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Greenhouse Gas Emissions from Forest Soils Reduced by Straw Biochar and Nitrapyrin Applications

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Abstract: Forestlands are widely distributed in the dominantly agricultural landscape in western Canada, and they play important ecological functions; such forestlands (e.g., shelterbelts) accumulate soil organic matter and may receive a substantial amount of nitrogen in the form of surface and subsurface runoff from adjacent croplands and become a significant source of emissions of greenhouse gases (GHGs) such as CO_2, N_2O, and CH_4. Biochar and nitrapyrin applications could potentially mitigate GHG emissions, but their co-application in forest soils has not been studied. We investigated the effect of the application of biochars produced at low (300 °C; BC300) and high temperatures (700 °C; BC700) using canola (*Brassica napus* L.) straw and the effect of their co-application with nitrapyrin on GHG emissions and soil properties in a 35-day laboratory incubation experiment using forest soils collected from five shelterbelt sites. Results showed no significant interaction effect of biochar and nitrapyrin on the global warming potential (GWP) of the GHG emissions, and the GWP was 15.8% lower in the soil with nitrapyrin than without nitrapyrin application treatments. The GWP was significantly enhanced by BC300 addition due to a 26.9% and 627.1% increase in cumulative CO_2 and N_2O emissions, respectively, over the 35-day incubation. The GWP significantly decreased by BC700 addition due to a 27.1% decrease in cumulative CO_2 emissions. However, biochar addition did not affect CH_4 emissions, while nitrapyrin decreased CH_4 uptake by 50.5%. With BC300 addition, soil-dissolved organic carbon and microbial biomass carbon increased by 26.5% and 33.9%, respectively, as compared to no biochar addition (CK). Soil pH increased by 0.16 and 0.37 units after the addition of BC300 and BC700, respectively. Overall, the effect of biochar and nitrapyrin was independent in mitigating GHG emissions and was related to the type of biochar applied and changes in soil properties.

Keywords: biochar; global warming potential; greenhouse gas emission; nitrification inhibitor; forest ecosystem

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1. Introduction

Forestlands such as shelterbelts are widely distributed in the agricultural landscape in western Canada and play critical ecological functions such as protecting crops and enhancing carbon (C) sequestration [1,2]. Soils in these forestlands are little disturbed by human activities, which may store large amounts of C and nitrogen (N) that come from plant debris and runoff from adjacent croplands, and potentially release greenhouse gases (GHGs) such as CO_2, N_2O, and CH_4 that influence climate change [3,4]. Reducing GHG emissions from such soils could help mitigate climate change [5].

Many strategies, such as adding amendments, have been developed to mitigate GHG emissions from soils [6–8]. Biochar, usually produced by pyrolysis of biomass, is increasingly being used as an amendment for improving soil quality and C sequestration [6] and for reducing GHG emissions in agricultural systems [6,9–11]. Compared to uncharred biomass, biochar could increase soil C stock and reduce atmospheric CO_2 due to its slower decomposition and mineralization rates [12]. On the other hand, the biochar's acid-buffering capacity and its liming effect can promote the last step of denitrification (the reduction of N_2O to N_2) and decrease N_2O emissions [13].

Biochar's impact on GHG emissions from soils may, however, vary depending on both biochar and soil characteristics [14,15]. The production condition such as pyrolysis temperature is a major factor that influences biochar properties [10,16,17]. For instance, biochars produced at high temperatures (e.g., 550 °C) usually have a greater surface area, pH, and porosity and a lower volatile matter concentration than biochars produced at low temperatures (e.g., 300 °C) when derived from the same feedstock [18,19]. These characteristics make biochars produced at high temperatures more effective in reducing GHG emissions than those produced at low temperatures [20]. Similarly, C and nutrient availabilities to microbes may be greater in biochars produced at low than at high temperatures, releasing more CO_2 when added to soils due to enhancement of microbial activities [21,22]. Canola (*Brassica napus* L.) straw is a by-product from agriculture that can be potentially used to produce biochars that will benefit the agriculture sector and the environment. However, the effect of canola straw biochars on GHG emissions has rarely been studied, especially with biochars that are produced under different pyrolysis temperatures [23].

