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EFFECTS OF BIOCHAR AND ITS REAPPLICATION ON SOIL PH AND SORPTION PROPERTIES OF SILT LOAM HAPLIC LUVISOL

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In this paper we investigate the effects of biochar alone and its reapplication and combination with N-fertilizer (1) on the soil pH, and (2) sorption parameters. The soil samples were taken during growing period in 2018 from plots with different biochar (first application in 2014 – A, reapplication in 2018 – B) at application rates: 0 t.ha⁻¹ (B0 control), 10 t.ha⁻¹ (B10) and 20 t.ha⁻¹ (B20) and different nitrogen fertilization: N0 (no nitrogen) and N40 (40 kg.ha⁻¹). Our results showed that the first application of biochar at the rate of 20 t.ha⁻¹ (B20A) without N-fertilizer significantly increased the values of soil pH in H₂O, soil pH in KCl, the sum of base cations (SBC) and cation exchange capacity (CEC) compared to control (B0). Similar effects were observed also after reapplication of biochar (B10B). All investigated parameters in fertilized control treatment (B0N40) were worst and the first application, as well as the reapplication of biochar with N, caused significant increase of soil pH in H₂O, soil pH in KCl, SBC, CEC, BS and decrease of hydrolytic acidity.

Keywords: soil acidity, cation exchange capacity, base saturation, biochar, fertilization

Soil acidity presents a world-wide problem as it reduces the soil fertility. Acidification is a slow, continual and natural process that considerably affects the sustainability of agriculture (Rengel, 2002; Guo et al., 2010). Approximately 50% of world's arable land is considered acidic (Kochian et al., 2015). Acidic soil is unsuitable for most field crops with the exception of some. Soil pH value expresses the degree of acidity and alkalinity of soil. Soil sorption is arguably the most important physico-chemical process that ensures the retention of nutrients, heavy metals and other chemical substances in soil (Thompson et al., 2012). According to Essington (2004), the ability of soil to retain cations increases with increasing pH. This is supported by Zhang et al. (2015) who claim that pH value and soil organic carbon content (SOC) are the main factors influencing the content of basic cations exchange. In the acidic soils the total content of cations is considerably lower. In addition, cation exchange capacity (CEC) is dependent on soil organic matter content (SOM). In general, SOM has a high content of basic cations exchange due to the presence of functional groups on the surface area of its particles.

According to Dai et al. (2017), application of biochar, to raise soil pH, could present an acceptable solution to high soil acidity. There is a consensus that biochar application raises the pH in acidic soils (Juriga and Šimanský 2018; Šimanský et al., 2018). Adding biochar into the soil could prove to be a valuable instrument in the efforts to increase the soil fertility and its use is deemed an important to counter the risks of soil acidification (Dai et al., 2017). Biochar represents a solid carbon-based product, which is produced during the thermal decomposition of different organic materials,

under conditions with limited access to oxygen (Lorenz and Lal, 2014). Biochar has specific properties which mainly depend on the type of material used for its production and producing conditions. Through its properties, biochar can influence various soil properties, such as: soil organic carbon content (Šimanský et al., 2018a; Juriga et al., 2018), aggregate stability (Šimanský et al., 2016), bulk density, soil pH, CEC, electric conductivity (Chintala et al., 2014), soil biota (Lehmann et al., 2011), etc.

There are several mechanisms that enable biochar to suppress the acidity of the soil and help to increase the soil pH (Dai et al., 2017). Biochar's specific properties reduce the soil acidity through its alkaline nature and high buffer capacity. The ability of biochar particles to absorb the H⁺ ions, as well as decarboxylation processes, are probably the main factors in soil acidity neutralization (Wang, Li and Liang, 2013). The biochar particles in soil are subject to gradual oxidation which leads to the production of functional groups containing oxygen (Hansen et al., 2016). During pyrolysis, the cations such as: Ca, Mg, K and Si which are contained in the organic materials used in bio-fuel production, form carbonates or oxides (Zong et al., 2018). When we apply biochar to the acidic soil, these carbonates and oxides react with H⁺ and Al³⁺ ions and thus increase the pH and decrease the soil's acidity (Novak et al., 2009). Yuan, Xu and Zhang (2011) have shown that functional groups such as COO⁻ and O⁻ can also react with H⁺ and Al³⁺ ions in the soil and significantly contribute to the alkalinity of soil. The range of changes in pH and acidity depends on biochar properties. As stated by Fidel et al. (2017), biochar alkalinity strongly correlates with the content of basic cations in

