

TEMPORAL VARIATIONS IN SOIL CHEMICAL PROPERTIES AND NUTRIENT AVAILABILITY IN RESPONSE TO MAIZE BIOCHAR PRODUCED AT DIFFERENT TEMPERATURES

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Biochar is a carbon-rich material produced through pyrolysis of biological material under controlled conditions. An incubation experiment was carried out in a calcareous soil to determine the temporal effect of maize biochar produced at three different temperatures 300, 400, and 500°C on soil chemical properties and nutrient availability. The variations in potassium (K), phosphorus (P), mineral nitrogen (MN), ammonium-nitrogen (NH₄⁺-N), nitrate-nitrogen (NO₃⁻-N), soil organic carbon (SOC), cation exchange capacity (CEC) and pH was evaluated by adding biochar in soil @ 0, 1.0 and 1.5% for incubation period (10, 20, 30, 40 and 50 weeks). Results revealed that soil pH was decreased with biochars (B300 and B400), particularly @ 1%. At the end of incubation, CEC was increased (12%) over control with B300 added @ 1%. The SOC and K contents significantly increased by increasing pyrolysis temperature, biochar rate and incubation time. The highest increase in SOC (51%) and K (367%) was observed with B500 @ 1.5% over control. The N contents (NH₄⁺, NO₃⁻) increased with increasing incubation time; highest NH₄⁺-N (97%) and NO₃⁻-N (118%) were observed @ 1.5% B300. Likewise, MN increased (107% over control) @ 1.5% B300. The available P increased in first 30 weeks but after that, it was decreased with increase in time. However, an increase of 65% in P over control was observed @ 1.5% B300. It is concluded that addition of B300 @ 1.5% improved the soil chemical properties and nutrient availability of the calcareous soil that needs to be verified further in field experiments.

Keyword: Biochar, soil fertility, organic matter, nitrogen, pyrolysis temperature, phosphorus, potassium

INTRODUCTION

The depletion of organic matter in soil disturbs its quality and fertility which is considered a notable environmental threat to agricultural productivity (Lal, 2006; Bashir *et al.*, 2018). This problem exists in vast areas of the world and is severe particularly in arid to semi-arid regions including Pakistan. Degradation of soil is the major factor contributing to agricultural productivity and food security (Lal, 2006). In soil management, the crucial aspect is to maintain the optimum amount of organic matter and nutrient status in soil. The management strategies protect our soil resources against severe environmental threats to meet the increased food demands of growing population. Organics (poultry manure, compost farmyard manure) and crop residues application to soil always remained the best refurbishment strategy to restore soil physical, biological and nutrient status but the quality and fast decomposition of these products offer limitation to get an advantage of their utilization. The best alternative to these strategies is the use of biochar as a soil amendment which provide a long-term solution to improve soil carbon sequestration, enhances soil

moisture content (Akhtar *et al.*, 2014) and to increase crop production (Akhtar *et al.*, 2015 a, b; Naeem *et al.*, 2017).

Biochar is a high-carbon material produced through pyrolysis and is considered as a soil amendment. Plant available forms of nutrients such as nitrogen (N), phosphorus (P) and potassium (K) are present in biochar (Naeem *et al.*, 2014, 2016, 2017, 2018). Furthermore, it also helps to enhance efficiency of N and P fertilizers (Cheng *et al.*, 2008; Hamdani *et al.*, 2017). Application of biochar to soils improves soil physicochemical properties (Naeem *et al.*, 2017), nutrient preservation, their availability and crop productivity (Chan and Xu, 2009; Naeem *et al.*, 2017).

Physical and chemical features of biochar are influenced by the type of raw material used, pyrolysis temperature and residence time (Gaskin *et al.*, 2008; Wu *et al.*, 2012). Biochar with poly-condensed aromatic structures is obtained through pyrolyzation of organic feedstock at high temperatures (400-700°C) (Glaser *et al.*, 2002). On the surface of its particles, ion exchange functional groups are present that restrict its usefulness in retaining soil nutrients (Glaser *et al.*, 2002). Biochar obtained at temperatures (250-400°C) has more C = O and C-H functional groups that after oxidation offers more exchange sites for nutrients (Glaser *et*

al., 2002). Moreover, pyrolysis at higher temperatures causes nutrients loss through volatilizations (Gaskin *et al.*, 2008). The type of biochar is specific for different types of soils owing to specific quality issues (Lehmann *et al.*, 2003) like biochar rich in aromatic compounds may be the best option for long-term C sequestration (Glaser *et al.*, 2002). Biochars with higher pH are generally applied to the acidic soils to maintain the quality of soil and enhance agricultural efficiency. It was reported by Yuan and Xu (2011) that the alkalinity of biochar was a fundamental element influencing their liming potential. However, based on nature of the raw material and conditions of pyrolysis, the pH of biochar may vary from 4-12. Moreover, the contents and availability of nutrients in organic amendments are changed by pyrolysis of crop residues as a result it influences the availability of nutrients to the soil. The present study was carried out to determine temporal variation in the availability of nutrients and chemical properties of a calcareous soil in response to application of maize biochar prepared at different temperatures.

