[Type text]

Biochar R	Research	and a	Case	Study	y in	Kansas

_	
ĸv	
υv	

Joe Wimmer

Submitted to the graduate degree program in Geography and the Graduate Faculty of the University of Kansas in partial fulfillment of the requirements for the degree of Master of Arts.

-		
Chairperson William I. Wo	S	
		Terry A. Slocum

Peter H. Herlihy

Date Defended: September 23, 2011

Date approved: December 2, 2011

Abstract:

As planet Earth's sustainability has become a foremost issue, different methods of prolonging sustainability have become prevalent in society, most prominently are alternative forms of energy and ways to help reduce the human impact on the environment. Another alternative that has become popular, mostly in the last decade, stems from decades of research conducted on ancient soils of the world, predominantly in the Amazon basin, soils of incredible fertility and mysterious properties that leave soil scientists wondering. The factor of greatest importance to these soils has been identified and termed biochar, the carbon remains of partially burned organic material. Biochar is now believed to have the potential not only help provide sustainability through fertile soils but also by providing relief from of the greatest threats to life on earth. This thesis will provide an outline of why biochar research is important, discuss all viable potentials for biochar and include the details and results of a case study in Kansas.

Acknowledgments

I would like to thank everyone who helped make this thesis possible, including Rolfe D. Mandel of the University of Kansas, Soren C. Larsen of the University of Missouri for their letters of recommendation of my admittance into the graduate department at the University of Kansas and Jerry Smith of Fort Scott Community College, both for his letter of recommendation and also for introducing to the academic world of geography. Without their letters of recommendation I would have never had the opportunity to be a graduate student at the University of Kansas. I would again like to thank Peter H. Herlihy and also Terry A. Slocum for serving on my graduate committee alongside my advisor, William I. Woods who accepted me as a student and provided me with the guidance and support needed to complete this thesis. I also thank Daniel R. Hirmas for his assistance and guidance with the laboratory portion of the project and Aaron Koop for his time and assistance with the maps found in the thesis.

Table of Contents:	P	ages ages
<u>Title Page</u>		
Acceptance Page	<u>ii</u>	
Abstract		1
Acknowledgements	2	
Table of Contents		3
Chapter 1: The Need for Change	<u>4-6</u>	
Chapter 2: Biochar Research and His	story	6-11
Chapter 3: The Physical Properties of	of Biochar	11-14
Chapter 4: Biochar as a Soil Amendr	ment 14-18	<u>3</u>
Chapter 5: Biochar to Mitigate Clima	ate Change, for Energ	y Production,
And Waste Management		18-20
Chapter 6: A Case Study with Result	s, Project Photos 2	<u>21-37</u>
Chapter 7: A Discussion of Results	37-4	<u>1</u>
Chapter 8: Outlook	41-43	<u>3</u>
Appendix of Data Tables	44-4	<u>6</u>
References Cited		47- <u>52</u>

Chapter 1: The Need for Change

Sustainability has become a foremost issue for our planet as an ever dwindling supply of resources combats a continually increasing need from an increasing human population that demands more resources for each person. Planet earth's human population has more than quadrupled in the past century alone from less than 1.7 billion people (Durand, 1977) to reach approximately seven billion people. That number is anticipated to rise to at least nine billion by 2050. Much of our need for change to provide prolonged sustainability centers on carbon. Human induced emissions of carbon in the form of carbon dioxide have proven to have a harmful effect in our atmosphere, promoting global climate change through global warming. This climate change is caused by the release of what are known as greenhouse gases, they include; carbon dioxide, methane, nitrous oxide and fluorinated gases (EPA, 2011), fluorinated gases being those that are emitted solely as result of human activity (EPA, 2011). As these gases are emitted they are held in the atmosphere and serve to reflect the radiated long wave energy that has been reflected by the earth after being emitted from the sun as shortwave radiation. Many of these gases are emitted by anthropogenic causes. Examples include carbon dioxide emissions from transportation vehicles and power plants. Or methane emissions caused by large scale cattle production for human consumption.

Recent years have seen increased scientific research in the field of greenhouse house gases as an attempt to lower our emissions. Solar and wind power have become increasingly popular as alternative power sources to help lower emissions while promoting sustainability just as electric and alternative fuels such as ethanol and hydrogen have served to lower

emissions from transportation vehicles. Even an increased trend towards vegetarianism is beneficial to help offset the increasing amount of livestock needed thus producing less methane emissions.

Our current global anthropogenic emissions contribute approximately thirty gigatons (one gigaton being equal to one billion tons) of carbon to the atmosphere annually (see Figure 1) (Chameides, 2007), the amount offset by the before mentioned alternatives is negligible at this point. However, there is much room for the expansion of such alternatives as can be deduced from the figure below.

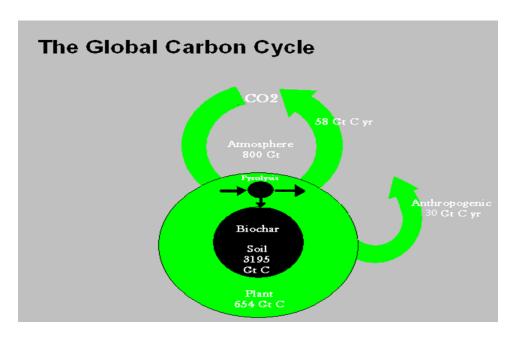


Figure 1: The Global Carbon Cycle by Joe Wimmer, Data from Biochar for Environmental Management

Figure 1 Shows that the earth's soils with 3,195 gigatons of carbon stored hold nearly four times as much carbon as the earth's atmosphere which has 800 gigatons of carbon dioxide stored with a 58 gigaton per year cycle. If we compare the amount of carbon currently in the soil with the amount in the atmosphere and consider how little carbon most of the earth's soils contain, it becomes clear that the earth's soils are easily able to sequester the excessive amounts of

atmospheric carbon dioxide and store it indefinitely to help mitigate climate change, which will be discussed more thoroughly in chapter 4.

Chapter 2: Biochar Research

Biochar is the product that remains once biomass is heated, within a certain temperature range with little to no available oxygen. Traditionally, biochar is made by digging an earthen pit that is then filled with biomass such as wood and crop residues, set to fire and then covered with soil, nearly eliminating the oxygen supply, creating a slow, low temperature burn. Although this is still practiced regionally, modern techniques are more widely used. The traditional method is known to emit considerably more pollutants than modern methods. Although advanced gasifying techniques exist, simple modern approaches are known that also create biochar while emitting few toxins. Biochar is made to be used as a soil amendment known traditionally for increasing fertility in soils, contemporarily, biochar has been found to have much greater potential.

Throughout recent history people have been changing their environment through pyrolysis for thousands of years. Ancient peoples around the world discovered that different methods of burning vegetation proved beneficial to the landscape, providing increased crop yields by more fertile soils. The earliest use, although not the most researched, use of charcoal fertilizer likely took place in East Asian countries (Glaser, 2002) where limited arable land coupled with dense populations led to the need for intensified agriculture. It is known that several thousand years ago, Asian farmers were producing rice husk charcoal and mixing it with an animal or human excrement as well as other ash and organic litter to be used as fertilizer

(Ogawa, 2010). Asian and other cultures have been researched but no culture has had more of an effect on the recent and dramatic increase in biochar interest than the discovery that substances extremely similar to biochar can explain the high amounts of organic carbon (Glaser et al., 2001) and sustained fertility of Amazonian Dark Earths, or Terra Preta do Indio (Lehmann et al, 2003a). Since, biochar has been related to the soil management practices of peoples living in the Amazon prior to the arrival of Europeans and the development of complex societies in the Amazon region (Peterson et al., 2001).

Spaniard Francisco de Orellana, traveling with creweastward along the Amazon River in search of the "City of Gold" in 1542 after having left present day Peru, described vast settlements that extended for miles, Of his journey Orellana said,

"there could be seen very large cities that glistened in white many roads that entered into the interior and besides this, the land is as fertile as our Spain."

However, subsequent travelers in the coming decades described lands free of settlement causing many to question the integrity of Orellana's account. Evidence would later suggest that perhaps Orellana's account may have been accurate as it is generally accepted the Europeans introduced multiple diseases to the area, nearly eliminating the population before subsequent travels were made.

