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ORIGINAL PAPER

Effect of biochar and nitrapyrin on nitrous oxide and nitric oxide emissions from a sandy loam soil cropped to maize

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Abstract

A field experiment was conducted to evaluate the combined or individual effects of biochar and nitrapyrin (a nitrification inhibitor) on N_2O and NO emissions from a sandy loam soil cropped to maize. The study included nine treatments: addition of urea alone or combined with nitrapyrin to soils that had been amended with biochar at 0, 3, 6, and 12 t ha^{-1} in the preceding year, and a control without the addition of N fertilizer. Peaks in N_2O and NO flux occurred simultaneously following fertilizer application and intense rainfall events, and the peak of NO flux was much higher than that of N_2O following application of basal fertilizer. Mean emission ratios of NO/N_2O ranged from 1.11 to 1.72, suggesting that N_2O was primarily derived from nitrification. Cumulative N_2O and NO emissions were 1.00 kg N_2O-N ha^{-1} and 1.39 kg NO-N ha^{-1} in the N treatment, respectively, decreasing to 0.81–0.85 kg N_2O-N ha^{-1} and 1.31–1.35 kg NO-N ha^{-1} in the biochar amended soils, respectively, while there was no significant difference among the treatments. NO emissions were significantly lower in the nitrapyrin treatments than in the N fertilization-alone treatments ($P < 0.05$), but there was no effect on N_2O emissions. Neither biochar nor nitrapyrin amendment affected maize yield or N uptake. Overall, our results showed that biochar amendment in the preceding year had little effect on N_2O and NO emissions in the following year, while the nitrapyrin decreased NO, but not N_2O emissions, probably due to suppression of denitrification caused by the low soil moisture content.

Keywords Biochar · Maize · Nitrification inhibitor · Nitrapyrin · Nitrification · Soil WFPS · Yield-scaled N_2O emission

Introduction

Nitrous oxide (N_2O) is an important contributor to global warming and is associated with the depletion of stratospheric ozone, whereas nitric oxide (NO) is a major precursor to atmospheric photo-oxidants that contribute to nitrogen (N) deposition and subsequent environmental acidification (Akiyama et al. 2010). Combined studies of NO and N_2O emissions from agricultural ecosystems are uncommon due to the differing roles of the compounds in atmospheric dynamics. The use of N fertilizer and animal manure is considered to be a driver of N_2O and NO emissions (Stehfest and Bouwman 2006) and agriculture accounts for almost 60 and 10% of global N_2O and NO emissions, respectively (Ciais et al. 2013), derived from 2.8 and 1.6 Tg of N_2O and NO emissions from fertilized agricultural fields, respectively (Bouwman et al. 2002). To satisfy the rising food demands of an increasing human population, especially in developing countries, greater inputs of N fertilizer not only reach levels of diminishing returns but also contribute to regional and global-scale environmental N-related issues (Chen et al. 2011).

The co-application of nitrification inhibitors with N fertilizer has been tested as an agronomic practice to decrease nitrate leaching and mitigate N_2O and NO emissions (Di and Cameron 2006; Wu et al. 2017). Nitrification inhibitors can

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effectively reduce the oxidation rate of NH_4^+ to NO_3^-, thereby decreasing N loss from soils and increasing N uptake by crops (Di and Cameron 2006; Zaman et al. 2008). Nitrapyrin (2-chloro-6-(trichloromethyl) pyridine) is similar to other frequently used nitrification inhibitors, such as dicyandiamide (DCD) and 3,4-dimethylpyrazole phosphate (DMPP), and has been shown to inhibit the ammonia monooxygenase enzyme that catalyzes the first, rate-limiting step of nitrification (McCarty 1999; Abbasi and Adams 2000; Chen et al. 2010). Field measurements by Burzaco et al. (2013) and Martins et al. (2017) found that nitrapyrin reduced N_2O emission by 49 and 24% with urea and urea-ammonium nitrate application during the maize growth season, respectively. The effectiveness of nitrification inhibitors on N_2O emissions depends on environmental parameters, e.g., temperature, soil moisture content (Menéndez et al. 2012), soil available carbon (C) (Wu et al. 2017), the proportion of clays in soil (Shi et al. 2016), and the timing of fertilization (Parkin and Hatfield 2010). It is generally accepted that nitrification inhibitors have no direct effect on denitrification (Müller et al. 2002). However, some studies have shown that nitrification inhibitors affect N_2O emissions more effectively under higher soil moisture levels by increasing the abundance of denitrifying genes (*narG*, *nirK*, and *nosZ*) (Barrena et al. 2017). Although the effects of nitrification inhibitor on N_2O emission have been extensively studied, those investigating mitigation effects on NO emissions are poorly known (Wu et al. 2017), including key factors that influence effects of nitrapyrin on N_2O and NO emissions from agricultural soils.

The addition of biochar to soil can be an effective mitigation technique for soil N_2O emissions. Meta-analyses of laboratory and field studies by Cayuela et al. (2014) estimated reduction potentials of biochar amendment of soil on N_2O emissions were 54 and 28%, respectively, where several mechanisms have been suggested. For example, biochar (1) improves soil aeration and immobilization of available N in the soil (van Zwieten et al. 2010b; Case et al. 2012), resulting in the suppression of denitrifier activities; (2) increases soil pH and the relative abundance of the bacterial N_2O reductase *nosZ* gene that reduces N_2O to N_2 more efficiently (Harter et al. 2014); (3) increases adsorption of organic compounds (Kuzyakov et al. 2009) and microbial inhibiting compounds, such as ethylene (Spokas et al. 2010); and (4) increases adsorption of N_2O, NO, and NH_3 onto the biochar surface (Taghizadeh-Toosi et al. 2012; Cornelissen et al. 2013). However, effects of biochar on N_2O emission may not be consistent among different types of biochar and soils (Ameloot et al. 2013; Cayuela et al. 2014); for example, Angst et al. (2014) did not observe effects on N_2O emissions of biochar application to a sandy loam soil cultivated with ryegrass at rates of 5.7 and 18.8 t ha^{-1}. To our knowledge, there have been few available studies on effects of biochar on NO emission (Nelissen et al. 2014; Obia et al. 2015). Data on biochar's effects on NO emission are scarce, variable impacts on soil NO emission range from nearly no effect in a rice-wheat rotation field experiment (Xiang et al. 2015) to obvious reduction under incubation experiments (Nelissen et al. 2014; Obia et al. 2015), suggesting that biochar's potential for reducing NO remains poorly regulated. The ingnored benefits of biochar applied on NO emission highlight the need for an improved understanding of the effect of biochar on the correlation bewteen N_2O and NO emissions in agricultural soil.

