

Effects of fertilizer and biochar applications on the relationship among soil moisture, temperature, and N₂O emissions in farmland (#55062)

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Effects of fertilizer and biochar applications on the relationship among soil moisture, temperature, and N₂O emissions in farmland

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Background. Soil N₂O emissions cause nonpoint-source pollution in farmland. The rates of soil biochemical reactions change depending on the moisture and temperature and thus affect the N₂O emissions. However, it remains unclear whether soil improvement measures change the response of N₂O emissions to soil moisture. **Methods.** To quantify the driving factors of N₂O emissions from farmland and explore the effects of different soil improvement measures on the N₂O emissions, three treatments (fertilization, fertilization + biochar, control) were implemented in the field experiments during 2019-2020. **Results.** The results of this study show that N₂O emissions strongly depend on the deep soil moisture and temperature (20–80 cm), in addition to the surface soil moisture and temperature (0–20 cm). However, changes in the soil environment due to fertilization and biochar application significantly affect the N₂O emissions despite the strong correlation between the soil moisture and N₂O emissions. Therefore, we established a model of the correlation between the soil moisture and N₂O emissions based on theoretical analysis. The results show that the N₂O emissions exponentially increase with increasing soil moisture regardless of fertilization or biochar application. Furthermore, the N₂O emissions initially increase and then decrease with nitrification and denitrification, respectively. Urea significantly increases the N₂O emissions in farmland. The biochar application significantly mitigates the N₂O emissions induced by urea based on the sensitivity coefficient (SC_B of 1.02 and 14.74; SC_U of 19.18 and 20.83), even if the soil moisture in the topsoil (0–20 cm) increases.

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Abstract

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Keywords: Biochar; N₂O emissions; Soil moisture; Soil temperature; Fertilization; sensitivity coefficient; multivariate nonlinear fitting; Exponential fitting.

Introduction

Soil N₂O emissions, representing a significant N loss, are inevitable products of chemical fertilizer application (Zou et al. 2005). Based on statistics, greenhouse gas emissions from

agricultural sources account for 11% of the global greenhouse gas emissions and thus exceed the 2020 emission target (Zhao et al. 2016). Soil N₂O emissions do not only depend on the soil characteristics (e.g., soil structure, available carbon sources, pH, and microbial activity) but also on the environmental conditions (e.g., temperature and precipitation). Nitrifying and denitrifying bacteria, affecting N₂O emissions by nitrification and denitrification, are aerobic and anaerobic soil microorganisms, respectively (Case et al. 2012; Gul et al. 2015). Soil aeration is restricted by soil moisture; therefore, when the soil moisture content changes, the soil microbial activity (~~nitrifying bacteria, denitrifying bacteria~~) and N₂O emissions also change. Denitrifying bacteria mainly produce N₂O emissions from farmland during precipitation. Under proper soil aeration, N₂O emissions are primarily produced by nitrifying bacteria (Shu et al. 2017; Wu et al. 2013). The soil temperature, another critical factor, directly influences the activities of the nitrifying and denitrifying microorganisms and urea hydrolysis (Alvarez et al. 2018). Soil N₂O emissions rapidly increase with increasing soil temperature (Sébastien et al. 2017).

At present, researchers have established the relationships among the soil temperature, moisture, and N₂O emissions to quantify the N₂O emissions on the farmland scale. The temperature response function (Q₁₀) of N₂O is greater than that of N₂ under anaerobic conditions (Phillips et al. 2015). The soil temperature and water-filled pore space (WFPS) regulate the soil N₂O emissions. The soil N₂O emissions and mean water content of the surface soil during the dry period are positively correlated (Saarnio et al. 2013). Weerden et al. (Weerden et al. 2012) also reported a pronounced linear correlation between the N₂O emissions and WFPS. A similar conclusion was drawn by (Wu et al. 2013). The relationship between the N₂O emissions and soil moisture has been described using an exponential first-order kinetics model in many studies (Prado et al. 2006; Weitz et al. 2001; Xue et al. 2012). However, it is difficult to clarify the response of the N₂O emissions to the increased WFPS using the above-mentioned models (linear correlation or exponential model). The N₂O emissions increase and reach a plateau when the WFPS is ~60%–70%. At the same time, the denitrification was maximal. When WFPS was >75%, a more anaerobic environment, the N₂O emissions decrease (Prado et al. 2006). This empirical model cannot predict the N₂O emissions at soil moisture concentration above 75% because the rates of the biochemical reactions (e.g., nitrification, denitrification, immobilization, and mineralization) are related to the variation in the soil moisture. Meanwhile, most studies ~~did~~ ~~not~~ consider the effect of the substrate on this process. In other words, it remains unclear if the response of the soil N₂O emissions to moisture and temperature would change with a change of the soil substrate characteristics such as the soil carbon and nitrogen concentrations. Thus, we still need to characterize the effect of exogenous organic matter improvement on the response (between N₂O emissions, soil moisture, and temperature) by establishing model.

