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Positive and negative effects of biochar from coconut husks, orange bagasse and pine wood chips on maize (*Zea mays* L.) growth and nutrition

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ABSTRACT

Transformation of organic waste into biochar for land application is a relatively new green technology management tool. Land-applied biochars can improve soil quality and plant growth. The aim of our study was to investigate the effects of biochars derived from coconut husk, orange bagasse and pine wood chips at different rates of application (0, 5, 10, 20 and 60 t ha^{-1}), on the biomass, nitrogen (N) and phosphorus (P) status of maize (*Zea mays* L) cultivated in a sandy soil, under greenhouse conditions. The treatments were arranged in a completely randomized block design with four replications. The effects of biochar addition on plant dry biomass and nutrition were dependent upon the biochar type and application rate. Soil treated with coconut husk biochar at an equivalent rate of 30 t ha^{-1} resulted in a 90% increase in maize biomass and plant N and P concentrations of 0.88 and 0.12%, respectively. Orange bagasse biochar applied at a similar rate had no effect on plant biomass, and resulted in plant N and P concentrations of 0.85 and 0.15%, respectively. Application of pine wood chip biochar to soil did not affect plant biomass or nutrition. Even though soil total N increased with an increasing application rate of orange bagasse biochar, N leaching may not have posed a problem since KCl extractable N decreased. However, the associated increase in soil pH may result in potentially greater N losses over time. Thus, the increase in plant biomass and nutrition indicates the superiority of the coconut husk biochar as soil amendment; yet, the application of orange bagasse biochar needs more investigation.

1. Introduction

A wide variety of organic residues and wastes have been converted into biochar, with the purpose of deliberately applying it to soils. Incorporated biochar stores carbon, improves soil quality and increases plant growth and productivity, especially in highly weathered soils with strong acidity, low clay content and poor fertility (Jien and Wang, 2013). Biochar, also known as black carbon, is a recalcitrant, carbon-rich material that when applied to soil, has the potential to store as much as 9 to 11 Gt C each year (Wang et al., 2013). According to Lehmann and Joseph (2015), one ton of dry biomass pyrolyzed at 300 to 700 °C, under a low oxygen atmosphere, can produce 400 kg of biochar containing 80 to 90% pure carbon. The recalcitrance of biochar allows its permanence in soil to be approximately 10–1000 times longer than the residence times of most soil organic matter (Lehmann and Joseph, 2009).

Orange bagasse and coconut husks are two agricultural by-products produced in large quantities in many warm-climate countries. Orange bagasse constitutes roughly 49% of the orange fruit mass and is a waste product of the orange juice industry. Considering that approximately 98.7 million tons of fresh citrus fruit are produced each year, on a global scale (Zirebwa et al., 2012), the amount of citrus waste generated by both, agricultural and industrial activities is remarkable. Citrus waste creates a severe environmental problem, as its carbohydrate content is highly fermentable (Van Heerden et al., 2002). Coconut husk corresponds to around 85% of the fruit weight and disposal is also problematic (Leitão et al., 2010). The conversion of these residues to biochar can provide an alternative strategy for managing agronomic waste disposal.

Feedstock composition translates into biochars with different elemental composition and release rates in soils, which directly impact crop growth. Therefore, there is a need to investigate the characteristics and effects of agricultural biochars developed from different feedstocks.

Many studies have addressed the production, characterization and application of woodchip biochar for agronomic and environmental use (Varela-Milla et al., 2013; Biederman and Harpole, 2013; Albuquerque

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et al., 2013; Agegnehu et al., 2015; Ippolito et al., 2015), and consequentially, woodchip biochar is often used as a reference for comparison purposes. Additionally, a few studies have addressed the use of coconut husk biochar (Sukartono et al., 2010; Dao et al., 2013; Hariz et al., 2015; Ippolito et al., 2015; Suman and Gautam, 2017). Sukartono et al. (2010) produced and characterized biochar from coconut shell but did not test it as a soil amendment. Suman and Gautam (2017) produced coconut shell biochar under different pyrolysis temperatures and observed high variability in biochar characteristics. Dainy et al. (2016) were one of the few who tested coconut husk biochar as a soil amendment. They performed biochar characterization and applied treatments to the field at different application rates. The authors observed a significant impact on soil chemical properties as well as on the yield of yard-long bean.

Some studies have reported the use of orange waste biochar as an adsorption matrix to remove organic and inorganic ionic species from contaminated water (Tran et al., 2016); however, few studies have tested this biochar as soil amendment. Tran et al. (2016) reported the potential of using orange peel biochar as a sorbent to remove Cd from aqueous solutions. The authors reported a maximum sorption capacity of 114.7 mg Cd g^{-1}, suggesting that this might be considered a new green adsorbent and a cost effective alternative to activated carbon. Abdelhafez et al. (2014) evaluated the potential effect of orange peel biochar on improving the physicochemical properties of a contaminated soil and reported increases in soil pH, CEC and water holding capacity. However, it was conducted as a soil incubation study where plants were not included.