Nitrification inhibitors such as nitrapyrin are widely used in croplands to increase the effectiveness of N fertilization and reduce N_2O emissions by decreasing nitrification rates [24,25]. Compared to cropland soils, forest soils are usually not fertilized. However, compared to natural forests, forestlands in the agricultural landscape may receive N input from surface and subsurface runoff from adjacent croplands that eventually cause more N_2O emissions. Furthermore, nitrification inhibitors might interact with biochar when they are co-applied [26]. For instance, Li et al. [27] showed that applying nitrapyrin and wheat straw biochar together increased N_2O emissions by 9% as compared with applying nitrapyrin alone, probably due to biochar adsorbing nitrapyrin and lowering the effectiveness of nitrapyrin in reducing nitrification rates. However, we tested the interaction effect of biochar and nitrapyrin on N_2O emissions in cropland soils in another study and did not find a significant interaction [23]. On the other hand, nitrapyrin and biochar may also interactively affect the emission of other GHGs, such as CO_2 and CH_4, which have not been fully investigated in previous studies.

The objectives of this study were (1) to examine the effect of canola straw biochar produced at different temperatures (300 and 700 °C) and nitrapyrin application on soil properties (i.e., pH, dissolved organic C (DOC), microbial biomass C (MBC), and nitrate concentration) and CO_2, N_2O, and CH_4 emissions from forest soils and (2) to examine the effect of biochar and nitrapyrin on the global warming potential (GWP) of GHG emissions to forest soils. We hypothesized that (1) the addition of the biochar produced at a high temperature (700 °C) would be more effective in reducing GHG emissions from the forest soils and that (2) the co-application of biochar and nitrapyrin would decrease more GHG emissions as compared with applying biochar alone.

2. Materials and Methods

2.1. Soil and Biochar

Soil samples were collected from five shelterbelt sites near Edmonton (53°32′0″ N, 113°30′0″ W), Alberta, Canada. The soils at all sites were black chernozemic soils according to the Canadian system of soil classification [28]. The distance between any two shelterbelts was greater than 20 km. At each shelterbelt site, 10 soil cores (0–10 cm layer) were collected at least 5 m apart from each other using an auger with a 5 cm diameter. These 10 soil cores were mixed to form a composite sample for each site; each sample represents one replicate

for the lab incubation experiment described below. Soil samples were kept in a cooler with ice bags and transported to the lab right away. Soil properties were determined after litter and plant roots were removed and gently sieved through a 2 mm sieve.

Biochars were produced using canola straw at low (300 °C) and high (700 °C) temperatures. The straw was oven-dried at 60 °C for 24 h and chopped into small pieces (less than 10 mm long) before pyrolysis. The heating rate was 10 °C min^{-1}. The low-temperature biochar had a pH of 7.68, an ash content of 8.1%, a surface area of 2.8 m^2 g^{-1}, and C and N contents of 632.5 and 15.8 g kg^{-1} (on a dry-weight basis), respectively. The high-temperature biochar had a pH of 10.93, an ash content of 15.9%, a surface area of 4.2 m^2 g^{-1}, and C and N content of 787.7 and 13.7 g kg^{-1}, respectively, based on data from Kwak et al. [19].

2.2. Experimental Design and Incubation Procedure

A two-factor completely randomized factorial design with five replicates for each treatment was used for the laboratory incubation experiment. One factor is biochar application, which had three levels: untreated soil with no biochar application (CK), low-temperature biochar application (BC300), and high-temperature biochar application (BC700). The other factor is nitrapyrin application, which had two levels: no nitrapyrin application and nitrapyrin application. Thus, there were six treatment combinations in total. The application rate of biochar and nitrapyrin was 2% (*w*:*w*; oven-dry-weight basis, equivalent to 4.5 Mg ha^{-1}) [20] and 80 mg kg^{-1} (*w*:*w*, equivalent to 180 kg ha^{-1}) [29], respectively.

For measuring GHG emissions, 100 g (oven-dry equivalent) of fresh soil was mixed with biochar and/or nitrapyrin thoroughly, as needed, and then was placed into a 500 mL Mason jar to measure GHG fluxes. A 3-day pre-incubation was conducted under 40% water-holding capacity (WHC) at 25 °C in the dark to activate microbial activities. The water content was then brought to 60% WHC and maintained at that level throughout the 35-day incubation period by adding deionized water periodically based on weight loss.

