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CARBON SEQUESTRATION IN WATER-STABLE AGGREGATES UNDER BIOCHAR AND BIOCHAR WITH NITROGEN FERTILIZATION

VLADIMÍR ŠIMANSKÝ; JÁN HORÁK; PETER KOVÁČIK; DANIEL BAJČAN
[1] *Slovak University of Agriculture, Department of Soil Science, Faculty of Agrobiology and Food Resources, 949 76 Nitra, Slovakia*
[2] *Slovak University of Agriculture, Department of Biometeorology and Hydrology, Horticulture and Landscape Engineering Faculty, 949 76 Nitra, Slovakia*
[3] *Slovak University of Agriculture, Department of Agrochemistry and Plant Nutrition, Faculty of Agrobiology and Food Resources, 949 76 Nitra, Slovakia*
[4] *Slovak University of Agriculture, Department of Chemistry, Faculty of Biotechnology and Food Sciences, 949 76 Nitra, Slovakia*

Abstract

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An experiment of different application rates of biochar and biochar combined with nitrogen fertilizer was conducted at the newly established experimental field (spring 2014) on Haplic Luvisol located in Nitra region of Slovakia during the growing season of spring barley. The aims of this study were to evaluate the effects of biochar and biochar combined with nitrogen fertilization (1) on the soil organic carbon (SOC) and labile carbon (C_L) contents in water-stable macro- (WSA_{ma}) and micro-aggregates (WSA_{mi}), and (2) on carbon sequestration in water-stable macro- (CSC_{ma}) and micro-aggregates (CSC_{mi}). The treatments (3 replicates) consisted of 0, 10 and 20 tha^{-1} of biochar application (B0, B10 and B20) combined with 0, 40 and 80 kg N ha^{-1} of nitrogen fertilizer applied (N0, N40, N80). There was observed significant increase of SOC in WSA_{ma} (by 11%) in B20N0 compared to B0N0. The biochar in both rates 10 and 20 t ha^{-1} together with 40 and 80 kg N ha^{-1} did not have effects on SOC in WSA. Significant increase of C_L in WSA_{ma} and C_L in WSA_{mi} were found only in B20N80 compared with B0N0. Overall, the highest values of CSC_{ma} were in the following order B10N80 > B20N0 > B0N0 > B20N40 > B10N0 > B20N80 > B10N40. Overall, the highest average values of CSC_{mi} were found in treatments with 10 t ha^{-1} of biochar combined with 80 kg N ha^{-1}.

Keywords: biochar; soil organic carbon; labile carbon; aggregates
Abbreviations: soil organic carbon (SOC), labile carbon (C_L), water-stable macro-aggregates (WSA_{ma}), water-stable micro-aggreggates (WSA_{mi}), carbon sequestration in water-stable macro-aggregates (CSC_{ma}), carbon sequestration in water-stable micro-aggregates (CSC_{mi}), no biochar and no N fertilization (B0N0), biochar at dose of 10 t ha^{-1} (B10N0), biochar at dose of 20 t ha^{-1} (B20N0), biochar at dose of 10 t ha^{-1} + fertilizer in dose of 40 kg N ha^{-1} (B10N40), biochar at dose of 20 t ha^{-1} + fertilizer in dose of 40 kg N ha^{-1} (B20N40), biochar at dose of 10 t ha^{-1} + fertilizer in dose of 80 kg N ha^{-1} (B10N80), biochar at dose of 20 t ha^{-1} + fertilizer in dose of 80 kg N ha^{-1} (B20N80)

**Corresponding author*: Vladimir.Simansky@uniag.sk

Introduction

Originally, after slight decline in soil organic carbon (SOC) at the beginning of soil monitoring system in Slovakia (1990s), its increase has been indicated on all arable soils during the last period. It could be probably caused by subsidies of Slovak government for increase of SOM in soils (Kobza and Gašová, 2014). The organic carbon content in arable land is typically unsatisfactory. In several of the most productive areas the soil organic carbon content has decreased to low levels. Soils with low (< 1.80 %), medium (1.81 – 2.30%) and high (> 2.30%) level of organic carbon represent 460 316, 770 318 and 1 215 336 hectares, respectively. The agricultural land of the Slovak Republic covers 2 432 979 hectares (Šimanský et al., 2013).

