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LOW TEMPERATURE PRODUCED CITRUS PEEL AND GREEN WASTE BIOCHAR IMPROVED MAIZE GROWTH AND NUTRIENT UPTAKE, AND CHEMICAL PROPERTIES OF CALCAREOUS SOIL

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In calcareous soils, the effects of biochar characteristics on maize growth are least understood. In a laboratory study, citrus peel biochar (CPB) and green waste biochar (GWB) were produced by slow pyrolysis at 300°C with 20 min residence time. Electrical conductivity, pH, ash, and nutrients i.e. N, P, K, Ca, Mg, S, Zn and Mn content in GWB were greater than CPB. Citrus peel biochar had wider C: N, C: P and C: S ratios than GWB. Efficacy of these biochars was tested for maize growth and nutrient uptake, and chemical properties of calcareous soil. Maize hybrid (Syngenta-6621) was grown in a greenhouse pot trial by using calcareous soil amended either with CPB or GWB at application rates of 0.0, 0.5, 1.0, 1.5 and 2.0% (w/w) along with NPK fertilizers. Our results revealed that increasing rates of CPB, effectively improved maize plant height; fresh and dry weight; chlorophyll content and photosynthetic rate; and N, P and K uptake. At varying GWB application rates, maize fresh and dry weight; and N and P uptake was improved. Regarding plant growth and nutrient uptake, the overall response of CPB was better than GWB. At 2.0% application rate, CPB resulted better fresh weight (19%), dry weight (24%), plant height (20%), N uptake (42%), P uptake (36%) and K uptake (30%), than from the treatment having same rate of GWB. Due to biochar addition, the highest percentage of N and P recovery (5.3 and 6.6%, respectively) was obtained at 2.0% CPB application rate, while the highest K recovery (9.8%) was obtained at CPB application rate of 0.5%. At 2.0% application rate, CPB decreased soil pH up to 7.96 and increased soil organic carbon up to 1.25%, and GWB increased soil electrical conductivity up to 1.45 dS m^{-1}. Conclusively, CPB produced at 300°C pyrolysis temperature with 20 min residence time, could be effectively used at the rate of 2.0%, for improving maize growth and nutrient uptake, and chemical characteristics of calcareous soil.

Keywords: Calcareous soil, green waste biochar, citrus peel biochar, maize

INTRODUCTION

For the success of any soil management, it is crucial to maintain an appropriate level of soil organic matter and biological cycling of essential nutrients. Compost, mulches, manure and cover crop have been used effectively for supporting rapid cycling of soil nutrients through microbial biomass activity and supplying these nutrients to different crops (Trujillo, 2002). The benefits of these soil amendments are, however, often short-lived, since decomposition rates are high and the added organic matter is usually mineralized to carbon dioxide (Bol, 2000). Biochar is composed of graphite-like, highly recalcitrant organic carbon (C) compounds together with variable proportions of minerals. It is formed during the thermal decomposition of biomass under low-oxic conditions (pyrolysis) between 300 to 1000°C (Verheijen *et al*. 2010), which leads to a C enriched, aromatic product obtaining features both suitable for C sequestration as well as an additive to agricultural soils (Lehmann and Joseph, 2009; Sohi *et al*., 2010). Biochar is a stable form of C and may last in the soil for thousands of years. Thus, it is possible, as part of a shift to organic farming practices, to use biochar to turn agriculture from a net emitter of C to a tool for drawing C back out of the atmosphere (Shenbagavalli and Mahimairaja, 2012). Biochar application to soil is increasingly investigated as a soil amendment and C sequestration strategy. Numerous studies have indicated that incorporation of biochar can dramatically enhance SOC content (Tammeorg *et al*., 2014; Yin *et al*., 2014). Biochar may directly enhance soil fertility by adding nutrients to the soil that had been previously stored in the biomass and such biochars may therefore act as an organic fertilizer (Chan and Xu, 2009; Farrell *et al*., 2014; Jiang *et al*., 2014). As a result of biochar application, increase in crop yields are observed by Yu *et al*. (2014) and Smider and Singh (2014). An indirect influence of biochar application to the soil is exerted by its pH, porosity, specific surface area, and cation exchange capacity (CEC) (Chan *et al*., 2007; Singh *et al*., 2010). Meta-analysis have revealed that slow pyrolyzed biochars produced from various feedstocks at temperatures from 300 to 600°C, may improve soil physico-chemical properties i.e. soil aggregation, pH and CEC (Gul *et al*., 2015).