MATERIALS AND METHODS

Soil collection: In order to characterize biochar and determine its effects on soil chemical properties and nutrient availability, an incubation experiment was performed in the Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad Punjab, Pakistan.

Bulk surface (0–15 cm) soil samples were collected from cultivated lands of research farm, University of Agriculture Faisalabad, Punjab, Pakistan. In order to remove coarse soil particles and plant parts, the soil was passed through a sieve (4.0 mm). The soil was completely mixed to get uniform structure and stored at 4°C (not more than 2 weeks). To perform physicochemical analysis, 0.5 kg soil subsample was air-dried, passed through a mesh (2.0 mm) and processed for analysis as given in Table 1.

Biochar preparation and characterization: Maize straw was obtained from the research station of the Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad, Pakistan. Oven dried maize straw was pyrolyzed using Muffle Furnace (Gallonghop, England) (Sanchez *et al.*,

Table 1. Physical and chemical properties of the soil.

Soil characteristic	Unit	Value	Reference system
Soil Great group	---	<i>Typic Calcargid</i>	USDA taxonomic system
Particle size distribution	Sand	35.8 ± 0.61	Hydrometer method (Gee and Bauder, 1986)
	Silt	38.5 ± 0.50	
	Clay	25.7 ± 0.70	
Textural class	---	Sandy clay Loam	USDA classification
pH _s	---	7.93 ± 0.18	pH of saturated soil paste (pH _s) Mclean (1982)
EC _e	dS m ⁻¹	1.93 ± 0.13	Electric conductivity of saturated soil paste extract Richards (1954)
Soluble cations	Ca ²⁺ + Mg ²⁺	mmol _c L ⁻¹	U.S. Salinity Laboratory Staff (1954)
	Na ⁺	mmol _c L ⁻¹	
	K ⁺	mmol _c L ⁻¹	
Aluminum (Al)	g Al kg ⁻¹ soil	0.65 ± 0.06	Oxalate-extractable Al and Fe oxides (Jackson <i>et al.</i> 1986)
Iron (Fe)	g Fe kg ⁻¹ soil	0.50 ± 0.05	
Cation exchange capacity	cmol _c kg ⁻¹ soil	16.20 ± 0.30	(Sumner and Miller 1996)
Soil organic carbon	g kg ⁻¹	3.42 ± 0.10	Walkley-Black method (Nelson and Sommers, 1982)
Calcium carbonates (CaCO ₃)	%	3.43 ± 0.08	(Leoppert <i>et al.</i> 1984)
Ammonium-nitrogen	mg kg ⁻¹ soil	4.88 ± 0.08	(Clare and Stevenson, 1964)
Nitrate-nitrogen		3.40 ± 0.10	(Soltanpour and Schwab, 1977)
Total Mineral N		8.28 ± 0.08	Soil NH ₄ ⁺ -N + NO ₃ ⁻ -N contents
Available P	mg kg ⁻¹ soil	7.30 ± 0.10	(Olsen and Sommers, 1982)
Extractable K	mg kg ⁻¹ soil	111 ± 5.00	(Richards, 1954)
Zn	mg kg ⁻¹ soil	1.01 ± 0.08	Micronutrients DTPA method
Fe		15.3 ± 0.10	(Lindsay and Norvell, 1978)
Mn		16.0 ± 0.20	
Cu		1.01 ± 0.05	

Values are mean of three replicates ± standard deviation (n = 3).

Table 2. Characteristics of biochar produced at different temperatures (300, 400 and 500 °C).

Pyrolysis Temperatures		300°C	400°C	500°C
Chemical properties				
Ash content	%	24 ± 1.14c	36 ± 1.50b	45 ± 1.53a
pH	-	6.85 ± 0.14c	7.50 ± 0.19b	8.15 ± 0.15a
EC	dS m ⁻¹	1.98 ± 0.13c	2.38 ± 0.07b	2.80 ± 0.08a
CEC	cmol _c kg ⁻¹	89 ± 3.10c	73 ± 3.75b	55 ± 4.00a
Nutrient composition				
Total carbon	%	42 ± 1.89c	52 ± 1.30b	66 ± 2.02a
Nitrogen	g kg ⁻¹	19.8 ± 0.72a	15.4 ± 1.05b	13.5 ± 0.89b
Phosphorus	g kg ⁻¹	2.4 ± 0.14a	2.0 ± 0.13ab	1.9 ± 0.15b
Potassium	g kg ⁻¹	20 ± 0.56b	25 ± 1.01b	35 ± 3.98a
Calcium	mg kg ⁻¹	8.5 ± 0.57b	9.3 ± 0.61b	12.8 ± 0.33a
Magnesium	mg kg ⁻¹	8.0 ± 0.10c	9.9 ± 0.19b	11.8 ± 0.28a
Zinc	mg kg ⁻¹	63 ± 1.90c	85 ± 2.00b	94 ± 2.15a
Manganese	mg kg ⁻¹	129 ± 8.39c	157 ± 6.34b	186 ± 11.70a
Iron	mg kg ⁻¹	171 ± 10.19c	305 ± 17.50b	407 ± 10.18a
Elemental ratio				
C:N	-	24 ± 1.55c	36 ± 3.19b	49 ± 4.61a
C:P	-	177 ± 18.01c	258 ± 23.12b	360 ± 38.78a
Surface functional groups (Boehm titration)				
Carboxylic	meq g ⁻¹	0.125 ± 0.005a	0.101 ± 0.007b	0.060 ± 0.005c
Lactonic	meq g ⁻¹	0.139 ± 0.002a	0.115 ± 0.005b	0.049 ± 0.007c
Phenolic	meq g ⁻¹	0.137 ± 0.004a	0.110 ± 0.005b	0.037 ± 0.006c
Total functional groups	meq g ⁻¹	0.401 ± 0.006a	0.326 ± 0.012b	0.146 ± 0.016c

