Effects of slow and fast pyrolysis biochar on N₂O emissions and water availability of two soils with high water-filled pore space

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Abstract: Biochars, depending on the types of feedstocks and technological conditions of pyrolysis, can vary significantly in their properties and, therefore, it is difficult to predict biochar-induced effects on nitrous oxide (N₂O) emissions from various soils, their physical properties and water availability. The objectives of this study were (1) to quantify effects of slow pyrolysis biochar (BC) and fast pyrolysis biochar (PYRO) on physical and hydro-physical properties of sandy soil (Haplic Arenosol) and clayey loam soil (Gleyic Fluvisol), and (2) to assess corresponding N₂O emissions from these two soils. The study included a 63-day long laboratory investigation. Two doses of BC or PYRO (15 t ha⁻¹ and 30 t ha⁻¹) were applied to the soils in combination or without nitrogen fertilizer (NH₄NO₃, 90 kg N ha⁻¹). The obtained results have shown a significant decrease in the bulk density of sandy soil after it was amended with either rate of BC or PYRO. Water retention capacity of the soils in all the treatments with BC or PYRO increased considerably although no changes was found in the soil water-filled pore space (WFPS) which was higher than 60%. BC was increasing N₂O emission rates from the sandy soil treated with N fertilizer, and reducing N₂O emission rates from the clayey loam soil treated with N fertilizer. PYRO was more efficient and was reducing N₂O emissions from both fertilized soils, but for the sandy soil the reduction was statistically significant only at higher dose (30 t ha⁻¹) of the biochar.

Keywords: Biochar; Sandy soil; Clayey loam soil; Bulk density; Water retention capacity; N₂O emission.

INTRODUCTION

Biochar is a carbon-rich, aromatic material produced by slow or fast pyrolysis of different organic wastes at high temperatures (up to 900 °C) in oxygen free or limited oxygen environment (Das et al., 2021; Kuppasamy et al., 2016; Lehmann et al., 2011; Lei and Zhang, 2013). Because of high chemical stability, biochar has a great potential to enhance atmospheric carbon sequestration (Laird et al., 2008; Lehmann et al., 2006). Soil amendments such as biochar, composts or their mixtures can decrease soil bulk density (Abd El-Mageed et al., 2021; Hardie et al., 2014), improve soil structure (Ajayi and Horn, 2016; Juriga et al., 2021), increase soil pH (Horák, 2015) cation exchange capacity (Igaz et al., 2018; Jien and Wang, 2013), soil N availability (Haider et al., 2017; Van Zwieten et al., 2010), organic carbon content (Ajayi and Horn, 2016; Šrank and Šimanský, 2020), soil porosity (Blanco-Canqui, 2017; Githinji, 2014), available water content (Głąb et al., 2016; Ibrahim et al., 2013) and saturated hydraulic conductivity (Jien and Wang, 2013; Toková et al., 2020).

Syakila and Kroeze (2011) reported that agricultural N₂O emission in 2006 reached 23–31% of the global emissions with the main source being nitrogen fertilizer and manure application to soils. Temperature, water-filled pore space (WFPS), O₂ concentration, pH, available soil organic carbon content (Dobbie and Smith, 2003; Wrage et al., 2001), mineral nitrogen content (Buchkina et al., 2012; Horák et al., 2019) affect microbial processes of nitrification and denitrification which are pathways of N₂O production in soils (Lee et al., 2009; Wrage et al., 2001).

Biochars produced under different conditions can have different physical (bulk density, porosity), physico-chemical (pH, CEC, BET surface area, oxygenated functional groups) and chemical (total carbon, nitrogen, hydrogen content) properties which, in due course, can have positive, neutral or negative effect on soil properties (Das et al., 2021; Liao et al., 2021; Novak et al., 2009; Rajapaksha et al., 2014) and crop yields (Murtaza et al., 2021). According to Bruun et al. (2012), application of fast pyrolysis biochar (produced from wheat straw) resulted in immobilization of soil N (43%) during the 65-day incubation, while application of slow pyrolysis biochar led to net N mineralization (7%) in soil. Application of biochar can be considered as one of the useful ways of mitigating N₂O emissions from soils (Buchkina et al., 2019; Horák et al., 2017; Ippolito et al., 2012; Rizhiya et al., 2019; Wang et al., 2013; Zhang et al., 2021). Biochar-induced improvement of soil physical and hydro-physical properties may mitigate microbial process of denitrification, which is the main process of N₂O production in soils (Wrage et al., 2001). Nevertheless, several studies have shown that biochar could stimulate N₂O emissions from soils under dry (Saarnio et al., 2013) and anaerobic conditions (Yanai et al., 2007) or had no effect on N₂O emissions (Karhu et al., 2011). According to Cayuela et al. (2013), there are four possible explanations for reduced N₂O emissions from soils after biochar application: binding of N₂O with metal ions (Fe, Cu) on the biochar surface; adsorption of organic substances by biochar and lower availability of this substances for microorganisms; liming effect of biochar resulting in an increase of soil pH and in a decrease of denitrification; improvement of soil aeration.