According to the results of the green report (2014), there is recorded continuous decline in the annual production of organic fertilizers as a primary source of SOC. In 1989, the dose of organic fertilizer from animal production reached 24.5 tons per year on cropland in the Slovak Republic. This value dropped almost three times (i.e. 7.8 tons of manure per year on cropland in SR) in 2011. In terms of sustainable agricultural production, it is extremely important to address the issue of equal balance of organic matter on the arable land. Since the production of organic fertilizers in Slovakia has a decreasing trend, the new solutions have been searched. It turns out that the application of biochar could be a beneficial solution.

Biochar is a carbon-rich product produced by the slow thermochemical pyrolysis of biomass materials (Zimmerman, 2010). Organic materials, such as livestock manures, sewage sludge, crop residues and composts are converted to biochars and then applied to soils as an amendment. Many studies have shown that biochar is a useful resource to improve the chemical and physicochemical (Yamato et al., 2006), biological (Lehmann et al., 2011) and physical (Kammann et al., 2011; Obia et al., 2016) properties of soil. Biochar used as a soil amendment improves soil fertility and plant growth (Zhu et al., 2014). Benefits of biochar as a soil amendment may vary with its properties, time after its application, and in relation to soil texture and mineralogy (Butman et al., 2015) and due to its mostly inert nature, is often applied to soils in conjunction with organic or mineral fertilizers (Asai et al., 2009; Laird et al., 2010).

Under these circumstances, the aims of this study were (1) to quantify the effects of added biochar and biochar with N fertilization to the soil on soil organic carbon contents in water-stable aggregates, and (2) to quantify the carbon sequestration in water-stable aggregates in relations to addition of biochar and biochar with N fertilization to the soil. The results of this experiment are discussed from the standpoint of possible organic carbon build up in the water-stable aggregates, with consequent improvement of both fertility and sequestration capacity of soil after application of biochar.

Materials and Methods

The field experiment was conducted at the experimental site of SAU-Nitra (Nitra-Malanta) in Nitra region of Slovakia (lat. 48°19´00´´; lon. 18°09´00´´) during the growing season of spring barley (March – July, 2014). Nitra-Malanta is situated in the lower part of Selenec creek basin and its tributaries, which belong to the central part of Nitra river basin. It is located on the east of Nitra, on the Žitavská upland. The geological substratum consisted of little previous rocks with high quantities of fine materials. Young Neogene deposits were composed of various clays, loams, sand gravels on which loess was deposited in the Pleistocene Epoch. The soil type is classified as Haplic Luvisol (WRB, 2006). Locality has a temperate climate. The average annual air temperature was 10.3°C and annual precipitation was 640 mm during the studied year. Soil samples from 10 random locations (experimental field trial) were taken on 4th of March before setting up the experiment from soil depth of 0-0.2 m. On average, soil contained 360.4 g kg^{-1} of sand, 488.3 g kg^{-1} of silt and 151.3 g kg^{-1} of clay (Šimanský et al., 2008). Soil carbon content was 9.13 g kg^{-1}, while the average soil pH (KCl) was 5.71.

The experiment was laid out few days later (7th of March) followed by biochar application (10th of March) and sowing of the crop (11th of March). The replicated (n = 3) trial plots (4 m x 6 m) were laid out in a randomized block design planted with the spring barley (*Hordeum vulgare* L.) on the experimental field that has been used for crop production over the last several years. The experiment consisted of following treatments which are shown in Table 1 separated by a protection row of 0.5 m in width. The field was ploughed, harrowed and biochar was evenly spread onto the soil surface and immediately incorporated into the soil (10 cm) combined with or without N fertilization using a combinator. To maintain consistency, ploughing and mixing treatments were also performed for the plots without biochar or N fertilization (Calc-Ammonium nitrate). Biochar used for the field experiment was produced from paper fiber sludge and grain husks (1:1 w/w) (company Sonnenerde, Austria) by pyrolysis at 550°C for 30 minutes in a Pyreg reactor (Pyreg GmbH, Dörth, Germany).