Between 1990 and 2014 in China, grain production and N fertilizer consumption increased by 36 and 46%, respectively, reaching 607 and 23.9 million t, respectively (China Agricultural Yearbook Editorial Committee 2015). It has been estimated that fertilizer-induced N_2O emissions from croplands increased from 115.7 Gg N_2O-N $year^{-1}$ in the 1980s to 210.5 Gg N_2O-N $year^{-1}$ in the 1990s (Zou et al. 2010), while fertilizer-induced NO emissions from croplands in 2012 were estimated to have been 336.97 Gg NO-N (Huang and Li 2014). Qin et al. (2017) found that excessive N fertilization had the potential to increase N_2O emissions due to reduction of N_2O reductase activity in soils. There is an urgent need to develop effective techniques to improve N use efficiency (NUE) and minimize N loss emissions in agricultural ecosystems, due to the environmentally degrading effects of reactive N enrichment of the atmosphere, soil, and water. Therefore, the objective of this study was to evaluate the field scale effects of biochar and nitrapyrin on N_2O and NO emissions, and how biochar's effect varied when the nitrapyrin was applied. We tested the hypotheses that (i) biochar can decrease N_2O and NO emissions and increase N uptake due to the relatively high N retaining capacity, and (ii) the combination of biochar and nitrapyrin further reduces N_2O and NO emissions, especially at high rates of biochar application.

Materials and methods

Experimental site

The study site was located at the Fengqiu National Station for Agroecological Observation and Research, Henan Province, China (35°00′ N, 114°24′ E), where the traditional cropping system is wheat (*Triticum aestivum* L.) grown in winter and maize (*Zea mays* L.) cultivated in summer. The region has a semi-arid, sub-humid monsoon climate, with a mean annual temperature of 13.9 °C and precipitation of 615 mm. Soils are derived from alluvial sediments of the Yellow River and classified as calcaric Fluvisol (Shi et al. 2010), with a pH of 8.41 in soil-water suspension (1:2.5 *v*/*v*), bulk density of 1.41 g cm^{-3}, and particle size distribution of 15.8% clay, 16.2% silt, and 68.0% sand, with 7.40 g kg^{-1} organic C, 0.85 g kg^{-1} total N, 1.06 mg kg^{-1} NO_3^--N, and 8.23 mg kg^{-1} exchangeable NH_4^+-N.

Experimental design

The field experiment was established on 9 June 2014 when maize was drilled, with the addition of maize straw biochar at 0, 3, 6, and 12 t ha^{-1}. The biochar, produced by the Sanli New Energy Company, was pyrolyzed at 450 °C in a vertical kiln constructed from refractory bricks, had a pH of 10.02, and comprised 38.3% ash, 450 g kg^{-1} total C, 14.8 g kg^{-1} total N, 2.82 mg kg^{-1} NO_3^--N, and 4.48 mg kg^{-1} exchangeable NH_4^+-N.

In June 2015, nine treatments were arranged in a randomized complete block design with three replicates, where experimental plots measured 9 m^2, except the control that was 18 m^2. N fertilizer (urea) was applied to the biochar amended plots, either alone or in combination with a nitrification inhibitor (nitrapyrin). Treatments comprised N fertilizer only (N), N fertilizer + 3 t ha^{-1} biochar (NB3), N fertilizer + 6 t ha^{-1} biochar (NB6), N fertilizer + 12 t ha^{-1} biochar (NB12), N + nitrapyrin (NI), NB3 + nitrapyrin (NB3I), NB6 + nitripyrin (NB6I), NB12 + nitripyrin (NB12I), and a control without N fertilizer. Urea applied at 200 kg N ha^{-1} was added as basal and supplemental fertilizers on 9 June and 22 July 2015, respectively, at a ratio of 2:3, and calcium superphosphate and potassium sulfate were applied at 120 kg P_2O_5 ha^{-1} and 120 kg K_2O ha^{-1}, respectively, as a basal dressing. The application rate of nitrapyrin (2-chloro-6-(trichloromethyl) pyridine) was equivalent to 0.26% of the applied urea N (*w*/*w*), namely 525 g ha^{-1}. Basal fertilizers were evenly broadcast onto the soil surface and immediately tilled into the surface (0–20 cm) soil. Unlike in local, conventional farming, irrigation was applied prior to tillage due to low soil moisture from low levels of precipitation. Maize was drilled on 9 June in rows 70 cm apart and was harvested on 25 September 2015, before it was dried at 60 °C to a constant weight for grain yield and aboveground biomass analysis.

Greenhouse gas flux measurement

Cylindrical polyvinyl chloride (PVC) plastic tubes (10 cm long, 10-cm outer diameter in the lower half, and 10-cm inner diameter in the upper half) were installed approximately 5 cm into the soil, and one maize plant per plot was subsequently established in the center of each plastic tube. Soil fluxes were measured using the closed chamber method, using a chamber that comprised two sections, which were joined using a hinge and airtight rubber seal, and was externally covered with plastic foam to minimize solar heating and temperature fluctuations (Ding et al. 2007). The stainless steel rectangular chamber base (70 cm × 30 cm × 10 cm), with a 5 cm groove around the upper edge, was inserted into the soil to a depth of 10 cm around the PVC tube in each plot, immediately after drilling. In order to exclude the plant from the gas sampling area and to avoid the need to raise the height of the chamber as the plant grew, a separate PVC pipe (35 cm long, 10 cm outer diameter) was inserted into the existing PVC tube, and upper end of the PVC pipe was sealed with a rubber seal. The stainless steel rectangular upper chamber (70 cm × 30 cm × 30 cm) with a 10-cm diameter central aperture (to accommodate the PVC pipe) was fitted to the base by inserting the flange of the upper chamber into the 5-cm groove. The chamber was equipped with two ports: A small, silicon-sealed vent for gas sampling and a second port for measuring chamber temperature and two battery-operated fans were placed in the upper chamber to ensure adequate gas mixing.

During the maize growth season, gas was sampled twice per week in the morning, between 09:00 and 12:00, to minimize the effects of diurnal variation in flux patterns. On each occasion, four samples of air were manually extracted, using a plastic syringe, from the chamber into pre-evacuated 20-ml glass vials fitted with butyl rubber stoppers at 0, 10, 20, and 30 min after chamber closure. The air temperature inside the chamber was simultaneously measured using a mercury thermometer. The gas samples were analyzed on an Agilent 7890D gas chromatograph equipped with an electron capture detector (ECD) for N_2O, using high-purity Ar-CH_4 carrier gases for the ECD.

NO fluxes were measured by the static chamber method. At the start and end of gas sampling, about 2 L of chamber gas was collected by a large syringe. The gas samples were stored in Teflon gas bags and immediately measured on a NO_x analyzer (Model 42i, Thermo Fisher Scientific Inc.).

Weather and soil physicochemical measurements

Precipitation and air temperature were monitored at a local meteorological station. Soil temperature at a depth of 5 cm was measured using a geothermometer, and soil moisture was measured using a time domain reflectometry probe (TDR), expressed as water-filled pore space (WFPS) determined by the following equation:

$$\text{WFPS}\ [\%] = (\text{volumetric water content}\ [\%]/\text{total soil porosity}\ [\%]) \times 100 \quad (1)$$

where total soil porosity = 1 − (soil bulk density / 2.65), based on the assumption that particle density of the soil was 2.65 g cm^{-3}.

Three replicate surface soil samples (0–20 cm) were taken weekly, at random from row and/or inter-row of each plot, using a 5-cm diameter auger. Nitrate and exchangeable NH_4^+ were extracted using 2 M KCl solution and quantified colorimetrically using a continuous-flow autoanalyzer (San++ System, Skalar Analytical BV, Breda, the Netherlands). Dissolved organic C (DOC) was determined using a TOC analyzer (vario TOC Cube, Elementar, Hanau, Germany), where fresh soil (equivalent to 10 g dry soil) was mixed with

50 ml of deionized water, shaken for 30 min, centrifuged for 15 min (7570×*g*), and filtered with a 0.45-μm polyethersulfone membrane filter. Soil pH was determined from soil-water suspensions (1:2.5 *v*/*v*), while soil organic C was measured using the wet oxidation-redox titration method and soil total N content was measured using an elemental analyzer (Vario Max CN, Elementar, Hanau, Germany). Particle size distribution was determined using a laser particle size analyzer (LS13320, Beckmann Coulter, Brea, USA).