We conducted a pot experiment study to test the hypothesis that a single application of biochar from orange bagasse will compare favorably to coconut husk- and woodchip-derived biochars, in terms of soil fertility and plant growth. Our objectives were to investigate: i) the effect of biochar source and application rate on corn growth and N and P nutrition; ii) the effect of biochar source and application rate on soil pH and N and P availability; and iii) develop a common set of recommendations from similar agronomic feedstocks.

2. Material and methods

2.1. Biochar production and characterization

Biochars were produced from coconut husks (CHB), orange bagasse (OBB) and pine woodchips (PWB) using slow pyrolysis in a Top-Lit Updraft retort unit, a micro-kiln that uses a reburner to eliminate volatile byproducts of pyrolyzation, developed by members of the International Biochar Initiative (IBI). Both, the vapors, as well as the non-condensable gases, were burned to provide heat for driving the pyrolysis reaction. All feedstocks were previously oven-dried at 40 °C for 2 days. The coconut husks and orange bagasse were pyrolyzed at a temperature of 500 °C, which was measured using an infrared thermal gun during the one h processing time. The wood chip biochar was pyrolyzed overnight, using the same process. After cool-down, the biochars were weighed, crushed, sieved to a 2 mm screen size and stored in airtight plastic bags. The biochars were stored at ambient temperature until analysis and experimentation.

Biochar yield was determined as the ratio of the biochar mass to feedstock mass:

Biochar yield (%) = (W2/W1) × 100, where W1 is the dry weight of feedstock sample prior to pyrolysis and W2 is the biochar weight.

The proximate analysis (ash content, volatile matter and fixed carbon) was determined according to ASTM standards [ASTM-E 1755, 1995; ASTM-E 872, 1982]. Ultimate analysis (elemental C, N, H and S) was determined using an elemental analyzer via flash combustion at 1020 °C. Percent oxygen was calculated, as follows:

$O = 100 - (C + H + N + S)$.

Biochar pH was determined at a 1:5 biochar:DI water ratio after 1.5 h shaking and 1 h equilibration (Gaskin et al., 2008). Electrical conductivity (EC) was determined in the same extract. Sample calorific value (HHV) was measured by the bomb calorimeter method, according to ASTM 5865. The specific surface-area was obtained according to the Brunauer–Emmett–Teller (BET) method (Zhang et al., 2011). Biochar porosity was determined using Nitrogen (N_2) adsorption isotherms (Zhang et al., 2011). Cation exchange capacity was determined by the ammonium acetate method (Thomas, 1982).

2.2. Greenhouse experiment

The soil used in this experiment was collected from a fallow field that had been out of cultivation for more than ten years, at the North Florida Research and Education Center (NFREC), Quincy, Florida, USA. The soil was air-dried and passed through a 2 mm sieve. The soil was classified as a Loamy, kaolinitic, thermic Grossarenic Kandiudult (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 P kg^{-1}, 65 mg K kg^{-1}, 345 mg Ca kg^{-1}, and 56 mg Mg kg^{-1}. 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 pipette method (Day, 1965). Concentrations of extractable P, K, Ca and Mg were determined by the Mehlich 3 method (Mehlich, 1984).

The experiment was a 3 × 5 factorial, completely randomized design, with 3 types of biochar (coconut husks, orange bagasse and wood chips), 5 biochar application rates (0, 5, 10, 20 and 60 t ha^{-1}), and 4 replications (n = 60). A known weight (2.0 kg) of air-dried and sieved (2 mm) soil was put into a plastic bag and thoroughly mixed with a given application rate of biochar, then transferred into a 2.5 L plastic pot. The pots were randomly positioned on benches. After two weeks of equilibrium under soil field capacity, three maize seeds were sown into the center of each pot, approximately 40 mm deep. At 9 days after germination, the two weakest seedlings were removed. The soil was kept at 80% field capacity during plant growth.

Each pot was given an identical dose of starter fertilizer via fertigation, as recommended by Rajkovich et al. (2012), consisting of 10 kg N ha^{-1}, as ammonium sulfate, 80 kg P ha^{-1} as triple super phosphate, and 60 kg K 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 control pots also received the same amount of fertilizer.

