biochar ages under various storage conditions. Over seven months, the chemical and thermal properties of six biochars made from three different feedstocks at two different treatment temperatures were analyzed at multiple time points using attenuated total reflectance (ATR) FTIR and simultaneous differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Fractions of each biochar produced were stored in different containers or under air or nitrogen atmospheres to help elucidate the impact packaging and storage may play in the aging process and identify the possible mechanisms and observed changes. We hypothesized that duration of storage would be associated with an increase in aromaticity and a decline in the labile carbon fraction, measured by a decrease in exothermicity at low temperatures in DSC, reduced mass loss between 200°C-400°C in TGA, and relative increase in aromatic regions and decline in aliphatic regions in FTIR, as these less stable carbon structures begin to decompose. We further hypothesized that these changes would be minimized through storage under an inert N₂ atmosphere and greatest when material was stored in air-permeable plastic due to increased exposure to oxygen, moisture, and air-borne organic compounds that would encourage chemical reactions within the biochar material.

2.2 Materials and Methods

2.2.1 Biochar

Biochar was produced from three feedstocks: *Miscanthus* straw feed through a Wiley mill fitted with 2mm mesh screen, fresh Douglas fir wood shavings produced by mechanical saw, and Oak wood pellets purchased from Sutton Lumber, Inc. Materials selected were intended to be common representatives of grass, softwood, and hardwood feedstocks used in biochar production. Materials were dried for at least 24 hours in a 105°C oven prior to pyrolysis. Pyrolysis was conducted in a muffle furnace flooded with nitrogen gas at a rate of 2 L/min to exclude oxygen with a heating rate of 10°C min⁻¹ and a dwell time of one hour at the highest treatment temperature (HTT). Biochar was produced for all feedstocks at both HTT = 300°C (MIS300, DF300, Oak300) and HTT=700°C (MIS700, DF700, Oak700) in Inconel crucibles.

Biochar material was characterized by Proximate Carbon Analysis (according to ASTM D-1762-84) to determine volatile carbon, fixed carbon, and ash content of all samples.

2.2.2 Experimental Design

Biochar was produced between 16 July 2018 and 3 August 2018. Upon the day of production, after cooling back to room temperature under N₂ atmosphere, each biochar was mixed to ensure homogeneity and a sub-sample collected for analysis. Remaining material was distributed into three storage conditions in triplicate; stored in glass under air (GA), stored in glass under nitrogen (GN), or stored in plastic Whirl-Pak bags under air (PA) for a total of 9

containers per biochar. Glass jars were acid-washed 8-ounce Ball canning jars with stainless steel lids, filled with biochar approximately half-way, while 7-ounce Whirl-Pak bags were filled half-way and sealed by folding over four times. Nitrogen preservation was accomplished by purging the biochar in glass containers with nitrogen gas for ten minutes through rubber septa installed in the container lids after filling with biochar. Containers were stored on a shelf within the laboratory, with room temperature ranging from 21-27° during experiment duration.

Timepoint	Time since production
T0	Day of production
T1	1 day (a)
T2	7 days (1 week)
T3	28 days (1 month)
T4	56 days (2 months)
T5	3 months
T6	7 months

Table 2.1: Analysis schedule used for subsampling of biochar. T-zero analysis was conducted prior to dividing biochar into distinct storage conditions. (a) Subsampling was conducted after one day, however due to analysis time of DSC/TGA, some samples were not analyzed until up to 30 hours after collection, which would have disproportionately impacted T1 results.

Subsamples were collected from each container after 1 day, 1 week, 1 month, 2 months, 3 months, and 7 months¹ had elapsed, ground with an agate mortar and pestle to pass through a 250 μm sieve, analyzed by DSC/TGA and FTIR, with excess material stored in glass scintillation vials. Biochar stored under nitrogen was sampled within a nitrogen-filled glove bag, however, no attempt was made to prevent the sampled portion from coming into contact with air after

¹ Final analysis was planned for six months after start of experiment, however due to the 2019 government shutdown laboratory was unavailable and analysis was delayed.

this point. All analyses were initiated on the day of subsample collection, but due to the long analysis time of DSC/TGA, up to 30 hours may have passed between subsample collection and completion the DSC/TGA analysis for some samples. This length of time may ultimately have some effect on the observed data.

2.2.3 Instrumental Analysis

Biochar samples were characterized by Proximate Carbon and Carbon/Nitrogen determination. Thermal properties were determined through combined differential scanning calorimetry– thermogravimetric analysis (DSC/TGA, carried out on Netzsch STA449 F3 equipped with automatic sample changer) within Al_2O_3 crucibles with Al_2O_3 lids with a small hole, to limit interaction with the lab atmosphere prior to analysis, at a heating rate of $10^\circ\text{C min}^{-1}$ to a final temperature of 950°C (Boguta et al, 2017; Li and Chen, 2018; Leng et al, 2018). Chemical analysis was conducted via attenuated total reflectance (ATR) Fourier-transform infrared spectroscopy (FTIR) on a Nicolet iS50 FTIR spectrometer at a 4 cm^{-1} (wavenumbers) resolution from 4000 to 400 cm^{-1} with 128 co-added scans per sample (Liu et al, 2015; Singh et al, 2016; Leng et al, 2018).

2.2.4 Data Analysis

The FTIR spectra were analyzed using The Unscrambler X (ver. 10.5.1, developed by CAMO Software) to perform baseline and scatter correction using Standard Normal Variate, conduct principal component analysis, and generate difference spectra via curve subtraction. DSC and TG thermogram comparative analyses were conducted via Netzsch Proteus Analysis

software (ver. 6.1) to evaluate changes in exo- and endothermic behavior and mass loss rates.

All replicate samples were averaged prior to analysis.

2.3 Results

2.3.1 Thermogravimetric Analysis

Typical thermal behavior of plant-based biochar includes mass loss from 100-200°C corresponding to evaporation of moisture, loss from 200-300°C from hemicellulose degradation, from 300-400°C as cellulose degrades, and lignin decomposition from 200°C through the end of heating without obvious peaks (Li and Chen, 2018; Boguta et al, 2017; Masto et al, 2013). Rates of decomposition of these components among different samples was compared using the first derivative of mass loss (dTG) over appropriate temperature ranges. It was assumed that all mass lost before 200°C was due to evaporation of water and volatile compounds, and its influence on mass loss from the solid material distinguished by dividing values by %Mass remaining at 200°C to produce an adjusted mass loss, which prevented dehydration effects from masking mass loss from decomposition during analysis. An example thermogram showing TG and dTG curves, with relevant decomposition temperature ranges marked, is provided in Figure 2.1.

Biochar made at $\text{HTT}=300^{\circ}\text{C}$ had significantly increased adjusted mass lost relative to baseline measurements over the duration of the study regardless of storage condition, while those with $\text{HTT}=700^{\circ}\text{C}$ showed reduced mass loss except for DF700, which had no change

(Table 2.3, Figure 2.2). Comparison of dTG curves suggests that the increased mass loss in HTT=300°C biochar is due to elevated rate of loss from 200-400°, corresponding to hemicellulose and cellulose degradation (Masto et al, 2013), but rate of lignin decomposition remains unchanged. Within HTT=700°C material, dTG show only discrepancies in maximum rate of loss around 100°C due to evaporation of water. While storage condition did not have a significant impact on adjusted mass loss, in all biochar samples storage in plastic was associated with increased mass loss from water and volatiles compared to other storage conditions, which seems to indicate that the plastic in the bags used are permeable to water and possibly other volatile materials that sorb onto the biochar. Biochar with HTT=300°C exhibited similar mass loss from 30-200°C to biochar stored in the same conditions, produced from the same feedstock, but at a higher temperature, however, the ratio of mass loss compared to baseline measurements was significantly higher due to low baseline mass loss within this region for all HTT=300°C biochar compared to HTT=700°C biochar (Table 2.4, Figure 2.3).

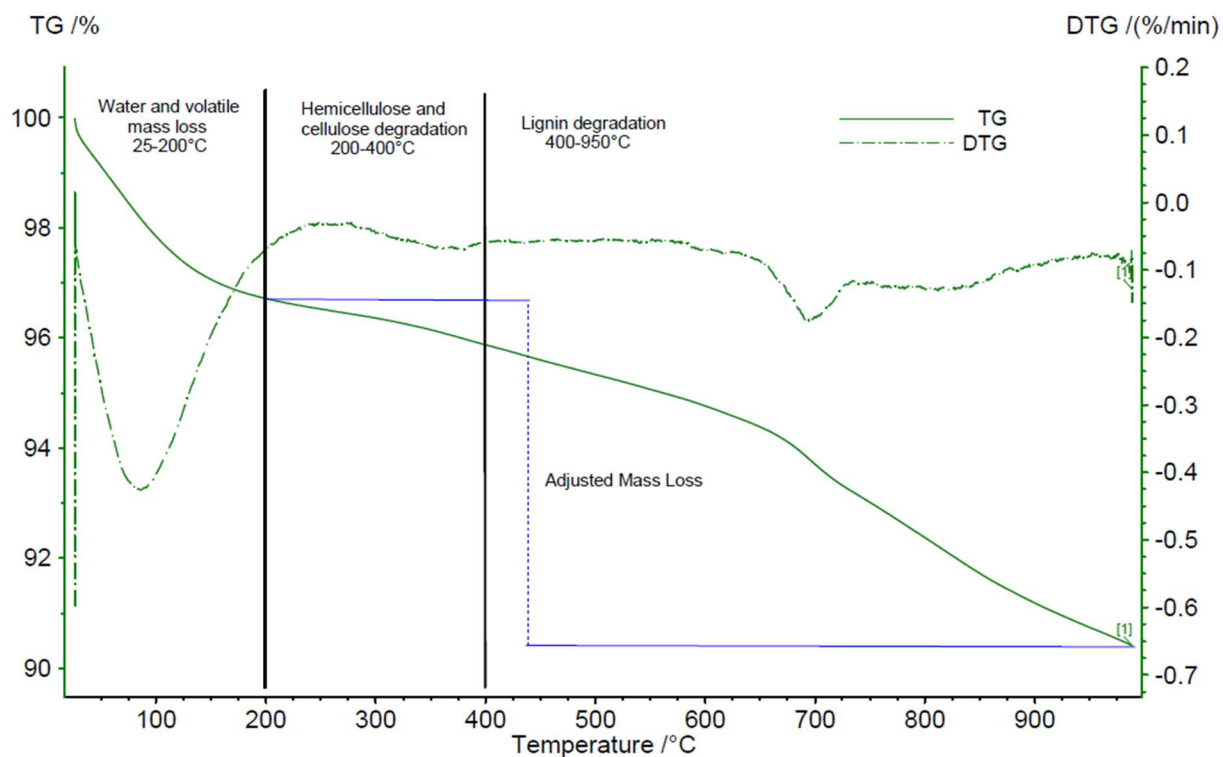


Figure 2.1: Example thermogram showing TG and dTG curves. Labeled ranges show temperatures at which common transformations occur. Mass loss before 200°C is typically associated with evaporation of water and loss of volatiles, loss from 200-400°C is due to degradation of cellulose and hemicellulose, and mass loss above 400°C is associated with degradation of lignin.

Ratio of Mean Percent Adjusted Final Mass Loss								
Feedstock	HTT	Storage	Mean	Std Err	HTT	Storage	Mean	Std Err
MIS	300	GA	1.40	0.04	700	GA	0.74	0.01
		GN	1.37	0.07		GN	0.73	0.01
		PA	1.38	0.02		PA	0.88	0.01
DF	300	GA	1.44	0.05	700	GA	0.94	<0.01
		GN	1.39	0.05		GN	0.92	<0.01
		PA	1.47	0.04		PA	1.01	<0.01
Oak	300	GA	1.52	0.09	700	GA	0.72	0.01
		GN	1.45	0.01		GN	0.71	0.01
		PA	1.41	0.02		PA	0.85	0.01

Table 2.2: Ratio of mean percent adjusted mass loss. Compares T6 values with T0. Values greater than 1.00 indicate more adjusted mass loss at T6 than T-zero. Adjusted mass loss is calculated by dividing total mass loss by percent mass remaining at 200°C to remove the influence of water and volatile losses.

Mean percent Mass Loss due to Water and Volatiles								
Feedstock	HTT	Storage	Mean	Std Err	HTT	Storage	Mean	Std Err
MIS	300	GA	2.97	0.07	700	GA	3.29	0.09
		GN	2.97	0.07		GN	3.17	0.12
		PA	3.98	0.07		PA	4.41	0.08
		T0	1.51	0.02		T0	3.64	0.04
DF	300	GA	2.91	0.07	700	GA	2.96	0.17
		GN	2.81	0.11		GN	3.00	0.13
		PA	3.46	0.04		PA	3.78	0.17
		T0	1.18	0.65		T0	3.44	0.20
Oak	300	GA	2.82	0.40	700	GA	1.79	0.04
		GN	2.90	0.05		GN	1.82	0.18
		PA	4.08	0.03		PA	2.50	0.06
		T0	0.97	0.13		T0	2.15	0.20

Table 2.3: Mean percent mass loss due to water and volatiles. Values presented are from samples at T6 for all three storage conditions (GA, GN, PA) and samples of the produced biochar prior to storage (T-zero).

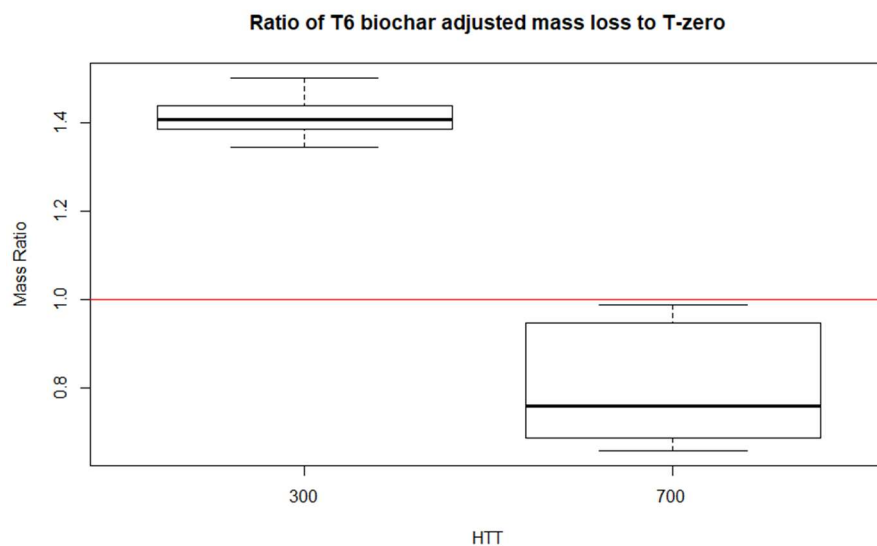


Figure 2.2: Boxplot displaying ratio of adjusted mass loss of all biochar samples at T6. Each box represents data from all samples produced at that HTT. Top and bottom of each box represent the first and third quartile, the dark line the median of each group, and the ends of the whiskers extending from the box 1.5 times the interquartile range. Red line indicates no net change from T-zero, above the red line an increase in mass loss and below the line a decrease in mass loss.

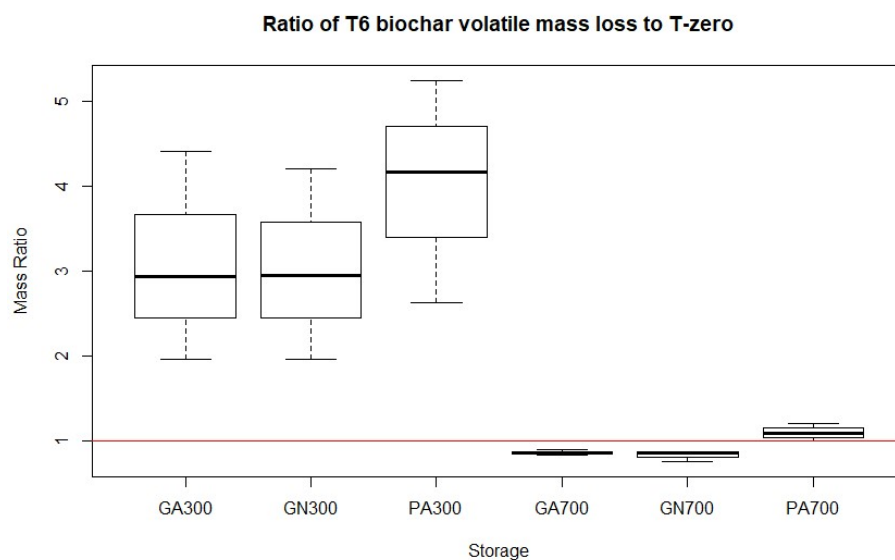


Figure 2.3: Boxplot displaying ratio of volatile mass loss for all samples. Ratio of T6 and T0 results. Samples grouped by HTT and storage condition. Results show less variation among high HTT biochar, significant increases in mass loss ratio among low HTT biochar, and an increase in mass loss associated with PA storage condition (plastic under air).

