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Research Article

HOW DOES BIOCHAR AND BIOCHAR WITH NITROGEN FERTILIZATION INFLUENCE SOIL REACTION?

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ABSTRACT

Biochar usually has a neutralizing effect, therefore, it is recommended for application to acid soils due to its potential to increase soil pH. The aims of this study were (1.) to quantify the role of different rates of biochar and biochar in combination with N fertilization on change of soil pH, and (2.) to evaluate the dynamic changes of soil pH in relation with doses of biochar and biochar with N fertilization. A field experiment was conducted with different biochar application rates: B0 control (0 t ha^{-1}), B10 (10 t ha^{-1}) and B20 (20 t ha^{-1}) and 0, 40 and 80 kg N ha^{-1} of nitrogen fertilizer (N0, N40, N80) on silt loam Haplic Luvisol at the locality of Dolná Malanta (Slovakia) in 2014. Their effects were investigated after vegetation season of spring barley and spring wheat (once a month: from April to July) in 2014 and 2016, respectively. Experimental results indicate that the soil pH_{H2O} in B0N0, B10N0, B20N0, B10N40, B20N40, B10N80 and B20N80 were 6.23, 6.45, 6.60, 6.77, 6.48, 6.36 and 6.60, respectively. The results of LSD test showed statistically significant differences between soil pH in control treatment and treatments with biochar and biochar with N fertilization. The most significant effect on increase of soil pH was observed in B10N40. During whole period, after application of biochar and biochar with N fertilization the values of pH_{KCl} were gradually decreased in all treatments.

Keywords: biochar, soil pH, neutralizing effect, N fertilization.

INTRODUCTION

The reaction of soils is significant in crop production and soil management practices because the various degree of soil reaction are produced by the chemical conditions which exist in soils, each set of chemical conditions causing its corresponding degree reaction. Each degree of soil reaction or set of chemical conditions in soils affects plant growth in a certain way owing to either a depressed solubility of some elements or to an increased solubility of others. The chemical conditions which accompany the different degrees of soil reaction, therefore, may be favourable to the growth of some crops, unfavourable to others, and in still other cases they may affect plant growth very little [Millar et al. 1962, Hanes 1999, Čurlík et al. 2003]. In the framework of agrochemical testing of soils in Slovakia, the soil pH is one of the most important parameters which is monitored. According to the results of the last monitored cycle ASP (XII.), Slovakia had 23.4, 35.2, 23.4 and 18.0% of soils acid, slightly acid, neutral and alkaline reaction, respectively. Most crop plants requires the pH value of 6–7 because this interval corresponds to the requirements of releasing nutrients from soil stocks and keeping them in accessible forms [Fecenko and Ložek 2000], so we have to lime mainly acid soils.

For liming except classic Ca fertilizers can be used biochar due to its neutralizing effects, high content of alkaline metals and basic cations in ash

[DeLuca et al. 2009, Yuan et al, 2011]. Effect of biochar on soil pH [Yuan et al. 2011, Zhang et al. 2012, Jones et al. 2012, Horák 2015] have been studied, but obtained results can be different due to different pH of biochar. The pH of biochar is influenced by the type of feedstock, production temperature, and production duration [Liu et al. 2012].

In this context, there are a few hypotheses: (1.) application of biochar to the soil would increase soil pH, however its effect can effected by rate of biochar as well as by dose of N fertilization. Biochar is source of stabile organic matter [Fischer and Glaser 2012], so there is a premise that its alkalizing effect will be of a longer term nature. Therefore, the objectives of this study were (1.) to quantify the role of different rates of biochar and biochar in combination with N fertilization on change of soil pH, and (2.) to evaluate the dynamic changes of soil pH in relation with doses of biochar and biochar with N fertilization.

MATERIAL AND METHODS

This study was carried out on an ongoing experiment with different application rates of biochar and its combination in different doses of N fertilization that had been running for three years at Dolná Malanta (48°19'00"N; 18°09'00"E). The geological substratum consisted of little previous rocks (biotite, quartz, diorite, triassic quartzites with phyllite horizonts, crinoid limestones and sandy limestone) with high quantities of fine materials. Young Neogene deposits were composed of various clays, loams and sand gravels on which loess was deposited in the Pleistocene epoch. The soil was classified as the Haplic Luvisol [WRB 2006]. Soil organic carbon content was 9.13 g kg^{-1} and soil pH (KCl) was 5.71. Soil texture was silt loam with content of sand 15.2%, silt 59.9% and clay 24.9%. The mean annual precipitation in the region is 573 mm and the mean annual temperature is 9.8 °C.

