



BIOMASS DERIVED, CARBON SEQUESTERING, DESIGNED FERTILIZERS

Kimberly A. Magrini-Bair^{*}, Stefan Czernik, Heidi M. Pilath, Robert J. Evans, Pin Ching Maness and Joel Leventhal

National Bioenergy Center, National Renewable Energy Laboratory, Golden, CO 80401, USA

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ABSTRACT

This work explores the hypothesis that functionalized biomass-derived chars (charcoal) can act as fertilizer-delivering, carbon-sequestering soil amendments. A naturally occurring precedent for this approach is based on recent results that clearly link increased soil productivity with charcoal-like Terra Preta deposits, which are characterized by enhanced microbial and fungal activity and are found in both temperate and tropical climates. In this work, peanut shell pellets were pyrolyzed under mild conditions (400°C). The resulting char retained nitrogen from the feedstock's high protein content. This char also provided the baseline material for further nutrient addition by reaction of pyrolysis oil with urea to add more bioavailable nitrogen. Replicated plant growth tests with corn conducted in a controlled greenhouse environment showed that these biomass-derived chars, as produced (raw) and chemically reacted (functionalized) with urea and pyrolysis oil, enhanced above and below ground plant growth similar to the periodic addition of an aqueous NPK fertilizer to the potting soil used for all experiments. We also found that char (raw and functionalized) addition to soil significantly enhanced root growth and that char could support the growth and subsequent release of nitrogen-fixing bacteria (*Azotobacter vinelandii*) into soils. These promising results provide the basis to design renewable time-release fertilizers for promoting above and below ground plant growth that also sequester carbon in the soil. Sustainable benefits

^{*} Corresponding author: Email <Kim.Magrini@nrel.gov>, Phone: 303-384-7706, Fax: 303-384-6363

of using these materials as targeted agricultural fertilizers include producing fertilizers from renewable biomass, eliminating conventional fertilizer nitrate runoff into watersheds (a severe and growing water quality problem), increasing soil organic matter accumulation from enhanced root growth, and sequestering carbon in soils.

Keywords: Biomass, char, soil amendment, nitrogen fixation, carbon sequestration.

1. INTRODUCTION

Soil organic matter or soil carbon is one component of mineral soils that makes plant growth possible and is one of our most important natural resources. Minimizing agriculture's impact on the global increase of atmospheric carbon dioxide requires carbon sequestration while maintaining productive and high levels of soil organic matter. The production and use of biofuels has led to the potential use of agricultural crop residues as a source of both energy and fuels. Thermal biomass processing via gasification or pyrolysis produces syngas and oil intermediates that are flexible feedstocks for fuel production. A significant byproduct of these processes is a charcoal-like substance (char) that may have potential as a soil amendment for adding carbon to the soil and, with process modifications, as a slow release form of nitrogen and phosphorous fertilizer or nitrogen fixing bacteria. This approach provides an opportunity to design fertilizers for specific crop and soil type.

Precedent for this approach exists in the Brazilian Amazon, where formerly forested land, now being used for cultivation and grazing, contains scattered patches of black soil among the predominant weathered, low fertility red soils. These dark areas, known as Terra Preta soils, are far more fertile than the adjacent red soil. Recent work has shown that the Terra Preta soils did not form from geological processes but are anthropogenic soils as they were found to contain significant amounts of charcoal. It is likely that pre-Columbian Indians cut the forest, buried the slash, and then burned it to produce charcoal. What is significant is that centuries later, these deposits are still fertile and preferred by local farmers. Surprisingly, the scientific rationale for this application of charcoal is unclear and researchers are now looking at why these deposits are so fertile. Glaser reported that the soil organic matter of Terra Preta consists of up to 30% black carbon, which remains as residue after incomplete burning of

biomass [1]. The Amazonian Terra Preta deposits contained 35 times more black carbon than adjacent soils. It is these soil characteristics that appear to confer fertility and provide the basis for designing biomass-derived char analogs as Terra Preta-like sustainable soil amendments.

