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Pyrolysis methods impact biosolids-derived biochar composition, maize growth and nutrition

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ABSTRACT

Land-applied biosolids (sludge) can improve food production sustainability through nutrient recycling. Biosolids-derived biochar may enhance soil fertility and overall soil health. However, there is little information on the conversion of biosolids to biochar using traditional kilns, or effects on biochar characteristics and plant growth. Biochar was produced from biosolids using two pyrolysis methods: 1) a traditional retort kiln (Top-lid Updraft-TLUD) intended for use by small farmers and gardeners, and 2) a laboratory muffle furnace, with the aim of evaluating biochar characteristics and its effects on *Zea mays* L. (corn) seed germination, growth and nutrition. Biochar produced in a muffle furnace contained 70% more ash, 78% more fixed carbon, and 63% less volatile matter than biochar produced by TLUD, which raised concern regarding TLUD-derived biochar toxicity The TLUD-derived biochar inhibited corn seed germination in a petri dish bioassay at biochar application rates from 2.5 to 100 Mg ha^{-1}. However, germination increased from 29% (control) to approximately 60%, at 60 Mg ha^{-1} or greater rates, with muffle furnace biochar. A greenhouse experiment was conducted to evaluate the growth and nutrition of corn grown in soil treated with 0, 5, 10, 20 and 60 Mg ha^{-1} biochar pre-incubated for two weeks in moistened soil. The muffle furnace biochar had no negative effect on plant growth and N nutrition, whereas the TLUD biochar at a 60 Mg ha^{-1}rate, reduced plant growth and increased plant N concentrations four-fold, compared to the control. Both biochars increased plant P concentrations with increasing application rates. Biosolids biochar produced via TLUD at rates below 20 Mg ha^{-1} may benefit crop production, although an incubation or weathering period may be necessary to limit potential short-term, phytotoxic effects. Future research needs include optimizing TLUD operational parameters and identifying weathering processes that improve biochar product quality for agronomic use.

1. Introduction

Biosolids, formerly known as sewage sludge or wastewater treatment residuals, is a major source of plant nutrients, especially nitrogen (N) and phosphorus (P). Land-applied, carbon-rich biosolids improve soil health (Singh and Agrawal, 2008; Usman et al., 2012). Municipal biosolids have undergone treatments, such as alkaline stabilization and thermal drying, to create a product safe for land application, a cost-effective method of waste disposal (Lu et al., 2012). Even so, fertilizer-grade biosolids (Class A and AA) must minimize human pathogens and inorganic contaminants that the US federal government regulates (EPA, 1999). Organic contaminants, such as pharmaceuticals and health care products may also be found in biosolids, but understanding and regulation of these materials are in their infancy. Furthermore, land-applied biosolids contribute to greenhouse gas emissions (Brown et al., 2010).

Thermally treating biosolids, via pyrolysis, reduces waste volume and mass, therefore, transport costs (Inguanzo et al., 2002). Manure-derived biochar further reduced pathogens and heavy metal bioavailability in soils (Cantrell et al., 2007). Additionally, soil-applied biochars often contribute to C sequestration, due to their inherent stability (Lehmann, 2007).

The chemical and physical characteristics of different biochars, in general, depend on the operating conditions of the pyrolysis unit (Mendez et al., 2013). Depending upon the pyrolysis operational

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conditions, biochar varies considerably in its elemental composition (C, N, H, S and O), ash content, pH, porosity, etc. (Enders et al., 2012).

Biochar effects on crop growth have been extensively reported (Gaskin et al., 2010; Major et al., 2010; Van Zwieten et al., 2010), but much less information is available about biochars derived from biosolids. Hossain et al. (2010) applied biosolids biochar at 10 Mg ha^{-1} to cherry tomatoes and observed a 64% increase in production. The authors attributed their results to increased N and P fertility. They also observed that the biochar mitigated some of the inherent soil acidity. Liu et al. (2014) tested biosolids biochar on Chinese cabbage and reported a significant increase in plant growth. Others have reported that biochars from different feedstocks will promote soil N immobilization and therefore alter N bioavailability (Lehmann et al., 2003; Steiner et al., 2008; Laird et al., 2010). Biochar applications also have been reported to enhance P bioavailability and consequently, plant growth (Xu et al., 2014), but according to Sandeep et al. (2013), the selected soil type may alter biochar's impact.

