CHARACTERIZATION OF NOVEL TORREFIED BIOMASS AND BIOCHAR AMENDMENTS

A Thesis

by

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ABSTRACT

Nutrient management is vital for food, feed, fiber, and fuel production. However, excessive application and loss (volatilization, leaching, run-off, etc.) of inorganic and organic sources of nutrients have significant, detrimental environmental impacts. Increasing prices for petroleum-based and mined fertilizers further limit opportunities for their utilization in developing nations. Torrefied and pyrolized biomass amendments can be used as alternative nutrient sources as well as carbon sequestration resources in cropping systems. The overall objective of this study was to convert high-biomass feedstocks into thermally modified, renewable soil amendments. Napiergrass, *Pennisetum purpureum* Schumach., (cv. Merkeron) and Pearl Millet x Napiergrass [*Pennisetum glaucum* [L.] R. Br. x *Pennisetum purpureum* Schumach. (PMN)] were converted under atmospheric pressure with minimal oxygen at 250° C and 400° C, ground to 1 mm and 2 mm particle sizes, and compared to inorganic fertilizer for yield response in maize and PMN in a full-season field trial and short-season nursery trial.

The thermally modified, pretreatment processes resulted in nutrient retention across feedstocks. When compared to the inorganic fertilizer in the full-season field trial, the renewable soil amendments had similar field responses in maize and PMN with a lower application rate. The short-season nursery trail produced on par yield responses from the inorganic fertilizer and renewable soil amendment in maize and PMN with the exception being nitrogen and yield. Finally, maize and PMN had higher phosphorus uptake with the thermally modified, renewable soil amendment in both trials.

DEDICATION

This thesis is dedicated to my sons, Bodan and Gunnar Burris. I decided to return to college to provide a better career for myself and my sons. It has been a sacrifice and they have readily supported me throughout it all. I love you more, boys. I would also like to dedicate this to my children's father, Sean Burris, without whom I would have never even considered returning to college. Thank you for your encouragement along the way. Lastly, I would like to dedicate this to my mother, Cynthia Baldi, for her words of wisdom, her help in getting me out of hard stalls and spots, and her being a constant in my life. You are the glue that holds me together and I cannot thank you enough for your friendship and love.

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CONTRIBUTORS AND FUNDING SOURCES

Contributors

This research was supervised by a thesis committee consisting of Associate Professor and Chair Dr. Russell Jessup, Professor Dr. Dirk Hays, and Professor Emeritus Dr. Sam Feagley of the Department of Soil and Crop Sciences, and Professor Dr. Fred Smeins of the Department of Ecosystem Science and Management.

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NOMENCLATURE

TBA	Torrefied Biomass Amendment
PMN	Pearl Millet – Napiergrass
N	Nitrogen
P	Phosphorus
K	Potassium
Ca	Calcium
Mg	Magnesium
T	Metric Ton
ha	Hectare
DAP	Days After Planting
C	Celsius
ADF	Acid Detergent Fiber
TDN	Total Digestive Nutrients
ANOVA	Analysis of Variance

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CHAPTER I

INTRODUCTION

Research Problem

Fertilizer use has increased dramatically over the years (Gunjal et al., 1980). The trend is rising largely to meet increasing global population demands for food and fiber. There is projected to be a 100-110% increase in global crop demands from 2005 to 2050 (Tilman et al., 2011). Inorganic fertilizer makes up the bulk of nutrient inputs needed to sustain current crop yields in the US alone (Stewart et al., 2005). To offset this increase of inorganic fertilizer use, alternative forms of renewable nutrient amendments need to be developed.

One alternative to inorganic fertilizers is the use of an inorganic nutrient amendment that can be created from thermally modified, high-biomass feedstocks. These pretreatment processes are pyrolysis and torrefaction. These processes break down plant structures while still retaining nutrients. These end result is carbon rich and can also benefit soil health by sequestering carbon, improving cation exchange capacity, increasing water retention, reduced leaching, and enhanced nutrient cycling (Laird, 2008; Malghani et al., 2013)). The carbon mineralization rate can last anywhere from hundreds of years to an excess of 1000 years depending on the temperature of pyrolysis (Harris, et al., 2013; Laird, 2008; Wu et al., 2016).

To see if torrefied and pyrolized biomass amendments can be used as a nutrient source in cropping systems, the first objective is to develop and characterize novel torrefied and pyrolized (biochar) biomass amendments. The second objective is to compare biomass yield responses and nutrient status from one torrefied biomass amendment, one biochar amendment, and urea in perennial pearl-millet x napiergrass hybrid [*Pennisetum glaucum* [L.] R. Br. x *Pennisetum purpureum* Schumach. (PMN)] and annual maize (*Zea mays* L.) in two environments. These environments will include a full growing season field trial and a partial growing season nursery trial.

LITERATURE REVIEW

Inorganic and Organic Nutrient Sources

The use of nitrogen (N) fertilizers has been a significant factor in tripling the food production globally over the past 50 years (Mosier et al., 2004) with cereal grain production being the driving factor for the demand of N fertilizer use globally (Cassman et al., 2012). Research has further shown that fertilization of crops increases nutritional quality in cereals, pulses, oilseed crops, tubers, and vegetables (Wang et al., 2008). As one example, 30-50% of higher yields in the US and England between the years 1930 – 2000 can be directly attributed to fertilizer use.

While crop fertilization is vital for food, feed, fiber, and fuel production, excessive application and loss (i.e. volatilization, leaching, run-off, etc.) of inorganic and organic sources of nutrients have significant, detrimental environmental impacts (Gilliam et al., 1985; Keeney and Follett, 1991). Excessive N from fertilizers can reduce nutritional quality in food crops, decreasing the concentration of vitamin C, soluble sugars, magnesium (Mg) and calcium (Wang et al., 2008). N is essential to increasing growth which leads to yield. However, when the N supply is increased it leads to a deficiency in other nutrients. This creates a demand for nutrients that can create concentrations less or greater than that needed (Fageria, 2001). Fertilizer needs also vary among different types of crops. This affects the price associated with fertilizer nutrients needed to produce a bushel of soybeans versus a bushel of maize (Gunjal et al., 1980).

Increasing prices for petroleum-based and mined fertilizers further limit opportunities for their utilization in developing countries (Brunelle et al., 2015; Huang et al., 2009). Production of N fertilizer has increased since 1962, yet its distribution is not globally uniform (Mosier et al., 2004). Agricultural development is crucial to the vitality of Africa in particular with regards to its economic growth, food security, and reduction in poverty. Yet, agricultural production is hindered by low soil fertility, low inputs of inorganic fertilizers, and fragile ecosystems (Henao and Baanante, 2006). As one indicative example, Ethiopian agriculture accounts for 90% of the labor force. It also consists of 56% of the gross domestic product (GDP), and 90% of export earnings (Croppenstedt et al., 2003). However, Ethiopia is one of the poorest countries in the world. As a result, farmers tend to not purchase fertilizer due to household cash constraints (Croppenstedt et al., 2003).

A lack of access to fertilizers affects all of Africa. In Southern Africa, with little to no access to fertilizers, farmers typically grow crops for a short period of time on one area of recently cleared land. After harvest, the land is fallowed to regain its fertility and another section of land is cleared. The fallowed time has decreased over the years from about 15 to five years due to population increase. This cycle creates nutrient-mined soils, and has become a key source for reduction in crop yields, per capita food decreases, and land degradation in Africa (Henao and Baanante, 2006). In fact, N depletion has been recorded at 22 kg/ha annually in sub-Saharan Africa and 112 kg/ha in Kenya (Smaling et al., 1997).

Increased fertilizer use has in turn led to a surge in organic farming practices and agronomic measures in order to both help offset costs associated with inorganic fertilizers as well as reduce loss of N on the agricultural landscape. In low-input traditional agronomic systems in developing countries, organic agronomic measures can increase productivity and restore the ecosystem (Scialabba, 2000). Approximately 50% of all applied N is lost through leaching, erosion, and denitrification (Tonitto et al., 2006). Combining conservation tillage and organic inputs like cover cropping systems with inorganic nutrients have been implemented to improve agricultural sustainability with regard to N fertilization management (Sarrantonio and Gallandt, 2003; Torbert et al., 2001). Research has shown that the incorporation of manure and crop residue can produce a higher percentage of water stable aggregates, lower bulk density, higher porosity, and greater water holding capacity (Bhagat and Verma, 1991).

In order to maintain optimal soil health and the balance of available nutrients for crops, inorganic and organic sources of nutrients should be combined (Clark et al., 1998; Hati et al., 2006). However, animal manures and crop residues cannot keep up with crop nutrient demands due to limited availability, low nutrient content, and high cost for processing and application (Palm et al., 1997). The application of compost or manure is also not economically viable with agronomic N rates in modern, high-input, mechanized cropping systems (Evanylo et al., 2008). In addition, research has shown that raw and composted manures may contain contaminants. These contaminants can include residual pesticides, hormones, and pathogens. Prolonged manure use can lead to excessive amounts of phosphorus (Barnett, 1994; Ju et al., 2007). Lastly, manure is associated with an increase in weed seed growth (Kuepper, 2003). Not only does manure and compost provide additional nutrients for the growth of weed seeds, but they also can be a source of incoming weed seeds if not treated well enough or long enough before application (Bàrberi, 2002).

Biochar

Novel alternatives to inorganic fertilizers and manures can offer renewable, pathogen free, and weed seed free soil amendments. These alternatives include forms of pyrolized biomass modeled after a process in the Amazon basin over 2500 years ago known as biochar. Anthropologists suggest that cooking fires along with the deliberate placement of charcoal in the soil resulted in ‘Terra preta de Indio’ or black earth of the Indians (Glaser and Birk, 2012). These are highly fertile soils containing carbon. The charcoal particles in the soil prevent nutrient leaching and therefore have higher concentrations of nutrients such as N, phosphorus (P), potassium (K), and calcium (Ca). These soils are still nutrient rich and hold carbon today, making them ideal for use in potting soils. They are highly sought after in Brazilian markets (Glaser et al., 2014).

Biochar conversion strategies can take diverse sources of agricultural waste and produce effective soil enhancers (Chan et al., 2007; Windeatt et al., 2014). Research is now confirming benefits that include: improved soil aggregate structure, increased water retention due to its hygroscopicity (or the ability to take up and retain water), increased cation-exchange capacity which results in improved soil fertility, increased number of beneficial soil microbes, moderating of soil acidity, and reduced leaching of nitrogen into ground water (Bargmann et al., 2014; Enders et al., 2012; Kavitha et al., 2018; Koide et al., 2015). Areas with low rainfall or nutrient-poor soils will most likely see the largest impact from addition of biochar. Additionally, biochar in soils can have in situ remediation benefits that include: stabilization of contaminants like copper and lead, the ability to act as liming agent, and carbon sequestration (Beesley et al., 2011; Karami et al., 2011; Manyuchi et al.; Rodríguez-Vila et al., 2015; Woolf et al., 2010). In clay-enriched, compacted soils, biochar can have a reduction in tensile strength (Chan et al., 2007).

Despite its many benefits, biochar is not widely adopted for use. This likely stems from the high cost associated with biochar being more energy intensive to produce. According to a study conducted in the UK, biochar can have a cost of US $197-584 per ton from production to application (Shackley et al., 2011). Biochar further has a high compositional variability dependent upon the conditions of pyrolysis and feedstock utilized (Kavitha et al., 2018; Spokas, 2010). Biochar effects may also prove to be soil specific (Zhu et al., 2015). To date, biochar utilization has been predominately focused in biocoal, syngas, bio-oil, and hydrothermal production of biomass under anaerobic conditions. Some research has utilized feedstocks from rice husks, miscanthus, pine needles, palm leaves, water hyacinth, switchgrass, and woody biomass for the creation of pyrochar and hydrochar (Cruz et al,. 2004; Fawaz et al., 2015; Gao et al., 2016; Gronwald et al., 2016; Hoekman et al., 2012; Kalderis et al., 2014). This research has shown significant increases in carbon content as well as calorific values (Kim et al., 2015) in the char for energy use. Research for agronomic biochar has utilized feedstocks from peanut hulls, poultry litter, pine wood chips, coconut husks, orange bagasse, cassava, and green waste (Gonzaga et al., 2018; Mohamed Noor et al., 2012; W. Gaskin et al., 2008). Ultimately, biochar application to soils is dependent upon parent material, temperature rates, and application rates (Gonzaga et al., 2018; Kavitha et al., 2018).

Torrefaction

Torrefaction is another novel approach towards renewable, pathogen free, and weed seed free soil amendments. Torrefaction is a milder form of pyrolysis requiring less energy and heat intensity than biochar. Torrefaction has the ability to reduce the heterogeneity of biomass (Nhuchhen et al., 2014). When biomass is torrefied, devolatilization, depolymerization, and carbonization of hemicellulose, lignin, and cellulose occur to varied degrees (Tumuluru et al., 2011). Lignin that is not devolatilized is loosened, and hemicellulose is broken down leaving an intermediate between biomass and charcoal. The torrefied biomass then retains the advantages of the nutrients in the biomass and charcoal (Mitchell and Elder, 2010). Torrefaction ranges are often reported in literature from 200-300° C in an inert environment at atmospheric pressure, whereas biochar is typically carried out at temperatures higher than 300° C (Chen and Kuo, 2011; Mitchell and Elder, 2010; Nhuchhen et al., 2014; Novak et al., 2009). In contrast to torrefaction, biochar temperatures above 300° C can decrease the cellulose and hemicellulose contents (Kavitha et al., 2018). Additionally, pyrolysis temperatures higher than 500 °C can decrease cation exchange capacity while increasing macronutrient concentrations (Harris et al., 2013).

While torrefaction can be completed without the presence of oxygen, it is interesting to note that it can also be carried out under minimal oxygen concentrations and still not spontaneously combust, making it a less expensive, more in situ approach. A study in 2012 (Rousset et al., 2012) found that biomass was not significantly affected by oxygen concentrations of 2, 6, 10, and 21% when torrefied at 240° C.

Post-torrefaction N concentration in TBA and biochar can be inversely proportional to its feedstock composition (Gaskin et al., 2008). This can be attributed to N volatilization in feedstocks like poultry litter and N being stored organically like in uric acid. However, lower N concentrations in feedstocks like pine chips can be retained in complex structures that do not easily volatilize (W. Gaskin et al., 2008). Field applications for torrefied biomass can come from high N feedstocks like pearl-millet – napiergrass, napiergrass, or legumes. This can result in soil amendments from a single feedstock with no pathogens and roughly 4-5% N. When compared to raw biomass, the carbon content of torrefied biomass increases by 15–25% and the moisture content decreases to less than 3% (Tumuluru et al., 2011). Torrefaction decreases the energy conversion by about 70%, improving grindability via fracturing cell walls, and increasing both particle surface area and size distribution. During torrefaction, 70-90% of the mass is retained as a solid product, containing 98% of the original energy content. Torrefaction can improve composition like moisture, carbon, hydrogen, and calorific value (Nunes et al., 2014; Pimchuai et al., 2010; Tumuluru et al., 2011). Like biochar, torrefied biomass has been predominantly utilized in the coal and energy industry (Chen et al., 2015; Junsatien et al., 2013). However, the highly recalcitrant torrefied carbon fraction provides all the benefits of biochar and additional opportunities without the additional energy inputs. Research has shown torrefied biomass to be an effective soil amendment by enhancing water retention and structural stability, while controlling soil metabolites and microbiota to promote plant growth (Ogura et al., 2016). Biochar or charification can also be effective in moderating nitrate levels when mixed with peat moss (Atland and Locke, 2012). Additionally, torrefied biomass has the potential to replace peat moss in potting media or soilless media due to increasing public pressure to find alternatives in horticultural rooting media (Blok et al., 2014). Torrefied biomass is hydrophobic similar to peat moss, but much more sustainable. A study conducted in 2014 (Blok et al., 2014) utilized a fast degrading nitrate fixing reed into an alternative pathogen free potting soil which could be added to potting soil mixes.