The application of nitrogen fertilizer to the soil notably promotes N₂O emissions because it increases the substrate volume available for nitrification and denitrification. Exogenous carbon provides energy for microbial proliferation and enzyme secretion (Alfred et al. 2018; Henrique et al. 2015). The mixing of exogenous carbon with the soil significantly increases the soil C/N ratio and promotes the immobilization of inorganic nitrogen (Baggs et al. 2000). Studies have shown

that exogenous carbon improvement indeed reduces soil N₂O emissions effectively (Bruun et al. 2014; Case et al. 2012; Kettunen et al. 2006; Ruser et al. 2006; Singh et al. 2010). However, it remains unclear whether fertilization or the application of exogenous carbon changes the response of N₂O emissions to soil moisture. Therefore, it is important to study the effect of soil improvement (fertilization or addition of exogenous carbon) on the soil N₂O emission process to prevent farmland gas pollution and facilitate sustainable agricultural development.

Biochar, a form of exogenous carbon, is produced by the pyrolysis of straw and branches. The amendment with biochar remarkably affects the physical soil properties (Nanda et al. 2016) as well as biochemical reactions (Gul et al. 2015; Henrique et al. 2015) and thus affects C and N cycles in soil. Biochar amendment of soil has many physical effects; for example, it improves the water holding capacity of the soil (Major et al. 2012), nitrate retention (Ghulam et al. 2017; Zhang et al. 2010), and soil aeration (Alfred et al. 2018). Biochar amendment significantly changes the nitrification and denitrification processes. Because the improvement of the water holding capacity of the soil due to biochar application is the primary factor inhibiting N₂O emissions (Basso et al. 2013). Thus, biochar application is a C resource and it is important to explore the effect of exogenous carbon on the N₂O emissions.

The aim of this work was to explore the effects of different soil improvement measures on the N₂O emissions. The central hypothesis was that the response of N₂O to soil moisture and temperature is independent of fertilization or the application of biochar. Thus, we conducted field experiments for three months to 1) explore the response of soil N₂O emissions to soil moisture and temperature under different conditions (no fertilization, fertilization, fertilization + biochar and 2) investigate the effects of fertilization and application of biochar on the relationship among soil moisture, temperature, and N₂O emissions.

Materials & Methods

Experimental site

The experiments were conducted between 2019-2020 at the experimental station of the China Agricultural University, China (latitude: 39°42'07.8"N, longitude: 116°41'48.0"E, altitude: 24 m) in loam soil (9.6% clay, 52.6% silt, and 37.8% sand). The mean temperature was 26.6 °C and the precipitation was 358 mm (April to September) in 2019. The mean temperature was 28.4 °C and the precipitation was 377 mm (July to September) in 2020. The experimental soil had a soil bulk density of 1.38 g cm⁻³ and the field capacity of the 0–20 cm soil layer was 22.87 % according to the method from Dane and Jacob (Dane & Jacob 2002).