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the soil. Ahmad et al. (2014) refers to surface absorption and electrostatic interactions as the main mechanisms in interaction between biochar particles and particles of organic matter. A large surface area, a high number of functional groups, a negative charge and also a porous structure have major functions in these processes (Dai et al., 2017; Yang, Ying and Kookana, 2009).

Based on the above context, we expect that application of biochar, biochar with N fertilizer and biochar reapplication could increase soil pH and improve soil sorptive properties in a silt loam Haplic Luvisol. Therefore, the aim of this study is to evaluate the effects of biochar, biochar with N fertilization and biochar reapplication on changes of soil pH and soil sorption parameters.

Material and methods

The study was conducted at the experimental station of Slovak University of Agriculture in Nitra (Dolná Malanta, 48° 10'00.0" N 18° 09'00.0" E) during the growing period of spring barley in 2018. The station is situated approximately 4 km from Nitra in Žitava highlands, with an altitude of 175 m a. s. l. The soil is classified as silt loam Haplic Luvisol and on average it contained 9.13 g.kg⁻¹ of soil organic carbon, while the average soil pH was 5.71 (Šimanský et al., 2018a). The studied area has a planar character with a slight south western facing of the slope. Climate is warm and dry with an average annual air temperature of about 9.5 °C and average annual sum of precipitation 540 mm.

The experiment was established in 2014, before the sowing of spring barley. This is when biochar was applied for the first time at the rate of 10 and 20 t.ha⁻¹. From the beginning of the experiment until now, the following crops were grown on the field in the years 2014, 2015, 2016, 2017 and 2018, respectively: spring barley, corn, spring wheat, corn and spring barley. Before the sowing of spring barley, biochar was reapplied at the same rates in 2018. The overview of the treatments is shown in Table 1. Biochar used in this experiment was produced from grains husks and paper, at the temperature of 500 °C. Its basic composition and properties are given in Table 2. The nitrogen fertilizer – LAD 27 is used every year at different rates based on the crop's needs. N fertilizer was used at the rates of 40 kg.N⁻¹.ha⁻¹ in 2018.

Table 2 The basic chemical composition and properties of applied biochar

Total C	531 g.kg ⁻¹
Total N	14 g.kg ⁻¹
Ca	57 g.kg ⁻¹
Mg	3.9 g.kg ⁻¹
K	15 g.kg ⁻¹
Na	0.7 g.kg ⁻¹
Ash	383 g.kg ⁻¹
pH in H₂O	8.8
Size of biochar	1–5 mm

The soil samples were collected at regular monthly intervals from all treatments during the growing season of spring barley in 2018 (from April to July). The sampling was carried out from the depth of 0–0.30 m. Subsequently, parts of plants were removed, and the samples were transported to the laboratory where they were dried. Finally, the following parameters in the soil samples were determined:

- soil pH in H₂O (ratio soil to distilled water, 1 : 2.5) and soil pH in 1 mol.dm⁻³ KCl (ratio soil to KCl, 1 : 2.5) – potentiometrically (Fiala et al., 1999);
- hydrolytic acidity (H), the sum of basic cations (SBC) according to Kappen method (Fiala et al., 1999);
- cation exchange capacity (CEC) and base saturation (BS) according to equations 1 and 2:

$$CEC = H + SBC \quad (1)$$

$$BS = \frac{SBC}{CEC} \cdot 100 \quad (2)$$

Average values of soil pH and soil sorptive parameters by ANOVA single-factor analysis (Statgraphic Centurion XV Program I.) were determined. The LSD test with the level of significance $P < 0.05$ was used to compare the effects of biochar, biochar with nitrogen fertilizer and biochar reapplication.

