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ORIGINAL ARTICLE

Fertilization strategies to reduce yield-scaled N_2O emissions based on the use of biochar and biochar-based fertilizers

Raúl Castejón-del Pino · **Miguel A. Sánchez-Monedero** · **María Sánchez-García** · **María L. Cayuela**

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Abstract Novel fertilization strategies, such as the use of biochar-based fertilizers (BBFs) and the co-application of biochar with mineral fertilizers, have shown promising results for mitigating nitrous oxide (N_2O) emissions and reducing N losses in agroecosystems. Two greenhouse experiments were performed with radish to evaluate: (1) the mitigation of yield-scaled N_2O emissions using BBFs, produced at either 400 or 800 °C and enriched with urea, compared to the co-application of raw biochars with urea; and (2) the N_2O mitigation potential of low rates of raw biochars, equivalent to those used with BBFs fertilization, co-applied with low and high N rates (90 and 180 kg N ha^{-1}). BBF produced at 800 °C reduced yield-scaled N_2O emissions by 32% as compared to the urea treatment, and by 60%, as compared to the combination of raw biochar with urea. This reduction was attributed to the slow rate of N release in BBF. On the contrary, the co-application of low rates of biochar with urea increased yield-scaled N_2O emissions as compared to the fertilization with urea alone. Low rates of biochar (1.4–3.1 t ha^{-1}) reduced yield-scaled N_2O emissions only with a high rate of N fertilization. High-pyrolysis-temperature biochar, co-applied with synthetic fertilizer, or used to produce BBFs, demonstrated lower yield-scaled N_2O emissions than biochar produced at a lower pyrolysis temperature. This study showed that BBFs are a promising fertilization strategy as compared to the co-application of biochar with synthetic fertilizers.

Keywords *Raphanus sativus* · GHG · Olive tree pruning · N-enriched biochar · Activated biochar · N_2O emission factor

Introduction

Fertilized soils represent the highest source of direct and indirect nitrous oxide (N_2O) emissions in agriculture (FAO 2020). This greenhouse gas (GHG) contributes to both increasing global temperatures and depleting the ozone layer (Myrold 2021). There is a high urgency to mitigate N_2O emissions from agricultural lands (Tian et al. 2020). However, in order to guarantee food security, mitigation practices need to address potential trade-offs with crop yields (Grados et al. 2022). Thus, in order to evaluate the mitigation potential of a given agricultural practice, the determination of yield-scaled N_2O emissions or N_2O-intensity is a better option than area-scaled N_2O emissions, as the former contemplates N_2O emissions

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R. Castejón-del Pino (✉) · M. A. Sánchez-Monedero · M. Sánchez-García · M. L. Cayuela
Department of Soil and Water Conservation and Organic Waste Management, CEBAS-CSIC, Campus Universitario de Espinardo, 30100 Murcia, Spain
e-mail: rcastejon@cebas.csic.es

per crop unit or N taken up by crops (Van Groenigen et al. 2010).

Recently, Grados et al. (2022) evaluated the efficiency of the most widely adopted N_2O mitigation practices. They identified some technology-driven solutions, such as the application of urease/nitrification inhibitors, the adoption of drip irrigation, and the use of biochar as the most promising strategies to reduce emissions without compromising crop production. The co-application of biochar with fertilizers is a well-documented strategy to mitigate GHG emissions, in particular N_2O, and to increase C sequestration in soil (Joseph et al. 2021). N_2O mitigation with biochar is associated with its ability to retain N and promote the last step of denitrification, thereby decreasing the $N_2O/(N_2O+N_2)$ ratio (Cayuela et al. 2013; Van Zwieten et al. 2014). In addition, the characteristics of the biochar influence its mitigation potential. Thus, the higher the aromaticity of biochar (due to high pyrolysis temperatures), the higher the reduction in N_2O emissions (Cayuela et al. 2015).

In order to guarantee the sustainability of biochar as a GHG mitigation strategy, several aspects need to be considered. First, it is important to avoid large scale biochar production from both biomass crops and forest wood, as this could lead to land use change and deforestation in some areas (IPCC 2023). In contrast, biochar produced from agroforestry residues is an environmentally and economically feasible practice that can contribute to a circular economy (Robb et al. 2020; Azzi et al. 2021). A second aspect to consider is biochar application rate. The cost of producing and applying biochar into soil may be economically unviable if the biochar application rate is high (Baveye 2023).