The history of how Terra Preta research began and would eventually lead to the coining of the term "biochar" begins in 1879 when explorer Herbert Smith wrote in *Scribners*Monthly(Marris, 2006) about something unusual about the soil along the Amazon River basin;

"the best [soil] on the Amazons...a fine, dark loam, a foot, and often two feet, thick..[which] owes its richness to the refuse of a thousand kitchens and maybe a

thousand years...[in one stretch] it forms almost a continuous line...thirty miles long...and strewn over it everywhere we find fragments of Indian pottery so abundant in some places they almost cover the ground...like shells in a surf-washed beach" (Woods and Denevan, 2004).

Terra Preta is an anthropogenic soil that was initially created by native Amazonian peoples as early as 7,000 years ago (Marris, 2006). What makes Terra Preta different from other soils of the region is its extremely high carbon content, as high as nine percent (Woods and McCann, 1999). The high carbon content is due to the native peoples' practice of "Slash and Char" agriculture. This is a process where vegetation is "slashed" during the wet season and burned soon after while the vegetation is still holding water. The water reduces the amount of oxygen available for the process, therefore reducing the temperature and decreasing the amount of carbon released as carbon dioxide, which, as a result increases the amount of carbon that will remain, thus increasing the carbon content of the soil. What also makes this soil unique is its ability to regenerate at a measurable rate, approximately one centimeter per year. Terra Preta's fertility is due not only to its high percentage of carbon, but because of high amounts of nutrients such as; nitrogen, phosphorus, calcium, zinc and manganese (Glaser, 2007).

Although Terra Preta is categorized as a type of Latisol, most of the Amazon consists of infertile soils known as Oxisols. The natural infertility of these soils leads many people to question the number of people that the area could have supported, being poor for agricultural use, but the presence of Terra Preta in settled areas totaling a land mass the size of France (Mann, 2005) could have made sustainability possible for a high population, as described by Orellana.

The term "biochar" developed more recently as soil management and carbon sequestration issues have become intensified. The earth's environmental needs have spurred great interest in biochar, as research has increased dramatically in the past decade (see Figure 2).

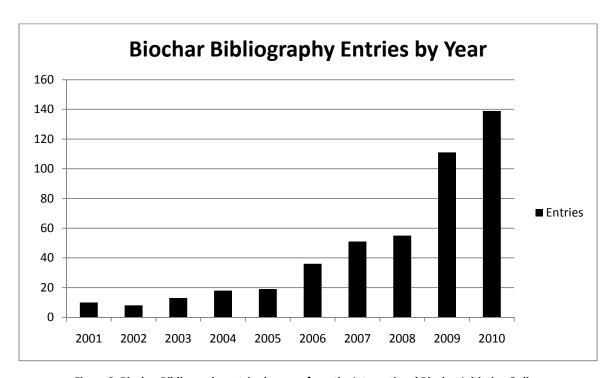


Figure 2: Biochar Bibliography entries by year, from the International Biochar Initiative Online

(Note: Biochar bibliography entries for previous years exist, but are few in number.)

Although familiar with the effects, these early people likely were not familiar with the carbon based product responsible for the increases in soil fertility, what is now known as biochar. Biochar allowed early environments to support civilizations that otherwise would have been beyond their means. With large-scale implementation modern society may be able to do the same for ourselves. However, at the current time, biochar is only manufactured on a small scale and sold as an additive for small lawns and gardens. However, if biochar can be produced on a large scale, the environmental impact would be profound. What biochar does is sequester

carbon for infinite amounts of time, while increasing soil fertility; two of the major needs of the planet. By sequestering carbon from the atmosphere, biochar mitigates climate change. By increasing soil fertility, biochar mitigates global hunger and a waning food supply.

Biochar is formally defined as the carbon-rich remnants obtained when biomass, including wood, manure, and leaves are heated in a contained environment in which little to no oxygen is available (Lehmann and Joseph, 2009). More specifically, biochar is the product of thermal decomposition or organic material under limited supply of oxygen at temperatures less than 700 degrees Celsius (Lehmann and Joseph 2009). Biochar should not be confused with charcoal, although the process by which charcoal is made is similar and is possibly the oldest industrial technology of mankind (Harris, 1999). The two are different in that biochar is produced with the intent to be used as a soil amendment, to store carbon, or filtrate percolating soil water. Charcoal is used as a fuel for heat, use as a filter, and is used in coloring agents and also in iron making. Also, biochar should not be confused with ash, considering the two are made differently, ash by burning, biochar by pyrolysis, and that their chemical composition differs greatly. Ash mainly consists of the minerals calcium or magnesium and inorganic carbonates (Lehmann and Joseph, 2009). Additionally, the majority of fires leave a limited portion of the vegetation only partially burned in areas where dioxide is limited with a portion remaining as char (Kuhlbusch and Crutzen, 1995). The outstanding property of the organic portion of biochar is the high carbon content that is composed of compounds with a high aromaticity (aromaticity refers to an increase in chemical strength (aromaticity, 2011)) which are characterized by rings of six C atoms linked together without oxygen or hydrogen (Lehmann and Joseph 2009).

Additional terms associated with biochar production are charring, burning, and pyrolysis. Charring is used to describe the process in which making charcoal or char originating from fires (Lehmann and Joseph, 2009). Pyrolysis is usually used to investigate the organic chemistry or organic substances (Leinweber and Schulten, 1999) or for analytical procedures. Burning however, is used when no char remains, only ash that does not contain organic carbon, although much of what is called ash does contain char or biochar. It should also be noted that burning differs greatly from charring and pyrolyses not only the physical remnants but the gaseous compounds emitted (Lehmann and Joseph, 2009). Recent years have proved that biochar is more stable than other soil amendments, increasing fertility beyond fertilizer effect (Lehmann, 2009). Additionally, the properties of biochar hold nutrients more effectively than other organic material in soil. This is what separates biochar from other types of manure or compost. Looking to the future, four main concepts motivate biochar research: soil improvement, waste management, climate change mitigation, and energy production.

Chapter 3:The Physical Properties of Biochar

Every soil has its own distinct physical properties. These properties depend on the nature of the mineral and organic matter within that soil, and their amounts (Brady and Weil, 2008). When biochar is a part of a soil mixture its contribution to the physical nature of the system may be substantial. It may influence depth, texture, structure, porosity and consistency through changing the bulk surface area, pore size distribution, density and packing (Downie et al., 2009). These effects of biochar then may have an impact upon plant growth by the penetration depth and availability of air and water within the root zone which is determined

largely by the make-up of soil horizons. By affecting the physical characteristics, biochar will affect the soils response to water, its aggregation, and workability during preparation, shrink/swell dynamics and its permeability (Brady and Weil, 2008). Much of biochar research is focused on the function of activated carbons in the biochar. These carbons are black carbon with high internal surface area and micro porosity and are widely used as adsorbents in separation and purification process for gases, liquids and solids (Downie et al., 2009).

The physical make-up of biochar will depend on what biomass was used and also on the pyrolysis system that was used. The degree of alteration of the initial structures of the biomass, processes as micro structural rearrangement, attrition during process and the formation of cracks all depend upon the conditions to which they are exposed during processing (Downie et al., 2009). Generally, the biochar will contain the imprint from the material in which it was made (Laine et al., 1991; Wildman and Derbyshire, 1991) and this has a great impact in its final physical and structural characteristics. Mass is lost mostly in the form of volatile organics during pyrolysis and an amount of shrinkage or volume reduction occurs. Hence, "during thermal conversion, the mineral and C skeleton formed retains the rudimentary porosity and structure of the original material. The residual cellular structures of botanical origin that are present and identifiable in biochars from woods and coals of all ranks contribute the majority of the macro porosity present (Wildman and Derbyshire, 1991)."

The temperature in which char is made will negate the structure of the char and what other materials have underwent thermal decomposition and have been gasified and which materials have not. At temperatures over 120 degrees Celsius organic materials begin to

undergo some thermal decomposition, losing moisture. Between 200 and 260 degrees Celsius hemicelluloses are degraded. Cellulose will begin to degrade between 240 and 350 degrees Celsius and lignin between 280 and 500 degrees Celsius (Sjöström, 1993). The proportions of these factors influence the degree of reactivity and the degree to which the physical structure is modified during processing (Downie et al., 2009).