Biochar amendments

Biochar was produced by pyrolysis (450 °C) of maize straw and used for the field experiment. The biochar had a pH of 8.2, total C content of 657 g kg⁻¹, total N content of 9 g kg⁻¹, available K of 16 g kg⁻¹, available P of 0.8 g kg⁻¹, and density of 0.297 g cm⁻³. The biochar was evenly applied to the surface soil (30 t ha⁻¹; top 20 cm of the soil) in April 2019 before sowing

maize. The initial soil had a pH of 8.14, SOC of 29.71 g kg⁻¹, SON of 2.3, NH₄⁺-N of 6.48 mg kg⁻¹, NO₃⁻-N of 28.00 mg kg⁻¹, available K of 38.14 g kg⁻¹, and available P of 1.70 g kg⁻¹.

Experimental Design

The maize cultivar Zhengdan 958 is widely used in China. Maize was planted on April 10, 2019 and June 15, 2020, with a 0.5 m line spacing and 0.3 m between plants and harvested on September 5 in 2019 and September 25 in 2020. A 1 m gap was left between adjacent plots. The experiment was carried out in three replicates; the plot size was 30 m × 6.5 m. This experiment included the following treatments: (1) RU: fertilization with urea, irrigation with reclaimed water; (2) BRU: soil amendment with 30 t ha⁻¹ biochar, fertilization with urea, and irrigation with reclaimed water; and (3) CK: irrigation with reclaimed water.

The N fertilizer (urea; 300 kg N ha⁻¹) was applied as follows: 40% before sowing, 30% during the silking stage, and 30% during the filling stage. The P (calcium superphosphate; 40 kg P ha⁻¹) and K (potassium sulfate; 80 kg K ha⁻¹) fertilizers were applied before sowing. The total irrigation amount for each treatment was 230 mm in 2019 and 250 mm in 2020, respectively.

The soil temperature and water content (0–80 cm) were measured with an ET-100 (Insentek, China). The WFPS was calculated with the following equation:

$$WFPS = \left(\frac{\theta_m \cdot \rho_0}{\rho_{H_2O} \cdot \rho_s} \right) \cdot 100\%, \quad (1)$$

where θ_m is the gravimetric water content (mg mg⁻¹), ρ_0 is the bulk soil density (mg m⁻³), ρ_{H_2O} is the density of water (mg m⁻³), and ρ_s is soil particle density (mg m⁻³).

Gas collection and analysis

The N₂O fluxes were measured at every plot using a static closed chamber method (Qi et al. 2015). The sampling chamber consisted of two parts: a soil ring without top and bottom (50 cm in diameter and 30 cm high) and a removable cover (50 cm in diameter and 50 cm high). The soil ring was directly inserted into the soil approximately 25 cm below the soil surface, leaving 5 cm to the soil surface, and the removable cover was placed on top during the sampling and was removed afterward. Two fans with diameters of 10 cm were installed on the sidewall of each cover to create turbulent airflow when the chamber was closed. Three gas samples were obtained during each treatment and sampling period, that is, three replicates of one treatment. The soil temperature from 9:00 to 11:00 a.m. was close to the daily mean soil temperature. Thus, we took gas samples during this period. The air temperature inside the static closed chamber was also measured. Gas samples (50 ml each) were collected in four time intervals (0, 10, 20, and 30 min) using 50 ml plastic syringes. The N₂O fluxes were measured after rainfall, fertilization, or every two days. The N₂O was analyzed using a gas chromatograph (GC 7890 A, Agilent, USA) and electron capture detector (ECD) within 48 h. The N₂O daily emissions were calculated with the following equation:

$$F = \rho \times V/A \times (dc/dt) \times 273/(273 + T), \quad (2)$$

where F is the N_2O flux ($g\ m^{-2}\ h^{-1}$), ρ is the density of the gas in a standardized state ($g\ m^{-3}$), V is the volume of the chamber (m^3), A is the cross-sectional area of the chamber (m^2), dc/dt is the rate of gas accumulation ($\mu g\ kg^{-1}\ h^{-1}$), and T is the chamber temperature ($^{\circ}C$).

The cumulative N_2O emissions ($kg\ ha^{-1}$) were calculated by using the linear interpolation method.