Biochar properties can be manipulated depending on feedstock characteristics and furnace design, such as potential highest treatment temperature and residence time (Collison *et al.*, 2009; Downie *et al.*, 2009). The pH of biochars may range from 4 to 12, depending on the feedstock used and the pyrolysis conditions (Lehmann, 2007). Pyrolysis causes some nutrients present in the original feedstock to volatilize (Deluca *et al.*, 2009). Different processing conditions (temperature) result different nitrogen (N) contents (Chan *et al.*, 2007), as the maximum N contents may be resulted at low temperature pyrolysis (Baldock and Smernik, 2002). Low temperature (<500°C) also favors the relative accumulation of available potassium (K) (Yu *et al.*, 2005), phosphorus (P), magnesium (Mg), sulfur (S) and silicon (Bourke *et al.*, 2007). Therefore, processing temperatures <500°C favor nutrient retention during pyrolysis (Chan and Xu, 2009). During the production of biochar, N starts to become volatile at ~200°C. Among all macronutrients, N is the most sensitive to high temperature (Tyron, 1948). As pyrolysis temperature decreases, extractable concentrations of ammonium (NH_4^+) generally increases (Gundale and Deluca, 2006). Due to high CEC, sorption of NH_4^+ to biochar may reduce ammonia volatilization from alkaline soils where N losses by this pathway are most problematic (Yuan *et al.*, 2011; Jiang *et al.*, 2014). Different scientists have reported an increase in total soil N after the application of biochar (Luo *et al.*, 2014; Doan *et al.*, 2015). Regarding P availability, the immediate positive effects of biochar addition may also be due to higher P availability (Lehmann *et al.*, 2003), because it may contribute as a source of available and exchangeable P, ameliorator of P complexing metals (Ca^{2+}, Al^{3+} and $Fe^{3+,2+}$), modifier of soil pH, as a promoter of microbial activity and P mineralization (Deluca *et al.*, 2009). Biochar have K in highly exchangeable form which is available for plant uptake (Chan *et al.*, 2007). Beside all this information, most of the research on pyrolysis of biomass has focused on energy and fuel quality, rather than on biochar as a soil amendment. However, biochar has nutrient value when used for soil application (Tsai *et al.*, 2006). The responses of biochar application mainly depend on the rate and type of biochar applied, as well as physicochemical characteristics of soil (Agegnehu *et al.*, 2015).

Regarding biochar, majority of the pot and field experimentation is conducted under acidic soils. For such type of soils, alkaline pH biochars have been produced as well as promoted to neutralize the effect of acidity. We hypothesized that in calcareous soils, low pyrolytic temperature biochars may play a constructive role for improving maize physiology and growth as well as nutrient uptake and soil properties. For investigating the efficacy of different biochars as soil amendment in more detail, our study pursued the subsequent objectives: (1) to produce two different biochars at low pyrolytic temperature; (2) to characterize the produced biochars for their nutrient content, elemental ratios and chemical properties; (3) to check the effect of varying levels of two different biochars on maize growth, physiology, nutrition, nutrient recovery and soil chemical properties and finally (4) to recommend the suitability of biochar and its application rate for calcareous soil.

MATERIALS AND METHODS

Biochar production

***Feedstock collection and preparation*:** Citrus peels were collected from the market area of University of Agriculture, Faisalabad (UAF). Green waste consisting of Indian devil (*Alestronia scholaris*) tree leaves and cuttings of Bermuda grass (*Cynodon dactylon*) were collected from the lawns of UAF. Both the feedstocks were selected, because these are not used for any special alternative purpose. If these feedstocks are not pyrolyzed, then these feedstocks may even cause some negative impacts on the surrounding environment. After removing dust and soil particles, both the feedstocks were sun-dried and then oven dried at 65°C in a forced air oven (Eyela WFO-600ND, Tokyo Rikakikai, Tokyo, Japan), until the moisture content were remained up to 10–15%. The dried samples were crushed into the particle size of 2–5 mm and stored in air tight zip bags.

***Pyrolysis process using muffle furnace*:** Two hundred grams of each crushed feedstock was pyrolyzed using the Muffle furnace (Gallonhop, England) as described by Sanchez *et al.* (2009). The pyrolysis was done in pyrex flask of 2 L capacity. For removal of gases and vapors from working area, bended outlet composed of glass rod was used. The junction of pyrex flask and glass rod was sealed with high temperature resistant silicon grease to completely avoid the entry of oxygen in reaction chamber. The increase in furnace temperature per unit time was adjusted at 8−9°C min^{-1}. After attaining 300°C temperature, 20 min residence time was maintained. After the completion of residence duration, the furnace was allowed to cool down until the temperature of reaction chamber had been reached up to 50°C. After cooling, the pyrex flask was removed from furnace chamber and biochar was collected from it.

***Characterization of biochars*:** Conversion efficiency of biochar was calculated by using the following formula:

$$\text{Conversion efficiency} = (\text{WCB} / \text{WFU}) \times 100$$

WCB = Weight of collected biochar (from pyrex flask)
WFU = Weight of feedstock used (for pyrolysis)

The ash content were determined by heating biochar samples in a muffle furnace according to the method proposed by Slattery *et al.* (1991) and calculated through following equation:

$$\text{Ash content (\%)} = (\text{WA} / \text{WB}) \times 100$$

WA = Weight of ash (obtained after heating)
WB = Weight of biochar (used for heating)

Moisture content of the biochar samples were determined gravimetrically by measuring the difference between fresh weight and weight after being dried for 24 h in an oven (Eyela WFO-600ND, Tokyo Rikakikai, Tokyo, Japan) at 65°C, then obtaining the ratio between this value and the biochar weight.

***Chemical analysis of biochars*:** The pH and electrical conductivity (EC) of biochar was measured by using 1:20 solid:solution ratio, after shaking for 90 min in de-ionized water on mechanical shaker. The CEC of biochar was measured by a modified ammonium acetate compulsory displacement method (Gaskin *et al*., 2008).