In systems that have higher oxidative gasification conditions, the burn off of the fixed carbon has the most effect on increasing the surface area. Thus, the surface area depends greatly on the carbon mass removed during processing, creating pores in the material (Zabaniotou et al., 2008). Another condition leading the structural complexity of biochar is the occurrence of cracking. Typically, biochar has macro cracks, which is related to feedstock properties and the rate at which carbonization is done (Byrne and Nagle, 1997). Biochar made from wood is normally cracked due to shrinkage during pyrolysis because the inside does not decompose as quickly as the outside (Brown et al., 2006). High temperature, 1,000 degrees Celsius, surface area is controlled primarily by low temperature, less than 450 degrees Celsius, cracking and high temperature micro structural rearrangement (Downie et al., 2009). Recent research has found that the cracks formed are too numerous and too large to be sealed off by micro structural rearrangement at higher carbonization temperatures (Brown et al., 2006). Other processes have proven to create carbon monoliths, biochars which have no cracks (Downie et al., 2009).

An important factor to consider when discussing the potential effect of biochar is that not all biochar consists of carbon of the same stability in the soil. Depending on the biomass

used and the pyrolysis conditions, biochars produced with contain carbon of varying aromacity, resulting in more and less stable forms of carbon. The more stable form, known as recalcitrant carbon is believed to be stable in soils for an unknown length of time, likely several thousand years or more. The other, low aromacity form is known as labile carbon, which can be quickly degraded by the soil and as a result be released to the atmosphere at carbon dioxide within a couple years of application. Biochars are known to contain labile carbon content ranging from two percent to twelve percent, a substantial amount when calculating potential carbon emission offsets. The main factor contributing the amount of labile carbon in biochars is the temperature at which the biochar is processes. At lower heating rates (slow pyrolysis), at a temperature of 475 degrees Celsius, carbohydrates are almost entirely converted to volatiles, whereas in fast pyrolysis systems certain limitations restrict the biochar formation process, resulting in a biochar that may contain a portion of unconverted biomass that will mineralize quickly in the soil (Yang et al., 2007).

Chapter 4: Biochar as a Soil Amendment

When considering the use of biochar as a soil amendment it is important to remember that the activated carbon that biochar consists of alone will not increase soil fertility (Tenanbaum, 2009) and thus will not increase crop yields as additional nutrients are also necessary. For example, the Amazonian peoples who were producing activated carbon to add to the soil were also adding remains from fish, plants, and other waste products that provided additional nutritional value. It is the combination of the biochar with its immense pore space

providing its high nutrient holding capacity, along with the addition of nutrients that give the soil its fertility.

Integrating biochar with fertilizers or forms of compost has been shown to cause a substantial increase in productivity in modern research as well. An extensive study on a highly weathered central Amazonian upland soil using fifteen combinations of biochar integrated with different nitrogen-phosphorus-potassium fertilizer, chicken manure, composts and agricultural lime (crushed limestone), each having five replicates resulted on average by doubling yields of rice and sorghum over the course of four harvests (Steiner et al., 2007). In another study, biochar used in conjunction with chemical fertilizer increased the growth of numerous vegetables, including winter wheat by 25-50% in comparison to just the fertilizer by itself (Guo, 2008).

Multiple variables contribute to the increases in fertility and thus, crop yield. Variables known to be changed or enhanced by the addition of biochar include: soil pH, cation exchange capacity (CEC), nutrient holding capacity (NHC), bulk density, carbon percentage, microbial environment, and water holding capacity (WHC). The alterations have important effects on the indirect nutrient value of the biochar such as the nutrient holding capacity of biochar is dependent on its cation exchange capacity (CEC) and anion exchange capacity (AEC)(Liang et al., 2006; Cheng et al., 2008). The CEC of biochars have proven to be dependent on the pyrolysis temperature at which it was produced, with higher pyrolysis temperatures making biochar with substantially higher CECs than the very low CECs of low pyrolysis temperature biochar (Lehmann, 2007). Recent research suggests that biochar has a minimal CEC in comparison to

soil organic matter (Cheng et al., 2006, 2008; Lehmann, 2007). As research continues to explore producing biochar to enhance CEC, it is known that once biochar has been exposed to oxygen and water that spontaneous oxidation reactions occur, likely as a result of microbial activity and can result in an unusually high CEC (Cheng et al., 2006, 2008; Liang et al., 2006). Modern research has also shown in low carbon, loamy sand soils of the southeastern United States that biochar additions have increased nutrient holding capacities, specifically phosphorus (Woods et al., 2009), the same study also suggests that biochar applied in high application rates could limit available nitrogen to plants.

As to the effect of biochar on pH, research shows that most biochars are alkaline but can be produced at basically any pH between 4 and 12 (Lehmann, 2007). It is known that the carbonates in biochar can have a liming effect on the soil. For example, one study applied biochar made from paper mill sludge to an acidic soil and the carbonates in the biochar promoted a 30-40% increase in wheat growth by overcoming the toxic effects of the exchangeable aluminum in the acidic soil (Van Swieten et al., 2007).

Bulk density of a soil is affected by biochar as biochar has a lower density than that of minerals common to a soil. For biochar, two types of density may be measured, solid density and bulk density, also known as apparent density. Solid density refers to a measure of density on the molecular level and is dependent on the degree of packing of the carbon structure. Bulk density is that of multiple particles and includes the macro porosity and inter-particle voids. Usually an increase in solid densities would foster a decrease in bulk density as it would develop greater porosity during pyrolysis. The highest known density of carbon in biochar is known to

be about 2.1 g/cm³ (Emmett, 1948), slightly lower than that of solid graphite. Due to their porosity and turbo static structure, most biochars have a much lower density (Oberlin, 2002) around 1.5-1.7g/cm³ (Janakowski et al., 1991; Oberlin, 2002). These densities being lower than that of mineral soils can change the hydrology of the soil in accordance with application rates of the changes in porosity and, eventually, aggregation (Watts et al., 2005).

The carbon percentage of biochar is largely dependent on the biomass used for production and the temperature at which the biomass pyrolysed. Carbon content is broken into three classes; high, medium, and low. High requiring a biochar with 80% or greater carbon, medium between 60% and 80% carbon and low, 59%-15% carbon. The carbon composition for wood produced at 500 degrees Celsius often exceeds 80% (Antal and Gronli, 2003) and some may achieve that percentage below 500 degrees. Biochars in the medium class may include maize stalks, cattle manure with sawdust. While low carbon achieving biochars include rice hulls and chicken litter (Lehmann and Joseph, 2009).

The amount and fineness of biochar, as well as the method used for application vary regionally and in different soils. Trace amounts of biochar in poor soils has proven to be substantially beneficial, while in productive agricultural soils, large quantities of biochar have proven to be largely irrelevant. The fineness or "dustiness" of biochar also has an impact on production as a finer biochar will result in more surface area and would presumably be more effective. Contrary to that common train of thought, biochar does reach a point of fineness where it too fine and therefore less productive. Many methods exist for biochar application and of those; several can be utilized with common agricultural implements. In some

agricultural systems where mechanical access to the soil is limited or limited-till or no-till farming practices are maintained a top dressing method is preferable. Top dressing is the method of applying the biochar to the top of the soil without incorporating it at any depth. This can be done by hand, as it was traditionally or by using modern machinery such as a fertilizer spreader. The biochar will be incorporated through natural processes such as rainfall and through macro faunal activity. The rate at which the biochar will incorporate itself into the soil is not known, but research suggests that substantial vertical transport has taken place in top-dressing application methods (Blackwell, 2009). Another popular method is the deep-banding application method. Deep-banding using a mechanical system to plant the biochar in bands from five to ten centimeters wide and twenty to sixty centimeters apart (Blackwell, 2009) at depths that best suit the particular agronomy where the biochar is being applied.

Chapter 5: Biochar to Mitigate Climate Change, for Energy Production, and Waste Management

Applying biochar to soil is known as a means of sequestering atmospheric carbon dioxide (Lehmann et al., 2006). For the carbon to be truly sequestered, two things must be accomplished. Plants have to be grown at the same rate as they are charred considering the actual step from atmospheric carbon dioxide to organic carbon is delivered by the photosynthesis taking place in plants. However, plant biomass that is formed on an annual basis typically decomposes quickly, releasing the carbon back into the atmosphere as carbon dioxide, but if the biomass is transformed into biochar that decomposes at a dramatically

slower rate, the cycle is slowed (Lehmann, 2007b). Secondly, the biochar must be more stable than the biomass which was made from.

Almost four times more organic carbon is stored in the Earths soils than in atmospheric carbon dioxide. The atmospheric carbon is on a 14 year cycle through the biosphere. The annual uptake of carbon dioxide by plants is eight times greater than the current anthropogenic carbon dioxide emissions. If we can divert even a small portion of the large amount of carbon cycling the biosphere into the biochar cycle, we would make a large difference to atmospheric carbon dioxide concentrations, yet a rather small contribution to the global soil carbon storage (Lehmann and Joseph, 2009).