Biomass is a complex polymeric material and its thermal decomposition via pyrolysis is a multistage process that forms solid, liquid, and gaseous products with yields, carbon content, and pore structure that depend on process conditions [2]. Transforming biomass into charcoal causes a 60-70% weight loss, rearrangement of the original sugars to aromatics, and formation of a porous and reactive carbon surface. The resulting charcoal has a variety of chemical functionalities on its surface that also depend on feedstock type and process temperature. Spectroscopic analysis (Fourier transform infrared - FTIR) shows the presence of alkyl aromatic units that contain hydroxyl, carboxyl, carbonyl, ether, and lactone structures [3]. The same functional groups are present at even higher concentrations in pyrolysis liquids. The carboxyl and carbonyl groups in bio-oil and char can easily react with ammonia, urea or other $-NH_2$ -containing materials to form amide and imide bonds. This inherent reactivity of both char and oil provides a facile chemical route to adding nutrients to char, which provides a basis for producing biomass-derived fertilizers.

Preliminary work on carbonization of agricultural wastes (peanut shells) showed that the surface area of the charcoal produced is a function of pretreatment and process temperature; at 400°C the surface area reached 225 m²/g. Nitrogen addition could be achieved by thermally reacting a raw char/pyrolysis oil slurry with urea. The resulting char then would contain metabolically accessible nitrogen for plant growth. This approach, which enhances the properties of charcoal as a soil conditioner by combining it with nitrogen amended bio-oil, produces a wholly biomass-derived, nitrogen-containing fertilizer (hydrogen for ammonia synthesis can also be thermochemically produced from biomass) that also adsorbs agrochemicals and provides long-term carbon storage.

In related work [4] Radlein et al. incorporated up to 10% nitrogen in an organic matrix formed from the polymerization of biomass pyrolyzate to produce an efficient biodegradable slow-release nitrogen fertilizer. This material leached less nitrogen than mineral fertilizers and reduced groundwater pollution. Radlein's product was also thought to be good soil conditioning material as it contained humic type matter in the form of lignin degradation products. Interestingly, the use of high-lignin fermentation

byproduct as a soil amendment in maize plant growth tests did not impact plant growth but did increase humic acid concentration, CO₂ emission, and water stable aggregates while decreasing bulk density [5]. The work reported here builds on Radlein's work by investigating the efficiency enhancement of several charcoal preparations on plant growth in controlled greenhouse tests. Our results provide strong support for the concept of using charcoal as a bifunctional tool to provide both carbon sequestration and soil amending properties.

Sustainable benefits of using these renewably-derived materials as targeted agricultural fertilizers are (a) eliminating conventional fertilizer nitrate runoff into watersheds (a severe and growing water quality problem), (b) increasing soil organic matter accumulation from enhanced root growth, and (c) sequestering carbon in soils. Taken together, the successful development and deployment of these materials could provide a sustainable approach to agriculture and eventually lead to decreasing CO₂ concentrations in the atmosphere [6-9].

Another approach to enriching chars with nitrogen is to take advantage of a microbe's ability to convert atmospheric nitrogen into ammonium via nitrogen fixation. When soil microbes are stressed with low nitrogen nutrients, they produce more nitrogenase enzyme, which converts atmospheric nitrogen into ammonium to support cell growth. Under anaerobic photosynthetic conditions in the presence of limited nitrogen nutrients, almost all photosynthetic bacteria induce their nitrogen-fixation pathway to convert nitrogen into its organic form to support cell growth [10]. Immobilizing nitrogen-fixing microbes within a char matrix ensures that their high populations are securely maintained when the char-microbe matrix is inoculated into soils. After introduction to the soil, the microbes replicate and carry out the nitrogen-fixation reaction as part of their nitrogen metabolism cycle. The presence of these nitrogen-fixing microbes in the char can thus improve any nitrogen limitation originally present in the ecosystem and subsequently enhance and interact with other native microbial community members for further soil enrichment.