The experiment was established in March 2014. More information about experiment was published by Šimanský et al. [2016]. The research comprised of seven treatments (Table 1) and the experiment was laid out in a randomized block design with three replicates.

The biochar was produced by pyrolysing paper fiber sludge and grain husks (1:1 w/w) (company Sonnenerde, Austria). Biomass was pyrolysed at 550 °C for 30 minutes in a Pyreg reactor (Pyreg GmbH, Dörth, Germany). The result was product with particle size of 1–5 mm. On average; it contained 57 g kg^{-1} of Ca, 3.9 g kg^{-1} of Mg, 15 g kg^{-1} of K and 0.77 g kg^{-1} of Na. Total C content of biochar was 53.1%, while total N content was 1.4%, the C:N ratio was 37.9, specific surface area (SSA) was 21.7 m^2 g^{-1} and content of ash was 38.3%. On average, the biochar pH($CaCl_2$) was 8.8. Calcium-ammonium nitrate was used as N fertilizer. The field was ploughed and biochar combined with or without N fertilization for all plots was incorporated to a depth of 10 cm. The spring barley (*Hordeum vulgare* L.) and spring wheat (*Triticum aestivum* L.) were sown in 2014 and 2016, respectively.

The soil was sampled repeatedly from the top layer (0–20 cm depth) to cover the whole spring barley growing season (17th April, 15th May, 16th June, and 13th July) in 2014 as well as in 2016 to cover the whole spring wheat growing season (20th April, 17th May, 22th June, and 18th July). Thus, for the 2014 treatments, sampling occurred 1, 2, 3 and 4 months after biochar application, while in 2016 treatments, sampling was conducted 26, 27, 28 and 29 months after biochar application. Soil samples were dried at laboratory temperature and grinded. We determined the pH_{H2O} and pH_{KCl} potentiometrically [Hanes 1999]. The pH in H_2O and in KCl were determined with a soil:distiled water ratio of 1:2.5 (g mL^{-1}) and with a soil:solution of 1M KCl ratio of 1:2.5 (g mL^{-1}) using a WTW inoLab pH 730.

Obtained data was analyzed by using the statistic software Statgraphics Centurion XV.I (Stat-

Table 1. The investigated treatments

Treatment	Description
B0N0	no biochar, no N fertilization
B10N0	biochar at rate of 10 t ha^{-1}
B20N0	biochar at rate of 20 t ha^{-1}
B10N40	biochar at rate of 10 t ha^{-1} with 40 kg N ha^{-1}
B20N40	biochar at rate of 20 t ha^{-1} 40 kg N ha^{-1}
B10N80	biochar at rate of 10 t ha^{-1} with 80 kg N ha^{-1}
B20N80	biochar at rate of 20 t ha^{-1} with 80 kg N ha^{-1}

point Technologies, Inc., USA). One-way ANOVA model was used for individual treatment comparisons at $P < 0.05$, with separation of means by LSD multiple-range test. To evaluate the trends of the soil pH during investigated period, the Mann-Kendall test and simple linear model were used.

RESULTS AND DISCUSSION

In this study, the addition of biochar to soil increased overall pH_{H2O} and the increase was highest for the treatment where biochar was applied at rate of 10 t ha^{-1} together with N fertilization in dose 40 kg ha^{-1} (Fig. 1a). The treatments increased the pH in the following order B0N0 < B10N80 < B10N0 < B20N40 < B20N80 = B20N0 < B10N40. Soil pH_{H2O} values in biochar (including N fertilization) treatments (except B10N0 and B10N80) were significantly higher than pH_{H2O} of control treatment. Effects of N fertilization in biochar treatments compared to biochar treatments were no observed. Paz-Ferreiro et al. [2014] found a lack of correlation between the initial biochar pH and the final pH of the biochar–soil mixture. A reason for the complex acid-basic equilibrium following biochar addition to the soil could lie in the mixture of organic and inorganic functional groups of alkali present in the biochar, which are dependent on the conditions of biochar production [Yuan et al. 2011]. The pH of biochar, similar with the other properties, is influenced by the type of feedstock, production temperature, and production duration [Liu et al. 2012]. The higher pH of the high temperature biochars is attributed to the accumulation of alkaline metals, formation of carbonates, and concentration of biomass-derived carbonates as a function of temperature [DeLuca et al. 2009, Yuan et al. 2011], which was also reflected in the higher ash contents in biochars produced at 600 °C. Pyrolysis leads to the accumulation of alkaline substances on the biochar surface, which increases the soil pH [Butterly et al. 2009]. In our case biochar

