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Research Article

Effect of biochar amendment and nitrogen fertilization on soil CO_2 emission during spring period

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Biochar application to agriculture soil has been recommended as a strategy to reduce increasing CO_2 emission in the atmosphere and mitigate climate change. In this study, we evaluated the impact of two doses of biochar (10 and 20 t.ha^{-1}) applied in 2014 and reapplied in 2018 combined with three fertilization levels (N0, N1, N2) on carbon dioxide emissions and selected physical and chemical soil properties in field conditions during spring season (April–June) in 2020. The field site is situated in the Nitra region of Slovakia (Malanta). The soil in the field was classified as a silt loam Haplic Luvisol. In this field research it was found that biochar application mostly in all treatments decreased cumulative CO_2 emissions in rage from 4.2% to 30.4% compared to controls (B0N0, B0N2), except treatments where biochar was applied with lower level of N-fertilizer (N1) and treatment B20N0. According to our study results, it was confirmed that biochar can be a promising material for improving soil physical and chemical properties. Mainly, it has very good impact on soil pH, even after seven years of field experiment established. However, the response of soil CO_2 fluxes to biochar application were regulated mainly by experiment length, biochar application rate, biochar properties, giving a new perspective for more comprehensive understanding on biochar.

Keywords: biochar, CO_2 emission, soil chemical and physical properties

1 Introduction

The global scientific community has generally regarded the greenhouse effect as a significant environmental concern. Carbon dioxide (CO_2), as a potent greenhouse gas (GHG), is responsible for global climate change due to an increasing concentration in the atmosphere. Fossil fuel combustion is considered responsible for more than 75% of human caused CO_2 emissions. Land use change (primarily deforestation) is responsible for the remainder (25%). In comparison to CH_4 and N_2O, CO_2 is cycling in the largest amounts through agricultural cropping systems. Plants consume large amounts of CO_2 through photosynthesis to make food, feed, fiber, and fuel – but all these plant products eventually convert back to CO_2 when consumed or when they decompose. The net emission of CO_2 is small compared to its total cycling in agriculture, and is mostly due to energy use on-farm and in the manufacture and transport of agricultural products.

Biochar application to agricultural soils is a promising management practice that has the potential to mitigate climate change and improve soil quality (Chintala et al., 2013). Still, it is not yet widely used in agricultural fields because the effects of biochar depend on soil and biochar properties (Van Zwieten et al., 2010). However, biochar is not completely inert and some parts of it, particularly the surface, contain significant amounts of bioavailable nutrients (Steiner et al., 2008). Therefore, the application of biochar to soil can influence the physical, chemical and biological properties of the soil (DeLuca & Sala, 2006). Effect of biochar also depend on the condition of the soil to which it was applied, application of biochar to soil with a high C content did not result in any application change in CO_2 emission (Cross & Sohi, 2011). In this study, we studied the effect of two rates of biochar application on CO_2 emissions from agriculture soil. The study included also the effect of biochar application on soil physical (soil temperature, and soil moisture) and chemical properties (soil pH, NO_3^- and NH_4^+) during the spring period. Here, we

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hypothesized that 1) biochar incorporated to soil would decrease soil CO_2 emissions and 2) biochar applied to the soil will improve soil chemical and physical properties.

2 Material and methods

2.1 Description of the research site

The field experiment was established in 2014 at the Dolná Malanta site in the Nitra region of Slovakia (coordinates: 48° 19′ 23″ N; 18° 09′ 01″ E). It is located in the west part of the Žitava Upland, through which stretches the Tribeč Mountains and belongs to the Nitra River basin. The altitude of the site is 175–180 m a. s. l. The site belongs to a temperate climate zone with an average annual air temperature of 10.8 °C and an average annual rainfall of 559 mm (30-year climatic normal, 1991–2020. In 2020, the mean annual air temperature was 8.8 °C and the annual precipitation was 669.4 mm. The soil at the research site Dolná Malanta is Haplic Luvisol. Before the establishment of the experiment, the area was cultivated conventionally and used for agricultural production. Before the commencement of field experiment the soil organic carbon had 9.13 $g.kg^{-1}$ and the average soil pH value was 5.71.