The energy captured during biochar production and applying that biochar to soils is beneficial for securing the production base for generating the biomass (Lehmann, 2007) and reducing overall emissions (Gaunt and Lehmann, 2008). Applying biochar to soil opposed to using it as a fuel reduces the efficiency of pyrolysis bioenergy production but the emission reductions that come with biochar additions to the soil seem to be greater than the fossil fuel offset in its use as fuel (Gaunt and Lehmann, 2008) In 2004, the global potential to produce ethanol from waste was estimated to be able to offset 32 percent of gasoline consumption (Kim and Dale, 2004). An assessment of the global potential of bioenergy from forestry yielded a theoretical surplus supply of 71 exajoules (one exajoule is equal to 1018 joules)in addition to other wood needs for 2050 (Smeets and Faaij, 2006). This is in comparison to a worldwide energy consumption of 489 exajoules in 2005 (EIA, 2007). Yet even a fraction of the global

potential would be an important contribution to an overall energy solution, on its own it will not be able to satisfy future global demand (Lehmann and Joseph, 2009).

Agricultural management of both crop and livestock wastes poses a substantial environmental concern that could lead to the pollution of water, above and below the surface (Carpenter et al., 1998; Matteson and Jenkins, 2007). Also, correct management of organic wastes can help mitigate climate change indirectly in numerous circumstances. These include decreasing methane emissions from landfills, reducing industrial energy use and emissions due to recycling and waste reduction, recovering energy from waste, decreasing energy used in long- distance transport of waste materials, and increasing carbon sequestration in due to decreased demand for paper and decreasing energy used in long-distance transport of waste (Ackerman, 2000).

One such waste management would be using pyrolysis to produce biochar from crop residues such as corn stalks, wheat straw or rice husks. This way we are using leftover crop residues to create stable carbon opposed to allowing the residues to decompose and be released back into the atmosphere. Opponents argue that removed the crop residues will result in the agricultural soil being deprived from nutrients that are returned to the soil be the decomposition of the residues either through being incorporated into the soils through tillage or what remains will incorporate themselves naturally in non-tillage applications, date from past studies confirmed that corn fields lost substantial amounts of nitrogen by the use of this method.

Chapter 6:A Case Study with Results

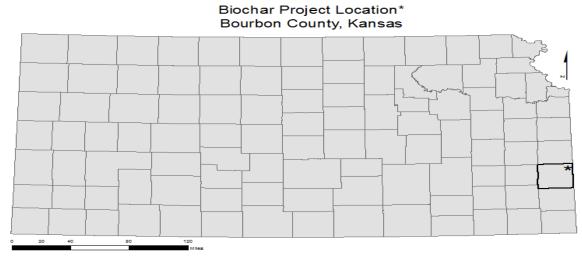


Figure 3: Project location, Bourbon County, KS, by the Author

Research to date has provided very little data for dry and temperate climate. Most biochar research has come from the tropical climates in South America and Southeast Asia (Blackwell et al., 2009) where the greatest consequence on crop production has been documented in both tropical and irrigation systems of the highly weathered, high acidity soils are most accepting of the relief provided through biochar application (Blackwell et al., 2009). It is known that some fertile soils with both biochar and fertilizer additions do not substantially impact yields, I felt the necessity to perform my own research on a common mollisol pasture soil of southeast Kansas (see Figure 3), the Tamaha silt loam (see Figure 4), using a variety of biochar treatment in order to test the effects of biochar in varying amounts over the course of a single growing season. It should be noted that biochar typically requires an inoculation period

before being an effective soil amendment, given the time restraints, this study will test biochars role in changing soil properties without any inoculation period.



Figure 4: Project Location and Soil Type. Data from the Web Soil Survey, edited by the Author

My project began by selecting an location that would provide the project with the necessary means. This included a level, well drained location for the construction of a biochar producing oven, as well as a location that could provide ample amounts of biomass, some of which would be converted to biochar, some of which would be used as fuel for biochar production. I decided on a wooded location near our home where I could construct an oven near the road and its dense timber would provide plenty of biomass from its native Oak and Ash tree forest. From this location I used multiple means, including a chain saw, hand saw, and hand gathering, to collect enough biomass for each batch, approximately of one hundred pounds, with all pieces no longer than three feet and no more than two inches in diameter. I only collected dead wood for the purpose of producing biochar as only wanted to use wood that would otherwise

decompose, emitting its carbon to the atmosphere at carbon dioxide. I also would use approximately one hundred pounds of fuel for each batch. This fuel also consisted of Oak and Ash wood with no size restrictions other than it must fit in the oven and also Hedge wood that I brought in from another location to provide increased heat and a more efficient pyrolysis process. Once the biomass was acquired, I then made the biochar using a self-made in-ground oven and steel barrel as a pyrolysis chamber. I dug the oven by hand three feet deep with an area of approximately twelve square feet, totaling 36 cubic feet (see PHOTO I). This oven would serve to hold a fifty-five gallon steel barrel containing the biomass to be pyrolysed to biochar as well as the biomass used as fuel. The barrel used as a pyrolysis chamber consisted of the main body of the barrel and a removable lid, which was sealed in place during production. It is important to keep the pyrolysis chamber, in this case a steel barrel, mostly sealed but not entirely. If the barrel is entirely sealed as the fuel heats the gases inside the barrel, pressure builds, and too much pressure will create an explosion. With this in mind I built a small vent on the barrel's lid by decreasing the size of the pre-existing vent by welding a series of washers with decreasing inside diameters over the top of the existing vent to ensure that the pressure inside the barrel during production was always greater than that outside the barrel so that gases were forced to escape and could not enter. During pyrolysis this creates a visually interesting effect as the hot, volatile gases escape the barrel they are introduced to oxygen and are immediately ignited (see PHOTO III), resulting in a constant flame.

Once the wood for fuel which was placed at the bottom of the oven, has been set to fire and is displaying a consistent burn, I then set the chamber in place, and covered the oven with metal sheeting for heat retention (see PHOTO II). The process of pyrolysis has completed once

the volatile gases being ignited outside the chamber are no longer being emitted, and the barrel has been given time to cool for safety purposes, the barrel could then be removed. This was consistently a three to four hour process between the time the barrel was introduced to oven through pyrolysis and cooling to the point of removal. The residual biochar from the initial biomass which, consistently lost two-thirds of its mass (see Figure 5), generally maintains its initial shape, but is fractured in many places, is very brittle, and is thoroughly black (see PHOTO IV).

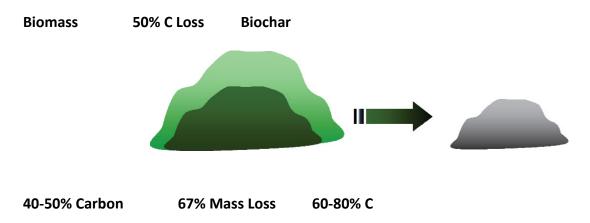


Figure 5: The Process of Pyrolysis by the Author

Once I had produced enough biochar for my project plots it was then necessary to incorporate the biochar with another material which contained water and nutrients so that when the biochar is introduced to the soil it does not compete with the plant for water and nutrients as it has collected them from the other material. For my project I decided to use mulch made from cotton burrs. The biochar was then mixed with its equal weight in cotton burr mulch, soaked with water, and left idle for several days to allow the biochar to absorb

water and nutrients from the cotton burr mulch. After that period, I applied the biochar to eight, twelve square foot plots, with a total of four treatments (see Figure 6).

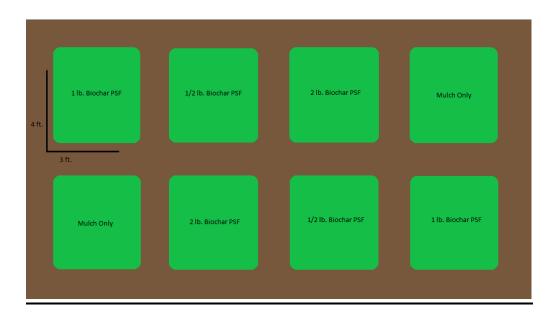


Figure 6: Project plots diagram, by the Author

Project Photographs

PHOTO I: Project oven





PHOTO II: Project oven, covered during production



PHOTO III: Gases escaping during production

PHOTO IV: Biochar just after production



Two of the plots received mulch only, one pound per square foot, while two plots received two pounds per square foot of the biochar/mulch mix. Two of the remaining four plots received one pound per square foot of the mixture, while the remaining two received four pounds per square foot of the mixture. I planted 30 seeds of sweet corn to each plot, each in three measured rows of ten to a determined planting depth, and germination rates were recorded. I maintained the plots over the course of the growing season by hand weeding. After the growing season, I removed the biomass from each plot and recorded the weight.