Despite the potential agricultural advantages and environmental benefits of biochar, its large-scale production under controlled conditions remains a constraint. Many small farmers, especially in developing and undeveloped countries, use conventional ovens and small retort kilns to produce biochar. In addition, it is unclear how well these systems and their products compare to products from more controlled conditions. Furthermore, the effect of biosolids biochar on plant growth and nutrient uptake has seldom been reported. Therefore, the aim of this study was to: 1) characterize and test biosolids biochar produced by two different pyrolysis units (TLUD retort kiln and muffle furnace); 2) evaluate the effect of different rates of the two biochars on corn seed germination using a soilless petri dish bioassay, and 3) evaluate corn growth, N and P nutrition in soil amended with different rates of the two biochars.

2. Materials and methods

2.1. Biochar production and characterization

Biosolids were collected from a tile-lined, drying bed, at a municipal wastewater treatment facility (WWTF), located in Tallahassee, Florida, U.S.A. The biosolids were the end-product of an activated sludge treatment process. Biosolids had the following composition (mean of three replicates ± std): 91 ± 2% moisture, 6.8 ± 0.3 pH units, and total elements (dry mass basis): 57 ± 9 g kg^{-1} N, 13 ± 5 g kg^{-1} P, 2 ± 0.1 g kg^{-1} K, 94.0 ± 21 mg kg^{-1}Cu, 88 ± 21 mg kg^{-1} Zn, 18 ± 3 mg kg^{-1} Mo, 4.0 ± 0.8 mg kg^{-1} As, 0.80 ± 0.26 mg kg^{-1} Cd, 20 ± 9 mg kg^{-1} Pb, and 3.6 ± 0.6 mg kg^{-1} Ni.

Biochars were produced using two types of slow pyrolysis units. The first unit was a Top-Lit Updraft retort unit (TLUD), which is a micro-kiln that uses a reburner to eliminate volatile byproducts of pyrolization (Nsamba et al., 2015). Both, the vapors, as well as the non-condensable gases, are combusted, to provide heat for driving the pyrolysis reaction. The sewage sludge was dried in an oven at 45 °C for 5 days and subsequently 20 kg of the feedstock was pyrolyzed over 3 h, at approximately 550–700 °C, which was measured using a thermal gun aimed at the center of the unit during operation. After cooling, biochar was weighed, ground with a mortar and pestal, sieved to pass through a 2 mm screen, and stored in airtight plastic bags. The second pyrolysis unit was a bench-scale, muffle furnace. The feedstock was oven-dried at 45 °C, ground with a mortar and pestal and sieved to pass through a 2 mm screen. Approximately 32 g of the dried biosolids were placed into ceramic crucibles with loose-fitting ceramic lids and pyrolyzed at 600 °C for 1 h. Subsequently, the oven was turned off and the material was allowed to cool (overnight) before collecting the biochar, in order to avoid auto-ignition when the lids were removed. The biochar was weighed and stored in sealed plastic bags.

Biochar yield was determined according to Gaskin et al. (2008) as the mass ratio of biochar product to oven-dried biosolids feedstock (Eq. (1)):

$$\mathrm{BCyield}(\%) = \frac{W_2}{W_1} X100 \tag{1}$$

Where W1 is biosolids dry mass prior to pyrolysis and W2 is the biochar product dry mass.

Biochar samples were ground in a ball mill to pass a 300 μm sieve and sent to a commercial laboratory (Huffman Labs, Boulder, CO, USA) for proximate analysis (ash content, volatile matter and fixed carbon). The determination of the volatile matter and ash content was conducted according to the American Society for Testing and Materials (ASTM) D1752-84, which is recommended by the International Biochar Initiative. The volatile matter was thus determined by measuring the weight loss that followed combustion of about 1 g of biochar in a crucible at 950 °C. Following the same procedure, the ash content was determined at 750 °C. The laboratory conducted ultimate analysis (elemental C, N, H and S) using a CNHS elemental analyzer, via flush combustion at 1020 °C and oxygen was determined by difference (Mukherjee et al., 2014). Sample caloric value (HHV) was measured by the ASTM bomb calorimeter method, according to ASTM5865.

Biochar pH was determined in a 1:5 (w/w) biochar:water ratio after 1.5 h shaking in a reciprocating shaker and one hour equilibration period (Gaskin et al., 2008). Electric conductivity (EC) was determined in the same extract.

2.2. Soilless germination bioassay

Fifteen corn (*Zea mays*) seeds were sown in petri dishes (8.5 cm diameter) on a layer of 41 mm filter paper moistened with 20 mL deionized water and containing biochar rates of 0, 2.5, 5, 10, 20, 60 and 100 Mg ha^{-1} on a volume basis, with three replications, according to the procedure described by Morrison and Morris (2000). All petri dishes were covered with lids and incubated in the dark at 25 °C for 72 h. The number of germinated seeds was counted and germination percent determined. Root and cotyledon lengths were measured and reported as the sum from each dish (cm per dish). Roots and cotyledons were dried at 60 °C for 48 h and weighed to determine dry mass.