Chemical analyses

The pH values of the biochar and soil were determined with a pH electrode (Thermo Orion, 420A plus). The biochar/deionized water and soil/deionized water ratios were 1:30 w/w and 1:10 w/w, respectively, after being stirred for 1.5 min and equilibrated for 1 h. The C and N concentrations of the biochar and soil were determined using an elemental analyzer (Flash 2000, Thermo Fisher, USA). The available P content was determined with an ultraviolet–visible spectrophotometer (TU-1901 UV–Vis, Beijing Puxi Instrument Company, China). The available K content was measured with a flame photometer (FAAS; Zennit 700P, Analytik Jena AG, Germany). The NH_4^+-N and NO_3^--N concentrations were measured using segmented flow analysis (SFA; Futura, Alliance, France).

Model

N_2O emissions are the result of soil biochemical reactions, and these reactions are slow. N_2O emission at a particular time may arise from the cumulative effects of water and temperature in the previous period. Therefore, the lag effects should be considered. We assume that the N_2O emission during sampling is caused by the influence of soil moisture and temperature in the previous 24 h. If sampling occurs at 9:00 am on July 23, the N_2O flux is affected by the soil moisture (or temperature) between 10:00 am on July 22 and 9:00 am on July 23. ET-100 can monitor a series of soil moistures and temperatures hourly. Therefore, we established a function between N_2O flux and the average of soil moisture (or temperature) in the past 24 h. This function was created to calculate the daily soil moisture and temperature at 9:00 as the node.

A) Relationship among the soil temperature, water content, and N_2O emissions

Principal component analysis is a statistical method. Based on orthogonal transformation, it transformed a group of correlated variables into a group of linearly unrelated variables. The transformed variables are called principal components (Stacklies et al. 2007). Through principal component analysis, we have synthesized numerous indexes and eliminated information overlapping of the sample (Granato et al. 2018; He et al. 2018; Imaizumi & Kato 2018). The expression of the principal component was as follows:

$$W1 = a \cdot W_{10}^* + b \cdot W_{20}^* + c \cdot W_{40}^* \quad (3)$$

$$T1 = d \cdot T_{10}^* + e \cdot T_{20}^* + f \cdot T_{40}^* \quad (4)$$

where W1 or T1 are the principal components obtained by extracting the soil water content or temperature from the 10, 20, and 40 cm soil layers, respectively; W_{10}^* , W_{20}^* , W_{40}^* , T_{10}^* , T_{20}^* , and T_{40}^* are the standardized soil water contents and temperatures corresponding to the 10, 20, and 40 cm soil layers, respectively; and a, b, c, d, e, and f are the coefficients of the standardized values, respectively.

Because the principal component 1 (PC1) accounts for more than 70% of the variation, only PC1 of the soil moisture content (or temperature) was used for multivariate nonlinear fitting. Table 1 shows that the PC1 covers the soil moisture content and temperature information of the 10, 20, and 40 cm soil layers. The moisture content and temperature of the 20 cm soil layer contribute the most to the PC1.

The parameter F_N^* was obtained by standardizing the daily N_2O emissions and fitting with W1 and T1:

$$F_N^*(W1, T1) = z_0 + k_1 \cdot W1 + k_2 \cdot T1 + k_3 \cdot W1^2 + k_4 \cdot T1^2 + k_5 \cdot W1 \cdot T1, \quad (5)$$

where k_1 (k_2 , k_3 , k_4 , k_5) is the coefficient and z_0 is the constant.

Table 2 shows the value of coefficient in Eq. (5).

Equations (3) and (4) were substituted into Eq. (5) to obtain:

$$F^*(W_{10}^*, W_{20}^*, W_{40}^*, T_{10}^*, T_{20}^*, T_{40}^*) = z_0 + k_1 \cdot a \cdot W_{10}^* + k_1 \cdot b \cdot W_{20}^* + k_1 \cdot c \cdot W_{40}^* + k_2 \cdot d \cdot T_{10}^* + k_2 \cdot e \cdot T_{20}^* + k_2 \cdot f \cdot T_{40}^* + k_3 \cdot (a \cdot W_{10}^* + b \cdot W_{20}^* + c \cdot W_{40}^*)^2 + k_4 \cdot (d \cdot T_{10}^* + e \cdot T_{20}^* + f \cdot T_{40}^*)^2 + k_5 \cdot (a \cdot W_{10}^* + b \cdot W_{20}^* + c \cdot W_{40}^*) \cdot (d \cdot T_{10}^* + e \cdot T_{20}^* + f \cdot T_{40}^*) \quad (6)$$

