# Impact of Bio-Char on Carbon Dioxide in the Atmosphere

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## Abstract

A review. A study of Terra Preta do Indio and bio-char was conducted to determine the technical feasibility of their use in sequestering atmospheric carbon dioxide as a summer undergraduate project for Dr. Tom R. Marrero. Properties of new and old Terra Preta were used. Literature of the last 40 years, including the electronic database SciFinder, was used. The educational component of this project included an assessment of different analytical methods to determine physical and chemical properties of bio-char. Lab tests of the bio-char include determination particle size distribution and elemental composition. The results obtained from literature for the carbon cycle mass balance indicates that 25-50% of carbon dioxide captured in biomass can be converted to solid bio-char or Terra Preta. The processes of converting bio-char to Terra Preta generate more energy than required for the process involved in making Terra Preta. This review indicates that sequestration of carbon dioxide is technically possible.

### Introduction

Bio-char sequestered soil, a soil based on the Amazonian Terra Preta do Indio from pre-Columbian times, has the potential to neutralize man-made CO<sub>2</sub> emissions at the current rate of emissions, 6 G tons C per year (see discussion below).

Terra Preta do Indio is a dark carbon rich soil that has been found to have up to 250 tons of C per hectare while being stable for over a thousand years.<sup>1</sup> While the method to make Terra Preta do Indio was buried with the Amazonians, progress has been made in the making new Terra Preta do Indio, Terra Preta Nova. For example, Oguntunde recently reported that the land under the charcoal kilns in Ghana, over time, has become a bio-char sequestered soil.<sup>2</sup> This dark soil in Ghana has an average temperature of 1.3-3°C higher than surrounding areas, depending on the moisture level. This increase in temperature enhances the seed growth and the production of crops.

In addition to the increased temperature of Terra Preta Nova soil, the Terra Preta soil has higher hydraulic conductivity that allows increased nutrient intake by the plants as shown in Table 1. The ability to hold water for plant life is also aided by the large surface area inside the bio-char that ranges between 200–400 m<sup>2</sup>/g.<sup>3</sup>

The CSS properties in Ghana compare with bio-char sequestered land in their dark nature and high carbon content.

For agriculture, however, char must be pyrolyzed at temperatures lower than 400°C to produce maximum yield of bio-char.<sup>4</sup> At temperatures above 400°C, the bio-char becomes fine soot that lacks the characteristic porosity of Terra Preta do Indio. The porosity has been hypothesized to prevent the ability of harmful fungi to build the bridges needed for expansion while allowing smaller, favorable bacteria and life forms to grow.<sup>5</sup> The porosity has also been used to explain the reduced emissions of nitrogen compounds from the soil. The bio-char enriched soil has also been shown to increase Mn, P, Ca, and neutralize the pH level of the soil.<sup>6</sup>

Soil Parameter	CSS	AFS
Hydraulic conductivity (cm/h)	11.4	6.1
Bulk density (g/cm <sup>3)</sup>	1.3	1.4
Total porosity (%)	50.6	45.7
Hue	2.9	3.2
Value	2.5	3.1
Chroma	1.7	2.1
Sand (%)	82.8	78.4
Silt (%)	14.2	15.9
Clay (%)	3.0	5.7

Table 1. Physical properties of charcoal-site soils (CSS) and adjacent field soils (AFS)<sup>2</sup>\*

\*Adapted from Oguntunde et al.(2008)

As part of a four-credit hour research class under the direction Dr. Tom R. Marrero, I conducted research into the use of Terra Preta and bio-char as a carbon sequestering using the resources of SciFinder, Endnote XI, and of the University of Missouri system, including staff. The goal was to obtain information on the feasibility of bio-char as a CO<sub>2</sub> sequestering agent; as well as to become familiar with university research resources.

A significant part of the learning for my undergraduate research project was done in various labs on Campus. Independent testing of a sample of bio-char (purchased from BuyActivatedCharcoal.com) was conducted for elemental composition and particle size distribution at the Soil Characterization Laboratory in College of Engineering. At the Research Core Facilities in the Veterinary Medicine School analysis by TEM (transmission electron microscope) was conducted for pore width and elemental composition. In the College of Arts and Sciences, Chemistry Department, analysis by XPS (X-ray photoelectron spectroscopy) was used to determine elemental composition of the sample. Finally, at the Missouri University Research Reactor (Nuclear), a fourth elemental analysis was conducted in an auxiliary laboratory by XRF (X-ray fluorescence).

# **Materials and Methods**

The sample of bio-char, propriety name Charcoal Green<sup>™</sup> Biochar, was obtained from BuyActivatedCharcoal.com. The bio-char purchased was a 9 lb. sample contained in a plastic pail.