Fast and slow pyrolysis biochars can demonstrate different effects on N₂O emissions from soils with different texture. Stewart et al. (2013) reported that the fast pyrolysis biochar (from oak pellets, 550 °C) caused several times higher N₂O emission from a coarse-textured soil than from a fine-textured soil. Slow pyrolysis is usually carried out at temperatures lower than 600 °C. Therefore, slow pyrolysis biochars, in comparison with fast pyrolysis biochars, often demonstrated higher porosity, higher content of nutrients and organic substrates, and, as a result, greater ability to mitigate N₂O emissions from soils (Das et al., 2021; Kuppasamy et al., 2016). So, up to date, mechanisms and reasons of biochar different effects on nitrogen transformation and relevant N₂O emissions from soils are still obscure.

The objectives of the study were: (1) to quantify the effects of slow and fast pyrolysis biochar on physical and hydro-physical properties of sandy and clayey loam soils, and (2) to assess the corresponding changes in N₂O emissions from both soils.

MATERIALS AND METHODS

The effect of two doses of slow pyrolysis biochar (BC) and fast pyrolysis biochar (PYRO) on N₂O emissions from two soils with different texture, their physical and hydro-physical properties was studied in a laboratory experiment. The soils of the experiment were classified as Haplic Arenosol (sandy soil) and Gleyic Fluvisol (clayey loam soil) according to WRB (2014). Disturbed field moist soil samples for the laboratory experiment were collected from the upper 0–20 cm layer of agricultural plots with Haplic Arenosol located in Rišňovce (N48° 21.788', E17° 54.685') and with Gleyic Fluvisol located in Janikovce (N48° 6.933', E18° 07.031'). The sandy soil contained 924 g kg⁻¹ of sand, 53 g kg⁻¹ of silt, and 5 g kg⁻¹ of clay while the clayey loam soil contained 288 g kg⁻¹ of sand, 417 g kg⁻¹ of silt and 295 g kg⁻¹ of clay. Soil organic carbon (SOC) content in the sandy soil ranged from 2.95 to 3.19 g C kg⁻¹ soil while in the clayey loam soil – from 5.86 to 6.20 g C kg⁻¹ soil. Values of pH (KCl) were equal to 6.83 and 6.25 for sandy soil and clayey loam soil, respectively.

BC was produced at a temperature of 500–600 °C in a Pyreg reactor, while PYRO was produced at a temperature of 900 °C in a Spanner Re2 wood power plant. PYRO and BC had particle diameters of ≤1 mm and ≤3 mm, respectively. The treatments investigated in the study are shown in Table 1.

For the experiment air-dried soil (120–125 g, dry weight) was mixed with the biochars or/and the nitrogen fertilizer according to the treatments and moistened to a field capacity. The field capacity of the soils was equal to 50–55% of their full saturation. The moistened soil was inserted into steel cores (95

cm⁻³). A 63-day incubation of the soil cores was carried out at a room temperature. The cores were regularly weighed and moistened to maintain the moisture content in both soils equal to 50–55% of full saturation in all the studied treatments. The full saturation of the soils (% of weight) with all the treatments was measured. For the sandy soil it was: 50% (control), 54% (15 t ha⁻¹ of BC or PYRO) and 58% (30 t ha⁻¹ of BC or PYRO) while for the clayey loam soil it was: 62% (control), 64% (15 t ha⁻¹ of BC or PYRO), 66% (30 t ha⁻¹ of BC or PYRO). The laboratory experiment was carried out in six replicates.