2.2 Designer of the experiment plots and treatments

Biochar was applied in March (2014) (starting of the experiment) at rate of 0,10 and 20 $t.ha^{-1}$ in combination with three levels of nitrogen fertilizer (N0, N1 and N2). The experiment after its setup included 9 treatments in three replications and was arranged in 27 experimental plots (4 × 6 m) in a randomized block design separated by 0.5 m wide buffer strips. Biochar was then again reapplied in April 2018 on half of the original experimental plots (4 × 3 m) at the same rates as in 2014 (0.10 and 20 $t.ha^{-1}$). Fig. 1 shows the design of the experimental plots and biochar treatments.

The sowing practice in 2020 included the cultivation of sowing peas (*Pisum sativum* L.). In 2020, N-fertilizer was applied at a rate of 30 kg. $N.ha^{-1}$ (fertilization level N1) and at a rate of 45 kg $N.ha^{-1}$ (fertilization level N2). In this research was used also insecticide Vastag and herbicide Corum.

The biochar used in this experiment was produced from paper fiber sludge and grain husks (1 : 1 ratio, Sonnenerde, Austria) by pyrolysis at 550 °C for 30 min in a Pyreg reactor (Pyreg GmbH, Dörthe, Germany). Table 1 shows the basic chemical and physical properties of the applied biochar.

Table 1 Basic properties of biochar used in current study

Biochar properties	Average value
Range of particle size (mm)	1–5
Bulk density ($g.cm^{-3}$)	0.21
Specific surface area ($m^2.g^{-1}$)	21.7
$pH_{(KCl)}$	8.8
Ash content (%)	38.3
Carbon (C) (%)	53.1
Nitrogen (N) (%)	1.4
C : N ratio	37.9

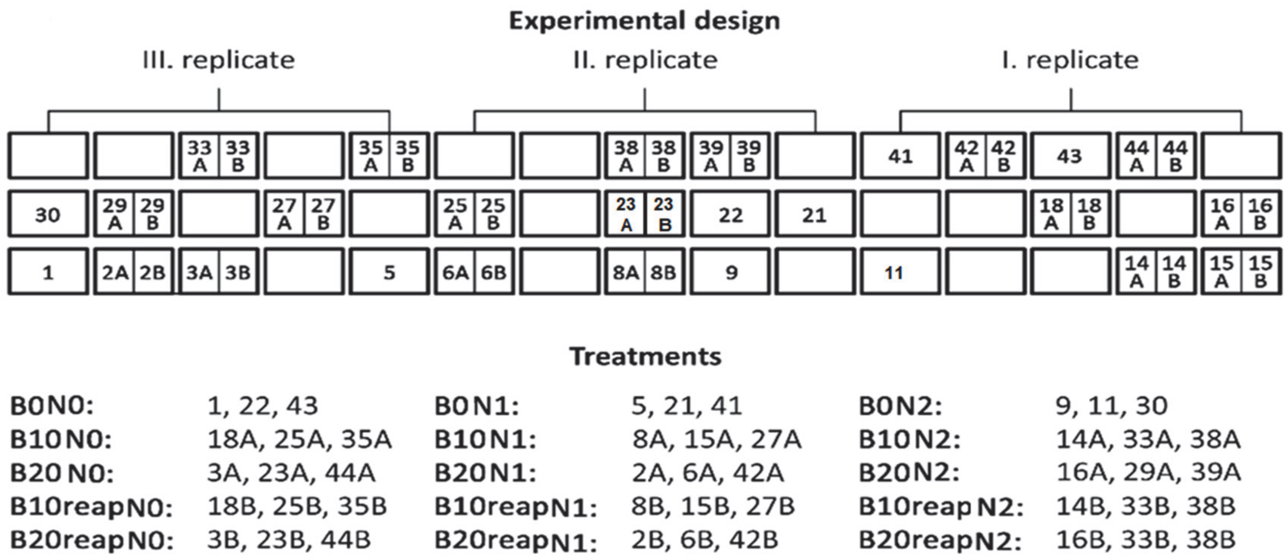

Figure 1 Schematic arrangement of the experimental site which were used in this study
A – plots with the biochar applied in 2014, B – plots with the biochar reapplied in 2018 and plots with control treatments without the biochar but with different rates of the N-fertilizer