B) Response of the N_2O emissions to WFPS

We assumed that the N_2O emissions exponentially increase with increasing WFPS and that the emission rate of N_2O initially increases and then decreases. Thus, dDE/dW initially is positive and then negative. The model of the N_2O emissions can be obtained as follows:

$$\frac{1}{DE} \frac{dDE}{dW} = B - AW, \quad (7)$$

where DE represents the daily emissions of N_2O ($kg \cdot hm^{-2}$), W is the WFPS, and A and B are constants.

To illuminate the mitigation of the N_2O emissions due to biochar amendment, we adopted the sensitivity coefficient (SC) to express the effect of the change in the soil water content on the N_2O emissions (Tan et al. 2017). The smaller SC is, the smaller is the response of the N_2O emissions to the change in the soil water content. The SC can be calculated as:

$$SC = \frac{\Sigma(\Delta DE/DE_0)}{\Sigma(\Delta W/W_0)}, \quad (8)$$

where ΔDE is the variation in the N_2O emissions between the BRU/RU and CK treatments, ΔW is the variation in the WFPS between the BRU/RU and CK treatments, and DE_0 and W_0 , represent the N_2O emissions and WFPS of treatment CK, respectively. Equation (9), obtained by integrating Eq. (7), is a numerical model describing the increase in the N_2O emissions for different WFPS values under irrigation.

$$DE = e^{-aW^2 + bW + c}, \quad (9)$$

where a is $A/2$, b is B , and c is an integral constant.

Statistical analysis

The data were analyzed with SPSS20.0 software. Variance analysis (ANOVA) was carried out by using the General Linear Model Univariate procedure. The analysis of significant differences ($p < 0.05$) between treatments was carried out using Tukey's range test. We also prepared figures and fitted the models using OriginPro 2019.

Results

Changes in the soil water content and temperature

The experimental area was irrigated with 60 mm reclaimed water after sowing. The next irrigation was conducted at the seeding stage. ~~We observed~~ a drastic fluctuation of the soil water content above a depth of 20 cm during each treatment. Such a fluctuation did not occur in the 60 and 80 cm soil layers. The average soil water content at 10 cm was ~1.31%, -0.04%, and 3.18% higher than that at 20 cm after the RU, BRU, and CK treatments, respectively (Fig. 1). The average soil water content at 20 cm was ~11.56%, 9.94%, and 17.89% higher than that at 40 cm after the RU, BRU, and CK treatments during 2019-2020, respectively. The average soil water content in the 20 cm soil layer of the BRU treatment was ~7.10% and 8.26% higher than that of the RU and CK treatments in 2019, respectively. ~~And~~ The average soil water content (20 cm) in BRU was ~15.69 % and 22.25 % higher than in RU and CK treatments in 2020. Thus, we can conclude that the soil amendment with biochar significantly promotes the water holding capacity.

Figure 1: Variation in the soil water content above a depth of 80 cm depth in the maize growth stage; (A), (B), and (C) show the soil water content of RU, BRU, and CK in 2019; (D), (E), and (F) show the soil water content of RU, BRU, and CK in 2020.

The variation in the soil temperature in the maize growth stage for each treatment is shown in Fig. 2. The temperature of the surface soil is higher than that of the deep soil. Although the temperature difference between each treatment above was not pronounced in 2020, the accumulative temperature difference between BRU and RU, BRU and CK were 463.24 and 455.46°C above 10 cm in 2019, respectively (Fig. 2). The accumulative temperature difference between BRU and RU, BRU and CK were 539.93 and 484.22°C in 20 cm, respectively. This can be explained by the remarkable heat-absorption of biochar, which increases the surface soil temperature.