Soil samples were collected from all treatments (soil depth of 0–0.2 m) during the whole spring barley growing season (19 March, 17 April, 15 May, 16 June, and 13

Table 1
The studied treatments

B0N0	no biochar, no N fertilization
B10N0	biochar (10 t ha^{-1})
B20N0	biochar (20 t ha^{-1})
B10N40	biochar (10 t ha^{-1}) + fertilizer (40 kg N ha^{-1})
B20N40	biochar (20 t ha^{-1}) + fertilizer (40 kg N ha^{-1})
B10N80	biochar (10 t ha^{-1}) + fertilizer (80 kg N ha^{-1})
B20N80	biochar (20 t ha^{-1}) + fertilizer (80 kg N ha^{-1})

July). For each sampled zone three different locations were chosen and the soil samples were always collected from these areas. Samples collected from each location were mixed (to avoid repeating: soil samples were collected) to make an average representative sample. Samples were taken with the aid of a spade to maintain the soil aggregates. Every root and large piece of litter was removed. The collected soil samples were transported to the laboratory and the large clods were gently broken up along natural fracture lines, followed by air-drying at the lab temperature. The size classes of water-stable aggregates (WSA) were determined using the Baksheev Method (Vadjunina and Korchagina, 1986). In fractions of water-stable macro- (WSA_{ma}) and micro- aggregates (WSA_{mi}), we analysed the total organic carbon by the Tyurin Method (Dziadowiec and Gonet, 1999) and the labile carbon by the Loginov Method (Loginow et al., 1987). The soil carbon sequestration capacities (Semenov et al. 2008) in WSA_{ma} (CSC_{ma}) and in WSA_{mi} (CSC_{mi}) were calculated according to the following equations:

$$CSC_{ma} = \frac{SOC - C_L}{C_L}, \tag{1}$$

where SOC is the content of organic carbon (g kg^{-1}) in the WSA_{ma}, and C_L is the content of labile carbon (g kg^{-1}) in the WSA_{ma}.

$$CSC_{mi} = \frac{SOC - C_L}{C_L}, \tag{2}$$

where SOC is the content of organic carbon (g kg^{-1}) in the WSA_{mi}, and C_L is the content of labile carbon (g kg^{-1}) in the WSA_{mi}.

The statistical evaluation of the data was performed using the Statgraphics Centurion XV.I programme (Statpoint Technologies, Inc., USA). Treatment differences (one-way ANOVA) were considered significant at *P* values < 0.05 by the LSD test. The interrelations between the soil carbon sequestration capacities of water-stable macro- and micro-aggregates and SOC in WSA as well as C_L in WSA were determined through a correlation matrix.

Results

The application of 20 t ha^{-1} of biochar without N fertilization significantly increased the SOC content in the WSA_{ma} by 11% compared with the B0N0 treatment (Figure 1). The B20N0 treatment significantly increased SOC content in the WSA_{ma} by 23% compared with the B10N0. We observed depressive effect of applied biochar at the dose of 10 t ha^{-1} on the SOC in WSA_{ma} compared to B0N0. Overall, the biochar treatment at dose of 10 with 40 kg N ha^{-1} increased the SOC content in WSA_{ma} by 8% compared to B10N0 treatment. On the other hand, the biochar treatment at dose of 20 t ha^{-1} combined with 40 kg N ha^{-1} decreased the SOC content in WSA_{ma} by 9% compared to B10N0 treatment. Similar trends, with significant increase of SOC in WSA_{ma} were observed as results of increased doses of biochar together with 80 kg N ha^{-1} compared with the B10N0 treatment. No significant differences in the SOC contents in the WSA_{mi} were determined in all biochar treatments without N fertilizer. No significant difference in the SOC in WSA_{mi} was found also between the B10N40 and B10N0 treatments as well as between the B20N40 and B20N0 treatments. One-way ANOVA analysis showed no significant differences in SOC content in WSA_{mi} between B10N80 and B10N0 treatments as well as between the B20N80 and B20N0. The SOC content in WSA_{mi} in B20N80 was higher by 11% compared to B0N0.