2.3 Soil and gas sampling and analyses

Soil water content (w) was measured gravimetrically (by drying soil at 105 °C), determined twice a month. The soil temperature was measured at a depth of 0.05 m by an electronic thermometer (Volcraft DET3R) twice a month. The pH values of the soil were measured once a month using the potentiometric method in 1 mol.L^{-1} KCl using a pH meter (HANNA instruments HI 2211). The concentrations of nitrate (NO_3^-) and ammonium (NH_4^+) of the soil were measured using a spectrophotometer (Spectroflex 6100) and were measured once a month.

CO_2 emissions were measured using the closed chamber technique of Elder and Lal (2008), two-times per month (the same days as measurement of SWC and soil temperature), during the spring season from April to June. In each experimental plot, the chamber consisted of a metal cylinder (frame) and a removable upper part – the chamber. After putting the chamber to the cylinder, the groove was flooded with water to provide gas tightness of the chamber to the external environment. Gas samples were taken with a plastic 60 ml gas-tight syringe in a rate of 20 ml, at regular time intervals of 0.30 and 60 minutes after the chamber was closed. A 12 ml glass evacuated vials (septa sealed) (Labco Exetainer) were used to transport the 20 ml gas sample to the laboratory. Gas samples were analyzed using a gas chromatograph (GC-2010 Plus, Shimadzu Corporation, Kyoto, Japan) with a thermal conductivity detector (TCD) for CO_2 concentrations in ppm. Cumulative CO_2 emissions were calculated by interpolating emissions between sampling days and are reported in kg.ha^{-1}. All soil properties and CO_2 emissions was analyzed for spring period from April to June (include).

2.4 Statistical analyses

A one-way analysis of variance (ANOVA) was used to evaluate the effects of different biochar application rate on the measured parameter. Differences between the treatment means were compared using least significant difference testing (LSD). Further, regression analyses to determine the interrelationships between the CO_2 emission and selected soil physical (soil temperature and soil water content) and chemical properties (pH, NO_3^-, NH_4^+) were used.

3 Results and discussion

3.1 Soil physical properties

The impact of biochar application and reapplication at rate of 0.10 and 20 t.ha^{-1} in combination with three levels of N-fertilizer on soil moisture (w) measured at spring season in 2020 is presented in Table 2. In 2020,

Table 2 Impact of biochar application on soil physical properties during spring season (April to June) in 2020

Treatments	T (°C)	w (% mass)	Percentage increasing/decreasing of w (% mass)
Not fertilized group N0 (0 kg.ha^{-1})			
B0N0	14.7 ±0.3 a	14.4 ±0.7 a	-
B10N0	14.8 ±0.4 a	14.7 ±0.7 a	+ 2.1 %
B20N0	14.6 ±0.4 a	14.5 ±0.9 a	+ 0.7 %
B10reapN0	14.6 ±0.2 a	15.2 ±0.9 a	+ 5.6 %
B20reapN0	14.8 ±0.3 a	15.1 ±1.2 a	+ 4.9 %
Fertilized group N1 (30 kg.ha^{-1})			
B0N1	14.8 ±0.5 a	14.3 ±0.8 a	-
B10N1	14.7 ±0.3 a	15.8 ±0.7 a	+ 10.5 %
B20N1	14.6 ±0.3 a	15.7 ±0.9 a	+ 2.8 %
B10reapN1	14.3 ±0.4 a	13.9 ±0.8 a	- 2.8 %
B20reapN1	14.3 ±0.3 a	14.4 ±0.9 a	+ 0.7 %
Fertilized group N2 (45 kg.ha^{-1})			
B0N2	14.6 ±0.4 a	14.5 ±0.8 a	-
B10N2	14.6 ±0.3 a	14.9 ±0.1 a	+ 2.8 %
B20N2	14.5 ±0.3 a	14.9 ±0.8 a	+ 2.8 %
B10reapN2	14.9 ±0.3 a	15.0 ±0.9 a	+ 3.5 %
B20reapN2	14.7 ±0.3 a	15.4 ±0.9 a	+ 6.2 %

