

## RESEARCH ARTICLE

# Influence of biochar on soil available nutrient contents in cropping sequence (Cotton-maize-mowpea)

■ R. Elangovan, S.R. Shri Rangasami, R. Murugaragavan and N. Chandra Sekaran

### SUMMARY

Application of biochar had significantly increased the available N, P and K contents in the post harvest soil of cotton field. However, the effect was increased with corresponding increase in the rate of application of biochar. Significantly highest values were recorded in biochar @ 10 t ha<sup>-1</sup> application. Similar trend of direct effect was also registered in the post harvest soil of maize under both the cumulative (continuous application) and residual (one time application) studies. Proving the biochar's ability in improving the soil physical, physico-chemical and chemical properties even in the succeeding maize crop soil. The application of biochar @ 10 t ha<sup>-1</sup> had increased the available N by 5.21 per cent, available P by 8.97 per cent and available K by 8.18 per cent over control. Thus, proving the biochar's ability to sustain the soil fertility status over long run.

**Key Words :** Biochar, Nitrogen, Phosphorus, Potassium, Soil nutrients, mobility

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India achieved spectacular agricultural growth since 1966. The increase in food grain production from a meager 51 million tonnes in 1950 to about 245 million tonnes in 2011-12 is a remarkable achievement unparalleled in the history of world agriculture. However, it contributes to only 14.4% of GDP and 10.23% of all exports.

Nevertheless, human ingenuity has helped us to overcome many agricultural challenges; one of the truly modern miracles is our agricultural system, which produces abundant food, fodder and fibre. High yields often come from the use of improved crop varieties, fertilizers and pest control measures, and irrigation, which have resulted in food and nutritional security. Despite

high productivity, farmers see various problems associated with our intensive agricultural systems.

Biochar can be produced by incomplete combustion of any biomass and it is a byproduct of the pyrolysis technology used for biofuel and bioenergy production. Biochar offers an opportunity for carbon sequestration, soil restoration, renewable energy production and waste reutilization. The global production of black carbon (biochar) has been estimated to be between 50 and 270 T g yr<sup>-1</sup>, with as much as 80% of this remaining as residues in the soil (Asai *et al.*, 2009).

The enhanced nutrient retention capacity of the soil not only reduces the total fertilizer requirements, but also the environmental damage associated with fertilizers, including nitrous oxide emissions, phosphorus runoff in to surface waters and nitrogen leaching in to ground water. Also been associated with increased nutrient use efficiency, either through nutrients contained in biochar or through physico-chemical processes that allow better utilization of soil-inherent or fertilizer derived nutrients importantly. It is apparent biological and chemical stability that allows biochar to both acts as carbon sink, as well as provide benefits to soil that are long – lived. Further and most importantly, biochar is relatively inert, with most of it remaining in the soil for orders of magnitudes longer than any other organic amendments.

This means that biochar offers one of the few tools available for removing carbon from the atmosphere, making it one of the only carbon negative renewable energy options at our disposal today (Lehmann, 2007). The use of biochar could allow the total soil organic carbon (SOC) sequestered in soils to be several magnitudes larger than is naturally possible. Again, it is relatively simple to verify for national carbon accounting and is more resistant to climate than the conventional SOC (Lehmann *et al.*, 2006). Carbon trading that include agricultural soil sequestration will enable farmers to trade their sequestered biochar soil applications and facilitate the expansion of a range of new technologies that improve farm productivity, energy security with potential for large positive environmental out comes. Though the practice of biochar application for agriculture is prevalent in India, the noval and scientific approach on biochar –based soil management strategies are new and have not been evaluated in the content of Indian agriculture.

Cotton - maize - pulse is a major cropping system practiced by farmers of the district of Coimbatore, Tamil Nadu, India. Cotton is considered as king of fiber in the world and India ranks first in its production with

production of 33.40 million tonnes from an area 11.61 millions hectares with the productivity of 489 kg ha<sup>-1</sup> during 2012-13. Maize, the third most important cereal crop next to wheat and rice in the world as well as in India. It is being cultivated to an extent of 8.67 million hectare with production and productivity of 21.60 million tonnes and 2492 kg ha<sup>-1</sup> respectively in the year 2012-13. Pulses play a vital role in human dietary and nutrition and it occupied 9.54 million hectares with the production of 5259.2'000 tonnes during the period 2011-12.

Maintenance of threshold level of organic matter in the soil is crucial for maintaining physical, chemical and biological integrity of the soil and also for the soil to perform its agricultural production and environmental functions. The application of biochar to the soil is proposed as a novel approach to establish a significant long term sink for atmospheric carbon dioxide in terrestrial ecosystems also to prove enhanced fertility and crop productivity, increased soil nutrients and water holding capacity, and reduced emissions of other green house gases from soils.

Biochar, a byproduct of the pyrolysis process, is biomass-derived black carbon intended for use as a soil amendment. It is analogous to charcoal manufactured through traditional or modern pyrolysis methods, and to black carbon found naturally in fire ecosystems. Biochar is used as a soil amendment to improve soil nutrient status, C storage and/or filtration of percolating soil water (Lehmann and Joseph 2009). Biochar from pyrolysis and charcoal produced through natural burning share key characteristics including long residence time in soils and a soil conditioning effect (Glaser *et al.*, 2002). Biochar has an inherent energy value which can be used to maximize the energy output of pyrolysis. However, research has shown that application of biochar to soil may be more desirable as it can increase soil organic carbon (SOC), improve the supply of nutrients to plants and there for enhance plant growth and soil physical, chemical, and biological properties (Glaser *et al.*, 2002; Lehmann *et al.*, 2003 and Rondon *et al.*, 2007). Regardless of its commercial market value, biochar presents an opportunity to return site nutrients lost from biomass removal projects, which may overshadow other potential uses.

Abebe Nigussie *et al.* (2012) reported that application of biochar on chromium polluted and unpolluted soils a significantly ( $p < 0.01$ ) increased the mean values of soil organic C and total N. The highest values of organic carbon and total nitrogen were observed

in soils amended with 10 t ha<sup>-1</sup> maize stalk biochar. The increase in organic carbon and total nitrogen due to addition of biochar could be resulted from the presence of high amount of carbon and nitrogen in the maize stalk. The highest values of organic carbon at biochar treated soils indicate the recalcitrance of C-organic in biochar. High organic carbon in soils treated with biochar has been also been reported by Lehmann (2007), Solomon *et al.* (2007) and Liang *et al.* (2006).