On the other hand, the biochar application rate is known to directly correlate with its N_2O mitigation potential (Cayuela et al. 2014; Rittl et al. 2021), with rates lower than 10 t ha^{-1} not having a significant effect on N_2O emissions (Borchard et al. 2019). Studies using lower rates showed a limited effect or even a promotion of N_2O emissions (Kaur et al. 2023). To date, research using biochar at low rates (<5 t ha^{-1}) is limited, and further knowledge is needed. Additionally, when biochar is co-applied in soil with synthetic fertilizers, the higher the N rate (such as those used in intensive agriculture), the higher the biochar N_2O mitigation (Sun et al. 2017; Wang et al. 2020). Studies that compared increasing N fertilization rates used moderate biochar application rates, but there is a need for information on biochar application rates $<0.5\%$ w/w (or <10 t ha^{-1}).

Recently, the interest on the application of biochar enriched with nutrients, such as N, is rapidly growing. Nutrient-enriched biochars are known as biochar-based fertilizers (BBFs), although some authors referred to them as BCFs or BFs. BBFs use has been described as an efficient strategy to mitigate GHG and to increase N use efficiency (Puga et al. 2020a; Rasse et al. 2022; Zhang et al. 2023). BBFs may reduce N_2O and CH_4 emissions with a moderate cost to farmers (Joseph et al. 2021). Thus, BBFs have been regarded as the most cost-effective option for biochar use, as they are usually applied at low rates (<5 t ha^{-1}) (Robb et al. 2020). Nonetheless, the associated generation of C credits is also small.

Several pre- and post-pyrolysis treatments have been developed to enrich biochar with N (Ndoung et al. 2021). Pre-pyrolysis treatments usually produce BBFs with highly recalcitrant N, whereas post-pyrolysis treatments commonly produce BBFs with slow-release N (Marcińczyk and Oleszczuk 2022). We have recently described post-pyrolysis activation and N-enrichment methods that efficiently incorporate different N forms that could be progressively released for plant nutrition (Castejón-del Pino et al. 2023). The present study tests some of these BBFs in soil. Our aim was to test N_2O mitigation using low rates of either (i) BBFs or (ii) biochar co-applied with N fertilization. We hypothesized that (1) BBFs and, to a lesser extent, the co-application of biochar with a synthetic fertilizer, will reduce yield-scaled N_2O emissions as compared to synthetic fertilizer alone and, (2) the higher the N rate co-applied with biochar, the higher the biochar mitigation potential, even at a low biochar application rate.

We performed two parallel experiments to validate these hypotheses. In experiment 1, we measured N_2O emissions, crop development, and N uptake, in a radish crop fertilized with either BBFs, urea, or biochar co-applied with urea. In experiment 2, we tested the co-application of low rates of biochar with a high N fertilization rate.

Materials and methods

Materials

The soil was sampled between crop rows in an irrigated fifty-year old lemon orchard located in

Santomera (Murcia, Spain), coordinates 38°04′17″ N, 1°03′08″ W. The soil was characterized by a low organic matter concentration (1.5%), a clay texture (15.5% sand, 48.7% clay, and 35.8% silt), and a high concentration of calcium carbonates (54%), which is common in our area and in some other Mediterranean regions (Durán et al. 2023). The main physico-chemical characteristics of the soil (0–300 mm depth) are presented in Table S1.

Biochars were prepared from olive-tree pruning residues at the highest pyrolysis temperatures of 400 °C (B400) and 800 °C (B800). Raw biochars, B400 and B800, had low N concentrations (0.68 and 0.81% N, respectively). BBFs were prepared from B400 (BBF400) and B800 (BBF800), activated with HNO_3 and N-enriched with urea (Castejón-del Pino et al. 2023). The nitrogen concentrations of BBF400 and BBF800 were 6.36% N and 2.87% N, respectively. About two thirds of the N in both BBFs were readily available to plants, whereas most of the N in the raw biochars was not available. The C concentration varied depending on the pyrolysis temperature. The C concentration in B400 and BBF400 was 73.2 and 56.8%, respectively, whereas in B800 and BBF800, it was 82.0 and 76.9%, respectively. A detailed description about the preparation and characterization of the biochars and the BBFs can be found in Castejón-del Pino et al. (2023).