Biomass-derived chars have been shown to increase microbial colonization in varied soil types. Yeast-derived chars promoted fungal growth in soils while glucose-derived carbon promoted the growth of gram negative bacterial colonies. Manipulating char properties may then provide convenient routes to designing the best possible amendments for a given soil type [11].

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Char Preparation

Charcoal was produced by pyrolysis of pelletized peanut shells provided by Birdsong, a peanut processing company plant located in Blakely, Georgia. These pellets, of elemental composition of 49.9% C, 5.9% H, 1.1% N, 3.0% ash, and 39.9% O, were pyrolyzed in a quartz rotary kiln operating in batch mode using 300-1000 g biomass per batch. The electrically heated reactor reached the temperature of 400°C after 20-30 minutes, during which period most of the volatile products were swept out from the reactor by a nitrogen stream. The condensable organic compounds and water were collected in a condenser while non-condensable gases were released to the ventilation system. The reactor was maintained in the desired temperature (380-450°C) for two hours and then cooled. The charcoal yield in those conditions was on average of 32 wt% of the feedstock.

The charcoal-based fertilizer was prepared by combining 50 g of peanut shell charcoal with 50 g of peanut shell fast pyrolysis oil produced in the NREL pilot plant and 25 g urea (aqueous solution). The slurry was heated to 200°C for 1 h with reaction of amine and carbonyl groups present in the oil, char and urea. During that time first water vapor and then white vapor, which was most likely a mixture of CO₂, NH₃, and H₂O (though the composition was not measured) was released, and finally 88 g of the solid product was recovered. The resulting material, crushed and sieved prior to incorporation in soil, contained 6.9% nitrogen (5.1% bound nitrogen that remained after leaching with water until pH 7 was achieved in collected leachate fractions) as determined by elemental analysis.

2.1.2. Microbially Amended Char

Microbe-containing chars were prepared by embedding char samples with an aqueous culture of nitrogen-fixing, photosynthetic *Azotobacter vinelandii*. The NREL Photobiology Laboratory screened a collection of photosynthetic bacteria for nitrogen fixation activity via nitrogenase assay under low light and anaerobic conditions similar to soil conditions. Nitrogenase activity was determined by acetylene reduction to ethylene via gas chromatographic analysis (Hewlett Packard 5890 Series II).

Azotobacter was found to be the most efficient strain. An aqueous solution of *Azotobacter vinelandii* (optical absorbance used to determine cell concentration) was added to incipient wetness to the char sample. Once immobilized, nitrogen-fixation activity was again assessed to ensure that the char did not inhibit microbial enzymatic activity. Approximately 65% of the cell dry weight of a microbe is protein, which itself is a nitrogen nutrient. To account for this high baseline, an aliquot of the char-microbe matrix was inactivated by heat treatment. The inactivated material was then used as an amendment to determine the effect of simply adding cellular protein as nutrient to soil. If cellular protein provides nutrients, then the char-microbe matrix has dual advantages, enriching the soil with microbes high in protein contents along with biological nitrogen-fixation capability.

2.2. Methods

2.2.1. Plant Growth Evaluation-Greenhouse Tests

Plant growth tests to assess the char amendments were conducted in NREL's greenhouse facility over a 6-week period. The greenhouse study evaluated 12 amendments (two controls and ten soil amendments) with 5 replicates each for a total of 60 pots. The amendments, pre- and post-plant growth soils, and associated compositional analyses are listed in Table 1. A generic top soil was used as a control test for marginal soil and for comparison with the potting soil-based plant growth tests. Potting soil (Sun Gro Peat/Perlite mix) was chosen as the base soil to bias the results against amendment improvement and to ensure that the plants avoided stress from any nutrient depletion. An average composition of this soil is given in Table 2.