The plants were allowed to grow for 60 days, when they were harvested and separated into roots and shoots. Plant tissues were washed thoroughly with tap water, and then rinsed with deionized water. The tissues were oven-dried for 3 days at 65 °C, weighed and ground, using a Wiley mill to pass through a 1 mm mesh screen for N and P analysis. Plant samples were digested in a hot block digestion system following the TKN protocol for N determination (Bremner, 1996). Analysis of total N was performed with a continuous flow diffusion and conductivity cell N analyzer (Timberland, Boulder, CO). Total P was determined using the molybdenum blue method (Murphy and Riley, 1962). Soil plant-available P was determined by extracting soil with sodium bicarbonate and the concentration in the extracts measured by the molybdenum-blue method (Murphy and Riley, 1962). Soil inorganic N (NH_4-N and NO_3-N) was extracted with 2 M KCl (Robertson et al., 1999) and analyzed as described for total N.

2.3. Statistical analyses

All results were expressed as an average of four replicates. Treatment effects were determined by a two-way analysis of variance (ANOVA) according to the General Linear Model procedure of the Statistical Analysis System (SAS, 2013). The two fixed factors were: type of biochar and application rates to soil. The Tukey-Kramer mean separation test was applied to treatment means at $P < 0.05$ probability level. Regression analysis was performed and a coefficient of

Table 1
Characteristics of the biochar from coconut husks (CHB), orange bagasse (OBB) and pine woodchips (PWB).

Biochar characteristics	CHB	OBB	PWB
Yield (%)	45.0	34.0	30.0
Ash (%)	10.1	16.1	2.48
Volatile matter (%)	15.0	17.3	13.4
Fixed C (%)	75.0	66.5	84.1
C (%)	79.8	72.1	88.2
N (%)	0.42	2.55	0.48
H (%)	2.21	1.83	2.74
S (%)	0.09	0.08	0.05
O (%)	7.42	7.29	6.09
P (%)	0.10	0.10	0.03
C/N	190	28.3	183.7
O/C	0.09	0.10	0.07
H/C	0.03	0.02	0.03
(O + N)/C	0.10	0.14	0.07
FC/(FC + VM)	0.83	0.80	0.86
pH	10.0	9.73	7.80
EC (dS m^{-1}, 25 °C)	0.43	0.33	1.04
Moisture (%)	16.5	1.70	–
CEC (cmolc kg^{-1})	69.7	63.5	11.5
Specific surface (m^{2} g^{-1})	77.2	99.1	72.2
Pore size (nm)	3.91	6.75	4.15

FC = fixed carbon; VM = volatile matter.

determination (R^2) was used as a measure of goodness of fit of least square fitted regression models.

3. Results and discussion

3.1. Biochar characteristics

Biochar characteristics derived from different feedstocks are shown in Table 1. The biochar yields varied from 30 to 45% and are within the normal range for biochars produced at 500 °C (Masek et al., 2013; Jindo et al., 2014). The type of feedstock affected ash content (2.48–16.1%), volatile matter (13.4–17.3%) and fixed C content (66.5–84.1%). According to classifications ratings by Iyer et al. (2002), the ash content was relatively low in the PWB ($< 5\%$), medium in the CHB (5–10%) and high in the OBB ($> 10\%$). A high quality biochar is signified by low ash content (Tran et al., 2016). The relative ash content of the PWB biochar was low compared with the other two biochars, agreeing with the results of Albuquerque et al. (2013).

The volatile matter content in the OBB was over 17% and was probably related to lower fixed C content. Of the biochar total C concentration (72.1–88.2%), the relative amount of fixed C was approximately 94%, which suggests that both, CHB and OBB may have potential C recalcitrance as great as the PWB. According to Ippolito et al. (2015), most plant-based biochars contain elevated C content (around 70%) as compared to biosolids and manure derived biochars (around 45%), however, the amount of fixed C will vary according to the temperature during pyrolysis. The OBB contained approximately 6 times more N than the other two biochars, reducing its C/N ratio. On the other hand, the PWB had a lower oxygen concentration, affecting the O/C and (O + N)/C ratios, suggesting a longer biochar half-life (Uras et al., 2012; Harvey et al., 2012). The very low H/C (0.02–0.03) and O/C (0.07–0.10) atomic ratios indicated a higher degree of C aromaticity, which tends to be associated with longer-term stability of biochar in soil. Similar proximate analytic results were reported by Mary et al. (2016) for orange peel biochar.

Biochars contain relic structures or combustion residues that correspond to O/C ratios < 0.6, which is related to the number and composition of the substituted functional groups. In our study, all three biochars had O/C ratios lower than 0.2 that according to Spokas (2010), estimates a half-life of over 1000 years. Elemental analysis, O/C and H/C ratios are useful indicators of potential biochar performance in the field (Nguyen and Lehmann, 2009).