The elemental analysis conducted by TEM was the first university resource used for the testing of the bio-char. Located at Research Core Facilities of the university, a sample of bio-char was analyzed by a staff member while I observed. A sample was prepared for the TEM by taking a thin layer of bio-char and placing in on the sampling device. The device was inserted into the TEM, where the machine was able to take readings by transmitting a ray of electrons through the sample. This produced images and spectrums for composition analysis.

Analyses conducted at the Soil Characterization Laboratory were done using the procedures for particle-size analysis according to the United States Department of Agriculture's <u>Soil Survey</u> <u>Laboratory Methods Manual</u>. A 10 g bio-char sample was ground to an acceptable size, then was sieved to less than 2 mm, and dried for testing of composition. In addition, a portion of the bio-char sample was sieved using 9 different sieves, mesh sizes were: 4, 6, 8, 10, 20, 30, 140, 170, and 250. Each portion of the sieved sample was weighed on a calibrated balance. Testing continues to be done to determine the composition of the bio-char by soil survey laboratory methods.

A portion of the subsequently used for both 30 mesh sample was used for both XPS and XRF.

The bio-char taken to the MURR was tested using X-Ray Florescence (XRF). For this analysis, a 3 g sample of the material was taken and mixed with .9 g of binder (a high quality paraffin material), and pressed to make a tablet like specimen. MURR's new tabletop XRF was used for testing. During XRF testing, x-rays are used to excite the electrons of the elements in the specimen. Then the excited electron undergo an energy decay, and the energy released is captured an analyzed by the XRF apparatus. The frequency, time delay, and other factors of this florescent energy leads to the determination of the elemental make up of the sample, as each element reacts slightly differently the frequency of the x-ray. Since a tabletop XRF was used, lighter elements like carbon and phosphorous were not detected by the machine.

In the Department of Chemistry, the bio-char sample was taken for elemental analysis using xray photoelectron spectroscopy (XPS). The sample was prepared on sample holder by placing a thin layer of bio-char on a slide of double-sided silver tape. The material was then inserted into the vacuum chamber where the pressure was lowered to 8 x 10-9 torr. At this extremely high vacuum, the x-rays could be used with minimum interference, and an electron spectrum could be read from the sample. This spectrum was input to software used to calculate the elemental atomic fractions.

A literature review was conducted on bio-char, Terra Preta do Indio, and the use of the two similar compounds in sequestration and agriculture. The database, SciFinder, was used to obtain articles from 1991 to 2009. In addition, Sombroek's (1966) <u>Amazon Soils: a reconnaissance of the soils of the Brazilian Amazon region</u>," is the original study on Terra Preta and was perused. Other key information was in the articles: "Energy Balance and Emissions Associated with Bio-char Sequestration and Pyrolysis Bioenergy Production" by Gaunt and Lehmann (2008) and "Sowing Fossil Hydrocarbons to Promote Bioenergy" by Laine (2009). Dr. Tom R. Marrero and the library staff also provided information on the various resources including Endnote XI and SciFinder.

#### **Results and Discussion**

#### 1. Laboratory Testing

At the EM Core, the bio-char was able to be seen under the electron microscope. Two images of the sample were taken as shown in Figure 1 and 2. Elemental composition was as taken as shown in Figure 3 and Table 2.



Figure 1. Sample of Bio-Char under TEM



Figure 2. Sample of Bio-Char under TEM



Figure 3. Composition analysis by TEM of Bio-Char Sample

Element	Net	Net	Counts	K-Ratio	Weight %	Weight %	Atom %	Atom %
Line	Counts	Error			Error			Error
C K	3648	+/-	76	0.47	43.52	+/- 0.91	52.90	+/- 1.10
O K	3064	+/-	94	0.28	45.70	+/- 1.40	41.70	+/- 1.28
Al K	2589	+/-	122	0.07	3.53	+/- 0.17	1.91	+/- 0.09
Si K	4172	+/-	135	0.12	5.20	+/- 0.17	2.70	+/- 0.09
S K	332	+/-	38	0.01	0.41	+/- 0.05	0.19	+/- 0.02
KK	495	+/-	75	0.02	0.77	+/- 0.12	0.29	+/- 0.04
Ca K	527	+/-	79	0.02	0.88	+/- 0.13	0.32	+/- 0.05
Total					100.00		100.00	

Table 2. Composition Analysis of Bio-Char by TEM

In the sample taken to the Soil Characterization Lab, the bio-char properties were determined as shown in Table 3. While the content of the sample was different than materials in literature, shown in Table 1, consideration must be taken into account that the bio-char sample was not mixed with the local soil and may have not shared the same pyrolyzed sources.

Table 3. Soil Characterization Laboratory Composition Analysis of Bio-Char Sample

Soil Composition	Sample (%)
Sand	72.3
Silt	8.7
Clay	19

The sieved sample particles average mass is shown in Table 4. The majority of the mass of the sample was from particles between a 10 and 30 mesh.