Figure 2: Variation in the soil temperature above a depth of 80 cm in the maize growth stage; (A), (B), and (C) show the soil water content of RU, BRU, and CK in 2019; (D), (E), and (F) show the soil water content of RU, BRU, and CK in 2020.

Soil N₂O emissions

Chemical fertilizer application significantly promotes the soil N₂O emissions (Fig. 3). The difference in the N₂O emissions between these treatments is not pronounced on June 13 and July 3 in 2019. However, the emission flux of N₂O is significantly higher for RU than for the BRU and CK treatments after fertilization. The cumulative N₂O emissions after the RU treatment are 3.61 kg ha⁻¹ compared with 1.72 and 1.59 kg ha⁻¹ for the BRU and CK treatments in 2019, respectively. The increment of N₂O emissions for RU treatment significantly were pronounced compared with CK treatment in 2020. And biochar application significantly alleviated N₂O emissions for the two year. The cumulative N₂O emissions were 8.96, 5.94, and 1.58 kg ha⁻¹ for RU, and BRU, and CK treatments in 2020, respectively.

Figure 3: N₂O emission flux in the maize growth stage. (A) and (B) show the N₂O emissions in 2019 and 2020, respectively.

Relationship among the soil water content, temperature, and N₂O emissions

The soil N₂O emissions significantly correlate with the soil water content at a depth above 40 cm in all treatments (Table 1). The correlation between the soil N₂O emissions and soil temperature of RU and BRU at depths above 40 cm is also pronounced. Both the soil water content and temperature affect the soil N₂O emissions. Thus, it is imperative to analyze the coupled effect of the soil water content and temperature on the N₂O emissions.

Table 1: Correlation among the soil water content, temperature, and N₂O emissions.

Based on Table 1, the soil water content and temperature at a depth above 80 cm affect the N₂O emissions. The correlations between the soil water content and temperature and N₂O emissions is pronounced at depths of 0–40 cm, while it is weak in the 60–80 cm soil layer. To simplify the calculation, we performed principal components analysis on the moisture content

and temperature in the 10, 20, and 40 cm soil layers. Table 2 and Table 3 show the value of coefficient in Eq. (3)-(5), respectively.

Table 2: Coefficient of PC1.

Table 3: Coefficient of multiple nonlinear regression.

Compared with a single soil layer (10, 20, or 40 cm), the soil N₂O emissions can be more accurately predicted by combining the moisture contents and temperatures of the three soil layers [Eq. (6)]. The water contents and temperatures of the three soil layers affect the N₂O emissions to different degrees. Therefore, we believe that the soil N₂O emissions are due to the combined effect of the moisture content and temperature of the 0–40 cm soil layer. It is not adequate to fit the three treatments with one regression equation (R^2 , 0.51 in 2019). When multivariate nonlinear fitting was applied to the three treatments, an R^2 value above 0.60 was obtained (Fig. 4). The results show that the N₂O emissions of the RU treatment are significantly higher than those of the BRU and CK treatments (Fig. 3), indicating that the change of the soil environment (two or more variables) significantly affects the response of the soil N₂O emissions to the moisture content and temperature.

Figure 4: N₂O emission observations and MNF-DR analysis during the growing period of maize; (A), (B), (C), and (D) show the MNF-DR analysis for RU + BRU + CK, RU, BRU, and CK treatment in 2019; (E), (F), (G), and (H) show the MNF-DR analysis for RU + BRU + CK, RU, BRU, and CK treatment in 2020.

When the soil environment was changed due to fertilization and biochar amendment, the accuracy of multivariate nonlinear fitting significantly decreased based on dimensionality reduction analysis (MNF-DR). This is due to the changes in soil biochemical reaction rate caused by fertilization or biochar amendment (Bruun et al. 2014; Saarnio et al. 2013) and changes in the response of the N₂O emissions to the moisture content and temperature. After the biochar application, the surface soil moisture content and temperature were higher than those of the RU and CK treatments, but the N₂O emissions were significantly lower than those of the RU treatment (Figs 1–3). Therefore, the N₂O emissions differently respond to changes in the water content and temperature under different conditions (fertilization, biochar amendment). Because the same volume was used for fertilization and biochar application in this experiment, studies should be carried out in the future to determine if the effects of the soil moisture and temperature on the N₂O emissions change depending on the amount of applied fertilizer or biochar.