Biochar pH tended towards neutral for PWB but more alkaline for CHB and OBB, probably due to carbonate formation and the release of alkali salts from the feedstock during pyrolysis. The lower pH with PWB may be related, in part, to its lower ash content. Sukartono et al. (2010) and Hariz et al. (2015) produced biochar from coconut shell in Indonesia and Malaysia, respectively, and found results similar to CHB of pH (9.9). Mary et al. (2016) and Tran et al. (2016) produced biochar from orange peel at the same temperature as in our study and reported similarly high pH values.

The measured values for biochar pore size (3.91–6.55 nm) and specific surface area (72.2–99.1 m^{2} g^{-1}) were typical of low temperature (< 600 °C) pyrolysis (Jindo et al., 2014). Both, porosity and specific surface area of PWB and CHB were similar, probably due to the relatively high lignin and cellulose content of the feedstocks. However, the OBB had 37% greater porosity and 63% greater specific surface area, as compared to the PWB which was used as reference. The cation exchange capacity values were 69.7 cmol$_c$ kg^{-1} (CHB), 63.5 cmol$_c$ kg^{-1} (OBB) and 11.5 cmol$_c$ kg^{-1} (PWB). Since the pyrolysis temperature was similar for all three biochars, the difference in CEC was likely related to the feedstock. The relatively high porosity, specific surface area and CEC of the OBB confirm its applicability as a sorption material for the clean-up of contaminated water (Rezzardori et al., 2012). In our study, the biochars produced from coconut husks, orange bagasse and pine wood chips had elemental composition and characteristics comparable to most biochars produced from plant feedstocks, which make them potentially eligible to be used as soil amendments and/or conditioners.

3.2. Effect of biochar on maize growth and nutrition

Maize plant response varied among biochar types and application rate (Table 2), where CHB resulted in greater growth. The CHB treatment, regardless of application rate, resulted in increased plant biomass by about 90%, as compared with the control treatment or other biochar treatments. Considering the CHB characteristics (Table 1) and yield response, CHB applied at moderate rates (up to 20 t ha^{-1}) may benefit maize growth. There appears to be diminishing response to greater rates. By 60 t ha^{-1}, CHB may potentially reduce plant growth, possibly due to increased soil alkalinity resulting in decreased nutrient availability and potentially Na toxicity. Rajkovich et al. (2012) applied different biochars from plant feedstock to fertile soil, at different

Table 2
Plant biomass (shoot and root) and shoot/root ratio of corn plants treated with coconut husk biochar (CHB), orange bagasse biochar (OBB) and pine wood chips biochar (PWB) at different rates of application.

Biochar	Application rate (t ha^{-1})	Shoot biomass	Root biomass	Shoot/root
		g pot^{-1}		
CHB	0	10.7 (0.26) a	8.97 (0.22) a	1.19 (0.04) a
	5	22.9* (1.17) a	8.85 (0.56) a	2.40 (0.06) a
	10	23.3 (2.09) a	10.2 (0.09) a	2.29 (0.23) a
	20	23.3 (1.83) a	11.1 (1.67) a	2.02 (0.36) a
	60	21.2 (0.95) a	8.57 (0.75) ab	2.44 (0.18) a
OBB	0	10.7 (0.26) a	8.97 (0.22) a	1.19 (0.04) a
	5	10.0 (0.26) b	9.97 (0.81) a	1.07 (0.10) b
	10	11.6 (0.43) b	10.7 (0.57) a	1.09 (0.74) b
	20	12.2 (0.05) b	10.3 (0.73) a	1.18 (0.06) a
	60	8.65 (0.45) b	7.80 (0.16) b	1.11 (0.03) b
PWB	0	10.7 (0.26) a	8.97 (0.22) a	1.19 (0.04) a
	5	11.0 (0.21) b	10.1 (0.62) a	1.08 (0.33) b
	10	12.0 (0.51) b	10.0 (1.10) a	1.09 (0.15) b
	20	11.4 (0.30) b	9.40 (0.32) a	1.21 (0.04) b
	60	10.9 (0.14) b	9.56 (0.21) a	1.14 (0.03) b

* Different letters indicate significant differences ($P < 0.05$) between treatment means within the same rate of application. Mean of 4 replicates and standard deviation.

application rates, and observed a slightly positive or no growth response in maize biomass with biochars produced at pyrolysis temperatures of 400 to 500 °C. Conversely, Dao et al. (2013) applied 80 t ha^{-1} of coconut shell biochar from an updraft gasifier, to a Feralite soil (pH 3.72) and observed over three-fold increase in maize aboveground biomass. Therefore, maize response to biochar depends not only on biochar type and application rate, but also on initial soil fertility and pH (Lehmann et al., 2003; Chan et al., 2008; Van Zwieten et al., 2010).