Using potting soil (Sun Gro Peat/Perlite mix) as the base material, the potting procedure was conducted as follows: five separate bins were assembled for each amendment type, then filled with the requisite amount of potting soil to fill five two-quart containers. Sufficient water was added to bring the soil moisture content to 50 wt%, followed by manual mixing for one minute. 5 wt% char was added then the soil was mixed again for two minutes. The wetted soils were transferred to a mesh lined, two-quart pot and further wetted until saturated. Amendments 7-8 (containing *Azotobacter vinelandii*) were prepared last to avoid cross contamination with the other pots.

Table 1 Soil amendments, pre- and post-plant growth soils, and compositional analyses used in plant growth tests

Sample	C (%)	H (%)	N (%)	P µg/g	K µg/g
Peanut shells ¹	49.9	5.9	1.1	606	6150
Peanut shell char	72.5	3.3	1.8	1840	18200
Char/bio oil/urea	66.3	3.9	6.9	1020	9970
Char/ <i>Azotobacter</i>	66.3	3.3	1.9	2100	8800
<i>Amended soils pre plant growth (t = 0 days)</i>					
Potting soil	38.4	4.3	0.8	349	1410
Potting soil + NPK ¹	38.3	4.2	1.0	1060	3680
Potting soil + 5 wt% char ²	39.6	4.3	0.9	440	2050
Potting soil + 5 wt% char + NPK	37.6	4.0	0.9	499	2870
Potting soil + 10 wt% char	39.4	4.1	0.8	406	2610
Potting soil + 5 wt% char (urea, pyrolysis oil)	40.1	4.4	1.0	353	1360
Potting soil + 5 wt% char (live <i>Azotobacter</i>) ³	36.	3.8	0.8	382	2100
Potting soil + 5 wt% char (sterilized <i>Azotobacter</i>) ⁴	39.4	4.3	0.8	442	2190
Potting soil + 5 wt% char (weathered) ⁵	40.1	4.1	0.8	441	1840
Potting soil + 5 wt% char (weathered) ⁵ + 2 wt% char	39.0	4.1	0.8	390	1400
Potting soil + 5 wt% softwood derived weathered char ⁶	39.3	4.4	0.8	360	1240
Top soil	32.5	3.7	0.6	2010	4300
<i>Amended soils post plant growth (t = 42 days)</i>					
Potting soil	30.0	3.6	1.1	520	2280
Potting soil + NPK ¹	36.4	4.1	1.0	1070	3020
Potting soil + 5 wt% char ²	38.6	4.1	0.8	439	2210
Potting soil + 5 wt% char + NPK	37.7	4.0	0.9	893	2900
Potting soil + 10 wt% char	39.9	4.0	0.9	489	2840
Potting soil + 5 wt% char (urea, pyrolysis oil)	32.3	3.5	1.5	547	2330
Potting soil + 5 wt% char (live <i>Azotobacter</i>) ³	37.8	4.0	0.8	447	2240
Potting soil + 5 wt% char (sterilized <i>Azotobacter</i>) ⁴	38.0	4.0	0.8	438	2270
Potting soil + 5 wt% char (weathered) ⁵	38.2	3.9	0.8	452	1980
Potting soil + 5 wt% char (weathered) ⁵ + 2 wt% char	37.3	3.9	0.7	347	1490
Potting soil + 5 wt% softwood derived weathered char ⁶	37.9	4.1	0.7	343	1430
Top soil	29.0	3.3	0.7	2200	4410

¹ NPK added as Miracle-Gro solution (2 wt %); ² All chars derived from peanut shells unless otherwise noted; ³ Char impregnated with live *Azotobacter vinelandii* culture; ⁴ Char impregnated with sterilized *azotobacter vinelandii* culture; ⁵ Weathered peanut shell derived char provided by Eprida; ⁶ Weathered char derived from softwood exposed to wildfire

Three sweet corn (*Zea mays*) seeds were planted in each pot at a depth of one inch and after 10 days the seedlings were thinned to one plant per pot. The harvested seedlings were examined for root growth and any anomalous growth patterns, which were not observed. Seedlings were grown under a controlled environment with a 14 h photoperiod and nighttime temperatures that did not fall below 52°F.