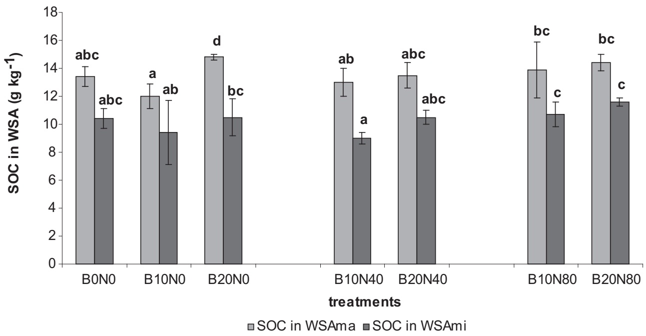

Fig. 1. Statistical evaluation of soil organic carbon contents in water-stable aggregates
Different letters between columns (a, b) indicate that treatment means are significantly different at P < 0.05 according to LSD test

The contents of C_L in WSA (micro- and macro-) were not significant changed by different rates of biochar application into the soil compared to control soil (B0N0). Also the application of 20 t ha^{-1} of biochar combined with 40 kg N ha^{-1} had no effect on the C_L in WSA compared to the control soil. However, a considerable increase of C_L in WSA_{ma} and C_L in WSA_{ma} were found in range of 12% and 27%, respectively in case of 20 t ha^{-1} of biochar application combined with 40 and 80 kg N ha^{-1} compared to B0N0 treatment (Figure 2). The same trends were observed in case of C_L in WSA_{mi}.

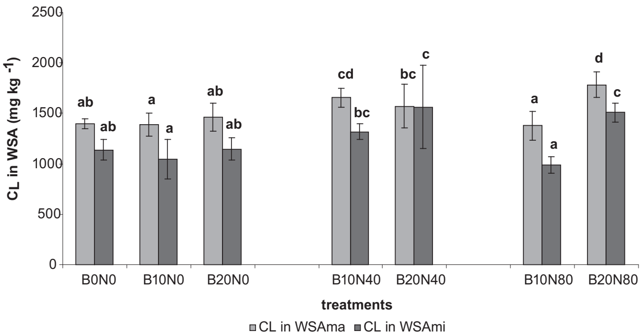

Fig. 2. Statistical evaluation of labile carbon contents in water-stable aggregates

Different letters between columns (a, b) indicate that treatment means are significantly different at P < 0.05 according to LSD test

The application of 20 t ha^{-1} of biochar and as well as 20 t ha^{-1} of biochar together with 80 kg N ha^{-1} had no a significant influence on the carbon sequestration capacities of water-stable macro-aggregates (Figure 3). On the other hand, the biochar at the dose of 10 t ha^{-1} without N fertilization significantly decreased the CSC_{ma} as compared to B0N0. The same trends were observed in B10N40, in B20N40 and also in B20N80 treatments. On the other hand, values of CSC_{ma} were higher in B20N0 by 5% than in B0N0. Overall, the highest values of CSC_{ma} were in the following order B10N80 > B20N0 > B0N0 > B20N40 > B10N0 > B20N80 > B10N40. No significant differences in the CSC_{mi} were determined in biochar treatments without N fertilizer as well

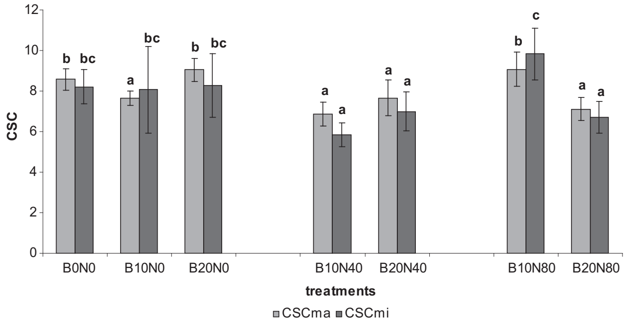

Fig. 3. Statistical evaluation of carbon sequestration capacity in water-stable aggregates