Compared with the control, OBB applied at 20 t ha^{-1} resulted in a small increase (16%) in plant biomass; however, the 60 t ha^{-1} rate reduced plant biomass by 15%. As with CHB, plant growth inhibition at the highest OBB application rates may be ascribed to inhibitory effects associated with micronutrient deficiencies induced by high soil pH (Nurhidayati, 2014). Additionally, biochar has high specific surface area and porosity, which might reduce nutrient availability when used at exceedingly high rates (Rezzardori et al., 2012). Furthermore, the OBB high volatile matter content (Table 1) may also have negatively influenced plant growth. Orange bagasse feedstock contains many essential oils, such as D-limonene, albedo and flavedo, especially in the orange peel (Donsì et al., 2011; Zanella et al., 2013). During pyrolysis, these compounds contribute to the release of volatile organic substances which eventually re-condense as liquids on the biochar surface during the cooling phase or become trapped within the pore spaces, which are significantly high in the OBB (Table 1). Many of those compounds are also soluble and can have deleterious effects on plant growth (Buss et al., 2015). In our study, we used an adapted TLUD retort to pyrolyze the feedstock, which may have resulted in potentially harmful by-products, such as phenols, volatile fatty acids, and polycyclic aromatic hydrocarbons to adsorb to the biochar surface (Spokas, 2010). During OBB production, a strong odor was detected when the inner chamber was opened, confirming the likely presence of volatile compounds. Detection and quantification of the volatile matter emitting from OBB requires further investigation.

Conversely, PWB did not affect plant biomass, probably due to its nutrient-poor characteristic, low ash content and high EC (Table 1). Varela-Milla et al. (2013) also reported a similar result with water spinach grown in wood chip biochar amended soil and concluded that there was not a significant amount of plant nutrients in the wood biochar that would influence plant growth. Even though all three biochars promoted more shoot than root growth (Table 2), the effect of the CHB was more pronounced, as is demonstrated in the shoot/root ratio values (Table 2).

Regardless of the feedstock type, biochar caused a reduction in plant shoot N content, except at the highest dose of CHB and OBB, which increased plant N concentration approximately 26%, as compared with the control or 61%, as compared to PWB at the same application rate. Lehmann et al. (2003) observed decreased N availability after addition of fresh biochar to soil. Rajkovich et al. (2012) reported a decrease in maize N content with increasing biochar application rates, regardless of biochar type. Even though plant tissue N concentrations decreased with most of our lower rate biochar treatments, it did not seem to impact plant productivity, compared to the control treatment.

Increasing rates of CHB and OBB beyond 25 t ha^{-1}, increased plant N concentrations (Fig. 1). Based upon the regressions, a dose equivalent to 25 t ha^{-1} resulted in a theoretic N content of 18.2 mg g^{-1} and 16.9 mg g^{-1} for CHB and OBB biochars, respectively. For the PWB, theoretical N concentration approached 16.5 mg g^{-1} with the application of approximately 35 t ha^{-1} biochar. The N concentrations were below the normal concentrations (27.0 to 40.0 mg g^{-1}) for maize plants (Jones, 1998); however, these values are also dependent on plant age. Aflakpui et al. (1998) and Rajkovich et al. (2012) observed values that varied from 10 to 35 mg g^{-1} in young maize plants (< 60 days), similar to our study. Even though N fertilizer was applied twice during the plant growth period, the low N concentration in plant tissue at lower rates of biochar application was likely a result of N immobilization in soil (Rajkovich et al., 2012; Steiner et al. (2008a); Zimmerman, 2010; Lehmann et al., 2011). Jones et al. (2012) observed low nitrate reductase enzyme activity in soil treated with biochar, which may have been caused by sorption of nitrate to the biochar particles. Ohe et al. (2003) reported significant nitrate adsorption onto bamboo and coconut shell biochar in one sorption study. Considering that N dynamics are highly complex, future studies need to address soil N interactions in biochar-treated soils.

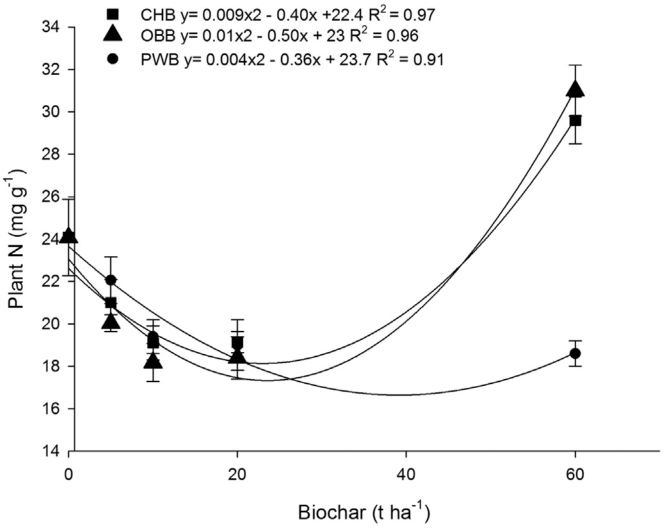

Fig. 1. Nitrogen concentration in maize plants treated with coconut husk biochar (CHB), orange bagasse biochar (OBB) and pine wood chips biochar (PWB) at different rates of application.