Different letters (a, b, c) within columns for each fertilized group indicate that treatments means are significantly different at P <0.05 according to the LSD multiple range test the treatments with biochar application combined with both levels of N-fertilization (N1 and N2) or without application of N-fertilizer (N0) showed higher (statistically insignificant) average soil moisture (w) over the spring season in most of the treatments from 0.7% to 10.5% compared to their respective controls (B0N0, B0N1, B0N2) (Table 2). Only treatment B10reapN1 showed lower soil moisture compared to control treatment B0N1. These results are in line with a study by Karim et al. (2020), which showed that soil moisture increased after the application of biochar. The positive effect of soil moisture increase could be attributed to biochar application to the soil, because soils with applied biochar have more micropores to hold water and thus improve aggregation, leading to the formation of more pores in the soil (Liao & Thomas, 2019).

Soil temperature is an important parameter that impacts a range of physical, chemical and biological processes in the soil (Khoshkhoo et al., 2015). Soil temperature is not only a key factor for plant growing, but also influences soil respiration and controls the transfer of water, salts and mineral nutrients (Xiong et al., 2020). In our research, no statistically significant effect of biochar application on soil temperature was found, during the studied period. Soil temperature decreased mostly in all treatments compare with their controls (B0N0, B0N1, B0N2), except treatments B10N0, B20reapN0, B10N2, B10 reapN2 and B20reapN2 where soil temperature in spring period increased to compare with control treatments (Table 2).

3.2 Soil chemical properties

Nitrogen is an essential component of organic compounds in crops and a key element for all living organisms. Soil fertility is usually measured by total nitrogen (Spokas, Novak & Venterea, 2012). The average concentrations of both forms of mineral nitrogen (NO_3^- and NH_4^+) over the study spring period in 2020 increased with application of N-fertilizer.

Concentrations of NO_3^- increased in all treatments, except treatments where biochar was applied without N-fertilizer and treatment B20N2 to compare with their respective control treatments (B0N0, B0N1, B0N2). No effect of biochar application was found in treatment B20reapN0. In other treatments was observed an increase concentration of NO_3^-. During spring period concentration of NO_3^- increased after application of spray (herbicide and insecticide) (data not shown). Study of Ullah et al. (2020) found that concentration of NO_3^- increased in treatments where biochar was applied with N-fertilizer.

Decreasing of NH_4^+ concentration was found in treatments where biochar was reapplied without N-fertilizer

Table 3 Impact of biochar application on soil chemical properties during spring season (April to June) in 2020

Treatments	NO_3^-	NH_4^+	pH
Not fertilized group N0 (0 kg.ha^{-1})			
B0N0	7.6 ±0.9 a	6.9 ±1.1 a	5.1 ±0.2 a
B10N0	6.9 ±0.4 a	7.0 ±1.5 a	5.3 ± 0.3 ab
B20N0	7.4 ±0.8 a	7.2 ±1.0 a	5.4 ±0.2 ab
B10reapN0	7.2 ±0.4 a	6.8 ±0.8 a	5.5 ±0.2 b
B20reapN0	7.6 ±0.4 a	6.5 ±1.2 a	5.5 ±0.1 b
Fertilized group N1 (30 kg.ha^{-1})			
B0N1	9.9 ±1.5 a	18.7 ±8.7 a	4.9 ±0.1 a
B10N1	11.8 ±1.2 a	11.2 ±3.3 a	5.3 ±0.4 a
B20N1	12.2 ±3.1 a	17.3 ±9.2 a	5.2 ±0.2 a
B10reapN1	15.5 ±2.1 a	21.5 ±5.2 a	5.3 ±0.5 a
B20reapN1	12.3 ±1.6 a	16.8 ±5.8 a	5.3 ±0.2 a
Fertilized group N2 (45 kg.ha^{-1})			
B0N2	12.6 ±1.2 a	22.5 ±2.5 a	4.2 ±0.1 a
B10N2	13.6 ±1.6 a	20.1 ±6.7 a	4.9 ±0.2 b
B20N2	11.3 ±1.2 a	12.3 ±4.7 a	5.3 ±0.4 bc
B10reapN2	16.1 ±2.5 a	16.5 ±5.4 a	4.9 ±0.3 bc
B20reapN2	15.4 ±1.8 a	17.9 ±4.4	5.3 ±0.3 c

