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RESPONSE OF SOIL CHEMICAL PROPERTIES TO BIOCHAR AND NITROGEN APPLICATION IN A FIELD EXPERIMENT

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ABSTRACT

A two-year field experiment was carried out with maize (*Zea mays* L.) at two biochar (BC) doses of (5 and 10 t. ha^{-1}) and two nitrogen fertilizer rates (130 and 260 kg. ha^{-1}) in Tsalapitsa village (Plovdiv) on Alluvial-meadow soil (Fluvisol). The aim of the study was to find out the influence of biochar as an aftereffect, as well as nitrogen fertilization on soil physicochemical and agrochemical properties. In order to observe the effect of biochar in the second year, the variants from the first year ($B_{(1)}$5N130, $B_{(1)}$10N130, $B_{(1)}$5N260 and $B_{(1)}$10N260, without the controls K1N130 and K2N260 were left without the addition of biochar, and for the second year, new variants were set up according to the same scheme. During the vegetation of maize, the influence of biochar as the aftereffect was observed with increase in pH values (0.2 - 0.3 units) in comparison with the control variants (without biochar, nitrogen fertilization only), which was confirmed by its application in the second year. There were positive changes in the mineral N content of the studied treatments as the aftereffect, compared to the controls and the second-year treatments, which may be related to the ability of the biochar to fix nitrogen and protect it from leaching, especially on vulnerable soils such as the Fluvisol studied. A slight increase in organic carbon (0.09-0.32 %) was also found at the lower N rate (130 kg. ha^{-1}) in the aftereffect variants. In these variants, a slight increase in cation exchange capacity, exchangeable Ca and the degree of base saturation was also observed. Biochar utilization had little effect on the investigated properties of the Fluvisol. Applying the lower doses of biochar in longer term would have a more significant impact.

Keywords: *pH, cation exchange capacity, organic carbon, soil mineral nitrogen, second year.*

INTRODUCTION

Globally, agriculture is identified as one of the most significant sources of anthropogenic loading on soils and water, causing negative effects on environmental components such as biodiversity loss, soil acidification, erosion, salinization, surface and groundwater pollution, eutrophication, increased gas emissions, etc. The need to implement effective measures to improve soil quality and mitigate climate change requires the use of soil improvers (Lal, 2004). Nowadays, the recovery of nutrients through the reintegration of organic waste into agriculture is a sustainable alternative that can contribute to the restoration of the natural balance of environment (Griffin *et al.,* 2003).

The Alluvial - meadow soil in the study area is characterized by light soil texture, poor water holding capacity and relatively high-water permeability. There is a relatively high-water exchange between the layers, which creates conditions for active migration of chemical elements in the profile. For this reason, the agricultural practices applied are of significant importance in regard to the nitrogen uptake. Studies have shown that the use of biochar improves physico-chemical, water-physical, biological properties and increases yields, as well as potential means of sequestering carbon in soil (Bista *et al.,* 2019, Liang *et al.,* 2006; Joseph *et al.,* 2010). Biochar can increase soil C storage and influence soil quality and function. Compared to other organic amendments, biochar has greater stability whereby it increases soil fertility, water holding capacity, crop growth and development (Yadav *et al.,* 2018). The aim of the study was to find out the influence of biochar as an aftereffect in relation with nitrogen fertilization on soil physicochemical and agrochemical properties.

MATERIALS AND METHODS

The two – year experiment (2019 and 2020) was conducted at the experimental field in the village of Tsalapitsa (Plovdiv region), in Bulgaria. The soil texture is sandy clay loam and the soils in the area are classified as Fluvisol in the WRB (2015) classification. Biochar was produced from oak peels at a pyrolysis temperature of 400 °C. The basic properties of the topsoil (0–0.15 m) are: pH (H_2O) 6.1, CEC 16.7 cmol.kg^{-1}, soil organic carbon (SOC) 0.68%, total N 0.052%, available N 20.17 mg.kg^{-1}, available P 17.13 mg.100^{-1} g, available K 22.40 mg.100^{-1} g. Biochar properties were: pH (H_2O) 9.7, organic C content 49 %, total N 0.59%, available N 72 mg.kg^{-1}, K 499.6 mg.100^{-1} g, available P 43.4 mg.100^{-1} g.