***Nutrient and elemental characteristics of biochar*:** Macronutrients i.e. P, K, Ca and Mg as well as micronutrients zinc (Zn), copper (Cu), iron (Fe) and manganese (Mn) were extracted from biochar samples after digestion in hydrogen peroxide and sulfuric acid (Wolf, 1982). Phosphorus concentration was measured on a UV-visible spectrophotometer (UV-1201, Shimadzu, Tokyo, Japan) using standard curve, after developing yellow color by vanadate-molybdate method (Chapman and Pratt, 1961). Potassium was determined on a flame photometer (PFP7, Jenway, Essex, UK) using standard curve. Calcium, Mg, Zn, Cu, Fe and Mn concentrations in biochar digest were determined on an atomic absorption spectrophotometer (AAnalyst 100, Perkin-Elmer, Norwalk, USA).

The C, hydrogen (H), N and S content in two different biochars were analyzed on Vario Micro CHNS-O Analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). The percentage of oxygen content was determined by difference method:

$$\text{Oxygen (\%)} = 100 - (\text{Ash+carbon+hydrogen+nitrogen})\%$$

The results obtained from Vario Micro CHNS-O analyzer were used to calculate elemental ratios i.e. C:N, C:P and C:S, and molar ratios i.e. H:C, O:C and (O+N):C.

Greenhouse study

***Soil properties*:** For an experiment, bulk surface (0–15 cm) soil sample was collected from the Experimental area, Institute of Soil and Environmental Sciences, UAF. The soil was air-dried and ground to pass through a 2-mm sieve. A sub sample of the sieved soil was analyzed for various soil physico-chemical properties. Soil texture was sandy clay loam (sand 56.3%; silt 22.5%; clay 21.2%) having pH, 8.23; EC_e, 1.13 dS m^{-1}; organic matter, 0.53%; calcium carbonate, 3.43%; CEC, 13.5 $cmol_c$ kg^{-1}; total N, 0.07%; extractable K, 127 mg kg^{-1} and Olsen P, 4.3 mg kg^{-1}.

***Experimental setup*:** A pot experiment was conducted in a greenhouse at the Institute of Soil and Environmental Sciences, UAF, to check the effect of varying biochar rates on maize growth, physiology, nutrient uptake, nutrient recovery and soil chemical properties. Two-factorial, completely randomized design was followed in such a way that five rates i.e. 0.0, 0.5, 1.0, 1.5 and 2.0% (of soil on w/w basis) of each citrus peel biochar (CPB) and green waste biochar (GWB) were used with three replicates. According to treatment plan, calculated amount of biochar was thoroughly mixed with the soil of each pot, separately. Before mixing, biochar of both feedstocks were ground into ≤2mm particle size. Basal dose of N, P and K fertilizers were uniformly applied in all treatments at the rate of 120, 90 and 60 kg ha^{-1} soil as urea, single super phosphate and sulfate of potash, respectively.

***Crop establishment*:** Five pre-soaked healthy seeds of maize hybrid (Syngenta-6621) were sown in each pot and thinning of seedlings into two plants pot^{-1} was done at plant establishment. The plants were root bounded in the pots. According to the requirement, de-ionized water was used to maintain moisture content of soil at field capacity in all the pots during whole experimental period. Plants were harvested after six weeks of germination, washed with de-ionized water and blotted dry with tissue paper.

Plant and soil measurements

***Agronomical measurements*:** Plant height was taken up by using measuring scale, just before harvesting. Immediately after harvesting, fresh shoot weight of each pot was recorded by using analytical balance. Shoot samples were air-dried and then oven dried at 65°C to a constant weight in a forced air driven oven (Eyela WFO-600ND, Tokyo Rikakikai, Tokyo, Japan). After achieving constant weight, dry weight of shoot samples was recorded.

***Physiological measurements*:** The plant physiological parameters of all the treatments were recorded in the morning (between 09:00 to 10:00am). Gas exchange parameters i.e. photosynthetic rate (A) and transpiration rate (E), were measured in fully expanded young leaves using a CIRAS-3 portable photosynthesis system (PP Systems, Hitchin, UK). The gas exchange response to CO_2 was measured from 60 to 2000 μmol mol^{-1} CO_2 at 1500 μmol m^{-2} s^{-1} PPF provided by a LED light (Long and Hallgreen, 1985). Fully expanded second leaf of each plant was selected for chlorophyll content and gaseous exchange measurements. Chlorophyll contents were measured by using SPAD-502 meter (Konica-Minolta, Japan).

***Nutrient measurements*:** Plant samples were finely ground with a wiley mill fitted with stainless steel chamber and blades. Ground samples (0.2 g) were digested through the method described by Wolf (1982). After digestion, final volume was made up to 50 mL with de-ionized water. The effect of treatments was evaluated for N, P and K. Nitrogen was determined with Kjeldhal method (Jackson, 1962). The P was determined on UV–visible spectrophotometer after developing yellow color by vanadate-molybdate method (Chapman and Pratt, 1961) at 410 nm using standard curve. Potassium concentration in plant samples was determined by flame photometer using a standard curve.