The laboratory portion of the project consisted of measuring the difference between the eight plots, pre-treatment and post-treatment from samples taken from the plots based on four soil characteristics: cation exchange capacity, pH, bulk density, and carbon composition.

Cation Exchange Capacity

I measured cation exchange capacity following the initial procedure from the soil survey laboratory methods manual by R. Burt (2004) and Mulvaney (1996). The process begins by adding 2.5g of air dried soil for each of the sixteen samples taken to 50ml centrifuge tubes and adding 40ml of ammonium acetate with a pH of 7, which are then balancing using DI water and placed on the shaker for 30 minutes. Then, I placed the tubes in the centrifuge at 2000 revolutions per minute for five minutes. This process results in the centrifuge tubes containing two elements: the soil concentrated in the bottom of the tube as a pellet, and the liquid supernatant on top of this. I discarded the supernatant, but kept the pellet and repeating the

process twice more to ensure that all the exchange sites were saturated with ammonium. I repeated the same process three more times using 95% ethanol to remove any excess ammonium that may be present. I was able to test this taking a sample of the supernatant from each of the 16 samples and adding Nessler's reagent to test for the presence of ammonium, which if present, results in a brown precipitate.

The next process is similar to the first two steps except using 40ml of 2 M potassium chloride and that the samples do not need to be shaken for each of the three rinses. Instead of discarding the supernatant, for this step I dispensed the 40ml of potassium chloride into separate beakers for each of the sixteen samples for each rinse, leaving 16 beakers each with 120ml of potassium chloride. This step replaces all of the ammonium on the exchange sites with potassium so that the equivalence concentration of ammonium in the beaker exactly equals the moles of charge in the weight solid fraction (2.5g).

The next step required that I transfer 1ml of each of the samples into 25ml beakers using a digital pipette. To those flasks I added 1ml of 6% EDTA solution and 4ml of sodium salicylate-sodium nitroprusside and 2ml of buffered sodium hypochlorite and then brought the flasks up to volume using DI water. This step also required that I made six standards using varying amounts of ammonium nitrate opposed the sample supernatant, as well as the other reagents. Once I had added all the reagents I placed all the flasks in 37 degree Celsius water bath for 30 minutes to help develop the desired emerald green color. For the final step before calculations I poured a sample from each flask into a cuvette and individually placed them into

the spectrophotometer and measured each samples absorbance at 667nm. I entered the results into a formula to find the cation exchange capacity, expressed in cmolc/kg.

Bulk Density

To calculate bulk density I used the clod method following Blake (1986). This procedure calls for large clods samples from each plot to be sampled. The weight of the clods are recorded and then the clods having been placed in a porous net are dipped into melted paraffin for a brief period, then removed and placed to hang freely to cool for 3-5 minutes. Once the paraffin had hardened I individually dipped the clods into a 1000ml beaker on a scale containing 600ml of DI water and recorded the weights. Ideally I would have used samples from each of the plots both pre- and post-treatment; however, I did not take samples for bulk density before applying the biochar treatment (trt.) and, therefore, used three samples near the plots for the pre-treatment average and the samples taken from each plot post treatment, totaling 11 samples. This procedure proves to be accurate as the weight of the beaker with the water plus the suspended clod is equal to the volume of the water displaced by the clod. I then entered each weight into a formula which computes the ratio of original mass of clod against the volume of the clod multiplied by its earlier recorded field moisture content plus 1.

рΗ

To measure pH I added 10g of each sample along with 10ml of DI water to a small paper cup and mixed them together. Then, I left the samples idle for 15 minutes before recording

their pH readings with a pH electrode meter. I repeated this process for all samples using 1M KCL opposed to DI water.

Carbon Analysis

I used the coulometer to measure the carbon percentage for all samples. A coulometer works by introducing the soil sample into a 936° C oven which effectively vaporizes all carbon. The vaporized carbon is then transferred as CO_2 through a chemical solution where it is quantifiably absorbed. The change in known absorbance automatically activates a titration current to return it to its initial state. The amount of current necessary to do so is measured, and from this measurement the coulometer calculates the carbon percentage of the sample which is displayed on a digital screen. I initially confirmed the coulometer accuracy by using a standard sample of calcium carbonate, which has a known Carbon percentage of 12%. My standard sample was measured at 12.07%.

Using the coulometer consisted of weighing out a small (20-40mg) sample of each sample which I placed into a small boat. Once in the boat, I carefully transferred the samples individually into a quartz and glass ladle which introduced them into the oven where titration process began, each sample requiring about eight minutes. I tested all eight post-treatment samples and used a mixed sample technique for my pre-application samples to find an average. I also tested one sample each of the cotton burr mulch, the cotton burr mulch/biochar mix, and

the biochar alone. Samples which had not been dried to 105 degrees were corrected to account for weight from moisture.

Results

Cation Exchange Capacity

The eight pre-treatment samples range from a C.E.C. in cmolc/kg of 35.4 to 61.0 with an average of 47.0 (see figure 7). The post treatment plots ranged in C.E.C. from 38.1-66.7 with an overall average of 49.0. More specifically, the mulch only plots have a slightly lower average of 46.5, and the ½ lb. treatment plots have an even lower average of 42.1. The average for the 1lb plots raises to 47.8 and the 2lb plot average rises to 59.8.

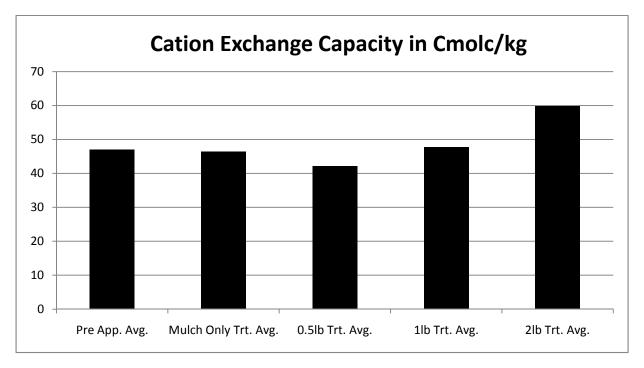


Figure 7: Results of cation exchange capacity laboratory testing

Comparing the post-treatment averages with their corresponding plots (see Figure 8) pretreatment averages the mulch only treatment has a loss of 1.25 cmolc/kg, and the 1/2 lb.

treatment has a loss of 4.1 cmolc/kg. The 1lb. treatment also has a loss of 5.4 cmolc/kg, yet the 2lb. plots have an increase of 18.9 cmolc/kg.

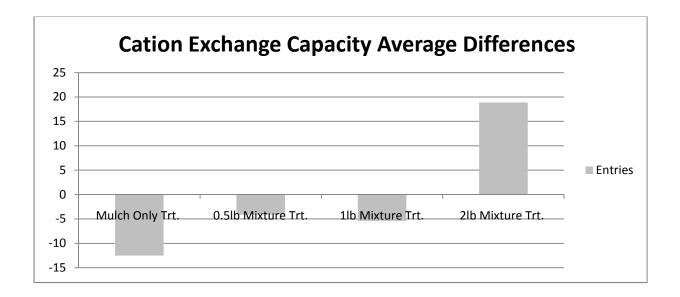


Figure 8: A comparison of the difference in cation exchange capacity between pre and post plot samples

рН

The pH measurements in both water and KCL increased as the amount of mulch/biochar mixture increased. For these results I'll first display the measured pH in water, with its corresponding measurement in KCL in parenthesis. The eight plots pre-treatment have an average pH of 5.3 (5.0), which increased substantially to 6.5(6.0) for the mulch only treatment average. From there, it remained mostly stable with slight, consistent increases. The 1/2lb. treatment plots average 6.6(6.0), while the 1lb. treatment plots average 6.8(6.2), with the 2lb. treatment plots averaging 7.0(6.4) (see Figure 9).