2.3. Greenhouse experiment

The soil used in this experiment was taken from a fallow field at North Florida Research and Education Center (NFREC), Quincy, Florida, from a depth of 0–20 cm (A horizon), air-dried and sieved to pass through a 2 mm screen. The soil was classified as Loamy, kaolinitic, thermic Grossarenic Kandiudults (Soil Survey Staff, 2007), with 90% sand, 6% silt and 4% clay, pH (ratio of 1:5 w/v) of 5.8, 0.72% organic matter, 3.70 Cmolc kg^{-1} CEC, 149 mg kg^{-1} P, 65 mg kg^{-1} K, 345 mg kg^{-1} Ca, and 56 mg kg^{-1} Mg. Cation exchange capacity was determined by the ammonium acetate method (Thomas, 1982); soil organic matter by the Walkley Black method (Nelson and Sommers, 1982); and soil texture by the pippete method (Day, 1965). Concentrations of extractable P, K, Ca and Mg were determined by the Mehlich 3 method (Mehlich, 1984).

The experiment was conducted as 2 × 5 factorial and completely randomized design, with two types of biosolids biochar (TLUD or muffle furnace), five biochar application rates (0, 5, 10, 20 and 60 t ha^{-1}), and four replications. For each observation, 2.0 kg of air-dried and sieved (2 mm) soil was put into a plastic bag and thoroughly mixed with the appropriate rate of biochar and then transferred into 2.5 L plastic pot. After a two week incubation period at field capacity, 3 corn seeds were sown (approximately 40 mm depth). At 9 days after emergence, the two weakest seedlings were removed. Soil in each pot was maintained at 80% of field capacity during the plant growth period by periodically (every two days) the pots and adding water accordingly.

Each pot was given an initial dose of starter fertilizer via fertigation, as recommended by Rajkovich et al. (2012). The solution contained 10 kg N ha^{-1}, as ammonium sulfate, 80 kg P_2O_5 ha^{-1} as triple super phosphate, and 60 kg K_2O ha^{-1} as potassium chloride. All of the pots received an additional application of N fertilizer (100 kg N ha^{-1}), via fertigation, 25 days after planting.

The plants were allowed to grow for 60 days, when they were harvested and separated into roots and shoots. Plant tissues were rinsed with tap water, followed by deionized water. The shoots and roots were oven-dried for 3 days at 65 °C, weighed and ground to pass through a 2 mm screen. Soil and shoot tissues were digested in a hot block digestion system, following the procedure for Total Kjeldahl N (TKN) determination (Bremner, 1996). Analysis of total N in soil and plant samples was performed with a Timberline continuous flow diffusion and conductivity cell N analyzer (Timberland, Boulder, CO). Total P concentration in soil and plant samples was determined in the TKN extracts colorimetrically by the molybdenum blue method (Murphy and Riley 1962). Plant available soil N (NH_4-N and NO_3-N) was determined by extracting air-dried soil with 2 M KCl (Keeney and Nelson, 1987) and analyzing with the Timberline instrument.

2.4. Statistical analysis

A two-way analysis of variance (ANOVA) with the factors biochar type and application rate, was performed using the Statistical Analysis System (SAS) (SAS, 2013). Post-hoc comparisons were conducted using Tukey test at $P < 0.05$ probability level. Regression analysis was computed at $P < 0.05$.

3. Results and discussion

3.1. Biosolids biochar characterization

Proximate and chemical compositions of the two biochars are given in Table 1. Approximately 90% more biochar was recovered from the TLUD oven (70%) than from the muffle furnace (36.5%). A range of 15–60% yield is generally reported for biochars, as a function of the feedstock and pyrolysis operating temperature (Abrego et al., 2008; Wang et al., 2012). More specifically, biosolids biochar yield of 46% was obtained by Liu et al. (2014), using a fixed-bed laboratory pyrolyzer at 450 °C for 30 min. Decreasing biochar yields are related to dehydration of hydroxyl groups and thermal degradation of ligno-cellulose structures, which is often due to high temperature pyrolysis (Amonette and Joseph, 2009). Although the jacket temperatures were similar between the two pyrolysis systems used in this study, yield differences between the two biosolids biochar is probably related to differences in the feedstock core temperature. This is suggested by the much higher concentration of volatile matter, H and O, in the TLUD derived biochar. Volatile matter is highly dependent on pyrolysis conditions, such as temperature and oxygen exposure, as well as the cool-down period (Spokas, 2010). The muffle furnace produced a biochar with 70% more ash and 78% more fixed C than the TLUD.