To measure N₂O emissions, the soil cores were inserted into plastic vessels (1000 cm³) with airtight lids equipped with sealed rubber septums. At every air sampling occasion the plastic vessels were sealed for 20 minutes and air samples were collected from the headspaces with a syringe and transferred to pre-evacuated 12-ml glass vials (Labco Exetainer, Lampeter, UK). The same technique was used earlier in other experiments (Buchkina et al., 2019). The collected air samples were analyzed for N₂O concentration using a gas chromatograph (GC-2010 Plus, Shimadzu) equipped with a ⁶³Ni electron capture detector (ECD). The gas chromatograph (GC) was calibrated using two certified standard gas mixtures (N₂O and N₂) in the expected concentration range. Analytical conditions of the GC were: carrier gas (Helium, 30 ml min⁻¹) and detector temperature: 330 °C for ECD.

Concentration of mineral nitrogen (in N-NO₃⁻ form) in the soil samples was determined by an extraction technique proposed by Yuen and Pollard (1954) using a spectrometer (SP-870 PLUS, Metertech Inc.) at wavelengths of 410 and 420 nm, respectively. Soil pH (at 1:2.5 ratio of soil to 1M KCl solution) was measured using pH meter (HI 9017 Microprocessor Benchtop, HANNA instruments). Water-filled pore space (WFPS), or a volume of soil pores filled with water as a percent of total soil porosity, was calculated using the data on the soil moisture content (% of weight) and soil bulk density measured at the last day of the incubation experiment.

Statistical assessment of the experimental results was carried out on the basis of the calculated means, standard deviations, and 95% confidence intervals. Spearman's rank correlation coefficients (Spearman, 1904) were used to assess the strength of associations between the sets of soil parameters in all the treatments at $P \leq 0.05$. One-way analysis of variance (ANOVA, available at <https://www.socscistatistics.com>) was applied to evaluate the significance of differences between means of normally distributed data. Mann-Whitney U test (Mann and Whitney, 1947) was applied to assess the significance of differences in means (at $P \leq 0.05$) if the distribution was not normal according to the Shapiro-Wilk test (Shapiro and Wilk, 1965). Calculation procedure is available at <https://scistatcalc.blogspot.com/2013/10/shapiro-wilk-test-calculator.html>.

Table 1. The investigated treatments of the experiment.

No. of treatment	Description
C	control (soils without biochars and nitrogen fertilizer)
F	soil with ammonium nitrate (NH ₄ NO ₃) fertilizer (90 kg N ha ⁻¹)
15 BC	soil with 15 t ha ⁻¹ of BC
15	soil with 15 t ha ⁻¹ of PYRO
15 BC F	soil with 15 t ha ⁻¹ of BC + NH ₄ NO ₃ (90 kg N ha ⁻¹)
15 PYRO F	soil with 15 t ha ⁻¹ of PYRO + NH ₄ NO ₃ (90 kg N ha ⁻¹)
30 BC	soil with 30 t ha ⁻¹ of BC
30 PYRO	soil with 30 t ha ⁻¹ of PYRO
30 BC F	soil with 30 t ha ⁻¹ of BC + NH ₄ NO ₃ (90 kg N ha ⁻¹)
30 PYRO F	with 30 t ha ⁻¹ of PYRO + NH ₄ NO ₃ (90 kg N ha ⁻¹)

RESULTS AND DISCUSSION

Physicochemical properties of biochars

Different pyrolysis conditions resulted in different physicochemical properties of the two biochars used in the study (Table 2). BC, the slow pyrolysis biochar, had higher organic carbon content compared to PYRO, the fast pyrolysis biochar. According to Keiluwert et al. (2010), slow pyrolysis contributes to a higher conversion of non-aromatic organic matter into aromatic carbon. The higher specific surface area of PYRO is in correlation with the biochar particle size: fast pyrolysis resulted in significant disintegration of the feedstock material and PYRO had a dust-like structure, while BC inherited some of the feedstock structure and consisted of bigger particles.

The H/C, O/C, and (O+N)/C atomic ratios are usually used as indicators of aromaticity and polarity of biochars (Das et al., 2021). BC was more carbonized and had higher number of aromatic compounds than PYRO. Based on the higher values of O/C and (O+N)/C of PYRO, it can be assumed that fast pyrolysis biochar had a greater number of oxygen-containing polar groups (carboxylic, phenolic, hydroxylic), which could contribute to its higher affinity to water, better water adsorption and retention (Das et al., 2021; Ren et al., 2016).