In summary, torrefied biomass provides a novel resource towards sustainable crop nutrient management. Despite it being renewable, having multiple soil restoration mechanisms, and requiring less production cost than biochar, the assessment and optimization of crop yield responses to utilization of TBAs as a source of nutrients is critical before widespread adoption.

CHAPTER II

MATERIALS AND METHODS

Pretreatment Processes

Torrefied Biomass Amendment

Based on availability, the development of the TBAs was from two feedstocks: pearl millet – napiergrass [*Pennisetum glaucum* [L.] R. Br. x *Pennisetum purpureum* Schumach. (PMN)] and napiergrass [(*Pennisetum purpureum* Schumach. (cv. Merkeron)]. The PMN TBA was utilized in the full growing season field trial. The Merkeron TBA was utilized in the partial growing season nursery trial.

PMN biomass was harvested in November 2016, while Merkeron biomass was harvested in May 2017. Due to the amount of biomass being harvested, each biomass sampling was then air-dried for a week. Air-dried biomass was then placed in a drying oven at 43° C for 24 hours to remove any residual moisture. The biomass was then ground down to a maximum particle size of 5.08 cm using a Cub Cadet chipper shredder model #24A-424M756. Ground material weighing 2.72 kg was placed into a 35 cm x 25.4 cm fixed bed stainless steel reactor and compressed to a bulk density of 200 kg/m³. The reactor was then placed under an Axner Model Heat Wave Raku Kiln model #A255655 and sealed with low oxygen. A propane torch was connected to a propane tank to provide the constant heat needed to achieve the 250° C for torrefaction. A Type K Thermocouple was placed inside the stainless steel reactor to monitor the temperature's rate of increase. A Bartlett Data Logger Pyrometer was used to monitor the temperature rise which was maintained at less than two degrees per minute. Once the target temperature of 250° C was reached, the reactor was held at a constant for a 45 minute incubation period. Once the incubation period was completed, the propane tank valve was closed to let the reactor cool. The reactor was then emptied of the biomass after cooling for a minimum of 12 hours. The treated biomass was then weighed on a digital scale for mass loss during torrefaction. Samples of the treated material were ground down to 2 mm and 1 mm particle sizes using a Wiley Mill standard model No. 3 serial #3720H-5.

Samples from the original (untreated) harvested feedstocks as well as the TBAs were sent for composition analyses and total carbon content analyses (See **Plant Analyses**).

Pyrolized Amendment

The development of the pyrolized (biochar) amendment was from the PMN feedstock. The PMN biochar was utilized in the full growing season field trial.

The overall methodology for the biochar was the same as that for the TBAs except for the target temperature. The temperature rise was maintained at less than four degrees per minute. Once the target temperature of 400°C was achieved, the reactor was held at that constant temperature for a 60 minute incubation period.

Sample analyses were also sent for the biochar as conducted for the TBAs and untreated feedstocks.

Experimental Design

Field Trial

The full growing season field trial was conducted at the Texas A&M Agricultural Research Farm in Burleson County in Snook, TX. There were three replications; two varieties: PMN10TX13 and VT Triple Pro Hybrid Corn: D57VP5; two soil amendments (TBA and biochar) and a control fertilizer: urea (46-0-0); and two amendment particle sizes: 2 mm and 1 mm. Individual plots were 0.5 m x 4.5 m, with each row being spaced 0.5 m, and alley spacing in between plots measuring 2.5 m. The total plot area was 2.25 m^2 and 7 m per block. The 36 plots account for 0.008 ha, with the trial size being 0.04 ha. The total cleared space was 0.07 ha.

The soil series at the field is a combination of Ships and Weswood. Ships is a very fine, mixed, active, thermic Chromic Hapluderts and Weswood is a fine-silty, mixed, superactive, thermic Udifluventic Haplustepts. The Ships series is a clayey soil with alluvial sediments whereas Weswood series is a stratified, loamy soil with alluvial sediments (Soil Survey, 2019). In order to determine residual nutrient content in the soil before planting, a representative soil sample of the field was taken. An Oakfield Company soil probe was used to take 10 random soil cores at a depth of 15.24 cm. The 10 soils cores were then put into a clean bucket and mixed together by hand to create a representative soil sample. The homogenized sample was sent for nutrient content analyses and soil test recommendations (See **Soil Analyses**).

Planting for the full growing season field trial took place on May 8, 2017 after the field has been disked. Planting followed a randomized complete block design (RCBD). The two varieties were planted differently due to their growth patterns. The maize was planted by seed with spacing of 2.54 cm between seed and a depth of 2.54 cm using a Jang Automation JP-1 Clean Seeder whereas the PMN was planted vegetatively. PMN plants had been growing from germinated seed in propagation trays for approximately a month before being planted. The PMN was spaced 30.48 cm apart in the 0.5 m x 4.5 m plot for a total of 13 plants per row.

Application rates for the TBA and biochar were 23 kg N/ha. The application rate for urea was 166 kg N/ha. The amendments and fertilizer were side dressed into the plots. The field was flood irrigated to field capacity at planting and two more times (July 12, 2017 and August 6, 2017) to ensure proper growth. The additional watering was completed in subsequent months from date of planting.

The field harvest for maize took place 106 days after planting (DAP) to ensure physiological maturity. The field harvest for PMN took place 205 DAP to ensure physiological maturity and prior to the season’s first frost. All plots were clipped to a 10 cm height and weighed wet using an Inscale DSWR load cell weigh rail. A subsample was taken from the total harvest of each plot. This subsample was then weighed wet and allowed to air-dry for three days before being put into a drying oven, at 43° C, for 24 hours to remove residual moisture. The subsamples were then weighed dry to calculate total moisture content before being ground to 1 mm particle size using a Wiley Mill. After grinding, 10 g of each subsample was used to determine total plant analyses including nutrient and forage content.

Nursery Trial

A partial growing season nursery trial was conducted at the Perennial Grass Breeding and Genetics Field Lab in Brazos County in College Station, TX. There were four replications; two varieties: PMN10TX13 and VT Triple Pro Hybrid Corn: D57VP5; one soil amendment (TBA) and a control fertilizer: urea (46-0-0); and one amendment particle size: 2 mm. Each variety was planted in an 11 L pot for a total of 16 pots. Each pot was filled with Redi-Earth Plug & Seedling Mix as soil media.

Planting of the nursery trial was completed on July 19, 2017. Planting followed a randomized complete block design (RCBD). The two varieties were planted by seed. The pots designated maize had two seeds placed in the middle of each pot at a depth of 2.54 cm to ensure germination. The pots designated PMN had three seeds placed in the middle of each pot in a hill seed approach at a depth of 1.27 cm to ensure germination. To avoid competition within the pot, each pot was thinned to one seedling post emergence. The pots were placed outside on corrugated cement boards to prevent weed encroachment. The pots were also placed in rows of 4 and columns of 2 for each replication. The spacing between each pot measured 10.16 cm x 12.7 cm with 60.96 cm between each replication.

The application rate for the TBA was 26.5 kg N/ha. The application rate for urea was 166 kg N/ha. To approximate side dressing in the field the amendment and fertilizer were applied in a circular furrowed perimeter around the seed with a diameter of 10.16 cm and a depth of 1.27 cm.

The pots were irrigated to field capacity as needed and observed daily to ensure proper growth. As the temperature increased outside, the pots were irrigated daily.

Harvesting took place 72 DAP on September 29, 2017. All pots were clipped at the crown of the plant. Each plant was weighed wet on a digital scale and allowed to air-dry for three days before being put into a drying oven, at 43° C, for 24 hours to remove residual moisture. The samples were weighed dry to calculate total moisture content before being ground down to 1 mm particle size using a Wiley Mill. After grinding, 10 g of each sample were used to determine total plant analyses as specified for the field test.

Soil and Plant Analyses

All testing for this study was completed by the Texas A&M Agrilife Extension Service: Soil, Water, and Forage Testing Laboratory in College Station, TX.

Soil Analyses

Soil testing for phosphorus (P) and potassium (K) nutrient availability were completed using the Mehlich III method and concentration of those nutrients were measured by inductively coupled plasma (ICP) (Mehlich, 1978; Mehlich, 1984). Soil nitrate is extracted from the soil sample using a 1 N KCl solution and determined by a reduction of nitrate (NO_3) to nitrite (NO_2) (Kachurina et al., 2000; Keeney and Nelson, 1982).

Plant Analyses

Composition

Nutrient content of P and K are determined by ICP analysis from a nitric acid digest (Isaac and Johnson, 1975; Havlin and Soltanpour, 1989). Total nitrogen (N) and total carbon (C) content are both determined by a high temperature combustion process (Nelson and Sommers, 1973; McGeehan and Naylor, 1988; Sheldrick, 1986; Storer, 1984; Sweeney, 1989).

Forage

Acid Detergent Fiber (ADF) is determined gravimetrically following a liquid digestion (Komarek, 1993). Total Digestive Nutrients (TDN) is based on ADF calculations and multiplied by a constant of 1.15. Crude protein is based on the N concentration and multiplied by a constant of 6.25.

Statistical Analyses

Data collected from the field and nursery trials was first tested for normal distribution and homogeneity of variance. Data was then submitted to analysis of variance (ANOVA) testing, an assumption check using Levene's test for equality of variances, and a post-hoc comparison using Tukey's honest significant difference test (HSD). The field trial analyzed ADF, TDN, yield (T/ha), percent macronutrient (N, P, K) content, percent micronutrient (Ca, Mg) content, and nutrient (N, P, K) uptake in biomass per plot. The nursery trial analyzed ADF, TDN, yield (g), and percent nutrient (N, P, K) content. Differences were considered significant at $p \leq 0.05$, 0.01, and 0.001. All statistical analyses were completed with JASP Version 0.8.3.1.

CHAPTER III

RESULTS AND DISCUSSION

Pretreatment Processes

Torrefied and Pyrolized Amendments

The forage analysis was conducted on the PMN and Merkeron feedstocks before pretreatment and at the 250° C torrefaction and 400° C pyrolysis (Fig. 1). The percentage of N retained in the feedstock increased minimally per each pretreatment process. Untreated PMN was 0.74%, whereas the TBA was 0.75%, and the biochar was 0.80%. Similarly, the percent of P retained in the feedstock increased with each pretreatment process. Untreated PMN started at 0.24% P, while the TBA retained 0.34% P, and biochar measured 0.57% P. Lastly, K had higher retention increases with each pretreatment process than N or P. Untreated PMN was measured at 1.52% K. The PMN TBA increased retention and was recorded at 1.97% K, while biochar almost doubled the amount of K available at 2.98%.

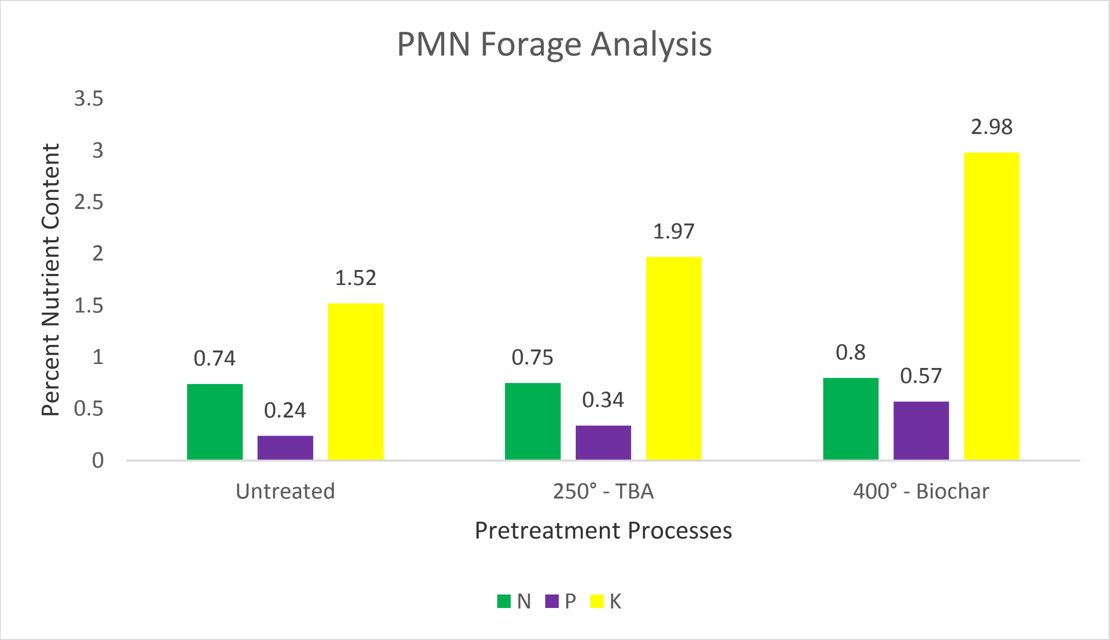

Fig. 1. Forage analysis for pretreatment processes (untreated, torrefied at 250° C, and pyrolized at 400° C) in pearl millet- napiergrass (PMN) feedstock. Nitrogen (N), phosphorus (P), and potassium (K) are shown in percent.

Unlike the PMN feedstock, the Merkeron feedstock did not increase retention across all macronutrients (Fig. 2).Nitrogen was slightly reduced after torrefaction, starting at 1.07% untreated and ending up at 0.94% N after torrefaction. Phosphorus increased slightly from 0.30% untreated to 0.35% torrefied. Similar to PMN feedstock pretreatments, the Merkeron pretreatments had the highest increase in K retention. The untreated Merkeron measured 3.69% while the TBA measured 4.54% K.

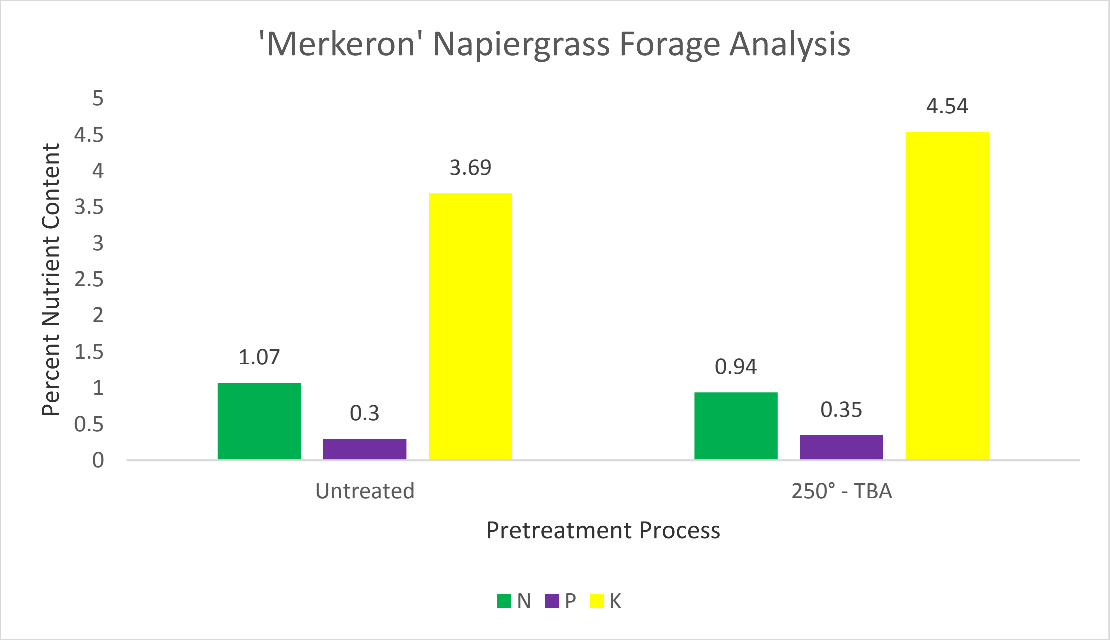

Fig. 2. Forage analysis for pretreatment processes (untreated and torrefied at 250° C) in 'Merkeron' napiergrass feedstock. Nitrogen (N), phosphorus (P), and potassium (K) are shown in percent.