Experimental design

Two parallel pot experiments were conducted under identical environmental conditions. The experiments were carried out in the summer of 2021 in a greenhouse at the Agroforestry Experimental Station of the University of Murcia (Spain). The climate conditions inside the greenhouse were stable over the experiments, with the average daily temperature ranging from 22.4 to 24.5 °C, and the average daily relative humidity ranging from 52.8 to 69.4%. The experiments followed a completely randomized design, and were established including the following treatments with three replicates.

The treatments in experiment 1 were the following:

(i) Control without fertilization (No fertilization);
(ii) Urea fertilization (U);
(iii) Co-application of urea fertilization with biochar pyrolyzed at 400 °C (U + B400);
(iv) Co-application of urea fertilization with biochar pyrolyzed at 800 °C (U + B800);
(v) Biochar-based fertilizer produced with biochar pyrolyzed at 400 °C (BBF400);
(vi) Biochar-based fertilizer produced with biochar pyrolyzed at 800 °C (BBF800).

The treatments in experiment 2 were the following:

(i) Double urea fertilization (2U);
(ii) Co-application of 2U fertilization with biochar pyrolyzed at 400 °C (2U + B400);
(iii) Co-application of 2U fertilization with biochar pyrolyzed at 800 °C (2U + B800).

In the first experiment, fertilized pots (U, U + biochars and BBFs) were adjusted to 90 kg N ha^{-1} according to radish N requirements. The fertilization treatments were applied once at the beginning of the experiment. In the second experiment, the rate of urea was doubled. Nitrogen fertilization treatments are presented in detail in Table S2. All the pots were fertilized with P and K (17 and 91 kg ha^{-1}, respectively). The pots were drip irrigated with tap water, taking into account the crop needs according to climatic conditions and crop stage (60–120 mL pot^{-1} every 2 days). We applied the same amount of BBF and raw biochar, considering the radish N requirements and the N in BBF. For instance, 0.06% w/w was applied for BBF400 and B400, and 0.14% w/w for BBF800 and B800. These proportions of application were comparable to 1.4 t ha^{-1} (BBF400 and B400) and 3.1 t ha^{-1} (BBF800 and B800).

Radish seeds (*Raphanus sativus* var. National 2) were sown at a depth of 10–15 mm (four per pot and only one seedling was left to grow). The pot dimensions were 100 × 100 × 120 mm and 800 mL in volume, and they were filled with 1000 g of soil. Plants grew for 11 weeks until most radish plants reached the minimum commercial diameter (20 mm).

Plants and soil measurements

The growth of radish plants was monitored weekly by measuring leaf length and width of all leaves and calculating the mean. At the end of the growing period, radishes were harvested, washed with deionized water and oven-dried at 60 °C. Radish fresh and dry yields were measured considering radish bulb and leaves. Nitrogen concentration was determined by elemental analysis of ball-milled samples (automatic elemental analyzer CHNS-932, LECO, USA).

At the end of the experiment, soils were air-dried, milled and sieved (< 2 mm) for elemental and water-soluble analyses. Fresh soil was used for NH_4^+–N determination. NH_4^+–N was measured in a 2 M KCl extract (1:20 w/v), after shaking soil for 2 h, centrifuging for 15 min at 2028 x *g* and filtered (< 0.45 µm). NH_4^+ was measured with a colorimetric method based on Berthelot's reaction (Sommer et al. 1992). Total N, total C, and total organic C were measured by elemental analysis of ball-milled soil samples as described for plant samples. Soil water extracts (1:20 w/v) were shaken for 2 h, centrifuged for 15 min at 2028 x *g* and filtered (< 0.45 µm). Dissolved total, inorganic, and organic C were determined by an aqueous elemental analyzer (multi N/C 3100, Analytik Jena, Germany), and NO_3^-–N was analyzed with ion chromatography (ICS 2100, Dionex, USA).