Data analysis

Rates of N_2O and NO increase in the chamber air were calculated using linear regression of gas concentration against time, using chamber air temperature and atmospheric pressure as follows:

$$F = \rho \times (V/S) \times (dC/dt) \times (273/273 + T) \quad (2)$$

where F is the flux in N_2O and NO (μg N_2O-N or NO-N m^{-2} h^{-1}); ρ is the gas density at standard temperature and pressure; V is the volume of the chamber; S is the area of the chamber; dC/dt is the change in gas concentration with time; and T is the mean temperature inside the chamber during sampling. Cumulative N_2O and NO emissions (E, N_2O-N kg ha^{-1} or NO-N kg ha^{-1}) were calculated using the following equation:

$$E = \left[\Sigma\left(f_i + f_{i+1}\right)/(2 \times (t_{i+1} - t_i))\right] \times \left(24 \times 10^{-5}\right) \quad (3)$$

where f represents the flux in N_2O or NO (μg N m^{-2} h^{-1}); i is the ith measurement; $(t_{i+1} - t_i)$ is the number of days between two adjacent measurements; and 24×10^{-5} was used for unit conversion. N_2O and NO direct emissions factor (EF, %) of N fertilizer applied to the soil, with adjustment to background levels, was calculated as follows:

$$EF = (E_{\text{fertilizer}} - E_{\text{control}})/\text{applied N} \quad (4)$$

where $E_{\text{fertilizer}}$ and E_{control} are cumulative N_2O or NO emissions (kg N ha^{-1}) in the N fertilizer treatments and the control, respectively, and applied N is the application rate of urea (200 kg N ha^{-1} for each treatment). Yield-scaled emissions (g N_2O-N kg^{-1} grain or g NO-N kg^{-1} grain) were calculated as (after Venterea et al. 2011):

$$\text{Yield} - \text{scaled emission} = \text{cumulative emission}/\text{grain yield} \quad (5)$$

where cumulative emissions is cumulative N_2O or NO emissions (kg N ha^{-1}) in all the treatments.

Soil inorganic N intensity of NH_4^+ (NH4I), NO_3^- (NO3I), and NH4I plus NO3I (IONI) was calculated as the summation of daily exchangeable NH_4^+-N, NO_3^--N, and (NO_3^- + NH_4^+)-N concentrations in the 0–20 cm layer soil over the same period as cumulative N_2O emissions, using linear interpolation between sample dates (Zebarth et al. 2008).

All data were analyzed using the SPSS software package for Windows (Version 18.0, SPSS Inc.). Differences among treatments were tested using one-way ANOVA followed by least significant difference (LSD) test at $P < 0.05$. Interaction effects of biochar and nitrapyrin on N_2O and NO emissions and grain yield were tested using two-way ANOVA, and Pearson correlation analysis was used to determine the relationship between N_2O or NO flux and other factors.

Results

Yield and N uptake

Compared with the control, maize grain yield was higher in all the urea-amended treatments ($P < 0.05$, Table 1). The highest grain yield and aboveground biomass were 12,287 and 21,649 kg ha^{-1} in the NB3I treatment, respectively. N uptake in the measures of aboveground biomass was consistently greater in each of the urea-amended treatments (223–236 kg

Table 1 Effects of N fertilizer, biochar, and nitrapyrin on maize biomass and N uptake

Season	Treatment	Biomass (kg ha^{-1})			Amount of N uptake (kg N ha^{-1})		
		Grain	Straw	Total	Grain	Straw	Total
Maize	Control	10,084 ± 269b	8828 ± 813a	18,913 ± 1035b	100 ± 0b	58 ± 9b	158 ± 9b
	N	11,787 ± 232a	9023 ± 831a	20,810 ± 928ab	138 ± 4a	85 ± 10a	223 ± 13a
	NB3	11,474 ± 348a	9653 ± 254a	21,127 ± 598a	133 ± 5a	97 ± 3a	230 ± 7a
	NB6	11,731 ± 168a	9490 ± 414a	21,221 ± 556a	135 ± 2a	100 ± 5a	235 ± 7a
	NB12	11,985 ± 136a	9309 ± 170a	21,294 ± 123a	142 ± 1a	94 ± 4a	236 ± 3a
	NI	11,900 ± 442a	9724 ± 350a	21,625 ± 684a	138 ± 7a	98 ± 4a	236 ± 10a
	NB3I	12,287 ± 293a	9362 ± 28a	21,649 ± 315a	138 ± 4a	94 ± 2a	232 ± 4a
	NB6I	11,682 ± 495a	9193 ± 388a	20,875 ± 446a	137 ± 6a	93 ± 6a	230 ± 1a
	NB12I	11,785 ± 445a	9168 ± 276a	20,954 ± 707a	142 ± 8a	90 ± 2a	232 ± 9a

Means ± SE ($n = 3$). Values followed by different letters within the same column denote differences between treatments at $P < 0.05$

N ha^{-1}) than the control (158 kg N ha^{-1}) ($P < 0.05$), and there were no treatment effects among urea-amended treatments.

Environmental and soil variables

Average air temperature was 24.5 °C, with a range of 15.7–30.4 °C and soil temperature that varied from 16 to 34 °C (Fig. 1), and was correlated with air temperature in the treatments ($R^2 = 0.73$–0.83, $n = 31$, $P < 0.01$). Total precipitation was 215.4 mm, and while soil moisture content ranged from 13 to 72% WFPS, there were no differences among the treatments. We recorded high soil WFPS values following irrigation events and/or heavy rainfall that were correlated with cumulative precipitation during the 3 days prior to the flux measurement ($R^2 = 0.25$–0.34, $n = 31$, $P < 0.05$).

Across all treatments, average exchangeable NH_4^+ concentration ranged between 7.59 and 15.91 mg N kg^{-1}. Soil exchangeable NH_4^+ concentration was higher in the NB3 treatment (48.83 mg N kg^{-1}) than the control (5.17 mg N kg^{-1}) after basal fertilization. After application of supplemental fertilizer, soil exchangeable NH_4^+ concentrations were higher in all the urea-amended treatments than the control, where peak concentration was 69% higher in the NB3I treatment than the NB3 treatment ($P < 0.05$, Fig. 2). Soil average NO_3^- concentrations ranged between 5.88 and 26.83 mg N kg^{-1} across all the treatments and were highest around 5 days after fertilizer application, before they gradually returned to background levels. After basal fertilization, the highest soil NO_3^- concentration was recorded in the NB3I treatment (29.25 mg N kg^{-1}). Nitrapyrin lowered soil NO_3^- concentrations by 3–25%, compared with the application of urea alone after application of supplemental fertilizer (Fig. 2). Concentrations of both soil exchangeable NH_4^+ and NO_3^- showed small peaks when soil WFPS was > 65% after heavy rainfall events (24–25 June 2015). Mean DOC concentration in the urea-amended treatments ranged between 20.66 and 27.97 mg C kg^{-1} and was 29.88 mg C kg^{-1} in the control, and no apparent difference was found between urea-amended treatments (Fig. 2).