2.3.2 Differential Scanning Calorimetry

Comparison of DSC curves indicate a shift of peak temperatures in all samples, with behavior connected strongly with HTT and seemingly unconnected to storage condition. All samples displayed an exothermic peak between 290-345°C that shifted to higher temperatures with biochar age, with an average shift of 33°C for HTT=300°C and 19°C for HTT=700°C biochars. As decomposition temperature is related to carbon stability, this suggests that cellulosic structures within the biochar becomes more stable and harder to degrade over time in storage (Masto et al, 2013). An example thermogram is provided in Figure 2.4 showing both T0 and T6 DSC curves for an Oak300 biochar.

Within the fresh DF300 and Oak300 biochar samples, an exothermic peak appearing at 436°C and 446°C respectively shifted to 396°C and 405°C, respectively, in aged samples, however the peak in question is not resolved in the MIS300 samples. These changes appear to be coupled with an endothermic peak which appeared at 510°C, 485°C, and 515°C in DF300, MIS300, and Oak300, respectively, and increased peak height above 600°C, which could indicate that a broad array of lignin structures have differentiated into a more labile fraction (indicated by the lower-temperature peak) and a less labile fraction. This peak shift was not observed until T4, requiring between one and two months of storage time to occur.

First derivatives of DSC curves (dDSC) of the HTT=700°C biochars indicate decreased rate of change within the 200°C-350°C region for samples at T6 compared to T0, however, the absence of difference in dTG curves suggests that these are structural changes, rather than decomposition into gaseous products. This would point towards decomposition of

hemicellulose and cellulose structures over time, or conversion into more stable forms requiring higher temperatures to degrade.

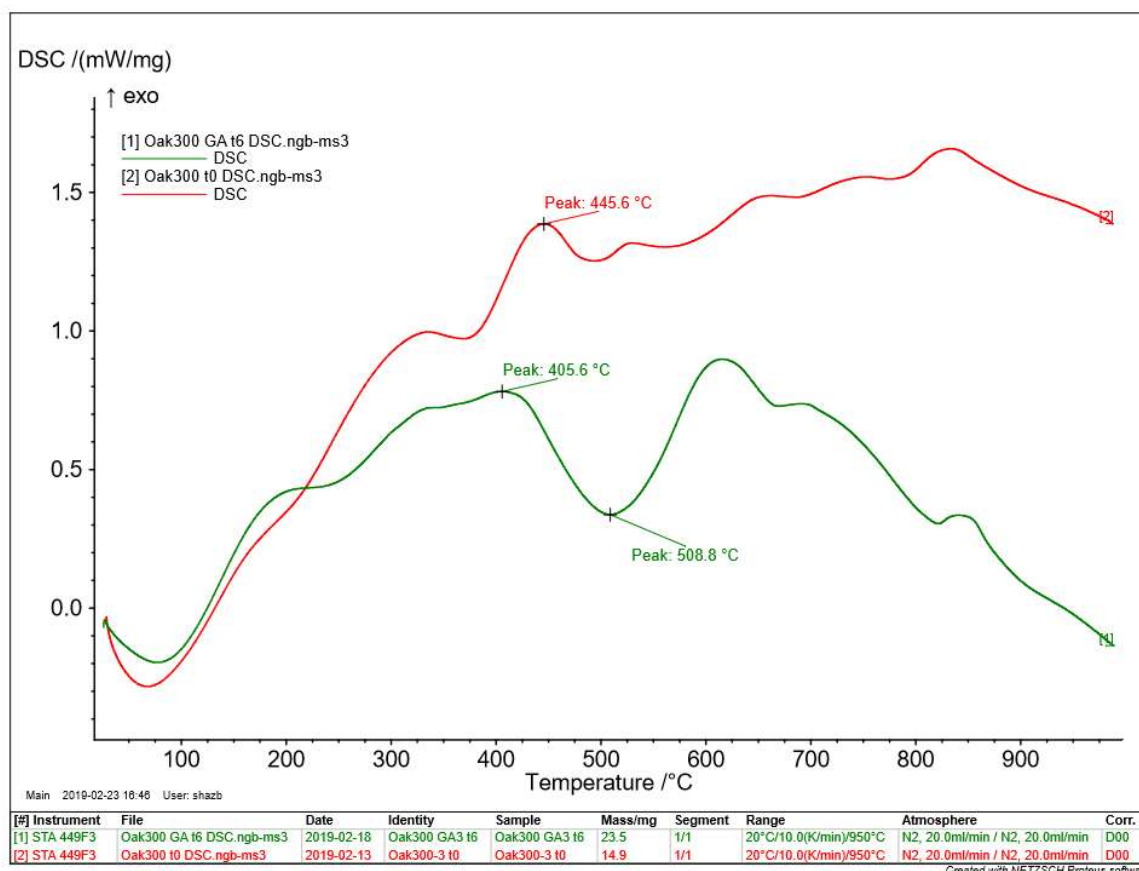


Figure 2.4: Example DSC thermogram. Figure displays peak shifts between T0 and T6 in Oak300 GA samples.

2.3.3 Infrared Spectroscopy

Prior to analysis, FTIR spectra were normalized using the Standard Normal Variate (SNV) to correct baseline drift and reduce the impact of scattering effects due to particle size without compromising signal that is chemical in origin (Rinnan et al, 2009; Barnes et al, 1989). From the resulting spectra, difference spectra were generated by subtracting the T0 spectra from the

corresponding T6 spectra according to feedstock and HTT to identify spectral regions that underwent change through time. Regions of interest were then compared at each time point to determine if the magnitude of difference from the initial biochar increased over time or varied due to other factors.

A significant increase in peak intensity was observed at 1025 cm^{-1} for DF300 samples and 1057 cm^{-1} for MIS300 samples regardless of storage condition due to C-O stretching (Nardon et al, 2014; Kloss et al, 2012; Liu et al, 2015; Sharma et al, 2004). The magnitude of change was roughly 22% of T0 peak in DF300 samples and 11% in MIS300 samples at T6, but peak intensity fluctuated with storage time rather than showing a consistent increase. This fluctuation is likely due to variation in instrument performance over the duration of the study, as the effect was observed at several wavenumbers of interest, rather than being associated with certain functional groups. MIS300 samples additionally displayed increased peak intensity at 1715 cm^{-1} , assigned to C=O stretching (Ramola et al, 2014; Boguta et al, 2017; Claoston et al, 2014) with the magnitude of the increase linked with storage time. Within the $3400\text{-}3200\text{ cm}^{-1}$ region associated with -OH functional groups and water (Nardon et al, 2014; Kloss et al, 2012; Claoston et al, 2014), changes were observed only in DF300 samples, indicating that for all other biochars produced, the water content of the material did not significantly change regardless of storage condition.

Change in peak intensities in high temperature (HTT=700°C) biochar samples were substantially smaller, and no significant deviations from the baseline measurement were

observed. Changes in all samples at all wavelengths were less than 10% of the baseline spectral intensities.

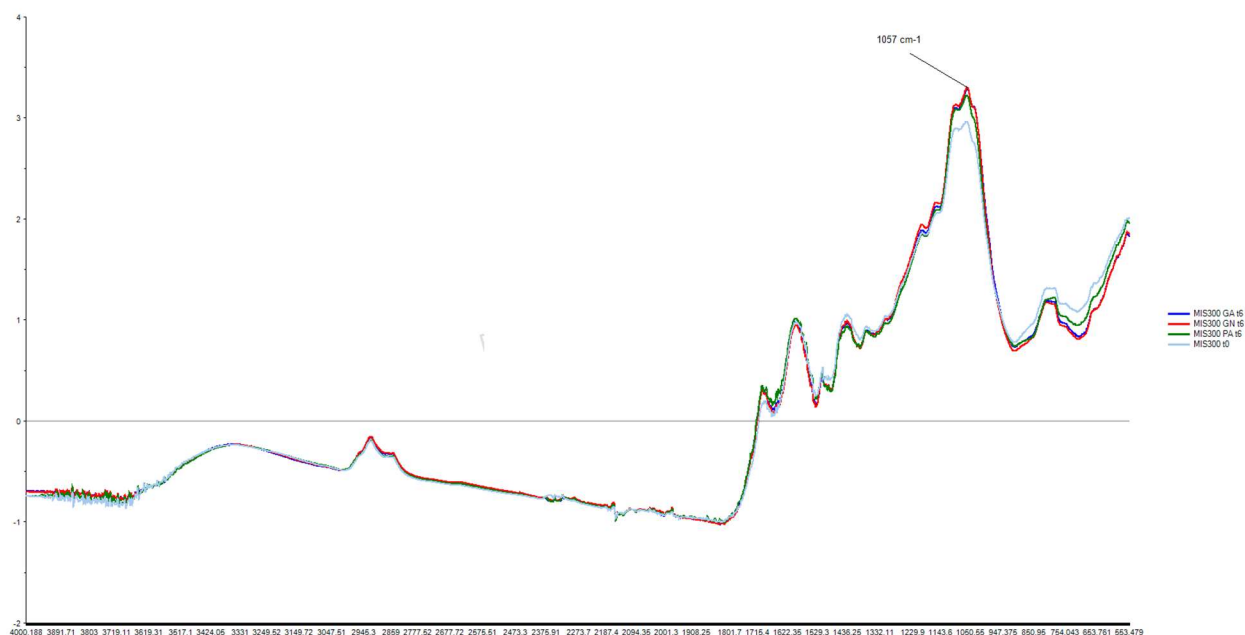


Figure 2.5: Example FTIR spectra (after normalization). Displays MIS300 at T6 under each storage condition and at T0. Marked peak at 1057 cm^{-1} exhibited substantial change in intensity.

Principal Component Analysis (PCA) was performed to differentiate samples based on observed variability. PCA creates several Loadings plots from the inputted spectra which identify regions of the spectral range that contribute to differences between the data set. Principal Component 1 (PC1) explains the greatest amount of variability, with each following Principal Component (PC) explaining less. Based on the degree of similarity to the Loadings

plot, individual spectra are assigned scores on that PC axis, and a plot of two components (such as PC1 vs. PC2) can visually display patterns within data. As shown in Figure 2.6 (top), PCA easily distinguished samples by HTT and feedstock, and readily shows that biochar made at 700°C remains more consistent over time under any storage condition and are more like material made from other feedstocks than lower-temperature biochar, where variance both between and within feedstock is larger. Conducting the same analysis on only the HTT=300°C biochar allows for more differentiation (Figure 2.6, bottom), as the large variance due to treatment temperature is removed but shows only minor difference within each feedstock due to storage condition. With no combination of principal components is there a clear trend with increasing biochar age. Based on this, after adjusting for differences from HTT and feedstock, storage condition seems to play a minor role in explaining variability, but much of the remaining variability is likely due to changes in instrument performance, testing conditions, and other external factors rather than the aging of biochar.

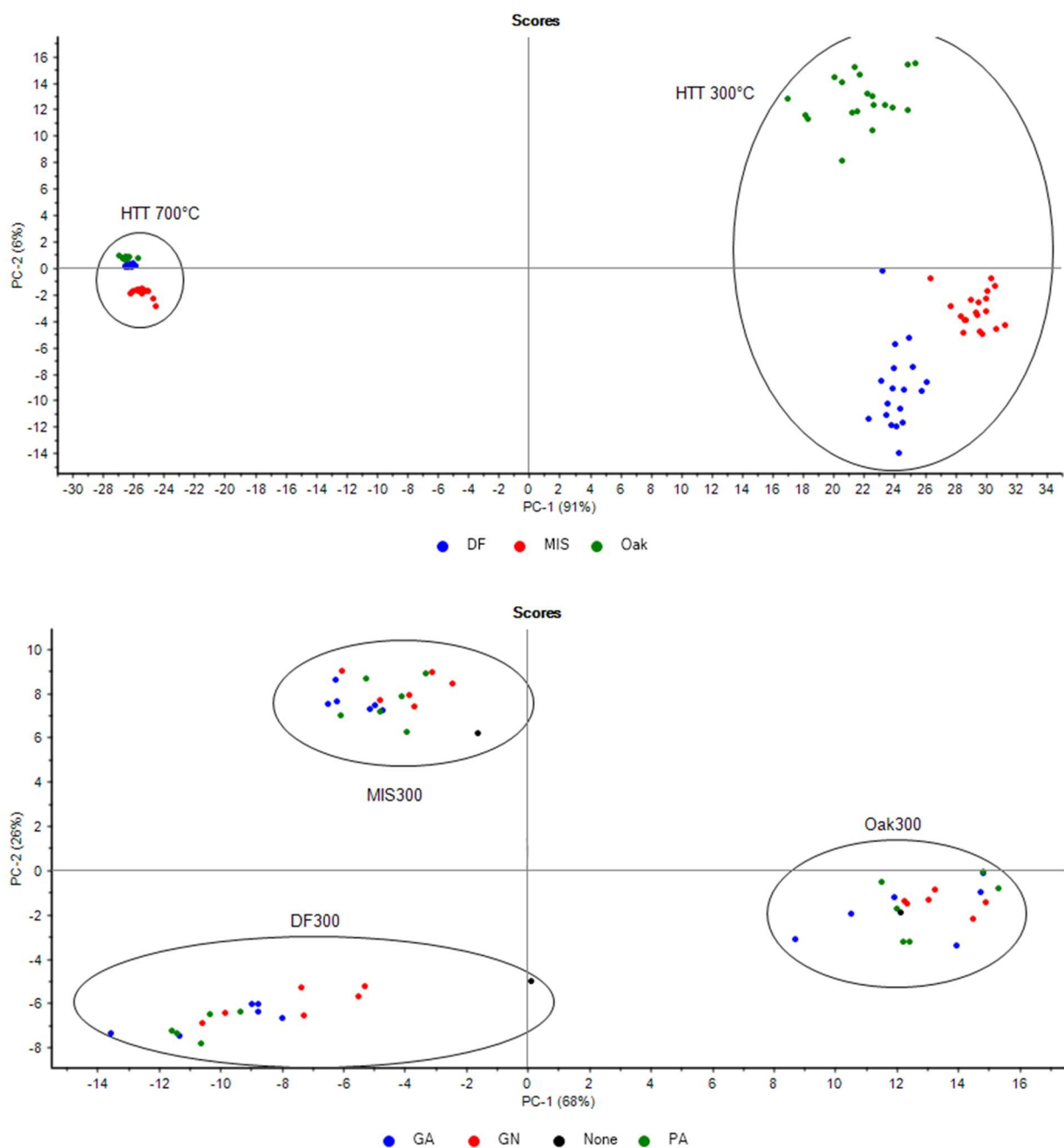


Figure 2.6: Results of PCA on entire FTIR dataset over the full spectral range. Clear grouping by feedstock and HTT are present (top). Separate analysis of only HTT=300°C samples (bottom) suggest minor influence due to storage condition. No trends emerged regarding time point in either set in first three PCs. Loadings plots in appendix.

2.3.4 Proximate Carbon Analysis

Biochar produced at 300°C had significantly higher volatile matter content than biochar produced at 700°C for all three feedstocks, see Table 2.4. Fixed carbon made up the major component in high-temperature biochar samples, with both DF700 and Oak700 containing about 90% fixed carbon, with about 75% in MIS700. Ash content of the biochar was similar between production temperature, except in MIS biochars, which had nearly twice the ash content at HTT=700°C than at HTT=300°C. The lower fixed carbon and higher ash content in MIS700 may be due to the lower presence of lignin-based compounds from grass-derived biochars compared to those produced from hardwoods or softwoods. Elevated volatile matter content in both DF300 and DF700 is likely due to the feedstock preparation; the freshly-generated Douglas fir shavings may have required a longer period of time in the 105°C drying oven to drive off moisture and volatiles to reach a comparable state to the other materials.