N_2O emissions monitoring

N_2O fluxes were regularly monitored during the experiments. Initially, we measured N_2O fluxes once or twice per day and, after 2 weeks, when emissions were low and stable, the measurements were performed twice per week. N_2O concentrations were measured at time 0 and 1 h after closing the chambers using a photo-acoustic gas monitor (1412i Lumasense Technologies A/S, Ballerup, Denmark). The chambers had a volume of 4.2 L and dimensions of 210 × 150 × 220 mm. The pots were introduced into the static polypropylene chambers only during gas accumulation and measurements, using a whole-plant static chamber technique (Clough et al. 2020) as shown in Figure S1. N_2O emissions were calculated by the linear increase in N_2O concentration during the accumulation period, expressed in mg N_2O–N m^{-2} soil, as shown in the Supplementary Material (Figure S2). The volume of the pot was subtracted from the volume of the chamber to calculate the N_2O emissions.

Calculations and statistical analysis

Yield-scaled N_2O emissions were calculated with the following equation:

$$\text{Yield-scaled } N_2O \text{ emissions} = \frac{\text{cum } N_2O \text{ emissions}}{\text{plant N uptake}}$$

where cumulative (cum) N_2O emissions and plant N uptake are expressed in g of N. Furthermore, N_2O intensity was calculated as the kg of N_2O emitted per ton of dry plant yield as follows:

$$N_2O \text{ intensity} = \frac{\text{cum } N_2O \text{ emissions}}{\text{dry product}}$$

where cum N_2O emissions are expressed in kg ha^{-1}, and dry product in t ha^{-1}.

The N_2O emission factor (EF) was calculated by subtracting the cumulative N_2O emissions of the treatments and the cumulative N_2O emissions of the no fertilization treatment, and dividing it by the N fertilization rate, as shown in the equation:

$$N_2O \text{ EF} = \frac{\text{cum } N_2O \text{ treatment } - \text{cum } N_2O \text{ control}}{\text{N applied}} \cdot 100$$

where the cum N_2O emissions are expressed in mg kg^{-1} of soil and the N applied with the fertilization treatment as mg kg^{-1} of soil. The N applied used in the estimation of the N_2O emission factor is either the N applied with urea or the available N fraction in the case of the BBFs; excluding the non-available N for plants applied with the biochar and BBFs.

Significant differences between treatments were analyzed through a one-way analysis of variance (ANOVA). Post-hoc analyses were performed with Tukey-b analysis, and significant differences were established at $p < 0.05$. Data were ln-transformed when necessary. Levene's test was used for homogeneity of variance, and the Shapiro-Wilk test for normality. Additionally, significant differences between treatments from paired samples were analyzed through *t* test analyses at $p < 0.05$. Analyses were performed with IBM SPSS Statistics v. 27.0.1., Sommers, USA.

Table 1 Cumulative N_2O–N emissions, plant dry yield and yield-scaled N_2O emissions and N_2O intensity

Treatment	Cumulative N_2O–N emissions (mg N m^2 $soil^{-1}$)	Dry plant yield (T ha^{-1})	Yield-scaled N_2O emissions (g N_2O–N kg N $uptake^{-1}$)	N_2O intensity (kg N_2O–N t dry $product^{-1}$)
No fertilization	52 ± 7 (a)	0.75 ± 0.12 (a)	5.62 ± 1.07 (a)	0.74 ± 0.23 (a)
U	224 ± 8 (c)	2.30 ± 0.26 (b)	8.68 ± 1.96 (ab)	0.90 ± 0.14 (a)
U + B400	410 ± 103 (d)	1.90 ± 0.66 (b)	18.49 ± 3.49 (c)	2.02 ± 0.41 (b)
U + B800	312 ± 80 (cd)	1.68 ± 0.51 (b)	14.57 ± 2.86 (bc)	1.90 ± 0.32 (b)
BBF400	194 ± 68 (bc)	1.59 ± 0.18 (b)	11.93 ± 3.68 (bc)	1.21 ± 0.37 (a)
BBF800	118 ± 13 (b)	2.08 ± 0.67 (b)	5.88 ± 0.61 (a)	0.59 ± 0.11 (a)
F-*ANOVA*	28.8***	17.9***	13.2***	13.4***

Letters in brackets indicate significant differences between treatments from one-way ANOVA analyses (Tukey's b test, $p < 0.05$). *** Significant difference between treatments at $p < 0.001$. U: urea. B400: untreated biochar produced at 400 °C. B800: untreated biochar produced at 800 °C. BBF400: biochar-based fertilizer produced with B400. BBF800: biochar-based fertilizer produced with B800. Data show average values ± standard deviations (n = 3)

Results

Experiment 1. Comparison of BBFs, urea and co-application of biochar with urea

Radish crop development

Plant yield showed significant differences between non-fertilized and fertilized plants. Although the differences among fertilized treatments were not statistically significant, BBFs tended to reduce crop yields (Table 1). This decline was only evident at the end of the experiment, when a reduction in plant development, measured as leaf length and width, was observed in both BBFs treatments (Figure S3). Figure 1 shows plant N uptake, plant-available N applied, as well as total N applied. The lower plant-available N in BBFs treatments influenced yield and N concentration in plant tissues, which was significantly lower in BBF400 as compared to the rest of fertilization treatments.

