



## RESEARCH PAPER

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## Effect of biochar on soil chemical properties and nutrient availability in sandstone and shale derived soils

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### Abstract

A field study was conducted at Pir Mehr Ali Shah Arid Agriculture university (Research Farm Koont Chakwal, Pakistan) to investigate the effect of two different types of biochar on soil chemical properties and nutrient availability during kharief season 2013-14. Two types of biochar were used wheat straw biochar (@ 5 and 10 t ha<sup>-1</sup> and sugarcane bagasse biochar @ 5 and 10 t ha<sup>-1</sup>. Both types of biochar had no significant ( $P < 0.05$ ) change on soil pH, while electrical conductivity (EC) and total organic carbon (TOC) differed significantly ( $P < 0.05$ ) at higher rates i.e. 10 t ha<sup>-1</sup> on both types of biochar. Nitrate-nitrogen and extractable potassium (K) did not significantly increased but available phosphorus (P), extractable zinc (Zn), iron (Fe), copper (Cu) and manganese (Mn) showed positive significant change. Soil treated with sugarcane bagasse biochar at @ 10 t ha<sup>-1</sup> had greater TOC, EC, available P, zinc and copper.

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## Introduction

Climate change is one of main problems of modern world besides increasing human population; waning food reserves (Lehmann and Joseph, 2009). In such a climate change it has been predicted that after next twenty years, in low rainfall areas such as semi-arid region, yield of primary foods (wheat, maize and rice) will decrease considerably due to drier and warmer conditions. Furthermore, soil infertility and degradation are threatening problems for crop production and causes the reduction in yield and quality of agricultural products (Chan and Xu, 2009). Keeping such problems in mind, the use of biochar has been brought forward to sustainably amend the soils which do not retain the nutrients (Laird, 2008; Lehmann and Joseph, 2009). The application of biochar to the soils has shown several agricultural benefits including increased sorption capacity of soil, reduced leaching of nutrients and less loss by runoff, and a slow nutrients release to the growing plant (Laird, 2008).

Nutrients content of biochar varies with feed stocks and different pyrolysis conditions. The nutrients which are chemically bound to organic matter such as nitrogen, do not necessarily show its actual availability to growing plants. For example, biochar of animal origin contains more nitrogen and phosphorus than the biochar produced from plant origin feedstock (Chan and Xu, 2009).

Biochar application can change soil bulk density with possible effects on soil water relations, rooting patterns and soil fauna. In low fertile soils, biochar application can positively affect both soil quality and productivity due to its ability to bind nutrient cations and toxic metals to increase pH and to improve soil structure (Atkinson *et al.*, 2010).

The biochar prepared from sewage sludge can avoid the solubilization of heavy metals of raw sewage sludge as compared to sewage sludge used as such in soil and can reduce the cost associated with transportation of sewage sludge (Mendez and Gasco, 2005). Biochar has been described as a possible means to improve soil fertility as well as other ecosystem services and sequester carbon to mitigate climate change (Sohi *et al.*, 2010).

The observed effects on soil fertility have been explained mainly by a pH increase in acid soils or improved nutrient retention through cations adsorption.

In Pothowar region, sandstone and shale are main soil parent material which contributes 90% soil development. This region is most productive for agriculture under rainfed area of Pakistan and has distinct agro-ecological significance. Soils of Pothowar are facing prevalent nutritional deficiencies that might be due to low rainfall, water erosion and less organic matter. In addition to this there is a lot of sugar cane bagasse and wheat straw waste in the fields every season produced by farmer community (Ahmed *et al.*, 2009). The purpose of this study was to utilize the sugar cane bagasse for the production of biochar and to investigate their effects on soil chemical properties and nutrient (N, P, K, Zn, Fe, Cu and Mn) availability in soil.

## Materials and methods

### Biochar Production

Sugarcane bagasse and wheat straw were collected and used for biochar production. Material was these were air dried and ground before the utilization of biochar production. After grinding, material was placed in a biochar production tank and heated at 350°C for 3 hours. Prepared biochar was collected from biochar production tank and stored in plastic bags.