The P content of maize plant tissue ranged between 1.80 and 3.00 mg g^{-1}, with average values of 2.10, 2.30 and 2.00 mg g^{-1} for CHB, OBB and PWB, respectively (Fig. 2), which was in the low sufficiency range for P concentrations reported in maize (2.50 to 5.00 mg g^{-1}) (Jones, 1998). A quadratic response (R^2 = 0.88) was observed for plant shoot P with increasing biochar application rates from 0 to 60 t ha^{-1}. A theoretical dose of 35 t ha^{-1} biochar resulted in an estimated P concentration of 3.6, 2.7 and 2.2 mg g^{-1} from OBB, CHB and PWB treatments, respectively. At a biochar dose of 20 t ha^{-1}, plant shoot tissue P ranking was OBB > CHB > PWB. Improvement in total soil P status with OBB and CHB biochar application (Table 3) probably positively influenced plant P nutrition and growth, whereas

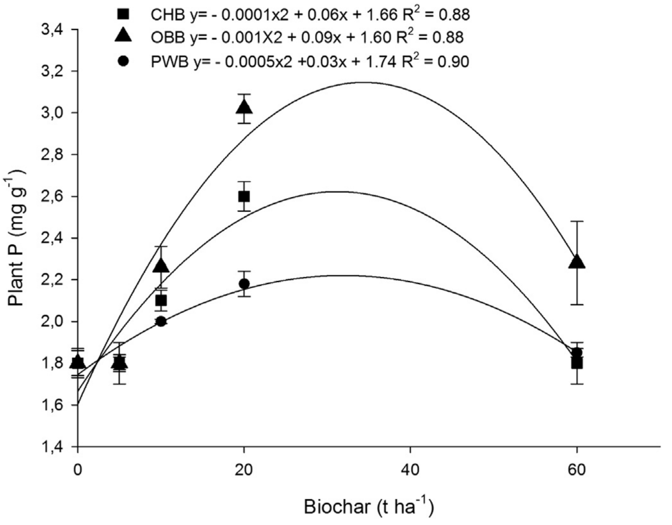

Fig. 2. Phosphorus concentration in maize plants treated with coconut husk biochar (CHB), orange bagasse biochar (OBB) and pine wood chips biochar (PWB) at different rates of application.

Table 3
Concentration of total nitrogen (N), total inorganic nitrogen (TIN), total phosphorus (P), extractable phosphorus (extract P) and pH in the soil treated with coconut husk biochar (CHB), orange bagasse biochar (OBB) and pine wood chips biochar (PWB) at different rates of application.

Biochar	Application rate (t ha^{-1})	Total N*	TIN**	Total P*	Extract P***	Soil pH
		mg kg^{-1}				
CHB	0	181 (16) a[a]	5.26 (0.7) a	335 (33) a	25.6 (0.7) a	5.82 (0.1) a
	5	185 (7.2) a	5.27 (0.8) b	370 (36) ab	25.1 (0.5) a	6.25 (0.2) a
	10	190 (9.2) c	5.28 (0.7) b	372 (31) b	21.1 (0.6) c	6.35 (0.1) a
	20	195 (14) b	5.89 (0.3) b	375 (28) a	20.9 (0.5) b	6.54 (0.1) b
	60	209 (19) b	6.61 (0.5) b	392 (42) a	20.0 (1.2) b	7.20 (0.1) b
	0	181 (16) a	5.26 (0.7) a	335 (33) a	25.6 (0.7) a	5.82 (0.1) a
OBB	5	214 (23) a	5.80 (0.8) b	380 (26) a	25.3 (0.8) a	6.33 (0.1) a
	10	227 (13) a	5.68 (0.7) ab	382 (8.7) a	37.2 (5.0) a	6.25 (0.2) ab
	20	243 (8.6) a	4.36 (0.7) c	386 (28) a	21.9 (0.6) b	6.97 (0.1) a
	60	289 (20) a	2.29 (0.2) a	402 (34) a	20.5 (0.6) b	8.36 (0.1) a
	0	181 (16) a	5.26 (0.7) a	335 (33) a	25.6 (0.7) a	5.82 (0.1) a
PWB	5	199 (20) a	7.03 (0.6) a	335 (22) b	26.4 (0.9) a	6.04 (0.1) b
	10	206 (14) b	7.08 (0.2) a	336 (21) c	26.9 (0.2) b	6.12 (0.1) b
	20	208 (24) b	7.22 (1.0) a	337 (26) b	28.8 (1.0) a	6.28 (0.2) c
	60	210 (2.3) b	8.90 (0.7) a	341 (11) c	29.0(1.1) a	6.30 (0.1) c

* Kjheldal N and P.