Tryon (1948) investigated the effect of biochar addition on available moisture in brown podzolic forest soils of three different textures - sandy, loamy and clayey. In this study, it was found that biochar addition may be ill-suited to soils that have high clay content (unless perhaps they are waterlogged) soil and useful tool in the reversal of desertification to sandy soils.

Lehmann *et al.* (2006) opined that conversion of biomass carbon leads to sequestration of about 50 per cent of the initial carbon compared to the low amounts retained after burning (3 %) and biological decomposition (<10 - 20% after 5- 10 years), therefore yielding more stable soil carbon than burning or direct land application of biomass. This efficiency of carbon conversion of biomass to biochar is highly dependent on the type of feedstock, but it is not significantly affected by the pyrolysis temperature (within 350 - 500° C). It also revealed that upto 12 per cent of the total anthropogenic carbon emissions by land use change (0.21 Pg C) can be offset annually in the soil. Agricultural and forestry wastes such as forest residues, mill residues, field crop residues or urban wastes add a conservatively estimated 0.16 Pg C Yr<sup>-1</sup>. The application of biochar to soil can deliver tradable carbon emissions reduction and the carbon sequestered and easily accountable.

### Nutrients retention and availability :

Higher nutrient availability for plants is the result of both the direct nutrient additions by the biochar and greater nutrient retention. Longer-term benefits for nutrient availability include a greater stabilization of organic matter, concurrent slower nutrient release from added organic matter and better retention of all cations due to a greater CEC (Lehmann *et al.*, 2003a).

Biochar is a high surface area, highly porous, variable charge organic material that has the potential to increase soil water-holding capacity, cation exchange capacity, surface sorption capacity and base saturation when added to soil (Glaser *et al.*, 2002; Bélanger *et al.*, 2004; Keech *et al.*, 2005 and Liang *et al.*, 2006). Also

biochar additions to soil have the potential to alter soil microbial populations and shift functional groups in soil organic compounds (Pietikäinen *et al.*, 2000). The broad array of beneficial properties associated with biochar additions to soil may function alone or in combination in order to influence nutrient transformations. Application of bark charcoal induced changes in soil chemical properties *viz.*, increasing the pH, total N and available P<sub>2</sub>O<sub>5</sub>, cation exchange capacity, amounts of exchangeable cations and base saturation and decrease in the content of exchangeable Al<sup>3+</sup> (Yamato *et al.*, 2006).

Glaser *et al.* (2002), Lehmann and Lehmann and Rondon (2005) reported that when biochar is applied to soil it helps to retain the nutrients which remain available to plants thus increasing the plant growth and yield; by contrast the response to effluent with the charcoal amender was linear with maximum yield requiring 100 kg N ha<sup>-1</sup>. On the un-amended soil there was no relationship between effluent level and biomass yield.

In contrast to other organic matter in soil, biochar also appears to be able to strongly adsorb phosphate, even though it is an anion (Lehmann *et al.*, 2005), although the mechanism for this process is not fully understood. These properties make biochar a unique substance, retaining exchangeable and therefore plant available nutrients in the soil and offering the possibility of improving crop yields while decreasing environmental pollution by nutrients. Addition of biochar to soil has shown definite increases in the availability of P and N concentrations (Glaser *et al.*, 2002). High rates of biochar addition in the tropical environment have been associated with increased plant uptake of P, K, Ca Zn and Cu (Lehmann and Rondon, 2006).

Lehmann (2007) provided that biochar is biologically stable, the benefit of higher CEC may be obtained without the risk of contributing to seasonal flushes of NO<sub>3</sub>. A beneficial impact of biochar on the plant-available P has been observed in soils enriched with biochar, which in contrast to NH<sub>4</sub>, is not a characteristics generally associated with soil organic matter, in the context of nutrient availability, the impact of biochar addition on pH may be important (Steiner *et al.*, 2007). Both CEC and pH are also frequently increased up to 40% of initial CEC and pH unit, respectively (Tryon, 1948).

Mbagwu and Piccolo (1997) reported that biochars also have been shown to have an extreme affinity for essential plant nutrients (Sanchez *et al.*, 2009) that can provide a slow release mechanism. The yields of annual crops such as maize (*Zea mays* L.) on Nigerian Alfisols

and Inceptisols with the application of charcoal caused an increase of soil pH that resulted in greater micro-nutrient availability and decreased deficiencies.

#### Nutrients mobility :

Biochar directly contributes to nutrient adsorption through charge or covalent interactions. Glaser *et al.* (2002) concluded that 'charcoal may contribute to an increase in ion retention of soil and a decrease in leaching of dissolved OM and organic nutrients' as they found higher nutrient retention and nutrient availability after charcoal additions to tropical soil. A possible contributing mechanism to increased N retention in soils amended with biochar is the stimulation of microbial immobilization of N and increased nitrates recycling back due to higher availability of carbon. Lehmann *et al.* (2003) reported on lysimeter experiments that the ratio of uptake to leaching for all nutrients increases with charcoal application to the soil. Therefore, nutrients must have been retained on electrostatic adsorption complexes created by the charcoal. Similarly, Steiner (2004) attributed decreased leaching rates of applied mineral fertilizer N in soils amended with charcoal to increased nutrient use efficiency. Lehmann *et al.* (2003) reported that cumulative leaching of mineral N, K, Ca and Mg was lower compared to that in unfertilized experiment effect of biochar on soil biological properties. A change in the balance of microbial activity between different functional groups could benefit crop nutrition, specifically enhancement of mycorrhizal fungi and this could feed back into higher net primary productivity and carbon input Ishii and Kadoy (1994). Biochar retains nutrients in the rooting zone and it reduces nutrient leaching through the soil profile (Ding *et al.*, 2010 and Laird *et al.*, 2010).