2.3. Gas Sampling and Analysis

Gas samples were collected from the headspace of the Mason jars on days 0 (after pre-incubation), 1, 3, 5, 7, 10, 13, 18, 23, 28, and 35. For gas sampling, the Mason jars were sealed tightly for 24 h on those sampling days. After the lid was closed, a 5 mL gas sample was taken using a 10 mL syringe four times: 0, 6, 12, and 24 h. The gas sample was then injected into a pre-evacuated 3 mL Labco exetainer to get a positive pressure for the GHG measurement. The Mason jars were covered with aluminum foils punched with several small holes on non-sampling days to minimize water loss from the jars and to allow the system to be maintained in an aerobic condition (Figure 1). The GHG concentrations were determined using a gas chromatograph (Varian CP-3800, Mississauga, ON, Canada) that was equipped with a thermal conductivity detector (for detecting CO_2), an electron capture detector (for detecting N_2O), and a flame ionization detector (for detecting CH_4). Linear interpolation was used to calculate GHG emissions on non-sampling days. The GWP was calculated after soil GHG units were converted to mg CO_2-C equivalent kg^{-1} of soil based on AR5 100-year GWP values as follows [3]: GWP = ($CO_2 \times 1$) + ($N_2O \times 265$) + ($CH_4 \times 28$).

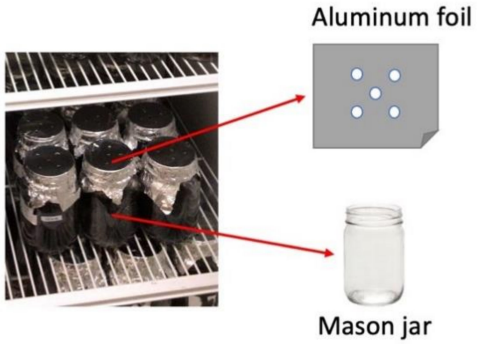

Figure 1. Schematic diagram of the incubation experiment.

2.4. Soil Analysis

Soil samples were collected destructively at the end of the incubation from the Mason jars on day 35. Soil pH was determined using a Thermo Scientific pH meter (710A, Beverly, MA, USA) in a 1:5 soil:water (*w*:*v*) supernatant. The soil DOC in a 1:5 soil:0.5 mol L^{-1} K_2SO_4 solution (*w*:*v*) filtrate was determined using a TOC-TNM1 analyzer (Shimadzu Corporation, Kyoto, Japan). For determining the soil MBC, chloroform-fumigated (at 25 °C, in the dark) and non-fumigated fresh soil samples were extracted using a 1:5 soil:0.5 mol L^{-1} K_2SO_4 solution (*w*:*v*). The extractions were then filtered, and the C in the filtrate was determined using the TOC-TNM1 analyzer described above to calculate the MBC with a coefficient of 0.45 [30,31]. For determining soil net nitrification rates, soil-extractable NO_3^- before and after the incubation was analyzed colorimetrically using the vanadium oxidation method [32]. The net nitrification rates were calculated by dividing changes in the extractable NO_3^- pool size by the number of days in the incubation [33].

2.5. Data Analysis

All data analysis was conducted using R software [34]. The assumptions of normality and homogeneity of variance were tested by evaluating the residual plots. Natural log-transform was performed for the cumulative N_2O data that were not normally distributed. The effects of the treatments on cumulative GHG emissions, GWP, soil pH, DOC, MBC, and net nitrification rates were tested using a linear mixed-effects model (LMM), with biochar and nitrapyrin as fixed factors and the sampling site (replication) as a random factor. Post hoc comparison of least-square means under different biochar treatments with and without nitrapyrin was conducted using the lsmean function in the emmeans package in R at a significance level of $\alpha = 0.05$. Tukey's test was used to conduct multiple comparisons among the biochar treatments.