Mesh No	Weight on Sieves (g)	Percent on Sieves
4	0.05	0.05
6	1.69	1.73
8	8.91	9.14
10	7.98	8.18
20	32.73	33.52
30	33.92	34.62
140	12.39	12.64
170	0.08	0.08
250	0.04	0.04

Table 4. Bio-Char Sample Average Weight Distribution Taken at Soil CharacterizationLaboratory

\*average of three samples

At the XRF, the sample of bio-char between 20-30 mesh particle size, the elemental analysis results are presented in Table 5. Only the elements heavier that K were detected, making the method impractical for carbon detection, but detailed analysis on materials not picked up by any other method were obtained.

Using XPS, peaks for six elements: C, O, N, Ca, S, and Si were found. The atomic fraction of each element in the sample is listed in Table 6. The XPS values have an error of  $\pm 10\%$ .

Table 5. Composition of 20-30 Mesh Particles of Bio-Char Sample from XRF (Test Done at MURR)

Element	Composition
Κ	0.65%
Ca	6.43%
Ti	1355. ppm
Mn	872. ppm
Fe	2268. ppm
Zn	58.4 ppm
Ga	19.3 ppm
Rb	9.5 ppm
Sr	218.0 ppm
Zr	19.8 ppm
Nb	0.4 ppm

	Atomic
Element	Fraction
С	0.60
0	0.25
Ν	0.08
Si	0.02
S	0.04
Ca	0.01

# Table 6. Composition of 20-30 Mesh Particles of Bio-Char Sample from XPS (Test Done in Chemistry Department)

# 2. Elemental Composition Analyses

Each method of elemental analysis had its unique advantage. The TEM was by far the most time efficient, taking less than an hour to prepare and analyze the sample; however, it didn't pick up any trace heavy materials. The XPS had similar limitations in measuring, picking up one less element than TEM. The XPS took about a day for full analysis, but matched up with the TEM values within the given error for XPS for each element except for oxygen. On the other end of the spectrum, the XRF picked up many trace material, but none of the light elements like carbon and oxygen that made up the majority of the compound.

The results of all three methods agreed within error on the amount of Ca and K in the samples. In addition, all of the analytical equipment and services were available to me as an undergraduate researcher through a professor. These resources took advantage of the various departments that university has to offer.

# 3. Carbon Dioxide Cycle

To establish the need for the sequestration of  $CO_2$ , the gradual increase of  $CO_2$  concentration in the atmosphere must first be addressed using literature. Whether this is caused by nature or human activity has not been successfully determined, but humans do emit around 6 G ton C per year in the form of  $CO_2$  with the atmosphere already containing 750 G ton C.<sup>1</sup>

The environment naturally sequesters most of the natural  $CO_2$  produced through the large forests and the ocean; however, over the years,  $CO_2$  has steadily been rising as an increasing percent of the atmosphere. If the assumption is taken that none of our emissions are sequestered naturally, in little over a century the atmospheric  $CO_2$  will double. A popular way of combating the rise in  $CO_2$  is reforestation. Reforestation, however, is only a temporary solution as shown in Figure 4. Mature forests cease to be a successful method of sequestering  $CO_2$  as their output of  $CO_2$  begins to match the input. In addition, when each tree dies, all of the biomass is released back into the atmosphere via degradation.

Carbon stabilization of this biomass is possible through pyrolysis. Although 50% of the initial biomass is immediately lost into the atmosphere, the ability to sequester carbon over a large time scale far outweighs the short term lose as shown in Figure 5. The ability to retain over 40% of biomass promises a way to sequester carbon successfully through charcoal.



Figure 4. Carbon cycle of biomass and biochar<sup>7</sup>



Figure 5. Description of biomass and bio-char degradation over time<sup>8</sup>

#### 4. Selected Carbon Dioxide Sequestration Methods

Many ways of sequestering carbon dioxide exist as shown in Figure 6. Aquatic sequestration promises vast amount of  $CO_2$  sequestration. It proposes  $CO_2$  be pumped into containers designed to sink to the bottom of the ocean.<sup>9</sup> While this allows for large amounts of  $CO_2$  to be removed, there is a potential for unknown environmental harm to the deep sea. In addition there is a large amount of work needed to ensure the containers sink deep enough into the ocean and do not leak  $CO_2$  from the deep sea pressure. Reforestation is another proposed sequestration method, however, the short term gains at the cost of long term loses mentioned before make reforestation alone ineffective. Another solution is filling depleted petroleum reservoirs with  $CO_2$ , a method of getting the last drops of petroleum out of a well. While this provides a practical and currently available way of sequestering carbon, there are concerns about leaks and the amount of room available for sequestration.



Figure 6. Methods of CO<sub>2</sub> sequestration<sup>10</sup>

Bio-char sequestration, however, has few limitations on the space needed. The bio-char can be applied to all farmland, grassland, oceanic silt, and any other landmass that is not being used otherwise. Bio-char is more stable in tropical climates<sup>11</sup> and retains the majority of sequestered carbon for long lengths of time, ranging from decades to millenniums. In addition, there are very few ways that the carbon can be released from the bio-char after it is formed as it is distributed into the ground by both natural and artificial methods, depending on the climate as shown in Figure 7.