Chan *et al.* (2008) showed that the biochar helps to retain the applied N and avoids N leaching, thus enhancing the soil N availability leads to enhanced yield. Significant additional yield increases, in excess of that due to N fertiliser alone were observed when N fertiliser was applied together with the biochar, highlighting the other beneficial effects of their biochar.

He *et al.* (2000) found a substantial reduction in the P mobility of animal manures when directly pyrolysing manures that need to be disposed off, but could presumably also convert the soluble inorganic phosphate contained in manure into adsorbed phosphate in biochar. There may be a downside to this if the available phosphate pool (usually in soluble inorganic phosphate form) becomes less available for crop uptake since it will be

adsorbed on to biochar.

Silber *et al.* (2010) indicated that rapid and constant rate P releases were significant, having the potential to substitute substantial proportions of P fertilizer and K releases were also significant and may replace conventional K fertilizers. Since native soil organic constituents have much higher CEC values average 2800 m mol. (kg C<sup>-1</sup>) at pH 7, improved soil fertility as a result of enhanced cation retention by the biochar probably will be favourable only in sandy and low organic matter soils, unless surface oxidation during aging significantly increases its CEC.

#### Biochar as soil nutrients :

Fertilizers have a definite place in soil fertility management, and more so from the point of sustaining soil organic carbon. Santhy *et al.* (2001) reported that the organic carbon content in *Vertic Ustrophept* soil increased with NPK doses and the highest organic carbon contents was observed in plots receiving 100 per cent NPK + FYM @ 10 t ha<sup>-1</sup>. The relative increase in organic carbon due to FYM can be attributed largely to increase the return of organic materials in the form of crop residues.

The availability of plant nutrients are strongly related to the properties of soil. The high content of organic carbon and cation exchange capacity (CEC) confer upon the soil, the capacity to hold the essential plant nutrients in sufficient amounts so as to provide the nutrient requirement of the crops. The increased organic carbon and CEC could be made possible through effective management of soils. Inclusion of organic materials such as biochar found to bring about changes in nutrient availability. Biochar being a component of soil organic carbon with high CEC and organic carbon content provides information on the nutrient fixation and release through ion exchange reaction besides acting as a nutrient reservoir.

Biochar application has resulted in increased nutrient availability in soils and increased nutrient uptake in plants (Hossain *et al.*, 2010 and Novak *et al.*, 2009). However, very few studies have attempted to isolate biochar effects on increasing nutrient availability (*i.e.*, increasing fertiliser use efficiency) from the nutrient additions concomitant with biochar application.

Liang *et al.* (2006) observed that the applied biochar and organic matter sorbed on to them contributed to the greater surface charge of terra preta soils when compared to adjacent unmodified soils. Lehmann *et al.*

(2006) reported that black carbon can produce significant benefits when applied to agricultural soils in combination with some fertilizers. Apart from positive effects in both reducing emissions and increasing the sequestration of greenhouse gases, the production of biochar and its application to the soil will deliver immediate benefits through improved soil fertility and increased crop production.

In recent years the field experiments revealed that greater soil CEC with biochar additions and nutrients remain to plants (Yamato *et al.*, 2006 and Peng *et al.*, 2011). Sellamuthu (2002) revealed that soil application of lignite humic acid increased the level of soil organic carbon, CEC and available status of macro and micro nutrients in soils of sugarcane. It also involved in major role for improving soil characteristics and nutrient availability, besides producing good quality crops especially in the presence of inorganics, organics and bio inoculants.

Afeng Zhang *et al.* (2011) reported that application of biochar to calcareous and infertile dry crop lands poor in soil organic carbon will enhance crop productivity and reduce GHGs emissions. Peng *et al.* (2011) reported that amendment of 1 per cent biochar increased pH by 0.1 - 0.46 ( $P < 0.01$ ) and CEC by 3.9 -17.3 per cent ( $P < 0.05$ ), but had no effect on aggregate stability.

Uzoma *et al.* (2011) reported that application of cow manure biochar improved the field-saturated hydraulic conductivity of the sandy soil, as a result net WUE also increased. Results of the soil analysis after the harvesting indicated significant increase in the pH, total C, total N, Olsen-P, exchangeable cations and cation exchange capacity. The results of this study indicated that application of cow manure biochar to sandy soil is not only beneficial for crop growth but it also significantly improved the physico-chemical properties of the coarse soil.

Tryon (1948) reported that nitrogen is the most sensitive to heating process thus the nitrogen content is low in biochar. Therefore, biochar is more important as a soil conditioner and a driver of nutrient transformations and less so as a primary source of nutrients (Glaser *et al.*, 2002 and Lehmann *et al.*, 2003).

Combined application of organics and NPK fertilizers enhanced the availability of  $\text{KMnO}_4$ -N, Olsen - P and  $\text{NH}_4\text{OAc}$ -K significantly in soil both during rhizome development stage (180 days after planting) and at harvest as compared to the addition of NPK fertilizers

in turmeric. The improvement in the availability of plant nutrients in the soil could be attributed to the release of nutrients from the native pool as well as from the manures (Selvakumari and Baskar, 1998). Sohi *et al.* (2009) observed that application of biochar increasing growth and nutrient supply especially nitrogen, as a determinant of plant growth response to soil amendment with biochar.

Allen *et al.* (2003) found that biochar addition did not appear to limit N availability in the soils because shoot biomass in biochar-only treatments was equal to, or better than, the controls or treatment receiving only fertilizer N. Seedling ECM are proficient at acquiring N and most likely not negatively impacted via competition with saprotrophic microflora for mineral N or organic sources of N. Biochar induced transformation of soil N may also differ between agricultural and forest soils. For example conifer forest soil had the greatest total extractable N following high rates of biochar addition, whereas temperate arable soils exhibited reductions in extractable N with increasing rates of biochar addition. Increased net N mineralization in black carbon-treated forest soils has been attributed to declines in inhibitory phenolic compounds or due to increased sorption of available C (DeLuca *et al.*, 2002, 2006 and Berglund *et al.*, 2004).

Robert Quirk and Paul Taylor (2010) showed that the trash biochar had high level of available phosphorus (P) and potassium (K). Since the biochar yield from trash is 33.6, which indicate 100 per cent retention of potassium in trash biochar, which is thus available for recycling back in to soil with almost 100 per cent efficiency. The ash in biochar contains plant nutrient, mostly bases such as Ca, Mg and K but also P and micronutrients including zinc and manganese (Novak *et al.*, 2009 and Gaskin *et al.*, 2010).