### Field Experiment

Soil samples were collected from surface 0-15 cm, dried, sieved through 2 mm sieve and used for analysis of pH, electrical conductivity, total organic carbon, soil texture and nutrients (nitrogen, phosphorus and potassium). The treatments were (i) wheat straw biochar at 5 t ha<sup>-1</sup>, (ii) 10 t ha<sup>-1</sup>, (iii) sugarcane bagasse biochar at 5 t ha<sup>-1</sup>, (iv) 10 t ha<sup>-1</sup>, (v) a control (no biochar). Samples were ground mechanically. Finally ground materials were again dried at 65°C to obtain constant weight.

### Analytical Methods

Soil pH was determined using soil to water ratio of 1: 2.5 suspensions using calibrated pH meter. Twenty gram soil was taken in 100 mL beaker, added 50 mL distilled water and shaken for 30 minutes.

Soil pH of the suspension was determined using pH meter (McLean, 1982). Electrical conductivity was determined with 1: 2.5 soil water suspension. In 20 g air dried soil 50 mL distilled water was added and shaken for 30 minutes on mechanical shaker. After that the suspension was allowed to stand for 30 minutes. Electrical conductivity was determined using EC meter (Rhoades, 1982).

In a 500 mL Erlenmeyer flask, 1 g soil was taken, added 10 mL of 1 N  $K_2Cr_2O_7$  and 20 mL of concentrated  $H_2SO_4$ , mixed gently for 1 minute and left to stand for 30 minutes. It was diluted by adding 200 mL of deionized water, then added 10 mL of ortho phosphoric acid. Afterwards, 10-20 drops of diphenylamine indicator was added and titrated against 0.5 N Ammonium iron (II) sulfate till the end point of sharp green color (Nelson and Sommers, 1982). Bouyoucos hydrometer method was used to determine soil texture. 40 g air-dried soil was taken with 60 mL of sodium hexa meta phosphate solution in a 600 mL beaker, left it for overnight. Afterwards, transfer of the suspension quantitatively to a 1 L Bouyoucos cylinder. The cylinder was filled with distilled water to 1-L mark. After mixing it well, inserted a hydrometer model 152 h in the suspension and recorded the first hydrometer reading after 40 sec for silt + clay, and then second reading after 4 hours for clay. The temperature was noted after every reading and made correction for corrected hydrometer reading. Percent silt and clay were calculated from hydrometer readings while % sand was calculated by difference method.

Percent sand, silt and clay were used to determine soil textural class on the USDA Soil Textural Triangle (Gee and Bauder, 1962). Salicylic acid method was used to determine nitrate nitrogen. Ten gram soil was taken and 20 mL of deionized water into a 50 mL Erlenmeyer flask. Then shaken the contents for one hour and filtered through Whatman No. 42 filter paper. Aliquot 0.5 mL was taken, added 1 mL of 5% salicylic acid reagent solution into test tube, mixed gently and left tubes for thirty minutes. Afterwards, 10 mL of 4 M NaOH reagent was added to each tube. Carefully mixed the contents and left the tubes for one hour for full color development.

Reading was recorded by using spectrophotometer at wavelength of 410 nm (Vendrell and Zupancic, 1990). Five gram soil and 100 mL of 0.5 M of  $NaHCO_3$  were mixed and shaken for 30 minutes into 250 mL Erlenmeyer flask. Ten mL of filtrate, 1 mL of 5 N  $H_2SO_4$  was added into 50 mL volumetric flask. Total volume was made up to 40 mL by addition of deionized water. Ammonium heptamolybdate, antimony potassium tartrate and ascorbic acid were used to develop colour. Absorbance was recorded after 10 minutes using Spectrophotometer at 882 nm wavelength. Standard curve was developed using range of phosphorus standards for computing phosphorus value from reading output (Olsen, 1954). Five gram of soil and 33 mL of 1 normal ammonium acetate solution were taken into 50 mL centrifuge tube and shaken for five minutes. The solution was centrifuged until the supernatant liquid was obtained.