Figure 7. Black carbon content of soils in different climates<sup>12</sup>

The formation of bio-char is dependent on inexpensive sources of biomass. The sources of biomass are everything from crop wastes such as pecan shells and coconut husks to coal. Since many of the sources are waste materials and have little or no cost, production is affordable.

If bio-char is produced in the quantities needed for widespread agricultural use, the added fertility of bio-char soil would increase production of crops, but also cause problems. Plots of Terra Preta do Indio are avoided as farmland in the Amazon because the fertility of the land leads to weed problems that choke out all intended crops.<sup>13</sup> Additional weeding may cause additional energy use, but the weeds could also be used as a source of bio-mass for the production of bio-char with the potential to balance out the cost of the weeds.

# 5. Converting Biomass into Bio-Char

The material of the biomass plays a large role in the making of bio-char along with the pressure and temperature. There are many choice in the agricultural products used to make bio-char as shown in Figure 8. Carbon can also be sequestered through pyrolysis of coals and other carbon rich inorganic materials.



Figure 8. Energy and sequestration of agricultural material<sup>14</sup>

The temperature that the biomass sources are pyrolyzed also is a determining factor. While high temperature pyrolysis is better for energy purposes, all biomass is lost into the atmosphere. To avoid using high temperatures to make the bio-char, higher pressures must be used. This allows more charcoal to be formed as shown in Table 7.

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Production temperature (°C)	Fraction weight lost	C content (%)	N content (%)	C/N	<sup>14</sup> C activity of charcoal (DPM g <sup>-1</sup> DM)	Fraction <sup>14</sup> C lost	<sup>14</sup> C activity of carbonate (DPM g <sup>-1</sup> DM)	Fraction of <sup>14</sup> C in carbonate
70	0.00	42.7	2.31	18.5	$4.1  imes 10^7$	0.00	$2.1  imes 10^4$	$5.1 imes10^{-4}$
225	0.21	41.2	2.62	15.7	$4.6 \times 10^{7}$	0.10	$4.6 \times 10^{4}$	$1.0  imes 10^{-3}$
300	0.52	37.8	5.45	6.9	$1.8 \times 10^{7}$	0.79	$8.4 \times 10^4$	$4.8 \times 10^{-3}$
375 <b>°</b>	0.60	-	-	-	$8.6 \times 10^5$	0.99	$9.8  imes 10^4$	0.11

<sup>a</sup> There was not enough charcoal produced at 375 °C to determine its composition.

One advantage of the changing properties of bio-char is that it can be optimized for energy, sequestration, or syngas output. Extracted oils can be used to power automobiles much in the same way as ethanol does from corn, and the heat used in making the bio-char can be used as a source of power. Gases such as  $H_2$  are also formed and can be collected. The net balance of  $CO_2$  emissions could make the fuel formed in the making of bio-char the first negative emission fuel.<sup>15</sup>

# 6. Mass Balance

To prove the effectiveness of bio-char as a sequestering agent, a mass balance, a staple of university teaching, must be performed. The atmosphere contains about 750 G ton kg of C currently and humans are adding to it at a rate of 6 G ton kg of C per year.<sup>1</sup> A quantitative estimate of the carbon dioxide captured is 250 ton of C per ha. For every ton of C sequestered, 20% of the sequestered carbon will be lost into the atmosphere as shown in Figure 1.<sup>7</sup> This leaves 200 tons of C per ha that will stay in the ground. To balance out emissions 30 x 10<sup>6</sup> ha of land per year must have bio-char applied to it at a rate of 250 tons C per ha as shown in Table 8. For selected other masses of C sequestered per ha refer to Figure 9.

	annual surface ground area used annually for carbon dioxide sequestration								
Year 0 ha		1 million ha	10 million ha	30 million ha	50 million ha				
	kg carbon in atmosphere, x 10^-15*								
2009	0.75	0.75	0.75	0.75	0.75				
2010	0.756	0.7558	0.754	0.75	0.746				
2015	0.786	0.7848	0.774	0.75	0.726				
2020	0.816	0.8138	0.794	0.75	0.706				
2030	0.876	0.8718	0.834	0.75	0.666				
2050	0.996	0.9878	0.914	0.75	0.586				
2075	1.146	1.1328	1.014	0.75	0.486				
2100	1.296	1.2778	1.114	0.75	0.386				

Table 8. Kilogram C in atmosphere over the 21<sup>st</sup> century at current emission rates and 250 tons C per ha

\*0.75 kg carbon in atmosphere =  $0.75 \times 10^{15}$  kg carbon in atmosphere



Figure 9. Atmospheric content of CO<sub>2</sub> based on density of the surface area used per year to sequester carbon

At 30 million ha per year, the FHC coke reserve, estimated at 1000 G tons,<sup>1</sup>would be exhausted in 33 years. In the 33 years, a system of harvesting agricultural waste and crops for sequestration could be designed and applied to make the system fully based on renewable resources.