Different letters (a, b, c) within columns for each fertilized group indicate that treatments means are significantly different at P <0.05 according to the LSD multiple range test

(B10reapN0, B20reapN0) and where biochar was applied in combination with lower rate of N-fertilizer (B10N1, B20N1, B20reapN1). All treatments where biochar was applied with higher level of N-fertilizer also decreased the concentration of NH_4^+ compared with control treatment (B0N2) (Table 3). These results are consistent with the study of Liu et al. (2020), where it was found that the NH_4^+ content of the soil was potentially lower after biochar application, during spring period. Concentration of soil NH_4^+ increased by 1.45%, 4.35% and 14.97% for treatments B10N0, B20N0 and B10reapN1, respectively.

The biochar combined with all fertilizer levels showed a positive effect on increase of soil pH in all treatments compared to the respective controls (B0N0, B0N1, B0N2). Statistically significant (P <0.05) increase of soil pH was found at some treatments where biochar was reapplied without N-fertilizer (B10reapN0, B20reapN0) and all biochar treatments with higher level of N-fertilizer as compared to its individual controls (B0N0, B0N2) (Table 3). Similar study (Aamer et al., 2020) to ours reported that application of biochar to the soil (at rate of 2%) increased soil pH. Biochar has positive effect on soil pH and can be used as an additive to modify soil acidity (Berek & Hue, 2016). For some treatments where biochar was applied without N-fertilizer and all treatments where biochar was applied with higher level of N-fertilizer soil pH increased with higher biochar application rate (B20 and B20reap).

3.3 CO_2 emission from the soil

The effect of application and reapplication of biochar in rates of 10 t.ha^{-1} and 20 t.ha^{-1} on the dynamics of carbon dioxide (CO_2) emissions at three different rates of N-fertilizer (N0, N1, N2) is shown in Fig. 2. In treatments with biochar combined with or without N-fertilization, emission peaks of CO_2 were identified in late spring due to precipitation (6 precipitation days – data not shown). Table 4 shown relationship between soil CO_2 emissions and soil temperature and soil moisture (w). Generally, our study showed that the temperature was the essential factor influencing soil CO_2 emission. Significant correlation was observed between soil CO_2 emission and soil temperature in all treatments, except treatments B0N0, B20N0, B10N1, B20N1, B20reapN1 and B10N2, B20N2. The most pronounced effect between temperature and CO_2 emission was found in treatment B10reapN0 (r = 0.90; P <0.01) (Table 4). Our results are in line with study Lopes de Gerenyu, Kurganova & Kudeyarov (2005), which found that significant linear trends (r = 0.46–0.55, P <0.001) reflecting the relationship between daily mean CO_2 emission and soil temperature through the whole period of observations and during spring and autumn seasons as well.

The significant effect on CO_2 emission had also soil moisture. The significant correlation between CO_2

Table 4 Pearson correlation coefficient between CO_2 emission and selected soil physical properties (soil moisture and soil temperature)

Treatments	**w (% mass)**	***T* (°C)**
Not fertilized group N0 (0 kg.ha^{-1})		
B0N0	0.55	0.62
B10N0	0.79*	0.80*
B20N0	0.75	0.75
B10reapN0	0.62	0.90**
B20reapN0	0.65	0.88*
Fertilized group N1 (30 kg.ha^{-1})		
B0N1	0.84*	0.85*
B10N1	0.75	0.74
B20N1	0.91**	0.71
B10reapN1	0.38	0.82*
B20reapN1	0.64	0.75
Fertilized group N2 (45 kg.ha^{-1})		
B0N2	0.91**	0.83*
B10N2	0.76	0.72
B20N2	0.79*	0.77
B10reapN2	0.38	0.83*
B20reapN2	0.85*	0.86*