Field Trial

The soil for the field trial was tested for residual macronutrient content (Fig. 3) and nutrient recommendations. The field location had extremely low residual nutrients available with N measuring at 0.0003%, P at 0.0021%, and K with 0.252%. Additionally, the micronutrients in the soil were 0.5595% Ca and 0.0237% Mg. The Soil, Water, and Forage Testing Laboratory at Texas A&M recommended nutrient application rates of 100.88 kg N/ha, 50.44 kg P_2O_5/ha, and 0 kg K_2O/ha to grow 6725.11 kg/ha of maize. The rates of the TBA, biochar, and urea were not applied per the recommended rates due to a comparison of slow-release and fast-release sources of nutrients. The urea was applied at rates similar to the standard application in Texas for maize of 133.83 kg/ha. The urea application rate of 166 kg/ha was slightly higher, but that was to at least partially offset the potential volatilization and leaching that can occur when using urea (Aarnio and Martikainen, 1994). The TBA and biochar application rate of equivalent N was considerably less than that of the standard rate at 23 kg/ha. This amount was chosen based on the crude protein of the feedstock selections and that the nutrient amendments would be slow-release. The application rate was set at a minimum to see yield response. Pine and poplar biochar have been noted to have a reduction in biomass with application rates of 5-19 T/ha (Marks et al., 2014). Another reason the application rate was lower than the standard of 133.83 kg/ha was to minimize cost that can be associated with high biochar inputs. Overall, urea had approximately seven times more elemental N than the TBA and biochar per plot.

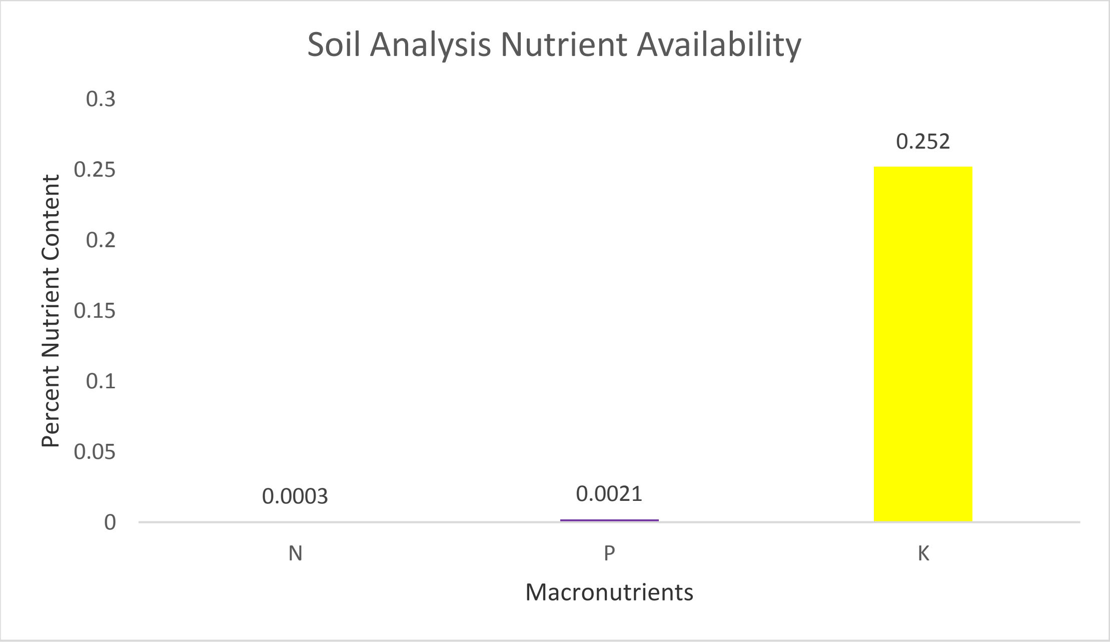

Fig. 3. Soil analysis of nutrient availability in Ships and Weswood soil series at the Texas A&M Agricultural Research Farm in Burleson County in Snook, TX. Nitrogen (N), phosphorus (P), and potassium (K) are shown in percent.

Individual variable effects from the ANOVA are summarized in Table 1. Significant effects are noted at $p \leq 0.05$, 0.01, or 0.001. Significant differences were noted for entry (PMN or maize) at $p \leq 0.001$ for ADF, TDN, N, P, K, and K uptake (%K). Biomass yield and Ca were significant at $p \leq 0.05$ by entry. All TBA and biochar amendments performed equivalent to urea. The only amendment to have a significant difference at $p \leq 0.05$ was Ca. The entry by amendment interaction was significant at $p \leq 0.01$ for P.

Table 1. Summary Table of analysis of variance in field trial of torrefied, biochar, and urea nutrient amendments in full-season maize and pearl millet – napiergrass measuring acid detergent fiber (ADF), total digestive nutrients (TDN), yield (T/ha), nitrogen, phosphorus, potassium, calcium, magnesium, nitrogen uptake (%N), phosphorus uptake (%P), and potassium uptake (%K).
NS (nonsignificant)
Significant at $p \leq 0.05$ (*), 0.01 (**), or 0.001 (***)

	ADF	TDN	Yield	N	P	K	Ca	Mg	%N	%P	%K
Entry	***	***	*	***	***	***	*	NS	NS	NS	***
Amendment	NS	NS	NS	NS	NS	NS	*	NS	NS	NS	NS
Entry * Amendment	NS	NS	NS	NS	**	NS	NS	NS	NS	NS	NS

ADF and TDN are important forage analyses used in relating to the digestibility of the forage to an animal. ADF relates to the cell wall portions of the forage that are cellulose and lignin. TDN is based on ADF and refers to the digestible energy of the forage. It is the sum of the digestible fiber, protein, lipid, and carbohydrate components (Belyea et al., 1993). The crops chosen for this research were based on forage use and seasonality. Maize was chosen for its widespread use as a food and forage annual crop. PMN was chosen for its adaptability as a ‘seeded-yet-sterile’ perennial biomass crop (Jessup, 2013). The results of the ANOVA that PMN had higher ADF, TDN, and T/ha than maize. These results are not surprising in that the relative maturity of the maize used was 117 growing days whereas PMN is still in vegetative growth stage at 117 days. The PMN used in this research was harvested at 205 DAP and had not entered the reproductive stage.

The ANOVA test measuring ADF found that the amendment and entry by amendment interaction did not produce significant differences. However, their p values were similar at 0.324 and 0.257, respectively (Table 2). Fig. 4 shows that the amendments were closely clustered together whereas the PMN had higher ADF results than the maize. This is expected based on digestibility of a full-season grass. PMN would typically be harvested at a much earlier time for greater digestibility. The only significant difference was shown to be $p < 0.001$ for entry with regard to ADF.

Table 2. Analysis of variance (ANOVA) table in full-season field trial measuring acid detergent fiber (ADF) by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment, biochar, and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - ADF

Cases	Sum of Squares	df	Mean Square	F	p
Entry	1846.37	1	1846.368	288.278	< .001
Amendment	31.41	4	7.852	1.226	0.324
Entry ✻ Amendment	36.24	4	9.061	1.415	0.257
Residual	166.53	26	6.405		

Note. Type III Sum of Squares

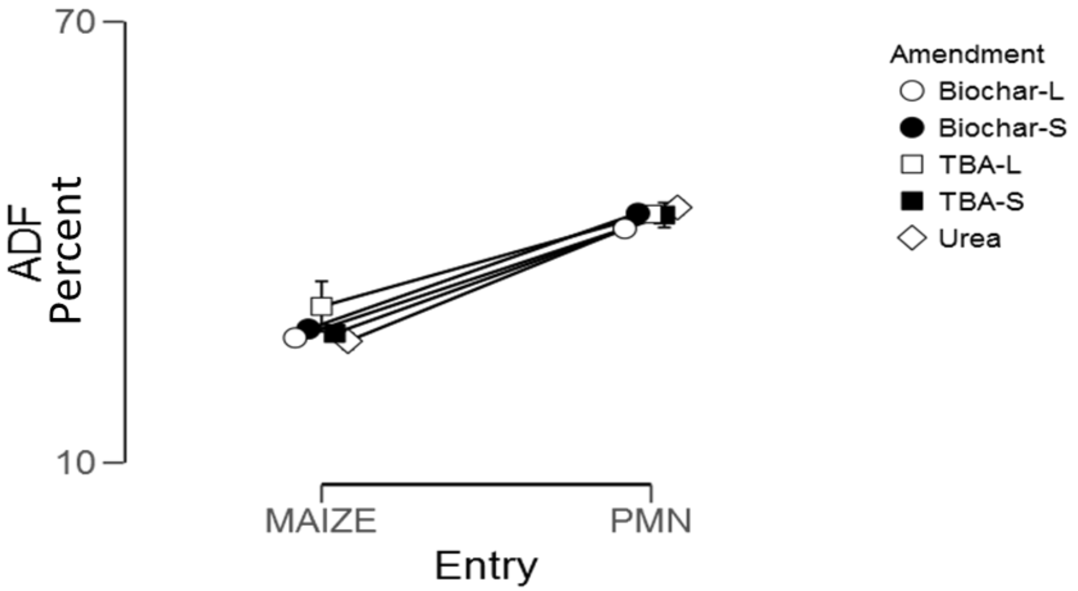

Fig. 4. Line graph of analysis of variance measuring percent acid detergent fiber (ADF) on the Y-axis by (amendment) torrefied biomass amendment (TBA), biochar, and urea with amendment sizes 2mm large (L) and 1mm small (S) in (entry) full-season maize and pearl millet – napiergrass (PMN) field trial on the X-axis.

Results from the ANOVA table (Table 3) measuring TDN had were similar to that of ADF. The only significant difference found was in the entries with PMN having a higher concentration of TDN than maize. The p value < 0.001 for the entry and just as seen in the ADF results, the amendment p value was 0.324 and the entry by amendment interaction was 0.258. Further illustration of these results can be seen in Fig. 5. The amendments are very closely clustered with the only significance being seen by the PMN.

Table 3. Analysis of variance (ANOVA) table in full-season field trial measuring total digestive nutrients (TDN) by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment, biochar, and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - TDN

Cases	Sum of Squares	df	Mean Square	F	p
Entry	2441.25	1	2441.249	288.120	< .001
Amendment	41.53	4	10.382	1.225	0.324
Entry ✻ Amendment	47.86	4	11.965	1.412	0.258
Residual	220.30	26	8.473		

Note. Type III Sum of Squares

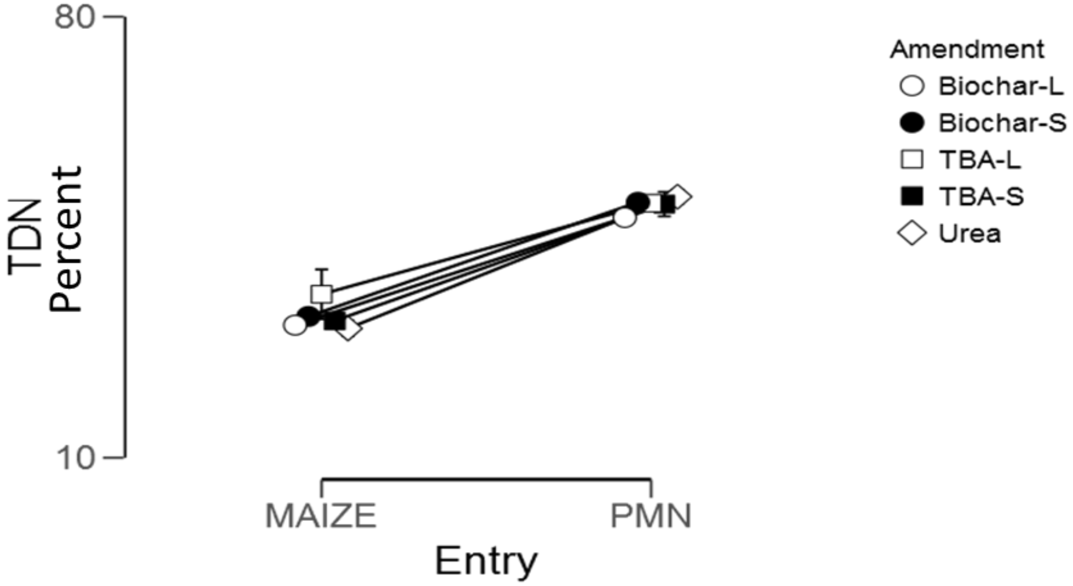

Fig. 5. Line graph of analysis of variance measuring percent total digestive nutrients (TDN) on the Y-axis by (amendment) torrefied biomass amendment (TBA), biochar, and urea with amendment sizes of 2mm large (L) and 1mm small (S) in (entry) full-season maize and pearl millet – napiergrass (PMN) field trial on the X-axis.

Overall yield, measured in T/ha, was only significant by entry. The perennial PMN outperformed the annual maize in terms of yield. Again, this was expected based on the relative maturity mentioned previous. All TBA and biochar amendments again performed as well as urea. The ANOVA table measuring T/ha (Table 4) has p values of 0.043 for entry, 0.054 for amendment, and 0.335 for the entry by amendment interaction. Fig. 6, shows all amendments in close proximity to one another.

Table 4. Analysis of variance (ANOVA) table in full-season field trial measuring yield (T/ha) by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment, biochar, and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - T-Ha

Cases	Sum of Squares	df	Mean Square	F	p
Entry	44299	1	44299	4.506	0.043
Amendment	105082	4	26270	2.672	0.054
Entry ✻ Amendment	47133	4	11783	1.199	0.335
Residual	255595	26	9831		

Note. Type III Sum of Squares

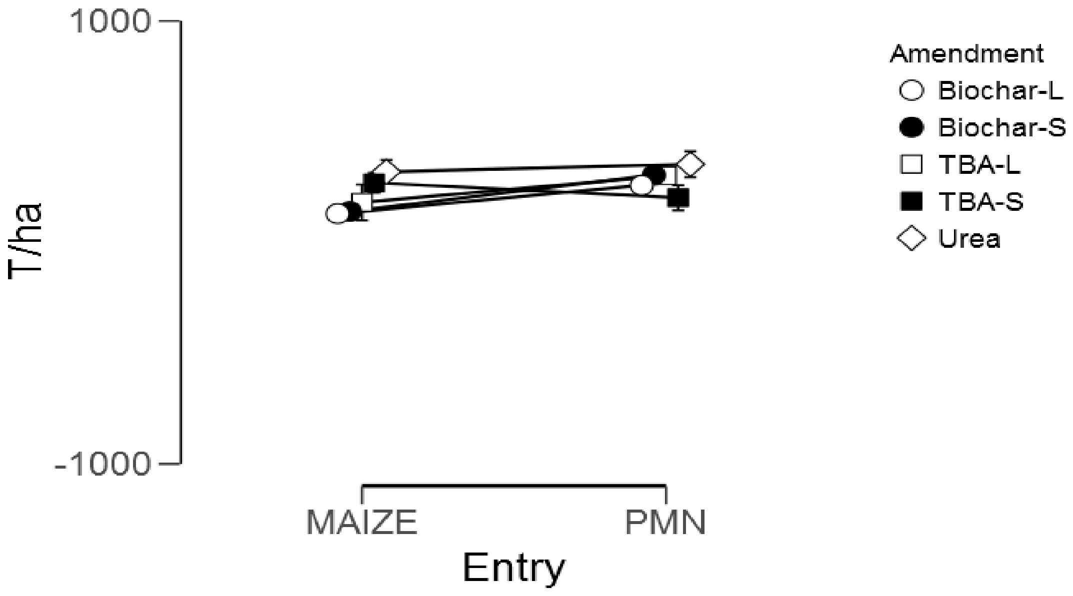

Fig. 6. Line graph of analysis of variance measuring yield (T/ha) on the Y-axis by (amendment) torrefied biomass amendment (TBA), biochar, and urea with amendment sizes of 2mm large (L) and 1mm small (S) in (entry) full-season maize and pearl millet – napiergrass (PMN) field trial on the X-axis.