Area and yield-scaled N_2O emissions

BBFs registered the lowest cumulative N_2O–N emissions of the fertilized treatments (Table 1). As compared to urea fertilization, BBF400 and BBF800 reduced N_2O emissions by 13 and 47%, respectively. The U + B400 treatment resulted in the highest emissions, being significantly higher than the U treatment. On the other hand, the U + B800 treatment resulted in an intermediate emission between U and U + 400.

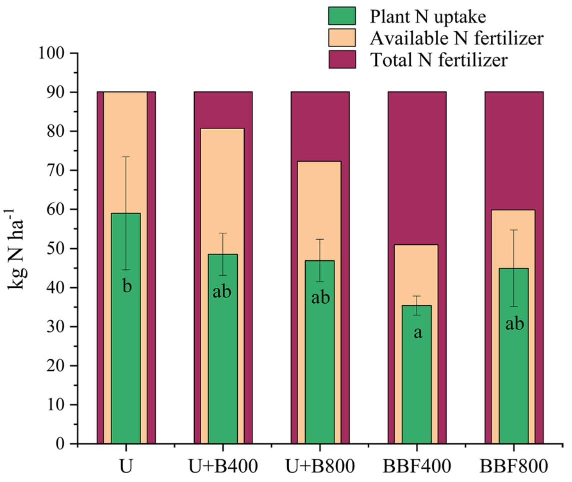

Fig. 1 Total N applied to soil with fertilization treatments, available N of the fertilization treatments and the N taken up by plants. B400: untreated biochar produced at 400 °C. B800: untreated biochar produced at 800 °C. BBF400: biochar-based fertilizer produced with B400. BBF800: biochar-based fertilizer produced with B800. Letters in brackets indicate significant differences between treatments from one-way ANOVA analyses (Tukey's b test, $p < 0.05$). Data shows average values ± standard deviations (n = 3)

The highest N_2O flux peaks of all treatments occurred between days 4 and 7 of the experiment (Fig. 2). However, the dynamics of N_2O fluxes varied depending on the fertilization treatment. The addition of urea alone or combined with biochar produced a single N_2O peak that reached 7.5 and 9 mg N_2O–N per kg of soil on days 4 and 5, respectively. However, the BBFs treatments showed two N_2O flux peaks that

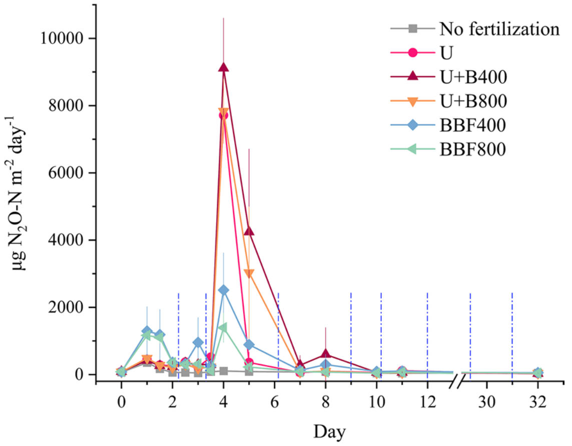

Fig. 2 Fluxes of N_2O emissions over the experiment. Vertical blue lines represent irrigation events. B400: untreated biochar produced at 400 °C. B800: untreated biochar produced at 800 °C. BBF400: biochar-based fertilizer produced with B400. BBF800: biochar-based fertilizer produced with B800. Error bars indicate standard errors (n = 3)