Treatments with two rates of BC (5 and 10 t.ha^{-1}) and two rates of nitrogen fertilizer (130 and 260 kg.ha^{-1}) in the first year (2019) were set. Each level of BC application was tested against each level of nitrogen fertilizer application. To observe the effect of BC in the second year (2020), the variants from the first year (without controls) are left for observation without adding BC, and 6 new variants are set for the second year according to the same scheme (Table 1).

Table 1. Scheme of variants

Variants	BC t. ha^{-1}	N kg. ha^{-1}	Variants	BC t. ha^{-1}	N kg. ha^{-1}
	from 1 st year - after effect			from 2 nd year	
$B_{(1)}$5N130	5	130	K1N130	0	130
$B_{(1)}$10N130	10	130	B $_{(2)}$5N130	5	130
			$B_{(2)}$10N130	10	130
$B_{(1)}$5N260	5	260	K2N260	0	260
$B_{(1)}$10N260	10	260	$B_{(2)}$5N260	5	260
			$B_{(2)}$10N260	10	260

Note: $_{(1)}$ - treatments from the previous year (without BC application, only with mineral fertilizers) for observation on the BC aftereffect; $_{(2)}$ - treatments with BC application during the second year.

Soil samples were taken during development of maize (at the 10-12 leaf phenophase - about 45 days after biochar and nitrogen fertilizer were applied in the second year) from the treatments. Mineral nitrogen was analysed by the method of Kjeldahl (Methods of Soil Analysis, 1982) and available P and K following the methods of (Ivanov, 1984). The physico-chemical soil properties were determined by the method of Ganev and Arsova (1980). Soil organic matter content and composition were obtained by a modified method of Turin (oxidation with dichromate and H_2SO_4 in a thermostat at 120 °C, 45 min., Ag_2SO_4 catalyst and back titration with $(H_4)_2SO_4$. $FeSO_4.6H_2O$ and Kononova - Belchikova method (Filcheva and Tsadilas, 2002).

RESULTS AND DISCUSSION

The results of the soil chemical analysis showed that pH values in the control treatments ranged from 5.6 (K2N260) to 6.1 (K1N130). After addition of BC, the pH values increased by 0.2 - 0.4 units. It was interesting to note the more pronounced aftereffect of BC, in the first year, compared to the control with the higher nitrogen rate. Many authors indicated that the application of BC increases pH of soil for acid soils (Pandian *et al.,* 2016, Zhao *et al.,* 2018, He *et al.,* 2021). Furthermore, previous studies of the relationship between soil pH and biochar dose have identified complex interactions (Hailegnaw *et al.,* 2019), requiring the long-term study of soil response.