Then the supernatant liquid was diluted to 100 mL with 1 normal ammonium acetate. The potassium concentration in the samples was determined using a standard curve, prepared from absorbance values of a series of potassium solution using flame photometer (Rhoades, 1982).

#### *Statistical Analysis*

The experimental design was two factors factorial. The data collected were analyzed statistically in two factors factorial and means were compared at 5 % level of significance (Steel *et al.*, 1997).

#### **Results and discussions**

Pre-treatment soil and biochar characteristics are summarized in Table 1.

#### *Effect of Biochar on Soil Chemical Properties*

Data on different biochar treatments for soil pH is presented in Table 2. The mean value for soil pH ranged from 7.78 to 8.04 and statistically non-significant increased from control. Maximum mean value (8.04) of soil pH was observed in soil treated with sugarcane bagasse biochar at 10 t ha<sup>-1</sup> after 120 days of application which was 3.3% more than control. The minimum mean value of soil pH (7.78) was recorded in control treatment.

Huang *et al.* (2013) evaluated to quantify the consequences of the biochar modification on soil eminence and crop production in the Chinese rice paddy and established that the accumulation of biochar to the paddy soils lead to increase in pH of soil by 6%. Biochar usually are alkaline in nature, depending on material, thus may have a little effect on most soils (Jeffery *et al.*, 2011). Verheijen *et al.* (2010) observed similar results that different types of biochar had positive effect on soil pH.

Results regarding effect of different biochar treatments for electrical conductivity of soil are depicted in Table 2. The mean value of soil electrical conductivity differ significantly ( $p < 0.05$ ) from control. The mean value for electrical conductivity ranged from 0.54 to 0.72 dS m<sup>-1</sup>. The maximum soil EC (0.72 dS m<sup>-1</sup>) was observed in soil treated with sugarcane bagasse biochar at 10 t ha<sup>-1</sup> which was 33 % higher than control, followed by (0.66 dS m<sup>-1</sup>) wheat straw biochar at 10 t ha<sup>-1</sup>. Hossain *et al.* (2011) studied the effect of different biochar application on soil electrical conductivity and concluded that biochar made up from different sources had various effect for electrical conductivity. Furthermore, they accomplished that different type of biochar had a significant rise in EC after biochar additions. Steiner *et al.* (2007) found in their experiment when biochar made from hardwood biochar have ability to increase the soil EC due to having higher concentration of carbonates.

Data regarding effect of different types of biochar on soil total soil organic carbon are presented in Table 2. The soil treated with sugarcane bagasse at rate of 10 t ha<sup>-1</sup> varied significantly ( $p < 0.05$ ) and mean value of total organic carbon ranged from 2.85 to 3.16 g kg<sup>-1</sup>. Maximum mean value of total organic carbon (3.16 g kg<sup>-1</sup>) was obtained in soil treated with 10 t ha<sup>-1</sup> sugarcane bagasse followed by 10 t ha<sup>-1</sup> wheat straw biochar representing 10.8 and 8.6 % respectively higher than control. Carbon is the major part in biochar. Kuzyakov *et al.* (2009) reported that biochar is stable for hundred to thousand years as it's the most stable form of organic carbon. Biochar has direct and indirect effect such as carbon

sequestration, physical and chemical properties of soil, plant growth and development, and energy production (Marris 2006). Sohi *et al.* (2010) studied and concluded that soil applied biochar had higher ability to store initial content of carbon. Biochar produced from different type of material revealed average 47.6% carbon concentration. Gaskin *et al.* (2010) determined that carbon concentration in biochar produced from poultry manure and pine chips can range from 40-78%.