Lehmann *et al.* (2003) reported that biochar had the most significant effects on the availability of Ca and Mg, as well as Sr which was applied with fertilizer. Sanchez Monedero *et al.* (2004) also reported that application of biochar could also be attributed to strong adsorption of Cu to biochar particles as confirmed by the sorption data. Rondon *et al.* (2007) attributed that the greater contribution of N derived from the atmosphere with biochar. Major (2009) reported that the low increase in CEC, Ca and Mg uptake by crops were greater and leaching lower with biochar and also the greater crop yield and nutrient uptake primarily to the 77 – 320 per cent greater available Ca and Mg in soil where biochar was applied.

## MATERIAL AND METHODS

The available nitrogen, phosphorus and potassium content were studied in cotton-maize-cowpea cropping sequence.

### Effects of biochar on soil :

*Analysis of available nutrient in soil samples :*

Soil samples collected from different field experiments were air dried, broken with wooden mallet and sieved through 2 mm sieve (0.2 mm for organic carbon), labeled and stored in cloth bags. Simultaneously undisturbed core sample were also taken for assessing soil physical parameters. The initial composite soil sample collected before initiating experiment was analyzed for various physical, physico-chemical and chemical properties and fertility status of the soil. The pre-sowing and the post-harvest soil samples (both disturbed bulk samples and undisturbed core samples) collected from the direct, cumulative, residual, cumulative residual and second residual trials were analyzed for soil available N, P and K contents by adopting standard procedures (Table 1).

## RESULTS AND DISCUSSION

The results obtained from the present investigation as well as relevant discussion have been summarized under following heads :

### Effect of biochar in post harvest soil of cotton :

*Soil available nutrients :*

Available nitrogen (Table 2) :

The application of different NPK and biochar levels

and their interactions significantly influenced the available nitrogen status in post harvest soil of cotton.

Among the NPK levels, the maximum mean available N of 235.0 kg ha<sup>-1</sup> was recorded at 100 % NPK + FYM and the minimum (222.6 kg ha<sup>-1</sup>) and was in control. Among the biochar levels, the available N increased with increasing levels and biochar @ 10.0 t ha<sup>-1</sup> recorded 237.7 kg N ha<sup>-1</sup> which was at par with biochar @ 7.5 t ha<sup>-1</sup> (234.0 kg N ha<sup>-1</sup>). The lowest value was recorded in the control (220.8 kg N ha<sup>-1</sup>) followed by biochar @ 2.5 t ha<sup>-1</sup> (226.7 kg N ha<sup>-1</sup>). Regarding the interaction between fertilizer and biochar levels, application of biochar @ 10 t + 100 % NPK + FYM recorded significantly highest value of 243.6 kg N ha<sup>-1</sup> and was on par with biochar @ 10 t + 75 % NPK + FYM (240.2 kg N ha<sup>-1</sup>).

The available nitrogen was conspicuously increased by about nine per cent due to the application of biochar @ 10 t ha<sup>-1</sup> over the unamended control. Both FYM and fertilizers along with biochar at all the levels enhanced the available nitrogen content in post harvest cotton soil. The higher nutrient availability for plants could be due to the result of both the direct nutrient additions by the biochar and greater nutrient retention. Since, biochar has high surface area, highly porous, variable charge organic material that has the potential to increase soil water-holding capacity, cation exchange capacity, surface sorption capacity and base saturation when added to soil. Also biochar additions to soil have the potential to alter soil microbial populations and shift functional groups in soil organic compounds. Similar findings were reported

**Table 1 : Standard procedures for soil analysis**

Sr. No.	Estimation	Author	Method/No. Extractant
1.	Available nitrogen	Subbiah and Asija (1956)	Alkaline permanganate method
2.	Available phosphorus	Olsen <i>et al.</i> (1954)	0.5 M NaHCO <sub>3</sub> extract method
3.	Available potassium	Stanford and English (1949)	N.N.NH <sub>4</sub> OAC extract method

**Table 2 : Effect of treatment on soil available nitrogen (Kg ha<sup>-1</sup>) in post harvest soil of cotton (Mean of three values)**

Rec. fertilizers (kg ha <sup>-1</sup> )	Biochar levels (t ha <sup>-1</sup> )					Mean
	B <sub>1</sub> Control	B <sub>2</sub> B @ 2.5	B <sub>3</sub> B @ 5.0	B <sub>4</sub> B @ 7.5	B <sub>5</sub> B @ 10.0	
F <sub>1</sub> (Control)	213.3	218.5	222.2	227.4	231.6	222.6
F <sub>2</sub> (100%)	221.2	227.4	231.3	233.6	235.5	229.8
F <sub>3</sub> (100% + FYM)	225.3	231.4	236.5	238.2	243.6	235.0
F <sub>4</sub> (75% + FYM)	223.4	229.5	234.3	236.6	240.2	232.8
Mean	220.8	226.7	231.1	234.0	237.7	
	F	B	F at B	B at F		
S.E.±	2.56	3.02	5.97	6.03		
C.D. (P=0.05)	6.27	6.14	12.61	12.28		

by Lehmann *et al.* (2003a), Keech *et al.* (2005), Liang *et al.* (2006), Lehmann (2007) and Sohi *et al.* (2009). Furthermore, this has been attributed to a high content of easily decomposable cellulose present in the FYM, which forms a readily available energy source for microorganisms to multiply and immobilize nitrogen. And also, the addition of fertilizer nitrogen could have reduced the loss of N, through immobilization of N or formation of ammonia complexes with the inorganic constituents of fertilizer nitrogen (Singh, 1987) which might be the reason for high content of available N in biochar @ 10 t + 100% NPK + FYM treatment.

Available phosphorus (Table 3) :

The results of available phosphorus revealed that the application of different fertilizer and biochar levels and their interactions had a significant influence in post harvest soil of cotton.