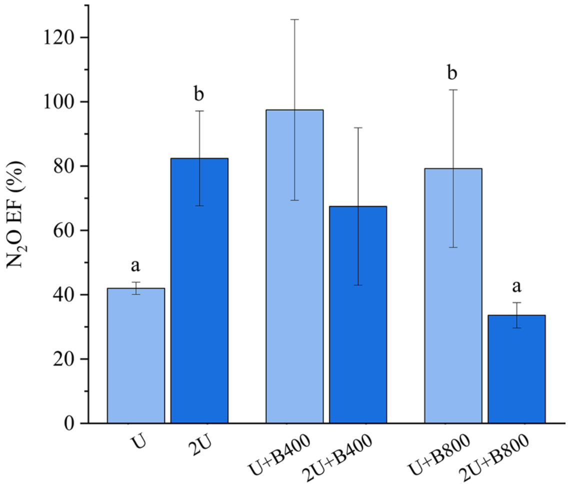

Fig. 3 N_2O emission factor (%) depending on treatment. Light blue bars depict treatments with a low urea rate (U), whereas dark blue bars show high N rate treatments (2U). B400: untreated biochar produced at 400 °C. B800: untreated biochar produced at 800 °C. Letters in brackets indicate significant differences between treatments from paired samples *t* test analyses ($p < 0.05$). The absence of letters indicates no significant differences. Data show average values ± standard deviations (n = 3)

reached 1 and 2.5 N_2O–N per kg of soil from day 0 to day 7. After day 10, no significant emissions were recorded for any treatment.

No fertilization and the BBF800 treatments showed the lowest yield-scaled N_2O emissions (Table 1), which were significantly lower than the rest of the treatments. BBF800 showed a similar yield as the U treatment, although significantly lower N_2O emissions, which were equivalent to the no fertilization treatment. Therefore, BBF800 increased radish yield without significantly raising N_2O emissions. The co-application of biochars with urea presented the highest N_2O–N intensity, which was statistically higher than the U treatment. BBF800 showed the lowest N_2O intensity, although no statistical difference was found when compared to the U treatment.

Relevant soil physicochemical characteristics at the end of the experiment.

At the end of the experiment, soils amended with biochars and BBFs presented a higher total N concentration than soils fertilized only with urea and non-fertilized soil, although this was not statistically significant (Table S3). Biochars and BBFs treatments also showed a lower plant N uptake than treatments fertilized with urea alone (Fig. 1). All the treatments showed low NO_3^-–N and NH_4^+–N concentrations at the end of the experiment (below 5.7 and 8.7 mg kg^{-1} respectively), with the BBF800 and U treatments exhibiting the highest NH_4^+–N concentrations. The pH and EC values were similar for all treatments at the end of the experiment. All treatments showed a slight decrease from the initial pH (9.1), and an increase in EC from the initial value (320 μS cm^{-1}) (Table S4). Changes in soil organic C concentration were not perceivable at the end of the experiment because of the low amount of applied biochar (Table S5).

Experiment 2: Biochar effect on N_2O emissions and crop yield under excessive N fertilization

The co-application of biochar (B400 or B800) with double urea fertilization significantly increased the radish yield compared to the 2U treatment (Table S6). However, the treatments showed a similar N uptake at a high N application rate, reaching N concentrations in the range of 37.0–41.6 mg N plant^{-1}.

The co-application of B400 or B800 with urea at a low N rate produced an increase of 51 and 33% of the N_2O emissions per kg of N fertilizer applied, as compared to fertilizing with urea alone. The N_2O emission factors of the treatments are shown in Fig. 3. Fertilizing with excess urea, resulted in a 14.9 and 48.8% reduction in the N_2O emission factor, with biochar use being an efficient strategy for the reduction of the emission factors, despite it being applied at a low rate (1.4–3.1 t ha^{-1}).

Similar to the N_2O emissions, the results of yield-scaled emissions were contrasting depending on the N application rate. Whereas treatments with biochar increased yield-scaled emissions at a low N rate, the same biochar treatments reduced the yield-scaled emissions at a high N rate. Treatments 2U + B400 and 2U + B800 showed yield-scaled N_2O emissions of 16.19 and 8.85 g N_2O–N kg N uptake^{-1}, respectively, while the 2U treatment showed 17.95 g N_2O–N kg N uptake^{-1} (Table S6).