Table 1 The overview of evaluated treatments

B0	without biochar	control	without N fertilizzer
B10A	10 t.ha ⁻¹ of biochar	first biochar application (2014)	
B20A	20 t.ha ⁻¹ of biochar		
B10B	10 t.ha ⁻¹ of biochar	biochar reapplication (2018)	
B20B	20 t.ha ⁻¹ of biochar		
B0N40	without biochar	N treatment	with N fertilizer
B10N40A	10 t.ha ⁻¹ of biochar	first biochar application (2014)	
B20N40A	20 t.ha ⁻¹ of biochar		
B10N40B	10 t.ha ⁻¹ of biochar	biochar reapplication (2018)	
B20N40B	20 t.ha ⁻¹ of biochar		

Results and discussion

The biochar application can be beneficial for soil pH enhancement (e. g. Chintala et al., 2013; Obia et al., 2015; Horák et al., 2017; Teutscheroova et al., 2017; Šimanský et al., 2018) as confirmed by our data. As shown in Fig. 1, in the case of treatments with the first biochar application without a nitrogen fertilizer, the statistically significant effect on soil pH increase was recorded in B20A treatment. Consequently, the soil pH in H₂O significantly increased from 6.06 (B0) to 6.47 (B20A) and pH in KCl from 5.66 (B0) to 6.0 (B20A). However, the addition of 10 t.ha⁻¹ of biochar did not have significant influence on pH changes. Zong et al., (2018) also confirmed that higher rates of biochar are more beneficial, stating that the volume of biochar added to the soil is crucial when trying to affect the pH values and acidity of the soil. Biochar reapplication had a statistically significant effect on the pH values in treatments at both rates (B10B and B20B). The higher values in B20B treatment: 6.71 (pH in H₂O) and 6.23 (pH in KCl) than in B10B treatment: 6.47 (pH in H₂O) and 6.0 (pH in KCl) were measured. The same values – pH in H₂O (6.47) and pH in KCl (6.0) were found in B20A and B10B treatments. For example, Cornelissen et al. (2018) also observed a significant increase in pH soon after the application of biochar

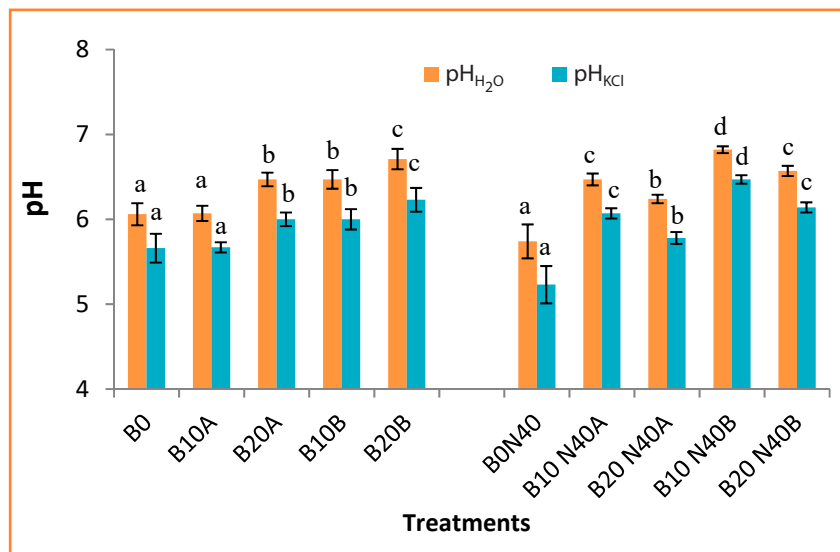


Figure 1 Statistical evaluation of soil pH the individual letters (a, b, c, d) in columns (at the same colour) represent the statistical significance ($P < 0.05$) of the application of biochar, biochar with N or biochar reapplication

into the soil, while pH values gradually decreased due to the weakening of the biochar's liming effect in the following years. According to Cornelissen et al. (2018) this decrease could be caused by the gradual leaching of alkaline compounds from biochar. They consider effective to apply biochar to the soil every three years to maintain the neutralizing effect. Castaldi et al. (2011) stated that the ability of biochar to affect the soil pH decreased as soon as 14 months after the application. It was proven that different kinds of biochar affect the soil pH differently. This depends on the specific biochar

properties, mainly on the used materials and production temperature (Keiluweit, Nico and Kleber, 2010; Ahmad et al., 2014; Masud, Li and Xu, 2014). Alkaline properties of biochar tend to increase with the pyrolysis temperature (Yuan, Xu and Zhang, 2011). In our case, the best results were recorded in the treatment with biochar reapplication at the rate of 20 t.ha⁻¹ which confirmed the data of above-mentioned authors (e.g. Castaldi et al., 2011; Cornelissen et al., 2018).