N is one of the most important nutrients needed for crop production, especially in maize. N is important with regard to protein within the plant itself so it is needed in high concentrations. N was measured post-harvest, and the levels were only significant by entry. As expected, maize had higher levels of N than PMN. The ANOVA table (Table 5) shows the significant difference to be $p < 0.001$. An interesting notation is that none of the amendments were significantly different with the p value being 0.512. The entry by amendment interaction was also not significant at 0.384. Fig. 7 shows that all amendments are very closely clustered around one another. This further illustrates that the TBA and biochar were providing equivalent N to the entries as synthetic urea.

Table 5. Analysis of variance (ANOVA) table in full-season field trial measuring nitrogen by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment, biochar, and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - Nitrogen

Cases	Sum of Squares	df	Mean Square	F	p
Entry	1.270	1	1.270	109.101	< .001
Amendment	0.039	4	0.010	0.841	0.512
Entry ✻ Amendment	0.051	4	0.013	1.086	0.384
Residual	0.303	26	0.012		

Note. Type III Sum of Squares

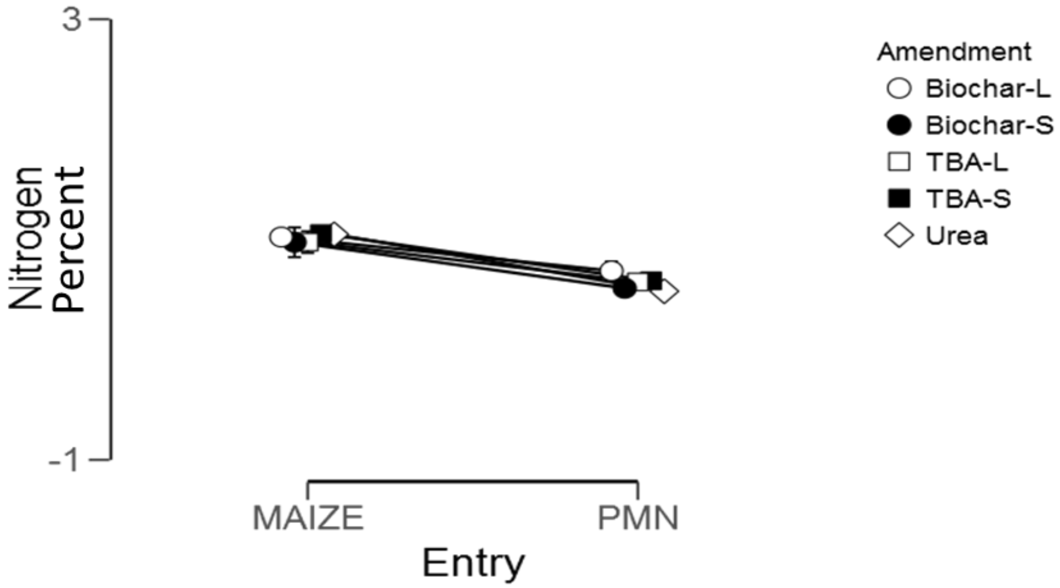

Fig. 7. Line graph of analysis of variance measuring percent nitrogen on the Y-axis by (amendment) torrefied biomass amendment (TBA), biochar, and urea with amendment sizes of 2mm large (L) and 1mm small (S) in (entry) full-season maize and pearl millet – napiergrass (PMN) field trial on the X-axis.

Table 6 shows the percent of P differs by entry and entry by amendment interaction. P is the only nutrient in the full-season field trial to have a significant difference in the entry by amendment interaction. This agrees with previous reports that biochar has the ability to help plants have better P uptake (Ok et al., 2015). Maize had higher percent P than PMN did with a p value of < 0.001. The amendment was nonsignificant at 0.497, but the entry by amendment interaction with a p value of 0.012. The biochar in maize and TBA in PMN showing slightly elevated levels in Fig. 8.

Table 6. Analysis of variance (ANOVA) table in full-season field trial measuring phosphorus by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment, biochar, and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - Phosphorus

Cases	Sum of Squares	df	Mean Square	F	p
Entry	0.072	1	0.072	41.688	< .001
Amendment	0.006	4	0.001	0.867	0.497
Entry ✻ Amendment	0.027	4	0.007	3.986	0.012
Residual	0.045	26	0.002		

Note. Type III Sum of Squares

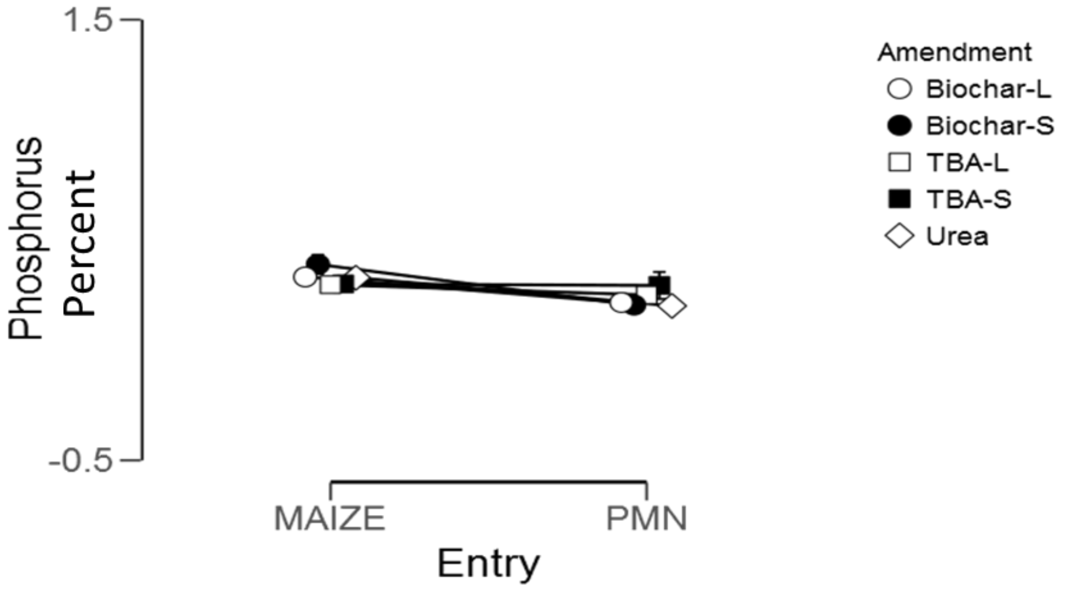

Fig. 8. Line graph of analysis of variance measuring percent phosphorus on the Y-axis by (amendment) torrefied biomass amendment (TBA), biochar, and urea with amendment sizes of 2mm large (L) and 1mm small (S) in (entry) full-season maize and pearl millet – napiergrass (PMN) field trial on the X-axis.

K levels were measured post-harvest (Table 7). ANOVA results show the only significant difference was found in the entry. PMN had elevated levels of K when compared to the maize samples. The p value of the entry is significant at < 0.001. Equivalent K was provided by all amendments. The amendment and entry by amendment interaction were not significant at 0.672 and 0.837 respectively. Fig. 9 shows all amendments closely grouped together.

Table 7. Analysis of variance (ANOVA) table in full-season field trial measuring potassium by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment, biochar, and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - Potassium

Cases	Sum of Squares	df	Mean Square	F	p
Entry	1.231	1	1.231	24.888	< .001
Amendment	0.117	4	0.029	0.591	0.672
Entry ✻ Amendment	0.070	4	0.018	0.356	0.837
Residual	1.286	26	0.049		

Note. Type III Sum of Squares

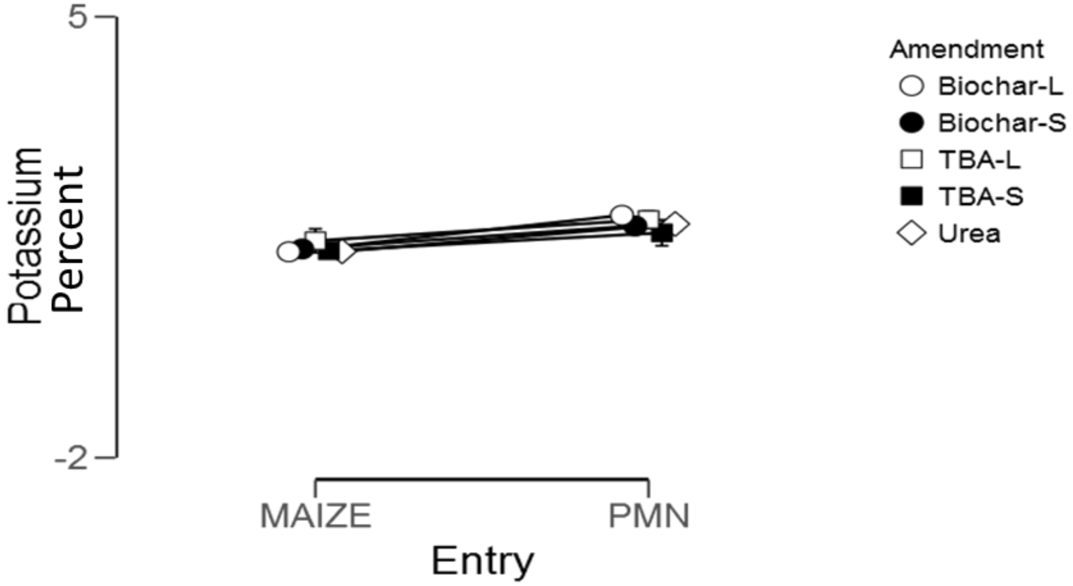

Fig. 9. Line graph of analysis of variance measuring percent potassium on the Y-axis by (amendment) torrefied biomass amendment (TBA), biochar, and urea with amendment sizes of 2mm large (L) and 1mm small (S) in (entry) full-season maize and pearl millet – napiergrass (PMN) field trial on the X-axis.

Ca is a vital macronutrient as it directly correlated to cell wall growth (Rorison and Robinson, 1984). Ca also reduces soil salinity and help with water retention. As discussed in the literature review, carbon rich soils can help prevent leaching and retain nutrients like Ca (Glaser et al., 2014). An additional benefit of using TBA or biochar would be to offset the effects of an ammonium fertilizer like urea which can lead to nitrification and soil acidification over time (Tong and Xu, 2012). Ca was measured post-harvest (Table 8) and the ANOVA results provide significant differences in the entry and amendment with a $p \leq 0.05$. Fig. 10 looks like the amendments are all grouped closely together and not statistically significant. However, the ANOVA p value is 0.043

and 0.054 for entry and amendment respectively. There was no statistical difference in the entry by amendment interaction with a p value of 0.335.

Table 8. Analysis of variance (ANOVA) table in full-season field trial measuring calcium by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment, biochar, and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - Calcium

Cases	Sum of Squares	df	Mean Square	F	p
Entry	4.430e -4	1	4.430e -4	4.506	0.043
Amendment	0.001	4	2.627e -4	2.672	0.054
Entry ✻ Amendment	4.713e -4	4	1.178e -4	1.199	0.335
Residual	0.003	26	9.831e -5		

Note. Type III Sum of Squares

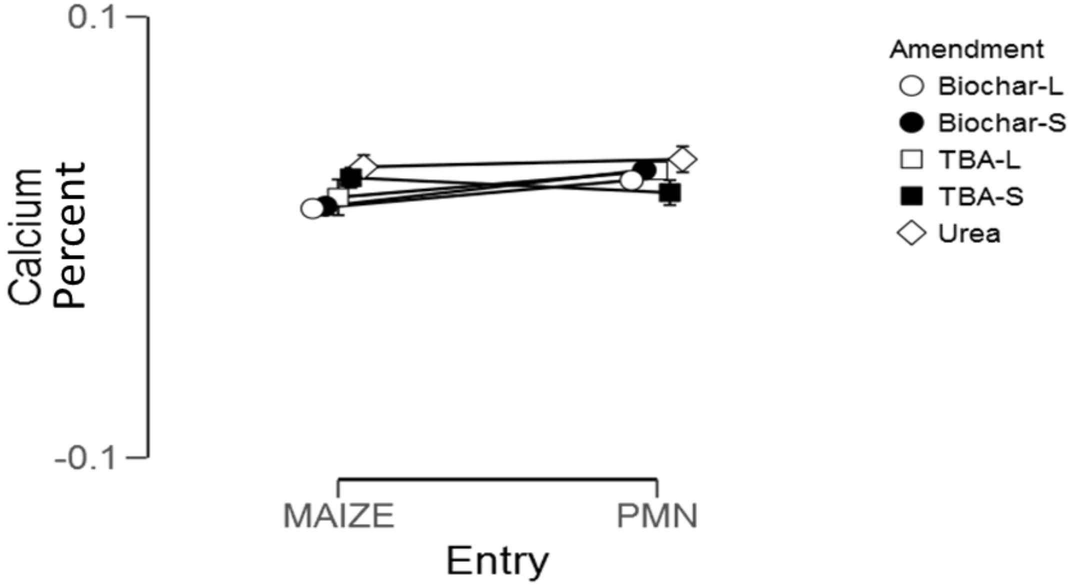

Figure 10. Line graph of analysis of variance measuring percent calcium on the Y-axis by (amendment) torrefied biomass amendment (TBA), biochar, and urea with amendment sizes of 2mm large (L) and 1mm small (S) in (entry) full-season maize and pearl millet – napiergrass (PMN) field trial on the X-axis.

Mg, like Ca, is required in quantities similar to K. Mg is also a key nutrient in the role of photosynthesis. Table 9 provides the ANOVA results which were nonsignificant. The entry p value was 0.153, while the amendment p value was 0.115. The entry by amendment interaction was not significant at 0.087. Fig. 11 appears to have variation in the amendments specifically in the maize crop, but the error bars overlap. All amendments are closely grouped together in the PMN crop.