Total uptake of N, P and K was calculated separately for each nutrient by using the formula:

$$\text{Nutrient uptake} = (NC \times DM) / 100$$

NC = Nutrient concentration (%)
DM = Dry matter (mg pot^{-1})

Due to biochar addition, change in nutrients (N, P and K) recovery was calculated by using formula described by Mengel and Kirkby (2001):

$$\text{Nutrient recovery (\%)} = (NUB - NUC) / NAB$$

NUB = Nutrient uptake in biochar amended treatment
NUC = Nutrient uptake in control (without biochar)
NAB = Nutrient added through biochar

***Post-harvest soil analysis*:** Soil samples were collected from each pot by using sampling auger. After air drying, samples were passed through 2 mm sieve. A sub sample of the sieved soil was analyzed for various soil chemical properties. The pH of saturated soil paste was measured by Calomel glass electrode assembly. Electrical conductivity of the saturated soil paste extract was measured by using EC meter (Cond 315i/SET, Weilheim, Germany). Soil organic C was determined by Walkley-Black method (Nelson and Sommers, 1982).

***Statistical Analysis*:** Statistical analysis and data computations were made on Microsoft Excel 2013® (Microsoft Corporation, Redmond, WA, USA) and Statistix 8.1® (Analytical Software, Tallahassee, USA). Significantly different treatment means were separated using least significant difference (LSD) test (Steel *et al.*, 1997).

RESULTS

***Characterization of citrus peel biochar and green waste biochar*:** Low temperature (300°C) pyrolysis of two different feedstocks, resulted biochars with different physical, chemical, nutritional, elemental/molar ratio characteristics (Table 1). Conversion efficiency, moisture content and CEC of CPB were 15, 82 and 54% greater, than PWB, respectively. As compared to CPB, GWB had 64, 23 and 50% more ash, pH and EC, respectively. Pyrolysis of citrus peel resulted biochar with more C and oxygen content as compared to GWB, while H percentage in GWB was greater, than CPB. Except Cu and Fe, all other macro and micro nutrients i.e. N, P, K, Ca, Mg, S, and Mn were comparatively greater in GWB. Elemental ratios i.e. C:N, C:P and C:S ratios of CPB were wider, than GWB. The H:C molar ratio of GWB was wider, than CPB, while O:C and (O+N):C molar ratio of CPB was wider than GWB.

***Agronomical trait measurements*:** Data regarding fresh weight reveals that in comparison with the respective control treatment (0.0% CPB), maximum statistical increase (33%) was observed in the treatment with 2% CPB (Table 2). As a result of 1% GWB addition, 18% more fresh weight was obtained over the respective control treatment (0.0% GWB), while further incremental doses of GWB (1.5 and 2.0%) were statistically unproductive. There was 19% more fresh weight as a result of 2.0% CPB addition, than the treatment having 2.0% GWB. Among all the treatments, 2.0% CPB addition resulted maximum statistical response regarding dry matter yield. As compare to control treatment, at 2.0% CPB rate, there was about 33% increase in dry matter yield, followed by 20% more dry matter yield as a result of 1.5% CPB addition. In case of GWB, maximum dry matter yield was obtained at 1.0% application rate with 10% better results, than control treatment. Data regarding plant height in Table 2, shows that maximum statistical increase in plant height (11%) was achieved from the treatment with 1.5% CPB, than the respective control treatment. Regarding plant height, at 1.5% application rate, the results of both biochar were statistically similar with each other; meanwhile a significant decrease in plant height was recorded in the treatment having 2.0% GWB.

Table 1. Characterization of citrus peel biochar and green waste biochar

Properties	Unit	Biochar	
		CPB*	**GWB****
Physical/Chemical properties			
Ash Content	%	7.61	12.5
Moisture Content	%	2.42	1.33
Conversion efficiency*	%	59.2	51.4
pH (1:20)	−	6.47	7.94
EC (1:20)	dS m^{-1}	1.54	2.31
CEC	cmol$_c$ kg^{-1}	43.6	28.3
Nutritional/Elemental composition			
C	%	58.7	56.4
H	%	3.08	3.24
O	%	29.1	25.9
N	%	1.52	1.88
P	g kg^{-1}	2.10	2.82
K	g kg^{-1}	8.29	11.1
S	g kg^{-1}	3.17	4.88
Ca	g kg^{-1}	11.9	17.9
Mg	g kg^{-1}	6.86	15.1
Zn	mg kg^{-1}	63.7	183
Cu	mg kg^{-1}	144	72.7
Fe	mg kg^{-1}	215	213
Mn	mg kg^{-1}	107	528
Elemental ratios			
C:N	−	38.6	30.0
C:P	−	280	201
C:S	−	185	116
H:C (molar ratio)	−	0.63	0.69
O:C (molar ratio)	−	0.37	0.34
(O+N):C (molar ratio)	−	0.39	0.37

All values are the means of three replicates
*CPB represents Citrus peel biochar
**GWB represents Green waste biochar

Table 2. Effect of citrus peel biochar and green waste biochar on fresh weight, dry weight and plant height of maize

Biochar rate (%)	Fresh weight (g pot^{-1})		Dry weight (g pot^{-1})		Plant height (cm)	
	CPB*	GWB**	CPB	GWB	CPB	GWB
0.0	65.0±3.61cd	63.7±4.73cd	10.1±0.42e	10.3±0.27de	73.0±3.61c	71.3±4.04c
0.5	70.0±3.61bc	60.7±2.08d	10.5±0.22de	10.8±0.57cd	69.3±1.53c	70.7±1.52c
1.0	73.7±0.58b	75.3±2.03b	10.9±0.29cd	11.3±0.44c	67.3±3.06c	80.0±3.61b
1.5	74.3±3.79b	75.7±5.86b	12.1±0.37b	11.3±0.85c	81.0±4.58ab	80.0±2.00b
2.0	86.3±3.51a	72.7±4.04b	13.4±1.15a	10.8±0.32cd	86.3±4.72a	72.0±2.65c