Different letters between columns (a, b) indicate that treatment means are significantly different at P < 0.05 according to LSD test

as biochar treatments with 80 kg N ha^{-1} compared to B0N0. There were observed statistical significant differences between treatments in contents of CSC_{mi} for B10N40, B10N40 and B0N0 treatments. Values of CSC_{mi} were lower by 29% and by 26% in B10N40 and B20N40 respectively, compared to B0N0 (Figure 3). Generally, the highest average values of CSC_{mi} were observed in the biochar treatments in dose of 10 t ha^{-1} with 80 kg N ha^{-1}.

Table 2 displays the correlation coefficients (r) between CSC in WSA and SOC and C_L in WSA. We found a significant positive correlation between CSC_{ma} and SOC in WSA_{ma} ($r = 0.816$, $P < 0.01$) as well as between CSC_{mi} and SOC in WSA_{mi} ($r = 0.708$, $P < 0.01$) at treatments with only biochar application. However, significant but negative correlation was found between the CSC_{mi} and C_L in WSA_{ma}. In case of biochar treatments combined with N-fertilizer (40 kg N ha-

Table 2

Correlation coefficients *(r)* between carbon sequestration capacities of water stable aggregates and soil organic matter in water stable aggregates

		SOC in WSA_{ma}	SOC in WSA_{mi}	C_L in WSA_{ma}	C_L in WSA_{mi}
Biochar without N fertilization	CSC_{ma}	0.816***	n.s.	n.s.	n.s.
	CSC_{mi}	n.s.	0.708**	-0.601*	n.s.
Biochar with N (40 kg ha^{-1})	CSC_{ma}	0.568*	n.s.	-0.717**	n.s.
	CSC_{mi}	n.s.	n.s.	n.s.	-0.873***
Biochar with N (80 kg ha^{-1})	CSC_{ma}	n.s.	n.s.	-0.724**	-0.698**
	CSC_{mi}	n.s.	n.s.	-0.643**	-0.910***

n.s. – non-significant; $^{*}p < 0.05$; $^{**}p < 0.01$; $^{***}p < 0.001$

CSC_{ma} – carbon sequestration capacity of water stable macro-aggregates, CSC_{mi} – carbon sequestration capacity of water stable micro-aggregates, SOC in WSA_{ma} – soil organic carbon in water stable macro-aggregates, SOC in WSA_{mi} – soil organic carbon in water stable micro-aggregates, C_L in WSA_{ma} – labile carbon in water stable macro-aggregates, C_L in WSA_{mi} – labile carbon in water stable micro-aggregates

[1]), we found a significant positive correlation only between CSC_{ma} and SOC in WSA_{ma}. There was also observed significant negative correlation between CSC_{ma} and C_L in WSA_{ma} and CSC_{mi} and C_L in WSA_{mi}. Significant negative correlation between CSC and C_L in WSA was determined at biochar treatment combined with 80 kg N ha^{-1}.

Discussion

Up to now, there were published several studies (Busscher et al., 2010; Laghari et al., 2015; Agegnehu et al., 2016) where authors concluded that biochar increased SOC in the soils. Soil minerals and organic matter associate with biochar tended to form aggregates in which the biochar turned occluded from chemical degradation or transport (Brodowski et al., 2006), which could be the main reason of C increase in the aggregates. Results of our study showed that added N had different effects on the SOC and C_L in WSA (Figures 1 and 2). Higher dose of biochar added to the soil with N at rates of 40 and 80 kg ha^{-1} resulted in higher SOC contents in WSA. There were determined a negative effect of biochar at dose of 10 t ha^{-1} without N fertilization treatment on content of SOC in WSA_{ma}. Biochar particles are 1-5 mm large and therefore they are part of WSA_{ma}. Effect of biochar without N fertilization on SOC change in WSA_{mi} and C_L in WSA was not significant. Higher dose of biochar together with 80 kg N ha^{-1} significantly increased the C_L in WSA. More significant effect was determined in WSA_{mi} (32%) than in WSA_{ma} (27%) (Figure 2). Biochar acts as a stable C compound being degraded only slowly with a mean residence time (Fisher and Glaser, 2012), however it is often applied to soils in conjunction with organic or mineral fertilizers (Laird et al., 2010). Addition of labile C (e.g. slurry) and chemical fertilizers - especially nitrogen to soil significantly increased biochar mineralization in the short-term (Kuzyakov et al., 2009; Yang, 2011).