Table 9. Analysis of variance (ANOVA) table in full-season field trial measuring magnesium by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment, biochar, and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - Magnesium

Cases	Sum of Squares	df	Mean Square	F	p
Entry	160.7	1	160.70	2.170	0.153
Amendment	609.9	4	152.48	2.059	0.115
Entry ✻ Amendment	678.3	4	169.57	2.290	0.087
Residual	1925.4	26	74.05		

Note. Type III Sum of Squares

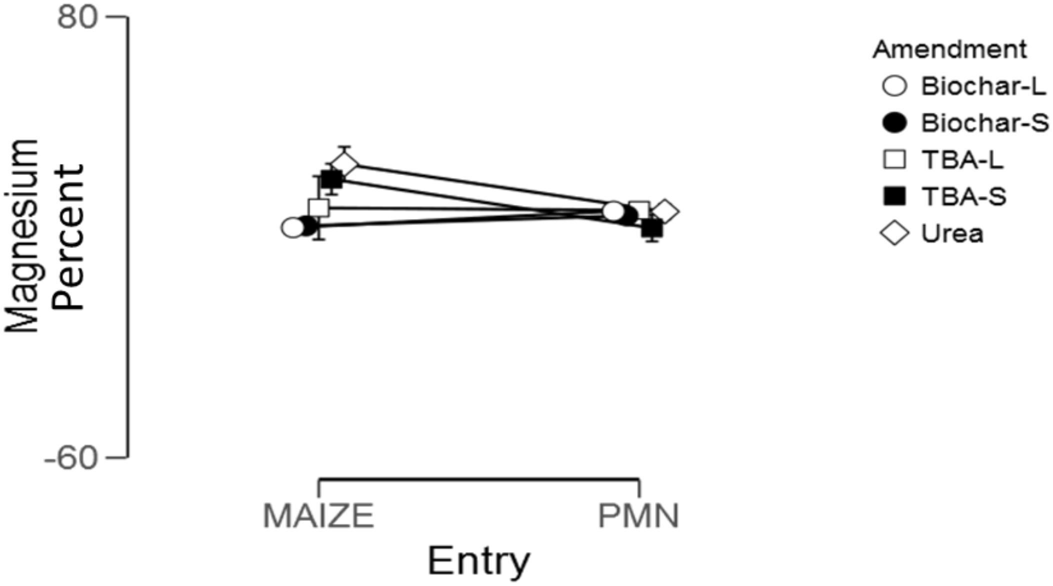

Figure 11. Line graph of analysis of variance measuring percent magnesium on the Y-axis by (amendment) torrefied biomass amendment (TBA), biochar, and urea with amendment sizes of 2mm large (L) and 1mm small (S) in (entry) full-season maize and pearl millet – napiergrass (PMN) field trial on the X-axis.

The overall nutrient uptake in harvested biomass per plot was also analyzed in the full-season field trial. The biomass yield per plot of nutrient uptake was measured for N, P, and K. Fig. 12 seems to show N to be visually higher in maize for the urea and biochar amendments. However, all p values are nonsignificant (Table 10). All numbers are closely related, but there is no significant differences between the entry at 0.153, amendments at 0.115, and the entry by amendment interaction at 0.087. Similar to nutrient content in the biomass, total nutrient uptake was equivalent for both crops irrespective of nutrient amendment.

Table 10. Analysis of variance (ANOVA) table in full-season field trial measuring nitrogen (N) biomass uptake (%) per plot by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment, biochar, and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - N Uptake

Cases	Sum of Squares	df	Mean Square	F	p
Entry	1.607e +10	1	1.607e +10	2.170	0.153
Amendment	6.099e +10	4	1.525e +10	2.059	0.115
Entry ✻ Amendment	6.783e +10	4	1.696e +10	2.290	0.087
Residual	1.925e +11	26	7.405e +9		

Note. Type III Sum of Squares

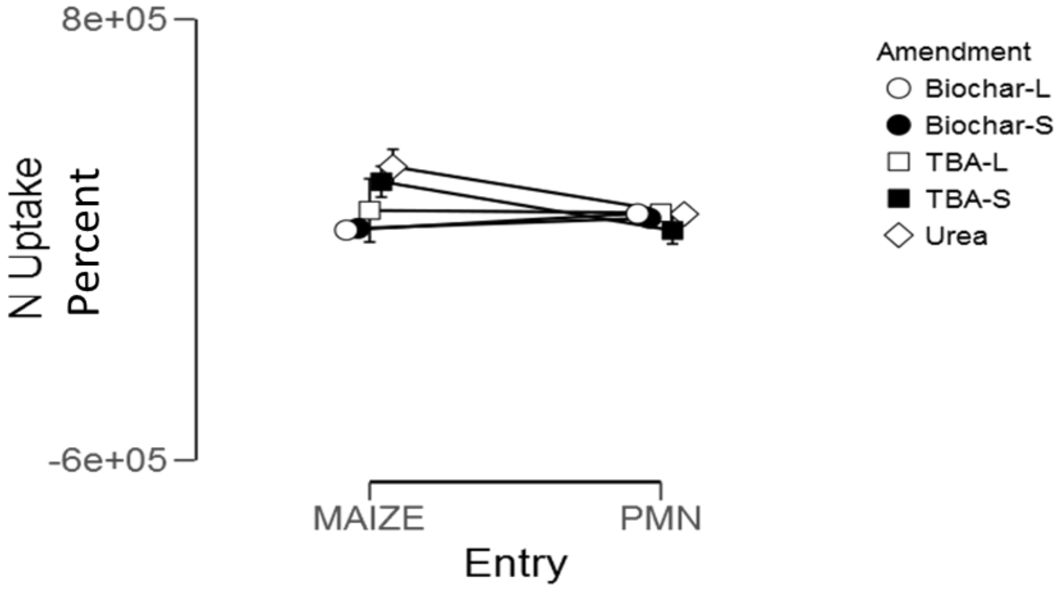

Fig. 12. Line graph of analysis of variance measuring nitrogen (N) biomass uptake (%) per plot on the Y-axis by (amendment) torrefied biomass amendment (TBA), biochar, and urea with amendment sizes of 2mm large (L) and 1mm small (S) in (entry) full-season maize and pearl millet – napiergrass (PMN) field trial on the X-axis.

P uptake had the same results as N uptake. Fig. 13 seems to be visually higher in maize with urea and TBA amendments. However, the ANOVA table (Table 11) has all nonsignificant p values. The entry p value is 0.803, the amendment is 0.070, and the entry by amendment interaction is 0.213. Finally, K is the only nutrient concentration in biomass per plot with any significance. The entry is higher in PMN with a p value of < 0.001 (Table 12). The amendment was nonsignificant with a p value of 0.101 and the entry by amendment interaction was also nonsignificant at 0.367. Fig. 14 shows all amendments are closely grouped together.

Table 11. Analysis of variance (ANOVA) table in full-season field trial measuring phosphorus (P) biomass uptake (%) per plot by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment, biochar, and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - P Uptake

Cases	Sum of Squares	df	Mean Square	F	p
Entry	4.084e +7	1	4.084e +7	0.063	0.803
Amendment	6.339e +9	4	1.585e +9	2.464	0.070
Entry ✻ Amendment	4.033e +9	4	1.008e +9	1.568	0.213
Residual	1.672e +10	26	6.432e +8		

Note. Type III Sum of Squares

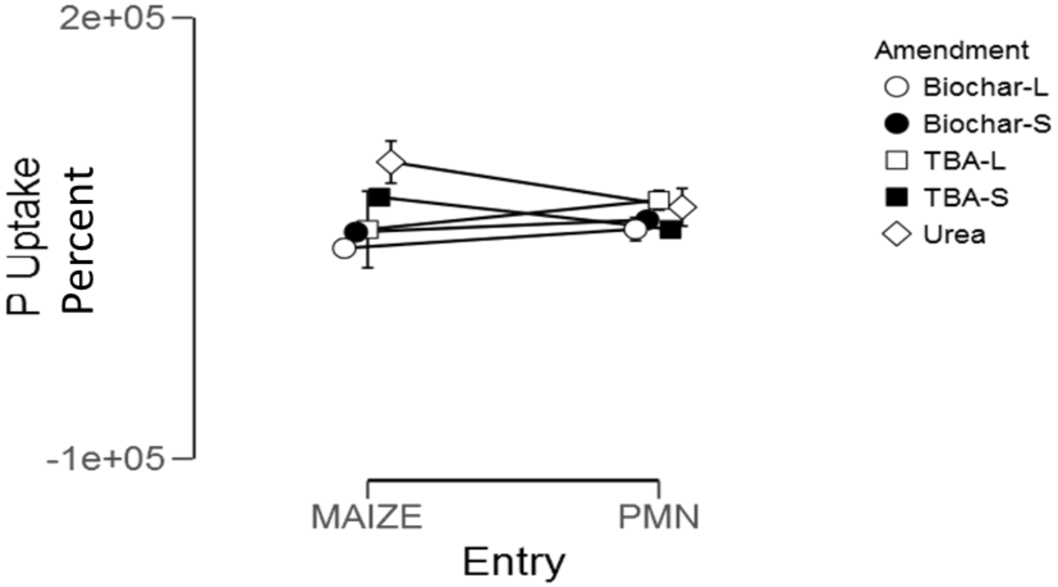

Fig. 13. Line graph of analysis of variance measuring phosphorus (P) biomass uptake (%) per plot on the Y-axis by (amendment) torrefied biomass amendment (TBA), biochar, and urea with amendment sizes of 2mm large (L) and 1mm small (S) in (entry) full-season maize and pearl millet – napiergrass (PMN) field trial on the X-axis.

Table 12. Analysis of variance (ANOVA) table in full-season field trial measuring potassium (K) biomass uptake (%) per plot by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment, biochar, and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - K Uptake

Cases	Sum of Squares	df	Mean Square	F	p
Entry	3.935e +11	1	3.935e +11	17.608	< .001
Amendment	1.938e +11	4	4.846e +10	2.168	0.101
Entry ✻ Amendment	1.005e +11	4	2.512e +10	1.124	0.367
Residual	5.811e +11	26	2.235e +10		

Note. Type III Sum of Squares

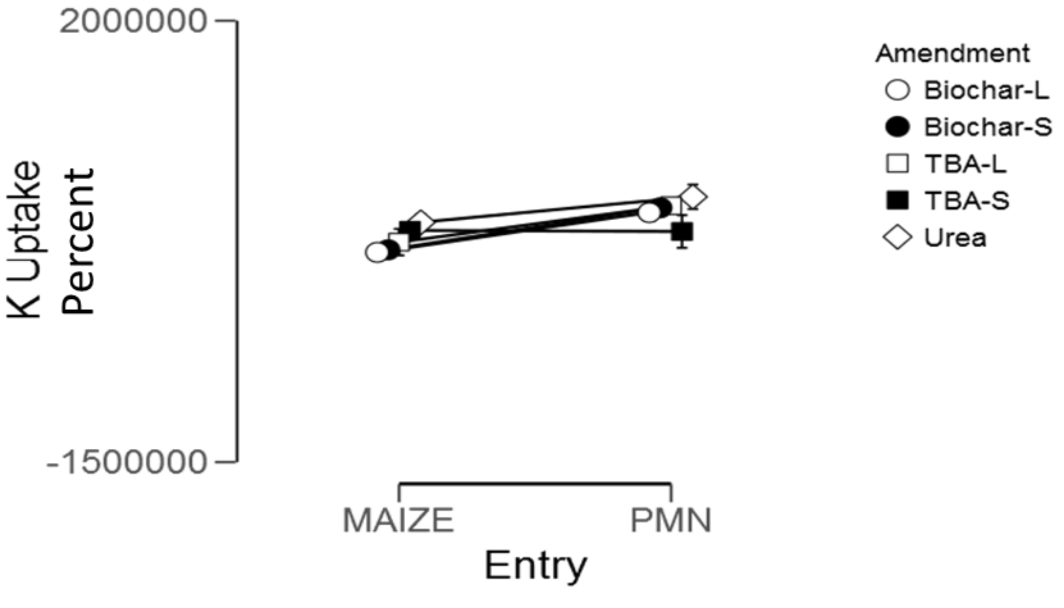

Fig. 14. Line graph of analysis of variance measuring potassium (K) biomass uptake (%) per plot on the Y-axis by (amendment) torrefied biomass amendment (TBA), biochar, and urea with amendment sizes of 2mm large (L) and 1mm small (S) in (entry) full-season maize and pearl millet – napiergrass (PMN) field trial on the X-axis.

Nursery Trial

Since the nursery trial was to be a partial-growing season, focusing on only 72 days, the amendment comparison only focused on TBA and urea. The urea fertilizer rate would remain the same as the field trial at 166 kg/ha while the TBA would increase slightly at 26.5 kg/ha. Following the same methodology and reasoning as the field trial, the urea would follow the Texas standard of 133.83 kg N/ha. The TBA would be applied at a minimum in order to see a yield response. Overall, urea had six times more elemental nitrogen than the TBA per pot.

Individual variable effects from the ANOVA are summarized in Table 13. Significant differences were noted by entry at $p \leq 0.001$ for N, K, and Mg. P and Ca were significant at $p \leq 0.01$ by entry. Yield was significant at $p \leq 0.05$ by entry. The amendment was significant at $p \leq 0.01$ for N and P. Amendment was also significant at $p \leq 0.05$ for yield. This was likely caused by the much shorter duration of the nursery trial versus the field trial and decreased time for the TBA derived nutrients to become available. The entry by amendment interaction was nonsignificant for all measurements.

Table 13. Summary Table of analysis of variance in nursery trial of torrefied and urea fertilizer amendments in partial-season maize and pearl millet – napiergrass measuring acid detergent fiber (ADF), total digestive nutrients (TDN), yield (g), nitrogen, phosphorus, potassium, calcium, and magnesium.
NS (nonsignificant)
Significant at $p \leq 0.05$ (*), 0.01 (**), or 0.001 (***)

	ADF	TDN	Yield	N	P	K	Ca	Mg
Entry	NS	NS	*	***	**	***	**	***
Amendment	NS	NS	*	**	**	NS	NS	NS
Entry * Amendment	NS	NS	NS	NS	NS	NS	NS	NS

As with the full-season field trial, forage analyses were conducted to determine if the TBA would have any interaction with the crop making it less digestible to animals. Fig. 15 shows PMN and TBA visually higher than maize and urea treatments. However, the error bars in the line graph are high for PMN. Per the ANOVA table (Table 14), ADF was nonsignificant across all criteria being measured. PMN and maize entries had a p value of 0.700. The amendment was 0.670 while the entry by amendment interaction was 0.792. Unlike the field trial, PMN did not have higher digestibility. This is most likely due to the fact that there was a difference from 205 DAP to 72 DAP for harvests.