** Total inorganic N (NH_4-N + NO_x-N) extracted with 0.2 M KCl.

*** Olsen P.

[a] Low case letters compare the effect of the different biochars within the same rate of application in a column. Mean of 4 replicates and standard deviation.

the PWB biochar was not a good source of P nutrition in this study. Several studies have demonstrated enhanced plant P nutrition in the presence of biochar. Sukartono et al. (2010) reported improvement in soil fertility, increased maize yield and P nutrition after an application of coconut shell biochar to a sandy loam soil in Indonesia. However, the mechanisms are still unclear. Biochar can be a direct source of soluble and extractable P (Gundale and DeLuca, 2006), it can modify soil pH and interact with P complexing metals (Al^{+3}, Fe^{+3} and Ca^{+2}) (Lehmann et al., 2003), and it can promote microbial activity and P mineralization (He et al., 2014; Mendes et al., 2014; Gull and Walen, 2016).

3.3. Effect of biochar on soil N and P concentrations and soil pH

Soil total N (TN) concentrations were affected by biochar type and application rates (Table 3). Higher TN was observed in soil amended with OBB, which was expected since the concentration of N in the OBB was much greater than in the other two biochars (Table 1). Applying 60 t ha^{-1} of OBB increased soil TN by 60%, as compared to the control and by 38%, as compared to CHB and PWB. In this study, the biochars were pyrolyzed at approximately 450 °C. Ippolito et al. (2015) reported that in the range of 300–399 °C, biochar concentrates total N and P content. The higher biochar N concentrations were probably due to the presence of recalcitrant heterocyclic N-containing compounds (Cantrell et al., 2012).

Soil total inorganic N (TIN) was low in all treatments, including the control, and ranged from 2.29 mg kg^{-1} (OBB at 60 t ha^{-1}) to 8.90 (PWB at 60 t ha^{-1}). Low TIN from biochar applications has been frequently reported (Belyaeva and Haynes, 2012; Zhen et al., 2012). Interestingly, TIN did not respond to increasing application rates of CHB and PWB, and there was a small decrease observed with increasing application rates of OBB (Table 3). A smaller TIN concentration in soil solution was to be expected if plants were taking up the TIN as quickly as it was being released from the biochar. Nishimaya et al. (1998) reported that pyrolysis at 400–500 °C resulted in biochars with additional acidic functional groups, such as carboxyls. These polar molecules can bind with soil NH_3. The OBB had relatively high atomic O/C and (O + N)/C values (Table 1) that can interact with polar molecules, such as ammonia (Wang et al., 2013). These interactions will likely result in less TIN in the soil solution. Furthermore, N will likely leave the biochar during pyrolysis, as N and S volatilization is common when organic materials burn.

In contrast, fresh biochar has been reported to increase short-term N mineralization, but the effects dissipated over time (Nelissen et al., 2015). Additionally, fresh or unweathered biochars are also a source of polyaromatic hydrocarbons (PAHs) that can act as microbial toxins, thereby lowering N mineralization rates for a time (Quilliam et al., 2012). Investigations into characterizing the organic matter (including volatile organic compounds) associated with biochars are needed, in order to elucidate what mechanisms are driving N sorption, immobilization and mineralization in biochar-amended (particularly OBB) soils. Biochars with greater TN, and therefore, potentially mineralizable N (PMN) such as OBB, also should be studied further as a sustainable, slow-release fertilizer alternative.

Soil total P concentrations ranged from 335 to 402 mg kg^{-1} (Table 3). The PWB did not affect soil TP, as compared with the control. However, addition of CHB or OBB increased soil TP by 12% and 15%, respectively. In comparison, soil extractable P decreased with increasing rates of CHB and OBB, but increased with increasing PWB application rates. Overall, soil available P decreased 32% after applications of CHB or OBB, and increased 8% when PWB was applied to soil. Soil P availability had a strong relationship with soil pH (Fig. 3) in all biochars.

The behavior of P in soil is influenced by soil organic matter, pH, and exchangeable and soluble Al, Fe, and Ca (Xu et al., 2014). Biochar addition to acidic soil is expected to reduce P fixation because organic amendments have a high affinity for Al and Fe. On the other hand, with increasing additions of high pH biochar, soil alkalinity may increase and precipitate P ions with Ca, as calcium phosphate (Nelson et al., 2011), which was likely the case of the OBB. Changes in soil P availability after biochar application have been reported in a number of papers (Novak et al., 2009; Sandeep et al., 2013) but the effect of biochar on P availability was very inconsistent. Therefore, each biochar/soil type combination requires further characterization in order to better predict nutrient retention and release.