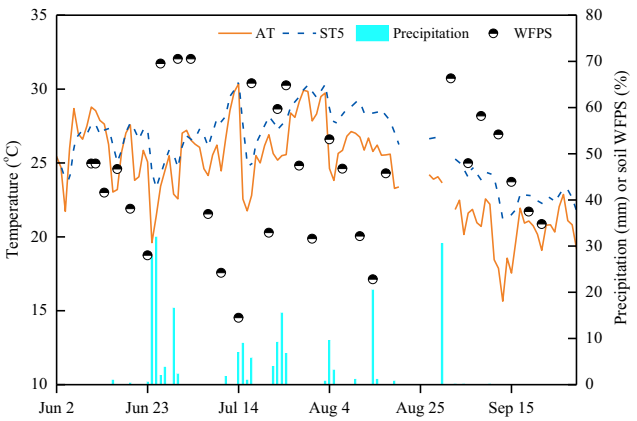

Fig. 1 Air temperature (AT), soil temperature at 5 cm depth (ST5), precipitation, and soil moisture content (measured as WFPS) during the maize growth season. Vertical bars are SE ($n = 3$)

Mean level of soil NH4I was higher in the urea-amended treatments than in the control ($P < 0.05$, Table 2). Soil NH4I level was higher in the NB3I treatment than in the NB3 treatment, while in contrast, it was lower in the NB6I and NB12I treatments than in the NB6 and NB12 treatments, respectively ($P < 0.05$, Table 2). Mean level of soil NO3I in the NB12 treatment was higher than in the other urea-amended treatments ($P < 0.05$, Table 2).

N_2O and NO fluxes

Mean N_2O flux in the urea-amended treatments varied from 38.04 to 46.82 μg N_2O-N m^{-2} h^{-1} and were higher than in the control ($P < 0.05$). Trends in N_2O fluxes were generally similar among the treatments, with three distinct low peaks occurring after application of urea, heavy rainfall, and irrigation (Fig. 3). The first N_2O flux peak was the day after application of basal fertilizer (10 June), when soil WFPS values ranged between 42 and 51% and soil temperature was > 28 °C; the highest peak was 153 μg N_2O-N m^{-2} h^{-1} in the NB3I treatment. A second peak in N_2O flux occurred on 26 June, when soil WFPS values increased to 67–72% following a heavy rainfall event (61.8 mm), where the highest peak, which was recorded in the N treatment, was 14% higher than the first peak. The third N_2O flux peak occurred after supplemental fertilizer application (23 July) and subsequent irrigation that resulted in 56–66% soil WFPS; the highest peak (284 μg N_2O-N m^{-2} h^{-1}) occurred in the NI treatment. Compared with the N treatment, application of biochar increased the peaks in flux by 14–45%, whereas application of nitrapyrin to the biochar-amended soils reduced the peaks by 30–39% compared with the NI treatment. We found that N_2O flux was correlated with soil WFPS in all the treatments and with soil exchangeable NH_4^+ concentration, except in the control ($P < 0.05$, Table 3). There was an exponential relationship between N_2O fluxes and soil WPFS (Fig. 4).

The NO flux in the control treatment was consistently low, with an average of 8.20 μg NO-N m^{-2} h^{-1} (Fig. 3). Following application of basal fertilizer, the highest NO flux peak of 696 μg NO-N m^{-2} h^{-1} occurred in the NB6 treatment and this peak was 129% higher than in the NB6I treatment. No peaks in NO flux were identified following the heavy rainfall in June 2015. Following application of supplemental fertilizer, the highest NO flux peak was observed in the NB3 treatment and this peak was 34% higher than that in the NB3I treatment. NO flux was correlated with soil temperature and exchangeable NH_4^+ concentration ($P < 0.05$, Table 3).

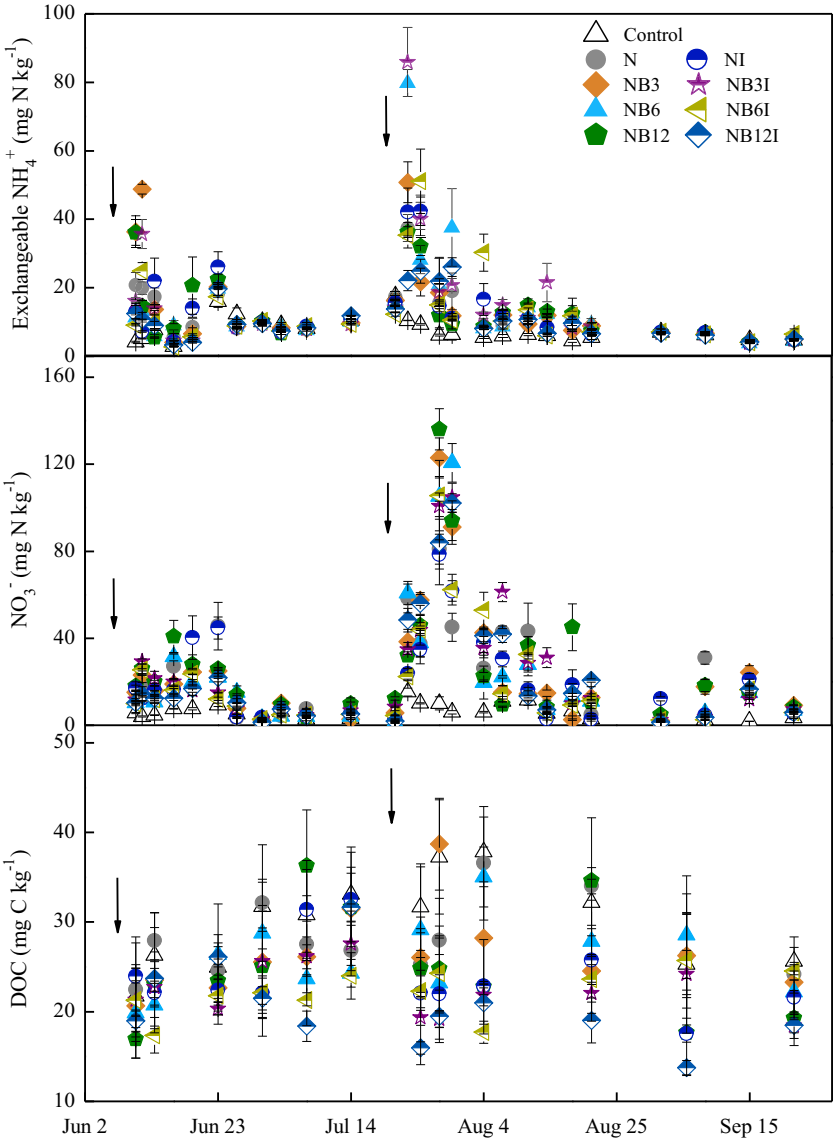

Fig. 2 Soil exchangeable NH_4^+, NO_3^-, and DOC concentrations during the maize growth season. Vertical bars are SE ($n = 3$). Arrows indicate fertilizer application