Means sharing similar letter(s) in a column for each parameter do not differ significantly at $P \leq 0.05$. Data are average of three replicates ± standard deviation (SD). *CPB represents Citrus peel biochar, ** GWB represents Green waste biochar

Table 3. Effect of citrus peel biochar and green waste biochar on chlorophyll content, photosynthetic rate and transpiration rate of maize

Biochar rate (%)	Chlorophyll content (SPAD Value)		Photosynthetic rate (µmol $CO_2 m^{-2} s^{-1}$)		Transpiration rate (mmol H_2O $m^{-2} s^{-1}$)	
	CPB*	GWB**	CPB	GWB	CPB	GWB
0.0	30.5±1.45d	30.1±1.45d	20.6±0.49c	20.5±1.02c	4.57±0.33bc	4.49±0.20c
0.5	30.4±0.95d	31.3±0.87cd	20.9±0.82c	20.7±0.90c	4.56±0.40bc	4.72±0.43a-c
1.0	31.5±2.21cd	32.4±1.89b-d	21.6±1.11bc	21.8±0.40bc	4.82±0.56a-c	4.90±0.35a-c
1.5	34.9±1.56ab	33.7±1.31a-c	23.0±0.25ab	22.3±1.64a-c	4.86±0.42a-c	4.97±0.32ab
2.0	35.1±0.93a	33.3±1.82a-c	24.3±1.46a	22.4±1.94a-c	5.03±0.40a	4.95±0.24ab

Means sharing similar letter(s) in a column for each parameter do not differ significantly at $P \leq 0.05$. Data are average of three replicates ± standard deviation (SD). *CPB represents Citrus peel biochar, ** GWB represents Green waste biochar

Physiological measurements: Data presented in Table 3 reveals that maximum statistical results regarding chlorophyll content were achieved from the treatments with 1.5% of either CPB or GWB. Maximum measured value of chlorophyll content was 35.1 in the treatment with 2.0% CPB, followed by 34.9 and 33.7 from the treatments with 1.5% CPB and GWB, respectively. Twelve and 15% increase in photosynthetic rate was recorded from the treatments with 1.5 and 2.0% CPB, respectively. Treatments with different rates of GWB, did not show any statistical increase in photosynthetic rate. With respect to control treatment, about 11% increase in transpiration rate was observed in the treatments with 2.0% CPB or 1.5% GWB.

***Nutrient uptake*:** It is cleared from Figure 1a that in comparison with control treatment, 2.0% addition of CPB resulted 55% more N uptake, followed by the treatment with 37% better N uptake as a result of 1.5% CPB addition. Increasing GWB rates were effective up to 1.0% for successful statistical increase in N uptake. Comparing the treatments having different rates of GWB, maximum N uptake (159 mg pot^{-1}) was calculated from the treatment with 1.5% GWB. Figure 1b shows that maximum P uptake was calculated when CPB was added at the rate of 2.0%, with 88% more P uptake, than control treatment. In case of GWB, regarding P uptake, maximum statistical outcome was achieved as a result of 1.0% GWB addition. At 1.5 and 2.0% application rate, the response of CPB for P uptake was statistically better, than GWB. It is cleared from Figure 1c that incremental rates of CPB were significantly effective for improving K uptake in maize straw. At 2% CPB, there was 52% increase in K uptake, than control treatment. Green waste biochar application at the rate of 0.5%, resulted about 10% better P uptake, than control treatment. Further incremental doses of GWB (upto 2.0%) did not show any further statistical increase in K uptake.

***Nutrient recovery parameters*:** It is evident from Figure 2a, that maximum N recovery (5.34%) was calculated from the treatment with 2.0% CPB, followed by 4.93% from the treatment with 1.5% CPB. In case of GWB, maximum N recovery (about 2.0%) was observed at 1.5% application rate. Figure 2b shows that maximum P recovery (6.63%) was achieved as a result of 2.0% CPB addition. However, these results were statistically matched with P recovery of treatment having 1.5% CPB. Green waste biochar indicated maximum response, at 1.0% application rate with 2.28% P recovery. The maximum K recovery was about 12% and then 9%, when CPB was added into the soil at the rate of 0.5 and 2.0%, respectively (Figure 2c). In case of treatments having different rate of GWB, maximum K recovery (5.62%) was calculated at 0.5% application rate.

***Post-harvest soil analysis*:** Data presented in Table 4 is clearly showing a decrease in soil pH with increasing rates of both, CPB and GWB. The lowest pH value i.e. 7.96 was obtained as a result of 2.0% CPB addition. Among different treatments of GWB, the lowest pH (8.10) was recorded from the soil of treatment with 2.0% GWB. With increasing both biochar rates, soil organic carbon (SOC) content were also increased significantly. As a result of 2.0% CPB and GWB addition, there was 3.8 and 3.0 fold increase in SOC content, respectively, over control treatment. Soil EC was significantly affected by the addition of both biochars. Increasing trend in soil EC was directly proportional to the increasing biochar rates. The highest EC value (1.45 dS m^{-1}) was measured from the soil of treatment with 2.0% GWB. Fifteen and 33% increase in soil EC was recorded from the soil of treatments with 2.0% CPB and GWB, respectively, over the respective control treatments (Table 4).