3. Results

3.1. Biochar and Nitrapyrin Effects on CO_2 Emissions

The CO_2 emission rates from the treatments with biochar application (regardless of BC300 or BC700) were greater in the first 5 days than in later periods (days 5 to 35) in the incubation (Figure 2a). However, there were no apparent peaks of CO_2 emission rates for the CK treatment during the incubation (Figure 2a). Regardless of the biochar treatment, the CO_2 emission rates were, on average, higher in treatments without than with nitrapyrin application during the entire incubation (Figure 2a).

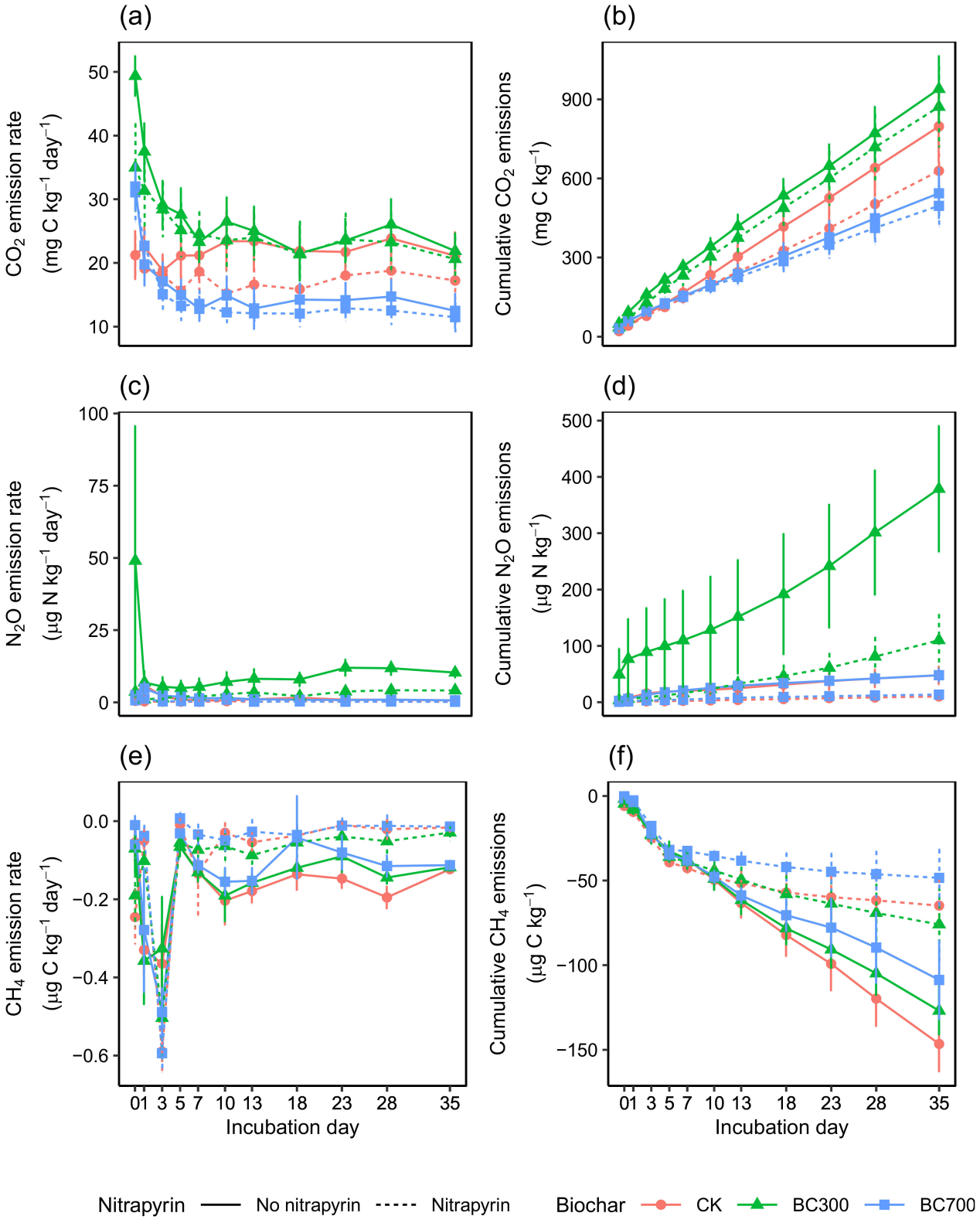

Figure 2. The effect of biochar and nitrapyrin applications on (**a**) CO_2 emission rate (mean ± standard error (SE), same below), (**b**) cumulative CO_2 emissions, (**c**) N_2O emission rate, (**d**) cumulative N_2O emissions, (**e**) CH_4 emission rate, and (**f**) cumulative CH_4 emissions from forest soils in a 35-day incubation. CK, no biochar addition; BC300, the application of biochar produced at 300 °C; BC700, the application of biochar produced at 700 °C.

There was no statistically significant effect of the interaction between biochar and nitrapyrin on cumulative CO_2 emissions (Table 1 and Figure 2b). The main effect of biochar was significant (Table 1), with cumulative CO_2 emissions in the BC300 treatment being 1.3 and 1.7 times, on average, greater than those in the CK and BC700 treatments, respectively (Table 2). The main effect of nitrapyrin was also significant (Table 1), with cumulative CO_2 emissions being 1.14 times, on average, higher in the treatment without nitrapyrin than that with nitrapyrin application (Table 2).

Table 1. Main and interaction effects (*F*-values) of biochar and nitrapyrin on cumulative greenhouse gas (GHG) emissions, global warming potential (GWP), soil pH, dissolved organic C (DOC), microbial biomass C (MBC), and net nitrification rates (NNR) in a 35-day incubation.