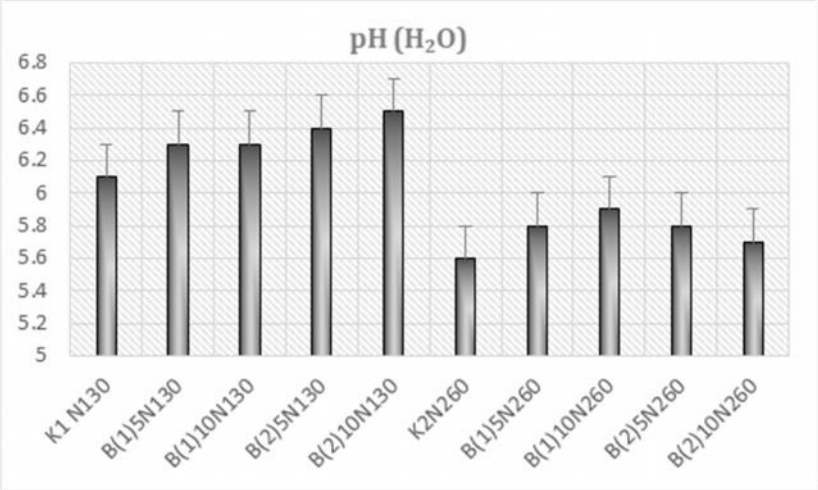

Fig. 1. Values of pH in Fluvisol by treatments during maize development

It is known that the cation exchange capacity (CEC) depends on soil texture, the organic matter content, and also the type of clay minerals that make up the fine-grained part soils. The Alluvial-meadow soil studied contains a relatively small amount of clay, and as can be seen from the data the sorption capacity values are low. Interestingly, the highest values of the cation exchange capacity were recorded in the variants with $B_{(1)}$5N130 and $B_{(1)}$10N130 aftertreatment - 16.5 and 16.6 cmol.kg^{-1} compared to the other variants studied (Table 2). According to (Karim *et al.*, 2020) BC is a porous material, with high surface area and significant negative charges. These are properties that can significantly increase the cation exchange capacity of soil and retain nutrients and water. CEC were found to have a positive correlation with total C content (r=0.85, P < 0.001) as a linear relationship with the biochar applied.

Table 2. Physico-chemical characteristics of Fluvisol by variants during the development of maize.

Variants	pH_{H2O}	EC	CEC	CEC_{CA}	CEC_A	exch.$H_{8.2}$	exch. Al	exch. Ca	exch. Mg	BS
		Ms/cm				cmol.kg^{-1}				%
K1N130	6.1	0.07	16.2	12.0	4.2	3.0	0	11.0	2.0	81.48
$B_{(1)}$5N130	6.3	0.08	16.5	12.6	3.9	2.8	0	11.8	2.0	83.03
$B_{(1)}$10N130	6.3	0.08	16.6	12.7	3.9	2.8	0	11.9	2.0	83.13
$B_{(2)}$5N130	6.4	0.09	16.2	13.3	2.9	1.6	0	12.4	2.1	90.12
$B_{(2)}$10N130	6.5	0.09	16.2	13.3	2.8	1.5	0	12.4	2.0	90.69
K2N260	5.6	0.06	16.0	11.1	4.9	4.0	0.5	9.5	1.8	71.87
$B_{(1)}$5N260	5.8	0.063	16.0	11.8	4.2	3.7	0.2	10.2	1.8	75.87

$B_{(1)}$10N260	5.9	0.063	16.2	12.4	3.8	3.5	0.1	10.5	1.9	78.40
$B_{(2)}$5N260	5.8	0.06	16.2	11.7	4.5	3.7	0.4	10.5	1.9	77.16
$B_{(2)}$10N260	5.7	0.06	16.2	11.7	4.5	3.7	0.5	10.0	1.8	74.07

The degree of base saturation (BS) increased compared to the controls, and this trend was more noticeable in the variants with a lower N rate and incorporation BC in the second year. The total acidity (exch.$H_{8.2}$), which covered all adsorbed cations with acidic functions, decreased relative to the controls with increasing pH values. In the variants with high nitrogen rate, acidification and the occurrence of exchange acidity were observed because even high biochar levels cannot provide sufficient basic cations (Ca, Mg) for precipitation of Al^{3+} to neutralise strongly acid exchangeable sites (CECca).

The application of a significant amount of nitrogen and other nutrients causes the accumulation of residual mineral nitrogen in the soil profile, which is a potential source of changes in the soil solid and liquid phase. The studied Alluvial-meadow soil is characterized by a light texture and accelerated water flow, which makes it more vulnerable to nitrate leaching from the soil. The addition of biochar is thought to have different, and sometimes conflicting, effect on nitrogen content and movement across the soil profile. Many researchers (Laird *et al.,* 2010; Libutti *et al,* 2016; Borchard *et al.,* 2019) found that the addition of biochar to arable soils can reduce nitrate and phosphate leaching. This may be explained by an increase in the anion exchange capacity of biochar, although the mechanisms are not yet well understood. In other studies (Yao *et al.,* 2012; Hollister *et al.,* 2013) found a limited ability of biochar to retain nitrate from the soil solution; furthermore, the authors believe that the material from which biochar is derived and the type of soil have a significant impact on nitrogen uptake.