With regard to the NPK levels, the maximum mean available phosphorus (17.69 kg ha<sup>-1</sup>) was recorded in 100 % NPK + FYM and the minimum mean of 16.41 kg ha<sup>-1</sup> and was in control. In the biochar levels, the incorporation of biochar @ 10.0 t ha<sup>-1</sup> resulted in the

highest availability of 18.17 kg of P ha<sup>-1</sup> and the least was recorded in control (16.00 kg ha<sup>-1</sup>). An increase in the levels of biochar increased the availability of P as in the case of available nitrogen. Among the interaction between fertilizer and biochar levels, application of biochar @ 10 t + 100% NPK + FYM recorded significantly maximum value of 18.75 kg P ha<sup>-1</sup> which was at par with biochar @ 10 t + 75 % NPK + FYM (18.44 kg P ha<sup>-1</sup>). A significant improvement in the status of available phosphorus was observed due to the application of biochar alone and biochar along with fertilizers and FYM treatments irrespective of biochar levels. The adsorption of both organic and inorganic compounds by biochar in soil environments alters the surface properties of the biochar (Liang *et al.*, 2006). Complexation of polyvalent metal cations by carboxylate and/or other oxygen-containing surface functional groups of biochar can transform a surface charge site from negative to positive, effectively creating anion exchange sites. Thus, increase the P availability. Steiner *et al.* (2007) also reported beneficial impact of biochar on the plant-available P in soils enriched with biochar, which in contrast to NH<sub>4</sub>, is not a characteristics generally associated with soil

Rec. fertilizers (kg ha <sup>-1</sup> )	Biochar levels (t ha <sup>-1</sup> )					Mean
	B <sub>1</sub> Control	B <sub>2</sub> B @ 2.5	B <sub>3</sub> B @ 5.0	B <sub>4</sub> B @ 7.5	B <sub>5</sub> B @ 10.0	
F <sub>1</sub> (Control)	15.21	15.83	16.54	17.02	17.45	16.41
F <sub>2</sub> (100%)	15.92	16.54	17.21	17.73	18.05	17.09
F <sub>3</sub> (100% + FYM)	16.53	16.84	17.91	18.42	18.75	17.69
F <sub>4</sub> (75% + FYM)	16.32	16.73	17.65	18.21	18.44	17.47
Mean	16.00	16.49	17.33	17.85	18.17	
	F	B	F at B	B at F		
S.E.±	0.19	0.23	0.45	0.45		
C.D. (P=0.05)	0.47	0.46	0.94	0.92		

Rec. fertilizers (kg ha <sup>-1</sup> )	Biochar levels (t ha <sup>-1</sup> )					Mean
	B <sub>1</sub> Control	B <sub>2</sub> B @ 2.5	B <sub>3</sub> B @ 5.0	B <sub>4</sub> B @ 7.5	B <sub>5</sub> B @ 10.0	
F <sub>1</sub> (Control)	286.2	290.3	293.4	297.5	300.6	293.6
F <sub>2</sub> (100%)	289.7	292.5	296.6	300.4	302.5	296.3
F <sub>3</sub> (100% + FYM)	295.5	297.6	301.4	304.9	307.2	301.3
F <sub>4</sub> (75% + FYM)	292.5	295.4	299.2	304.1	305.6	299.4
Mean	291.0	294.0	297.7	301.7	304.0	
	F	B	F at B	B at F		
S.E.±	3.32	3.90	7.72	7.80		
C.D. (P=0.05)	NS	7.94	16.32	15.88		

NS= Non-significant

organic matter, in the context of nutrient availability, the impact of biochar addition on pH may be important. The increase in pH and CEC increased the availability of P in the soil. Similar trend of result was also observed by Tryon (1948) and Glaser *et al.* (2002). Further, the addition of manures with biochar might have increased the solubilization of phosphate due to decomposition processes of easily degradable portion of FYM might have reduced the binding energy and phosphorus sorption capacity of the manure, favouring higher available P content in the soil. It is also evident from the results that the application of biochar along with fertilizers and

manures (biochar @ 10 t + 100% NPK + FYM) had further increased the available phosphorus contents of soil which might be ascribed to the availability of phosphorus from fertilizer source and increased biological activity.

Available potassium (Table 4) :

The application of different NPK and biochar levels and their interactions significantly affected the available potassium status in post harvest soil of cotton.

Among the NPK levels, the maximum mean available K (301.3 kg ha<sup>-1</sup>) was recorded at 100 % NPK

**Table 5 : Residual and cumulative effect of treatments on available nutrients status in post harvest soil of maize (Mean of three values)**