Table 2 Effects of biochar and nitrapyrin on intensity (g N day kg^{-1}) of soil ammonium (NH4I), nitrate (NO3I), and inorganic N (IONI)

Treatment	NH4I	NO3I	IONI
Control	0.80 ± 0.0.02d	0.52 ± 0.01f	1.32 ± 0.03 g
N	1.14 ± 0.03b	1.94 ± 0.08cd	3.09 ± 0.05de
NB3	1.17 ± 0.01b	2.08 ± 0.06bc	3.25 ± 0.06bc
NB6	1.27 ± 0.03a	1.93 ± 0.03d	3.20 ± 0.03cd
NB12	1.17 ± 0.02b	2.32 ± 0.06a	3.49 ± 0.04a
NI	1.19 ± 0.02b	1.81 ± 0.04de	3.00 ± 0.06ef
NB3I	1.31 ± 0.03a	2.09 ± 0.02b	3.40 ± 0.05ab
NB6I	1.18 ± 0.02b	1.71 ± 0.03e	2.89 ± 0.05f
NB12I	1.04 ± 0.02c	1.93 ± 0.05d	2.97 ± 0.07ef

Means ± SE ($n = 3$). Values followed by different letters within the same column denote differences between treatments at $P < 0.05$

Cumulative N_2O and NO emissions

The lowest N_2O emission was recorded in the control (0.31 kg N_2O-N ha^{-1}) and the highest in the N treatment (1.00 kg N_2O-N ha^{-1}) (Table 4). NO emissions recorded in all the urea-amended treatments were higher than the control ($P < 0.05$), and the highest emission was recorded in the N treatment (1.39 kg NO-N ha^{-1}). While NO emissions were only reduced by 3–6% in plots that were treated with biochar alone (NB3, NB6, and NB12) compared with the N treatment, application of nitrapyrin significantly reduced NO emissions by 20–30% compared with the urea-amended-alone treatments. Cumulative NO emissions were higher than N_2O emissions in the urea-amended treatments; however, an opposite pattern was observed in the control ($P < 0.05$).

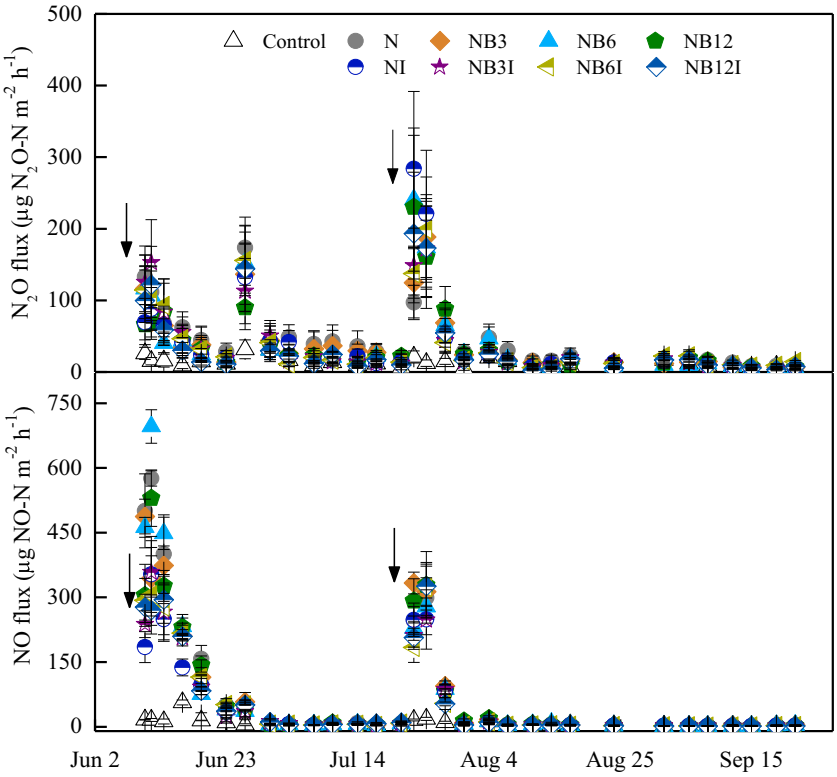

Fig. 3 Temporal dynamics of nitrous oxide and nitric oxide fluxes during the maize growth season. Vertical bars are SE (n = 3). Arrows indicate fertilizer application

The ratios of NO/N_2O emission ranged between 1.11 and 1.72 in the urea-amended treatments. There were no nitrapyrin × biochar interaction effects on N_2O or NO emissions (Table S1).

Emission factors and yield-scaled emissions

The N_2O emission factor of applied N was 0.34% in the N treatment, and the addition of biochar and nitrapyrin

Table 3 Correlation between N_2O flux and soil WFPS, soil temperature at 5 cm depth (T_5), soil inorganic N concentration, dissolved organic C (DOC), or total N

	Treatment	T_5	WFPS	Exchangeable NH_4^+-N	NO_3^--N	Total N	DOC
N_2O flux	Control	0.252	0.525**	0.168	0.117	0.199	− 0.006
	N	0.421*	0.462*	0.607**	0.129	0.314	− 0.326
	NB3	0.373*	0.460*	0.566**	0.274	0.443*	− 0.014
	NB6	0.408*	0.465**	0.688**	0.277	0.458*	0.003
	NB12	0.423*	0.384*	0.657**	0.266	0.431*	− 0.181
	NI	0.345	0.387*	0.780**	0.085	0.379	− 0.183
	NB3I	0.418*	0.415*	0.674**	0.086	0.371	− 0.303
	NB6I	0.331	0.437*	0.655**	0.136	0.346	− 0.270
	NB12I	0.354	0.451*	0.493**	0.260	0.317	− 0.327
NO flux	Control	0.251	− 0.004	− 0.068	0.324	0.047	− 0.043
	N	0.473**	0.187	0.584**	0.114	0.287	− 0.437
	NB3	0.518**	0.246	0.742**	0.148	0.399*	− 0.323
	NB6	0.464**	0.175	0.216	0.018	0.071	− 0.494
	NB12	0.518**	0.134	0.565**	0.133	0.273	− 0.341
	NI	0.548**	0.179	0.564**	0.124	0.307	− 0.223
	NB3I	0.469**	0.201	0.558**	0.114	0.327	− 0.335
	NB6I	0.448*	0.146	0.529**	0.120	0.273	− 0.407
	NB12I	0.452*	0.202	0.358*	0.113	0.152	− 0.134