Values are mean of three replicates ± standard deviation (n = 3). Different letters within column indicate significance between pyrolysis temperature at $\alpha = 0.05$ according to LSD test.

2009). Physico-chemical properties of biochar are presented in Table 2. The ash content was estimated by heating biochar samples in a muffle furnace following Slattery *et al.* (1991). The Electrical conductivity (EC) and pH of biochar were measured at 1:20 biochar: water ratio by shaking with a mechanical shaker for 90 min at 180 rpm. The CEC of biochar was determined by using method of Gaskin *et al.* (2008). The elemental analysis (P, K, Ca, Mg, Fe, Zn, Mn, and Cu) of biochars was performed after wet digestion with HNO₃-HClO₄ (Jones and Case, 1990). The Ca, Mg, and micronutrients (Fe, Zn, Mn, and Cu) were determined by atomic absorption spectrophotometer (AAAnalyst 100, Perkin-Elmer, Norwalk, America). Phosphorus concentration was measured by the vanadate-molybdate method (Chapman and Pratt, 1961) on UV-visible spectrophotometer (UV-1201, Shimadzu, Japan). Potassium was determined on flame photometer (PFP7, Jenway, UK). Nitrogen and carbon content in biochar were analyzed on Vario Micro CHNS-O Analyzer (Elementar Analysensysteme GmbH, Germany). The surface functional groups (i.e. carboxylic, lactonic and phenolic groups) were determined by using Boehm Titration (Boehm, 1966).

Biochar-amended soil incubation: Sieved biochars (<0.5 mm) were well mixed with soil (equivalent to 1000 g oven-dried weight) at a rate of 10 g biochar kg⁻¹ soil. There were three rates of biochar (1 and 1.5%) which was produced at

three different temperatures (300, 400, and 500 °C) along with control (no biochar). The 1000 g soil from each pot was put into five plastic cups. A completely randomized design was used with three replicates. Fifteen plastic films per treatment were set up to examine the soil properties at 10, 20, 30, 40 and 50 weeks. After incorporation of biochar, all the cups were weighed and covered with plastic sheet. To allow gaseous exchange and maintain moisture loss, a small hole was made in the center of plastic covering. The material was placed at a temperature (25 °C) and water-holding capacity (70%). When loss of moisture exceeds from 0.05 g, a small volume of distilled water was added to maintain soil moisture contents at every two days interval. After every incubation interval selected soil properties and nutrient status (pH, SOC, CEC, MN, NH₄⁺, NO₃⁻, P, and K) were estimated according to methods described in Table 1.

Statistics analysis: Data were recorded using Microsoft Office Excel 2013 (Microsoft Corporation, Redmond, WA, USA). The different effects of biochar at different application rates were examined by three-way analysis of variance (ANOVA) using Statistix 8.1 statistical software. To compare the means, Tukey's multiple comparison tests were adopted.

RESULTS

Effect of biochar on soil chemical properties: Significant decline in soil pH was observed by addition of low temperature biochars (B300, B400) over control after 30 days and later on it was increased (Fig. 1a,b). The soil pH significantly increased with B500 up to 30 days and then it decreased at both biochar rates 1 and 1.5%. The application

of biochar at the rate of 1% showed a pronounced effect in decreasing soil pH rather than its rate 1.5%. Consequently, a clear decline in pH (0.20 units) was observed after 10 weeks in soil containing B300 at 1%. In addition, after 20 and 30 weeks further decrease in pH was demonstrated. Additionally, a prominent decline in pH from 7.86 to 7.71 was noticed in B300 at the rate of 1% over control after the 50th week.