Rec. fertilizers (kg ha <sup>-1</sup> )	Biochar Levels (t ha <sup>-1</sup> )											
	B <sub>1</sub> Control	B <sub>2</sub> B @ 2.5	B <sub>3</sub> B @ 5.0	B <sub>4</sub> B @ 7.5	B <sub>5</sub> B @ 10.0	Mean	B <sub>1</sub> Control	B <sub>2</sub> B @ 2.5	B <sub>3</sub> B @ 5.0	B <sub>4</sub> B @ 7.5	B <sub>5</sub> B @ 10.0	Mean
Available nitrogen (Kg ha <sup>-1</sup> )												
	Biochar Residual						Biochar Cumulative					
F <sub>1</sub> (Control)	199.5	205.5	210.6	215.5	221.4	210.5	199.5	220.6	225.1	231.4	237.3	222.8
F <sub>2</sub> (100%)	205.2	216.8	221.5	226.7	231.4	220.3	205.2	231.4	236.4	242.1	246.2	232.3
F <sub>3</sub> (100% + FYM)	208.8	219.2	224.6	229.4	234.5	223.3	208.8	234.6	239.4	244.4	249.3	235.3
F <sub>4</sub> (75% + FYM)	206.6	217.3	222.4	227.6	232.7	221.3	206.6	232.8	237.5	242.3	247.4	233.3
Mean	205.0	214.7	219.8	224.8	230.0		205.0	229.9	234.6	240.1	245.1	
	F	B	F at B	B at F				F	B	F at B	B at F	
S.E.±	2.46	2.87	5.69	5.73				2.65	3.04	6.04	6.07	
C.D. (P=0.05%)	6.02	5.84	12.02	11.68				6.48	6.18	12.78	12.37	
Available phosphorus (Kg ha <sup>-1</sup> )												
	Biochar Residual						Biochar Cumulative					
F <sub>1</sub> (Control)	14.42	14.75	15.16	15.57	15.96	15.17	14.42	15.65	16.88	18.01	19.22	16.84
F <sub>2</sub> (100%)	15.13	15.44	15.85	16.26	16.64	15.86	15.13	16.32	17.52	18.74	19.95	17.53
F <sub>3</sub> (100% + FYM)	15.68	16.01	16.46	16.84	17.21	16.44	15.68	16.86	18.02	19.28	20.49	18.07
F <sub>4</sub> (75% + FYM)	15.49	15.77	16.16	16.57	16.96	16.19	15.49	16.72	17.95	19.18	19.36	17.74
Mean	15.18	15.49	15.91	16.31	16.69		15.18	16.39	17.59	18.80	19.76	
	F	B	F at B	B at F				F	B	F at B	B at F	
S.E.±	0.178	0.209	0.413	0.417				0.206	0.230	0.460	0.461	
C.D. (P=0.05%)	0.436	0.425	0.873	0.850				0.503	0.469	0.975	0.938	
Available potassium (Kg ha <sup>-1</sup> )												
	Biochar Residual						Biochar Cumulative					
F <sub>1</sub> (Control)	264.5	269.2	274.2	279.2	284.2	274.3	264.5	275.6	286.3	297.1	308.2	286.3
F <sub>2</sub> (100%)	276.5	281.5	286.5	292.1	297.4	286.8	276.5	288.2	299.5	309.4	320.2	298.8
F <sub>3</sub> (100% + FYM)	280.4	285.3	290.4	295.4	300.2	290.3	280.4	302.5	304.5	313.6	324.5	305.1
F <sub>4</sub> (75% + FYM)	278.2	283.3	288.4	293.2	298.4	288.3	278.2	300.3	302.4	311.2	316.3	301.7
Mean	274.9	279.8	284.9	290.0	295.1		274.9	291.7	298.2	307.8	317.3	
	F	B	F at B	B at F				F	B	F at B	B at F	
S.E.±	3.18	3.73	7.40	7.46				3.38	3.90	7.76	7.81	
C.D. (P=0.05%)	7.79	7.60	15.63	15.20				8.26	7.95	16.41	15.91	

+ FYM and the minimum mean (293.6 kg ha<sup>-1</sup>) was in control. In the biochar levels, application of biochar increased available K significantly and registered available K as 304.0, 301.7, 297.7, 294.0 and 291.0 kg ha<sup>-1</sup> for 10.0, 7.5, 5.0, 2.5 t ha<sup>-1</sup> biochar levels and control respectively. Significant increase in available K was registered with the increasing levels of biochar. Among the interaction between fertilizer and biochar levels, application of biochar @ 10 t+100 % NPK + FYM (307.2 kg K ha<sup>-1</sup>) and biochar @10 t + 75 % NPK + FYM (305.6 kg K ha<sup>-1</sup>) were found to be on par.

The status of available potassium was also found to be favourably influenced by biochar addition. Lehmann and Rondon (2006) also observed that high rates of biochar addition in the tropical environment have been associated with increased plant uptake of P, K, Ca Zn and Cu. This might be due to the biochar was made by pyrolysis process and contained at least 0.3 per cent of ash and their application to soils registered an increase in availability of K. The effect of biochar with fertilizers and organic manures was highly significant at all levels of biochar wherein the highest available potassium

**Table 6 : Second residual and cumulative residual effect of treatments on available nutrients content in post harvest soil of cowpea (Mean of three values)**

Rec. fertilizers (kg ha <sup>-1</sup> )	Biochar levels (t ha <sup>-1</sup> )											
	B <sub>1</sub> Control	B <sub>2</sub> B @ 2.5	B <sub>3</sub> B @ 5.0	B <sub>4</sub> B @ 7.5	B <sub>5</sub> B @ 10.0	Mean	B <sub>1</sub> Control	B <sub>2</sub> B @ 2.5	B <sub>3</sub> B @ 5.0	B <sub>4</sub> B @ 7.5	B <sub>5</sub> B @ 10.0	Mean
Available nitrogen (Kg ha <sup>-1</sup> )						Available phosphorus (Kg ha <sup>-1</sup> )						
	Biochar II <sup>nd</sup> Residual						Cumulative Biochar residual					
F <sub>1</sub> (Control)	182.5	184.8	187.1	189.4	192.0	187.2	182.5	203.4	220.4	223.3	232.4	212.4
F <sub>2</sub> (100%)	191.4	193.8	198.2	200.1	203.1	197.3	191.4	222.3	225.6	233.3	237.2	222.0
F <sub>3</sub> (100% + FYM)	205.6	208.6	213.8	216.2	219.1	212.7	205.6	225.5	228.4	234.4	238.8	226.5
F <sub>4</sub> (75% + FYM)	201.2	203.4	208.7	211.4	214.3	207.8	201.2	223.4	226.7	233.4	236.4	224.2
Mean	195.2	197.7	202.0	204.3	207.1		195.2	218.7	225.3	231.1	236.2	
	F	B	F at B	B at F				F	B	F at B	B at F	
S.E.±	2.18	2.65	5.22	5.30				2.54	2.90	5.78	5.80	
C.D. (P=0.05%)	5.33	5.40	11.00	10.79				6.22	5.91	12.23	11.82	
	Biochar II <sup>nd</sup> Residual						Cumulative Biochar residual					
F <sub>1</sub> (Control)	13.05	13.32	13.64	13.95	14.22	13.64	12.05	14.55	15.76	16.95	18.15	15.49
F <sub>2</sub> (100%)	14.05	14.35	14.69	14.94	15.25	14.66	13.05	15.23	16.41	17.63	18.82	16.23
F <sub>3</sub> (100% + FYM)	14.78	15.05	15.40	15.69	16.02	15.39	13.78	15.76	17.00	18.14	19.35	16.81
F <sub>4</sub> (75% + FYM)	14.56	14.85	15.16	15.44	15.78	15.16	13.56	15.68	16.87	18.09	18.24	16.49
Mean	14.11	14.39	14.72	15.01	15.32		13.11	15.31	16.51	17.70	18.64	
	F	B	F at B	B at F				F	B	F at B	B at F	
S.E.±	0.162	0.193	0.381	0.386				0.193	0.214	0.429	0.428	
C.D. (P=0.05%)	0.396	0.393	0.805	0.787				0.473	0.436	0.909	0.871	
	Biochar II <sup>nd</sup> Residual						Cumulative Biochar residual					
F <sub>1</sub> (Control)	250.5	255.5	260.8	266.2	271.0	260.8	240.5	269.4	280.6	290.5	302.2	276.6
F <sub>2</sub> (100%)	261.4	266.6	271.6	277.5	282.8	272.0	251.4	282.5	293.3	303.4	315.2	289.2
F <sub>3</sub> (100% + FYM)	264.6	269.6	274.2	280.5	286.6	275.1	254.6	297.1	300.2	308.8	316.6	295.5
F <sub>4</sub> (75% + FYM)	262.7	267.4	272.6	277.4	274.3	270.9	252.7	294.4	297.2	300.3	311.1	291.1
Mean	259.8	264.8	269.8	275.4	278.7		249.8	285.9	292.8	300.8	311.3	
	F	B	F at B	B at F				F	B	F at B	B at F	
S.E.±	3.01	3.52	6.99	7.05				3.33	3.79	7.55	7.57	
C.D. (P=0.05%)	7.38	7.18	14.77	14.36				8.14	7.71	15.97	15.42	