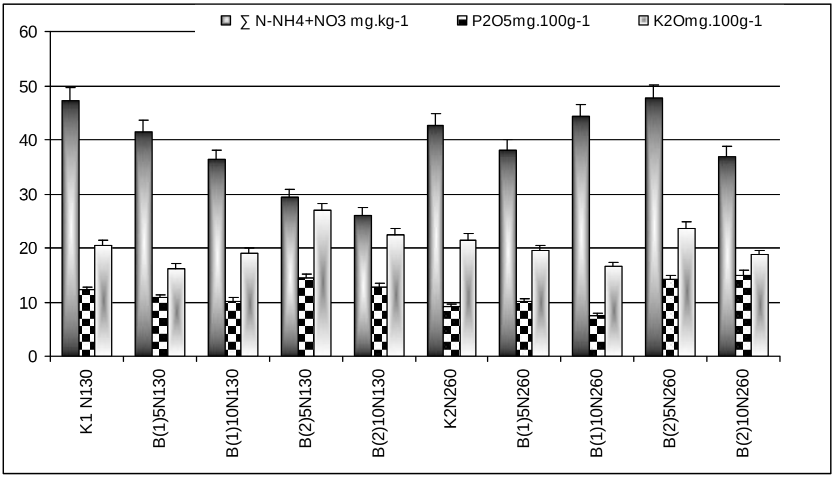

Fig. 2. Content of mineral nitrogen, available phosphorus and potassium (mg.kg^{-1}) in Fluvisol by variants in maize cultivation

The agrochemical soil data showed that the mineral nitrogen content of the control treatments ranged in the interval (47.23- 42.62 mg.kg^{-1}). It was observed that in the B$_{(1)}$5N130 and B(1)10N130 after-treatments, the mineral nitrogen content was higher (41. 47 mg.kg^{-1}) at the lower rate of BC compared to the treatment with higher amount of BC (B$_{(1)}$10N130 36. 29 mg.kg^{-1}). In the other two treatments (B$_{(2)}$5N130 and B$_{(2)}$10N130) in the second year, the mineral nitrogen content was about 1.5 times lower (Fig. 2). In the variants with nitrogen rate of 260 kg ha^{-1}, no significant difference was observed in the mineral nitrogen content of the soil, perhaps reflecting the more significant effect of fertilisation. The studies of Li *et al.*, (2019a), Paetsch *et al.*, (2018) found that monitoring N in soil can effectively reveal the impact of biochar on agroecosystems during its application, which is associated with aging processes and changes in its functional groups and specific surface area.

From the results obtained for the available phosphorus content, it was found that they did not vary significantly. It was necessary to note its higher content in the variants in the second year studied, with the highest values reaching B$_{(2)}$10N260 (15.05 mg.100g^{-1}). It is known that many factors significantly affect the availability of phosphorus in soil, such as soil solution pH, adsorption reactions, organic matter, phosphatase activity, etc., and that the organic inputs and their interaction with soil phosphorus content are not well understood. Regarding the potassium content (Fig. 2), the highest values were observed in the variants with the low doses of BC (B$_{(2)}$5N130 and B$_{(2)}$5N260, 26. 9 mg. 100g^{-1} and 23.7 mg.100g^{-1}, respectively). In their research Bista *et al.*, (2019) found the better effectiveness of lower doses of BC on the properties of certain soil types.