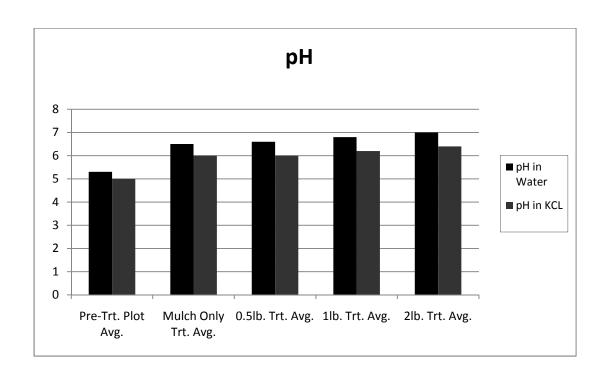


Figure 9: pH test results

Just as I did for cation exchange capacity, I compared the averages of the post treatment plots with their corresponding pre-treatment plots and found the average differences (see Figure 10). The mulch only treatment plots increased an average of 1.3(1.0) and the .5lb treatment plots increased by a slightly lower margin of 1.2(1.0) on average. The 1lb treatment plots increased by an average of 1.4(1.2) and the 2lb treatment plots increased by an average of 1.7(1.4).

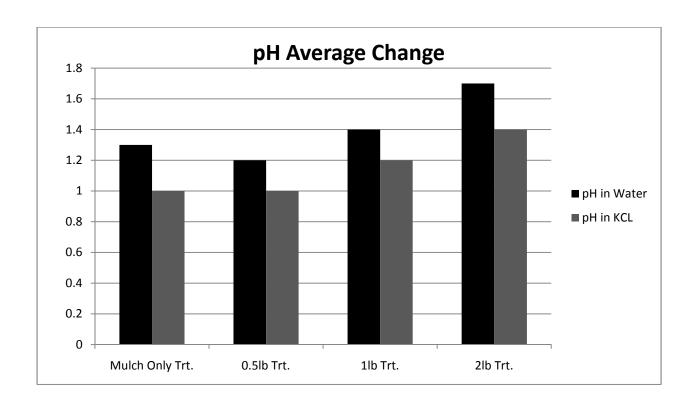


Figure 10: A comparison of the difference in pH between pre and post test samples

Bulk Density

Results for bulk density are averages of the two post treatment plots for each treatment, and the pre-treatment average is an average of three pre-treatment samples. All bulk densities are expressed as grams/cubic centimeter. The pre-treatment samples average 1.22 and increases slightly to 1.28 for the mulch only treatment plots. Nearly the same is the .5lb treatment plots with an average of 1.27. From here, the bulk densities decline to 1.01 for the 1lb treatment plot average and 1.10 for the 2lb treatment plot average (see Figure 11).

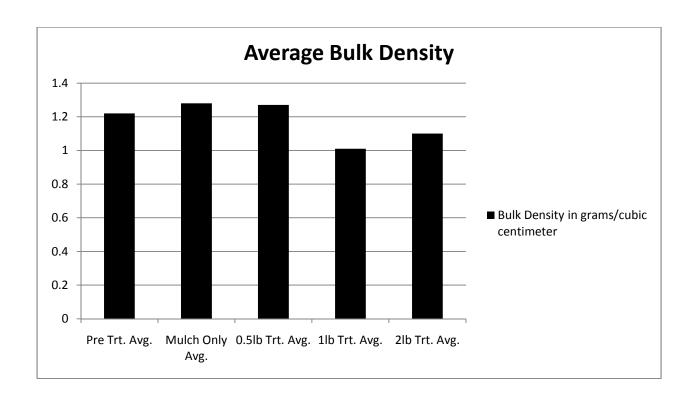


Figure 11: Results of bulk density laboratory testing

Carbon Analysis

My carbon analysis data is also provided in averages of the two plots for each of the four treatments. The pre application average is an average of two samples taken from a sample consisting of samples from all eight plots before treatment. The two pre-treatment samples provide carbon percentages of 1.94 and 1.60 for an average of 1.77%. The eight post-treatment plots range from 2.00% to 13.94%. The mulch only treatment plots average 2.25% and the .5lb treatment plot average jumps to 4.94%. The 1lb treatment plots increase to 6.86%, and the 2lb treatment plots again jump to 10.72%. The sample of cotton burr mulch is 29.50%, and the cotton burr mulch mixed in equal portions with biochar is 47.60%. The biochar sample alone is 78.0% carbon (see Figure 12).

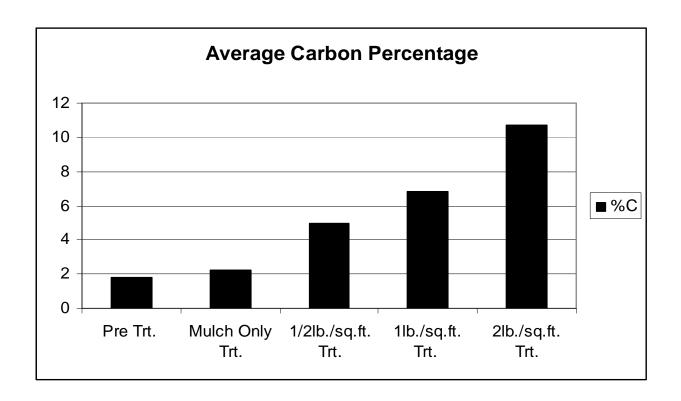


Figure 12: Results of carbon percentage laboratory testing

Chapter 7: A Discussion of Results

Cation Exchange Capacity

I cannot quantify the exact degree to which the biochar had on changing the soil composition to either increase, or decrease cation exchange capacity due to the equal portion of mulch that was applied along with the biochar. This being considered, the results must be interpreted as an effect of the applied mulch/biochar mix, not just the biochar.

The cation exchange capacities obtained do not indicate a substantial increase over the course of one growing season, except for the case of the 2lb treatment plots. Two of the other three treatments (mulch only and .5 lb. plots) experienced a decrease in cation exchange

capacity while the 1lb treatment plots exchange capacity only rose slightly. Although the 2lb plots display a substantial increase in exchange capacity, adding to two pounds of biochar is only feasible in a study such as mine and is not realistic on a large scale due to production and financial restraints. Based on the results of my study over the course of one growing season, biochar is not a feasible means for increased cation exchange capacity.

рΗ

In general, pH increased with the amount of biochar applied, but this is problematic as it also increased with the amount of mulch applied and increased substantially with only mulch applied. The pre-treatment plots averaged, in water, a pH of 5.3; the mulch only plots averaged a pH of 6.5. From there the pH increases only 0.1, 0.2, and 0.4 between each treatment as biochar/mulch mix application rates increase. For a more effective comparison, the pretreatment plots increased in pH with 1lb of mulch per square foot only, an average of 1.2. The 2lb plots which received an application of two pounds of mulch and two pounds of biochar increased an average of 1.7, twice the mulch and its equivalent in biochar for an increase of 0.5 more. The range of pH in the pre-treatment plots (in water) from 5.0-5.7 with no consistency makes interpreting the corresponding treatment averages difficult. Yet again, the mulch only plots have the greatest average increase (1.3) with the least amount of treatment. Given these results, mulch and not biochar is more effective at raising pH in this soil.

Bulk Density

My study resulted in consistent bulk densities for the pre-treatment average along with the mulch only average and the 0.5lb plot average. The 1lb. plot average does decrease substantially although the 2lb plot rebounds slightly, providing no linear relationship between a decreasing bulk density and treatment rates applied. The only positive relationship can be found by averaging the pre-treatment averages with the averages for the mulch only and 0.5 lb. plots together, and comparing that to an average of the 1lb and 2lb plots. This results in a bulk density of 1.25 for the pre-treatment (/mulch only/½ lb. average and a bulk density of 1.05 for the 1lb trt. /2lb trt. average). Considering such a result as conclusive would be ignoring data, the results which depict both substantial and unsubstantial results for bulk density must be deemed inconclusive.