Table 1
Characteristics of biosolids biochar produced from muffle furnace and retort kiln (TLUD).

Biochar characteristics	Muffle furnace biochar	TLUD biochar
Moisture (%)	5.0	8.1
Yield (%)	36.5	70.0
Ash (%)	43.7	25.6
Volatile matter (%)	20.2	54.2
Fixed C (%)	36.1	20.2
C (%)	42.4	45.5
N (%)	6.39	7.43
H (%)	1.91	4.85
S (%)	0.74	1.14
O (%)	4.83	15.5
C/N	6.64	6.12
O/C	0.11	0.34
H/C	0.05	0.11
(O + N)/C	0.26	0.50
FC/(FC + VM)	0.64	0.27
pH[a]	8.0	7.5
EC[a] (uS cm^{-1}, 25 °C)	157	729
HHV (BTU/lb)	6610	7728

FC = fixed carbon; VM = volatile matter; HHV = high heating value.
[a] pH and EC measured at 1:5 (deionized water:biochar).

The elemental composition of the biosolids biochars were used to calculate atomic ratios as predictors of char stability and ability to interact with polar compounds. The C and N concentrations were comparable among the two biochars, resulting in similar C/N ratios. However, biochar from the TLUD resulted in 3.0, 2.5, and 1.5 greater O, H and S concentrations, respectively. The greater TLUD values are likely related to uncontrolled and incomplete chemical and physical transformations during the pyrolytic process, as a function of temperature, feedstock and cooling conditions (Antal and Grønli, 2003).

The oxygen concentration in biochar is related to the surface chemistry and its potential for chemical reactions and degradation (Boehm, 1994). Therefore, O:C values may help predict biochar stability by inferring the presence of functional groups (Uras et al., 2012). In general, biochars with O:C below 0.6 demonstrate greater stability and potentially a longer C mineralization half-life. For comparison, an O:C value of 0 is assigned to graphite (Harvey et al., 2012). In the present study, the O:C ratio was greater in the TLUD biochar (0.34) than in the muffle furnace biochar (0.11), therefore, the muffle furnace-derived biochar may mineralize more slowly in soil. For comparison purposes, Novak et al. (2010) reported that pecan shell biochar pyrolyzed in a laboratory oven had a O:C ratio of 0.01 and an estimated half-life of 1400 years, whereas Major et al. (2010) measured an O:C ratio of 0.23 and estimated a half-life of 600 years for a biochar produced in a retort kiln. However, this association is not as strong when assessing high alum and high ash biochars, such as biosolids that may contain significant amounts of inorganic C, H, and O (Enders et al., 2012).

The H:C ratio of the biosolids biochar followed the same trend as the O:C ratio, that is the TLUD biochar had a higher H:C ratio (0.11) than the muffle furnace biochar (0.05). The H:C ratio typically varies from 0.3 to 1.0 in biochars (Hammes et al., 2006), where lower values indicate higher biochar stability. Enders et al. (2012) proposed a combination of volatile matter and O:C or H:C ratios to classify the stability of biochar and established ratings of low stability (volatile matter > 80%), moderate stability (volatile matter < 80% and O:C > 0.2 or H:C > 0.4), and high stability (volatile matter < 80%, O:C < 0.2 or H:C < 0.4). According to this classification and if high ash content is not a factor, then the muffle furnace biochar had a high stability rating and a high potential to sequester C, while the biochar produced in the TLUD retort had a moderate stability rating. Furthermore, applying the equation FC/(FC + VM) (Wang et al., 2012), the higher stability of the biochar produced in the muffle furnace was confirmed (Table 1). Based upon the data, it is likely that the TLUD method for pyrolyzing biosolids requires further refinement to improve feedstock conversion to char, but it also provides an example of the quality of product (incomplete

Table 2
Muffle furnace-derived biosolids biochar effects on corn seed germination characteristics in a soilless, petri dish bioassay.

Biochar ($Mg\,ha^{-1}$)	Germination (%)	Shoot length (cm)	Root length (cm)	Total biomass (g dw)
0	28.9b[a]	20.5c	21.4d	0.09c
2.5	55.6a	41.5b	44.7b	0.12bc
5	55.6a	47.5bc	51.8bc	0.13bc
10	60.0a	53.1ab	44.9b	0.13bc
20	60.0a	58.5ab	50.7b	0.16ab
60	62.2a	60.4a	74.0ab	0.17a
100	64.0a	63.4a	76.0a	0.20a

[a] Means followed by the same letter within a column are not statistically different, according to Tukey-HSD test at 5% level.

charring) that might be produced using homemade pyrolyzers, under real-world conditions.