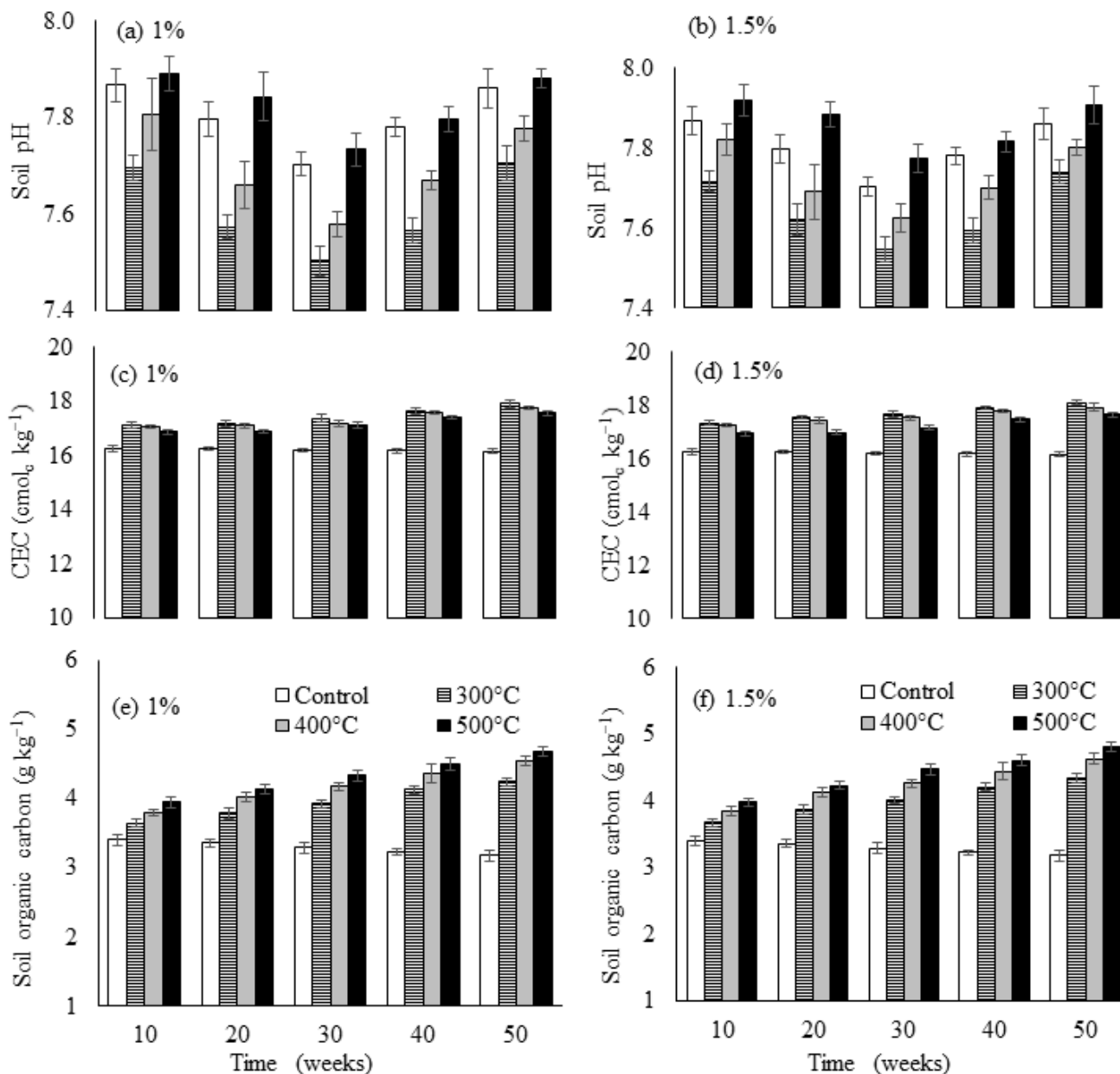


Figure 1. Temporal changes in pH (a-b), CEC (c-d), soil organic carbon (e-f) with respect to control (0.0% biochar addition (treatment without biochar) as a result of various rates (1.0 and 1.5%) of maize straw biochar produced at different temperatures 300, 400, 500 °C. Error bars represent standard errors; all the treatments were replicated thrice (n = 3).

The application of different biochars at both 1 and 1.5% levels significantly increased soil CEC as compared to control and incubation time (Fig. 1c-d). Furthermore, the comparison of pyrolysis temperatures, low pyrolysis produced biochar (B300) demonstrated the higher value of soil CEC at all biochar levels (1 and 1.5%) than biochars (B400 and B500). It was observed that soil CEC increased with increasing incubation time and it increased up to 12% over control by application of B300 at the rate of 1.5%. It was observed that application of different biochars

significantly increased SOC content (Fig. 1e-f). The increase in temperature caused increase in SOC and highest SOC content of 3.98 g kg⁻¹ was noticed in B500 at the rate of 1.5%. Whereas, minimum SOC content (3.40 g kg⁻¹) was evaluated in B300 at the rate of 1% after 10 weeks. The SOC noticeably increased during the period of incubation and soil incubated with B500 at the rate of 1.5% had the highest increase in SOC (4.80 g kg⁻¹) as compared with control after 50 weeks.