Material	Volatile Matter (%)	SD Volatile Matter	Fixed Carbon (%)	SD Fixed Carbon	Ash Content (%)	SD Ash Content
MIS300	45.0	1.0	45.3	0.5	9.7	0.5
DF300	66.5	4.0	34.3	3.4	-0.8	0.6
Oak300	40.9	4.1	57.1	4.9	2.0	1.1
MIS700	7.4	1.3	74.9	1.6	17.7	0.4
DF700	9.1	0.4	90.6	0.3	0.3	0.0
Oak700	7.7	2.4	90.6	2.4	1.7	0.1

Table 2.4: Summary of proximate carbon analysis results. Values of volatile matter, fixed carbon, and ash content are averages of three replicate analyses.

2.4 Discussion

Initial interpretation of TG data was that biochar samples pyrolyzed at low temperatures were hydrating either during storage or between subsampling and analysis, however, the results of DSC and FTIR do not support this conclusion. The consistently exothermic thermogram between 100-200°C and stable IR intensity over the 3400-3200 cm^{-1} region in FTIR in all samples except DF300 point to increased mass loss from something other than water; decomposition of labile structures and devolatilization (i.e., loss of adsorbed volatile components) (Boguta et al, 2017). The connection with HTT indicates that biochar produced at lower temperatures retain more compounds vulnerable to aging than high-temperature biochars, and the higher loss associated with storage in plastic could be due to compounds absorbed from the atmosphere or the plastic itself, or changes induced with higher exposure to oxygen over time.

Observed changes in biochar aromaticity or labile carbon fraction were not linked to storage time as hypothesized. Inability to detect trends over storage time are likely the combination of small changes being difficult to assess and long inter-sampling periods in which laboratory climate conditions and instrument performance can introduce additional variability that cannot be easily compensated for across the entire spectral or thermal range. Influence of storage condition is likely to become more distinct over greater periods of time, however, over the duration of this study the hypothesized trends of fewer changes under an N_2 atmosphere and more changes associated with storage in plastic were detected only within TGA

measurements from 25-200°C. Additional testing over longer timeframes may make differences between storage conditions more apparent.

Storage conditions tested represent what would reasonably be observed within a laboratory or storage room, and not the complete range of possible conditions. Consequently, these results cannot be extrapolated to conditions such as exterior storage, where exposure to higher temperature variation and local precipitation could have substantial and immediate impact on biochar properties.

2.5 Conclusion

The changes observed over seven months of storage in biochar produced at a high temperature were quite small in all analyses, thus storage of these biochars for long periods, regardless of the precise method of storage, is likely to result in performance similar to freshly-made biochar. Low-temperature biochar is more susceptible to changes as measured by TGA, DSC, and FTIR. Except for volatile mass loss, changes do not appear to correlate strongly with storage condition, thus the extra expense of packing material under nitrogen seems to be unwarranted. How critical the properties associated with storage in plastic are to intended applications is not determined within this study but could influence biochar behavior after long periods of storage time in this medium.

Chapter 3: Biochar as a Carbon Sequestration Tool in the United States

Abstract

Biochar and charcoal have been applied to soil to improve its fertility for thousands of years, but its role in modern farming practices has been small. Recent exploration of carbon sequestration has renewed interest in biochar as a stable form of carbon that can be applied to agricultural soils to store carbon while simultaneously improving soil quality. Here, the capacity of soils to hold biochar is evaluated along with the quantity of suitable materials from which to produce biochar in the United States without requiring modification of current land use. An estimated 836 million metric tons (Mt) of feedstock resources are available, which could produce approximately 224 Mt of biochar carbon. This is well below the lower estimated soil capacity to store biochar at 16,200 Mt, so production of excess unusable biochar is unlikely for decades to come. Conversion of all available raw feedstocks to biochar could potentially sequester carbon equivalent to 12.6% of annual U.S. greenhouse gas emissions on long time scales. Modeling of feedstock decomposition was conducted using a single exponential decay model to assess the viability of biochar production as a means of storing atmospheric carbon in the soil by comparing the amount of carbon present in unmodified biomass versus the biochar which could be produced from it over time. This assessment determined that material with decay rate-constants above 0.20 yr^{-1} , which include some forest residues and most crop residue, would result in positive net carbon sequestration after less than 10 years. Material with decay constants between $0.05\text{--}0.20 \text{ yr}^{-1}$ yield enhancements within the 10-50 year range, but material with decay constants below 0.05 yr^{-1} require excessive lengths of time to show

carbon sequestration benefits. Establishing a threshold decomposition rate, below which material would be deemed unsuitable for conversion to biochar for carbon sequestration, would be necessary to ensure that climate goals are met within the appropriate time frame, but would decrease the available feedstocks as estimated in this study.

3.1 Introduction

To avert climate disaster, the concentration of carbon dioxide (CO₂) in the atmosphere must remain below a critical threshold, after which the compounding effects of warming will cause dangerous environmental shifts (IPCC, 2018). Current approaches towards this limit have largely and unsuccessfully focused on emissions reductions, which would require the world to reach zero net carbon emissions by the year 2050 (Woolf et al., 2010; IPCC, 2018). A supplemental strategy is carbon sequestration, the capture of atmospheric carbon through various means for long-term storage in a form that cannot contribute to global warming. While this cannot replace the need for emissions reductions, it might provide necessary time for the development of technologies or strategies that will provide long-term climate stability.

Carbon sequestration happens naturally as a result of both a terrestrial and oceanic carbon cycle. The terrestrial cycle includes four major pools; the atmosphere, biomass, soil carbon, and geologic stores. Plants, algae, and cyanobacteria transfer 123 Gt atmospheric carbon per year on a global scale from the atmospheric pool into biomass through photosynthesis (US DOE, 2008). About 60 Gt yr⁻¹ are returned to the atmosphere as a result of plant respiration, and another 60 Gt yr⁻¹ convert back to CO₂ due to decay of dead biomass and microbial respiration (US DOE, 2008). The result is a small increase in the pool of soil carbon of

about 3 Gt yr⁻¹ globally, insufficient to offset the 9 Gt yr⁻¹ of fossil fuels consumed globally (US DOE, 2008). Over thousands to millions of years, a small portion of soil carbon will convert to fossil fuels such as coal and petroleum, which can remain stable within the geosphere for further millions of years until released by volcanic activity or extracted by humans. While the ideal method of carbon sequestration would be to replenish these long-lived, isolated geologic carbon pools, this is impossible with current technologies, and impractical at a time in which we are still actively extracting these reserves. Three major approaches to terrestrial carbon sequestration are currently being employed are:

- I. Capture of CO₂ emissions to be injected into underground soil or groundwater (Carbon Capture and Storage, CCS)
- II. Increasing the biomass storage pool through revegetation, reforestation, and wetland restoration
- III. Increasing soil carbon pool through improved agricultural techniques and soil amendment

CCS has shown some promise in reducing emissions from electricity generation and other industrial activities, however, the technology as it is being applied can only reduce CO₂ emissions in industrial scenarios and would be expensive to implement by small producers. Identifying appropriate locations for storage of the collected CO₂ is an additional challenge, as regions with porous soil, areas susceptible to seismic activity, or vulnerable to cracking due with the addition of highly pressurized gases could release this carbon back into the atmosphere with little or no retention. Afforestation, reforestation, and wetland restoration hold great

promise in increasing both soil carbon pools and biomass pools in transformed areas (Griscom et al., 2017; Nave et al., 2018), however, this competes with other land use activities.

Conversion of agricultural land into forest land has been found to have little effect on the soil carbon pool, but did enhance total carbon stored in soil and biomass by an average value of 21 Mg C ha⁻¹ in the United States (Nave et al., 2018), or to be associated with between 0.20-0.66 Mg C ha⁻¹ added to the soil pool per year (Post and Kwon, 2000). However, if converted cropland is “outsourced”, with other countries making up for the decrease in US production by converting forests into cropland, there would be no benefit to the process, and may in fact result in higher CO₂ emissions due to transportation costs of agricultural products to the United States. US farms are therefore required to produce an equal or greater yield of food products with reduced land area in order for afforestation, reforestation, and other restoration activities to be effective.

Implementation of programs designed to enhance the soil carbon pool can enhance total carbon sequestration without changing the designated use of land. Modification of agricultural practices from conventional tillage to no-till has been associated with an increased quantity of soil carbon within the 0-30 cm depths due to higher aggregate concentrations, slower breakdown of labile carbon from crop residues, and increase microbial and fungal activity (Sundermeier et al., 2011). Increases in surface soil carbon under no-till cultivation are partially offset by decreases in carbon pools of deeper soil (Baker et al., 2007; Luo et al., 2010) and show substantially decreased carbon sequestration after periods

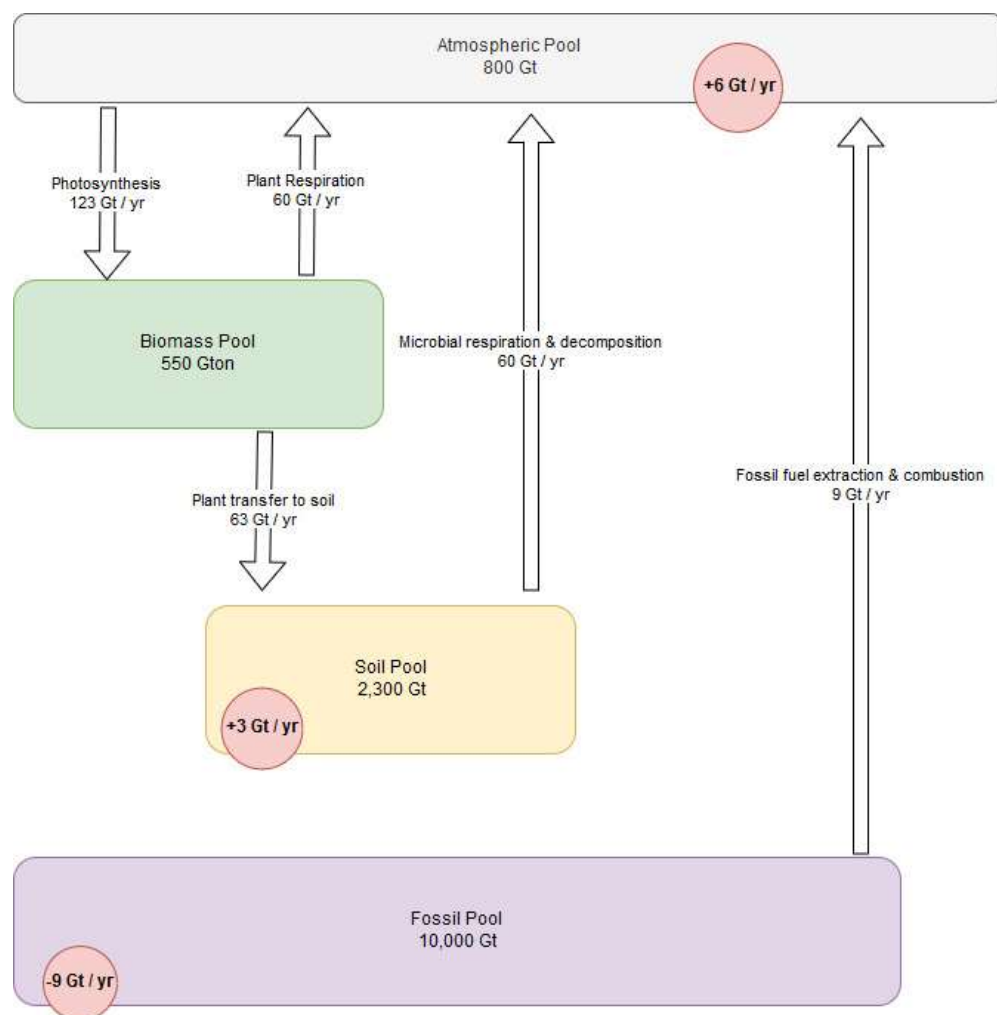


Figure 3.1: Simplified diagram of terrestrial carbon cycle. Boxes represent global carbon pools in Gigatons (Gt) Carbon, arrows yearly fluxes between pools in Gt yr^{-1} , and circles net changes to carbon pools in Gt yr^{-1} . Data adapted from US DOE, 2008.

of 10-30 years (Sundermeier et al., 2011; Johnston et al., 2009) as the soil reaches a natural equilibrium. Amendment of soil with biochar provides a direct route for increasing soil carbon at a level beyond what can be achieved through no-till agriculture, and without the need to wait for carbon to accumulate over three decades.

Biochar, a charcoal-like material produced by heating biomass in the absence of oxygen, is composed primarily of carbon (up to 80% C), exhibits increased stability (i.e., resistance to decomposition) compared to the feedstocks from which it was produced, and can provide a number of chemical, physical, and biological benefits to soil fertility (Barrow, 2012). Like charcoal naturally produced as a result of wildfires, or ancient amendment as seen in the soil of the Amazonian *terra preta de Indio*, biochar can remain in soil for thousands of years after its production (Spokas et al., 2010) and thus represents a suitable material for long-term storage of carbon within soil.

This study attempts to estimate the capacity of biochar to be used to sequester carbon in soil within the United States of America through application at a moderate rate, selected to emphasize secondary benefits to land use such as enhancing crop yield, and at a high rate at which the addition of biochar may not produce meaningful benefits, but do not result in decrease productivity in primary land use or other measures of soil health. Limitations due to the availability of low-cost feedstocks are considered to determine whether shifting focus from historical uses of material, such as bioenergy production, to biochar production would be worthwhile. Viability of carbon sequestration is estimated using a simple exponential decay model to compare decomposition of feedstock material stores versus biochar stores under different scenarios. Similar studies to this have been produced, however, typically focus on a global scale (Woolf et al., 2009; Lehmann, et al., 2006; Smith, 2016), are primarily concerned with energy production rather than carbon sequestration (Laird, 2008), and lack modeling of the fate of feedstock carbon. This study could be more relevant for public policy discussions

than a global analysis, and captures the unique carbon-negative potential of biochar compared to other biofuel options. The inclusion of the decomposition model can inform decisions about feedstocks or locations to implement a biochar management strategy based on the required time for decomposition to emit greater amounts of CO₂ into the atmosphere than the biochar production process. Additionally, it is the opinion of this author that additional studies using biochar are beneficial, if only to keep the idea within the forefront of the discussion on climate change and carbon sequestration.

3.2 Agricultural Application

Agricultural land makes up 915 million acres (370 million hectares) according to the 2012 Census of Agriculture, 40.5% of the total land area of the United States, so improvement in the capacity of agricultural soils to retain carbon could have substantial cumulative impacts (USDA-NASS, 2014). The effects of biochar addition to agricultural plots is the most-studied application of biochar, and has been associated with improving water retention (Pandit et al., 2018b; Zhu et al., 2014; Laird et al., 2010), adjusting soil pH (Zhu et al., 2014; Cornelissen et al., 2018; Mete et al., 2015; Laird et al., 2010), improving potassium and phosphorus availability (Pandit et al., 2018b; Zhu et al., 2014; Mete et al., 2015; Laird et al., 2010), and direct improvements to crop yield (Yeboah et al., 2016; Pandit et al., 2018b; Cornelissen et al., 2018; Agegnehu et al., 2015). Because of these potential benefits, the incorporation of soil biochar amendments into farming practices in the United States will likely occur without outside involvement eventually, however as atmospheric CO₂ levels rise, the value of additional carbon

sequestration may lead to the introduction government sponsored incentive programs for biochar application rates above those that are otherwise commercially viable.

Rate of biochar application to fields found in literature vary widely, with many studies having tested rates around 10 tons biochar ha⁻¹ (Agegnehu et al., 2015), several have ventured up to 40-50 t ha⁻¹ (Pandit et al., 2018a; Lehmann et al., 2006; Egamberdieva et al., 2016), but a reliable maximum application rate has not been established. This is partially because biochars produced from different feedstocks or at different temperatures have distinct properties, which may interact differently with the soil or vegetation at any particular site, but also because high application rates typically do not result in crop performance below that of an unamended plot at any rate viable for field studies (Lehmann et al., 2006). For the purpose of this analysis, a beneficial application rate in agricultural fields of 40 tons ha⁻¹ is used due to studies demonstrating its benefits to corn (Pandit et al., 2018a), soybean (Egamberdieva et al., 2016), wheat (Alburquerque et al., 2013), and no difference in cotton yields (Sorensen and Lamb, 2016). Combined, these four crops make up more than 70% of harvested cropland in the United States (USDA-NASS, 2014). A maximum application rate of 140 tons ha⁻¹ is used because literature showing the effects on crop growth above this rate have not been located and studies near this rate have not shown detrimental effects on crop yields (Lehmann, 2006; Sorensen and Lamb, 2016).