The pH values increased with biochar formation, from 6.6 (feedstock) to 7.5 (TLUD) and 8.0 (muffle furnace). It is interesting to note that the electrical conductivity of the biochar produced in the TLUD oven was 4.6 times higher than in the muffle furnace biochar. As EC is a measurement of soluble inorganic compounds, it is possible that the muffle oven biochar has most of its ash in an insoluble form. The pH and electrical conductivity of the biochar is related to the content and composition of the ash fraction (Singh et al., 2010).

3.2. Corn seed germination in the soilless petri dish bioassay

The soilless petri dish bioassay results are presented in Table 2. Percent germination was low (under 30%) in the control treatment, which likely reflects the quality of the corn seeds. Almost none of the seed germinated in any of the TLUD biochar dosage treatments. In comparison, muffle furnace biochar, regardless of the application rate, increased corn seed germination by 106% from that of the control (Table 2). Few have reported on biosolids biochar effects on seed germination. Liu et al. (2014) applied biosolids biochar as soil amendment at a 3:1 ratio (soil:biochar) and observed 100% germination in Chinese cabbage, indicating that biochar did not inhibit seed germination.

The muffle furnace biochar resulted in greater shoot and root lengths, compared with the control. In fact, shoot length increased by 209% with the addition of 100 $t\,ha^{-1}$ biochar, with no signs of toxicity (Table 2). It is interesting to note that the greatest root length was observed with the highest rate of biochar application. In comparison, the few seeds that germinated in the TLUD biochar had roots lengths less than 3 mm, so these data were not collected.

The high volatile matter content and electrical conductivity likely affected germination and early growth in the TLUD biochar treatments. The bioassay results raised concern over the risk of using TLUD-derived biosolids as a soil amendment. Biosolids biochar had been reported to contain some toxic and volatile compounds, including dioxins and PAHs (Hale et al., 2012), which might pose some negative environmental impact. Additionally, Biederman and Harpole (2013) and Spokas (2010) suggest that some re-condensation may occur during the pyrolysis process, resulting in a less favorable biochar product. Washing or weathering fresh biochar may alleviate some of these concerns.

3.3. Corn growth using biosolids biochar

In the soil experiment, the muffle furnace biochar had no effect on corn above-ground dry mass, with values ranging from 10.02 to 10.7 $g\,pot^{-1}$ (Table 3). The growth promotion observed in the petri-dish bioassay did not translate to potted corn plants. Unlike the inhibition of the TLUD biochar on germination, application of 20 $Mg\,ha^{-1}$ TLUD biochar increased root and total dry mass by 35, and 25%, respectively, compared to the control (Table 3).

In comparison, application of 60 $Mg\,ha^{-1}$ of TLUD biochar reduced above-ground biomass by almost 20%, compared to the control, while the root biomass was unaffected. Borchard et al. (2014) applied biochar to temperate sandy and silty soils and observed no effect on maize yield at an application rate of 15 g biochar $kg^{-1}$of soil. However, when they applied 100 $g\,kg^{-1}$, plant biomass significantly declined, probably as a result of nutrient imbalances and N-immobilization. Even though the biochar used by Borchard et al. (2014) was not biosolids, it seems that application of high doses in soil is not beneficial for maize plants. In this experiment, the soil was mixed with biochar, watered to field capacity and left to incubate for two weeks, with periodic mixing in open bags. Mixing biochar with soil probably diluted water soluble substances and the pre-plant incubation may have encouraged volatile matter dissipation or degradation, thereby reducing the potential negative effects of the TLUD biochar on plant growth.

Shoot:root were somewhat low in all treatments, ranging from 1.04 to 1.19, which were two to three times lower than expected for corn plants at eight weeks after planting. According to Eghball and Maranville (1993), a lower shoot:root might be a result of environmental stress, such as water or fertility limitations, especially N. Above-ground, whole plant tissue N was below the leaf critical concentration of 30 $g\,N\,kg^{-1}$, reported by Campbell and Plank (2009) at early growth, and Fageria (2004), reported shoot N concentrations of 25–45 $g\,N\,kg^{-1}$ for 8 wk old corn plants. It is interesting to note that tissue N in the 60 $Mg\,ha^{-1}$ TLUD treatment was excessively high (100 $g\,kg^{-1}$), but it had no reversal effect on shoot:root. Potassium (K) can also reduce shoot:root, but reported effects are mixed for K and several other nutrients, while low P does not seem to affect shoot:root significantly (Andrews et al., 1999). Even though shoot:root values were below expectations, shoot yields were similar to what others have reported for 8-week greenhouse studies with corn (Deenik and Cooney, 2016).