Factor	CO_2	N_2O	CH_4	GWP	pH	DOC	MBC	NNR
Biochar	46.2 **	30.6 **	1.25	72.4 **	22.9 **	10.5 **	4.89 *	2.27
Nitrapyrin	8.36 **	34.8 **	18.2 **	17.2 **	31.5 **	0.02	2.47	22.3 **
Biochar × nitrapyrin	1.30	0.16	0.36	1.41	0.06	0.06	0.78	0.54

* $p < 0.05$, ** $p < 0.01$.

Table 2. Multiple comparisons of the least-square means of the main effects (biochar and nitrapyrin) on cumulative GHG emissions, global warming potential (GWP), soil pH, dissolved organic C (DOC), microbial biomass C (MBC), and net nitrification rates (NNR) in a 35-day incubation.

Treatment	CO_2 (mg C kg^{-1})	N_2O (μg N kg^{-1})	CH_4 (μg C kg^{-1})	GWP (mg CO_2-C kg^{-1})	pH	DOC (mg kg^{-1})	MBC (mg kg^{-1})	NNR (mg N kg^{-1} day^{-1})
CK [1]	713.1 b	19.5 [2] b	−105.7 a	718.8 b	5.87 c	653.1 b	739.1 b	0.49 a
BC300	905.2 a	141.9 a	−101.4 a	975.3 a	6.03 b	825.9 a	989.5 a	0.90 a
BC700	520.0 c	23.2 b	−78.6 a	526.9 c	6.24 a	769.8 a	810.4 ab	0.34 a
No nitrapyrin	760.1 A	78.8 A	−127.4 B	803.7 A	5.92 B	747.5 A	899.2 A	1.17 A
Nitrapyrin	665.5 B	20.3 B	−63.1 A	677.0 B	6.17 A	751.7 A	793.5 A	−0.01 B

[1] Different lowercase letters (a, b, c) indicate significant differences between different biochar treatments across nitrapyrin application treatments; different uppercase letters (A, B) indicate significant differences between without and with nitrapyrin application treatments across biochar application treatments. [2] Data were back-transformed.

3.2. Biochar and Nitrapyrin Effects on N_2O Emissions

Peaks of N_2O emissions were observed on days 1, 0, and 1 in the CK, BC300, and BC700 treatments, respectively, without application of nitrapyrin (Figure 2c). With nitrapyrin application, there were no apparent peaks of N_2O emissions for all biochar treatments (Figure 2c).