Carbon sequestration through biochar adition to the soil is rather great (Heitkötter and Marschner, 2015), and therefore lately its application to the soil has received attention. Added biochar increase soil carbon sequestration (Singh and Cowie, 2014; Han et al., 2016). One of the most effective mechanisms is based on sequestration of C in WSA. There can be C physically and physico-chemically protected. Our findings did not point to C sequestration clearly in WSA (Figure 3). Biochar at dose of 10 t ha^{-1} without N significantly decreased the CSC_{ma} compared to B0N0 and the CSC_{mi} was not significantly changed. Franzluebbers (2005) reported that fertilization has been proved to improve C sequestration. In this experiment the added N had a different effect on the CSC in WSA. In B20N80, the values of CSC_{ma} and CSC_{mi} significantly decreased by 17% and by 18%, respectively, compared to B0N0 treatment. The results of Šimanský (2013) confirmed significant effect of NPK fertilization on the CSC in the size fractions of WSA, while the highest values of CSC_{ma} were observed in NPK1 (lower doses of fertilizers) than in NPK3 (higher doses of fertilizers) which is consistent with our findings (Figure 3).

A high C input leads to linear increase of C sequestration in the soil (Li et al., 2010; Ghosh et al., 2012). Semenov et al. (2008) reported that the amount of C sequestered in the soil depends on the balance between the C input rate and the decomposition rate of soil organic matter. In this study CSC_{ma} correlated with SOC in WSA_{ma} and CSC_{mi} correlated with SOC in WSA_{mi} in the biochar treatments without N fertilizer. The same effect was not observed in the biochar treatments with 80 kg N ha^{-1}. Higher contents of C_L in WSA_{ma} and WSA_{mi} resulted in lower values of CSC_{ma} and CSC_{mi}, respectively in the biochar with 40 kg N ha^{-1} treatments. Contents of C_L in WSA had negative effects on CSC in the biochar with 80 kg N ha^{-1} treatments (Table 2). The differences in CSC_{ma} and CSC_{mi} could be due to different C stabilization mechanisms. Stabilization and protection of C is controlled by three mechanisms: (1) C association with clay minerals or Fe and Al oxides, (2) C sequestration into macro- and micropores of aggregates; and (3) C biochemical stabilization (Chenu and Plante 2006; Mikutta et al. 2006; Six et al., 2002; von Lützov et al. 2008; Pronk et al., 2011). In addition, the fertilization can influence carbon sequestration (Franzluebbers, 2005; Šimanský, 2013) - especially the added nitrogen (Table 2).

Conclusion

A positive response of soil organic carbon, labile carbon in water-stable aggregates and the carbon sequestration capacity of water-stable aggregates to the application of the biochar and biochar combined with nitrogen fertilizer are emphasized in this study. The most favourable effect on soil organic carbon in water-stable macro-aggregates was determined when 20 t ha^{-1} of biochar was applied. The same, the most favourable effects on labile carbon in water-stable macro-aggregates and micro-aggregates were observed when 20 t ha^{-1} of biochar with 80 kg N ha^{-1} and when 10 t ha^{-1} of biochar with 40 kg N ha^{-1} were applied. However, the highest increase of carbon sequestration capacity of water-stable aggregates was observed when 10 t ha^{-1} of biochar with 80 kg N ha^{-1} was applied to the soil.

In the view of agriculture sustainability, the combined biochar and nitrogen fertilization is a promising practice through which high carbon sequestration in water-stable aggregates could be obtained. Since the interaction between biochar and mineral fertilizer applied to soil is a complex process, additional studies included long-term field experiments are needed to support our understanding of their effects on changes of soil parameters.

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