Carbon Analysis

My carbon analysis is the least trivial of my tests as it comes as no surprise that adding carbon to the soil increases the carbon percentage in the soil, and the more carbon added the more that percentage increases. The purpose of this study is more to determine how much carbon percentages increase with varying applications of biochar in the soil. Again, any increase in C percentage must not be attributed solely to the function of biochar as all of the plots also received their compliment of cotton burr mulch. The amount of influence that each variable, the mulch or the biochar, had on the soil carbon percentage can be roughly quantified as the pre application average of 1.77 increased to 2.25 for the mulch only plots. An increase of not quite half a percent with 1lb of mulch applied per square foot. The ½ lb. treatment plots

which received one half pound of mulch per square foot averaged a soil of which was 4.94% carbon. If we use 0.5% as a standard for change from no treatment to 1 pound of mulch per square foot, than it may be assumed that 0.5lbs of mulch per square foot would cause an increase of 0.25%. If we compute the difference of the ½ pound plots and that of the pretreatment plots we have a sum of 3.17% of which 0.25% will be credited to mulch, leaving 2.92% of increase in soil carbon credited to biochar, assuming the standard is accurate. The data of my study would be most useful when attempting to raise soil carbon to certain percentage when the carbon percentage of the soil is known. The biochar measuring 78% carbon helps tell me about my production procedure. As discussed before most hardwoods pyrolysed at 500°C or greater produce a biochar of 80% or greater. Considering I used a combination of hardwood biomass for my biochar, it may be deduced that my oven was operating near the 500% mark, as was hoped for, although not measured as I did not possess the necessary instrumentation.

Study Conclusions

To conclude, my study did provide some compelling data considering the small sample size and short duration of the study. Although the cation exchange capacity did not increase as expected, it does tell us that the addition of biochar is not a means to increase exchange capacity substantially, at least not within the first growing season. The most compelling of the results is the increase in pH caused by the cotton burr mulch. As biochar is known to have a liming effect, it was expected to see such an increase in the plots where the biochar was applied, but I did not anticipate the bulk of the increase to come because of the mulch. It is

surprising to see little to no change in bulk density in the lower application plots and then such a decrease in the two highest application plots, this may however be a flaw in the data due to the small sample size. The biochar being 78% carbon is a strong indication of a well-made char, which is fortunate as that is imperative to the relevance of this study.

Chapter 8: Outlook

History provides that what is contemporarily known as biochar did wonders for the ancient Amazonian people who implemented its use. The creation of the Terra Preta soils made life sustainable for more people than the area should have been able to support. Today were looking to biochar to do the same, yet on a dramatically larger scale, and scale isn't the only major difference between the ancient Amazon and our modern society. The society and lifestyle of the Amazonian people allowed for nearly the entire population to contribute in the production of their food, while today in our modern society, the lifestyles of most people does not allow them to do so, and the tremendous responsibility of feeding the world is handled by just a few. If biochar production is implemented on a large scale, it will be much the same way, with few producers constantly battling an increasing global population.

As the earth's population continues to grow and our carbon footprint increases, humans will soon be demanding more resources from the earth than it can provide. The data and information provided in this thesis is shows that while biochar is currently making a difference on a small scale, biochar research, even if implemented on a large scale in the coming decades

is not the one response to this global concern. However, with continued interest, research, and most importantly, implementation, biochar technologies will be able to help provide the Earth with the resources necessaries for the continuation of sustainable production. The first step to solving a problem is recognizing that a problem exists. With recent swelling in biochar research confirms that we have recognized the problem and are taking steps toward solving it. It is my hope that biochar will not only serve to promote research in itself but that biochar research may also serve indirectly as a gateway to other sustainable research in agricultre and industry.

Personally, through experience with my project, feel that if biochar research is going to be effective it must take place place on a large scale. Using the same technique I used, or those similar requires too much effort to produce biochar. Larger, more efficient ovens which also cycle the exhaust gases into energy will be the only way this is feasible. On average, the batches I produced would require over one hundred pounds of wood to produce approximately 30 pounds of biochar from approximately 100 pounds of pyrolysed material. All together, the system used over 200 pounds of wood to produce 30 pounds of biochar. Considering I only used dead wood from the timber that would have degraded anyway, the system still functions as a carbon sink, but the effects are minimal. Another reason that it is unlikely to function by being implemented on a smaller scale, such as individual farmers producing their own supply is the time investment. Biochar requires roughly four hours to pyrolysize from wood. Once that process has been completed then the biochar must be broken down to the desired grain size; mixed with another soil, mulch, or compost, and given an adequate inoculation period before application. This time and effort commitment, along with the poor experiences of the process

deem it undesirable. These factors will cause potential producers to not maintain the motivation necessary to continue long-term biochar production on a smalle scale.



Data Tables Appendix

рΗ

Pre Plot Numbers	Measured pH in Water	Measured pH in KCL
1	5.5	5.2
2	5.4	5.0
3	5.3	4.9
4	5.1	4.8
5	5.0	4.8
6	5.2	5.0
7	5.5	5.0
8	5.7	5.2

Post Plot Numbers

Measured pH in Water

Measured pH in KCL

1	6.5	6.0
2	6.8	6.2
3	6.5	5.9
4	6.4	5.9
5	6.5	5.9
6	7.1	6.6
7	6.6	6.0
8	7.1	6.5

pH Average

Pre Plots	5.3	5.0
Mulch only treatment	6.5	6.0
½ lb. biochar w/ mulch	6.6	6.0
treatment		
1lb. biochar w/ mulch	6.8	6.2
treatment		
2lb. biochar w/ mulch	7.0	6.4
treatment		

pH Average Change (units)

Pre Plots		
Mulch only treatment	1.25	.95
½ lb. biochar w/ mulch	1.15	1.0
treatment		
1lb. biochar w/ mulch	1.35	1.2
treatment		
2lb. biochar w/ mulch	1.65	1.4
treatment		

Average Bulk Density (Grams per Cubic Centimeter)

Pre Application Average	1.22
Mulch Only Treatment Average	1.28
½ lb. Treatment Average	1.27
1lb. Treatment Average	1.01
2lb. Treatment Average	1.10

Carbon Analysis (%)

Pre plot mixed average 1	1.94
Pre plot mixed average 2	1.60
Post 1	2.60
Post 2	7.50
Post 3	4.72
Post 4	4.90
Post 5	2.00
Post 6	13.94
Post 7	5.15
Post 8	8.81
Mulch	29.49
Biochar/ Mulch Mixture	47.35
Biochar	78.06

Carbon Average (%)

Pretreatment average	1.77
Mulch only average	2.25
1/2lb. biochar w/ mulch treatment average	4.94
1lb. biochar w/mulch treatment average	6.86
2lb. biochar w/mulch treatment average	10.72

C.E.C. Pre Treatment Plots in Cmolc

1	58.9
2	35.4
3	47.4
4	61.0
5	36.6
6	46.4
7	45.0
8	45.4

C.E.C. Post Treatment Plots in Cmolc

1	49.6
2	52.9
3	38.9
4	38.1
5	43.3
6	66.7
7	45.3
8	57.5

C.E.C. Average Difference in Cmolc

Mulch Only Treatment	-1.25
1/2lb. Biochar w/ Mulch Treatment	-4.1
1lb. Biochar w/ Mulch Treatment	-5.4
2lb. Biochar w/Mulch Treatment	18.9

References Cited

Ackerman, F. (2000) 'Waste management and climate change', *Local Environment*, vol 5, pp223-229

Antal, M.J. and Gronli, M. (2003) 'The art, science, and technology of charcoal production', Industrial Engineering and Chemical Research, vol 42, pp1619-1640

aromaticity. 2011. In *Merriam-Webster.com*. Retrieved June 14, 2011, from http://www.merriam-webster.com/dictionary/aromaticity

Blackwell, P., Riethmuller, G., Collins. (2009) Biochar Application to Soil, *Biochar for Environmental Management; Science and Technology*, pg. 207-222

Blake, G.R., and K.H. Hartge. (1986) Bulk density. p. 363-375. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods, 2nd ed. SSSA Book Series no. 9. SSSA, Madison, WI.

Brady, N.C. and Weil, R. R. (2008) *An Introduction to the Nature and Properties of Soils*, 14th edition, Prentice Hall, Upper Saddle River, NJ

Brown, R. A., Kercher, A. K., Nguyen, T. H., Nagle, D.C. and Ball, W. P. (2006) 'Production and characterization of synthetic wood chars for use as surrogates for natural sorbents', *Organic Geochemistry*, vol 37, pp321-333

Burt, R. (ed.). 2004. Soil Survey Laboratory Methods Manual. Soil Surv. Invest. Rep. No. 42, Ver. 4.0. U.S. Dept. Agric., U.S. Gov. Print. Office, Washington, DC.