There was no significant effect of the interaction between biochar and nitrapyrin on cumulative N_2O emissions (Table 1 and Figure 2d). The main effect of biochar was significant (Table 1), with the cumulative N_2O emissions in the BC300 treatment being 7.3 and 6.1 times, on average, greater than those in the CK and BC700 treatments, respectively (Table 2). The main effect of nitrapyrin was significant as well (Table 1), with the cumulative N_2O emissions being 3.9 times, on average, higher in treatment without nitrapyrin than that with nitrapyrin application (Table 2).

3.3. Biochar and Nitrapyrin Effects on CH_4 Emissions

Unlike CO_2 and N_2O emissions, CH_4 emission rates were negative, indicating that the soil took up CH_4 (Figure 1e,f). The CH_4 uptake rates increased (under all treatments) sharply from days 1 to 3 and then decreased sharply from days 3 to 5 (Figure 2e). Furthermore, on day 3, CH_4 uptake rates were, on average, higher with nitrapyrin application than without nitrapyrin application ($F = 17.52$, $p < 0.001$, Figure 2e). However, from day 7 to the end of the incubation, the CH_4 uptake rates were higher in the treatment without nitrapyrin application (Figure 2e).

There was no significant effect of the interaction between biochar and nitrapyrin on cumulative CH_4 uptake (Table 1 and Figure 2f). The main effect of biochar was not

significant (Table 1). However, the main effect of nitrapyrin was significant (Table 1), with the cumulative CH_4 uptake being 2.02 times, on average, higher in the treatment without nitrapyrin than that with nitrapyrin application (Table 2).

3.4. Biochar and Nitrapyrin Effects on Global Warming Potential (GWP)

There was no significant effect of the interaction between biochar and nitrapyrin on the GWP (Table 1). The main effects of biochar and nitrapyrin were significant (Table 1), with the GWP in the BC300 treatment being 1.4 and 1.9 times, on average, greater than that in the CK and BC700 treatments, respectively (Table 2), and 1.2 times, on average, greater in the treatment without nitrapyrin than that with nitrapyrin application (Table 2).

3.5. Biochar and Nitrapyrin Effects on Soil Properties

At the end of the incubation, there was no significant effect of the interaction between biochar and nitrapyrin on soil pH, DOC and MBC concentrations, and net nitrification rates (Table 1). The main effect of biochar was significant on soil pH, DOC concentration, and MBC concentration (Table 1) but not on net nitrification rates. The main effect of nitrapyrin on soil pH and net nitrification rates was significant (Table 1). Soil pH, DOC concentration, and MBC concentration were, on average, higher in the BC300 and BC700 treatments than in the CK treatment at the end of the incubation (Table 2). Furthermore, soil pH was, on average, significantly higher in the BC700 than in the BC300 treatment (Table 2).

4. Discussion

The higher GWP in the BC300 than in the BC700 treatment via increased CO_2 and N_2O emissions supports our hypothesis that canola straw biochar produced at a high temperature is more effective in reducing GHG emissions and lowering the GWP of GHG emissions from forest soils.

The greater CO_2 emissions in the BC300 than in the BC700 treatment is consistent with results reported in a meta-analysis that biochars produced at <600 °C increase, while those produced at ≥600 °C decrease CO_2 emissions when applied to soils in laboratory studies [35]. The difference in the effect on CO_2 emissions is mainly attributed to the properties of the different biochars. Biochar application is likely to cause a priming effect that contributes to changes in the soil organic C pool [36]. Both positive and negative priming effects have been reported [21,37]. The greater the labile matter concentration in the biochar, the more likely it is to have a positive priming effect when applied to the soil [37–39]. Increasing pyrolysis temperature leads to decreased labile matter concentration [38–40]. The BC300-amended soils also had higher DOC and MBC concentrations than the BC700-amended soils (Table 2). The high labile C concentration in the BC300 treatment might stimulate microbial activity [41,42] and cause a higher C mineralization rate [37], leading to more CO_2 release from the soil, especially in the early phase of the incubation (Figure 2a).

Compared to no biochar addition, the application of BC700 treatment significantly reduced cumulative CO_2 emissions (Table 2). Similarly, Pokharel et al. [20] observed a 16.4% reduction in cumulative CO_2 emissions in forest soils amended with a sawdust biochar produced at 550 °C. However, this reduction did not occur in BC300-amended soils. However, these studies were all conducted under laboratory conditions, and results may be different under field conditions due to some other important factors such as improvement in soil aeration and structure, changes in soil water availability, and interactions with plants that are difficult to be studied in laboratory experiments [36,43].