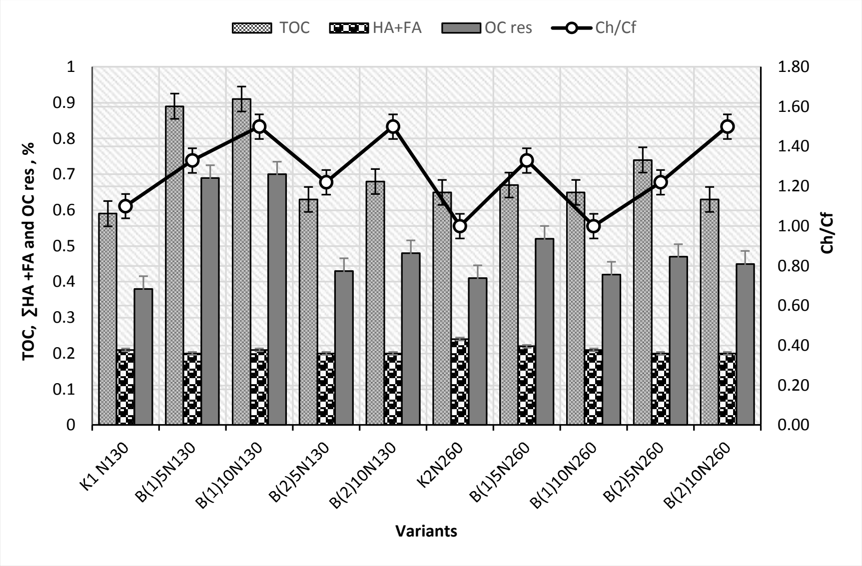

Fig. 3. Content and composition of TOC in Fluvisol by variants

The studied soil was characterized by a low content of humus (1.17 %) of humate-fulvic type (Ch/Cf = 1), low content of humic acids, 100 % bound with Ca and weak degree of humification (13.5 % of total carbon) (Benkova *et al.*, 2022). The results for total carbon content and organic matter composition (Fig. 3), indicate that there was a slight increase in carbon, and this change was the highest (0. 89 and 0. 91 %) in the variants with low dose of N in the first year, $B_{(1)}5N130$ and $B_{(1)}10N130$. The humus system in soil changed from humate-fulvate (C_{HA}/C_{FA} 0.5 - 1) to fulvate - humate type (C_{HA}/C_{FA} 1.5) (Orlov, 1985). Biochar application to soil resulted in an increase in C_{HA}/C_{FA} ratio and hence soil organic matter quality compared to controls. The application of biochar increased the amount of humin from 0. 38 % in the control to 0. 69-0. 70 % in the variants $B_{(1)}5N130$ and $B_{(1)}10N130$ in the first year. In other studies, Uzoma *et al*. (2011), Van Zwieten *et al*. (2010) and Oladele *et al.* (2018) also observed an increase in soil TOC after the application of biochar. Van Zwieten *et al*. (2010) found that biochar significantly increased total soil C in the range of 0.5 – 1.0 %. Oladele *et al.* (2018) reported that biochar amendments to soil significantly increased total C with increasing application rates.

CONCLUSIONS

The obtained results indicate that an increase in pH values was found in the BC and lower N rate treatments. There was divergent behaviour between mineral nitrogen content, available forms of phosphorus and potassium and applied BC rates. The mineral-N was lower at the higher rate of BC (10 $t.ha^{-1}$) than at the lower dose (5 t.ha-1) after the first year, and it is possible that biochar ageing processes alter its influence on soil physico-chemical properties compared to recently applied biochar. A higher available phosphorus content was observed in the variants of the second year studied compared to the after-effect variants. The results showed that the C content was higher in the biochar treatments compared to the controls (K1N130, and K2N260), with the highest values obtained in the first year of the experiment, when biochar was applied at the low rate of 130 $kg.ha^{-1}$ N as an after-treatment. A slight increase in cation exchange capacity, exchangeable calcium and degree of base saturation was also found in the same variants. These results indicate that long-term additions of BC have the beneficial effects on the soil physico-chemical and agrochemical properties. Further research is needed to clarify the complex influence between fertilization rates and BC doses on light-textured soils such as Alluvial-meadow soils, due to their vulnerability to anthropogenic loading.

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