The result of biochar application at rates of 40 or 140 t ha⁻¹ to all agricultural fields in the United States would be 14.8 and 51.8 Gt of biochar, respectively, applied to the soil. Carbon content of biochar varies depending on the feedstock it is produced from and the

temperature at which the biochar is produced, however typically ranges between 60-80% of the total biochar mass (Kloss et al., 2012; Cornelissen et al., 2018; Pandit et al., 2018a). Using a mid-range estimate of 70% carbon content, this would mean 10.4 and 36.3 Gt carbon (38-133 Gt CO₂-equivalents) sequestered within the soil due to application of biochar, compared to the total US emissions of 6.5 Gt CO₂-equivalents in 2017 (US EPA, 2019). However, this is reduced by emissions due to biochar production and transportation of feedstocks and biochar products, limited by the availability of feedstock materials and the fate of those materials were they not used in biochar production, which shall be examined further in this analysis. Additionally, this represents the total stored carbon, not the net carbon, which would require the carbon content of the feedstock material to be released back into the atmosphere through decomposition or combustion before the full sequestration value is realized.

The effect on agriculture of these levels of biochar application is impossible to predict with certainty, but increased crop yield and improved fertilizer use efficiency are very common results from both pot and field studies. Improved crop yields would provide a direct financial benefit to growers, and improved fertilizer use efficiency would provide both an economic and an environmental benefit by reducing fertilizer application rates and decreasing the risk of fertilizer transportation or leaching into surface water or groundwater. Soils amended with biochar exhibit improved water retention in nearly all cases, which would reduce the requirement for irrigation in some areas and could boost agricultural outputs. Economic assessment by Pandit et al. (2018a) suggests that a biochar application rate of 15 t ha⁻¹ is most economically beneficial to corn production without any consideration of the value of carbon

sequestration, though this value could be enhanced by improving production efficiency to reduce biochar costs or by providing landowners credit for increased soil carbon storage.

3.3 Forestry Application

Forest land available for timber harvest in the United States accounts for 514 million acres (208.2 million hectares), 22.8% of the country's total land area (Oswalt et al., 2014). The effects on forest growth due to biochar addition are less widely-studied than agricultural impacts, although these studies are supplemented by additional research assessing the impacts of wildfire-produced charcoal. Makoto et al. (2010) found positive effects on growth for *Larix gmelinii* (Dahurian larch), a fire-associated tree species, due to charcoal additions, with improved growth from distribution of charcoal onto the surface of the soil compared to distribution throughout the entire soil, suggesting that plowing to incorporate applied biochar may not be necessary to produce positive effects in forests. Biochar additions have also been associated with greater biomass production in lodgepole pine and sitka alder (Robertson et al., 2012), Scots pine, Norway spruce, aspen, and downy birch (Pluchon et al., 2014), sugar maple and honey locust (Scharenbroch et al. 2013), *Moringa oleifera* (Fagbenro et al., 2013), and others. Meta-analysis conducted by Thomas and Gale (2015) of 17 studies on 36 tree species found positive effects of biochar application on plant growth in boreal, tropical, and temperate forests, for both conifer and hardwoods, with both short (less than 6 months to 1 year) and longer (1-4 years) studies, and found no statistical difference between results of field studies and those of pot or greenhouse studies. Large variability was observed in results of different

studies which included the same tree species, so while it appears that biochar amendment is beneficial to tree growth, determining an economically viable level of intentional biochar addition is not currently possible.

As with agricultural studies, while the majority of studies on forests and tree growth have assessed the influence of biochar application rates of 0-50 t ha⁻¹ (Thomas and Gale, 2015), a maximum level has not been determined and positive effects on shoot height and root volume were observed even in growing media composed of 60% biochar (Heiskanen et al., 2013). This is equivalent to an application rate of several hundred t ha⁻¹, far beyond what would be feasible to apply to soil in field conditions. Since plowing of forest soils is not typical, a maximum biochar application rate of 40 t ha⁻¹ to forested land was selected to avoid excessive layering of biochar upon the surface.

A single application of 40 t ha⁻¹ of biochar to all timberland in the United States would require 8.3 Gt of biochar and result in 5.8 Gt carbon sequestered (21.3 Gt CO₂-equivalents) assuming 70% C content of biochar, approximately 90% of US annual total CO₂ emissions (US EPA, 2019). The effects of this application on forest growth and other relevant considerations is unclear. Although increases in biomass production have been observed in a number of studies, these are often focused on growth of young trees (Thomas and Gale, 2015), and the effects on older forests are likely to be diminished or absent. Studies on long-term effects of biochar addition on other forest properties are lacking, and therefore this proposal does carry additional risks compared to agricultural applications from unforeseen interactions (McElligott et al., 2011).

3.4 Biochar Production

Production of biochar is typically conducted using either “fast” pyrolysis, using high temperatures for durations as short as seconds (Bridgwater et al., 1999) to produce primarily a liquid fraction known as bio-oil, or “slow” pyrolysis that typically takes place over an hour or more but favors production of gaseous products, called syngas, and the solid biochar (Al Arni, 2018). Because bio-oil and syngas, a mixture of carbon monoxide, carbon dioxide, methane, and hydrogen gases, lack applications apart from combustion as a fuel source, their yield is irrelevant to carbon sequestration goals, but could be used to offset fossil fuel use as a biofuel. Slow pyrolysis is the typical method used for biochar production and is the one evaluated for pyrolysis of feedstocks in this study (Gaunt and Lehmann, 2008).

During pyrolysis, about 50% of the carbon contained within the feedstock material is converted to bio-oil or syngas, which will return to the atmosphere when consumed (i.e., vented or burned), but about 50% of the carbon is converted to biochar (Lehmann, 2007). In contrast to this, the burning of biomass, as frequently conducted in clearing of agricultural fields or during forest thinning for fuel reduction, instantly releases 97% of the biomass carbon. Natural decomposition of biomass releases carbon gradually over time, but under most conditions will continue until most or all of the contained carbon has been returned to the atmosphere and the input and loss of carbon to soil is at a steady state. Within agricultural systems, 90% of biomass carbon returns to the atmosphere in 5-10 years (Lehmann et al., 2006). Decomposition of forest slash is more varied, but estimated half-lives of debris, the time required for half of the material present to decompose, have been estimated around 10 years

for hardwoods and 18 years for conifers located in the eastern United States (Russell et al., 2014), with typical decomposition rates higher in the warm and humid southeast and lower in the Pacific Northwest, where conditions are usually either cool and wet or warm and dry, but rarely warm and wet. The long-term carbon sequestered by biochar is equal to 80-90% of its total carbon content, as a fraction of the biochar decomposes, while the remainder is stable over timescales in the hundreds to thousands of years (Lehmann et al., 2006). Although there is an energy cost associated with pyrolysis of feedstocks to produce biochar, studies indicate that combustion of the syngas produced is often sufficient to make up for the energy inputs to the system without considering the energy content of the bio-oil fraction (Cong et al., 2018), although this does not include energy costs for feedstock collection, processing, or transportation. The net carbon sequestration associated with biochar production is therefore the difference between carbon content of the biochar produced versus the biomass that would have resisted decomposition, minus any production-associated carbon costs.

A critical component of any large-scale biochar production effort would be the acquisition of mobile pyrolysis units. These units, mounted into truck beds or built within shipping containers, can be hauled to farms, timber harvest sites, or other remote locations and convert biomass into biochar on-site. This allows the use of raw material that is otherwise too costly to transport, such as treetops and small woody debris, that is typically left at the harvest site. Additionally, mobile pyrolysis units decrease the economic barrier to entry, as individual farmers would not be required to operate pyrolysis kilns themselves but could contract with a company or government organization to convert crop wastes into biochar. A study of financial

viability of mobile pyrolysis using a prototype system developed by The Biochar Solutions Inc. found that it was possible, though unlikely, to make a profit through conversion of sawmill residue into biochar to be resold (Kim et al., 2015). However, this study did not capture the syngas or bio-oil generated during pyrolysis, nor consider the value of carbon sequestration. The authors note several mechanical changes, some of which the manufacturer was already implementing for the next iteration of the portable pyrolyzer design, that would enhance the likelihood of profitability, making it reasonable to assume that more advanced mobile pyrolysis units would be a profitable venture. Other studies have confirmed economic viability of mobile pyrolysis at current market values using different feedstock materials and note the increased profitability if carbon subsidies or other appropriate programs are introduced (Sahoo et al., 2018; Meyer et al., 2011).

3.5 Feedstock Availability

Sequestration of large quantities of carbon will require larger quantities of feedstock materials from which to make the biochar. The selection of feedstock for biochar production has implications on the properties of the final product which are critical for certain applications, but not so for the goal of carbon sequestration. Ideal feedstock materials should have little economic value or few competing uses and be collectable with minimum investment of energy in order to maximize net carbon storage while minimizing cost. Feasible biochar feedstocks would include residues associated with the harvesting and processing of timber, crop waste or residues that are frequently burned or left in the field, or yard trimmings collected as municipal

solid waste. Potential feedstocks that are not considered feasible are animal manures, which have value as a fertilizer and soil amendment, merchantable timber, and crops themselves.

Agricultural residues, the portions of plants left on the field after crop harvest or removed during processing, are an attractive feedstock for biochar production. The Harvest Index (HI) of a crop is the ratio of dry crop yield to total plant biomass, and typically ranges from 0.4-0.6 for commercial crops in the United States (Smil, 1999), indicating that roughly half of the produced biomass is residue. An HI value of 0.4 for cereal crops (Smil, 1999) would calculate that the United States produces approximately 435 million tons of crop residue from the growth of corn alone (USDA-NASS, 2014). Farming operations typically leave a significant portion of this residue on the field to be plowed into the soil to return key nutrients, nitrogen, phosphorus, and potassium, and to protect soil from erosion until new plants are established (Doran et al., 1984; Smil, 1999), although an estimated 15% of residues are burned in-field in developed countries (Smil, 1999). Although the removal of crop residues would necessitate additional application of fertilizers, the return of the produced biochar would provide similar level of most nutrients as the removed residues, although a portion of contained nitrogen compounds are lost during pyrolysis. As improved fertilizer use efficiency is a frequent result of biochar application, this conversion is not expected to significantly change nutrient dynamics so long as the biochar produced remains within the same agricultural system, although supplemental nitrogen fertilization may be required. An estimate of the annual production of crop residues in the United States, calculated from annual crop production (USDA-NASS, 2014) and estimated HI values (Smil, 1999), yields 645 million tons of dry residue per year from the

top five agricultural products (USDA-NASS, 2014), summarized in Table 3.1. This value matches those found in literature of 550 (Johnson et al., 2011) to 660 million tons (Lehman, 2007) of total residue.

Potential biochar feedstocks from forested land consists of two primary groups: logging residue and processing residue. Logging residue is the portion of trees deemed unsuitable for commercial processing, including treetops, branches, limbs, rotted or dead trees, small trees and trees of non-commercial species, all of which are typically left at the site of harvest (US DOE, 2011). Reported estimates of the dry mass of logging residues produced annually in the United States vary significantly, with low values of 45-52 Mt (Walsh et al., 1999; Gan and Smith, 2006), mid-range estimates of 68 Mt (US DOE, 2011), and one particularly high estimate of 700 Mt (Lehmann, 2007). Assuming 75% of the 68 Mt of residue reported by the

Crop	Harvest Index (a)	Annual Production (Mt) (b)	Residue Production (Mt)
Corn	0.40	290	435
Soybean	0.49	88	92
Sorghum	0.40	7	10.5
Wheat	0.40	66	99
Cotton	0.33 (c)	4	8
Total			645

Table 3.1: Annual crop and residue production in the United States. Units in millions of dry tons. (a) Harvest Indices obtained from Smil, 1999. (b) Mass of crop production from USDA, 2014. (c) Value obtained from Gifford et al., 1984.

US Department of Energy is recovered, to account for residues distant from roads, particularly minute wood fragments, or other unrecoverable components of harvest residue, there would

be 51 Mt of timber residue available annually that is currently unused. Harvest guidelines typically suggest that 30% of logging residues should be left on-site to prevent nutrient deficits, provide habitat for wildlife, and prevent soil erosion (US DOE, 2011; Helmisaari et al., 2011). Returning the produced biochar to the soil where the feedstock is from would likely be more effective at preventing nutrient deficiencies than retaining 30% of slash at the location of harvest, but it would be ineffective at resolving these other issues, thus these estimates of available biomass may not properly account for essential residues which should remain on-site. Thinning of overstocked forests within fire-prone areas of the United States could generate an additional 29 Mt of feedstock per year, and conversion of timberland to other land uses generates 25 Mt of unused residue annually (US DOE, 2011).

Additional wood residues are produced during processing of harvested timber, such as bark and sawdust, which could be converted to biochar. However, the majority of this residue is either converted into high-value products or co-fired in boilers to generate energy at the production site. The reported mass of primary mill residue (produced from the conversion of raw logs into lumber, plywood, or pulp) is 51-87 Mt annually in the United States (Walsh et al., 1999; US DOE, 2011; Oswalt et al., 2014) with as little as 0.8% of that going unused (Oswalt et al., 2014). However, the majority of these residues are consumed as fuel in cofiring boilers, which are relatively inefficient and capture only 33-37% of the energy content of the wood (US DOE, 2000). Depending on the process parameters used, pyrolysis of the same feedstock can result in 38-50% energy efficiency without consuming any of the produced char (Gaunt and Lehmann, 2008) resulting in equal or greater energy production and a valuable secondary

product for sale or use. Therefore, it is assumed that both unused residues and those consumed as fuel are available as pyrolysis feedstocks, approximately 41 Mt annually (Walsh et al., 1999; US DOE, 2011). Studies of secondary mill residues are sparse, however the one published inventory found estimates 15.6 Mt of these residues are generated annually (US DOE, 2011) of which 67% are unused or consumed as fuel (Rooney 1998).

Forestry-derived Feedstocks	Annual Availability (Mt)
Harvest Residue	51
Timberland Conversion	25
Forest Thinning	29
Primary Mill Residue	41
Secondary Mill Residue	10
Total	156

Table 3.2: Summary of available wood-derived biomass for use in biochar production annually. Values are based upon literature from US DOE (2011), Walsh et al. (1999), Oswalt et al. (2014), and Rooney (1998). Total value calculated is similar to that reported by US DOE (2011) of 142 Mt and differs due to modified assumptions regarding alternative uses.

A fraction of Municipal Solid Waste (MSW) is suitable for use as biochar feedstocks, including wooden pallets and packing material, yard waste, and construction or demolition debris. Making use of these materials is difficult, as it cannot be reliably processed due to size differences, may contain wildly varying levels of moisture, and could be contaminated by other waste. However, many localities offer distinct collection of yard cuttings, which could be utilized without facing the same issues. National estimates based on state environmental

agency reports indicate approximately 35 Mt of yard waste is collected as MSW annually (US EPA, 2018) which could be converted to biochar at centralized pyrolysis units.

3.6 Modeling of Biochar Carbon Dynamics

3.6.1 Model Setup

To assess the net carbon sequestration potential of biochar compared with natural decomposition, a simple exponential decay model was created according to the equation:

$$\text{Equation 3.1} \quad C_{slash} = A * e^{-Rs*t}$$

where C_{slash} is the total carbon store as slash, A an arbitrary value of biomass input, Rs the decomposition rate-constant for slash, and t the time. To account for the carbon lost during the pyrolysis process, the store of biochar carbon follows the equation:

$$\text{Equation 3.2} \quad C_{bioch} = (Eff * A * e^{-Rb*t}) * (1 - P)$$

with Rb the decomposition rate-constant for biochar, Eff the efficiency of biochar carbon conversion (i.e., the percentage of biomass carbon that is retained in the biochar) and P the production offset, the percentage of biochar which must be burned as fuel to produce energy equivalent to that consumed in the transportation of equipment and feedstocks, delivery of biochar products, and powering pyrolysis. A “mixed” scenario is created in which a set percentage of slash is converted to biochar, while the remainder is left as slash, according to the equation:

$$\text{Equation 3.3} \quad C_{mix} = (A * e^{-Rs*t})(1 - M) + (Eff * A * e^{-Rb*t}) * (1 - P)(M)$$

with M the percentage of slash to be converted to biochar. A Harvest Frequency is set which adds A units of biomass, or $A \cdot Eff$ units of biochar, to each system whenever the set duration has elapsed. The model was allowed to reach a stable equilibrium with zero biochar production to estimate the carbon stores of sustainably managed lands without interference and better represent the starting point of site conditions before the alteration of management practices. A landscape-level approximation of feedstock residue and biochar present is produced by averaging the values of each over the most recent fifty years to simulate fifty plots at different stages in the harvest cycle. A summary of parameters and their tested ranges is presented in Table 3.3. Decomposition rates evaluated ranged from 0.01 - 0.30 yr^{-1} for forest systems, indicating between 1% and 30% of harvest residue or slash present decays each year, as typical literature values fall within this range (Fasth et al., 2011; Russell et al., 2014; Wagener and Offord, 1972; Spaulding and Hansbrough, 1994; Gill and Andrews, 1956; Childs, 1939). Decomposition rates for agricultural systems were determined by testing values to reach appropriate concentrations of remaining residue over time matching literature, ranging from 0.30 - 0.90 yr^{-1} on a yearly basis or scaled to appropriate monthly rates. Harvest interval, the frequency that harvest residue is generated, was varied between 1 and 100 years. A conversion factor of 50% was applied to biochar production, resulting in biochar with only half of the carbon content of the material from which it is generated, to approximate typical modern conversion yields.