Since the biochar is alkaline, it might increase of soil pH, but this effect could be softened with adding

Table 3 Statistical evaluation of soil sorption parameters

Treatments	H	SBC	CEC	BS
	mmol.kg ⁻¹			%
B0	16.65±3.00 ^{bc}	137.28±8.29 ^a	153.93±6.45 ^a	89.14±2.24 ^{ab}
B10A	19.81±3.52 ^c	140.34±12.30 ^{ab}	160.15±10.40 ^{ab}	87.55±2.51 ^a
B20A	14.17±1.72 ^b	164.06±14.29 ^b	177.70±13.33 ^b	91.47±1.31 ^{bc}
B10B	15.20±3.01 ^b	163.80±8.97 ^b	179.25±6.29 ^b	91.99±1.92 ^{bc}
B20B	11.47±2.46 ^a	194.66±30.86 ^c	206.12±29.43 ^c	94.29±1.74 ^c
B0N40	27.53±1.11 ^d	117.90±10.67 ^a	145.43±10.58 ^a	80.99±1.60 ^a
B10 N40A	14.10±3.08 ^b	167.63±6.68 ^b	181.73±4.53 ^{bc}	92.22±1.80 ^b
B20 N40A	20.22±1.77 ^c	152.59±7.94 ^b	172.80±8.75 ^b	88.30±0.87 ^b
B10 N40B	6.29±2.89 ^a	226.28±6.03 ^d	232.57±7.67 ^d	97.32±1.19 ^c
B20 N40B	13.57±1.67 ^b	195.68±20.88 ^c	202.49±26.86 ^c	97.01±9.39 ^c

the individual letters (a, b, c, d) in lines represent the statistical significance ($P < 0.05$) of the effect of the application of biochar, biochar with N or biochar reapplication, H – hydrolytic acidity, SBC – the sum of basic cations, CEC – cation exchange capacity, BS – base saturation

of nitrogen fertilization. Therefore, we evaluated also the changes in soil pH under treatments with N fertilization (Fig. 1). The lowest values of pH in H₂O and pH in KCl in treatments with N fertilization were measured in B0N40 treatment. However, when combined with biochar, the values increased significantly. Yu et al. (2017) compared the effects of N ammonium fertilizer alone at the rate of 30 kg.N⁻¹.ha⁻¹, but also the effect of its combination with 19.5 t.ha⁻¹ of biochar. After addition of N alone, the pH value was 5.3, while pH increased from 5.3 to 6.0 after the application of biochar with N. Long-term use of nitrogen fertilizers in the ammonium form can be the reason of soil acidification. This is initiated by the release of H⁺ ions in the process of nitrification (Zhang, Zhang and Li, 2002). In our case, the effect was stronger after adding 10 t.ha⁻¹ rather than 20 t.ha⁻¹ (Fig. 1). The values of soil pH in H₂O in B10N40A, B20N40A, B10N40B and B20N40B treatments were higher than in B0N40 by 11.3%, 8.0%, 15.4% and by 12.6%, respectively. The values of soil pH in KCl in the same treatments were higher by 13.8%, 9.5%, 19.2% and 14.8%, respectively.