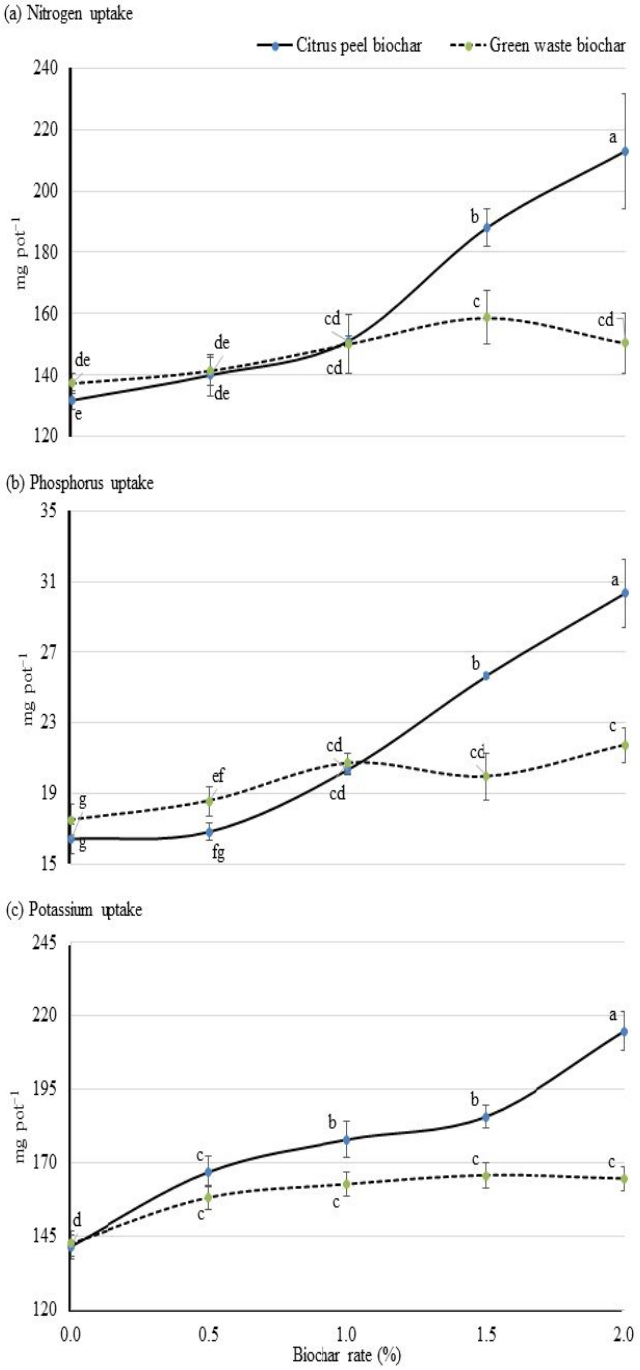

Figure 1. Effect of different citrus peel biochar and green waste biochar on nitrogen, phosphorus and potassium uptake of maize

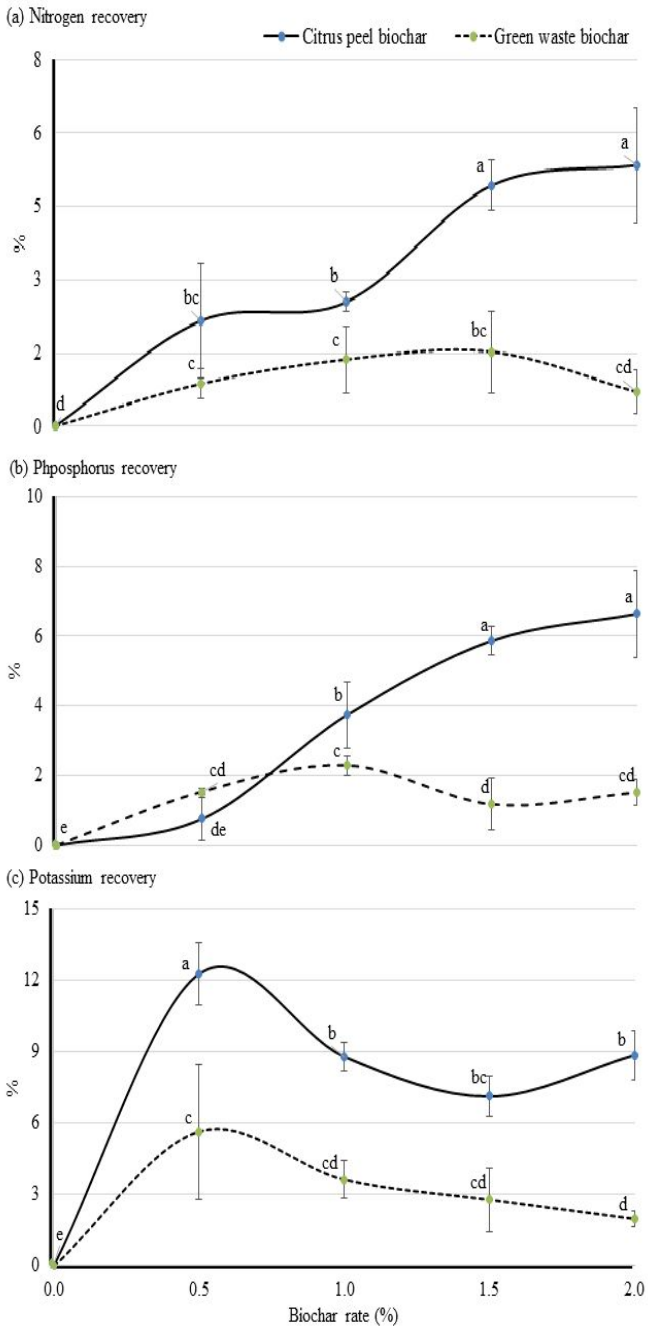

Figure 2. Nitrogen, phosphorus and potassium recovery due to citrus peel biochar and green waste biochar