Parameter	Range	Source
Decomposition Rate	0.01-0.30 yr ⁻¹ (forest) 0.30-0.90 yr ⁻¹ (crop)	Fasth et al. (2011), Lehmann & Gaunt (2006)
Harvest Frequency	1-100 years	Oswalt et al. (2014)
Percent Slash Converted	0, 50-100%	Assumed
Production Offset	0-50%	Assumed
Biochar Carbon Conversion Efficiency	50%	Lehmann (2007)
Biochar Decomposition Rate	0.001-0.002	Wang et al. (2016)

Table 3.3: Model parameters and range of tested values.

3.6.2 Results of Modeling Analysis

The most significant factor in positive carbon sequestration under biochar production is the natural decomposition rate of the slash or crop residue generated. Observed decomposition rates within forest stands depend upon local temperature and precipitation, degree of shading, tree species, types of fungi present, diameter of the slash debris, and additional factors (Fasth et al., 2011; Wagener and Offord, 1972), making it difficult to establish typical or average decomposition rates at any large scale. Studies of the residence time of forest slash indicate that under conditions found within some Northeast and Southwest forests, complete decomposition can occur within 20 years (Spaulding and Hansbrough, 1994; Gill and Andrews, 1956) and as much as 90% of Douglas fir slash can decompose within 16-20 years (Childs, 1939), corresponding to approximate decomposition rates of 0.20 and 0.11 yr⁻¹, respectively. Observations by Fasth et al. (2011) in North Carolina measured decomposition rates ranging from 0.06-0.33 yr⁻¹ for fine woody debris. When decomposition rate exceeds 0.20

yr^{-1} , carbon content of residues decreases below that of the biochar that could be produced within 4 years. At a decay rate of 0.10 yr^{-1} , this break-even point occurs between 6-7 years after harvest, after which biochar production results in enhanced carbon storage relative to unmodified slash. With a rate of 0.05 yr^{-1} , there is an estimated 30-50 years to realize a net benefit from biochar production depending on frequency of harvest, which extends beyond 100 years as decomposition rates further decrease.

At the landscape level, the level of carbon storage depends on the rate of decomposition of the residue and the frequency of harvest. A decay rate of 0.2 with a harvest every 25 years results in a stable carbon store equivalent to 20% of the residue generated per harvest, while biochar production results in a continuous increase equal to 47-48% of residue carbon per harvest cycle. Lower decomposition rates result in a higher baseline carbon at the landscape level, but all tested combinations of conditions reached a steady carbon storage level, while biochar application results in a near-linear increase in carbon storage for hundreds of years. More frequent harvests result in a higher baseline carbon storage from harvest residue which requires longer periods of biochar production to match, but also increase the rate of biochar accumulation, and thus has a mixed impact on the viability of biochar

application compared to decomposition rate at the landscape level. Harvest frequencies of 10, 25, and 50 years require 30, 18, and 16 years, respectively, for biochar production to store equal quantities of carbon at the landscape level with a slash decomposition rate of 0.10.

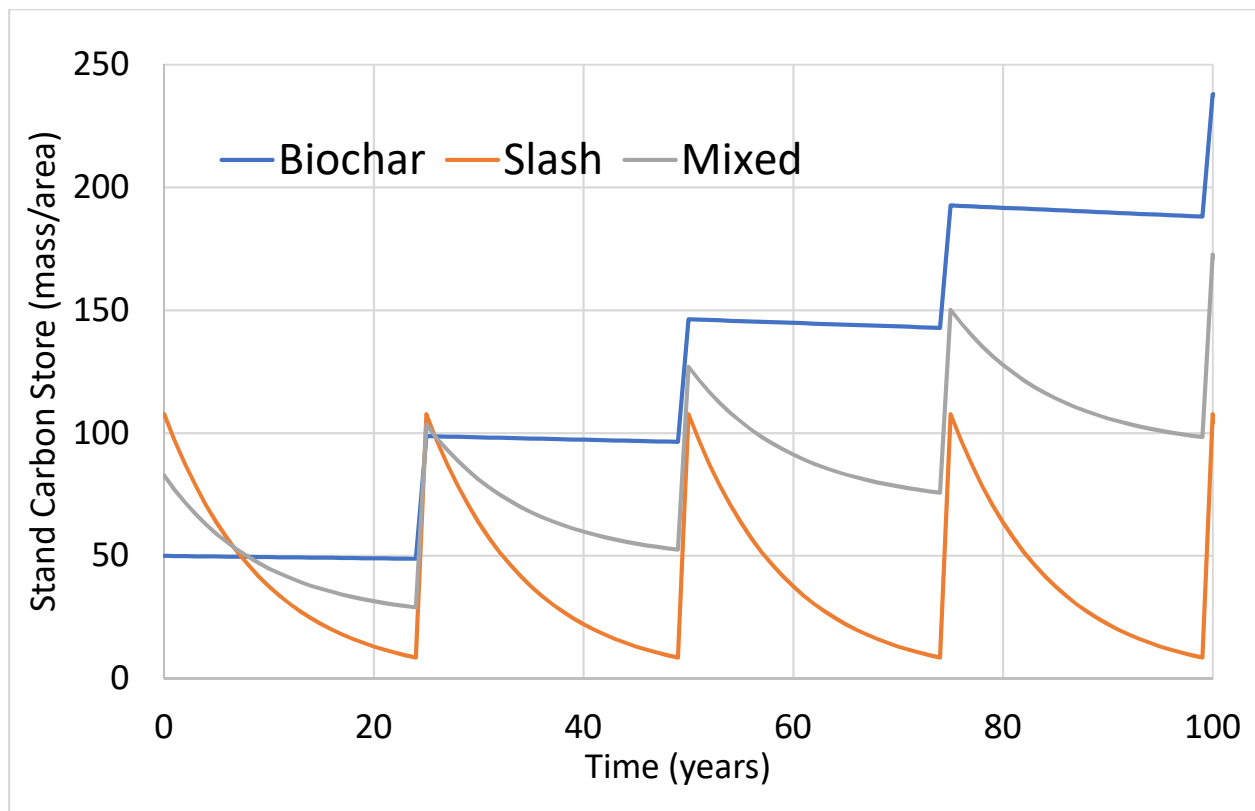


Figure 3.2: Example of Stand-level Carbon Stores over time. Decomposition rate = 0.1, Harvest Interval = 25 years. At each harvest, 100 arbitrary units of residue are generated and either left without alteration (slash) or converted to biochar with 50% yield. Under this Mixed scenario, 50% of residue is converted to biochar and 50% is unmodified. A break-even point occurs between 7-8 years, after which biochar carbon exceeds slash carbon.

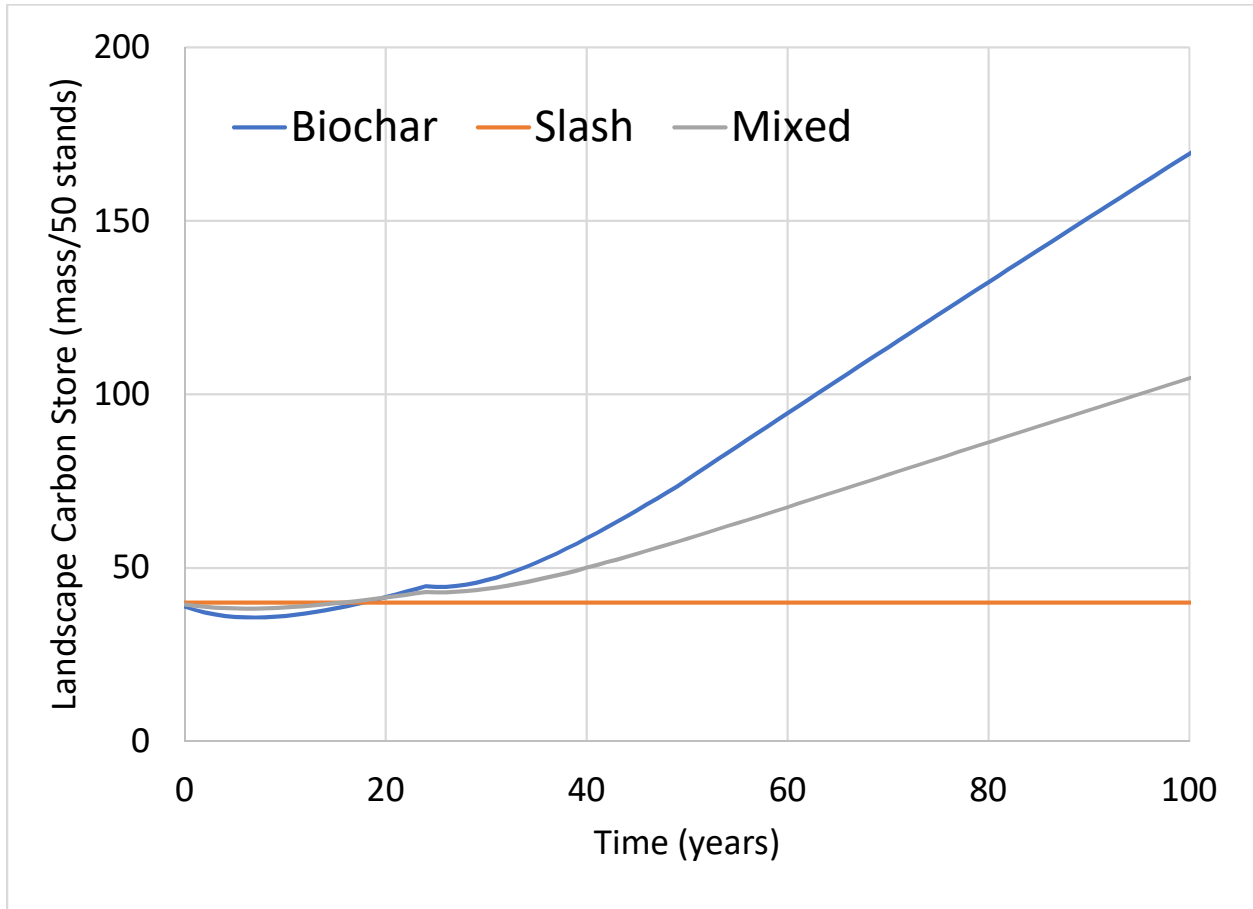


Figure 3.3: Example of Landscape-level Carbon Stores over time. The average carbon store of fifty identical forest stands at different stages of production with Decomposition Rate = 0.10, Harvest Interval = 25 years. Leaving residue as slash results in a constant, stable store of carbon, while switching from this to a biochar-based management strategy results in a relatively small carbon debt during the initial period, followed by substantial accumulation of landscape carbon over time. The mixed scenario results in a reduced carbon debt but does not substantially change the time required to repay that debt. Mixed scenario displayed is 50% slash, 50% biochar.

Converting only a portion of the generated residue into biochar results in an intermediate scenario in which the initial carbon loss from biochar production is reduced, but the long-term carbon accumulation is also diminished. This would shorten the time required to achieve equal carbon storage, particularly under conditions of low decomposition, however there are relatively few borderline scenarios in which the difference in time seems to justify the reduced carbon sequestration rate. In one low-decomposition scenario, conversion of 50% of feedstock to biochar rather than 100% reduces the time to break even on carbon storage from 82 years to 59 years, however both of these are still beyond the time scales appropriate for climate change mitigation. At decomposition rates above 0.05, the reduction in time to yield benefit between a pure-biochar and a 50% mixed scenario maximizes at only 1-2 years but halves the rate of stable carbon accumulation.

To account for the carbon emissions from equipment transportation, collection of feedstock material, and biochar production, a production offset was tested which reduced the quantity of biochar produced. Because biochar can be burned as a fuel, this is conceptualized as the percent of biochar that must be combusted to replace the energy consumed in its production. This factor reduces initial carbon storage and reduces the rate of carbon accumulation from biochar production, but ultimately has relatively small influence on biochar viability. With a decomposition rate of 0.10 yr^{-1} and a harvest interval of 25 years, production offsets of 0%, 10%, and 20% result in biochar favorability at the stand level occurring after 8 years, 9 years, and 10 years, respectively. A 50% production offset approximately doubles the time required to enhance carbon stores for short time scale scenarios, with an even greater

impact in longer time scales. The magnitude of difference between scenarios is smaller with higher residue decomposition rates and lower harvest frequency, and larger with slow decomposition and frequent harvests, conditions which accumulate significant quantities of harvest residue. Because low decomposition rate is already prohibitive to effective biochar sequestration strategies, the relationship between harvest frequency and production efficiency is of greater interest. If harvest frequency increased from every 25 years to every 10 years, with decomposition rate held at 0.10 yr^{-1} , the time to break even will increase from 20 years without an offset to 30 years with a 20% production offset, and 54 years with a 50% production offset, which suggests that sites harvested more frequently require more efficient production to be viable. Current pyrolysis technology often includes the combustion of syngas and collection of bio-oil, both of which could potentially replace fuel consumption that would contribute towards the production offset, which would contribute towards smaller production offset values. Particularly for feedstocks that require substantial time investment to yield benefits in ideal cases, a case-specific analysis should be performed to determine whether these production-related carbon costs would shift the carbon balance into an unfavorable position within the desired timeframe for enhancing storage.

Decomposition rate of biochar within the tested range only had noticeable impacts on extremely long time scales. With slash decomposition rate of 0.05 and a harvest frequency of 25 years, the difference in time required to break even on carbon storage changes by less than one year when biochar decomposition rate increases from 0.001 to 0.002, approximately 32 years in either case. The difference in carbon storage is 10-15% less after 300 years of biochar

production at the higher decomposition rate, however after this period of time both scenarios have resulted in substantial increases in carbon storage versus the alternative methods, therefore this parameter does not influence the conclusions drawn.

Within agricultural systems, harvest could occur one or multiple times per year, with typically high decomposition rates capable of breaking down the majority generated residues over 5 years, and the potential for more than 80% of material to decompose within one year (Al-Kaisi and Guzman, 2013). Under these conditions, the time required for biochar to result in improved carbon storage can be measured in months, rather than years. When 90% of crop residue decays within the first year, a net benefit from biochar production is found after just four months. If it requires two years to reduce residue by 90%, the advantage of biochar over residue is observed after 16 months. At this rate but two harvests per year, each generating equal amounts of residue, every 14 months of biochar production accumulates carbon equal to that present in each harvest's residue.

3.6.3 Limitation of the Model

This model was intended only to provide a rough approximation of the decomposition of biochar and crop or forest residues under generalized conditions. More sophisticated models which distinguish labile and recalcitrant components of biomass and biochar, or further differentiate components of feedstock such as leaves, small branches, and logs, could provide more accurate representation of biomass decomposition, but this level of detail was not considered necessary to draw the desired conclusions of this study. Decomposition rate is

modeled as a constant exponential decay, however changes to local conditions including temperature and precipitation may cause significant fluctuations in rates of decomposition over the modeled time, which are not accounted for. The range of decomposition rates tested was intended to represent the range of values reported in literature, however such literature is often restricted to small geographic regions, incomplete, or unclear, thus the values tested may not be appropriate for all conditions. This model considers only the carbon content of biomass and biochar, which may overlook other aspects of biochar production, such as differences in nutrient content, that would necessitate additional inputs to forest or agricultural systems. It is assumed that the modeled land is managed in the same way for sufficient time to reach a steady state, and that no major disturbances occur. Events such as floods, wildfires, or drought could result in significant alteration in the quantity and timing of feedstock materials and the decomposition rates of both feedstock and biochar present. In particular, wildfires may result in the combustion of biochar present on or near the surface of the soil, thus caution should be taken when applying these results to fire-prone forests. The Mixed scenario assumes that the two fractions, the one to be converted to biochar and the one to be left to decompose, are the same, whereas a practical application would likely choose rapidly-decomposing materials for biochar and retain materials which decompose more slowly, resulting in more favorable outcomes than modeled.