Table 3
Shoot biomass (g dry weight), root biomass (g dry weight), total biomass (g dry weight) and shoot:root of corn plants after 60 days of growth in soil treated with different rates of biosolids biochar produced in muffle furnace or TLUD oven.

Plant variable	Biochar application rate ($Mg\,ha^{-1}$)				
	0	5	10	20	60
	(Muffle furnace biochar)				
Shoot biomass	10.7Aa*	10.2Aa	10.4Ba	10.6Ba	10.5Aa
Root biomass	8.97Aa	8.92Ba	9.67Ba	10.02Ba	9.01Aa
Total biomass	19.7Aa	18.9Ba	20.7Ba	20.6Ba	19.5Aa
Shoot/root	1.19Aa	1.12Aa	1.08Aa	1.06Aa	1.16Aa
(TLUD biochar)					
Shoot biomass	10.7Aab	10.9Ab	12.0Aab	12.6Aa	8.72Bc
Root Biomass	8.97Acd	10.2Abc	11.6Aab	12.1Aa	7.6Bd
Total biomass	19.7Ac	21.0Abc	23.5Aab	24.6Aa	16.32Bd
Shoot/root	1.19Aa	1.07Aa	1.05Aa	1.04Aa	1.15Aa

Means followed by the same upper case letter within a column (between muffle furnace and TLUD) and by the same lower case letter within a row, are not statistically different, according to Tukey-HSD test at 5% level.

3.4. Fate of nitrogen and phosphorus

Biochar application rates from the muffle furnace did not affect corn N content (Fig. 1), but the 60 Mg ha^{-1} biochar application rate from the TLUD increased corn N content nearly five-fold (Fig. 2). Soil extractable N (inorganic N) was exceptionally high at the 60 Mg ha^{-1} TLUD biochar application rate (Fig. 3), and supports the tissue results. In comparison, soil TKN increased with increasing biochar application rates, regardless of source, but trended higher with the TLUD biochar (Fig. 4). These data suggest that the biochars at moderate application rates may have been immobilizing or adsorbing inorganic soil N and they were not mineralizing sufficient N to supply crop demand. Similar results were reported by Rajkovich et al. (2012). In comparison, Deenik and Cooney (2016) reported increased corn N uptake with a biosolids biochar application rate of 25% (w/w), in their first production cycle, but the response had dissipated by the third crop cycle (no additional biochar was applied).

A large proportion of N in the biosolids is released as N_2, NH_3 and other types of volatile matter during the pyrolysis process (Cao and Harris, 2010; Hossain et al., 2010). In addition, heterocyclic N-containing structures are formed as a result of the pyrolysis process, limiting the conversion of N to bioavailable forms and reducing microbial decomposition of the recalcitrant biochar (Lehmann et al., 2003; Knicker, 2007). According to Van Zwieten et al. (2010) and Zheng et al. (2013), application of biochar as a soil amendment may affect N availability through increasing retention, which includes adsorption of NH_4-N and organic-N onto biochar, thereby enhancing N immobilization. Deenik and Cooney (2016) reported that their biosolids biochar NO_3-N concentrations were below detection limit, while the soil inorganic N measured at the end of our study was comprised entirely of NH_4-N (NO_3-N below detection limit). Hua et al. (2009) observed a significant increase in N retention in compost when they applied biochar into a sludge composting system, and others have reported NH_4-N retention when biochars are mixed with soil (Yao et al., 2012; Hollister et al., 2012).

Phosphorus concentrations in shoot (above-ground) biomass increased with increasing biochar application rates, regardless of the pyrolysis method employed (Fig. 5). However, the control treatment, as well as treatments with biochar rates at or below 20 Mg kg^{-1}, resulted in critically low (<3 g P kg^{-1}) tissue P concentrations, as reported by Campbell and Plank (2009). In comparison, the 60 Mg ha^{-1} biochar application rate resulted in tissue P near 4 g kg^{-1}, or two times greater than tissue P at the 20 Mg ha^{-1} application rate (Fig. 5). The highest biochar application rates also resulted in the highest soil P concentration when muffle furnace-derived biochar was applied (Fig. 6), agreeing with the results of Xu et al. (2014). However, this was not the case with the TLUD biochar, where increasing biochar application rates had little effect on soil P. Deenik and Cooney (2016) found ammonium acetate extractable soil P concentrations unaffected by biosolids biochar addition after their first crop cycle, even though it resulted in greater P uptake in corn. However, by the second cycle, both,

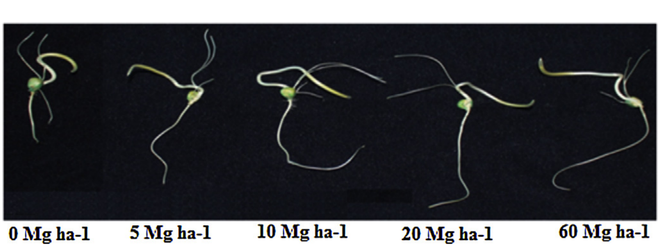

Fig. 1. Image of the effect of the muffle furnace biochar applied at different rates on corn seed germination and growth in a soilless petri dish bioassay.