Discussion

BBFs as a fertilization strategy to reduce N_2O emissions and maintain crop yields

BBFs reduced N_2O emissions as compared to urea, supporting our first hypothesis. Many recent studies have found a decrease in GHG and NH_3 emissions after the application of BBFs as compared to fertilizers alone (Puga et al. 2020b; Zhou et al. 2021; Pereira et al. 2022; Zhang et al. 2023). We expected both BBFs and the co-application of biochar with urea to decrease N_2O emissions as compared to the urea treatment, and hypothesized even lower N_2O emissions for BBFs due to the controlled-release of N from these materials. A slow N-release from BBFs has been proposed as the main mechanism explaining low N losses after BBF application (Shi et al. 2020). However, the comparison between the application of BBF and the co-application of biochar with synthetic fertilizers has been less investigated. In our study, BBFs were characterized by (a) a low water-soluble N (10–15%), (b) a high proportion of slowly available N (45–55%) and (c) a relevant proportion of N that is strongly embedded in the biochar structure and not available in the medium term (35–45%) (Castejón-del Pino et al. 2023).

The presence of several small peaks observed in the N_2O fluxes of the BBF treatments (Fig. 2) demonstrates that BBFs released N at different rates, which was dependent on their chemical composition. In contrast, the urea treatments only showed a high peak of N_2O fluxes, which accounted for most of the cumulative N_2O emissions. Zhang et al. (2023) hypothesized that BBFs could reduce N emissions through other mechanisms aside from N retention, often associated with the impact of biochar itself on soil microorganisms. They proposed a reduction of the urease/protease activities by the adsorption of soil enzymes and a reduction of the denitrification activity because of the improved soil aeration. Rasse et al. (2022) also reported enhanced characteristics of BBFs and other engineered biochars, in comparison to raw biochars, to reduce GHG emissions, but mainly associated with N retention and slow-release of N.

Contrary to our first hypothesis, the co-application of biochar with urea increased the total cumulative N_2O emissions as compared to the urea treatment. Although meta-analyses showed an average decrease of N_2O emissions after biochar application, a few studies have reported an increase in N_2O emissions (Sánchez-García et al. 2014; Wells and Baggs 2014), where biochar enhanced N_2O emissions through nitrification pathways. Thus, in soils prone to N_2O emissions by nitrification, which could be our case, the use of BBFs might represent an advantage to the co-application of biochar with urea.

Biochar usually reduces N_2O emissions by either directly decreasing the denitrification process or by promoting the last step of denitrification (Joseph et al. 2021). However, most studies use higher biochar application rates (between 0.5 and 10% w/w) than the rates used in this study (0.06% w/w of BBF400 and B400 and 0.14% w/w of BBF800 and B800). Biochar application rates > 10 t ha^{-1} have been found to significantly reduce N_2O emissions (Cayuela et al. 2014; Kaur et al. 2023). Lower amounts of biochar (as < 0.5%) have been previously reported to not affect or even increase N_2O emissions (Borchard et al. 2019). Our study confirms that a low rate of biochar may increase N_2O emissions, especially when the biochar is produced at a low temperature.

Pyrolysis temperature influences the effect of biochar on N_2O emissions, since biochars produced at high temperatures (> 500 °C) usually show higher N_2O mitigation potential than biochars produced at lower temperatures (Cayuela et al. 2014; Weldon et al. 2019). In the case of the BBFs, the influence of the pyrolysis temperature had not been studied before. Nevertheless, we observed a similar trend as that of raw biochars: BBF800 led to lower N_2O emissions than BBF400. This might represent an important advantage of BBFs produced at a high temperature when considering the trade-offs between C sequestration and N_2O emissions. Biochars produced at a high temperature are much more recalcitrant to microbial degradation in soil, leading to longer-term C storage (Ippolito et al. 2020). Nonetheless, the lower biochar yields at higher pyrolysis temperatures should also be considered when assessing overall CO_2 removal. Apart from the reduction in N_2O emissions, BBFs synthesized with high-temperature biochars have shown a better performance as slow-release fertilizers (Jia et al. 2020). In addition, Melo et al. (2022), in a recent meta-analysis, showed that BBFs with a high C concentration, such as the ones produced at high temperatures, led to higher crop productivity.