All pots were periodically fed a standard in-house

prepared macro/micronutrient solution [12] (30 mL of 30% aqueous dilution of Hoagland's solution) in addition to water or Miracle-Gro solution (50 mL of 50% aqueous dilution) for the NPK treatments (potting soil and potting soil + 5 wt% unamended char were the positive NPK controls – amendments 2 and 4). All plants were fed the same volume of liquids to minimize this variable. Nutrient solution compositions are listed in Table 3.

Table 2 Sun Gro potting soil composition

Nutrient	Typical Extractable Nutrient Range
pH	5.0-6.7
Ec (mmhos), cm	0.5-1.15
Nitrate Nitrogen, NO ₃ -N (ppm)	0-7
Ammonium Nitrogen, NH ₄ -N (ppm)	0-15
Phosphorous (ppm)	0-8
Potassium (ppm)	0-25
Calcium (ppm)	29-113
Magnesium (ppm)	17-72
Sulfur (ppm)	70-225
Manganese (ppm)	0-0.45
Iron (ppm)	0-1.10
Copper (ppm)	0-0.03
Boron (ppm)	0-0.08
Zinc (ppm)	0-0.07
Molybdenum (ppm)	0-0.07

Table 3 Nutrient composition of Hoagland's and Miracle-Gro solutions

Hoagland's		Miracle-Gro	
<i>Macronutrients</i>			
		Total N ¹	15%
KNO ₃	1M	K ₂ O	15%
CaCl ₂	1M		
MgSO ₄	1M		
FeNaEDTA	1M	Chelated Fe	0.15%
NaH ₂ PO ₄	1M	P ₂ O ₅	30%
<i>Micronutrients</i>			
H ₃ BO ₄	0.04M	B	0.02%
MnSO ₄	0.008M	Chelated Mn	0.05%
ZnSO ₄	0.008M	Zn	0.06%
CuSO ₄	0.003M	Cu	0.07%
MoO ₃	0.003M	Mo	0

At final harvesting, each plant was soaked in water to remove as much soil as possible. The greater the level of root growth, the more difficult the soil removal, but washing qualitatively indicated the extent of fine root development achieved with the char amended soils. Even at 10 days post germination, we found that root growth appeared to be enhanced in char amended soils. Stalk diameter at 21 days was measured between the 0 and 1st internode at 1 cm down from the 1st leaf; at 35 days between the 2nd and 3rd internode and 1 cm down from the 3rd leaf; and at 42 days between leaves 3 and 4 and at 1 cm down from the 4th leaf.

3. RESULTS AND DISCUSSION

3.1. Plant Growth Tests

Figure 1 shows averaged plant height measured after 21, 35, and 42 days of growth in all soil samples. Stalk diameter mirrored the plant height results (Figure 2). The addition of 50 mL of a 50:50 solution of NPK (as aqueous Miracle-Gro solution) to potting soil (amendment 2) and to 5 wt% unamended char in potting soil (amendment 4) produced the tallest corn plants at 42 days post germination (106 and 104 cm, respectively) with the widest stalk diameters (19.3 and 19.2 mm). The urea and pyrolysis oil amended char (amendment 6) produced plants of similar growth characteristics with an average height of 94 cm and width of 16.7 mm. Note that this treatment contained no NPK: any nitrogen supplied to the plant came from the urea and pyrolysis oil amended char. The potting soil and top soil controls had plant height and widths at 42 days of 71 cm, 11.4 mm and 27 cm, 4.2 mm, respectively. Intermediate results (better than potting soil alone) were achieved with 5 wt% char, 5 wt% weathered softwood derived char, and 5 wt% char containing nitrogen fixing *Azotobacter*. Potting soil containing 10 wt% char, 5 wt% char with sterilized *Azotobacter*, and 5 wt% weathered peanut char produced plants that were statistically similar to those grown in potting soil only.