Byrne C. E. and Nagle, D. C. (1997) 'Carbonized wood monoliths- characterization', *Carbon*, vol 35 pp. 267-273

Carpenter, S. R., Caraco, N. F., Coreell, D. L., Howarth, R. W., Sharpley, A. N. and Smith, V. H. (1998) 'Nonpoint pollution of surface waters with phosphorus and nitrogen', *Ecological Applications*, vol 8, pp 559-568

Chameides, Bill. (2007) 'Picturing a ton of CO2' Basic Science of Global Warming

Cheng, C.H., Jehmann, J., Thies, J.E., Burton, S.D. and Engelhard, M.H. (2006) 'Oxidation of black carbon by biotic and abiotic processes', *Organic Geochemistry*, vol 37, pp1477-1488

Lehmann, J. and Engelhard, M. (2008) ,Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence', *Geochimica et CosmochimicaActa*, vol 72, pp1598-1610

Conway, G. (1999) The Doubly Green Revolution, Cornell University Press, Ithaca, NY, US

Downie, A., Crosky, A., and Munroe, P. (2009) 'Physical Properties of Biochar', *Biochar for Environmental Management*, pp 13-32

Durand, J. (1977) 'Historical Estimates of World Population: An Evaluation', *Population and Development Review*, Vol. 3, No. 3 (Sep., 1977), pp. 253-296

EIA (US Energy Information Administration) (2007) 'International total primary energy consumption and energy intensity', Energy Information Administration, US Government, www.eia.doe.gov/pub/international/iealf/tablee1.xls, accessed 10 August 2008

Emmett, P.H. (1948) 'Adsorption and pore-size measurements on charcoal and whetlerites', *Chemical Reviews* vol 43, pp69-148

Environmental Protection Agency. (2011) 'Greenhouse Gas Emissions' *Greenhouse gas* overview, http://epa.gov/climatechange/emissions/index.html#ggo

FAO (United Nations Food and Agriculture Organization) (2006) The State of Food Insecurity in the World, FAO, Rome, www.fao.org/docrep/009/a0750e/a0750e00.htm, accessed 7 August 2008

Gaunt, J. and Lehmann, J. (2008) 'Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production', *Environmental Science and Technology*, vol 42, pp 4152-4158

Glaser, B., Haumaier, L., Guggenberger, G. and Zech, W. (2001) 'The Terra Preta phenomenon: A model for sustainable agriculture in the humid tropics', *Naturwissenschaften*, vol 88, pp 37-41

Glaser B, Lehman J, Zech W (2002) Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal –a review. *Biology and Fertility of Soils* **35**, 219–230. doi: 10.1007/s00374-002-0466-4

Guo, M. (2008) 235th national meeting of the American Chemical Society

Harris, P. (1999) 'On charcoal', Interdisciplinary Science Reviews, vol 24, pp 301-306

Jankowska, H., Swiatkowski, A. and Choma, J. (1991) *Active Carbon*, Ellis Horwood, New York, NY

Kim, S. and Dale, B. E. (2004) 'Global potential bioethanol production from wasted crops and crop residues', Biomass and Bioenergy, vol 26, pp 361-375

Kuhlbusch, T. A. J., and Crutzen, P.J. (1995) 'Toward a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO2 and a source of O2', *Global Biogeochemical Cycles*, vol 9, pp 491-501

Laine, J., Simoni, S. and Calles, R. (1991) 'Preparation of activated carbon from coconut shell in a small scale concurrent flow rotary kiln', *Chemical Engineering Communications*, vol 99, pp 15-23

Lehmann, J., Kern, D.C., Glaser, B. and Woods, W. I. (2003a) *Amazonian Dark Earths: Origin, Properties, Management*, Kluwer Academic Publishers, The Netherlands

Gaskin, J.W., Das, K.C., Tassistro, A.S., Sonon, L., Harris, K., Hawkins, B., (2009) 'Characterization of Char for Agricultural Use in the Soils of the Southeastern United States' *Amazonian Dark Earths: WimSombroek's Vision*, Chapter 25, pp 433-443

Gaunt, J. and Rondon, M. (2006) 'Biochar-char sequestration in terrestrial
ecosystems- a review', Mitigation and adaptation Strategies for Global Change, vol 11, pp 403-
427
(2007a) 'Bio-energy in the black', Frontiers in Ecology and the Environment, vol 5, pp
381-387
(2007b) 'A handful of carbon', <i>Nature</i> , vol 447, pp 143-144
Joseph, S. (2009) Biochar for Environmental Management: An Introduction, <i>Biochar for Environmental Management</i>
Environmental Management; Science and Technology, pg. 1
(2009) 'Terra preta Nova – where to from here?', in W.I. Woods, W.G. Teixeira, J.
Lehmann, C. Steiner and A. WinklerPrins (eds) Terra preta Nova: A tribute to WimSombroek,
Springer, Berlin, pp 473-486
Leinweber, P. and Schulten, HR. (1999) ,Advances in analytical pyrolysis of soil organic matter
Journal of Analytical and Applied Pyrolysis, vol 49, pp 359-383
Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J. O., Theis,
J., Luizao, F.J., Petersen, J. and Neves, E.G. (2006) 'Black carbon increases cation exchange
capacity in soils', Soil Science Society of America Journal, vol 70, pp1719-1730
Mann, Charles. 2005. 1491: New Revelations of the Americas Before Columbus, p. 307
Marris, Emma. 2006. Black is the new green. Nature 442:624-626. August 10, 2006.
Mulvaney, R.L. 1996. Nitrogen - Inorganic Forms. p. 1123-1184. <i>In</i> D. Sparks et al. (eds.)
Methods of soil analysis. Part 3. Chemical methods. SSSA Book Series no. 5. SSSA, Madison, WI.
Oberlin, A. (2002) 'Pyrocarbons-review', Carbon, vol 40, pp7-24
Ogawa M, Okimori Y (2010) Pioneering works in biochar research, Japan. Soil Research 48, 489–
500. doi:10.1071/SR10006

O'Grady, R. and Rush R. (2007) 'The Terra Pretaphonomenon' *Managing the Carbon Cycle' Katanning Workshop 21-22 March 2007* www.amazingcarbon.com

Petersen, J. B., Neves, E. and Heckenberger, M.J. (2001) 'Gift from the past: Terra Preta and prehistoric Amerindian occupation in Amazonia', in C. McEwan, C. Barreto and E. Neves (eds) *Unknown Amazonia*, British Museum Press, London, UK, pp 86-105

Sjöström, E. (1993) *Wood Chemistry: Fundamentals and Applications*, second edition, Academic Press, San Diego, US

Smeets, E. M. W. and Faaij, A. P. C. (2006) 'Bioenergy potentials from forestry in 2050', *Climatic Change*, vol 81, pp 353-390

Stiener, C., Teixeira, W., Lehmann, J., Nehls, T., Vasconcelos de Macedo, L., Blum, W., Zech, W., (2007) 'Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil', *Plant Soil*(2007) 291:275-290

Tenanbaum, D. (2009) 'Biochar: Carbon Mitigation from the Ground Up', *Environ News*, innovations. Environ Health Perspect. 2009 February; 117(2): A70–A73.

Tilman, D. (1998) 'The greening of the green revolution', Nature, vol 396, pp 211 -212

Un.org. (2005) *UN News Centre. World Population to Reach 9.1 Billion in 2050, UN projects.*http://www.un.org/apps/news/story.asp?NewsID=13451&Cr=population&Cr1

Van Zwieten, L., Kimber, S., Downie, A., Chan, K.Y., Cowie, A., Wainberg, R. and Morris, S. (2007) 'Papermill char: Benefits to soil health and plant production', in *Proceedings of the Conference of the International Agrichar Initiative*, 30 April-2 May 2007, Terrigal, NSW, Australia

Watts, C.W. Whalley, W.R., Brookes, P.C., Devonshire, B.J. and Whitemore, A.P. (2005) 'Biological and physical process that mediate micro-aggregation of clays', *Soil Science*, vol 170, pp573-583 Wildman, J. and Derbyshire, F. (1991) 'Origins and functions of macroporosity in activated carbons from coal and wood precursors', *Fuel*, vol 70, pp 655-661

Woods, W. I. & McCann, J. M. (1999) in Yearbook Conf. Latin Am. Geogr. Vol. **25** (ed. Caviedes, C.) 7–14. (Univ. Texas, Austin)

Yang, H., Yan R., Chen, H., Lee, D., Zheng, C., (2007) 'Characteristics of hemicellulose, cellulose and lignin pyrolysis' *Fuel*, Volume 86, Issues 12-13, August 2007, pp. 1781-1788

Zabaniotou, A., Stravropoulos, G. and Skoulou, V. (2008) 'Activated carbon from olive kernels in a two-stage process:' *Industrial improvement*. Bioresource Technology, 99(2): pp. 320-326