content was recorded by the biochar @ 10 t + 100 % NPK + FYM treatment which was at par with biochar @ 10 t + 75 % NPK + FYM treatment. The present findings corroborated with the findings of Oguntunde *et al.* (2004), Lehmann and Rondon (2006) and Rondon *et al.* (2007).

Literature on the effect of biochar addition on nutrient availability is too voluminous; nevertheless, there is close agreement with findings of Chan *et al.* (2008), Silber (2010), Ding *et al.* (2010) and Laird *et al.* (2010).

#### *Effect of biochar in post harvest soil of maize*

##### *Soil available nutrients :*

##### Available nitrogen (Table 5) :

The application of different levels of fertilizers and biochar and their interactions significantly influenced the available nitrogen status at harvest in both the studies.

Among the biochar levels, the highest mean available N of 230.0 and 245.1 kg ha<sup>-1</sup> was recorded at biochar @ 10.0 t ha<sup>-1</sup> in residual and cumulative studies respectively. Among the fertilizers levels, the maximum mean available N of 223.3 and 235.3 kg ha<sup>-1</sup> was recorded at 100 % NPK + FYM and the minimum (210.5 and 222.8 kg ha<sup>-1</sup>) was at control. Regarding the interaction between fertilizers and biochar levels, the available N was higher (234.5 and 249.3 kg ha<sup>-1</sup>) in the treatment with biochar @ 10 t + 100 % NPK + FYM in both the studies and the lowest was at control with 195.5 kg ha<sup>-1</sup> respectively. The treatments biochar @ 10 t + 100 % NPK + FYM and biochar @ 10 t + 75 % NPK + FYM were found statistically on par with each other in both the studies. Compared to residual study the cumulative study mean available N was marginally higher.

##### Available phosphorus (Table 5) :

The results revealed that the application of different fertilizers and biochar levels and their interactions had a significant influence on the available phosphorus status in both the studies at post harvest stage of maize.

In the biochar levels, the highest mean available P of 16.69 and 19.76 kg ha<sup>-1</sup> was recorded in biochar @ 10.0 t ha<sup>-1</sup> in residual and cumulative studies, respectively and which was at par with biochar @ 7.5 t ha<sup>-1</sup> treatment. With regard to the fertilizer levels, the maximum mean available P (16.44 and 18.07 kg ha<sup>-1</sup>) was recorded at 100 % NPK + FYM with the minimum mean available P of 15.17 and 16.84 kg ha<sup>-1</sup> and was at control. Among the interaction between fertilizers and biochar levels, the available P was higher (17.21 and 20.49 kg ha<sup>-1</sup>) in

biochar @ 10 t + 100 % NPK + FYM in both the residual and cumulative studies, respectively and which was at par with biochar @ 10 t + 75 % NPK + FYM treatment and the lowest (14.42 kg ha<sup>-1</sup>) at control in the both the studies. Compared to residual study the cumulative study soil available phosphorus status was marginally higher.

##### Available potassium (Table 5) :

Irrespective of the studies, the application of different levels of fertilizers and biochar and their interactions significantly affected the available potassium status in post harvest soil of maize.

Among the biochar levels, the maximum mean available K (295.1 and 317.3 kg ha<sup>-1</sup>) was recorded at biochar @ 10.0 t ha<sup>-1</sup> in residual and cumulative studies respectively with the minimum mean available K of 274.9 kg ha<sup>-1</sup> was at control in both the studies. In the fertilizer levels, the highest mean available K of 290.3 and 305.1 kg ha<sup>-1</sup> was recorded at 100 % NPK + FYM. Among the interaction between fertilizers and biochar levels the available K was the highest (300.2 and 324.5 kg ha<sup>-1</sup>) in biochar @ 10 t + 100 % NPK + FYM in both the residual and cumulative studies respectively and which was at par with biochar @ 10 t + 75 % NPK + FYM treatment. Compared to residual study the available K of the post harvest soil was slightly higher in cumulative study.

In tune with direct effect, the available nutrients contents of post harvest soil of maize were also positively influenced by different levels of biochar application under both cumulative and residual studies. Significant improvement in the available N, P and K status at post harvest soil of maize was evidenced with the conjoint application of biochar with fertilizers and FYM (biochar @ 10 t + 100 % NPK + FYM) under both the studies. The treatments received fertilizers which could have resulted in increase in available nutrients status of soil might be due to the residual effect of added fertilizers. The effect was further improved with the application of FYM, which had not only increased the buildup of nutrients of the soil but also the ability of the soil to sustain the fertility status over long run. This result is consistent with the results of Sukartono *et al.* (2011) confirmed that higher nutrient concentrations of biochar and cattle manure treated plots compared to control is suggestive of the positive contribution of organic amendments to improve soil nutrient availability. However, to sustain these positive effects, cattle manure should be applied for every planting season, whereas a direct application of biochar can maintain these positive attributes for a

longer period of time revealed by Islami *et al.* (2011). Among the studies cumulative study found to register significantly higher available nutrients than residual study.