Effect of biochar on soil nutrients availability: Soil NH₄⁺-N

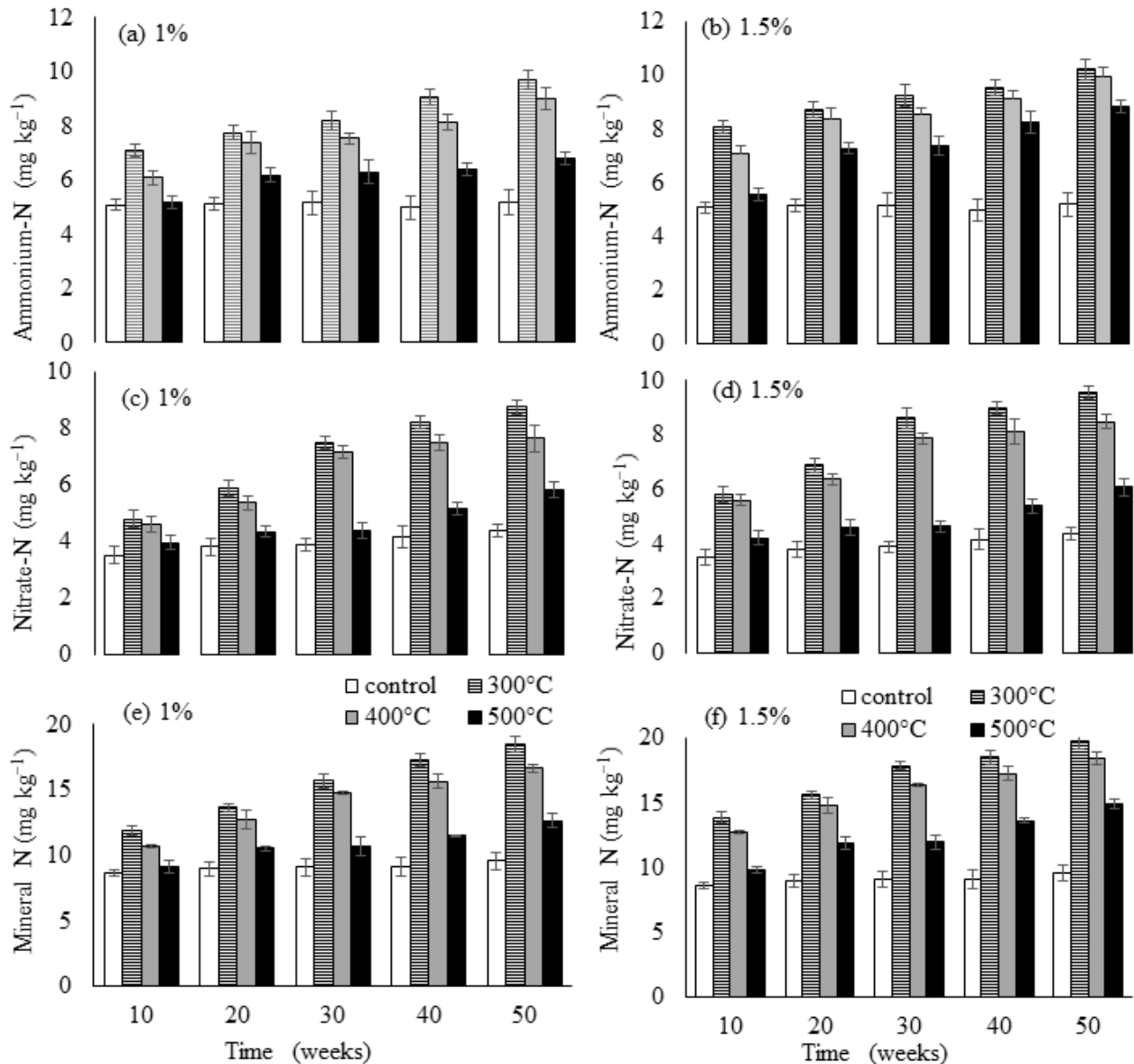


Figure 2. Temporal changes in ammonium-nitrogen (a-b), nitrate-nitrogen (c-d), mineral nitrogen (e-f) with respect to control (0.0 % biochar addition (treatment without biochar) as a result of various rates (1.0 and 1.5%) of maize straw biochar produced at different temperatures 300, 400, 500°C. Error bars represent standard errors; all the treatments were replicated thrice (n = 3).

contents were increased significantly up to 8.08 mg kg⁻¹ soil as compared to the control treatment after 1.5% of B300 addition at 10-week as shown in Figure 2a,b. The soil NH₄⁺-N content significantly increased with time during the whole incubation period. Application of B300 at the rate of 1%

increased soil NH₄⁺-N content up to 40, 51, 58, 82 and 87 % over control after 10, 20, 30, 40 and 50 weeks, respectively. At the end of incubation study (after 50 weeks), highest NH₄⁺-N (10.23 mg kg⁻¹ soil) contents were obtained from 1.5% B300 amended treatment, followed by 9.97 NH₄⁺-N

Table 3. Analysis of variance table (p-values) of different soil parameters for Temperature (T), Rates (R), time (t) and their interactions in incubation experiment.

Parameters	Temperature (T)	Rates (R)	Time (t)	T × R	T × t	R × t	T × R × t
pH	0.000*	0.000*	0.000*	0.000*	0.110 ^{NS}	0.721 ^{NS}	0.965 ^{NS}
CEC	0.000*	0.000*	0.000*	0.000*	0.828 ^{NS}	0.000*	0.995 ^{NS}
SOC	0.000*	0.000*	0.000*	0.000*	0.470 ^{NS}	0.000*	0.997 ^{NS}
NH ₄ ⁺ -N	0.000*	0.000*	0.000*	0.000*	0.432 ^{NS}	0.000*	0.032*
NO ₃ ⁻ -N	0.000*	0.000*	0.000*	0.000*	0.000*	0.000*	0.000*
Mineral N	0.000*	0.000*	0.000*	0.000*	0.000*	0.000*	0.004*
Available P	0.000*	0.000*	0.000*	0.000*	0.338 ^{NS}	0.000*	0.626 ^{NS}
Extractable K	0.000*	0.000*	0.000*	0.000*	0.282 ^{NS}	0.000*	0.986 ^{NS}

Here, ‘*’ indicate the significant difference while ‘NS’ stand for nonsignificant. P < 0.05.