3.7 Carbon Sequestration Potential

The capacity of forest and agricultural soils to sequester carbon is substantial and exceeds the annual greenhouse gas (GHG) emissions several times over, however, there is simply not enough available feedstock to realize more than 1.4% of this capacity annually. To achieve even this level of carbon sequestration would require a monumental effort to construct a network of pyrolysis units, both centralized and mobile, to efficiently collect raw materials across the country from thousands of private individuals, including materials typically used for alternative purposes, and to redistribute the produced biochar back onto the areas from which it was sourced. Based on the mass of feedstock available, assuming 50% C content for all feedstocks and 53.5% of feedstock C is retained in produced biochar (Lehmann et al., 2006), 223.6 Mt of C can be converted to biochar and sequestered annually by the United States, equivalent to 819.4 Mt of CO₂. This would comprise 12.6% of annual emission of GHG in the United States (US EPA, 2019). While the pyrolysis of feedstock material would result in the instantaneous emission of significant amounts of carbon dioxide that would otherwise remain tied up in biomass, the decomposition of biomass from agricultural residues and yard waste would likely equal or exceed pyrolysis emissions in under three years (Lehmann and Gaunt, 2006; Al-Kaisi and Guzman, 2013), and forest residues within 10-20 years (Russell et al., 2014; Fasth et al., 2011). The upside to the feedstock limitation on carbon sequestration is that repeating the cycle of collection, pyrolysis, and distribution every year will likely never reach the maximum beneficial concentrations of biochar within the soil, as older material sinks within

the soil profile, extending the time required for excessive application of biochar to cause damage to soil systems.

Feedstock Source	Annual Available Mass	Biochar Carbon (a)	Soil Capacity
Agricultural Residue	645	172.5	10,400-36,300
Forestry Residue	156	41.7	5,800
MSW	35	9.4	NA
Total	836	223.6	16,200-42,100

Table 3.4: Summary of biochar carbon sequestration potential. Total available feedstock materials, estimated mass of carbon in biochar produced, and the estimated capacity of agricultural and forest soils for biochar amendment, units in Mt yr⁻¹. (a) Calculated assuming 50% C content of feedstock and 53.5% of total feedstock carbon retained in biochar, per Lehmann et al., 2006.

Improvements to pyrolysis technology may result in less expensive and more energy efficient systems, however, the proportion of biomass carbon that can be retained as biochar is unlikely to change significantly. Instead, the focus should be on increasing availability of feedstock materials, particularly those which decompose relatively quickly, to increase carbon sequestration potential. One substantial source not considered previously is the diversion of bioenergy crops for biochar production. Woolf et al. (2010) found that the emission mitigation potential of biochar production using bioenergy crops is 22-27% higher than use of those crops for biofuel production, a difference they ascribe to improved crop yield and reduction in soil GHG fluxes associated with biochar application. Further, the mitigation potential of bioenergy is largely connected with the emissions impact of replaced fuels, with large mitigation for replacing coal firing, but next to no mitigation for replacing renewable or nuclear power (Woolf et al., 2010). As much as 800 Mt of bioenergy crops can be produced annually by 2030 (US DOE, 2011) which could be converted to biochar to nearly double the total carbon

sequestration with an additional 214 Mt carbon if sufficient alternative energy capacity was developed. Carbon sequestration could further be enhanced through strategic application of biochar to degraded or contaminated soils to increase biomass, such as infertile farmland, abandoned mine sites, or other inhospitable soils.

3.8 Conclusion

Modeling of carbon dynamics show that conversion of crop residue, forest slash, and other biomass will sequester greater quantities of carbon than allowing these feedstocks to decompose naturally when compared on long time scales. The viability of these processes to mitigate climate change becomes a question of speed, in which the long-term stability of biochar must be balanced with the immediate emission of half of the feedstock carbon as CO₂. This simple modeling shows that when decomposition rate is above 0.05 yr⁻¹, as would be expected for much of forest slash and likely all crop residue, carbon storage above that provided by unmodified biomass is possible within 30-40 years and rapidly accumulates after this break-even point is reached. This time frame may be sufficient, assuming substantial CO₂ emission reduction strategies are also enacted in the meantime, to avoid runaway climate change. Should more rapid sequestration of carbon be imperative, targeting feedstocks that are decompose quickly could yield benefits within just a few years. With an understanding of the decomposition rates of different biomass components in a given location, decisions could be made to leave the fractions which decompose more slowly, such as coarse woody debris, to tailor management strategies to maximize carbon storage within a given period of time.

Focusing implementation within agricultural systems appears more promising with the current understanding of carbon cycling and the effects of biochar application. The breadth of research on the effects of biochar within agricultural soils is greater than within forests, leading to less uncertainty with its application. Crop residues are particularly suited to biochar production, as typical decomposition rates are sufficiently high that conversion to biochar shows benefits within as little as two years. Frequent harvests result in a steady supply of feedstock material for biochar production, which can be collected, processed, and reapplied to fields with substantially less effort than the same process in a forest stand.

Converting timber harvest residues into biochar does appear to be viable as a carbon sequestration method, however, the time required for this to be beneficial is longer than with crop residues. Additionally, as the effects of biochar application within forests is less thoroughly understood, the introduction of this variable must be carefully considered. Analysis of slash decomposition would be necessary to identify areas and materials suitable for biochar production, as well as an analysis of the effects of biochar application at whatever rate is sustainable for those identified sites.

Considerations regarding the time to enhance carbon storage assume that the feedstock material would otherwise be left to decompose over time. A significant portion of these materials are burned to clear fields or reduce fuel in forests. Under these circumstances, production of biochar enhances both immediate and long-term carbon sequestration. Although these potential feedstocks make up a small portion of the total available, they could

be used to generate biochar for further research with reduced risk to ecosystem stability associated with removal of habitat or substantial changes to local carbon cycling conditions.

It will undoubtedly take time to establish the framework necessary and develop the relationships with landowners required for implementation of a large-scale biochar sequestration strategy, and thus it should not be delayed if biochar is to be a part of future climate solutions. Integration of biochar production and application into management of agricultural and forested lands could sequester enough long-term carbon to offset one-eighth of U.S. GHG emissions annually while enhancing productivity of farms and restoring degraded land. As the country and the world transitions to renewable energy and eliminating GHG emissions, biochar continues to maintain efficacy in enhancing carbon storage and could be a critical factor in reversing the accumulation of atmospheric carbon dioxide.

Chapter 4: Conclusion

This study found that biochar produced at high temperatures underwent only very minor chemical and thermal changes during storage over a period of seven months as measured by FTIR and DSC/TGA. This is beneficial for centralized production facilities as it is not necessary to produce biochar to-order, instead it can be produced as feedstock becomes available and distributed according to customer demand over the following year. Biochar produced at lower temperatures underwent greater chemical and thermal changes during storage ascribed to degradation of cellulose and hemicellulose structures, however, it is unclear how these changes will influence biochar applications without additional study. Low temperature biochar may be more suitable to production in mobile pyrolysis systems, as it can be immediately applied to soil, but until the effects of fresh biochar versus aged biochar are better understood, this is uncertain. Storage in plastic was associated with an increase in water and volatile compounds in both high and low temperature biochars. Seven months of storage did not appear to cause any changes that would preclude such conditions, which is promising for expanded production and applications.

With the right incentives to encourage construction of production facilities, and credits for use of biochar as a soil amendment to sequester carbon, there is significant potential to offset up to 12.6% of GHG emissions in the United States. Because the capacity for biochar in soil far exceeds potential production, any type of biochar produced is likely to find a beneficial application, and biochar can be directed to maximize environmental or economic benefits according to the project goals. If the share of renewable and nuclear energy grows, shifting

bioenergy crops towards biochar production would provide even greater emissions mitigation, and nearly double the carbon sequestration potential. Production of biochar is associated with a short-term increase in atmospheric CO₂ compared with leaving feedstock material to decompose, but modeling conducted herein has estimated that increase is offset in less than five years for agricultural residues and between 10-50 years for most forest residues as these materials decompose. This period of time could be minimized through selection of materials which decompose more rapidly to tailor the carbon management strategy to suit the time available for climate change mitigation. Because the model utilized was designed for a nation-scale analysis, it required simplification and generalization of several factors which may prove critical to effective carbon sequestration. Before any biochar management program would be implemented, a more sophisticated model that takes into account local influences such as forest species composition, climate, and transportation distances, should be consulted to more accurately assess the net effects of biochar production. Without immediate action to reduce CO₂ emissions in the short-term, the continued rise of atmospheric carbon levels will require more rapid mitigation in the future, precluding the use of potential biochar feedstocks until only those with near-immediate benefits would be viable.

Bibliography

- Abiven, Samuel, Pascal Hengartner, Maximilian P.W. Schneider, Nimisha Singh, and Michael W.I. Schmidt. "Pyrogenic Carbon Soluble Fraction Is Larger and More Aromatic in Aged Charcoal than in Fresh Charcoal." *Soil Biology and Biochemistry* 43, no. 7 (July 2011): 1615–17. <https://doi.org/10.1016/j.soilbio.2011.03.027>.
- Agegehu, Getachew, Adrian M. Bass, Paul N. Nelson, Brian Muirhead, Graeme Wright, and Michael I. Bird. "Biochar and Biochar-Compost as Soil Amendments: Effects on Peanut Yield, Soil Properties and Greenhouse Gas Emissions in Tropical North Queensland, Australia." *Agriculture, Ecosystems & Environment* 213 (December 2015): 72–85. <https://doi.org/10.1016/j.agee.2015.07.027>.
- Al Arni, Saleh. "Comparison of Slow and Fast Pyrolysis for Converting Biomass into Fuel." *Renewable Energy* 124 (August 2018): 197–201. <https://doi.org/10.1016/j.renene.2017.04.060>.
- Alburquerque, José Antonio, Pablo Salazar, Vidal Barrón, José Torrent, María del Carmen del Campillo, Antonio Gallardo, and Rafael Villar. "Enhanced Wheat Yield by Biochar Addition under Different Mineral Fertilization Levels." *Agronomy for Sustainable Development* 33, no. 3 (July 2013): 475–84. <https://doi.org/10.1007/s13593-012-0128-3>.
- Al-Kaisi, Mahdi M., and Jose G. Guzman. "Effects of Tillage and Nitrogen Rate on Decomposition of Transgenic Bt and Near-Isogenic Non-Bt Maize Residue." *Soil and Tillage Research* 129 (May 2013): 32–39. <https://doi.org/10.1016/j.still.2013.01.004>.
- Barnes, R. J., M. S. Dhanoa, and Susan J. Lister. "Standard Normal Variate Transformation and De-Trending of Near-Infrared Diffuse Reflectance Spectra." *Applied Spectroscopy* 43, no. 5 (July 1989): 772–77. <https://doi.org/10.1366/0003702894202201>.
- Barrow, C.J. "Biochar: Potential for Countering Land Degradation and for Improving Agriculture." *Applied Geography* 34 (May 2012): 21–28. <https://doi.org/10.1016/j.apgeog.2011.09.008>.
- Baker, John M., Tyson E. Ochsner, Rodney T. Venterea, and Timothy J. Griffis. "Tillage and Soil Carbon Sequestration—What Do We Really Know?" *Agriculture, Ecosystems & Environment* 118, no. 1 (January 1, 2007): 1–5. <https://doi.org/10.1016/j.agee.2006.05.014>.
- Boguta, Patrycja, Zofia Sokołowska, and Kamil Skic. "Use of Thermal Analysis Coupled with Differential Scanning Calorimetry, Quadrupole Mass Spectrometry and Infrared Spectroscopy (TG-DSC-QMS-FTIR) to Monitor Chemical Properties and Thermal Stability of Fulvic and Humic Acids." Edited by Amitava Mukherjee. *PLOS ONE* 12, no. 12 (December 14, 2017): e0189653. <https://doi.org/10.1371/journal.pone.0189653>.
- Bridgwater, A.V., D. Meier, and D. Radlein. "An Overview of Fast Pyrolysis of Biomass." *Organic Geochemistry* 30, no. 12 (December 1999): 1479–93. [https://doi.org/10.1016/S0146-6380\(99\)00120-5](https://doi.org/10.1016/S0146-6380(99)00120-5).

- Childs, Thomas. Decay of Slash on Clear-Cut Areas in the Douglas Fir Region. Vol. 37, 1939.
- Cong, Hongbin, Ondřej Mašek, Lixin Zhao, Zonglu Yao, Haipo Meng, Erfeng Hu, and Teng Ma. "Slow Pyrolysis Performance and Energy Balance of Corn Stover in Continuous Pyrolysis-Based Poly-Generation Systems." *Energy & Fuels* 32, no. 3 (March 15, 2018): 3743–50. <https://doi.org/10.1021/acs.energyfuels.7b03175>.
- Cornelissen, Gerard, Jubaedah, Neneng L. Nurida, Sarah E. Hale, Vegard Martinsen, Ludovica Silvani, and Jan Mulder. "Fading Positive Effect of Biochar on Crop Yield and Soil Acidity during Five Growth Seasons in an Indonesian Ultisol." *Science of The Total Environment* 634 (September 2018): 561–68. <https://doi.org/10.1016/j.scitotenv.2018.03.380>.
- Claoston, N, Aw Samsuri, Mh Ahmad Husni, and Ms Mohd Amran. "Effects of Pyrolysis Temperature on the Physicochemical Properties of Empty Fruit Bunch and Rice Husk Biochars." *Waste Management & Research* 32, no. 4 (April 2014): 331–39. <https://doi.org/10.1177/0734242X14525822>.
- Dong, Xinliang, Guitong Li, Qimei Lin, and Xiaorong Zhao. "Quantity and Quality Changes of Biochar Aged for 5 Years in Soil under Field Conditions." *CATENA* 159 (December 2017): 136–43. <https://doi.org/10.1016/j.catena.2017.08.008>.
- Doran, J. W., W. W. Wilhelm, and J. F. Power. "Crop Residue Removal and Soil Productivity with No-Till Corn, Sorghum, and Soybean1." *Soil Science Society of America Journal* 48, no. 3 (1984): 640–45. <https://doi.org/10.2136/sssaj1984.03615995004800030034x>.
- Egamberdieva, Dilfuza, Stephan Wirth, Undine Behrendt, Elsayed F. Abd_Allah, and Gabriele Berg. "Biochar Treatment Resulted in a Combined Effect on Soybean Growth Promotion and a Shift in Plant Growth Promoting Rhizobacteria." *Frontiers in Microbiology* 7 (February 25, 2016). <https://doi.org/10.3389/fmicb.2016.00209>.
- Fagbenro, Ja, So Oshunsanya, and Oa Onawumi. "Effect of Saw Dust Biochar and NPK 15:15:15 Inorganic Fertilizer on *Moringa Oleifera* Seedlings Grown in an Oxisol." *Agrosearch* 13, no. 1 (September 6, 2013): 57. <https://doi.org/10.4314/agrosh.v13i1.6>.
- Fasth, Becky G., Mark E. Harmon, Jay Sexton, and Peter White. "Decomposition of Fine Woody Debris in a Deciduous Forest in North Carolina 1." *The Journal of the Torrey Botanical Society* 138, no. 2 (April 2011): 192–206. <https://doi.org/10.3159/TORREY-D-10-00009.1>.
- Gan, Jianbang, and C.T. Smith. "Availability of Logging Residues and Potential for Electricity Production and Carbon Displacement in the USA." *Biomass and Bioenergy* 30, no. 12 (December 2006): 1011–20. <https://doi.org/10.1016/j.biombioe.2005.12.013>.
- Gaunt, John L., and Johannes Lehmann. "Energy Balance and Emissions Associated with Biochar Sequestration and Pyrolysis Bioenergy Production." *Environmental Science & Technology* 42, no. 11 (June 2008): 4152–58. <https://doi.org/10.1021/es071361i>.
- Glaser, Bruno. "Prehistorically Modified Soils of Central Amazonia: A Model for Sustainable Agriculture in the Twenty-First Century." *Philosophical Transactions of the Royal Society B:*