#### *Effect of Biochar on Nutrient Availability*

Data regarding the effect of different biochar treatments on soil nitrate-nitrogen is presented in Table 2. Mean value of nitrate-nitrogen for treated soil with different type of biochar revealed statistically at par from each other. Maximum nitrate-nitrogen (6.67 mg kg<sup>-1</sup>) was observed in soil treated with wheat straw biochar at the rate of 10 t ha<sup>-1</sup> treatment representing 6.5% relative to control. Minimum nitrate-nitrogen was recorded (6.26 mg kg<sup>-1</sup>) in control treatment where no biochar was applied. Chan *et al.* (2008) determined that manure biochar addition to soil had substantial effect for increasing nitrogen availability. Lehmann *et al.* (2003) recorded that biochar application to soil increases C/N ratio which may causes nitrogen immobilization. So for better production additionally nitrogen in from of fertilizer must be applied. Biochar made from plant material consists of various form of structural nitrogen like amino acid, amines and amino sugar when subjected to high heat lose most of nitrogen which increase C/N ratio thus may not be available for plant uptake (Cao and Harris 2010; Koutcheiko *et al.* 2006). Biochar amendments increases soil total nitrogen content but these had no significant effect on soil mineral nitrogen contents (Zhang *et al.*, 2012).

Results regarding soil extractable phosphorus is presented in Table 1. The mean value of extractable phosphorus for different type of biochar treated soil ranged from 4.11 to 5.45 mg kg<sup>-1</sup> and varied significantly from control. Maximum mean value of extractable phosphorus ranged from 5.45 mg kg<sup>-1</sup> in soil treated with 10 t ha<sup>-1</sup> sugar cane bagasse biochar

followed by wheat straw biochar at rate of 10 t ha<sup>-1</sup> representing 32.6 and 31.6 % respectively higher than control. Organic material when subjected to pyrolysis do not lose their phosphorus thus having higher concentration of P in biochar than the original material (Kloss *et al.* 2012). Petter *et al.* (2012) concluded that wood based biochar application to soil had positive effect on availability of phosphorus in sandy soils. Biochar of different feedstock's varies for total phosphorus content from 160 to 1560 mg kg<sup>-1</sup> (Miller *et al.*, 2013).

Results for extractable potassium are summarized in Table 2. The mean value of extractable potassium increased non-significantly in soil treated with different type of biochar after 120 days of application. The mean value of extractable potassium ranged from 133 to 149 mg kg<sup>-1</sup>. Maximum mean value (149.33 mg kg<sup>-1</sup>) for extractable potassium observed in soil treated with wheat straw biochar at 10 t ha<sup>-1</sup> followed by sugarcane bagasse biochar at 10 t ha<sup>-1</sup> representing 12% and 6.8% respectively higher relative to control.

Ro *et al.* (2010) observed that potassium content totally recovered when plant based material is subject to pyrolysis. Potassium content in biochar made up from different feedstock's varies from 0.039% to 1.83% which alters the concentration of potassium in soils. (Miller *et al.*, 2013). Results regarding zinc concentration in soil treated with different type of biochar are presented in Table 3. Zinc concentration in soil treated with different type of biochar varied significantly (p<0.05) after 120 days of application from control and ranged from 0.74 to 1.20 mg kg<sup>-1</sup>. Maximum Zinc concentration was observed in soil treated with 10 t ha<sup>-1</sup> sugarcane bagasse biochar followed by 10 t ha<sup>-1</sup> wheat straw biochar.

Therefore, soil T5 (sugarcane bagasse) and T3 were statistically at par from each other, and T4 and T2 had no significant difference from each other but varied from control. Novak *et al.* (2009) established that extractable Zn concentration varied greatly depending on feedstock used when compared three different types of biochar.

**Table 1.** Basic characteristics of soil and biochar.

Parameters	Soil	Wheat straw biochar	Sugarcane bagasse Biochar
Texture	Sandy loam	----	----
pH	7.79	7.66	8.80
EC (dS m <sup>-1</sup> )	0.54	1.64	1.78
N (mg kg <sup>-1</sup> )	6.34 (mg kg <sup>-1</sup> )	1.38 (%)	0.92 (%)
P (mg kg <sup>-1</sup> )	4.09 (mg kg <sup>-1</sup> )	0.26 (%)	0.24 (%)
K (mg kg <sup>-1</sup> )	134 (mg kg <sup>-1</sup> )	3.00 (%)	2.91 (%)
Zn (mg kg <sup>-1</sup> )	0.74	39	41
Fe (mg kg <sup>-1</sup> )	2.24	92	84
Mn (mg kg <sup>-1</sup> )	1.82	106	77
Cu (mg kg <sup>-1</sup> )	0.16	13	11