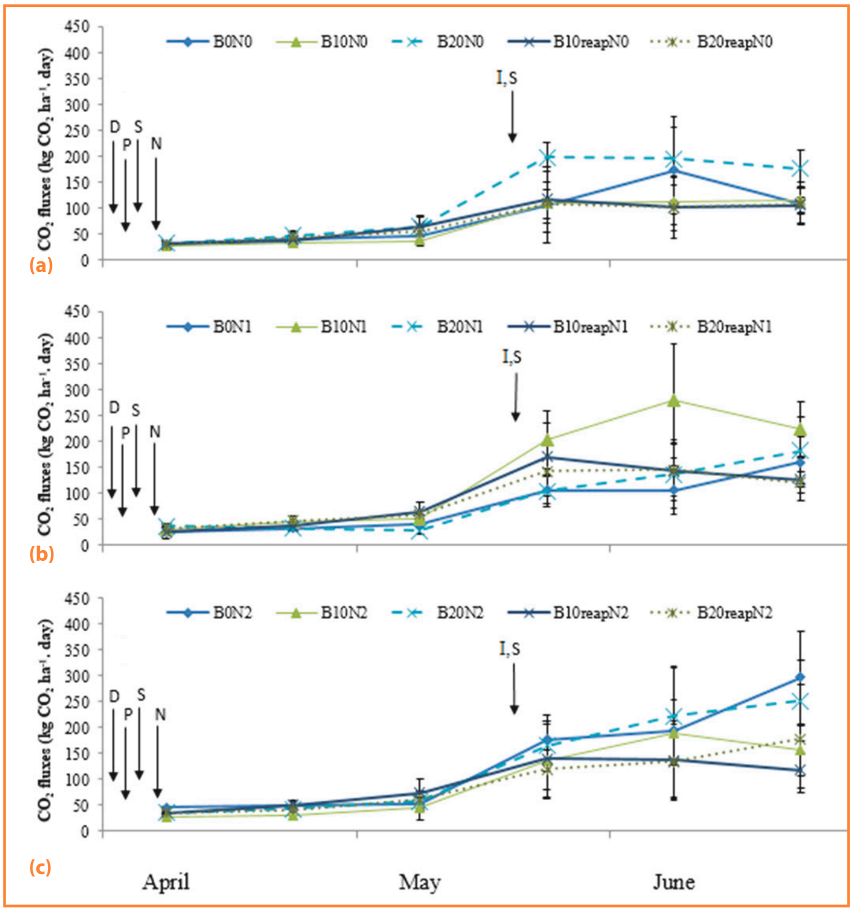

Figure 2 Fluxes of CO_2 emission from unfertilized treatment N0 (a), fertilized treatment N1 (b) and fertilized treatment N2 (c) with or without the biochar

Error bars denote the standard error of the mean (n = 3). D – disking (19. 3. 2020); P – planting of peas (20. 3. 2020); N – nitrogen fertilizer application (6. 4. 2020); S – spray herbicide application (1. 4. 2020); I, S – spray herbicide and insecticide application (19. 5. 2020)

emission and soil moisture was found for treatments B10N0, B0N1, B20N1, B0N2, B20N2 and B20reapN2 what indicating that the soil moisture was also factor limitative the rate of CO_2 emission from soil for this period.

In all three levels of N-fertilizer we found the differences in CO_2 fluxes (Fig. 2 – a, b, c). Concentration of CO_2 emissions in treatments where biochar was applied without N-fertilizer was lower compared with biochar treatments with N-fertilizer. Generally, daily CO_2 fluxes from the treatments with biochar combined with or without N-fertilizer (N2 and N0 level, respectively) were lower as compared to the control treatments.

Increased CO_2 emissions were found at treatments where biochar was applied in combination with lower rate of N-fertilizer compared with control treatments (Table 5).

The results for the unfertilized treatments showed that mostly all biochar treatments (B10N0, B10reapN0, B20reapN0) decreased the cumulative CO_2 emissions by 16.1%, 11.2%, and 14.2%, respectively, compared to control (B0N0). Only treatment B20N0 increased cumulative CO_2 emissions by 39.4%. The similar trend was found for treatments fertilized at the N2 fertilization level where all biochar-amended treatments (B10N2, B20N2, B10reapN2, B20reapN2) decreased cumulative CO_2 emissions by 26.1%, 4.2%, 29.8%, and 30.4% compared to control (B0N2) (Table 5). Our results are particularly in line with study Bovsun et al. (2021), where the measurement of CO_2 emissions during the growing season showed a significant decrease in the cumulative CO_2 flux in the treatments of the experiment with rates of biochar application. A decrease in the CO_2 flux indicates a recultivation effect of biochar. The reason for the recultivation action is due to the high sorption properties which affect the sequestration capacity of the soil.