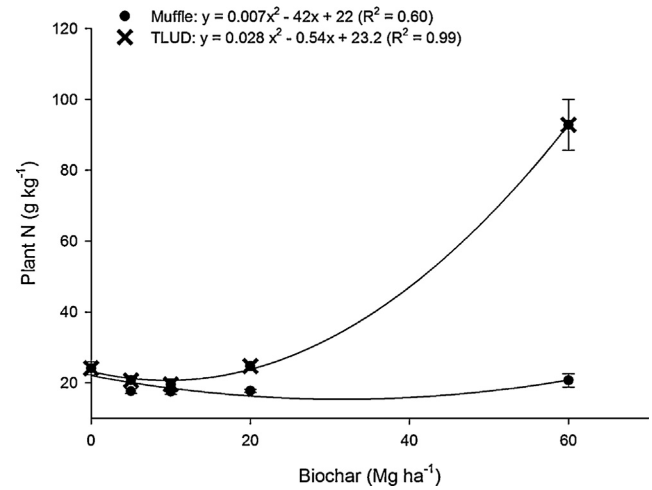

Fig. 2. Nitrogen concentration in corn plants at 60 days after planting, in soil treated with different rates of application of biosolids biochar produced in a muffle furnace and in a TLUD oven (Results are mean and SE, n = 4).

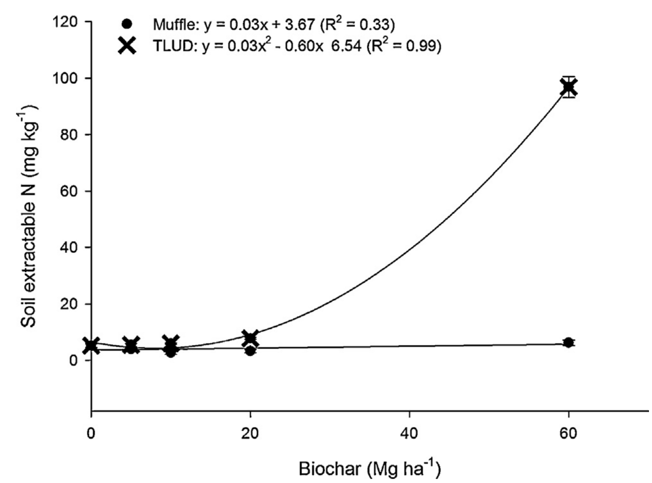

Fig. 3. Extractable N in the soil treated with different rates of biosolids biochar produced in a muffle furnace and in a TLUD oven. (Rresults are mean and SE, n = 4).

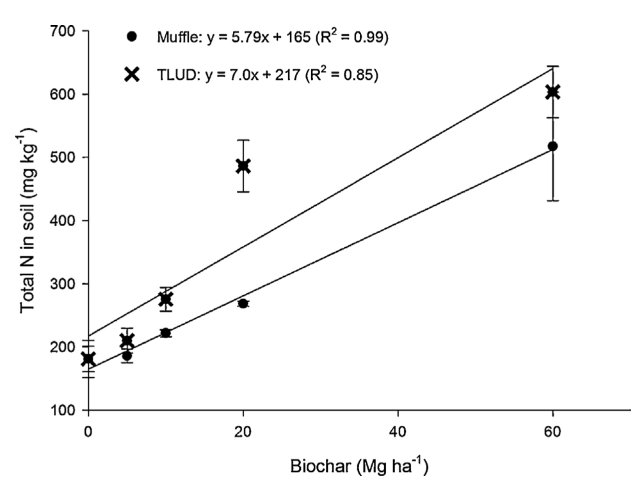

Fig. 4. Total N in the soil treated with different rates of biosolids biochar produced in a muffle furnace and in a TLUD oven (Results are mean and SE, n = 4).