*$P < 0.05$; **$P < 0.01$

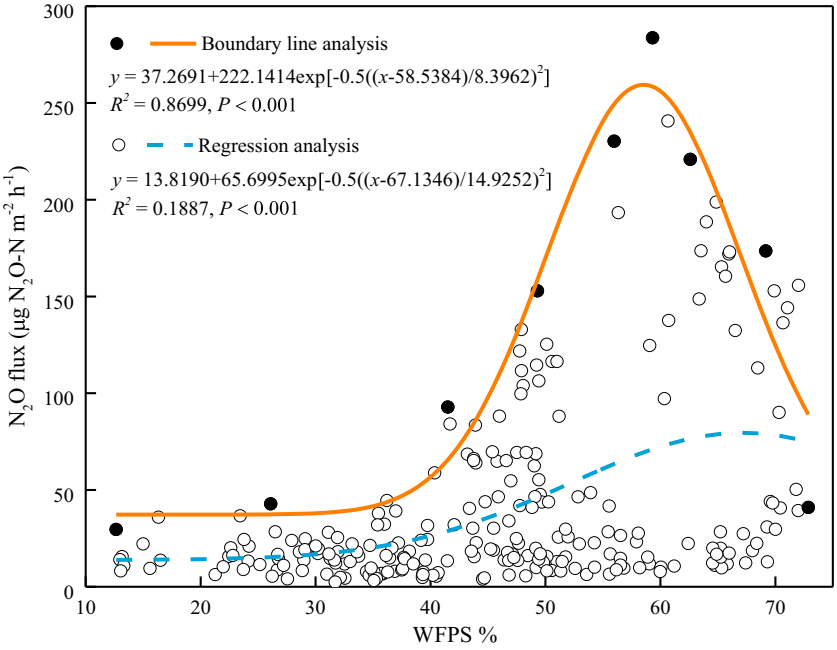

Fig. 4 Relationship between N_2O flux and soil WFPS in the urea-amended treatments during the maize growth season

reduced this to between 0.22 and 0.28% (Table 4). The highest NO emission factor of applied N was 0.60% in the N treatment, and although there was no effect of the addition of biochar, application of nitrapyrin reduced NO emission factors by 23–34% compared with the urea-amended treatments ($P < 0.05$). The yield-scaled N_2O emissions ranged from 0.064 to 0.085 g N_2O-N kg^{-1} grain and were lower in the NB12I treatment than in the N treatment ($P < 0.05$). The highest yield-scaled NO emission was 0.118 g NO-N kg^{-1} grain in the N treatment, and the addition of nitrapyrin reduced this to 0.082–0.093 g NO-N kg^{-1} grain ($P < 0.05$, Table 4).

Discussion

Effect of nitrapyrin on N_2O and NO emissions

We found that the N_2O emission factor of applied N of 0.34% was much lower than the IPCC default value of 1.00% (IPCC 2006), and that measured in the neighboring field (1.06%) in a previous study (Cai et al. 2013). Nitrous oxide can increase due to denitrification (including nitrifier denitrification) following irrigation and/or intense rainfall (Wan et al. 2009; Zhou et al. 2016). In our study, irrigation was carried out prior to application of basal fertilizer to ensure germination under

Table 4 Effects of N fertilizer, biochar, and nitrapyrin on N_2O and NO emissions, emission factors of applied N as N_2O and NO, and yield-scaled N_2O emissions

Treatment	Emission (kg N ha^{-1})		Emission factor (%)		NO/N_2O ratio	Yield-scaled emission (g N kg^{-1} grain)	
	N_2O	NO	N_2O	NO		N_2O	NO
Control	0.31 ± 0.03bx	0.18 ± 0.02cy	–	–	0.57	0.031 ± 0.003c	0.018 ± 0.001e
N	1.00 ± 0.07ay	1.39 ± 0.02ax	0.34 ± 0.05a	0.60 ± 0.01a	1.40	0.085 ± 0.004a	0.118 ± 0.005a
NB3	0.84 ± 0.10ay	1.30 ± 0.04ax	0.26 ± 0.03a	0.55 ± 0.02a	1.57	0.073 ± 0.008ab	0.113 ± 0.006ab
NB6	0.85 ± 0.03ay	1.35 ± 0.07ax	0.27 ± 0.03a	0.58 ± 0.0 3a	1.58	0.073 ± 0.003ab	0.115 ± 0.004ab
NB12	0.81 ± 0.15ay	1.31 ± 0.07ax	0.25 ± 0.05a	0.56 ± 0.03a	1.72	0.068 ± 0.013ab	0.109 ± 0.006abc
NI	0.87 ± 0.06ax	0.97 ± 0.12bx	0.28 ± 0.02a	0.39 ± 0.06b	1.11	0.073 ± 0.004ab	0.082 ± 0.010d
NB3I	0.80 ± 0.14ax	1.01 ± 0.05bx	0.24 ± 0.06a	0.41 ± 0.03b	1.32	0.065 ± 0.010ab	0.083 ± 0.004d
NB6I	0.84 ± 0.01ax	1.08 ± 0.13bx	0.26 ± 0.02a	0.45 ± 0.07b	1.29	0.072 ± 0.004ab	0.093 ± 0.013bcd
NB12I	0.75 ± 0.04ay	1.05 ± 0.06bx	0.22 ± 0.01a	0.43 ± 0.03b	1.41	0.064 ± 0.001b	0.089 ± 0.009cd

Means ± SE ($n = 3$). Values followed by letters a, b, and c within the same column, and x and y within the same row, denote differences between treatments and between N_2O and NO emissions for the same treatment, respectively, at $P < 0.05$

the low rainfall conditions. This practice reduced soil WPFS peak to c. 50%, due to the longer time available for evaporation, and contrasts with values of 65–85% that are typically recorded when irrigation is applied at the time of basal fertilizer application (Ding et al. 2007; Cai et al. 2013). Cai et al. (2013) suggested that irrigation prior to plowing minimized the formation of anaerobic conditions for denitrification, leading to a decrease in N_2O emissions. Thus, management practices, such as tillage following appropriate irrigation to avoid excessive saturation of arable soils, may reduce conversion of applied N into N_2O by denitrification.

We found that the estimated NO emission factor of 0.60% was within the previously reported range of 0.52–0.66% (Yan et al. 2003; Cui et al. 2012). The highest NO flux peaks occurred at 40–55% WFPS following the application of basal fertilizer, which was within the range of the optimal WFPS (40–60%) for NO emissions (Abalos et al. 2014), but much lower than the optimal WPFS (60–70%) for N_2O emissions (Davidson et al. 2000). The relationship between N_2O fluxes and soil WFPS indicated that optimal soil moisture for N_2O emission in the experimental soils was 60–70% WFPS (Fig. 4). The ratio of NO/N_2O emissions was > 1 in all the urea-amended treatments, suggesting that NO and N_2O were primarily derived from nitrification (Anderson and Levine 1986) and confirmed previous studies that found nitrification was the dominant process (Ding et al. 2007; Cui et al. 2012). Thus, irrigation prior to plowing could contribute to increased NO emissions, creating a trade-off with N_2O emission.

We found that nitrapyrin amendment significantly reduced NO emission by 20–30%, compared with the only N treatment, and this was slightly lower than the range of 35–84% reported previously (Baumgärtner and Conrad 1992; Akiyama et al. 2010). The use of nitrification inhibitors results in NH_4^+ retention by blocking the ammonia mono-oxygenase enzyme and preventing N_2O and NO emissions through longer retention of N in the NH_4^+ form (Abbasi and Adams 2000; Wolt 2004). Using the ^{15}N trace technique, Russow et al. (2009) found that NO_2^- was the main intermediate product for NO production under aerobic conditions and contributed 70% of the total emitted NO emissions. Nitrapyrin may effectively inhibit NO_2^- accumulation in alkaline soils (Shen et al. 2003) that would subsequently lead to the inhibition of conversion of NO_2^- to NO_3^- (Chen et al. 2010; Cui et al. 2013). In our study, lower soil NO_3^- intensity in the nitrapyrin-amended treatments, with the exception of the NB3I treatment, indicated that nitrapyrin effectively contributed to the inhibition of conversion of NH_4^+ to NO_2^- and NO_3^-. Fu et al. (2018) and Shi et al. (2016) have also confirmed negative responses of ammonia-oxidizing bacteria activity and nitrification to nitrification inhibitors in arable soils.