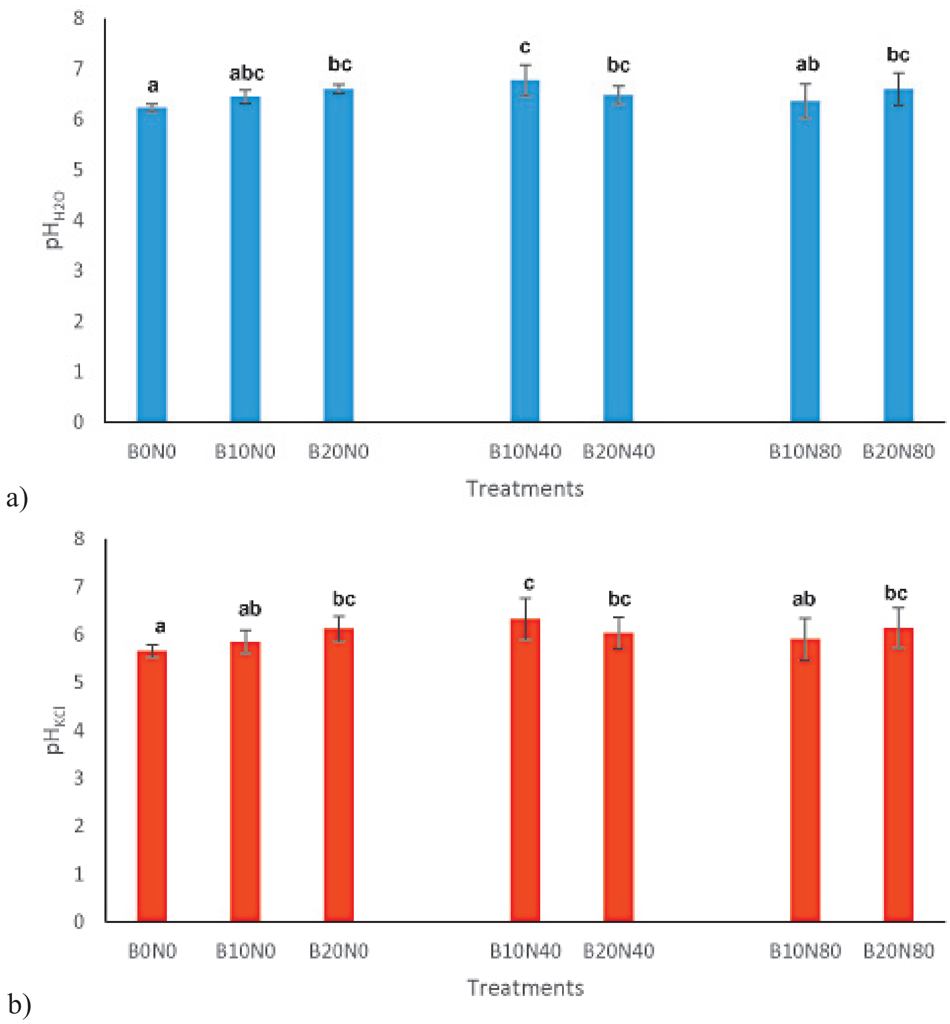

Fig. 1. Statistical evaluation of a) soil pH in H_2O, and b) soil pH in KCl

used in the experiment was produced from the paper fiber sludge and grain husks by pyrolysis at 550°C for 30 minutes in a Pyreg reactor. On average; it contained 57 g kg^{-1} of Ca, 3.9 g kg^{-1} of Mg, 15 g kg^{-1} of K and 0.77 g kg^{-1} of Na. On average, the biochar pH was 8.8. Initial soil pH on average was 5.71 – slightly acidic and our results confirmed the findings of other authors recording neutralizing effect of biochar in the soils [Jeffery et al. 2011, Kim et al. 2015]. The same effects were observed in case of soil pH_{KCl} (Fig. 1b). The B20N0, B10N40, B20N40 and B20N80 treatments significantly increased pH from 5.66 to 6.13, 6.33, 6.04 and 6.14, respectively. One-way ANOVA analysis showed no significant differences in soil pH_{KCl} between B10N0, B10N80 and control treatment (B0N0). Statistical significant differences in soil pH_{KCl} between treatments with applied biochar and treatments with biochar and N fertilization were determined only in case of B10N40 and B10N0.