### **Cumulative residual and second residual effect of biochar in post harvest soil of cowpea :**

#### *Soil available nutrients :*

Available nitrogen (Table 6) :

The residual effect of application of different fertilizers and biochar levels and their interactions significantly influenced the available nitrogen status at post harvest stage of cowpea in both the second residual and cumulative residual studies, respectively.

Among the biochar levels, significantly highest mean available N of 207.1 and 236.2 kg ha<sup>-1</sup> was recorded at biochar @ 10.0 t ha<sup>-1</sup> in second residual and cumulative residual studies, respectively. Among the fertilizers levels, the significantly maximum mean available N of 212.7 and 226.5 kg ha<sup>-1</sup> was recorded at 100 % NPK + FYM and the minimum (187.2 and 212.4 kg ha<sup>-1</sup>) was at control. Regarding the interaction between fertilizers and biochar levels, the available N was higher (219.1 and 238.8 kg ha<sup>-1</sup>) in the treatment with biochar @ 10 t + 100 % NPK + FYM in both the studies and the lowest was at control with 182.5 kg ha<sup>-1</sup> respectively. The treatments biochar @ 10 t + 100 % NPK + FYM and biochar @ 10 t + 75 % NPK + FYM were found statistically on par with each other in both the studies. Compared to second residual study the cumulative residual study mean available N was marginally higher.

Available phosphorus (Table 6) :

The results revealed that the residual effect of application of different fertilizers and biochar levels and their interactions had a significant influence on the available phosphorus status in both the studies at post harvest stage of cowpea.

In the biochar levels, the highest mean available P of 15.32 and 18.64 kg ha<sup>-1</sup> was recorded in biochar @ 10.0 t ha<sup>-1</sup> in second residual and cumulative residual studies respectively. With regard to the residual effect of fertilizer levels, the maximum mean available P (15.39 and 16.81 kg ha<sup>-1</sup>) was recorded at 100 % NPK + FYM with the minimum mean available P of 13.64 and 15.49 kg ha<sup>-1</sup> was at control. Among the interaction between fertilizers and biochar levels the available P was higher (16.02 and 19.35 kg ha<sup>-1</sup>) in biochar @ 10 t + 100 % NPK + FYM in both the second residual and cumulative residual studies respectively and which was at par with

biochar @ 10 t + 75 % NPK + FYM treatment and the lowest (13.05 kg ha<sup>-1</sup>) at control in second residual study and the biochar cumulative at control (12.05). Compared to second residual study the cumulative residual study soil available phosphorus status was marginally higher.

Available potassium (Table 6) :

Irrespective of the studies, residual effect of application of different fertilizers and biochar levels and their interactions significantly affected the available potassium status in post harvest soil of cowpea.

Among the biochar levels, the maximum mean available K of 278.7 and 311.3 kg ha<sup>-1</sup> were recorded at biochar @ 10.0 t ha<sup>-1</sup> in second residual and cumulative residual studies, respectively. The minimum mean available K of 260.8 kg ha<sup>-1</sup> and 276.6 was at control in second residual and cumulative residual studies respectively. In the fertilizers levels, the highest mean available K of 275.1 and 295.5 kg ha<sup>-1</sup> was recorded at 100 % NPK + FYM. Among the interaction between fertilizers and biochar levels the available K was the highest (286.6 and 316.6 kg ha<sup>-1</sup>) in biochar @ 10 t + 100 % NPK + FYM in both the second residual and cumulative residual studies, respectively and which was at par with biochar @ 7.5 t + 75 % NPK + FYM treatment. The available K of the post harvest soil was slightly higher in cumulative biochar residual study.

The cumulative residual and second residual effects of biochar on soil available nutrients *viz.*, N, P and K was conspicuous in the succeeding post harvest soil of cowpea as well and the trend of results was similar to that of main crop. Comparing the studies, relatively higher available N, P and K was registered under cumulative residual than second residual study. Thus, in a nutshell, the biochar proved to be not only a conditioner but also a fertilizer. It has become clear that biochar is likely more important as a soil conditioner and a driver of nutrient transformations and less so as a primary source of nutrients. Biochar can act as a soil conditioner enhancing plant growth by supplying and retaining nutrients and by providing other services such as improving soil physical and biological properties.

### **Conclusion :**

In cotton crop at all the levels, application of biochar had significantly increased the available N, P and K contents in the post harvest soil. However, the effect was increased with corresponding increase in the rate of application of biochar. Significantly highest values

were recorded in biochar @ 10 t ha<sup>-1</sup> application. Significant improvement in soil physical, physico-chemical, chemical properties and fertility status of post harvest soil of cotton was found when biochar was applied in conjunction with fertilizers and FYM. Among the treatments, the trend of results were significantly higher in biochar @ 10 t + 100 % NPK + FYM followed by biochar @ 10 t + 75% NPK + FYM treatment which was statistically on par with biochar @ 7.5 t + 100 % NPK + FYM treatment. Similar trend of direct effect was also registered in the post harvest soil of maize under both the cumulative (continuous application) and residual (one time application) studies. Proving the biochar's ability in improving the soil physical, physico-chemical and chemical properties even in the succeeding maize crop soil.

The residual effect of biochar on soil properties were conspicuous in the succeeding post harvest soil of cowpea and it is on par with direct, cumulative and residual studies, similar trend of results were also registered in the post harvest soil of cowpea under both the cumulative residual (residual effect of continuous application) and second residual (second residual effect of one time application) studies.

The significant improvement in the soil physical, physico-chemical and chemical properties even in the post harvest soil of cowpea under second residual study was also recorded. The application of biochar @ 10 t ha<sup>-1</sup> had increased the available N by 5.21 per cent, available P by 8.97 per cent and available K by 8.18 per cent over control. Thus, proving the biochar's ability to sustain the soil fertility status over long run. Comparing the residual effects of biochar, the impact was relatively greater in cumulative residual soil (residual effect of continuous application) as against second residual soil (second residual effect of one time application).

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