Table 14. Analysis of variance (ANOVA) table in partial-season nursery trial measuring acid detergent fiber (ADF) by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - ADF

Cases	Sum of Squares	df	Mean Square	F	p
Entry	0.833	1	0.833	0.156	0.700
Amendment	1.018	1	1.018	0.191	0.670
Entry ✻ Amendment	0.390	1	0.390	0.073	0.792
Residual	58.570	11	5.325		

Note. Type III Sum of Squares

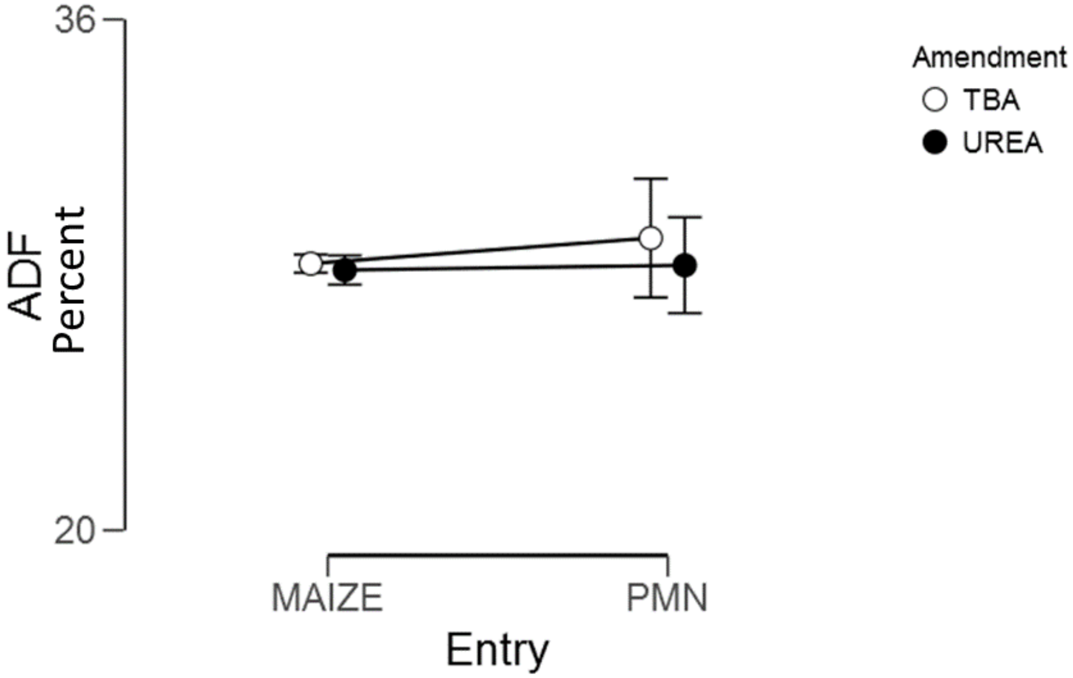

Fig. 15. Line graph of analysis of variance measuring percent acid detergent fiber (ADF) on the Y-axis by (amendment) torrefied biomass amendment (TBA) and urea in (entry) partial-season maize and pearl millet – napiergrass (PMN) nursery trial on the X-axis.

TDN (Table 15) had the same results as ADF. There was no significance across all measurements. The ANOVA p values for entry were 0.700, amendment was 0.670, and the entry by amendment interaction was 0.792. The only difference between ADF and TDN was shown in Fig. 16. The visual representation of ANOVA for TDN shows maize having higher TDN numbers. Yet, as with ADF, the error bars are high in PMN causing overlap between the entries and amendments.

Table 15. Analysis of variance (ANOVA) table in partial-season nursery trial measuring total digestive nutrients (TDN) by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - TDN

Cases	Sum of Squares	df	Mean Square	F	p
Entry	1.102	1	1.102	0.156	0.700
Amendment	1.346	1	1.346	0.191	0.670
Entry ✻ Amendment	0.516	1	0.516	0.073	0.792
Residual	77.459	11	7.042		

Note. Type III Sum of Squares

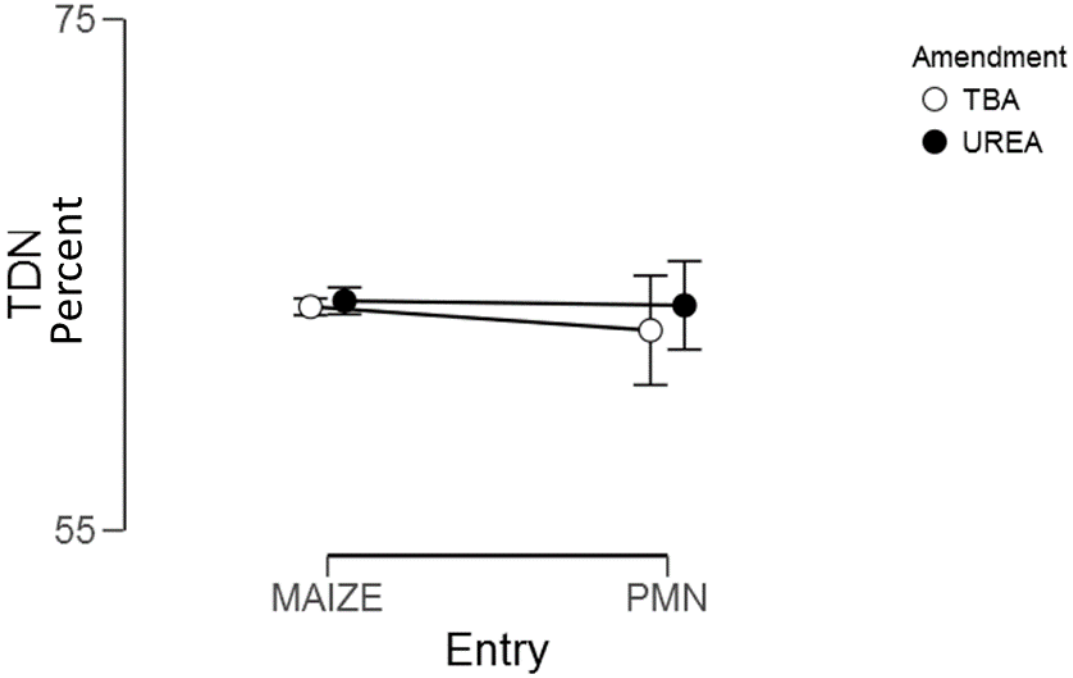

Fig. 16. Line graph of analysis of variance measuring percent total digestive nutrients (TDN) on the Y-axis by (amendment) torrefied biomass amendment (TBA) and urea in (entry) partial-season maize and pearl millet – napiergrass (PMN) nursery trial on the X-axis.

Yield (g) for the nursery trial was significant in entry and amendment. Maize yielded more than PMN in both urea and TBA treatments. This coincides with the relative maturity of the maize seed used as well as urea being a fast-release fertilizer. The ANOVA table (Table 16) shows a p value of 0.032 for entry and 0.045 for amendment. There was no entry by amendment interaction which had a p value of 0.458. Fig. 17 illustrates urea with maize having a higher yield, but maize with TBA isn't statistically significantly lower.

Table 16. Analysis of variance (ANOVA) table partial-season nursery trial measuring yield (g) by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - Yield (g)

Cases	Sum of Squares	df	Mean Square	F	p
Entry	1072.9	1	1072.9	6.004	0.032
Amendment	917.5	1	917.5	5.134	0.045
Entry ✻ Amendment	105.5	1	105.5	0.590	0.458
Residual	1965.9	11	178.7		

Note. Type III Sum of Squares

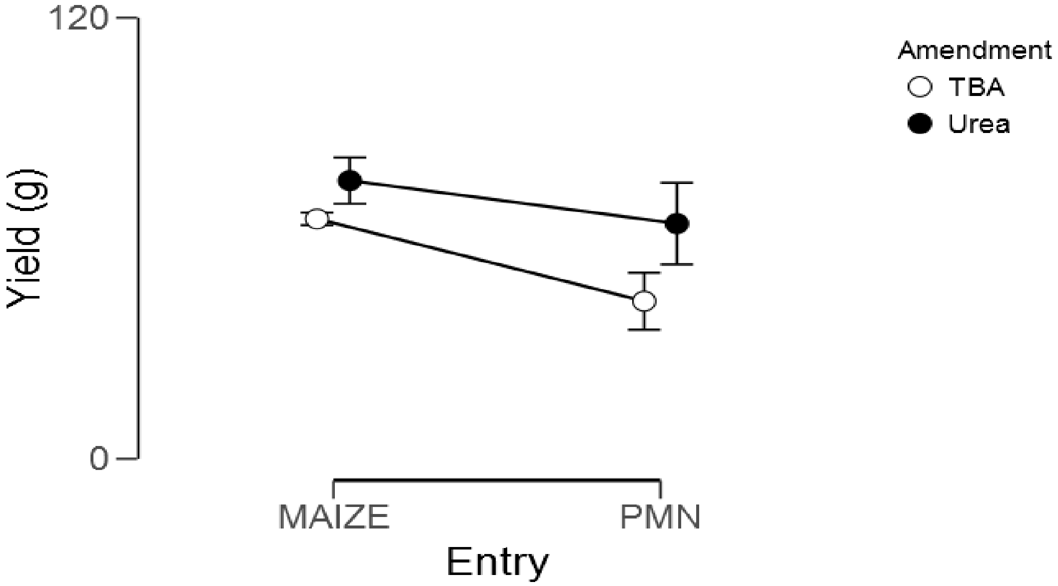

Fig. 17. Line graph of analysis of variance measuring yield (g) on the Y-axis by (amendment) torrefied biomass amendment (TBA) and urea in (entry) partial-season maize and pearl millet – napiergrass (PMN) nursery trial on the X-axis.

N was analyzed post-harvest and it was found to have significant differences in both entry and amendment. The entry with significance in the nursery trial differed from that of the maize in the field trial. PMN had a higher amount of N uptake than the maize in both urea and TBA treatments. Table 17 shows the ANOVA results for N and the entry had a p value of < 0.001. The amendment had a p value of 0.002 and the entry by amendment interaction had no significance at 0.132. Fig. 18 highlights the differences between PMN and maize being significant. It also further illustrates that the urea, being a fast-release fertilizer, has the higher availability of nitrogen to the plant in a shorter period of time.

Table 17. Analysis of variance (ANOVA) table partial-season nursery trial measuring nitrogen by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - Nitrogen

Cases	Sum of Squares	df	Mean Square	F	p
Entry	0.739	1	0.739	30.264	< .001
Amendment	0.390	1	0.390	15.963	0.002
Entry ✻ Amendment	0.065	1	0.065	2.653	0.132
Residual	0.269	11	0.024		

Note. Type III Sum of Squares

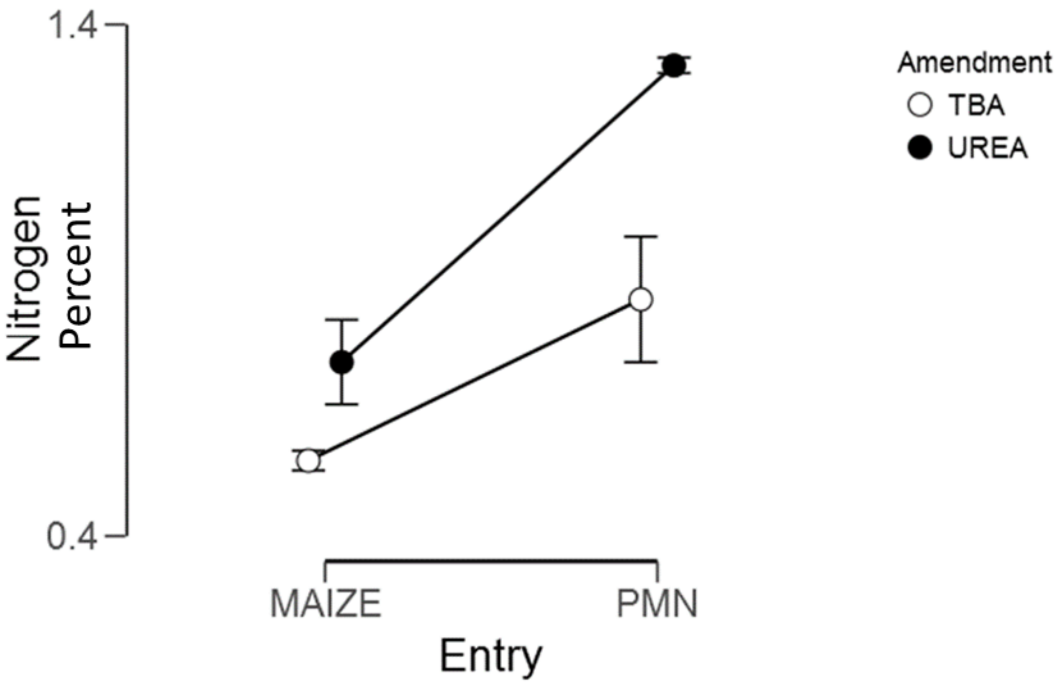

Fig. 18. Line graph of analysis of variance measuring percent nitrogen on the Y-axis by (amendment) torrefied biomass amendment (TBA) and urea in (entry) partial-season maize and pearl millet – napiergrass (PMN) nursery trial on the X-axis.

Similar to the results in the field trial, P had more retention in the PMN. TBA was also significant as an amendment. This coincides with the results found in the field trial with regard to biochar. As torrefaction has the same beneficial properties as biochar, it too would help plants have better P uptake. The ANOVA table in Table 18 shows a significant difference for entry at 0.002 and amendment at 0.005. The entry by amendment interaction had no significant difference with a p value of 0.282. Fig. 19 illustrates the high result of percent phosphorus in PMN and TBA.

Table 18. Analysis of variance (ANOVA) table partial-season nursery trial measuring phosphorus by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - Phosphorus

Cases	Sum of Squares	df	Mean Square	F	p
Entry	0.026	1	0.026	16.468	0.002
Amendment	0.019	1	0.019	12.118	0.005
Entry ✻ Amendment	0.002	1	0.002	1.280	0.282
Residual	0.017	11	0.002		

Note. Type III Sum of Squares

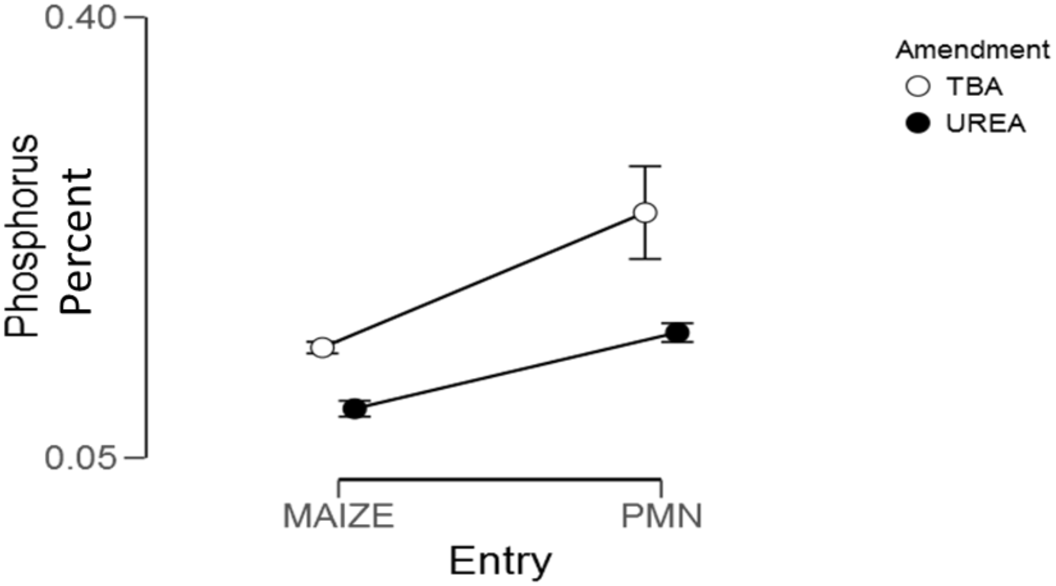

Fig. 19. Line graph of analysis of variance measuring percent phosphorus on the Y-axis by (amendment) torrefied biomass amendment (TBA) and urea in (entry) partial-season maize and pearl millet – napiergrass (PMN) nursery trial on the X-axis.

The final macronutrient analyses completed in the partial-season nursery trial is percent potassium. Potassium only had a significant difference in entry. The ANOVA table has a p value of < 0.001 for entry (Table 19), while the amendment and entry by amendment interaction were nonsignificant at 0.551 and 0.785 respectively. As with the findings in the field trial, PMN had a higher percentage of potassium in both urea and TBA treatments. However, the amendments are shown closely clustered in Fig. 20. This falls along the same pattern as the field trial in that the TBA was on par with the urea fertilizer despite it being a slow-release nutrient amendment.