Table 1 lists the C, H, N, P, and K content of the amendments and the pre- and post-plant growth soils. The amended chars have slightly increased N, P, and K compared to unamended char, though these nutrient levels were only slightly elevated in the amended soils compared with the control potting soil. All of the soils had higher PK levels than either control and we can only speculate that the enhanced growth achieved with the NPK and pyrolysis oil-urea char amendments may be attributed to enhanced nutrient delivery.

Figure 3 shows pictures of root growth during plant and root harvesting at 42 days for the replicates conducted in potting soil, potting soil with periodic NPK additions, and potting soil with 5 wt% urea and pyrolysis oil amended char. Enhanced root growth is observed in the NPK and amended char containing soils. Figure 4 shows pictures of individual corn plants at 42 days post germination grown in potting soil, potting soil with periodic NPK additions, and potting soil containing 5 wt% urea and pyrolysis oil amended char. Plant heights are similar for the NPK and char amended soils.

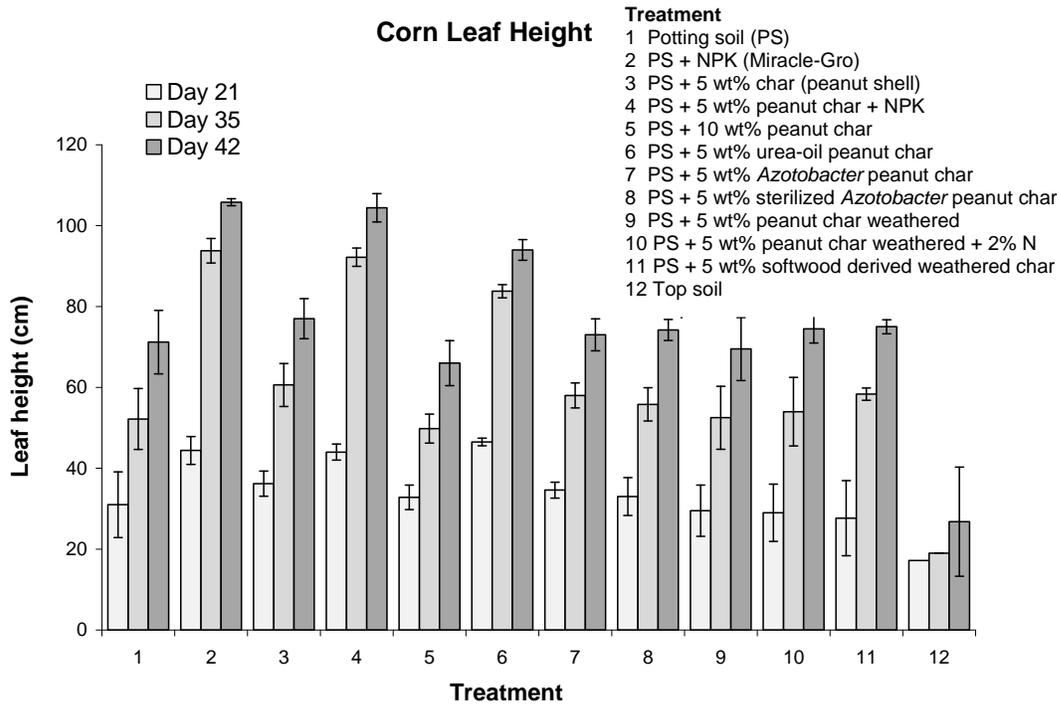


Figure 1 Corn plant height (longest leaf) 21, 35, and 42 days post germination. Longest leaves obtained with NPK, NPK and 5% char, and 5% urea and pyrolysis oil-amended char.