There is only limited information about the impact of BBF on yield-scaled N_2O emissions. BBFs are expected to play a role in the reduction of N_2O emissions, as there is some evidence on increasing N use efficiency (Shi et al. 2020; Puga et al. 2020a). In our study, the yield-scaled N_2O emissions of the BBF800 treatment were similar to the no fertilization treatment, whereas the yield was significantly higher (Table 1). Additionally, we observed a trend in which the BBFs treatments increased the total N concentration in soil at the end of the experiment, which was not readily available for plants (Table S3). This is especially relevant in the case of short-term crops, where all the N supplied by the BBF may not be available for plants during their period of growth. Our results suggest that in short-cycle crops, N fertilization rates should be adjusted considering the available N in the short term (water soluble N and hydrolyzable N). This would imply an increased N input with BBFs, which would result in reduced fertilization requirements for subsequent crops under rotation. However, this hypothesis requires further field studies to be validated.

High nitrogen application rates lead to increased biochar N_2O mitigation

In our study, low rates of biochar co-applied with the recommended rate of urea for radish growth (90 kg N ha^{-1}) increased N_2O emissions. In contrast, the same biochars reduced the N_2O emission factor when the rate of urea was doubled (Fig. 3). This finding confirms our second hypothesis, especially with the biochar produced at a high temperature (B800), as this treatment was efficient in mitigating N_2O emissions at a high N rate, although not at a low N rate. Although meta-analyses have shown that N fertilization rate does not significantly change the effect of biochar on N_2O emissions, this result could be due to confounding factors. For instance, studies with high N rates may have been carried out with low C:N biochars, in very acidic or very alkaline soils, or in combination with organic amendments, where mitigation is known to be less efficient (Borchard et al. 2019). However, experimental studies analyzing the co-application of biochar with increasing rates of N under identical environmental conditions found a higher mitigation efficiency with increasing N fertilization (Sun et al. 2017; Wang et al. 2020).

In a controlled soil column experiment, Wang et al. (2020) showed that whereas the co-application of biochar with a low N rate increased N_2O emissions, the application of biochar with high N concentrations significantly reduced the emissions, even at low biochar rates (0.5% w/w). Similarly, Sun et al. (2017) showed that by increasing N fertilization, biochar progressively reduced N_2O emissions. However, all the previous studies applied higher biochar rates than the rates used in this study, i.e. 0.5–2% w/w (Wang et al. 2020) and 10 t ha^{-1} (Sun et al. 2017).

In our study, we used very low biochar rates (0.06–0.14% w/w equivalent to 1.4–3.1 t ha^{-1}), but we still found lower yield-scaled N_2O emissions and N_2O intensity with the co-application of biochar with urea at a high N rate, as compared to the application of urea alone, especially for 2U + B800 (Table S6). This finding contrasted with the results obtained with the application of 90 kg N ha^{-1}, where U + B800 did not significantly decrease yield-scaled N_2O emissions as compared to U. The co-application of biochar with urea at a high N rate not only reduced N_2O emissions, but also increased the plant yield (Table S6); in contrast to other studies that did not find a significantly higher crop yield or N uptake by plants (Sun et al. 2017). In our study, fertilizing plants with twice the amount of urea reduced the germination rate in treatment 2U as compared to U (data not shown), but pots that contained biochar were not affected by the large amount of urea. This could be due to the ability of biochar to adsorb the excess N, as reflected in the N retained in soil at the end of the experiment (Table S6).

Soil N_2O emissions are known to increase exponentially with N application rates, and several studies found that under the same experimental conditions, the higher the N_2O emissions, the higher the biochar mitigation (Cayuela et al. 2013; Thomazini et al. 2015), which is consistent with our results. The reason for this may be related to a shift in N_2O formation pathways with increasing N concentration in soil. Further studies are needed to test this hypothesis.

Conclusions

Our findings suggest that using small amounts of BBF800, which is produced with biochar pyrolyzed at a high temperature, leads to yields similar to synthetic fertilizers, and lower yield-scaled N_2O emissions. BBF800 showed N fertilization comparable to synthetic fertilizers, providing at the same time additional stable organic N (as shown it Table S1), which could be subsequently used by crops as it slowly mineralizes in soil. Our results indicate that N fertilization rates should be calculated considering the available N in the BBFs during the crop growing period to avoid a decline in crop yield. In addition, the application of low rates of high-temperature biochar might represent a cost-effective option for decreasing the yield-scaled N_2O emissions in commercial fields with high N inputs, such as those under vegetable crop production.

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Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

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