Opposite was found for treatments at the N1 fertilization level (B10N1, B20N1, B10reapN1, B20reapN1) where cumulative CO_2 emissions were higher by 79.1%, 6.0%, 21.6%, and 17.1%, respectively compared to the control treatment (B0N1) (Table 5). Statistically significant (p <0.05) increase was found for treatment B10N1 as compared to control treatment (B0N1). These results are in agreement with the findings of other studies by Jones et al. (2012) and Ameloot et al. (2013), which also found that soil CO_2 emission increased after biochar application. The CO_2 dynamics were strongly dependent on soil temperature, with a higher correlation with the temperature at a depth of 10 cm (Table 5). The tendency of biochar to increase CO_2 efflux, observed in our study was probably due to increased soil microbial activity as well as plant growth.

4 Conclusion

Our field study provided important insights into the effects of N-fertilizer applied with biochar on CO_2 emission and soil properties. Under temperate climate conditions of Slovakia (field site Malanta) CO_2 emissions were effectively reduced by application of biochar and

Table 5 The effect of biochar application and reapplication on daily and cumulative CO_2 emissions. Different letters within columns indicate that treatment means over the sampling dates are significantly different at $p < 0.05$

Treatments	Average CO_2 emission	Cumulative CO_2 emission	Increase/decrease of cumulative CO_2 emission
Not fertilized group N0 (0 kg.ha^{-1})			
B0N0	84.2 ±33.7 a	6,786.9	–
B10N0	72.8 ±20.9 a	5,693.8	-16.1 %
B20N0	119.2 ±19.5 a	9,458.0	+39.4 %
B10reapN0	76.7 ±31.9 a	6,029.7	-11.2 %
B20reapN0	74.2 ±23.1 a	5,822.4	-14.2 %
Fertilized group N1 (30 kg.ha^{-1})			
B0N1	78.70 ±22.4 a	6,212.1	–
B10N1	139.32 ±39.64 b	1,1124.3	+79.1 %
B20N1	87.0 ±28.5 ab	6,586.6	+6.0 %
B10reapN1	94.6 ±32.6 ab	7,550.4	+21.6 %
B20reapN1	91.5 ±26.7 ab	7,271.0	+17.1 %
Fertilized group N2 (45 kg.ha^{-1})			
B0N2	135.7 ±36.7 a	10,465.6	–
B10N2	97.3 ±45.9 a	7,731.5	-26.1 %
B20N2	129.1 ±41.3 a	10,029.8	-4.2 %
B10reapN2	92.5 ±37.7 a	7,352.4	-29.8 %
B20reapN2	94.7 ±39.6 a	7,285.2	-30.4 %

Different letters (a, b, c) within columns for each fertilized group indicate that treatments means are significantly different at $P < 0.05$ according to the LSD multiple range test

N-fertilizer. Compared to control treatment, biochar had inhibitory effect on cumulative CO_2 emissions during spring period in range from 4.2% to 30.4%. In treatments where biochar was applied with lower level of N-fertilizer (N1) cumulative CO_2 emission increased by 6.0% to 79.1% as compared to control treatment (B0N1). Increasing was found also in one treatment B20N0 by 39.4% to compare with control (B0N0). Contradictory effect between treatments where biochar was applied with higher and lower N-fertilizer can be explaining by microbial activity and plant root respiration were the regulators of CO_2 emissions in this experiment. For soil chemical and physical properties, it was found that biochar had the most significant and positive effect (during spring period) on the pH of the soil. Based on the results of this study, we can conclude that addition of biochar into soil in combination with N-fertilizer is still able to improve soil CO_2 emission seven years after its first addition into the soil. However, its further recommendation to farmers needs more investigation of different types of biochar application at different soil-climatic conditions.

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