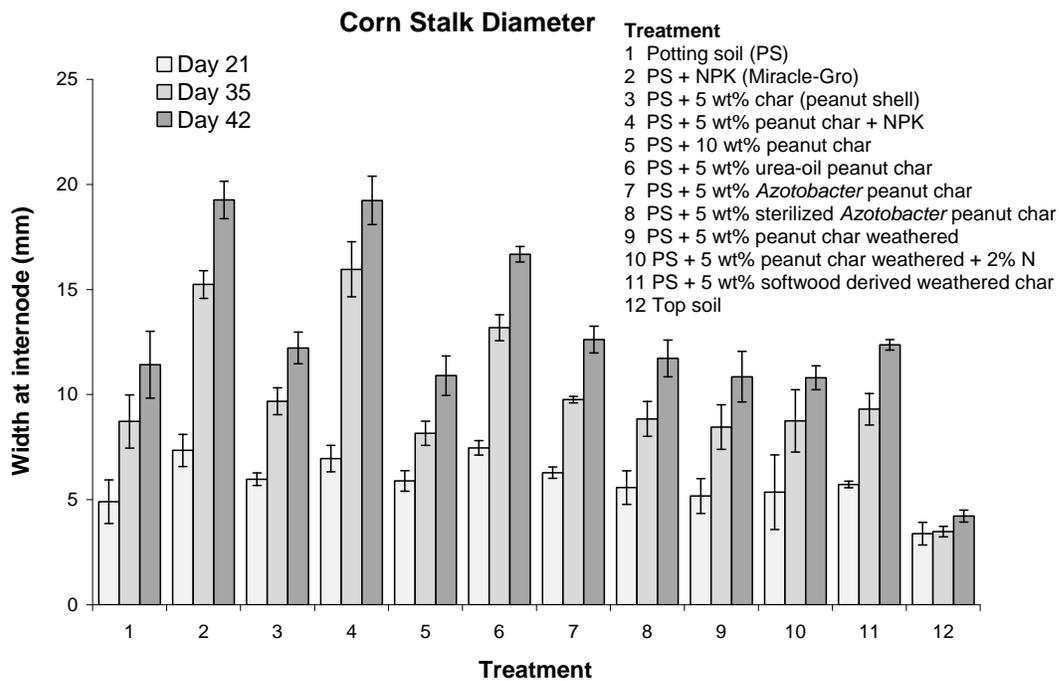


Figure 2 Corn plant diameter measured at the internode between the 2nd, 3rd, and 4th leaf at 21, 35, and 42 days post germination. Largest diameter stalks obtained with NPK, NPK and 5% char, and 5% urea and pyrolysis oil amended char.

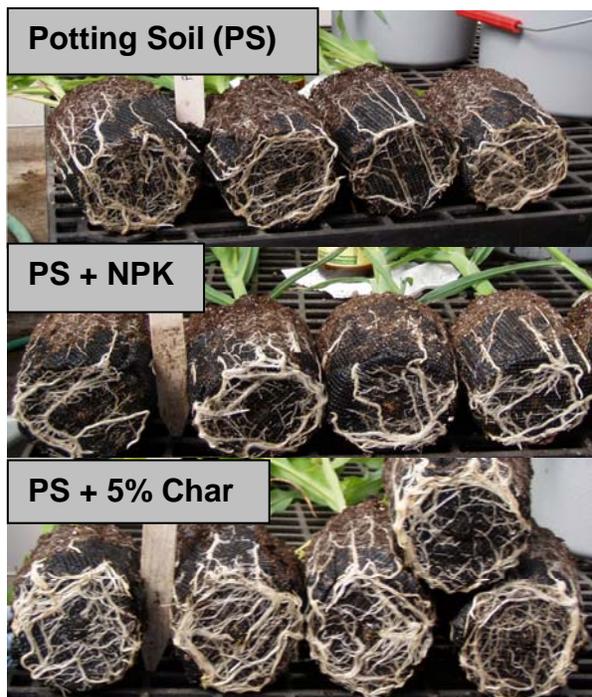


Figure 3 Corn plant roots 42 days post germination in potting soil (PS), PS and NPK addition, PS and 5% peanut char.