Table 4. Effect of different citrus peel biochar and green waste biochar on pH, organic carbon and electrical conductivity of soil

Biochar rate (%)	pH		Soil organic carbon (%)		Electrical conductivity (dS m^{-1})	
	CPB*	GWB	CPB	GWB	CPB	GWB
0.0	8.21±0.02a	8.19±0.03ab	0.28±0.012f	0.31±0.012f	1.11±0.021f	1.09±0.021f
0.5	8.16±0.01b	8.17±0.02ab	0.54±0.033e	0.52±0.033e	1.18±0.044e	1.28±0.067cd
1.0	8.10±0.01d	8.15±0.02bc	0.85±0.024d	0.82±0.052d	1.19±0.040e	1.33±0.025bc
1.5	8.04±0.04e	8.11±0.04cd	1.14±0.124c	1.09±0.089c	1.25±0.045de	1.37±0.028b
2.0	7.96±0.04f	8.10±0.03d	1.35±0.062a	1.25±0.039b	1.28±0.035cd	1.45±0.046a

Means sharing similar letter(s) in a column for each parameter do not differ significantly at $P \leq 0.05$. Data are average of three replicates ± standard deviation (SD). *CPB represents Citrus peel biochar, ** GWB represents Green waste biochar

DISCUSSION

In our laboratory study, during biochar characterization we found that percentage of elements i.e. C and O in CPB was relatively greater, than GWB, while, GWB had more O content, than CPB. According to Deluca *et al*. (2009), biochar composition varied with feedstock type, as in our case, overall GWB had more nutrient content than CPB. Ash is inorganic portion of biochar, so overall, higher nutrient content in GWB also justified the reason of greater ash content in GWB, as shown in Table 1. The pH of biochar depends upon feedstock type and pyrolysis conditions (Shinogi and Kanri, 2003). In our case, pH and EC of GWB was comparatively higher, than CPB, while CPB had greater CEC, than GWB. The elemental composition of each feedstock was used to calculate atomic ratios as a predictor of their polarity and potential interaction with water. One would expect a biochar possessing higher H:C, O:C and (O+N):C molar ratios to be more interactive with polar compounds (Wang *et al*., 2007). The atomic ratios of the biochars, because of dissimilar O and H losses, varied considerably between both feedstocks (Table 1). Spokas (2010) suggested that O:C molar ratio is the most reliable predictor of biochar stability. As in our case, biochars with O:C ratio <0.6 produced at low pyrolytic temperature (300^{O}C) with short residence time (20 min), may have a very long half-life (100-1000 years). Recently Schimmelpfennig and Glaser (2012) proposed the combined use of H:C and O:C molar ratios as a tool to assess the biochar stability with threshold limits of H:C (<0.6) and O:C (<0.4). In the present study, both CPB and GWB had H:C and O:C molar ratios within above mentioned threshold limits. Different pyrolytic temperatures result different nutrient content in produced biochars (Chan *et al*., 2007). Low pyrolytic temperature favors higher N (Baldock and Smernik, 2002) because N is the most sensitive for heating (Tyron, 1948); available P (Bourke *et al*., 2007) and extractable K (Yu *et al*., 2005) contents in biochar. In our study, to get maximum benefit from the nutrient content of both biochar feedstocks, we used low pyrolytic temperature (300^{o}C) for biochar production.

After production as well as characterization (Table 1), we tested the efficacy of these biochars for maize crop. In this experiment, with increasing biochar rates (especially CPB), a positive response was observed in physiological traits i.e. chlorophyll contents and photosynthetic rate (Table 3). Anten (2005) explained that improvement in photosynthetic rate has a significant impact on crop growth and dry matter. Improvement in chlorophyll content, indicates the improved nutrient availability and vigorous plant growth in CPB amended treatments. Chlorophyll content, an indicator of photosynthetic activity, is related to the N concentration in green plants and serves as a measure of the response of crops to soil N status (Minotta and Pinzauti, 1996). In our case, better N status in plants of CPB amended treatments (Figure 1a) was the indication of better chlorophyll content and other physiological traits of maize plant. Moreover, despite of having more ash content in GWB, the overall performance of CPB was more pronounced for improving growth parameters (Table 2). In our case, overall response of CPB was better for decreasing alkaline soil pH (Table 4). Pyrolysis temperature influences the impact of biochar on maize growth. Yu *et al*. (2014) reported that biochar produced at low temperature have generally positive effect on maize dry matter. With the aim of evaluating the relationship between biochar and crop productivity (either yield or above-ground biomass), a meta-analysis study was undertaken by Jeffery *et al*., (2011). According to that meta-analysis, biochar application may increase crop productivity (on an average) upto 10%. However, the mean results for each analysis performed within the meta-analysis covered a wide range from −28 to 39%. In the present study, 2.0% CPB addition resulted an increase of 33% in dry biomass relative to control treatment.