Soil bulk density and water retention capacity

Incorporation of biochars into soils often leads to a decrease in their bulk density (Abd El-Mageed et al., 2021; Hardie et al., 2014). A degree of biochar-induced decrease in soil bulk density depends on soil texture and biochar application dose (Murtaza et al., 2021). In the conducted experiment the biochars

application affected the bulk density of the coarse-textured soil more than that of heavy-textured soil. The data on the bulk densities of the two soils studied in the experiment with all the treatments are presented in Fig. 1 and Fig. 2.

Bulk density of the sandy soil was reduced significantly due to application of both doses of BC or PYRO in comparison to the control treatment. Application of 15 t ha⁻¹ of PYRO to sandy soil with or without N-fertilizer resulted in considerably lower soil bulk density compared to similar treatments with BC ($P < 0.05$). Marginal differences were found in the bulk density of the sandy soil with various treatments after application of the higher dose (30 t ha⁻¹) of biochar irrespective of the biochar type.

Very negligible changes in the clayey loam soil bulk density were found under any of the studied treatments of the experiment in comparison to the control treatment. Therefore, both biochars were more effective in decreasing the bulk density of the sandy soil than the clayey loam soil. This might be attributed to the higher content of fine clay particles of the latter soil.

Figures 3 and 4 show the water retention curves of the two soils treated with two doses of BC or PYRO. The readily available water content is being held by soils in the range of water potentials from -5 to -300 kPa (the latter is the water potential of the first signs of plant wilting) and can be assessed using the water retention curves. The obtained results for the control treatments indicate that water retention capacity corresponding to the readily available water was significantly lower in the sandy soil in comparison to the clayey loam soil (at $P < 0.001$). Incorporation of either dose of BC or PYRO to the sandy soil significantly increased its water retention capacity (at $P < 0.05$). The increase after PYRO application was significantly higher ($P < 0.05$) than after BC application for both doses of the

Table 2. Properties of biochars used in the laboratory experiment.

Biochar	Specific surface area, m ² g ⁻¹	Oxygen (O), %	Hydrogen (H), %	Carbon (C), %	Nitrogen (N), %	O:C molar ratio	H:C molar ratio	(O+N)/C	pH KCl
PYRO	258	16.25	1.63	58.7	0.29	0.21	0.33	0.28	10.4
BC	123	6.20	0.63	76.7	0.64	0.06	0.10	0.09	9.1

Fig. 1. Bulk density of the sandy soil with different treatments. Bars show the 95% confidence intervals. Different letters indicate the significance of differences (at $P < 0.05$) according to one-way ANOVA. C – control; F – 90 kg N ha⁻¹; 15 BC PYRO – 15 t ha⁻¹ of BC or PYRO; 15 BC PYRO F – 15 t ha⁻¹ of BC or PYRO with 90 kg N ha⁻¹; 30 BC PYRO – 30 t ha⁻¹ of BC or PYRO; 30 BC PYRO F – 30 t ha⁻¹ of BC or PYRO with 90 kg N ha⁻¹.

Fig. 2. Bulk density of the clayey loam soil with different treatments. Bars show the 95% confidence intervals. Different letters indicate the significance of differences (at $P < 0.05$) between treatments according to one-way ANOVA. C – control; F – 90 kg N ha⁻¹; 15 BC PYRO – 15 t ha⁻¹ of BC or PYRO; 15 BC PYRO F – 15 t ha⁻¹ of BC or PYRO with 90 kg N ha⁻¹; 30 BC PYRO – 30 t ha⁻¹ of BC or PYRO; 30 BC PYRO F – 30 t ha⁻¹ of BC or PYRO with 90 kg N ha⁻¹.

biochars (Fig. 3). There was no significant difference in the water retention capacity of the sandy soil between the treatments with two doses of BC while application of PYRO resulted in a significant difference in water retention capacity between the treatments with 15 and 30 t ha⁻¹.

Greater specific surface area of PYRO and higher number of polar groups on the biochar surface could be the reason for higher water retention capacity of the sandy soil amended with this type of biochar (Ren et al., 2016).