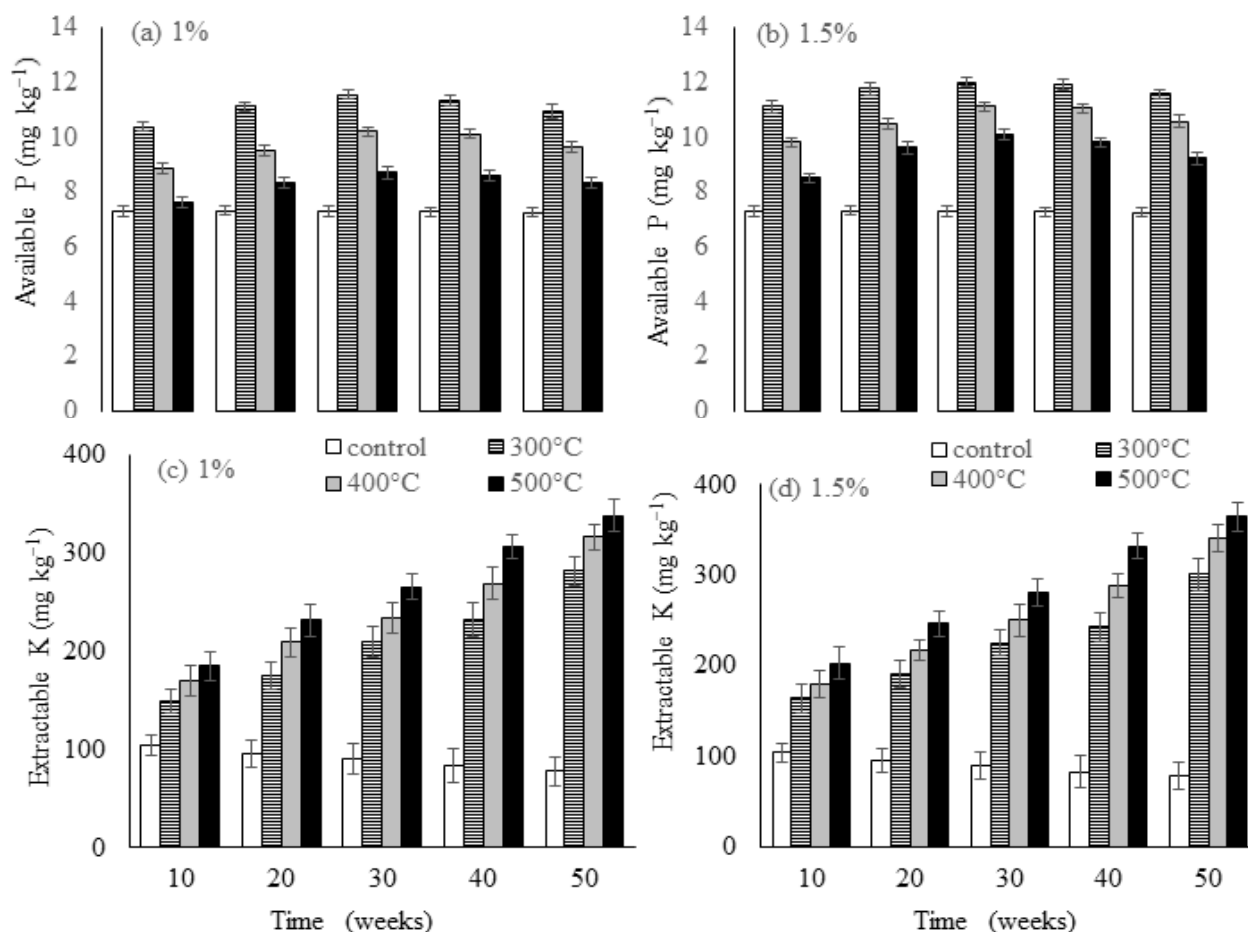


Figure 3. Temporal changes in available P (a,b), extractable K (c,d) with respect to control (0.0% biochar addition (treatment without biochar) as a result of various rates (1.0 and 1.5%) of maize straw biochar produced at different temperatures 300, 400, 500°C. Error bars represent standard errors; all the treatments were replicated thrice (n = 3).

kg⁻¹ soil from B400 at rate of 1.5%

The low temperature biochars (B300 and B400) increased NO₃⁻-N content than high temperature biochar (B500) (Fig. 2c-d). Similarly, application of biochar at rate of 1.5% significantly increased soil NO₃⁻-N content as compared with biochar at the rate of 1%. Therefore, soil with B300 at rate of 1.5% demonstrated the highest increase (39%) in soil NO₃⁻-N content after 10 weeks. Most eminent increment (9.55 mg kg⁻¹) was noticed in soil NO₃⁻-N content after 50 weeks over control with B300 at the rate of 1.5%.