- Biological Sciences 362, no. 1478 (February 28, 2007): 187–96.
<https://doi.org/10.1098/rstb.2006.1978>.
- Grand View Research. “Biochar Market Size Worth \$3,146.1 Million by 2025 | CAGR: 13.2%.” May 2017. Accessed March 14, 2019. <https://www.grandviewresearch.com/press-release/global-biochar-market>.
- Griscom, Bronson W., Justin Adams, Peter W. Ellis, Richard A. Houghton, Guy Lomax, Daniela A. Miteva, William H. Schlesinger, et al. “Natural Climate Solutions.” *Proceedings of the National Academy of Sciences* 114, no. 44 (October 31, 2017): 11645–50.
<https://doi.org/10.1073/pnas.1710465114>.
- Heiskanen, J., P. Tammeorg, and R.K. Dumroese. “Growth of Norway Spruce Seedlings after Transplanting into Silty Soil Amended with Biochar: A Bioassay in a Growth Chamber.” *Journal of Forest Science* 59, no. No. 3 (March 22, 2013): 125–29.
<https://doi.org/10.17221/44/2012-JFS>.
- Helmisaari, Heljä-Sisko, Kjersti Holt Hanssen, Staffan Jacobson, Mikko Kukkola, Jukka Luro, Anna Saarsalmi, Pekka Tamminen, and Bjørn Tveite. “Logging Residue Removal after Thinning in Nordic Boreal Forests: Long-Term Impact on Tree Growth.” *Forest Ecology and Management* 261, no. 11 (June 2011): 1919–27.
<https://doi.org/10.1016/j.foreco.2011.02.015>.
- Intergovernmental Panel on Climate Change (IPCC). “Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty.” 2018. Masson-Delmotte, V., P. Zhai, H.-O. Pörtner, D. Roberts, J. Skea, P.R. Shukla, A. Pirani, Moufouma-Okia, C. Péan, R. Pidcock, S. Connors, J.B.R. Matthews, Y. Chen, X. Zhou, M.I. Gomis, E. Lonnoy, Maycock, M. Tignor, and T. Waterfield (Editors). World Meteorological Organization, Geneva, Switzerland, 32 pp.
- Johnson, Jane M.-F.. “Chapter 5 Crop Residues of the Contiguous United States : Balancing Feedstock and Soil Needs With Conservation Tillage , Cover Crops , and Biochar.” (2011).
- Johnston, A.E., P.R. Poulton, and K. Coleman. 2009. Soil organic matter: Its importance in sustainable agriculture and carbon dioxide fluxes. *Adv. Agron.* 101:1–57.
doi:10.1016/S0065-2113(08)00801-8
- Kim, Dongyeob, Nathaniel McLean Anderson, and Woodam Chung. “Financial Performance of a Mobile Pyrolysis System Used to Produce Biochar from Sawmill Residues.” *Forest Products Journal* 65, no. 5–6 (September 2015): 189–97. <https://doi.org/10.13073/FPJ-D-14-00052>.
- Kloss, Stefanie, Franz Zehetner, Alex Dellantonio, Raad Hamid, Franz Ottner, Volker Liedtke, Manfred Schwanninger, Martin H. Gerzabek, and Gerhard Soja. “Characterization of Slow Pyrolysis Biochars: Effects of Feedstocks and Pyrolysis Temperature on Biochar

- Properties.” *Journal of Environment Quality* 41, no. 4 (2012): 990.
<https://doi.org/10.2134/jeq2011.0070>.
- Kumar, Abhay, Stephen Joseph, Ludmila Tsechansky, Karen Privat, Inga J. Schreiter, Christoph Schüth, and Ellen R. Graber. “Biochar Aging in Contaminated Soil Promotes Zn Immobilization Due to Changes in Biochar Surface Structural and Chemical Properties.” *Science of The Total Environment* 626 (June 2018): 953–61.
<https://doi.org/10.1016/j.scitotenv.2018.01.157>.
- Laird, David A., Pierce Fleming, Dedrick D. Davis, Robert Horton, Baiqun Wang, and Douglas L. Karlen. “Impact of Biochar Amendments on the Quality of a Typical Midwestern Agricultural Soil.” *Geoderma* 158, no. 3–4 (September 2010): 443–49.
<https://doi.org/10.1016/j.geoderma.2010.05.013>.
- Laird, David A. “The Charcoal Vision: A Win–Win–Win Scenario for Simultaneously Producing Bioenergy, Permanently Sequestering Carbon, While Improving Soil and Water Quality.” *Agronomy Journal* 100, no. 1 (2008): 178. <https://doi.org/10.2134/agronj2007.0161>.
- Lehmann, Johannes. “A Handful of Carbon.” *Nature* 447, no. 7141 (May 2007): 143–44.
<https://doi.org/10.1038/447143a>.
- Lehmann, Johannes, John Gaunt, and Marco Rondon. “Bio-Char Sequestration in Terrestrial Ecosystems – A Review.” *Mitigation and Adaptation Strategies for Global Change* 11, no. 2 (March 2006): 403–27. <https://doi.org/10.1007/s11027-005-9006-5>.
- Leng, Lijian, Huajun Huang, Hui Li, Jun Li, and Wenguang Zhou. “Biochar Stability Assessment Methods: A Review.” *Science of The Total Environment* 647 (January 2019): 210–22.
<https://doi.org/10.1016/j.scitotenv.2018.07.402>.
- Li, Simeng, and Gang Chen. “Thermogravimetric, Thermochemical, and Infrared Spectral Characterization of Feedstocks and Biochar Derived at Different Pyrolysis Temperatures.” *Waste Management* 78 (August 2018): 198–207.
<https://doi.org/10.1016/j.wasman.2018.05.048>.
- Liu, Yongliang, Zhongqi He, and Minori Uchimiya. “Comparison of Biochar Formation from Various Agricultural By-Products Using FTIR Spectroscopy.” *Modern Applied Science* 9, no. 4 (March 9, 2015). <https://doi.org/10.5539/mas.v9n4p246>.
- Luo, Zhongkui, Enli Wang, and Osbert J. Sun. “Can No-Tillage Stimulate Carbon Sequestration in Agricultural Soils? A Meta-Analysis of Paired Experiments.” *Agriculture, Ecosystems & Environment* 139, no. 1–2 (October 15, 2010): 224–31.
<https://doi.org/10.1016/j.agee.2010.08.006>.
- Makoto, K., Y. Tamai, Y. S. Kim, and T. Koike. “Buried Charcoal Layer and Ectomycorrhizae Cooperatively Promote the Growth of *Larix Gmelinii* Seedlings.” *Plant and Soil* 327, no. 1–2 (February 2010): 143–52. <https://doi.org/10.1007/s11104-009-0040-z>.

- Masto, R. Ebhin, Sandeep Kumar, T.K. Rout, Pinaki Sarkar, Joshy George, and L.C. Ram. "Biochar from Water Hyacinth (*Eichornia Crassipes*) and Its Impact on Soil Biological Activity." *CATENA* 111 (December 2013): 64–71. <https://doi.org/10.1016/j.catena.2013.06.025>.
- McElligott, Kristin, Debbie Dumroese, and Mark Coleman. "Bioenergy Production Systems and Biochar Application in Forests: Potential for Renewable Energy, Soil Enhancement, and Carbon Sequestration." Ft. Collins, CO: U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station, 2011. <https://doi.org/10.2737/RMRS-RN-46>.
- Mete, Fatima Z., Shamim Mia, Feike A. Dijkstra, Md. Abuyusuf, and A.S.M. Iqbal Hossain. "Synergistic Effects of Biochar and NPK Fertilizer on Soybean Yield in an Alkaline Soil." *Pedosphere* 25, no. 5 (October 2015): 713–19. [https://doi.org/10.1016/S1002-0160\(15\)30052-7](https://doi.org/10.1016/S1002-0160(15)30052-7).
- Meyer, Sebastian, Bruno Glaser, and Peter Quicker. "Technical, Economical, and Climate-Related Aspects of Biochar Production Technologies: A Literature Review." *Environmental Science & Technology* 45, no. 22 (November 15, 2011): 9473–83. <https://doi.org/10.1021/es201792c>.
- Nave, L. E., B. F. Walters, K. L. Hofmeister, C. H. Perry, U. Mishra, G. M. Domke, and C. W. Swanston. "The Role of Reforestation in Carbon Sequestration." *New Forests* 50, no. 1 (January 2019): 115–37. <https://doi.org/10.1007/s11056-018-9655-3>.
- Oswalt, Sonja N., W. Brad Smith, Patrick D. Miles, and Scott A. Pugh. "Forest Resources of the United States, 2012: A Technical Document Supporting the Forest Service 2010 Update of the RPA Assessment." Washington, DC: U.S. Department of Agriculture, Forest Service, 2014. <https://doi.org/10.2737/WO-GTR-91>.
- Pandit, Naba Raj, Jan Mulder, Sarah E. Hale, Andrew R. Zimmerman, Bishnu Hari Pandit, and Gerard Cornelissen. "Multi-Year Double Cropping Biochar Field Trials in Nepal: Finding the Optimal Biochar Dose through Agronomic Trials and Cost-Benefit Analysis." *Science of The Total Environment* 637–638 (October 2018a): 1333–41. <https://doi.org/10.1016/j.scitotenv.2018.05.107>.
- Pandit, Naba Raj, Jan Mulder, Sarah Elizabeth Hale, Vegard Martinsen, Hans Peter Schmidt, and Gerard Cornelissen. "Biochar Improves Maize Growth by Alleviation of Nutrient Stress in a Moderately Acidic Low-Input Nepalese Soil." *Science of The Total Environment* 625 (June 2018b): 1380–89. <https://doi.org/10.1016/j.scitotenv.2018.01.022>.
- Pluchon, Nathalie, Michael J. Gundale, Marie-Charlotte Nilsson, Paul Kardol, and David A. Wardle. "Stimulation of Boreal Tree Seedling Growth by Wood-Derived Charcoal: Effects of Charcoal Properties, Seedling Species and Soil Fertility." Edited by Nick Ostle. *Functional Ecology* 28, no. 3 (June 2014): 766–75. <https://doi.org/10.1111/1365-2435.12221>.
- Post, W. M., K. C. Kwon. "Soil carbon sequestration and land-use change: processes and potential." *Global Change Biology* 6 (2000): 317-327.

- Pourhashem, Ghasideh, Shih Yu Hung, Kenneth B. Medlock, and Caroline A. Masiello. "Policy Support for Biochar: Review and Recommendations." *GCB Bioenergy* 11, no. 2 (February 2019): 364–80. <https://doi.org/10.1111/gcbb.12582>.
- Ramola, S., T. Mishra, G. Rana, and R. K. Srivastava. "Characterization and Pollutant Removal Efficiency of Biochar Derived from Bagasse, Bamboo and Tyre." *Environmental Monitoring and Assessment* 186, no. 12 (December 2014): 9023–39. <https://doi.org/10.1007/s10661-014-4062-5>.
- Rechberger, Maria V., Stefanie Kloss, Harald Rennhofer, Johannes Tintner, Andrea Watzinger, Gerhard Soja, Helga Lichtenegger, and Franz Zehetner. "Changes in Biochar Physical and Chemical Properties: Accelerated Biochar Aging in an Acidic Soil." *Carbon* 115 (May 2017): 209–19. <https://doi.org/10.1016/j.carbon.2016.12.096>.
- Ren, Xinhao, Hongwen Sun, Fei Wang, Peng Zhang, and Hongkai Zhu. "Effect of Aging in Field Soil on Biochar's Properties and Its Sorption Capacity." *Environmental Pollution* 242 (November 2018): 1880–86. <https://doi.org/10.1016/j.envpol.2018.07.078>.
- Rinnan, Åsmund, Frans van den Berg, and Søren Balling Engelsen. "Review of the Most Common Pre-Processing Techniques for near-Infrared Spectra." *TrAC Trends in Analytical Chemistry* 28, no. 10 (November 2009): 1201–22. <https://doi.org/10.1016/j.trac.2009.07.007>.
- Robertson, Susan J., P. Michael Rutherford, Juan C. López-Gutiérrez, and Hugues B. Massicotte. "Biochar Enhances Seedling Growth and Alters Root Symbioses and Properties of Sub-Boreal Forest Soils." *Canadian Journal of Soil Science* 92, no. 2 (February 2012): 329–40. <https://doi.org/10.4141/cjss2011-066>.
- Rooney, T. Tue. "Lignocellulosic feedstock resource assessment". United States. doi:10.2172/672163. <https://www.osti.gov/servlets/purl/672163>.
- Russell, Matthew B., Christopher W. Woodall, Shawn Fraver, Anthony W. D'Amato, Grant M. Domke, and Kenneth E. Skog. "Residence Times and Decay Rates of Downed Woody Debris Biomass/Carbon in Eastern US Forests." *Ecosystems* 17, no. 5 (August 2014): 765–77. <https://doi.org/10.1007/s10021-014-9757-5>.
- Sahoo, Kamalakanta, Edward Bilek, Richard Bergman, and Sudhagar Mani. "Techno-Economic Analysis of Producing Solid Biofuels and Biochar from Forest Residues Using Portable Systems." *Applied Energy*. 235: 578-590. 235 (2019): 578–90. <https://doi.org/10.1016/j.apenergy.2018.10.076>.
- Sharma, Ramesh K, Jan B Wooten, Vicki L Baliga, Xuehao Lin, W Geoffrey Chan, and Mohammad R Hajaligol. "Characterization of Chars from Pyrolysis of Lignin." *Fuel* 83, no. 11–12 (August 2004): 1469–82. <https://doi.org/10.1016/j.fuel.2003.11.015>.
- Singh, B., Y. Fang, and C.T. Johnston. "A Fourier-Transform Infrared Study of Biochar Aging in Soils." *Soil Science Society of America Journal* 80, no. 3 (2016): 613. <https://doi.org/10.2136/sssaj2015.11.0414>.
- Smil, Vaclav. "Crop Residues: Agriculture's Largest Harvest." *BioScience* 49, no. 4 (April 1999): 299–308. <https://doi.org/10.2307/1313613>.

- Smith, Pete. "Soil Carbon Sequestration and Biochar as Negative Emission Technologies." *Global Change Biology* 22, no. 3 (March 2016): 1315–24. <https://doi.org/10.1111/gcb.13178>.
- Sorensen, Ronald B., and Marshall C. Lamb. "Crop Yield Response to Increasing Biochar Rates." *Journal of Crop Improvement* 30, no. 6 (November 2016): 703–12. <https://doi.org/10.1080/15427528.2016.1231728>.
- Spaulding, Perley, and J. R. Hansbrough. "Decay of Logging Slash in the Northeast." United States Department of Agriculture, Economic Research Service, September 1944. <https://EconPapers.repec.org/RePEc:ags:uerstb:169720>.
- Spokas, Kurt A. "Review of the Stability of Biochar in Soils: Predictability of O:C Molar Ratios." *Carbon Management* 1, no. 2 (December 2010): 289–303. <https://doi.org/10.4155/cmt.10.32>.
- Sundermeier, A. P., K. R. Islam, Y. Raut, R. C. Reeder, and W. A. Dick. "Continuous No-Till Impacts on Soil Biophysical Carbon Sequestration." *Soil Science Society of America Journal* 75, no. 5 (2011): 1779. <https://doi.org/10.2136/sssaj2010.0334>.
- Tang, Jingchun, Wenying Zhu, Rai Kookana, and Arata Katayama. "Characteristics of Biochar and Its Application in Remediation of Contaminated Soil." *Journal of Bioscience and Bioengineering* 116, no. 6 (December 2013): 653–59. <https://doi.org/10.1016/j.jbiosc.2013.05.035>.
- Thomas, Sean C., and Nigel Gale. "Biochar and Forest Restoration: A Review and Meta-Analysis of Tree Growth Responses." *New Forests* 46, no. 5–6 (November 2015): 931–46. <https://doi.org/10.1007/s11056-015-9491-7>.
- Uchimiya, Minori, Lynda H. Wartelle, K. Thomas Klasson, Chanel A. Fortier, and Isabel M. Lima. "Influence of Pyrolysis Temperature on Biochar Property and Function as a Heavy Metal Sorbent in Soil." *Journal of Agricultural and Food Chemistry* 59, no. 6 (March 23, 2011): 2501–10. <https://doi.org/10.1021/jf104206c>.
- U.S. Department of Agriculture, National Agricultural Statistics Service (USDA-NASS). 2014. 2012 Census of Agriculture. T. Vilsack and C. Clark. AC-12-A-51. USDA-NASS, Washington, D.C.
- U.S. Department of Agriculture, National Agricultural Statistics Service (USDA-NASS). 2014. 2012 Census of Agriculture Highlights: Farms and Farmland. ACH12-13. USDA-NASS, Washington, D.C.
- U.S. Department of Energy (US DOE). "Biomass Cofiring: A Renewable Alternative for Utilities," 2000. Shepherd, P (Author), DOE/GO-102000-1055. National Renewable Energy Laboratory, Golden, CO.
- U.S. Department of Energy. "Carbon Cycling and Biosequestration: Integrating Biology and Climate Through Systems Science," 2008. DOE/SC-108