The average values of the sorption parameters in this study are shown in Table 3. We did not find any significant effects on hydrolytic acidity (H) in treatments with initial added biochar without N, however the values of sum of basic cations (SBC) and cation exchange capacity (CEC) in B20A treatment significantly increased by 16.3% and 13.4% compared to B0 treatment. On the other hand, B10A treatment showed no significant changes. In several studies (e.g. Wang, Li and Liang, 2013) the positive impact of biochar on the content of CEC has been demonstrated. The biochar effect increased along with its applied rate. The re-addition of biochar without N with the lower rate also significantly increased the SBC by 16.2% and CEC by 14.13% compared to B0 treatment (Table 3). Furthermore, the reapplication of biochar with higher rate suppressed H from 16.65 mmol.kg⁻¹ (B0) to 11.47 (B20B) mmol.kg⁻¹. The SBC value increased from 137.28 mmol.kg⁻¹ (B0) to 194.66 mmol.kg⁻¹ (B20B), CEC value from 153.93 mmol.kg⁻¹ (B0) to 206.12 mmol.kg⁻¹ (B20B) and the BS value from 89% (B0) to 94% (B20B). Better results were observed in B20B treatment than in B20A. After the biochar adding, it is subject to a whole range of biochemical reactions which can be reflected in a change in its properties over time (Liang et al., 2006). The study of Šimanský et al. (2018) also observed the gradual decline of biochar efficiency during the first three years in this experiment after its first application. The values of SBC, CEC and BS gradually decreased in almost all treatments. According to Ren, Yuan and Sun (2018), some biochar pores are blocked by fine soil particles. These gradually migrate from the outer to the inner portions of the pores. It may result in a reduction in surface area of biochar particles. As a result, it reflects on the suppression of its sorption capacity. In addition, the action of soil organisms can influence the structural properties of biochar, which is also shown to change its sorption capacity. At the same time, Ren, Yuan and Sun (2018) added that the effect of biochar increased in pollutant sorption in the first months after application. However, the biochar surface area gradually decreased over time, thereby decreasing its sorption capacity. It reached the

control level within 2.5 years after adding biochar. A similar finding was also found by Martin et al. (2012). Our results showed that the greatest positive effects on the changes of sorption parameters were determined after the biochar reapplication at the rate of 20 t.ha⁻¹.

In the case of treatment with N fertilizer without biochar (B0N40), we found the highest value of H and the lowest values of SBC, CEC and BS. On the other hand, when the N fertilizer was used in combination with biochar, there was a significant decrease of H and the SBC, CEC and BS increased in of all four treatments (Table 3). Yu et al. (2017) stated that after the addition of N with biochar, the content of exchange cations was significantly higher than the addition of N fertilizer itself. Both rates of originally applied biochar: 10 t.ha⁻¹ and 20 t.ha⁻¹, respectively decreased H by 48.8% and 26.6%, increased SBC by 29.7% and 22.7%, CEC by 20%, and 15.8%, BS by 12.2% and 8.3% compared to B0N40 treatment. After the reapplication of biochar at both rates the H values dropped from 27.53 mmol.kg⁻¹ (B0N40) to 6.29 mmol.kg⁻¹ (B10B40B) and to 13.57 mmol.kg⁻¹ (B20N40B). The SBC values increased by 47.9% and 39.8%, CEC by 37.5% and 28.2%, BS by 16.8% and 16.5% compared to the B0N40 treatment. The most favourable effect of biochar in combination with N fertilizer was achieved in B10N40B treatment (H value – the lowest and opposite the highest values of SBC and CEC).

Conclusion

The results of our study showed the contrasting effects of the first application and the reapplication of pure biochar and biochar in combination with N fertilizer on improving of soil pH and soil sorption parameters.

In the case of the first biochar application without N, in B20A treatment we observed significant increase in pH in H₂O, pH in KCl, SBC and CEC by 6.3%, 5.7%, 16.3% and 13.4% compared to B0 treatment. The reapplication of lower biochar rate had a similar effect to the initial application of higher biochar rate. Additionally, the most beneficial effect in B20B treatment was achieved. We conclude that biochar reapplication at the higher rate had the most significant effect on increase of soil pH.

We found the higher values of pH in H₂O, pH in KCl, SBC, CEC, BS and lower value of H in B10N40A, B20N40A, B10N40B and B20N40B treatments compared to B0N40 treatment. In this case, the adding of fresh biochar was also more effective than the first application at the beginning of the experiment. The addition of 10 t.ha⁻¹ of fresh biochar had the most beneficial effect on soil pH and soil sorption parameters.

Based on the results of this study, we conclude that the addition of biochar into soil mainly at a higher rate or in combination with N every four years could be effective for increase of soil pH and improve soil sorption properties. In addition, we anticipate that shorter interval between biochar application could be even more advantageous.

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