Results indicated that the pyrolysis temperature, application rate, and incubation period affected MN and, in general, B300 displayed significantly higher MN (107%) as compared to the B500 after 50 weeks (Table 3). Among different biochar applications, the B300 at rate 1.5% exhibited significantly higher (7% and 32%, respectively) MN as compared to the B400 and B500 at same rate (1.5%). Analysis of variance indicated that pyrolysis temperature, application rates and sampling time had a significant (P<0.05) effect on available P (Table 3). It is demonstrated in the data of P that amendment of low temperature biochar (B300) raised the P in soil significantly as compared with high temperature biochars (B400 and B500) after the 10 weeks (Fig. 3a-b). Application of B300 at the rate of 1.5% resulted in the highest soil P increase (52%) over control, on the other hand, the lowest increment in soil P (4%) was observed in soil containing B500 at rate 1% over control. The increase in incubation period also caused increase in soil P and acquired most prominent values (14.2 mg kg⁻¹) in soil amended with B300 at the rate of 1.5% after 30 weeks. However, soil P was observed in decreasing trend with increasing incubation period from 30 to 50 weeks) at all biochars. The highest increase (60%) in soil P was observed with treatment B300 at the rate of 1.5% over control after 50th weeks.

In soils containing biochars, the extractable K was highest at a temperature of 500°C as compared to lower temperatures (Fig. 3c-d). After 10 weeks, it was observed that soil with biochar B500 at the rate of 1.5% had highest extractable K (203 mg kg⁻¹). Furthermore, a significant increase in K was measured during the whole incubation period. After 50 weeks it was observed that soil with biochar B500 at the rate of 1.5% (364 mg kg⁻¹) had most eminent extractable potassium (K) and comparatively this extractable K was 80% more than 10 weeks of incubation time.

DISCUSSION

Effect of biochar on chemical properties of soil: Yuan and Xu (2011) reported that there was an increase in pH of acidic soils after addition of biochar. On the other hand, some researchers reported a decreasing trend of pH in alkaline soil after adding alkaline biochar (Liu and Zhang, 2012; Naeem *et al.*, 2017). In this study, the liming effect of biochar could

have been stopped by alkaline soil (pH 7.93) as demonstrated in the results, for example, B300 and B400 had lower pH as compared to control. Similarly, decreasing trend in soil pH was observed with respect to pyrolysis temperature; the biochar produced at a low pyrolysis temperature (300°C) showed a decrease in pH of the soil. Cheng *et al.* (2008) reported that decline of pH in the soil can be attributed to slow oxidation of biochar with carboxylic and other acidic functional groups that possibly resulted in the neutralization of alkalinity of the soil. Biochar produced at 300°C is probably more oxidized than 500°C, because of its less aromaticity (Abrishamkesh *et al.*, 2015). Therefore, production of acidic material with higher oxidation of B300 might have caused lower soil pH in the B300 amended soil. Consequently, this also correlates with the fact that acid material is incremented by functional groups that contain high oxygen at low temperature (B300) (Table 2) and hence result in a decrease of soil pH. The cation content of biochar can be the reason for an initial decrease in pH of the soil (Figure 1 a, b). Liu and Zhang (2012) reported that decline in hydroxyl ions can occur from a combination of soil carbonates with biochar cation, leading to the formation of somewhat soluble carbonates in soil that can possibly restrict the hydroxylation of carbonates. Furthermore, Cheng *et al.* (2008) reported that the acidic matter can be produced by oxidation of organic matter present in the soil and it can be supplemented by biochar addition. Nevertheless, an increase in soil pH was noticed after an increase in incubation time. Moreover, Liu and Zhang (2012) and Naeem *et al.* (2017) reported that pH of the soil can be changed due to the potential interaction of pH and biochar in extremely alkaline conditions owing to the presence of inorganic carbonates and organic ions (Yuan and Xu, 2011). Therefore, it can be concluded that there is increase in pH during incubation period after an initial decline. Elements in soil are not carried away from the soil by the evaporation during incubation period and this may lead to an increase in soil pH and possibly results into soil salinization (Liu and Zhang, 2012).

In this study, the addition of biochar resulted in an increase of CEC (up to 18.10 cmol_c kg⁻¹). These results correlate with old findings and indicate a good buffering capacity of the soil (Cheng *et al.*, 2008; Yuan and Xu, 2011). Cheng *et al.* (2008) reported that CEC of biochar increases with time with the fact that in fresh biochar CEC is mostly low. Slow oxidation of biochar in soil results in higher number of exchange sites, which ultimately increase soil CEC (Cheng *et al.*, 2008). Highly porous nature and greater surface area of biochar increase the CEC and base saturation of soil (Glaser *et al.*, 2002). There is higher inherent CEC of biochar as compared to soil, clay or soil organic matter (Sohi *et al.*, 2009). This study also shows a similar behavior of biochar for CEC. Furthermore, this information also correlates with increased biochar CEC because of high

oxygen-containing functional groups at low temperature (B300) (Wu *et al.*, 2012) (Table 2) and therefore result into an increase of soil CEC.