#### 7. Energy Balance

The energy needed to produce bio-char must not cause more emission than the amount of  $CO_2$  sequestered. Using the energy balance from Gaunt and Lehmann's "Energy Balance and Emissions Associated with Biochar Sequestration and Pyrolysis Bioenergy Production," the energy efficiency of pyrolysis with the sources of switchgrass, miscanthus, and forage corn prove favorable. The energy inputs and outputs in Table 9 show a net positive production of energy even when the process is optimized for the bio-char sequestration of the non-annual crops switchgrass and miscanthus.

These crops provided additional profitability in the 12.6-17.3 thousand kg of  $CO_2$  emissions that are avoided as shown in Table 10. Forage corn provides far less energy production with respect to the input necessary due to its annual nature of the crop; however, it provides 16.9-18.6 kg of  $CO_2$  sequestration. These avoided emissions included not only the sequestered carbon, but the savings in fertilizer, the carbon sequestered in the changing field, and the energy offsets from coal or natural gas. These offset emissions include the minimal amount of emissions produced in the making of the bio-char.

Table 9. Energy balance of switchgrass, miscanthus, and forage corn<sup>16</sup>

•					
	switchgrass	miscanthus	forage corn	wheat straw	corn stover
		i	nputs (MJ ha <sup>−1</sup> y⁻	<sup>-1</sup> )	
field production	5521	6505	20789	2024	2352
transportation and processing	3671	4430	11990	2410	2440
subtotal inputs	9192	10935	32779	4434	4792
		o	utput (MJ ha <sup>-1</sup> y	-1)	
pyrolysis optimized for energy	64225	80050	99425	40056	43456
pyrolysis optimized for biochar	48811	60838	75563	30442	33027
		net	output (MJ ha <sup>-1</sup>	y-1)	
pyrolysis optimized for energy	55033	69115	66646	35622	38665
pyrolysis optimized for biochar	39619	49903	42784	26008	28235
		e	nergy yield MJ/M	ſIJ	
pyrolysis optimized for energy	7.0	7.3	3.0	9.0	9.1
pyrolysis optimized for biochar	5.3	5.6	2.3	6.9	6.9
		cha	r yield (kg C ha <sup>−1</sup>	V <sup>−1</sup> )	
pyrolysis optimized for energy	0	0	0	0	0
pyrolysis optimized for biochar	867	1081	1338	534	599

TABLE 1. Energy Inputs and Outputs for Each Feedstock Production Scenario, Comparing a Slow Pyrolysis System Optimized for Energy and Biochar Production TABLE 3. Avoided Emissions (kg CO2 ha<sup>-1</sup> y<sup>-1</sup>) for Bioenergy Crop (BEC) Scenarios, Comparing a Slow Pyrolysis System Optimized for Energy and Biochar Production

	energy			biochar					
	switchgrass	miscanthus	foragecorn	switchgrass	miscanthus	corn stover			
	feedstoo	k: switch fro	m winter w	heat to bioen	ergy crop pro	oduction			
emissions due to changes in crop production	1141	1107	338	1141	1107	338			
		applic	ation of bio	char on cerea	l land				
avoided soil nitrous oxide emissions	0	0	0	1901	2369	2933			
reduced fertilizer requirement	0	0	0	218	272	337			
subtotal	0	0	0	2119	2641	3269			
			bioenerav	production					
C stabilization	0	0	0	7065	8806	10 900			
	emissions for electricity generated using natural gas								
carbon dioxide	3087	3877	3739	2223	2800	2400			
nitrous oxide	2	2	2	1	2	1			
methane	4	5	5	3	4	3			
subtotal	3093	3884	3746	2227	2805	2405			
		emissions	for electrici	ty generated (	using coal				
carbon dioxide	5228	6566	6331	3764	4741	4064			
nitrous oxide	26	32	31	18	23	20			
methane emissions	4	5	5	3	4	3			
subtotal	5258	6603	6367	3785	4768	4087			
total avoided emissions - offsets natural gas total avoided emissions - offsets coal	4234 6399	4992 7710	4083 6705	12 551 14 109	15 358 17 321	16 912 18 595			

#### 8. Selected Applications

After bio-char is produced, it has many positive applications. It can be used as a soil additive for agricultural land. No detrimental effects have been found for bio-char addition, while many positive ones have been found. Bio-char addition has routinely been found to reduce N emissions, reducing the need for fertilizer by 30%.<sup>16</sup> The cation exchange capability also increases, allowing for the crop to be well fed. Production of bio-mass also has been shown to increase in fertilized soil as shown in Figure 10.