Particle diameter of PYRO (up to 1 mm) was smaller than particle diameter of BC (up to 3 mm). Therefore, incorporation of PYRO to the sandy soil at the dose of 30 t ha⁻¹ led to a two-fold decrease in the volume of capillary macro- and meso-pores (the intervals of water potentials between -5 kPa and -55 kPa) compared to that after application of 15 t ha⁻¹ of PYRO. At the same time, the incorporation of either dose of BC did not cause similar changes in the volume of macro- and meso-pores of this soil.

Incorporation of both doses of PYRO or BC into the clayey loam soil also resulted in a significant (at $P < 0.05$) increase in the soil water retention capacity, compared to the control treatment (Fig. 4). The higher was the dose of either biochar, the higher was the water retention capacity (at $P \leq 0.05$) of the clayey loam soil in the range of water potentials from -5 to -300 kPa.

Fig. 3. Water retention curves of the sandy soil with different treatments. Bars show the 95% confidence intervals. Different letters indicate the significance of differences according to one-way ANOVA (at $P < 0.05$).

Fig. 4. Water retention curves of the clayey loam soil with different treatments. Bars show the 95% confidence intervals. Different letters indicate the significance of differences according to one-way ANOVA (at $P < 0.05$).

The difference in water retention capacity of clayey loam soil amended with 15 t ha⁻¹ of either biochar was not statistically significant, as well as there was no difference in water retention capacity of the soil amended with 30 t ha⁻¹ of BC or PYRO.

In the studies of N₂O emission from soils, WFPS is being often used as an important indicator of soil conditions favorable for microbial processes of nitrification or denitrification. These conditions are observed in soils at WFPS being lower than 60% (mainly aerobic conditions) and higher than 60% (mainly anaerobic conditions), respectively (Dobbie and Smith, 2003; Wrage et al., 2001). The data on the WFPS (%) of the studied soils are given in Table 3. During the experiment, the WFPS of the sandy soil was higher than 60% in all the treatments including control and control + N-fertilizer. Incorporation of BC or PYRO in two studied doses did not result in any significant increase of WFPS in the sandy soil compared to control treatment. WFPS of the sandy soil was considerably higher after application of 15 t ha⁻¹ of BC than 15 t ha⁻¹ of PYRO. There were negligible differences in WFPS between treatments with 30 t ha⁻¹ of BC and PYRO.

In the clayey loam soil, values of WFPS were also higher than 60%. Application of BC or PYRO did not significantly change WFPS of this soil compared to the control treatment. Application of 30 t ha⁻¹ of PYRO resulted in significantly (at $P < 0.001$) higher values of WFPS compared to the treatments with 30 t ha⁻¹ of BC. As the WFPS values during the experiment were always higher than 60% (anaerobic conditions) in both soils under all the studied treatments, microbial process of denitrification was likely to be the main pathway of N₂O formation in these soils (Dobbie and Smith, 2003).

Table 3. Average values of WFPS, %, (mean $\pm$ 95% confidence interval) for the sandy and clayey loam soils with different treatments. Letters a, b and c, d show significant differences among values of WFPS in sandy soil and clayey loam soil, respectively, by one-way ANOVA (at $P < 0.05$).

Treatment	Sandy soil	Clayey loam soil
Control	64.4 $\pm$ 3.9a	79.0 $\pm$ 6.5c
Control + N-fertilizer	61.9 $\pm$ 2.7a	71.4 $\pm$ 7.6c
15 t ha ⁻¹ of BC	69.4 $\pm$ 5.5a	66.4 $\pm$ 4.4d
15 t ha ⁻¹ of BC + N-fertilizer	64.6 $\pm$ 3.1a	73.1 $\pm$ 6.7c
30 t ha ⁻¹ of BC	59.4 $\pm$ 4.8a	67.4 $\pm$ 3.1d
30 t ha ⁻¹ of BC + N-fertilizer	58.1 $\pm$ 4.8b	71.9 $\pm$ 4.4c
15 t ha ⁻¹ of PYRO	61.0 $\pm$ 4.0a	72.9 $\pm$ 4.4c
15 t ha ⁻¹ of PYRO + N-fertilizer	57.1 $\pm$ 3.0b	72.3 $\pm$ 4.3c
30 t ha ⁻¹ of PYRO	62.7 $\pm$ 3.6a	78.2 $\pm$ 3.1c
30 t ha ⁻¹ of PYRO + N-fertilizer	66.0 $\pm$ 5.5a	83.1 $\pm$ 4.2c

N₂O emissions and soil mineral nitrogen

N₂O emission rates from the soils with different treatments are shown on Fig. 5 and 6 while the average values of N₂O emission rates – in Table 4. There was a very high variability of N₂O emissions from both soils under all the studied treatments during the entire period of the experiment and, for this reason, some differences in N₂O emission rates, which were found during the experiment, were not statistically significant. Still, the obtained results provide a good possibility to see the main directions of the changes in N₂O emission rates, related to the biochars application to fertilized and unfertilized soils of different texture.