**Table 2.** Effect of biochar treatments on selected chemical properties and extractable nutrients.

Treatments	pH	EC	TOC	N	P	K
		-dS m <sup>-1</sup> -	-g kg <sup>-1</sup> -	-----mg kg <sup>-1</sup> -----		
Control	7.78B	0.54C	2.85B	6.26A	4.11C	133B
Wheat Straw Biochar 5 t ha <sup>-1</sup>	7.80B	0.606BC	3.03B	6.46A	4.70B	138AB
Wheat Straw Biochar 10 t ha <sup>-1</sup>	7.78B	0.666AB	3.82A	6.67A	5.41A	149A
Sugarcane Biochar 5 t ha <sup>-1</sup>	7.89AB	0.643B	2.91B	6.29A	4.67B	39AB
Sugarcane Biochar 10 t ha <sup>-1</sup>	8.04A	0.720A	4.03A	6.64A	5.45A	142AB

Effect of different type of biochar in soil application on iron concentration were observed and presented in Table 3. The mean value of iron varied significantly (p<0.05) from control and ranged from 2.15 to 5.40 mg kg<sup>-1</sup>. Maximum mean value of iron concentration was observed in soil treated with 10 t ha<sup>-1</sup> wheat straw

biochar (5.40 mg kg<sup>-1</sup>) followed by sugarcane bagasse biochar applied at rate of 10 t ha<sup>-1</sup> and minimum iron concentration was observed in control treatment. Copper concentration of soil treated with different type of biochar was observed and data is presented in Table 3.

The mean value of copper concentration ranged from 0.15 to 0.62 mg kg<sup>-1</sup> and varied significantly from control after 120 days of application. Maximum concentration of copper was observed in soil treated with wheat straw biochar at rate of 10 t ha<sup>-1</sup> followed by sugarcane bagasse at rate of 10 t ha<sup>-1</sup>. Therefore, T2 and T4 were statistically at par from each other and different from control.

Treatment T3 and T5 were statistically similar and different from control. Novak *et al.* (2009) found in their experiment that Cu content did not change significantly in soil after biochar application which might be due to higher content of Cu in soil, while Gaskin *et al.* (2008) observed significant increase in

soil copper content which correlates our findings. Results regarding Mn concentration of soil treated with different type of biochar are presented in Table 3. The mean value of manganese concentration varied significantly (p<0.05) and ranged from 1.76 to 3.76 mg kg<sup>-1</sup>. Maximum manganese concentration (3.76 mg kg<sup>-1</sup>) was observed in soil treated with wheat straw biochar at rate of 10 t ha<sup>-1</sup> followed by sugarcane bagasse at rate of 10 t ha<sup>-1</sup>. Novak *et al.* (2009) exhibited that Mn concentration in soil increase after two month of biochar application. The higher content of Mn retention in biochar might be due to its association with organic and inorganic form in plant based material (Amonette and Joseph., 2009).

**Table 3.** Effect of biochar treatment on soil micronutrient (Zn, Fe, Cu, Mn).

Treatments	Zinc	Iron	Copper	Manganese
	-----mg kg <sup>-1</sup> -----			
Control	0.74C	2.15E	0.15D	1.76D
Wheat Straw Biochar 5 t ha <sup>-1</sup>	1.09B	3.80C	0.46BC	2.12C
Wheat Straw Biochar 10 t ha <sup>-1</sup>	1.19A	5.40A	0.62A	3.76A
Sugarcane Biochar 5 t ha <sup>-1</sup>	1.09B	3.07D	0.40C	2.16C
Sugarcane Biochar 10 t ha <sup>-1</sup>	1.20A	5.09B	0.55A	3.37B

**Conclusion**

From current experiment it is concluded that biochar of any type if applied to the soils low in organic matter and other nutrients, can improve the soil nutritional status. Only nitrate-nitrogen is reduced in soil, while other nutrients P, K, Fe, Zn, Cu and Mn were increased. So to agricultural lands minerals nitrogen must be applied with biochar to ensure better production.

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