It has been widely reported that biochar applications can increase soil pH (Liang et al., 2006; Nurhidayati, 2014). The degree of change is a function of both, the initial soil pH, pH of the biochar and their buffering abilities (Biederman and Harpole, 2013). The results from this study support these findings (Fig. 4). The pattern of response differed somewhat among biochars. The PWB had the least effect on soil pH, raising the soil pH by < 0.5 units, as compared to the control. Similar

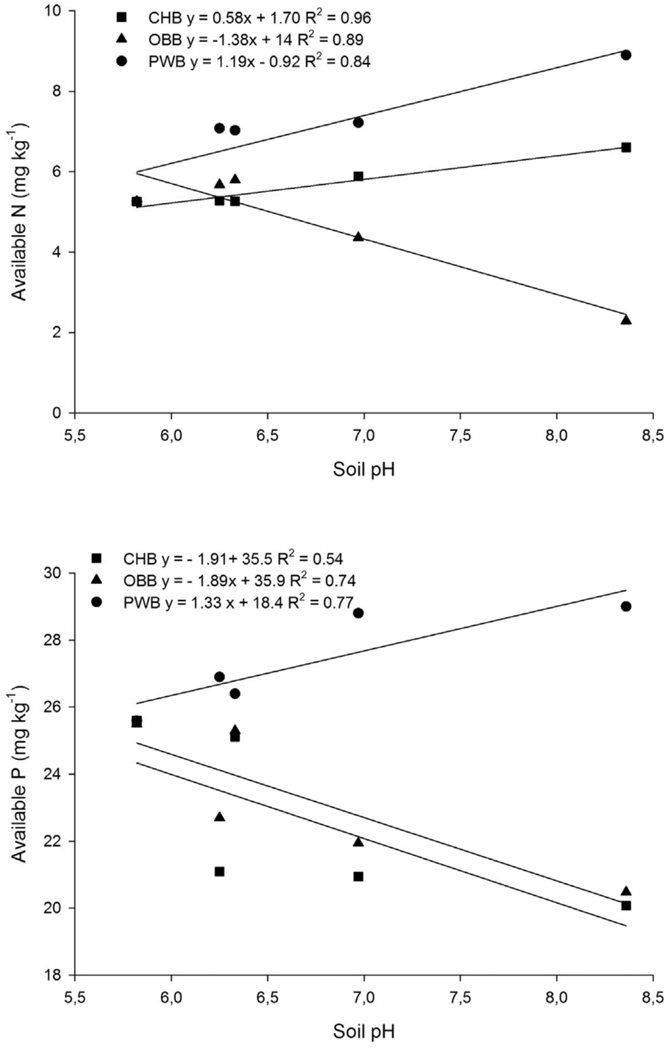

Fig. 3. Relationship between nitrogen and phosphorus concentration and soil pH.

results were observed by Rajkovich et al. (2012) and Albuquerque et al. (2013) when using pine wood chips biochar as a soil amendment. Application of 60 t ha^{-1} of CHB and OBB significantly increased soil pH by 1.4 and 2.5 units, respectively. Large increases in soil alkalinity can reduce the availability of some plant nutrients such as Ca, Mg, P and micronutrients, resulting in reduced plant yields (Nurhidayati, 2014). Based on the resulting soil pH from high (60 t ha^{-1}) biochar application rates, one might expect OBB and perhaps CHB to negatively impact crop growth. Therefore, lower application rates are recommended.

4. Conclusions

Results of this study confirmed differences in biochar feedstock imparting varying effects on soil fertility and plant growth. Pine wood chip biochar (PWB) did not have any effect on plant growth, and had a slight positive effect on plant P nutrition but it also reduced plant N nutrition. The low O/C ratio and high fixed C value suggest that PWB has the potential to be used in soil as a conditioner as well as to sequester C, but these attributes did not appear to translate to yield increases in an ultisol soil type. The coconut husk biochar (CHB) had a positive impact on maize growth, especially the aboveground biomass, even though it had limited fertilizer (N or P) value. Its proximate analysis was more similar to PWB than OBB and may exhibit some soil conditioner and/or soil C sequestration benefit. In comparison, the orange bagasse biochar (OBB) contained the greatest ash content and might function as a liming agent, as well as provide a source of slow-release N and P. This was supported by measurable maize yield increases from product application. Future studies need to address the impact of nutrient-rich biochar sources on long-term soil chemistry, especially C, N and P dynamics and potential contributions to crop nutrition.

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