Table 19. Analysis of variance (ANOVA) table partial-season nursery trial measuring potassium by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment and urea), and entry by amendment.
Significant at $p \leq 0.05$, 0.01, or 0.001

ANOVA - Potassium

Cases	Sum of Squares	df	Mean Square	F	p
Entry	7.348	1	7.348	115.207	< .001
Amendment	0.024	1	0.024	0.377	0.551
Entry ✻ Amendment	0.005	1	0.005	0.078	0.785
Residual	0.702	11	0.064		

Note. Type III Sum of Squares

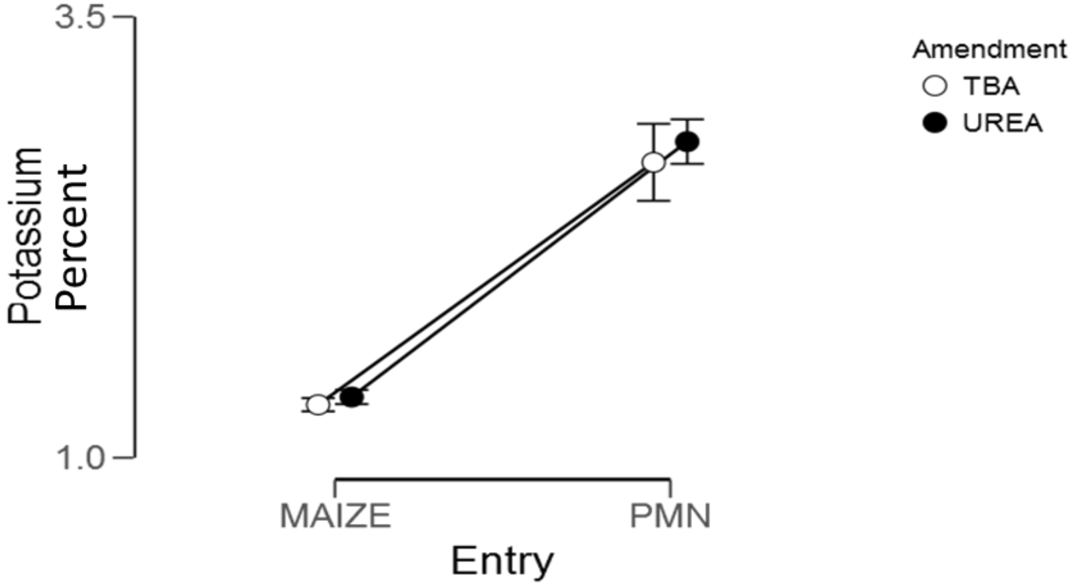

Fig. 20. Line graph of analysis of variance measuring percent potassium on the Y-axis by (amendment) torrefied biomass amendment (TBA) and urea in (entry) partial-season maize and pearl millet – napiergrass (PMN) nursery trial on the X-axis.

The final two macronutrients to be analyzed are Ca and Mg. PMN had more retention of Ca than maize (Table 20). There were significant differences found in the entry with a p value of 0.002. There is a clear demarcation between PMN and maize (Fig. 21). However, unlike the field trial, Ca had nonsignificant differences in the amendment, p value of 0.440. There is a greater error bar overlap in the nursery trial. Finally, there was no entry by amendment interaction at 0.289.

Table 20. Analysis of variance (ANOVA) table partial-season nursery trial measuring calcium by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - Calcium

Cases	Sum of Squares	df	Mean Square	F	p
Entry	0.047	1	0.047	17.292	0.002
Amendment	0.002	1	0.002	0.642	0.440
Entry ∗ Amendment	0.003	1	0.003	1.243	0.289
Residual	0.030	11	0.003		

Note. Type III Sum of Squares

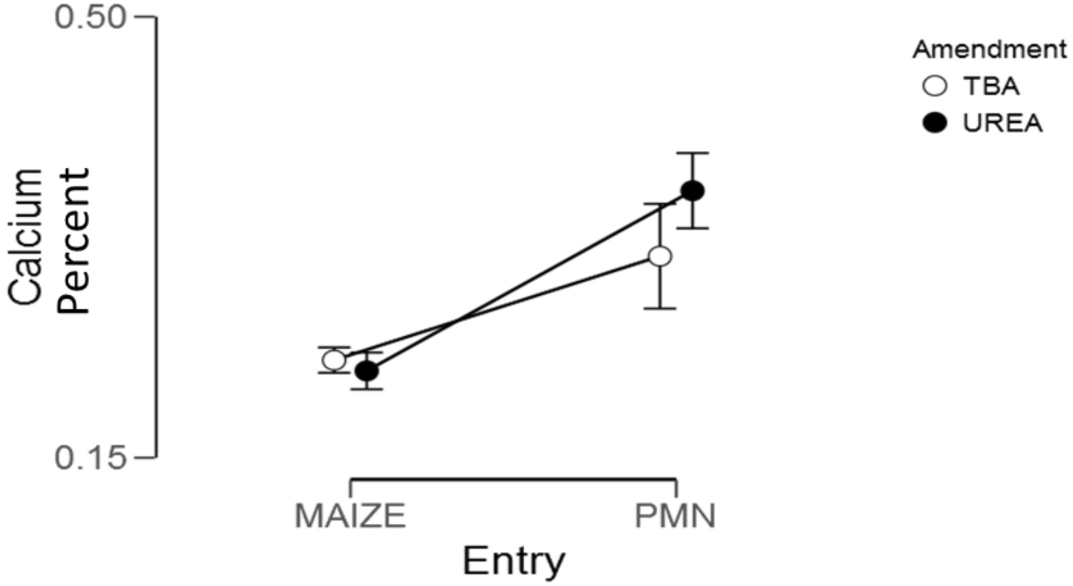

Figure 21. Line graph of analysis of variance measuring percent calcium on the Y-axis by (amendment) torrefied biomass amendment (TBA) and urea in (entry) partial-season maize and pearl millet – napiergrass (PMN) nursery trial on the X-axis.

Unlike the full-season field trial, Mg results (Table 21) were significant in the entry. The field trial produced all nonsignificant differences, but PMN had a higher retention of Mg. The p value of the entry was < .001. Similar results were found via amendment and the entry by amendment interaction as the field trial. The p value was 0.662 for the amendment and 0.979 for the entry by amendment interaction. Fig. 22 shows the amendments had similar retention in both the maize and PMN crops.

Table 21. Analysis of variance (ANOVA) table partial-season nursery trial measuring magnesium by entry (pearl millet – napiergrass and maize), amendment (torrefied biomass amendment and urea), and entry by amendment.
Significant at p ≤ 0.05, 0.01, or 0.001

ANOVA - Magnesium

Cases	Sum of Squares	df	Mean Square	F	p
Entry	0.110	1	0.110	22.472	< .001
Amendment	9.891e -4	1	9.891e -4	0.202	0.662
Entry ✻ Amendment	3.391e -6	1	3.391e -6	6.936e -4	0.979
Residual	0.054	11	0.005		

Note. Type III Sum of Squares

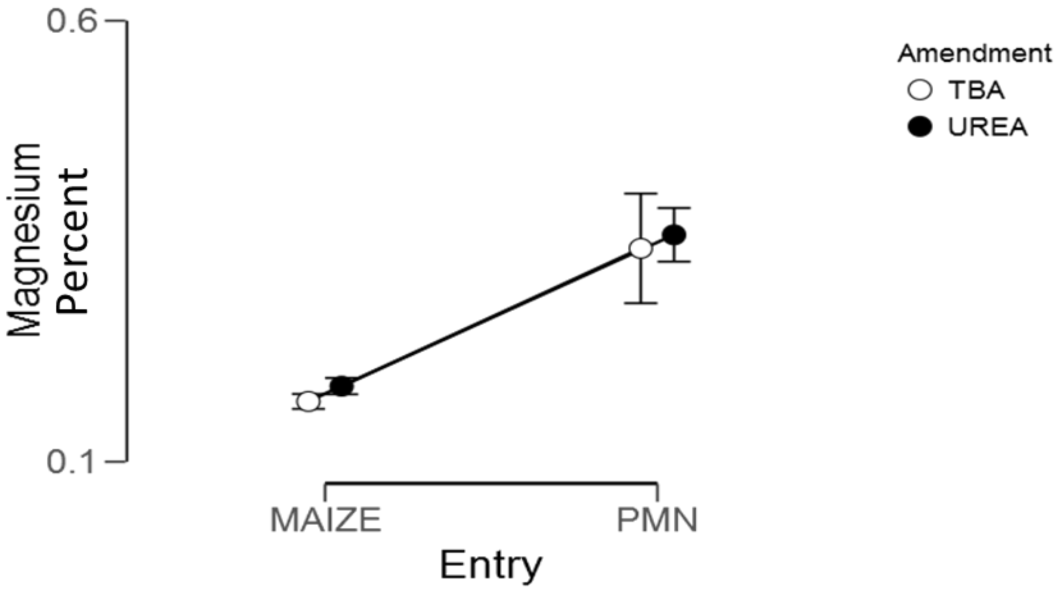

Figure 22. Line graph of analysis of variance measuring percent magnesium on the Y-axis by (amendment) torrefied biomass amendment (TBA) and urea in (entry) partial-season maize and pearl millet – napiergrass (PMN) nursery trial on the X-axis.

CHAPTER IV

SUMMARY AND CONCLUSIONS

The pretreatment processes of torrefaction and pyrolysis resulted in higher nutrient retention among the feedstock selections of PMN and Merkeron. Torrefaction has been shown to increase the energy density of biomass (Medic et al., 2010). Further research should be conducted to include multiple feedstock selections to determine optimal nutrient content for use in TBA and biochar amendments as there is a high compositional variability dependent upon the conditions of pyrolysis and feedstock utilized (Kavitha et al., 2018; Spokas, 2010). Torrefaction can break down the polymers in the plant which is beneficial. However, high temperature torrefaction can also result in a loss of aromatic hydrocarbon (Mahadevan et al., 2016). Therefore, different temperatures should be taken into consideration for further research as torrefaction can occur at multiple temperature settings within 200 – 300° C.

The TBA and biochar nutrient amendments both performed as well as urea in the full-season field trial with a lower application rate. Further research would need to be conducted to determine the proper application rate to quantify an improved crop response. It is important that TBA and biochar be used in full-season plantings, as the partial-growing season nursery trial showed that crop response would only be beneficial with regard to phosphorus retention. Testing TBA and biochar amendments across more diverse crops and soil types would further optimize cropping systems incorporating these amendments.

While further research would need to be conducted to see if different temperatures, feedstocks, incubation times, and additional application rates have any further effect on a cropping system, the overall takeaway from this research is that the TBA and biochar created could be used as a nutrient amendment to help with macronutrients N, P, and K retention. Additionally, it can help with micronutrients, Ca and Mg, retention and use in affecting soil pH. Finally, TBA and biochar have been tested with a minimal application rate and there was still a crop response similar to that of an inorganic fertilizer at an application rate standard in Texas.

REFERENCES

Aarnio, T., and Martikainen, P. J. (1994). Mineralization of Carbon and Nitrogen in Acid Forest Soil Treated with Fast and Slow-Release Nutrients. *Plant and Soil* **164**, 187-193.

Altland, J. E., and Locke, J. C. (2012). Biochar affects macronutrient leaching from a soilless substrate. *HortScience* **47**, 1136-1140.

Bàrberi, P. (2002). Weed management in organic agriculture: Are we addressing the right issues? *Weed Research* **42**, 177-193.

Bargmann, I., Rillig, M. C., Kruse, A., Greef, J.-M., and Kücke, M. (2014). Effects of hydrochar application on the dynamics of soluble nitrogen in soils and on plant availability. *Journal of Plant Nutrition and Soil Science* **177**, 48-58.

Barnett, G. (1994). Phosphorus forms in animal manure. *Bioresource Technology* **49**, 139-147.

Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J. L., Harris, E., Robinson, B., and Sizmur, T. (2011). A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. *Environmental Pollution* **159**, 3269-3282.

Belyea, R. L., Steevens, B. J., Garner, G. B., Whittier, J. C., and Sewell, H. B. (1993). Using NDF and ADF to balance diets. *Extension publications (MU)*.

Bhagat, R., and Verma, T. (1991). Impact of rice straw management on soil physical properties and wheat yield. *Soil Science* **152**, 108-115.

Blok, C., Rijpsma, E., and Ketelaars, J. (2014). New growing media and value added organic waste processing. *In* "XXIX International Horticultural Congress on Horticulture: Sustaining Lives, Livelihoods and Landscapes (IHC2014): 1112", pp. 269-280.

Brunelle, T., Dumas, P., Souty, F., Dorin, B., and Nadaud, F. (2015). Evaluating the impact of rising fertilizer prices on crop yields. *Agricultural economics* **46**, 653-666.

Cassman, K. G., Dobermann, A., and Walters, D. T. (2002). Agroecosystems, nitrogen-use efficiency, and nitrogen management. *AMBIO: A Journal of the Human Environment* **31**, 132-141.

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

Chen, W. H., and Kuo, P. C. (2011). Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass. *Energy* **36**, 803-811.

Chen, W. H., Peng, J. H., and Bi, X. T. T. (2015). A state-of-the-art review of biomass torrefaction, densification and applications. *Renewable & Sustainable Energy Reviews* **44**, 847-866.

Clark, M. S., Horwath, W. R., Shennan, C., and Scow, K. M. (1998). Changes in soil chemical properties resulting from organic and low-input farming practices. *Agronomy Journal* **90**, 662-671.

Croppenstedt, A., Demeke, M., and Meschi, M. M. (2003). Technology adoption in the presence of constraints: the case of fertilizer demand in Ethiopia. *Review of Development Economics* **7**, 58-70.

Cruz, D. C., Baddour, C. E., Ferrante, L., Berruti, F., Briens, C., Cruz, D. C., Ferrante, L., Briens, C., Berruti, F., and Cruz, D. C. (2004). Bio-coal Production from the Torrefaction of Maple Wood Biomass. *Energy Fuels* **18**, 590-598.

Enders, A., Hanley, K., Whitman, T., Joseph, S., and Lehmann, J. (2012). Characterization of biochars to evaluate recalcitrance and agronomic performance. *Bioresource Technology* **114**, 644-53.

Evanylo, G., Sherony, C., Spargo, J., Starner, D., Brosius, M., and Haering, K. (2008). Soil and water environmental effects of fertilizer-, manure-, and compost-based fertility practices in an organic vegetable cropping system. *Agriculture, Ecosystems & Environment* **127**, 50-58.

Fageria, V. D. (2001). Nutrient interactions in crop plants. *Journal of Plant Nutrition* **24**, 1269-1290.

Fawaz, Y., Holail, H., Hammud, H., Khalil, Z., and Hourani, N. (2015). Characterization Of Biocoal From Hydrothermal Carbonization Of Pine Needles And Palm Leaves. *Journal of Multidisciplinary Engineering Science and Technology* **2,** 3088-3093.

Gaskin, J.W., Steiner, C., Harris, K., C. Das, K., and Bibens, B. (2008). Effect of Low-Temperature Pyrolysis Conditions on Biochar for Agricultural Use. *Transactions of the ASABE* **51**, 2061-2069.

Gao, Y., Yu, B., Wu, K., Yuan, Q., Wang, X., and Chen, H. (2016). Physicochemical, pyrolytic, and combustion characteristics of hydrochar obtained by hydrothermal carbonization of biomass. *BioResources* **11**, 4113-4133.