Figure 10. Rate of dry matter production at different levels of char<sup>17</sup>

With work, bio-char can also be applied to infertile land to change it into fertile land. While irrigation would be necessary in desert land, the dark color of the soil leads to proper heating of *Proceedings of the 2009 Midwest Section Conference of the American Society for Engineering Education* 

the seed and the potential for crop growth on previously infertile lands.<sup>1</sup> This would prove beneficial unless the high UV content of desert lightened the color of the soil; however, the bio-char would still contain sequestered carbon even if no agricultural land was added.

Two bio-char based trial plants have already been made or are in the planning stages, one in Japan and one in Australia. A full scale Australian plant would contain 50,000 ha of mallee, and the trial plant in Australia was capable of producing "7500 MWh of electricity, 690 t of activated carbon, and 210 t of eucalyptus oil."<sup>14</sup>A full scale plant would produce "40,000 MWh of electricity, 1050 t of eucalyptus oil, 2720 t of granular activated carbon, 1090 t of pelletised activated carbon and 294 t of powdered activated carbon."<sup>14</sup> The net present value of this plant would be \$7.8 million dollars. The Japanese plant contains 1,000 ha of mallee trees and will be scaled up to 10,000 ha if successful. The goal is to establish a carbon sink which will sequester more than 1 million tons carbon over 35 years.

Bio-char can also be used to replace slash and burn. Slash and burn is currently used in the Amazon and is one of the major causes of deforestation. The soil quickly degrades after the first year of harvest as shown in Figure 2. To avoid this degradation, a system of slash and char could be used, and the land would sacrifice the peak soil fertility of the first year in exchange for good soil for decades to come.

### Conclusion

Using the resources at the University of Missouri, the literature review and experimental measurements of bio-char were successful as an undergraduate research project. The undergraduate research project provided many opportunities to learn from many different specialists. An understanding of the many different techniques for measuring similar properties, and the limitations of a few methods was also achieved. Using the resources of the Soil Characterization Laboratory, Research Core Facilities, the Chemistry Department, and MURR, the physical-chemical properties of the bio-char sample were readily determined. Each piece of equipment had its own unique advantage for finding out the exact composition. In the literature review, the use of the software, Endnote XI and SciFinder, aided in the acquisition of information, and provided information on efficient ways to research materials. With current technology, a system that will help to balance the man-made carbon emissions using a combination of slash and char, pyrolysis of crop waste, and energy crops like miscanthus, switchgrass, and forage corn can be put into full production. The production of the bio-char would cause sequestration of carbon from the atmosphere and a positive amount of energy production. Using a small portion of surface land mass, atmospheric CO<sub>2</sub> could be sequestered in the form bio-char. This sequestration could immediately be implemented to provide more time to study the potential of greenhouse effects of CO<sub>2</sub> on the environment.

After all, the environment is affected by a "long causal chain stretching from the implementation of emissions abatement policies to emissions reductions to changes in atmospheric GHG concentrations to surface warming to changes in ice sheets, sea level, agricultural productivity, extinction rates, and other impacts",<sup>18</sup> and delays in addressing climate change issues may cause irreversible changes to the Earth.

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#### References

1. Laine, J., Sowing Fossil Hydrocarbons to Promote Bioenergy. *Center for Applied Energy Research* **2009**, 20, (2), 1-3.

2. Oguntunde, P. G.; Abiodun, B. J.; Ajayi, A. E.; van de Giesen, N., Effects of charcoal production on soil physical properties in Ghana. *J. Plant Nutr. Soil Sci.* **2008**, 171, (4), 591-596.

3. Kishimoto, S.; Sugiura, G., Charcoal as a soil conditioner. *Symp. For. Prod. Res. Int.: Achiev. Future* **1985**, 5, 12/23/1-12/23/15.

4. Bruun, S.; Jensen, E. S.; Jensen, L. S., Microbial mineralization and assimilation of black carbon: Dependency on degree of thermal alteration. *Org. Geochem.* **2008**, *39*, (7), 839-845.

5. Warnock, D. D.; Lehmann, J.; Kuyper, T. W.; Rillig, M. C., Mycorrhizal responses to biochar in soil - concepts and mechanisms. *Plant Soil* **2007**, 300, (1-2), 9-20.

6. Novak, J. M.; Busscher, W. J.; Laird, D. L.; Ahmedna, M.; Watts, D. W.; Niandou, M. A. S., Impact of Biochar Amendment on Fertility of a Southeastern Coastal Plain Soil. *Soil Sci.* **2009**, 174, (2), 105-112.

7. Lehmann, J., A handful of carbon. Nature (London, U. K.) 2007, 447, (7141), 143-144.

8. Lehmann, J.; Gaunt, J.; Rondon, M., Bio-Char Sequestration in Terrestrial Ecosystems-A Review. *Mitigation and Adaptation Strategies for Global Change* **2006**, 11, 403-427.