- U.S. Department of Energy (US DOE). "U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry." 2011. R.D. Perlack and B.J. Stokes (Leads), ORNL/TM-2011/224. Oak Ridge National Laboratory, Oak Ridge, TN. 227p.
- U.S. Environmental Protection Agency (US EPA). "Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990-2017." 2019. EPA430-P-19-001.
- U.S. Environmental Protection Agency (US EPA), "Yard Trimmings: Material-Specific Data." Environmental Protection Agency, 17 July 2018, www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/yard-trimmings-material-specific-data.
- Wagener, W.W. and H.R. Offord. "Logging slash: its breakdown and decay at two forests in northern California." USDA Forest Service Research Paper PSW-83 (1972).
- Walsh, Marie E., Robert L. Perlack, Anthony Turhollow, Daniel de la Torre Ugarte, Denny A. Becker, Robin L. Graham, Stephen E. Slinsky, and Daryll E. Ray. "Biomass Feedstock Availability in the United States: 1999 State Level Analysis," January 1, 2000. <https://doi.org/10.2172/1218318>.
- Wang, Jinyang, Zhengqin Xiong, and Yakov Kuzyakov. "Biochar Stability in Soil: Meta-Analysis of Decomposition and Priming Effects." *GCB Bioenergy* 8, no. 3 (May 2016): 512–23. <https://doi.org/10.1111/gcbb.12266>.
- Woolf, Dominic, James E. Amonette, F. Alayne Street-Perrott, Johannes Lehmann, and Stephen Joseph. "Sustainable Biochar to Mitigate Global Climate Change." *Nature Communications* 1, no. 5 (August 2010): 1–9. <https://doi.org/10.1038/ncomms1053>.
- Yeboah, Edward, Gideon Asamoah, Boafo Kofi, and Akwasi Adutwum Abunyewa. "Effect of Biochar Type and Rate of Application on Maize Yield Indices and Water Use Efficiency on an Ultisol in Ghana." *Energy Procedia* 93 (August 2016): 14–18. <https://doi.org/10.1016/j.egypro.2016.07.143>.
- Zhang, Xueyang, Bin Gao, Yulin Zheng, Xin Hu, Anne Elise Creamer, Michael D. Annable, and Yuncong Li. "Biochar for Volatile Organic Compound (VOC) Removal: Sorption Performance and Governing Mechanisms." *Bioresource Technology* 245 (December 2017): 606–14. <https://doi.org/10.1016/j.biortech.2017.09.025>.
- Zhao, Rudong, Neil Coles, and Jiaping Wu. "Carbon Mineralization Following Additions of Fresh and Aged Biochar to an Infertile Soil." *CATENA* 125 (February 2015): 183–89. <https://doi.org/10.1016/j.catena.2014.10.026>.
- Zhu, Qiao-Hong, Xin-Hua Peng, Tai-Qing Huang, Zu-Bin Xie, and N.M. Holden. "Effect of Biochar Addition on Maize Growth and Nitrogen Use Efficiency in Acidic Red Soils." *Pedosphere* 24, no. 6 (December 2014): 699–708. [https://doi.org/10.1016/S1002-0160\(14\)60057-6](https://doi.org/10.1016/S1002-0160(14)60057-6).

Appendix

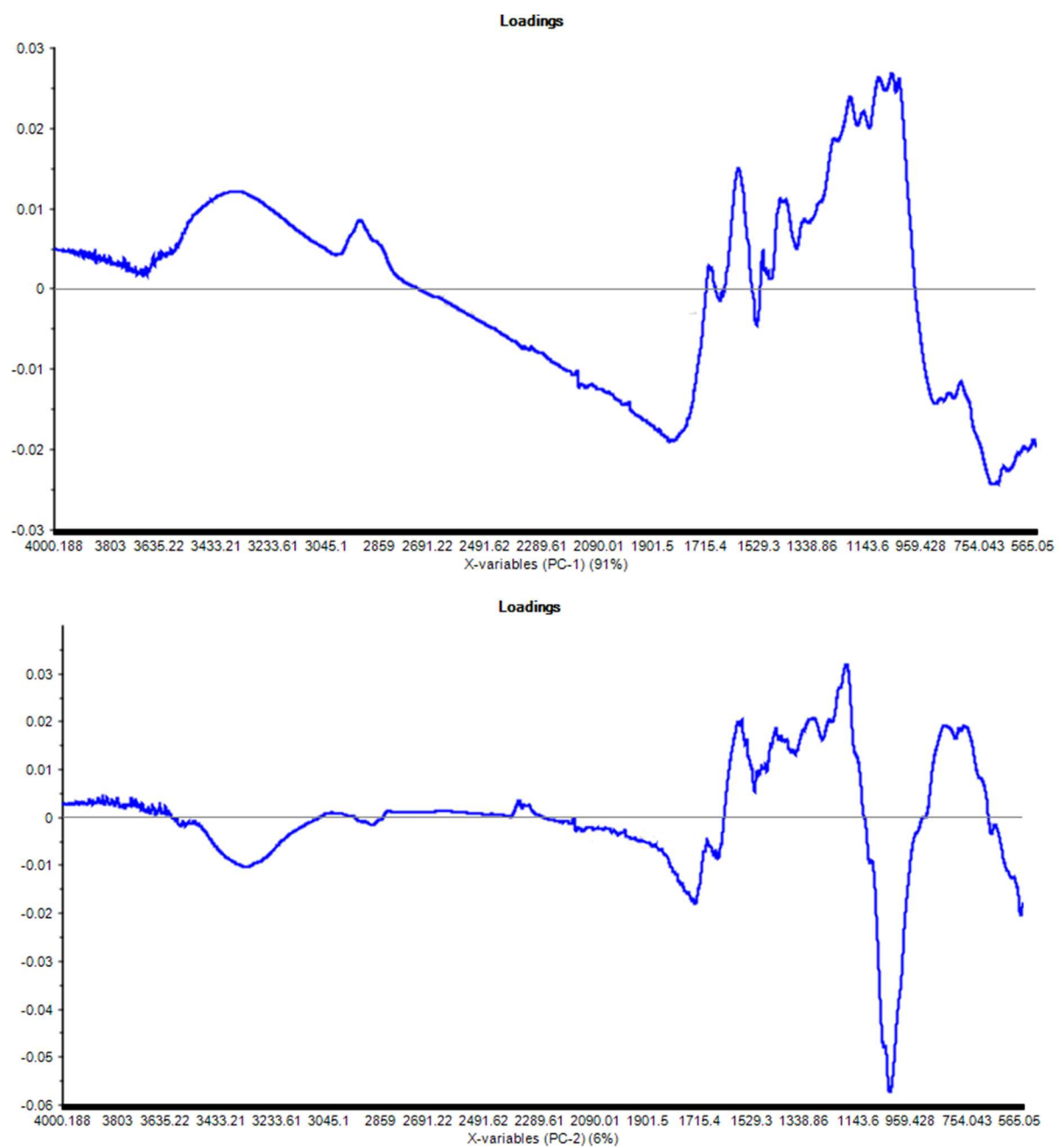


Figure A.1: Principal Components 1 and 2 from analysis shown in Figure 2.6 (top).

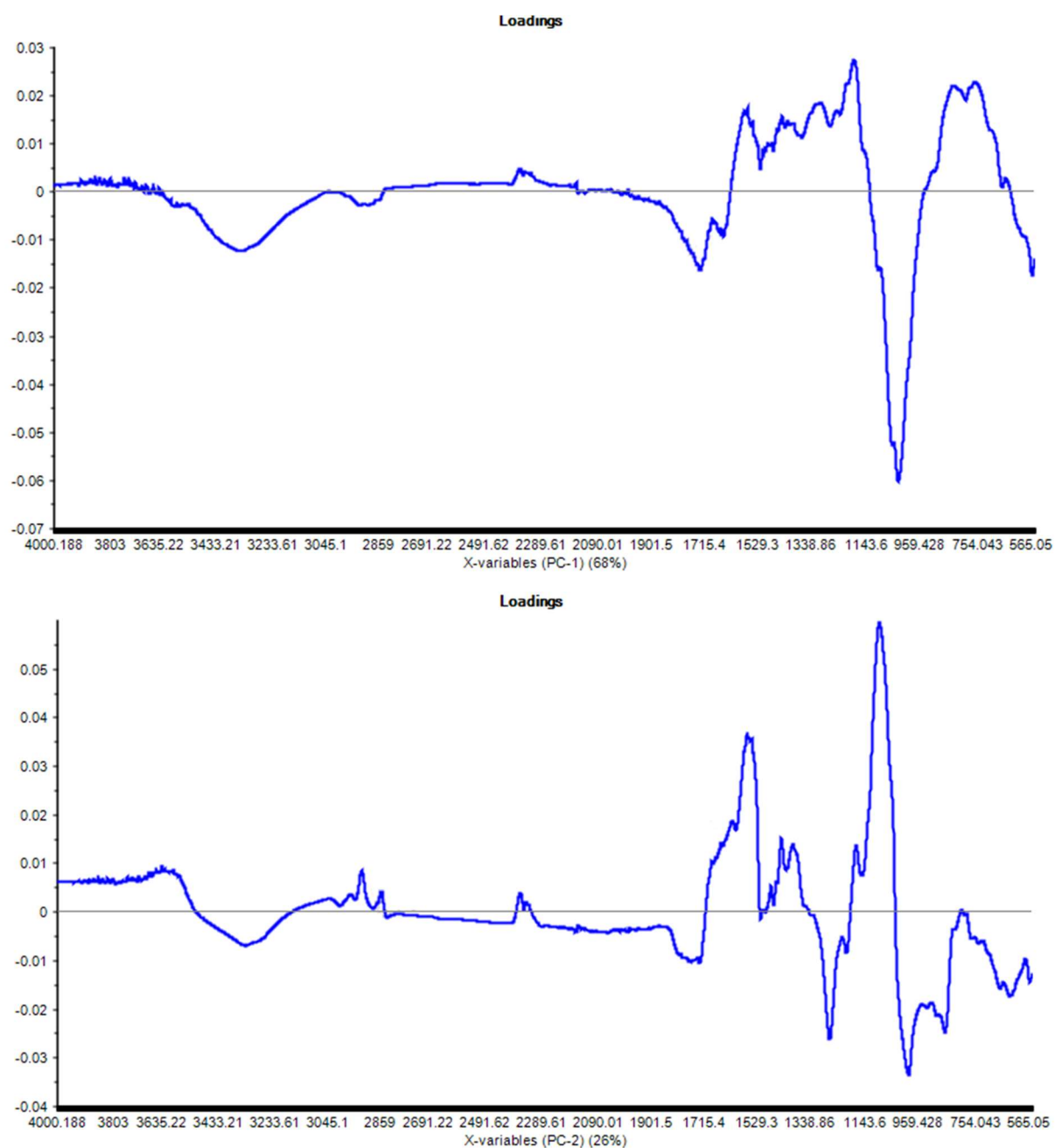


Figure A.2: Principal Components 1 and 2 from analysis shown in Figure 2.6 (bottom).

A3 Usage of Carbon Store Model

The carbon store model used was created in Microsoft Excel. In the top-left of the first Excel sheet (“model”) are a list of model parameters which can be varied to create different scenarios by changing the values in the yellow boxes. No cells apart from those colored yellow should be edited. In the top-center are the results of the model warm-up, in which the model runs with the parameters provided for the number of years selected to determine the level of slash accumulation which would be present. This value should only be set to a multiple of your harvest frequency (i.e., if your harvest frequency is 25, you could set the model warm-up time to 475 or 500 years, but not 480). The warm-up is processed identically to the Slash Stores model and takes place on the “Model Warm-Up” Excel sheet. No edits are required on this sheet, but a graph is provided to determine the time required to reach equilibrium with the entered parameters.

In the area below the parameters are the model output. Each row represents one timestep (one year by design, but equally valid as months or days with appropriate decomposition rate-constants). Slash input, Biochar input, and Mixed input are the quantity of new material added to the store in a given year. Slash store, Biochar store, and Mixed store are the result of the previous year’s total, minus decomposition, plus any inputs, the results of which are plotted on the “stores” Excel sheet. Slash decomposition, Biochar decomposition, and Mixed decomposition are the quantities of the previous row’s store which are lost due to decomposition. Char-Slash Difference and Char-Mix Difference are the result of subtracting a given row’s Biochar Store from the Slash Store or Mixed Store, respectively, the results of which are plotted on the “difference” Excel sheet.

Landscape-level modeling is performed by averaging a given row’s values for the appropriate Stores column with the values of the previous 50 rows, to simulate 50 identical plots at different stages

in the production cycle. If 50 previous rows are not available, values from the appropriate number of rows of the Model Warm-up are used.

The “time of biochar implementation” parameter was used in a previous iteration of the model and is no longer used but has not been removed from cell calculations. It has been preserved to ensure that other parameters are not placed on the same line which could cause errors in calculated values.

AutoSave On Biochar Model 4 - Excel

File Home Insert Draw Page Layout Formulas Data Review View Help Search

Clipboard Font Alignment Number Styles Cells Editing Ideas

Share Comments

Normal Bad Good Neutral Calculation Check Cell Explanatory... Input Linked Cell Note

Insert Delete Format

AutoSum Fill Clear Sort & Find & Filter Select Ideas

C5 25

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	This is a simple spreadsheet model to look at one aspect of biochar use in forests														
2	This is at the stand or plot level														
3															
4	Parameters					Model Warm-up					Landscape				
5	Harvest Interval	25	years			Time	Slash Input	Slash Store	Slash Deco	Slash Store					
6	Slash Generated per Harvest	100	store/area			500	100	107.7342	0.859358	40					
7	slash decomposition rate	0.1	per time												
8	Biochar Carbon Conversion	50	%												
9	Percent Slash to Biochar (Mixed)	75	%												
10	Production Offset	20	%												
11	biochar decomposition rate	0.001	per time												
12	time of biochar implementation	0	year												
13								Char-Slash	Mixed	Mixed	Mixed	Char-Mix	landscape	landscape	landscape
14	Time	Slash input	Slash store	Slash decomposition	Biochar input	Biochar store	Biochar decomposition	difference	Input	Store	Decompos	Difference	SlashStore	BiocharStore	MixedStore
15	0	100	107.73422	0.859357535	40	40	0	-67.73422	55	77.7342	0.85936	-37.73422	40	38.645316	39.4
16	1	0	96.960796	10.77342178	0	39.96	0.04	-57.0008	0	72.9308	4.80342	-32.9708	40	37.5053	38.9194
17	2	0	87.264716	9.696079604	0	39.92004	0.03996	-47.34468	0	68.6047	4.32605	-28.68471	40	36.558406	38.5462
18	3	0	78.538245	8.726471643	0	39.88012	0.03992004	-38.65812	0	64.7083	3.89641	-24.82821	40	35.785244	38.2696
19	4	0	70.68442	7.853824479	0	39.8402398	0.03988012	-30.84418	0	61.1986	3.50973	-21.35836	40	35.16836	38.0799
20	5	0	63.615978	7.068442031	0	39.8003996	0.03984024	-23.81558	0	58.0369	3.16172	-18.23648	40	34.692049	37.9683
21	6	0	57.25438	6.361597828	0	39.7605992	0.0398004	-17.49378	0	55.1884	2.84851	-15.42777	40	34.342173	37.927
22	7	0	51.528942	5.725438045	0	39.7208386	0.039760599	-11.8081	0	52.6218	2.56661	-12.90092	40	34.106011	37.9488
23	8	0	46.376048	5.152894241	0	39.6811178	0.039720839	-6.69493	0	50.3089	2.3129	-10.62774	40	33.972112	38.0275
24	9	0	41.738443	4.637604817	0	39.6414366	0.039681118	-2.097007	0	48.2243	2.08456	-8.582855	40	33.930172	38.1572
25	10	0	37.564599	4.173844335	0	39.6017952	0.039641437	-2.037196	0	46.3452	1.87905	-6.743444	40	33.970916	38.3328
26	11	0	33.808139	3.756459901	0	39.5621934	0.039601795	-5.754054	0	44.6511	1.69409	-5.088955	40	34.085997	38.5497

model Model Warm-Up Partial Biochar Model stores landscape store difference

145%

Figure A.3: Screenshot of Carbon Store Model.