Ding et al. (2011) and Zhou et al. (2016) reported a 31–39% reduction of N_2O emissions under DCD amendment of maize, compared with the application of N fertilizer alone. However, in our study, there was no reduction in N_2O emissions following nitrapyrin amendment, supporting observations by Parkin and Hatfield (2010) in corn field, and was likely due to the reduction in denitrification activity in the experimental soil (Wan et al. 2009; Cai et al. 2013). We compiled data from the literature on N_2O emissions under the application of N fertilizer with (N_2O_{Ni}) and without (N_2O_N) nitrification inhibitors in the local region (North China Plain) for comparison with our data (Table 5) and analyzed the relationship between the response ratio of N_2O emissions to nitrification inhibitor ($RR_{Ni} = (N_2O_N - N_2O_{Ni}) / N_2O_N$) and soil WFPS. We found that efficacy of inhibitors on N_2O emissions increased with soil WFPS (Fig. 5). Xue et al. (2012) found that DMPP (3,4-dimethylpyrazole phosphate) more efficiently reduced oxidation of NH_4^+ to NO_3^- at 40% water holding capacity (WHC) than at 60 and 80% WHC in an incubation experiment on brown soil, probably as a results of slower DMPP degradation in the drier conditions. In contrast, Balaine et al. (2015) observed the higher efficacy and longer half-time of DCD at wetter soil when targeted at urine-induced N_2O emissions. The low efficacy of nitrapyrin can be explained by (1) biological process: microbial or plant uptake of the nitrification inhibitor (Marsden et al. 2016; Pal et al. 2016) and microbial degradation in warm conditions (Weiske et al. 2001); and (2) physicochemical process: solubility/leaching with rainfall or irrigation and sorption onto soil components (Shi et al. 2016; Marsden et al. 2016). We suggest that the small inhibitive effects of nitripyrin on N_2O emission we found in this study were primarily driven by the low levels of soil moisture that reduced the denitrification process and N_2O production and masked the potential effect of inhibitors. Further study is required to evaluate the effect of inhibitors on the relative contributions of nitrification and denitrification to N_2O emissions at different levels of the soil moisture.

Combined effects of biochar and nitrapyrin on N_2O and NO emissions

There are studies with conflicting results on the influence of biochar on N_2O emissions, showing that inhibition (van Zwieten et al. 2010a; Zhang et al. 2012), stimulation (Saarnio et al. 2013), and no effect (Karhu et al. 2011) have been reported. Here, we found no effects of biochar on soil N_2O or NO emissions during the maize growth season, unlike Niu et al. (2017) who reported significant reductions in emissions of N_2O, and Nelissen et al. (2014) and Obia et al. (2015) who recorded reductions in NO emission under aerobic conditions and anaerobic conditions. It is known that biochar inhibits NO emissions due to an increase in N immobilization and non-electrostatic sorption of NH_4^+ and stimulation of ammonia volatilization (Nelissen et al. 2014).

Table 5 Summary of a literature review of N_2O emissions from N fertilized croplands, with or without the addition of nitrification inhibitors, in the North China Plain

Site	Year	SOC (g C kg^{-1})	WFPS (%)	Crop	N fertilizer		Nitrification inhibitor		N_2O emission (kg N_2O-N ha^{-1})	RR_{Ni}	Reference
					Type	Application rate (kg N ha^{-1})	Type	Application rate (% N)			
Shanxi	2009	16.3	54.70	M	Urea	180	–	–	1.25		Zhu et al. (2016)
	2009	16.3	54.70	M	Urea	180	DCD	10	1.04	0.17	
	2010	16.3	56.83	M	Urea	180	–	–	1.21		
	2010	16.3	56.83	M	Urea	180	DCD	10	1.00	0.17	
	2011	16.3	69.99	M	Urea	180	–	–	1.76		
	2011	16.3	69.99	M	Urea	180	DCD	10	0.66	0.61	
	2012	16.3	62.31	M	Urea	180	–	–	1.77		
	2012	16.3	62.31	M	Urea	180	DCD	10	1.24	0.30	
Shandong	2012/2013	25.7	54.90	W/M	Urea	300	–	–	5.01		Zhao et al. (2016)
	2012/2013	25.7	54.90	W/M	Urea	300	DMPP	2	2.59	0.48	
Hebei	2012	7.71	65.00	M	Compound	176	–	–	5.80		Zhou et al. (2016)
	2012	7.71	65.00	M	Compound	176	DCD	10	4.00	0.31	
Henan	2009	12.0	58.00	M	Urea	200	–	–	0.77		Ding et al. (2011)
	2009	12.0	58.00	M	Urea	200	DCD	10	0.47	0.39	
Henan	2015	7.40	44.61	M	Urea	200	–	–	1.00		This study
	2015	7.40	46.14	M	Urea	200	Nitrapyrin	0.26	0.87	0.13	
	2015	7.40	44.74	M	Urea	200	–	–	0.84		
	2015	7.40	47.31	M	Urea	200	Nitrapyrin	0.26	0.80	0.05	
	2015	7.40	45.69	M	Urea	200	–	–	0.85		
	2015	7.40	47.18	M	Urea	200	Nitrapyrin	0.26	0.84	0.02	
	2015	7.40	44.68	M	Urea	200	–	–	0.81		
	2015	7.40	45.45	M	Urea	200	Nitrapyrin	0.26	0.75	0.07	

$RR_{Ni} = (N_2O_N - N_2O_{Ni}) / N_2O_N$, where N_2O_{Ni} and N_2O_N are N_2O emissions in the N fertilizer + inhibitor and N fertilizer-alone treatments, respectively

SOC soil organic carbon, *WFPS* soil water-filled pore space, *M* maize, *W* wheat, *DCD* dicyandiamide, *DMPP* 3,4-dimethylpyrazole phosphate

The increased soil pH caused by biochar may alter the product stoichiometry of the denitrification process (reducing N_2O/N_2 ratio) by increasing the relative abundance of *nosZ* genes that encode for N_2O reductase in acid soils (Harter et al. 2014; Obia et al. 2015). The soil acidification in our study (Table 6) due to the excessive use of fertilizer may lead to the higher N_2O/N_2 ratios during denitrification (Qu et al. 2014). Wang et al. (2018) demonstrated that the N_2O emission increased by 21–119% under one unit decreasing of soil pH, based on a global meta-analysis of 1104 field experiments. As discussed above, N_2O emission was mainly derived from nitrification in our study; thus, stimulation effect of soil acidification on N_2O emission may be low. Baggs et al. (2010) reported that acidification of fertilized soil with H_2SO_4 lowered soil N_2O emission, while liming of the acid soil with $CaCO_3$ increased N_2O emission with nitrification. The lower pH reduced the NH_3 availability during nitrification (Blum et al. 2018). In this study, addition of biochar did not affect soil pH (Table 6), suggesting that there was absence of liming effect of biochar on N_2O emission in the test alkaline soil, which was consistent with the finding of Liu et al. (2014). In addition, other mechanisms of biochar-mediated reductions in N_2O emissions have been suggested: Firstly, the adsorption of inorganic N through abiotic or biotic processes by biochar decreases the availability of substrates for nitrifiers and denitrifiers (van Zwieten et al. 2010b; Kammann et al. 2012); secondly, reduction in the soil bulk density by biochar increases soil aeration and decreases soil WFPS, which in turn lowers the denitrification potential and N_2O emissions (van Zwieten et al. 2010b; Harter et al. 2014). We found no significant difference in inorganic N and DOC concentrations between plots treated with urea alone and biochar, but soil bulk