The dynamics of soil pH_{H2O} showed a stable trend with time during investigated period in control and treatments with applied biochar at the rate of 10 and 20 t ha^{-1} as well as in treatment with biochar in dose of 10 t ha^{-1} combined with 40 kg N ha^{-1}. However, in B20N40 and treatments at both biochar application rates (10 and 20 t ha^{-1}) with 80 kg N ha^{-1} showed a decreasing trend with the time according to the results of the Mann-Kendall test. In B10N0, B10N40, B20N40 and B10N80 treatments, soil pH_{H2O} was increasing (during vegetation season 2014) after the application of biochar and during the next investigated period (vegetation season 2016) the soil pH_{H2O} was decreasing, however, statistically significant linear trend was observed only in case of B20N40. Several authors [DeLuca et al. 2009, Yuan et al. 2011, Rajkovich et al. 2012] pointed out on the fact that in ash of biochar are high levels of Ca^{2+} and Mg^{2+} and other alkaline elements, which are responsible for current neutralizing effect, but in the future they (alkaline elements) can increase the intensity of physico-chemical sorption of soil resulting in decrease in soil pH_{KCl}. Biochar is very stable in soil compared to other organic matter additions [Fischer and Glaser 2012]. Management practices such as addition of labile C (e.g. slurry) to soil significantly increased biochar mineralization [Kuzyakov et al. 2009]. After addition to soils, non-aromatic C fractions in biochar are potentially oxidized [Nguyen et al. 2010], which leads to subsequent decline in soil pH [Joseph et al. 2010]. Additionally, nitrification may also contribute to the decrease in pH [Horák et al. 2017]. Above mentioned findings confirms our results (Table 2). The dynamics of soil pH_{KCl} showed a decreasing trend with time in all treatments including control according to the results of the Mann-Kendall test. Statistically significant linear trends were observed in treatments with applied biochar in both rates as well as in treatment with applied lower dose of biochar with combination of higher dose of N and opposite in treatment with applied higher dose of biochar with lower N fertilization.

CONCLUSION

Overall, biochar is a soil additive that increased the soil pH. This effect (on soil pH in H_2O and in KCl) was the most intense after application of biochar at rate of 10 t ha^{-1} in combination with 40 kg ha^{-1} of nitrogen. Higher dose of biochar to the soil without N fertilization resulted in higher increase of soil pH. During whole period, after application of biochar and biochar with N fertilization the val-

Table 2. Dynamics of soil pH according to the results of the Mann-Kendall test and correlation coefficient (linear model)

Treatment	pH		pH	
	H_2O	KCl	H_2O	KCl
	Mann-Kendall trends: 8 quarter evaluation		Linear model (r)	
B0N0	Stable / no trend	Decreasing	0.439	0.568
B10N0	Stable / no trend	Decreasing	0.413	0.725*
B20N0	Stable / no trend	Decreasing	0.550	0.910**
B10N40	Stable / no trend	Decreasing	0.379	0.484
B20N40	Decreasing	Decreasing	0.747*	0.828*
B10N80	Decreasing	Decreasing	0.649	0.754*
B20N80	Decreasing	Decreasing	0.424	0.600

B0N0 – no biochar, no N fertilization, B10N0 – biochar at rate of 10 t ha^{-1}, B20N0 – biochar at rate of 20 t ha^{-1}, B10N40 – biochar at rate of 10 t ha^{-1} with 40 kg N ha^{-1}, B20N40 – biochar at rate of 20 t ha^{-1} 40 kg N ha^{-1}, B10N80 – biochar at rate of 10 t ha^{-1} with 80 kg N ha^{-1}, B20N80 – biochar at rate of 20 t ha^{-1} with 80 kg N ha^{-1}.

ues of pH_{KCl} were gradually decreased in all biochar and biochar with N fertilization treatments. No significant linear decreasing trends were observed only after application biochar at rate 10 t ha^{-1} with 40 kg N ha^{-1} as well as in treatment with biochar at rate 20 t ha^{-1} together with 80 kg^{-1} ha^{-1} of nitrogen. In other words, lower dose of biochar with lower dose of N and on the other hand, higher dose of biochar with higher dose of N fertilization can be used to amend acidic soils in this region, but the effectiveness will decrease with time after its application. Thus, application of biochar to the soil does not address treatment of acidic soils for a longer period of time.

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