Increased dry matter yield of 1.5 and 2.0% CPB amended treatments, provided an evidence for more N uptake in maize straw. Performance of CPB at the rate of 1.5 and 2.0%, was the best among all the treatments because of the highest significant results regarding straw N uptake (Figure 1a). It could be directly due to comparatively higher N content (1.52%) present in CPB, than GWB (Table 1). At low pyrolysis temperature, an extractable concentration of NH_4^+

generally increases (Gundale and Deluca, 2006). Chan and Xu (2009) reported that the availability and rate of mineralization of organic N found in biochar applied to soil provides an indication of the biochar's ability of being a slow release N fertilizer. For agronomic purposes, to counter the potentially unavailable biochar N, it has been found that, there is a positive effect when biochar is applied together with the addition of N fertilizer (Chan *et al*., 2007; Steiner *et al*., 2008). Biochar due to high CEC has potential to retain NH_4^+ present in the soil (Sohi *et al*., 2010). We also observed the ability of both biochars to improve N recovery. Our results indicate the positive effect of added biochar on plant nutrient availability. According to the study reported by Lehman *et al*. (2006), availability of total N was also increased as a result of biochar application. High CEC of produced biochar might also be another reason for increasing N retention capacity of soils and ultimately decreasing N losses from calcareous soils, in the form of ammonia volatilization and denitrification.

Additions of biochar to soil have shown an increase in the availability of P (Glaser *et al*., 2002; Lehmann *et al*., 2003). In our pot study, incremental biochar rates enhanced P content in plant tissue. The immediate positive effects of biochar could be due to higher P availability (Lehmann *et al*., 2003). Various mechanisms, including: biochar as a source of available and exchangeable P; ameliorator of P complexing metals (Ca^{2+},Al^{3+} and Fe^{3+2+}); modifier of soil pH and as a promoter of P mineralization and microbial activity, may be involved for improving P availability (Deluca *et al*., 2009). It is expected that P availability improves with raising biochar application rates (Novak *et al*., 2009). In the current experiment, with increasing biochar rates, an improvement in P recovery indicates the positive role of biochar for enhancing P availability to plant. It is reported that increased P availability may be due to high concentrations of available P found in the biochar (Nigussie *et al*., 2012).

Increase in K uptake was might be due to better plant growth and as well as directly or indirectly due to improved availability of N and P as a result of biochar addition. Maximum K recovery was observed at 0.5% CPB application rate. It might also be due to the reason that soils which have been developed from micaceous parent material and have undergone a considerable degree of weathering, contain already sufficient plant available K. The soils of Pakistan are rich in mica minerals, which are the major source of natural K (Bajwa and Rehman, 1996). Due to this reason, indigenous soil K content as well as K fertilizer content were sufficient to fulfill the K requirement of maize crop during vegetative growth stage.

In our study, pH of CPB was slightly acidic, while GWB had alkaline pH (Table 1). According to the post-harvest soil analysis, treatments with increasing level of CPB showed a consistent decrease in soil pH. Pakistani soils are alkaline in nature and pH of these soils is already high. So, the addition of any amendment which have low pH, may be helpful to decrease the alkalinity of such soils as well as ultimately may play a role to increase the availability of soil nutrients for plant uptake. Cheng *et al*. (2006) also proved the reduction in soil pH, with the application of biochar. In our case, GWB also reduced soil pH, but comparatively due to its high pH, than CPB, its impact on soil pH was comparatively lower. Soil organic carbon content were improved in line with increasing biochar rates. Carbon content of biochar are present in highly stable form (Shenbagavalli and Mahimairaja, 2012). It is well known that soil organic matter plays important roles in both soil fertility and the global C balance. Increased soil organic matter can thus sequester C and dramatically enhances SOC content (Lal, 2004; Lehmann and Gaunt 2006; Kuzyakov *et al.,* 2009). Electrical conductivity is largely dependent on the ash content and ash composition of biochar. High ash and metal content result in high EC of GWB. The alkali-earth metals of Ca and Mg may determine the EC of biochar. High EC of biochar is strongly related to feedstock (Yuan *et al*., 2011). In our experiment, due to high EC (2.31 dS m^{-1}) of GWB (Table 1), a significant increase in soil EC was noticed with increasing GWB rates. However, CPB had comparatively low EC (1.54 dS m^{-1}) and ultimately as a result of CPB application, there was only a negligible increase in soil EC.

Conclusion: We confirmed that ash and total nutrient content define the efficacy of biochar for calcareous soil, beside these, properties i.e. pH, EC and CEC of biochar does also matter. Instead of having more nutrient content in GWB, CPB is more effectual to enhance maize growth, physiology, as well as N and P uptake and recovery. The improved plant physiology and nutrient recovery ultimately lead to enhanced maize growth and nutrient uptake. Possible reasons behind the comparatively low outcome of GWB amended treatments were: less nutrient release from GWB during cropping period, high EC and pH, and low CEC, than CPB. Moreover, pH of Pakistani soils is already high, so due to comparatively lower pH of CPB, its performance remained better than GWB. Finally, it can be concluded that CPB produced at low pyrolytic temperature (300°C) with short residence time (20 min), may play a significant role for improving maize growth and nutrient uptake, under calcareous soil condition.

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