Fig. 5. N₂O emission rates for the sandy soil with BC application (a and b) and with PYRO application (c and d). Bars show the 95% confidence intervals.

Fig. 6. N₂O emission rates for the clayey loam soil with BC application (a and b) and with PYRO application (c and d). Bars show 95% confidence intervals.

The rate of N₂O emission from the control soils was not very high and the reason for that was, presumably, the very low N-content in the soils. Despite of the six-fold difference in the numbers, the difference in N₂O emission rates between control treatments of the sandy soil and the clayey loam soil was not statistically significant due to the high variability of the flux. Application of the biochars to the unfertilized soils either did not significantly change the rate of N₂O emission (for the sandy soil: treatments 15 t ha⁻¹ of BC, 30 t ha⁻¹ of PYRO; for the

clayey loam soil treatment 30 t ha⁻¹ of BC) or significantly increased it (for the sandy soil: treatments 30 t ha⁻¹ of BC or 15 t ha⁻¹ of PYRO; for the clayey loam soil: treatments 15 t ha⁻¹ of BC and 30 t ha⁻¹ of PYRO). Nitrogen content in the biochars could be the main reasons for N₂O flux increase in the circumstances when the soil water content was kept at the same level throughout the experiment.

Application of N-fertilizer (90 kg N ha⁻¹) to both soils resulted in a significant increase in the rate of N₂O emission and

Table 4. Average values of N₂O emission rates ($\mu\text{g m}^{-2} \text{h}^{-1}$) for the sandy and clayey loam soils with different treatments (means $\pm$ 95% confidence intervals). Different letters indicate the significance of differences according to one-way ANOVA within each column (at $P < 0.05$).

Treatment	Sandy soil	Clayey loam soil
Control	2.4 $\pm$ 6.1a	12.3 $\pm$ 22.8a
Control + N-fertilizer	124.5 $\pm$ 92.5c	1423.5 $\pm$ 617.4d
15 t ha ⁻¹ of BC	-0.6 $\pm$ 3.5ab	76.6 $\pm$ 55.1b
15 t ha ⁻¹ of BC + N-fertilizer	797.5 $\pm$ 255.3e	219.9 $\pm$ 127.3c
30 t ha ⁻¹ of BC	16.3 $\pm$ 9.0b	15.4 $\pm$ 13.4a
30 t ha ⁻¹ of BC + N-fertilizer	368.1 $\pm$ 185.3d	159.5 $\pm$ 63.5c
15 t ha ⁻¹ of PYRO	19.3 $\pm$ 3.9b	66.4 $\pm$ 77.4ab
15 t ha ⁻¹ of PYRO + N-fertilizer	216.0 $\pm$ 104.9cd	208.7 $\pm$ 207.9bc
30 t ha ⁻¹ of PYRO	14.2 $\pm$ 12.0ab	216.3 $\pm$ 166.5b
30 t ha ⁻¹ of PYRO + N-fertilizer	24.5 $\pm$ 11.3b	175.5 $\pm$ 173.8bc

Table 5. Average N-NO₃⁻ content (mg kg⁻¹ of soil) for the sandy and clayey loam soils with different treatments (means $\pm$ 95% confidence interval). Different letters indicate the significance of differences according to one-way ANOVA within each column (at $P < 0.05$).