Naeem *et al.* (2017) reported that addition of biochar significantly enhances SOC reserves. The B500 had a greater amount (66%) of total carbon (C) content (Table 2), and after the soil application of B500 particularly at rate of 1.5%, increase in SOC content was observed (Fig. 1e-f). Yuan and Xu (2011) reported that the higher resistance to oxidation and recalcitrant nature of biochar is clearly indicated by the highest values of organic carbon in soils containing biochar, and by that means protecting the organic carbon (C) from being utilized (Glaser *et al.*, 2002). A significant increase in total SOC content was reported because of biochar addition in calcareous soil (Naeem *et al.*, 2017). Moreover, more prominent increase in carbon (C) mineralization was observed in biochar produced at low temperatures as compared with biochars produced at high temperatures, since there is a more incomplete pyrolyzed fraction of feedstock material biochars produced at low-temperature (Bruun *et al.*, 2011).

It is reported that because of the biochar treatment having higher C/N ratio, a decline in soil respiration after application of biochar over control was observed (Zahra *et al.*, 2017). With the increasing pyrolysis temperature, the stability and chemical recalcitrance of biochars also increased, mainly because of a greater amount of C-C bonds. It means the presence of more available substances in biochars is indicated by more aliphatic C-H bonds in biochars produced at lower pyrolysis temperatures (Yuan and Xu, 2011).

Effect of biochar on soil nutrients availability: This study indicates that increase in pyrolysis temperature shows decreasing trend in nutrient contents. The biochar produced at a temperature of 300°C had more nutrient contents (NH₄⁺-N, NO₃⁻-N, MN, and P). Furthermore, a comparison between 1 and 1.5% showed that rate of 1.5% had higher levels of MN, P and K. Nutrient levels in biochar are highly affected by temperature and duration of pyrolysis (Gaskin *et al.*, 2008; Naeem *et al.*, 2016). The highest nitrogen mineralization during incubation was showed by biochar produced at a low temperature (300°C) owing to high nitrogen (N) concentration and low C/N ratio (Table 2). The temperature during pyrolysis is directly correlated with retention of nutrients in feedstock biochar (Naeem *et al.*, 2017). Glaser *et al.* (2002) reported that condensation of aromatic structures happens in the process of pyrolysis of feedstock material at a higher temperature (>400-500°C). Additionally, it is reported by Glaser *et al.* (2002) that there is reduction of ion exchange functional groups because of decarboxylation there by mimicking nutrient retention capacity of the material. Presence of more functional groups and exchange sites after oxidation is the reason for higher nutrient retention ability of biochar produced at a lower

temperature as compared to the biochar acquired at a higher temperature (Table 2) (Wu *et al.*, 2012). Gundale and Deluca (2006) reported that the decrease in pyrolysis temperature of feedstock results in an increase of extractable NH₄⁺ concentration from the feedstock. Likewise, the decrease in pyrolysis temperature leads to increase in nitrogen (N) hydrolysable content present in biochar (Wang *et al.*, 2012). Therefore, it is possible that B300 had more eminent fraction of hydrolysable nitrogen (N) content (amino acids ammonia and amino sugars) (Wang *et al.*, 2012). Moreover, adsorption of NH₄⁺-N is caused by cation exchange capacity of biochar. As compared to control, the B300 amended soil showed a relatively slower decline in NH₄⁺-N content, primarily because of enhanced soil CEC. A significant ($p \leq 0.05$) increase in soil NO₃⁻-N content was noticed as a consequence of biochar addition (Figure 2 c, d). Furthermore, this can be because of transformation of hydrolysable N content into NH₄⁺-N and finally its conversion into NO₃⁻-N form. It has been reported that higher NO₃⁻-N concentration in the soil was achieved after application of biochar (Prendergast-Miller *et al.*, 2011). The nitrification rates in the soil are increased with the application of biochar (Ball *et al.*, 2010). Furthermore, the residence time for NO₃⁻-N in the soil can be improved as a result of weakly adsorbed NO₃⁻-N onto biochar surface (Kameyama *et al.*, 2012). Atkinson *et al.* (2010) reported that increased microbial activity, variations in soil pH and avoiding fixation of P with cations in soil might be a reason for increased level of available P. Amongst nutrients; P is most directly influenced by soil pH. Soil pH showed a significant decline after application of B300 (Fig. 1a,b). It was observed that B300 indirectly enhanced P availability and it is proven by a significant rise in P (Fig. 3a,b), perhaps because of Ca²⁺ amelioration and alteration in pH of the soil. It has been reported by Naeem *et al.* (2017) that increase in incubation period results in improvement of K contents in biochar.

Conclusions: It is concluded that the biochars produced at a low temperature (B300 and B400) caused a decline in soil pH in the range of 0.6-2.0 units compared with the control. On the other hand, all the types of biochars used in this study caused a clear increase in available P, K and SOC, CEC, mineral N, NH₄⁺-N and NO₃⁻-N contents. Incubation of soil with B300 at the rate of 1.5% reduced the soil pH and improved CEC and nutrient content (NO₃⁻-N, NH₄⁺-N, MN, and P) of soil. However, application of B500 improved the SOC and K. Hence, a practical approach to sustain soil fertility and productivity would be the use of biochar at the rate of 1.5% produced at low temperature (300°C) and this needs to be verified further in field experiments.

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