Gilliam, J., Logan, T. J., and Broadbent, F. (1985). Fertilizer use in relation to the environment. *Fertilizer Technology and Use*, 561-588.

Glaser, B., and Birk, J. J. (2012). State of the scientific knowledge on properties and genesis of Anthropogenic Dark Earths in Central Amazonia (terra preta de Índio). *Geochimica et Cosmochimica Acta* **82**, 39-51.

Glaser, B., Haumaier, L., Guggenberger, G., and Zech, W. (2014). The 'Terra Preta' phenomenon: A model for sustainable agriculture in the humid tropics. *Naturwissenschaften* **88**, 37-41.

Gonzaga, M. I. S., Mackowiak, C., de Almeida, A. Q., de Carvalho Junior, J. I. T., and Andrade, K. R. (2018). Positive and negative effects of biochar from coconut husks, orange bagasse and pine wood chips on maize (Zea mays L.) growth and nutrition. *Catena* **162**, 414-420.

Gronwald, M., Vos, C., Helfrich, M., and Don, A. (2016). Stability of pyrochar and hydrochar in agricultural soil - a new field incubation method. *Geoderma* **284**, 85-92.

Gunjal, K. R., Roberts, R. K., and Heady, E. O. (1980). Fertilizer demand functions for five crops in the United States. *Journal of Agricultural and Applied Economics* **12**, 111-116.

Harris, K., Gaskin, J., Cabrera, M., Miller, W., and Das, K. (2013). Characterization and mineralization rates of low temperature peanut hull and pine chip biochars. *Agronomy* **3**, 294-312.

Hati, K., Mandal, K., Misra, A., Ghosh, P., and Bandyopadhyay, K. (2006). Effect of inorganic fertilizer and farmyard manure on soil physical properties, root distribution, and water-use efficiency of soybean in Vertisols of central India. *Bioresource Technology* **97**, 2182-2188.

Havlin, J.L. and P.N. Soltanpour. (1989). A nitric acid and plant digest method for use with inductively coupled plasma spectrometry. *Communications in Soil Science and Plant Analysis* **14**, 969-980.

Henao, J., and Baanante, C. (2006). Agricultural production and soil nutrient mining in Africa: Implications for resource conservation and policy development. *IFDC Technical Bulletin Agricultural Production and Soil Nutrient Mining in Africa: Implications for Resource Conservation and Policy Development*, 1-6.

Hoekman, S. K., Broch, A., Robbins, C., Zielinska, B., and Felix, L. (2012). Hydrothermal carbonization (HTC) of selected woody and herbaceous biomass feedstocks. *Biomass Conversion and Biorefinery* **3**, 113-126.

Huang, W.-Y., McBride, W. D., and Vasavada, U. (2009). Recent volatility in US fertilizer prices: causes and consequences. *Amber Waves: The Economics of Food, Farming, Natural Resources, and Rural America* **7**, 28-31.

Isaac, R.A. and W.C. Johnson. (1975). Collaborative study of wet and dry ashing techniques for the elemental analysis of plant tissue by atomic absorption spectrophotometry. *Journal – Association of Official Analytical Chemists* **58**, 436-440.

Jessup, R. (2013). Seeded-Yet-Sterile'Perennial Biofuel Feedstocks. Adv Crop Sci Tech 1: e102. doi: 10.4172/2329-8863. 1000e102 Page 2 of 2 Volume 1• Issue 2• 1000e102 Adv Crop Sci Tech ISSN: 2329-8863 ACST, an open access journal 4. Heaton E, Voigt T, Long SP (2004) Quantitative review comparing the yields of two candidate C4 perennial biomass crops in relation to nitrogen, temperature and water. *Biomass Bioenergy* **27**, 212-30.

Ju, X. T., Kou, C. L., Christie, P., Dou, Z., and Zhang, F. (2007). Changes in the soil environment from excessive application of fertilizers and manures to two contrasting intensive cropping systems on the North China Plain. *Environmental Pollution* **145**, 497-506.

Junsatien, W., Soponpongpipat, N., and Phetsong, S. (2013). Torrefaction reactors. *Journal of Science and Technology Mahasarakham University* **32**, 84-91.

Kachurina, O.M., H. Zhang, W.R. Raun, and E.G. Krenzer. (2000). Simultaneous determination of soil aluminum, ammonium- and nitrate-nitrogen using 1 M potassium chloride extraction. *Communications in Soil Science and Plant Analysis*. **31**, 893-903.

Kalderis, D., Kotti, M. S., Méndez, A., and Gascó, G. (2014). Characterization of hydrochars produced by hydrothermal carbonization of rice husk. *Solid Earth* **5**, 477-483.

Karami, N., Clemente, R., Moreno-Jiménez, E., Lepp, N. W., and Beesley, L. (2011). Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. *Journal of Hazardous Materials* **191**, 41-48.

Kavitha, B., Reddy, P. V. L., Kim, B., Lee, S. S., Pandey, S. K., and Kim, K.-H. (2018). Benefits and limitations of biochar amendment in agricultural soils: A review. *Journal of Environmental Management* **227**, 146-154.

Keeney, D., and Follett, R. (1991). Managing Nitrogen for Groundwater Quality and Farm Profitability: Overview and Introduction 1. *Managing Nitrogen for Groundwater Quality and Farm Profitability*, 1-7.

Keeney, D.R. and D.W. Nelson. (1982). Nitrogen - inorganic forms. p. 643-687. In: A.L. Page, et al. (ed.). *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties-Agronomy Monograph* **9**. 2nd ed. ASA and SSSA, Madison, WI.

Kim, D., Yoshikawa, K., and Park, K. (2015). Characteristics of Biochar Obtained by Hydrothermal Carbonization of Cellulose for Renewable Energy. *Energies* **8**, 14040-14048.

Koide, R. T., Nguyen, B. T., Skinner, R. H., Dell, C. J., Peoples, M. S., Adler, P. R., and Drohan, P. J. (2015). Biochar amendment of soil improves resilience to climate change. *GCB Bioenergy* **7**, 1084-1091.

Komarek, A.R. 1993. An improved filtering technique for the analysis of neutral detergent and acid detergent fiber utilizing the filter bag technique. Publication #101. Ankom Company®, Fairport, NY 14450.

Kuepper, G. (2003). Manures for Organic Crop Production. *ATTRA National Sustainable Agriculture Inofrmation Service* **IP127**, 1-12.

Laird, D. A. (2008). The Charcoal Vision: A Win–Win–Win Scenario for Simultaneously Producing Bioenergy, Permanently Sequestering Carbon, while Improving Soil and Water Quality. *Agronomy Journal* **100**, 178-181.

Mahadevan, R., Adhikari, S., Shakya, R., Wang, K., Dayton, D. C., Li, M., Pu, Y., and Ragauskas, A. J. (2016). Effect of torrefaction temperature on lignin macromolecule and product distribution from HZSM-5 catalytic pyrolysis. *Journal of Analytical and Applied Pyrolysis* **122**, 95-105.

Malghani, S., Gleixner, G., and Trumbore, S. E. (2013). Chars produced by slow pyrolysis and hydrothermal carbonization vary in carbon sequestration potential and greenhouse gases emissions. *Soil Biology and Biochemistry* **62**, 137-146.

Manyuchi, M., Stinner, W., Mbohwa, C., and Muzenda, E. Integrated Biomass Utilization for Energy Efficiency and Nutrient Recycling. *IEOM Society International*, 120-128.

Marks, E. A., Alcañiz, J. M., and Domene, X. (2014). Unintended effects of biochars on short-term plant growth in a calcareous soil. *Plant and soil* **385**, 87-105.

McGeehan, S.L. and D.V. Naylor. (1988). Automated instrumental analysis of carbon and nitrogen in plant and soil samples. *Communications in Soil Science and Plant Analysis* 19, 493-505.

Medic, D., Darr, M., Potter, B., and Shah, A. (2010). Effect of torrefaction process parameters on biomass feedstock upgrading. *In* "2010 Pittsburgh, Pennsylvania, June 20-June 23, 2010", pp. 1. American Society of Agricultural and Biological Engineers.

Mehlich, A. (1978). New extractant for soil test evaluation of phosphorus, potassium, magnesium, calcium, sodium, manganese, and zinc. *Communications in Soil Science and Plant Analysis* **9**(6):477-492.

Mehlich, A. (1984). Mehlich-3 soil test extractant: a modification of Mehlich-2 extractant. *Communications in Soil Science and Plant Analysis* **15**, 1409-1416.

Mitchell, D., and Elder, T. (2010). Torrefaction? What's that? *In* "In: Proceedings of 2010 COFE: 33rd Annual Meeting of the Council on Forest Engineering. Auburn, AL: June 6-9, 2010.[CD-ROM] 1-7.", pp. 1-7.

Mosier, A. R., Syers, J. K., and Freney, J. R. (2004). Nitrogen fertilizer: an essential component of increased food, feed, and fiber production. *Agriculture and the nitrogen cycle: assessing the impacts of fertilizer use on food production and the environment* **65**, 3-15.

Nelson, D.W. and L.E. Sommers. (1973). Determination of total nitrogen in plant material. *Agronomy Jounal* **65**, 109-112.

Noor, N. M., Shariff, A., and Abdullah, N. (2012). Slow pyrolysis of cassava wastes for biochar production and characterization. *Iranica Journal of Energy & Environment 3 (Special Issue on Environmental Technology)* **3**, 60-65.

Nhuchhen, D. R., Basu, P., and Acharya, B. (2014). A comprehensive review on biomass torrefaction. *International Journal of Renewable Energy & Biofuels* **2014**, 1-56.

Novak, J. M., Lima, I., Xing, B., Gaskin, J. W., Steiner, C., Das, K., Ahmedna, M., Rehrah, D., Watts, D. W., and Busscher, W. J. (2009). Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. *Annals of Environmental Science* **3**, 195-206.

Nunes, L. J. R., Matias, J. C. O., and Catalão, J. P. S. (2014). A review on torrefied biomass pellets as a sustainable alternative to coal in power generation. *Renewable and Sustainable Energy Reviews* **40**, 153-160.

Ogura, T., Date, Y., Masukujane, M., Coetzee, T., Akashi, K., and Kikuchi, J. (2016). Improvement of physical, chemical, and biological properties of aridisol from Botswana by the incorporation of torrefied biomass. *Scientific Reports* **6**:28011.

Ok, Y. S., Uchimiya, S. M., Chang, S. X., and Bolan, N. (2015). "Biochar: Production, characterization, and applications," CRC press.

Palm, C. A., Myers, R. J., and Nandwa, S. M. (1997). Combined use of organic and inorganic nutrient sources for soil fertility maintenance and replenishment. *Replenishing Soil Fertility in Africa*, 193-217.

Pimchuai, A., Dutta, A., and Basu, P. (2010). Torrefaction of Agriculture Residue To Enhance Combustible Properties†. *Energy & Fuels* **24**, 4638-4645.

Rodríguez-Vila, A., Asensio, V., Forján, R., and Covelo, E. F. (2015). Chemical fractionation of Cu, Ni, Pb and Zn in a mine soil amended with compost and biochar and vegetated with Brassica juncea L. *Journal of Geochemical Exploration* **158**, 74-81.

Rorison, I., and Robinson, D. (1984). Calcium as an environmental variable. *Plant, Cell & Environment* **7**, 381-390.

Rousset, P., Macedo, L., Commandré, J. M., and Moreira, A. (2012). Biomass torrefaction under different oxygen concentrations and its effect on the composition of the solid by-product. *Journal of Analytical and Applied Pyrolysis* **96**, 86-91.

Sarrantonio, M., and Gallandt, E. (2003). The role of cover crops in North American cropping systems. *Journal of Crop Production* **8**, 53-74.

Scialabba, N. (2000). Factors influencing organic agriculture policies with a focus on developing countries. *In* "IFOAM 2000 Scientific Conference, Basel, Switzerland", pp. 28-31.

Shackley, S., Hammond, J., Gaunt, J., and Ibarrola, R. (2011). The feasibility and costs of biochar deployment in the UK. *Carbon Management* **2**, 335-356.

Sheldrick, B.H. (1986). Test of the Leco CHN-600 Determinator for soil carbon and nitrogen analysis. *Canadian Journal of Soil Science* **66,** 543-545

Smaling, E., Nandwa, S. M., and Janssen, B. H. (1997). Soil fertility in Africa is at stake. *Replenishing soil fertility in Africa*, 47-61.

Soil Survey Staff, Natural Resources Conservation Service, United States Department of Agriculture. Official Soil Series Descriptions. Available online. Accessed June, 2019.

Spokas, K. A. (2010). Review of the stability of biochar in soils: predictability of O:C molar ratios. *Carbon Management* **1**, 289-303.

Stewart, W., Dibb, D., Johnston, A., and Smyth, T. (2005). The contribution of commercial fertilizer nutrients to food production. *Agronomy Journal* **97**, 1-6.

Storer, D.A. (1984). A simple high volume ashing procedure for determining soil organic matter. *Communications in Soil Science and Plant Analysis* **15**, 759-772.

Sweeney, Rose A. (1989). Generic combustion method for determination of crude protein in feeds: Collaborative Study. *Journal – Association of Official Analytical Chemists* **7**2: 770-774.

Tilman, D., Balzer, C., Hill, J., and Befort, B. L. (2011). Global food demand and the sustainable intensification of agriculture. *Proceedings of the National Academy of Sciences* **108**, 20260-20264.

Tong, D., and Xu, R. (2012). Effects of urea and (NH4) 2SO4 on nitrification and acidification of Ultisols from Southern China. *Journal of Environmental Sciences* **24**, 682-689.

Tonitto, C., David, M., and Drinkwater, L. (2006). Replacing bare fallows with cover crops in fertilizer-intensive cropping systems: A meta-analysis of crop yield and N dynamics. *Agriculture, Ecosystems & Environment* **112**, 58-72.

Torbert, H. A., Potter, K. N., and Morrison, J. E. (2001). Tillage system, fertilizer nitrogen rate, and timing effect on corn yields in the Texas Blackland Prairie. *Agronomy Journal* **93**, 1119-1124.

Tumuluru, J. S., Wright, C. T., Hess, J. R., and Kenney, K. L. (2011). A review of biomass densification systems to develop uniform feedstock commodities for bioenergy application. *Biofuels, Bioproducts and Biorefining* **5**, 683-707.

Wang, Z. H., Li, S. X., and Malhi, S. (2008). Effects of fertilization and other agronomic measures on nutritional quality of crops. *Journal of the Science of Food and Agriculture* **88**, 7-23.

Windeatt, J. H., Ross, A. B., Williams, P. T., Forster, P. M., Nahil, M. A., and Singh, S. (2014). Characteristics of biochars from crop residues: potential for carbon sequestration and soil amendment. *Journal of Environmental Management* **146**, 189-197.

Woolf, D., Amonette, J. E., Street-Perrott, F. A., Lehmann, J., and Joseph, S. (2010). Sustainable biochar to mitigate global climate change. *Nature Communications* **1,** 1-9.

Wu, M., Han, X., Zhong, T., Yuan, M., and Wu, W. (2016). Soil organic carbon content affects the stability of biochar in paddy soil. *Agriculture, Ecosystems & Environment* **223**, 59-66.

Zhu, Q., Peng, X., and Huang, T. (2015). Contrasted effects of biochar on maize growth and N use efficiency depending on soil conditions. *International Agrophysics* **29**, 257-266.