9. Strand, S. E.; Benford, G., Ocean Sequestration of Crop Residue Carbon: Recycling Fossil Fuel Carbon Back to Deep Sediments. *Environ. Sci. Technol.* **2009**, 43, (4), 1000-1007.

Lal, R., Sequestering Atmospheric Carbon Dioxide. *Critical Reviews in Plant Sciences* 2009, 28, (3), 90 - 96.

11. Duenisch, O.; Lima, V. C.; Seehann, G.; Donath, J.; Montoia, V. R.; Schwarz, T., Retention properties of wood residues and their potential for soil amelioration. *Wood Sci. Technol.* **2007**, 41, (2), 169-189.

12. Czimczik, C. I.; Masiello, C. A., Controls on black carbon storage in soils. *Global Biogeochem. Cycles* **2007**, 21, (3), GB3005/1-GB3005/8.

13. Mann, C. C., The real dirt on rainforest fertility. *Science (Washington, DC, U. S.)* **2002,** 297, (5583), 920, 922-923.

14. McHenry, M., Agricultural bio-char production, renewable energy generation and farm carbon sequestration in Western Australia: Certainty, uncertainty and risk. *Agriculture, Ecosystems & Environment* **2009**, 129, (1-3), 1-7.

15. Marris, E., Putting the carbon back: Black is the new green. *Nature (London, U. K.)* **2006,** 442, (7103), 624-626.

16. Gaunt, J. L.; Lehmann, J., Energy Balance and Emissions Associated with Biochar Sequestration and Pyrolysis Bioenergy Production. *Environmental Science and Technology* **2008**, 42, (11), 4152-4158.

17. Chan, K. Y.; Van Zwieten, L.; Meszaros, I.; Downie, A.; Joseph, S., Agronomic values of greenwaste biochar as a soil amendment. *Aust. J. Soil Res.* **2007**, 45, (8), 629-634.

18. Sterman, J. D., Risk Communication on Climate: Mental Models and Mass Balance. *Science (Washington, DC, U. S.)* **2008,** 322, (5901), 532-533.

#### Bibliography

Bruun, S., E. S. Jensen, et al. (2008). "Microbial mineralization and assimilation of black carbon: Dependency on degree of thermal alteration." Org. Geochem. **39**(7): 839-845.

Chan, K. Y., L. Van Zwieten, et al. (2007). "Agronomic values of greenwaste biochar as a soil amendment." <u>Aust. J.</u> <u>Soil Res.</u> **45**(8): 629-634.

- Czimczik, C. I. and C. A. Masiello (2007). "Controls on black carbon storage in soils." <u>Global Biogeochem. Cycles</u> 21(3): GB3005/1-GB3005/8.
- Duenisch, O., V. C. Lima, et al. (2007). "Retention properties of wood residues and their potential for soil amelioration." <u>Wood Sci. Technol.</u> 41(2): 169-189.