Treatment	Sandy soil	Clayey loam soil
Control	0.10 $\pm$ 0.01a	0.10 $\pm$ 0.01c
Control + N-fertilizer	1.0 $\pm$ 0.8a	40.3 $\pm$ 16.3d
15 t ha ⁻¹ of BC	0.4 $\pm$ 0.3a	2.3 $\pm$ 3.8c
15 t ha ⁻¹ of BC + N-fertilizer	12.6 $\pm$ 6.7b	24.4 $\pm$ 23.5d
30 t ha ⁻¹ of BC	0.9 $\pm$ 0.8a	2.2 $\pm$ 2.0c
30 t ha ⁻¹ of BC + N-fertilizer	9.9 $\pm$ 3.7b	13.2 $\pm$ 3.2d
15 t ha ⁻¹ of PYRO	1.2 $\pm$ 0.6b	2.8 $\pm$ 2.3c
15 t ha ⁻¹ of PYRO + N-fertilizer	24.8 $\pm$ 5.0b	55.6 $\pm$ 9.8d
30 t ha ⁻¹ of PYRO	1.5 $\pm$ 0.6b	12.8 $\pm$ 8.4d
30 t ha ⁻¹ of PYRO + N-fertilizer	0.5 $\pm$ 0.3a	24.0 $\pm$ 23.1d

the increase was significantly higher for the clayey loam soil compared to the sandy soil (at $P < 0.05$). Application of N-fertilizer also resulted in an increase of N-NO₃⁻ content in both soils (Table 5) and that was the main reason of the increased N₂O emission rates from the fertilized soils of the experiment compared to the control. Another factor that could affect N₂O emission rate from the soils was WFPS but values of WFPS were about the same for different treatments of the same soil (>60%) and therefore had about the same effect on N₂O emissions independent of the treatment, providing conditions suitable for the process of denitrification. Combination of high values of WFPS and high N-content are the main factors promoting processes of denitrification, which is the main source of N₂O in wet soils.

Application of BC to the fertilized sandy soil resulted in a significant increase of N₂O emission rates for both doses of the biochar while application of the same biochar to the fertilized clayey loam soil resulted in significant decrease of N₂O emission rates compared to the control + fertilizer treatment. In general, BC application did not help to mitigate N₂O emissions from N-fertilized sandy soil at WFPS >60% and even was most likely to increase the N₂O flux. At the same time, BC application to the fertilized clayey loam soil was effective in reducing N₂O emission rates compared to the fertilized treatment with no BC at WFPS >60%.

PYRO was reducing N₂O emission rates from both fertilized soils. For the sandy soil, the 5-fold reduction was statistically significant only for the higher rate of PYRO, while for the clayey loam soil N₂O emission rates were 6–9 times lower and the reduction was statistically significant for both rates.

It was shown earlier that biochars can influence the process of microbial denitrification through the improvement of soil

aeration and lower mineral nitrogen utilization by denitrifying microorganisms, but that was not the case in the conducted experiment where the WFPS of the studied soils was kept at quite a high level and N₂O emissions were studied in the conditions of no water deficiency.

According to Liao et al. (2021), biochars with the larger specific surface area decrease soil N₂O emission by affecting the diversity, abundance, and composition of total bacteria and N₂O-producing microbial communities. That could be the reason of more pronounced N₂O emission rate reduction from both fertilized soils after PYRO application.

The obtained experimental results indicate a high efficiency of the biochars to mitigate N₂O emissions from the N-fertilized clayey loam soil but not from the N-fertilized sandy soil.

When the mean N₂O emission rates from all the treatments with BC or PYRO and mineral fertilizer were analyzed together, the Spearman's rank correlation coefficients did not distinguish any significant relationship between N₂O emissions and WFPS for either soil studied in the experiment; showed a significant (at $P < 0.01$) relationship with N-NO₃⁻ content for the sandy soil but not for the clayey loam soil at WFPS higher than 60%.

CONCLUSIONS

The results of the study have shown that application of BC and PYRO resulted in a significant reduction in bulk density of the sandy soil but not the clayey loam soil. Addition of BC or PYRO increased water retention capacity of the two soils used in the study. However, incorporation of BC or PYRO was not affecting the soils' water-filled pore space, which was > 60% for all the studied treatments.

BC did not significantly reduce N₂O emission rates from the N-fertilized sandy soil and was even increasing the flux. In the N-fertilized clayey loam soil BC was more efficient and significantly reduced N₂O emission rate at WFPS >60%.

The mitigating effect of PYRO application on N₂O emission rate was less pronounced in the sandy soil, where only the higher dose of the biochar was successfully reducing the flux from the N-fertilized soil. In the clayey loam soil N₂O emission rates were significantly reduced by PYRO at both rates.

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