The N_2O emissions were mainly from denitrification and nitrification in soils [44–46]. Many studies have documented that biochar application is one of the strategies to mitigate N_2O emissions from soils by affecting these processes [13,47]. However, some also found that biochar increases N_2O emissions [48]. In this study, compared to CK, adding BC300 increased the cumulative N_2O emissions, while adding BC700 did not affect cumulative N_2O emissions (Table 2). One possible mechanism is the positive priming effect caused by BC300 addition leading to more soil organic C decomposition, supplying substrates

for denitrifiers and nitrifiers [37]. The increased N_2O emissions mainly occurred in the early phase of the incubation, in line with the timing of CO_2 emissions. On the other hand, BC700 had a higher pH itself and its application increased soil pH as compared to BC300 application. The increase in soil pH may enrich some denitrification-related genes such as *nirK* and *nosZ* [49] and favor the last step of denitrification that produces N_2 instead of N_2O [13,50,51]. Thus, BC700 has a greater ability to mitigate N_2O emissions. Furthermore, the C/N ratio of biochars has been shown to be highly correlated with its function in affecting N_2O emissions from soils; a lower C/N ratio will most likely enhance N_2O emissions [52]. The C/N of BC300 was 40, which was much lower than that of BC700, which was 57, indicating that the C/N ratio of the biochars most likely affected N_2O emissions.

The lack of biochar effect on CH_4 emissions was probably due to the incubation being conducted under aerobic conditions, causing no significant change in CH_4 oxidation activity [48,53]. Furthermore, methanogens are known as strict anaerobes and do not grow in aerobic conditions [54]. Thus, CH_4 uptake was observed in all treatments.

The role of nitrapyrin in inhibiting the activities of nitrifiers and reducing the oxidation of NH_4^+ to NO_3^- [24,55,56] is confirmed by the difference in net nitrification rates between treatments with and without nitrapyrin application. Furthermore, nitrapyrin might also affect the denitrification process, as the NO_3^- produced from the nitrification process could be a substrate for denitrification, which will eventually reduce N_2O emissions from both denitrification and nitrification processes [57]. The lack of the effect of the interaction between biochar and nitrapyrin on N_2O emissions (Table 1) indicates that the effectiveness of nitrapyrin in reducing N_2O emissions is not affected by biochar application; this is consistent with our earlier study on cropland soil [23]. Co-application of biochar and nitrapyrin does emit less N_2O than the application of biochar alone, especially for the application of BC300 (Figure 2d). Nitrapyrin can act against the CH_4 monooxygenase enzyme system and inhibit CH_4 oxidation [58]; thus, the CH_4 uptake decreased by nitrapyrin application in the studied soils (Figure 2f and Table 2).

Overall, BC300 application resulted in a greater GWP as compared to BC700 application to the forest soils. Adding nitrapyrin to the biochar-amended forest soils can help to further reduce the GWP of GHG emissions from the soils.

5. Conclusions

Our results highlight that the effect of biochar on the global warming potential of greenhouse gas emissions depends on the properties of biochar that are affected by its production temperature. With the application of the straw biochar produced at low temperature, greater CO_2 and N_2O emission rates in the early incubation stage caused a greater global warming potential relative to the control and application of straw biochar produced at high temperature, indicating that the greater labile carbon concentration in the low-temperature biochar caused a greater priming effect in the forest soils. However, the CH_4 emissions were not significantly affected by different biochar additions as this incubation experiment was conducted under aerobic conditions. Nitrapyrin effectively reduced N_2O emissions from the forest soils by inhibiting the nitrification process, as indicated by the significantly reduced net nitrification rates. In addition, the effectiveness of nitrapyrin in reducing N_2O emissions was not affected by biochar addition in the forest soils. Thus, we conclude that the application of biochar produced at high temperatures (e.g., 700 °C) and nitrapyrin can be potential techniques to employ to reduce greenhouse gas emissions from forestlands widely distributed across the agricultural landscape.

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