- Gaunt, J. L. and J. Lehmann (2008). "Energy Balance and Emissions Associated with Biochar Sequestration and Pyrolysis Bioenergy Production." Environmental Science and Technology **42**(11): 4152-4158.
- Glaser, B. (2006). "Prehistorically modified soils of central Amazonia: a model for sustainable agriculture in the twenty-first century." Philosophical Transactions of the Royal Society of London, Series B 362: 187-196.
- Glaser, B. and K.-H. Knorr (2008). "Isotopic evidence for condensed aromatics from non-pyrogenic sources in soils - implications for current methods for quantifying soil black carbon." <u>Rapid Commun. Mass Spectrom.</u> 22(7): 935-942.
- Glaser, B., J. Lehmann, et al. (2002). "Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal- a review." <u>Biology and Fertility of Soils</u> **35**: 219-230.
- Kimetu, J. M., J. Lehmann, et al. (2008). "Reversibility of Soil Productivity Decline with Organic Matter of Differing Quality Along a Degradation Gradient." <u>Ecosystems</u> 11(5): 726-739.
- Kishimoto, S. and G. Sugiura (1985). "Charcoal as a soil conditioner." <u>Symp. For. Prod. Res. Int.: Achiev. Future</u> 5: 12/23/1-12/23/15.
- Laine, J. (2009). "Sowing Fossil Hydrocarbons to Promote Bioenergy." <u>Center for Applied Energy Research</u> 20(2): 1-3.
- Laine, J. and A. Calafat (1991). "Factors Affecting the Preparation of Activated Carbons from Coconut Shell Catalized by Potassium." <u>Carbon</u> 29(7): 949-953.
- Laine, J., S. Simoni, et al. (1991). "Preparation of Activated Carbon from Coconut Shell in a Small Scale Cocurrent Flow Rotary Kiln." <u>Chemical Engineering Communications</u> 99: 15-23.
- Laird, D. A., M. A. Chappell, et al. (2008). "Distinguishing black carbon from biogenic humic substances in soil clay fractions." <u>Geoderma</u> 143(1-2): 115-122.
- Lal, R. (2009). "Sequestering Atmospheric Carbon Dioxide." Critical Reviews in Plant Sciences 28(3): 90 96.
- Lehmann, J. (2007). "A handful of carbon." Nature (London, U. K.) 447(7141): 143-144.
- Lehmann, J., J. Gaunt, et al. (2006). "Bio-Char Sequestration in Terrestrial Ecosystems-A Review." <u>Mitigation and</u> <u>Adaptation Strategies for Global Change</u> 11: 403-427.
- Leifeld, J. (2008). "Biased 14C-derived organic carbon turnover estimates following black carbon input to soil: an exploration with RothC." <u>Biogeochemistry</u> **88**(3): 205-211.
- Litynski, J. T., S. M. Klara, et al. (2006). "An Overview of Terrestrial Sequestration of Carbon Dioxide: the United States Department of Energy's Fossil Energy R&D Program." <u>Clim. Change</u> 74(1-3): 81-95.
- Lorenz, K. and R. Lal (2008). "Biogeochemical C and N cycles in urban soils." Environ. Int. 35(1): 1-8.
- Mann, C. C. (2002). "The real dirt on rainforest fertility." <u>Science (Washington, DC, U. S.)</u> **297**(5583): 920, 922-923.
- Marris, E. (2006). "Putting the carbon back: Black is the new green." Nature (London, U. K.) 442(7103): 624-626.
- McHenry, M. (2009). "Agricultural bio-char production, renewable energy generation and farm carbon sequestration in Western Australia: Certainty, uncertainty and risk." <u>Agriculture, Ecosystems & Environment</u> 129(1-3): 1-7.
- McLauchlan, K. (2006). "The Nature and Longevity of Agricultural Impacts on Soil Carbon and Nutrients: a Review." <u>Ecosystems</u> 9(8): 1364-1382.
- Novak, J. M., W. J. Busscher, et al. (2009). "Impact of Biochar Amendment on Fertility of a Southeastern Coastal Plain Soil." <u>Soil Sci.</u> 174(2): 105-112.
- Oguntunde, P. G., B. J. Abiodun, et al. (2008). "Effects of charcoal production on soil physical properties in Ghana." J. Plant Nutr. Soil Sci. 171(4): 591-596.
- Preston, C. M. and M. W. I. Schmidt (2006). "Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions." <u>Biogeosciences</u> **3**(4): 397-420.
- Ramirez, S., D. Ferreira, et al. (2003). "Adding a micropore framework to a parent activated carbon by carbon deposition from methane or ethylene." <u>Carbon</u> 41: 2653-2689.
   Reeves, J. B., III, G. W. McCarty, et al. (2007). "Near infrared spectroscopic examination of charred pine wood,
- Reeves, J. B., III, G. W. McCarty, et al. (2007). "Near infrared spectroscopic examination of charred pine wood, bark, cellulose and lignin: implications for the quantitative determination of charcoal in soils." <u>J. Near</u> <u>Infrared Spectrosc.</u> 15(5): 307-315.
- Reeves, J. B., III, G. W. McCarty, et al. (2008). "Mid-infrared diffuse reflectance spectroscopic examination of charred pine wood, bark, cellulose, and lignin: implications for the quantitative determination of charcoal in soils." <u>Appl. Spectrosc.</u> 62(2): 182-189.
- Schiermeier, Q. (2006). "Putting the carbon back: The hundred billion ton challenge." <u>Nature (London, U. K.)</u> 442(7103): 620-623.
- Sombroek, W. G. (1966). "Amazon soils. A reconnaissance of the soils of the Brazilian Amazon region." <u>Versl.</u> Landbouwkd. Onderz. No. 672: 292 pp.
- Sterman, J. D. (2008). "Risk Communication on Climate: Mental Models and Mass Balance." <u>Science (Washington, DC, U. S.)</u> **322**(5901): 532-533.

- Strand, S. E. and G. Benford (2009). "Ocean Sequestration of Crop Residue Carbon: Recycling Fossil Fuel Carbon Back to Deep Sediments." <u>Environ. Sci. Technol.</u> 43(4): 1000-1007.
- Thiffault, E., N. Belanger, et al. (2007). "Investigating the soil acid-base status in managed boreal forests using the SAFE model." <u>Ecol. Modell.</u> **206**(3-4): 301-321.
- Titirici, M.-M., A. Thomas, et al. (2007). "Back in the black: Hydrothermal carbonization of plant material as an efficient chemical process to treat the CO2 problem?" <u>New J. Chem.</u> **31**(6): 787-789.
- Warnock, D. D., J. Lehmann, et al. (2007). "Mycorrhizal responses to biochar in soil concepts and mechanisms." <u>Plant Soil</u> **300**(1-2): 9-20.
- Yanai, Y., K. Toyota, et al. (2007). "Effects of charcoal addition on N2O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments." <u>Soil Sci. Plant Nutr. (Carlton, Aust.)</u> 53(2): 181-188.

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