These preliminary and qualitative results support the concept that nitrogen-containing chars produced from pyrolysis oil can function as a renewably derived fertilizer that additionally sequesters carbon in soils. Similar enhancements with maize and cowpea were obtained in tropical infertile soils amended with wood bark derived char, which additionally increased root development and enhanced fungal colonization [13]. In those tests, bark charcoal application was also found to induce soil chemical changes by increasing pH, total nitrogen and P_2O_5 content, and cation exchange capacity, while reducing exchangeable Al^{3+} content.

Enriching chars with nitrogen by using photosynthetic microorganisms' ability to convert atmospheric nitrogen into ammonium via the nitrogen fixation reaction was a novel approach tested in this work. The presence of viable nitrogen-fixing microbes in the char was expected to improve any nitrogen limitation originally present in a soil and subsequently enhance and interact with other native microbial communities for further soil enrichment. This work demonstrated that chars from peanut shells are effective media in retaining soil microbes and further that the adsorbed microbes can propagate once released into an appropriate environment, including soils.



Figure 4 Potted corn plants at 42 days post germination.

Azotobacter vinelandii, a soil nitrogen fixing bacterium, was 99.8% immobilized on peanut shell char and retained its nitrogen fixing capability while adsorbed as measured by the acetylene reduction assay, a direct measurement of microbial N₂-fixation activity. The *Azotobacter*-amended chars (live and inactivated) produced a positive plant growth response compared to potting soil, though we determined that addition of Hoagland's solution to the pots suppressed nitrogen fixation activity due to the presence of 5 mM nitrate nutrient in the feed. Qualitatively, root growth enhancement in the microbially amended plants was very similar to root growth in the char-amended soils. Similar enhanced root growth was observed in corn plants grown in fertile soil and associated subsoil containing 5 wt% char derived from sugarcane. While plant height was only slightly greater, plant and root weight was significantly higher in the fertile soil containing char [14].

Microbial activity is known to be enhanced in the presence of chars. Pietikainen et al. [15] found greater bacterial growth rates in charcoal layers than in the underlying organic horizon in a temperate forest soil. Char addition to highly weathered tropical soil significantly enhanced microbial growth rates when nutrients were supplied by fertilizer addition [16]. In addition, char has been found to improve biological nitrogen fixation in common beans (*Phaseolus vulgaris* L.) [17]. Other work has shown that char and pyroigneous acid (smoke from char pyrolysis) addition to highly weathered soil substantially increased microbial biomass and respiration rates [18].

Similar results have been demonstrated in temperate soils as well [19]. Our work, which adds nitrogen fixation capability to renewably derived chars, provides a future framework for tailoring chars to specific soil needs.

4. CONCLUSIONS

Replicated plant growth tests with corn (*Zea mays*) confirmed that biomass-derived charcoal addition to fertile soil improves plant growth when measured as plant and root weight. The best results of plant growth enhancement were obtained with charcoal-based fertilizer prepared by reacting a charcoal/pyrolysis oil slurry with urea. The biomass derived chars may also help bind added nutrients until the plant requires them and this property may ultimately reduce the amount of fertilizers required while protecting our watersheds from runoff. Microbial nitrogen fixation is a promising option that needs more study to optimize the

fertilizing effect on plant growth. From a carbon sequestration perspective, this concept of thermochemical biomass fuel production with charcoal byproduct utilization as a fertilizer delivering, carbon sequestering soil amendment may provide the opportunity to remove millions of tons of CO₂ from the atmosphere.

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