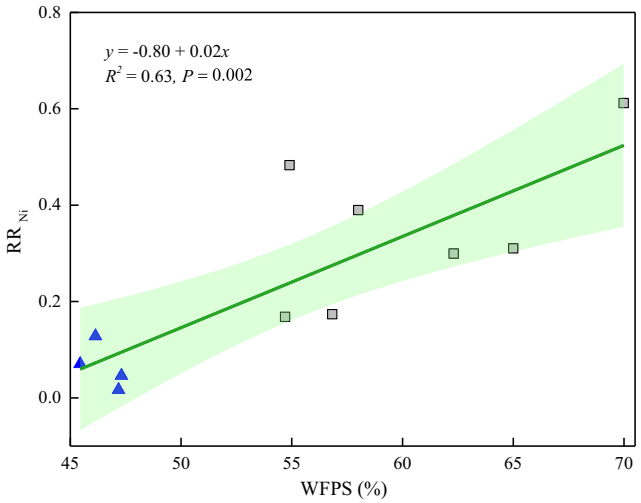

Fig. 5 Correlation between the response ratio of N_2O emissions to nitrification inhibitor (RR_{Ni}) and soil WFPS during the maize growth season. Squares and triangles represent the results from previous studies and the present study, respectively, as detailed in Table 6. Shaded sections indicate the 95% confidence intervals of the regression models

density reduced by biochar (Table 6). Thus, we suggest that the lack of effect of biochar on N_2O emissions in this study may have been a result of a reduced denitrification process and N_2O production in the low moisture experimental soils. A decrease in N immobilization and associated reduced effect on NO emission suppression caused by biochar in our study may have stemmed from the age of the biochar (degradation) and/or saturation with N.

Fuertes-Mendizábal et al. (2017) found that combined amendment with biochar and DMPP diminished the inhibition effect of the nitrification inhibitor on N_2O emission at 40 and 80% WFPS, probably due to the adsorption of DMPP by the biochar (Shi et al. 2015). In comparison to DMPP, we speculate that the adsorption of the nitrapyrin might also occur after application of biochar. In the present study, no significant interactions of nitrapyrin and biochar on N_2O and NO emissions were found mainly due to the small effect of the biochar. Continuous measurement in the deployed plots is required to evaluate the long-term effect of biochar on N_2O and NO emission.

Table 6 Effect of biochar and nitrapyrin on soil properties after maize harvest

Treatment	Soil bulk density (g cm^{-3})	Soil pH	SOC (g C kg^{-1})
Control	1.40 ± 0.01	8.38 ± 0.01a	7.06 ± 0.12d
N	1.38 ± 0.01	8.20 ± 0.03b	7.07 ± 0.17cd
NB3	1.35 ± 0.03	8.19 ± 0.08b	8.64 ± 0.19bc
NB6	1.30 ± 0.03	8.14 ± 0.02b	8.94 ± 0.23b
NB12	1.31 ± 0.02	8.16 ± 0.04b	10.37 ± 0.43a
NI	1.38 ± 0.03	8.19 ± 0.07b	7.03 ± 0.09d
NB3I	1.35 ± 0.05	8.19 ± 0.04b	7.97 ± 0.04bcd
NB6I	1.35 ± 0.02	8.11 ± 0.05b	8.75 ± 0.19bc
NB12I	1.34 ± 0.06	8.16 ± 0.02b	10.93 ± 0.81a

Means ± SE ($n = 3$). Values followed by different letters within the same column denote differences between treatments at $P < 0.05$

Impact of biochar and nitripyrin on grain yield and yield-scaled N_2O emissions

Whereas we found that grain yield and N uptake increased in N fertilized treatments but were unaffected by the addition of biochar, Zhang et al. (2012) observed that biochar amendment at 20–40 t ha^{-1} increased maize yield by 12–18%. However, biochar has also been found to decrease crop yield (Rajkovich et al. 2012) or have no effect on maize growth (Nguyen et al. 2016). The N immobilization has been suggested as an important mechanism for decreasing availability of N, since biochar tends to have high C/N ratios (> 25) (van Zwieten et al. 2010b), but this may not have been applied in this study because mean levels of soil NO3I and IONI in the NB3 and NB12 treatments were shown to be high. It is likely that the high application rate of N fertilizer masked the negative effects of N immobilization in the subsequent year (Liu et al. 2014). Major et al. (2010) found a 3-year increase in maize yield following a single application of 8–20 t ha^{-1} of biochar to an infertile soil, and Yamato et al. (2006) similarly found an increase in maize yield following biochar amendment of an infertile soil, but not in fertile soils. Thus, we postulate that, under biochar amendment, an increase in crop yields may be expected in infertile, nutrient-poor, or acid soils (Major et al. 2010; Jeffery et al. 2011; Liu et al. 2013), but not in fertile or alkaline soil (Tammeorg et al. 2014; Hagemann et al. 2017).

We found that crop grain yield and N uptake did not increase in the NI treatment, compared with the N treatment. Chatterjee et al. (2016) found a similar phenomenon, where the combined addition of nitrapyrin with urea had no effect on corn yield or NUE; however, nitrapyrin combined with urea had a greater effect on yield in a vegetable system and paddy soil by increasing NUE (Ma et al. 2013; Li et al. 2014). We found that aboveground biomass and N uptake were lower in the NB6I and NB12I treatments than in the NI treatment (Table 1), and since the application of nitrification inhibitors may cause retention of NH_4^+ and induce higher NH_3 emissions in alkaline soils (Kim et al. 2012), the supply of N at the rapid crop growth stage may have been reduced (Ding et al. 2015).

In our study, yield-scaled N_2O emissions ranged from 0.031 to 0.085 g N_2O-N kg^{-1} grain, which was within the range reported by Venterea et al. (2011), but lower than that found in the study of Ma et al. (2013). The lowest yield-scaled and lowest cumulative N_2O emissions were recorded in the

NB12I treatment, suggesting that this treatment may offer the optimal mitigation of N_2O emissions.

Conclusions

We found that irrigation prior to plowing reduced the levels of soil moisture following application of basal fertilizer, compared with irrigation following fertilizer application, and this approach mitigated more effectively N_2O emissions than NO emissions. Although biochar decreased soil bulk density, there was no effect on both N_2O and NO emissions, whereas application of the nitrification inhibitor mitigated NO emissions, but not N_2O emissions. We suggest that the potential effects of amendment with biochar in the previous year and addition of nitrapyrin on mitigating N_2O emissions were probably offset by the low levels of moisture in the experimental soils that suppressed soil denitrification. Both biochar and nitrapyrin did not show any significant effect on maize yields and the N uptake in plant. Overall, we suggest that the NB12I treatment could be used as a "win-win" strategy with more agricultural income for farmers and less N_2O emission for the environment in the North China Plain.

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