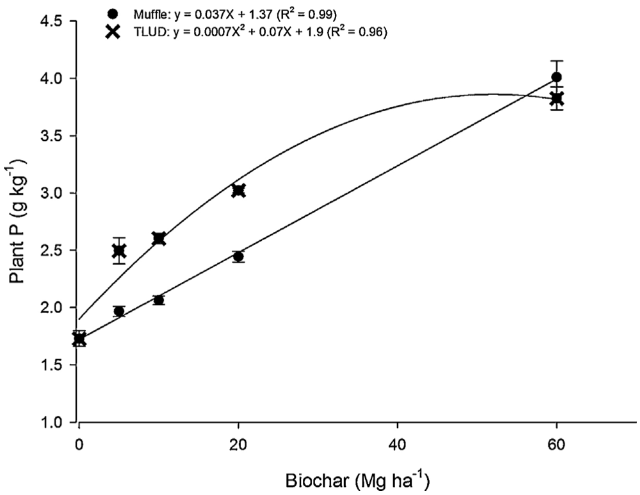

Fig. 5. Phosphorus concentration in corn plants at 60 days after planting, in soil treated with different rates of biosolids biochar produced in a muffle furnace and in a TLUD oven (Results are mean and SE, n = 4).

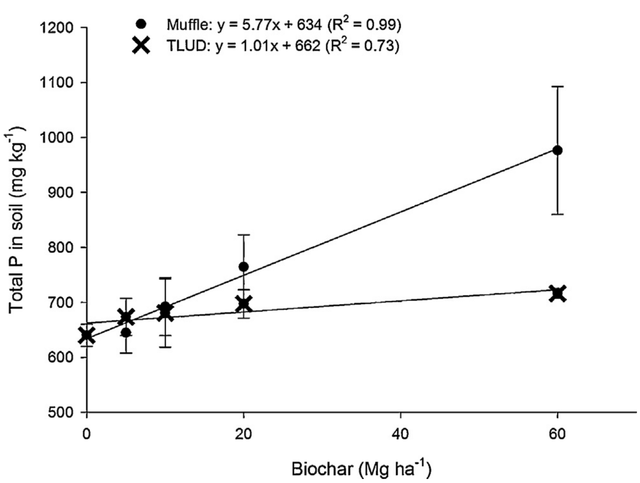

Fig. 6. Total P in the soil treated with different rates of biosolids biochar produced in a muffle furnace and in a TLUD oven (Results are mean and SE, n = 4).

crop uptake and soil P concentrations were higher with biosolids biochar treatment. Soil total P was analyzed in the Total Kjeldahl Nitrogen (TKN) extracts and this method has been reported to be a good estimate of P in soils (Taylor, 2000). Therefore, it is not clear why the highest application rate of muffle furnace biochar was not reflected by the soil total P measurement. Additional soil testing and comparison of total P methods are needed to address this discrepancy.

Biochar additions to soil often enhance soil P bioavailability (De Luca et al., 2009; Sohi et al., 2010), especially in acidic soils such as the one used in this study. Generally, biosolids contain relatively high concentrations of P (often 3% or more) and therefore, the resulting biochar are also high in P (Atkinson et al., 2010; Wang et al., 2012). Xu et al. (2014) studied the sorption of P in different soils amended with biochar and observed that more acidic soils fixed more P, even with increasing soil pH. Additionally, increased soil solution ionic strength and calcium resulted in less available P. Since biosolids biochars contain relatively large amounts of P, as well as other cations, it will be important to determine how these biochars will affect short- and long-term P availability and whether other biochar constituents will impact the inherent soil controlling mechanisms.

4. Conclusions

Biosolids biochar produced in a top-lid updraft retort (TLUD) kiln inhibited corn germination in a petri plate bioassay, while the same biosolids pyrolized in a muffle oven improved germination and early shoot and root growth. Biosolids biochar applied to soil had no deleterious effects on vegetative corn growth at rates up to 20 Mg ha^{-1}, but the TLUD biochar inhibited corn growth at a 60 Mg ha^{-1} application rate. The poorer response of corn to the TLUD-derived biochar may be due, in part, to less complete pyrolysis. Volatile matter was greater and fixed C was less in biochar from the TLUD than from the muffle furnace. In the potted corn experiment, soil extractable N concentration was greater with TLUD biochar applications, particularly at the 60 Mg ha^{-1} rate. However, the TLUD is the biochar production method most commonly available to small villages and individuals. Identifying the degree of variability of product coming from personal-sized pyrolysis units should be considered, as well as developing inexpensive and simple assessment tools to verify if biochar is adequately pyrolyzed. Biosolids biochar interactions with soil and its effects on agronomic production and soil health are in the initial stages of understanding. Exciting topics for future research include the fate of biosolids biochar nutrients and organic contaminants in soil and changes that weathering have on biochar performance in the field.

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