The soil moisture content and temperature data for the 0–40 cm soil layer were synthesized using MNF-DR analysis. The predictions are more stable than those based on the surface soil moisture content and temperature only. However, with MNF-DR analysis, only the N₂O emissions at the farmland scale can be predicted from the perspective of statistics. The N₂O emission trends depending on changes in the water content or temperature at the microscale

cannot be explained. Therefore, a N_2O emission model based on theoretical analysis should be proposed.

Studies have also suggested that the soil water content (or temperature) at 5 cm can be identified as the single trigger for N_2O emission (Lognoul et al. 2019). We acknowledge that most N_2O emissions originate from biochemical reactions in the topsoil, but some N_2O emissions still arise from deep soil. Deep soils also produce N_2O via nitrification and denitrification. The N_2O in the deep soil will diffuse to the surface, and the rate of diffusion depends on the soil moisture content and the N_2O concentration gradient (Shcherbak & Robertson 2019). Furthermore, storage fluxes occurred in the deep soil. Lognoul et al. (2019) assumed that storage fluxes were negligible. However, the soil moisture content and temperature in the 0-40 cm soil layer were significantly correlated with N_2O emissions; therefore, it is not accurate to identify physical factors from topsoil as the single trigger for N_2O emissions.

The correlation between the WFPS and N_2O emissions

The emission rate of N_2O increases with increasing soil moisture content based on this field experiment, while the increase in the N_2O emissions slows down after the WFPS exceeds 80%. Previous studies showed that the N_2O emissions increase until the WFPS reaches ~75% (Lan et al. 2013). However, the N_2O emissions rate decreases when the soil water content exceeds a WFPS of 75% (Prado et al. 2006) because the anaerobic environment accelerates the reduction of N_2O to N_2 in the soil (Wu et al. 2013). The soil represents a N_2O sink when the WFPS is below 25% (Flechard et al. 2007; Goldberg & Gebauer 2008; Wu et al. 2013).

Thus, we assume that the rate of N_2O emissions varies with the WFPS. The rate of N_2O emissions is low at a low WFPS. The N_2O emission rate then sharply increases with increasing WFPS. When the WFPS exceeds a particular value, the increase in the soil N_2O emissions slows down despite the continuous increase in the WFPS. The WFPS ranges from 0 to 1; the emitted nitrous oxide responds to a variation in the WFPS.

The soil was amended with biochar at a depth above 20 cm and we fitted the model for the 20 cm soil layer to reduce the influence of soil water evaporation. For each treatment, the N_2O emissions were plotted against the WFPS (Fig. 5). These values were fitted using Eq. (9), yielding a strong positive correlation (Table 4). Thus, Eq. (8) explains the N_2O emissions well. The N_2O emissions significantly increase with increasing WFPS after fertilization (Fig. 6). However, this increase slows down remarkably after biochar application (Fig. 6). To quantify the effect of biochar on the N_2O emissions, the SC [Eq. (9)] was determined, which has been applied in many previous studies (Engel et al. 2017; Joby & Mahanthesh 2019; Tan et al. 2017). The SC of RU versus CK (SC_U) is 19.18 and 20.83 in 2019, respectively. and The SC of BRU versus CK (SC_B) is 1.02 in 2019 and 14.74 in 2020, respectively. Biochar significantly reduces the sensitivity of the N_2O emissions to the soil water content, which efficiently inhibits the N loss.

Figure 5: Observed and simulated N_2O emissions during the growth period of maize; (A), (B), and (C) show the observations for RU, BRU, and CK treatment in 2019; (D), (E), and (F) show the observations for RU, BRU, and CK treatment in 2020.

Table 4: Coefficients, determinative factor, and F value of Eq. (4).

Discussion

N₂O is an intermediate product that forms during both denitrification and nitrification (Dobbie & Smith 2001). Soil moisture is the most critical factor governing N₂O and NO when mineral N sources in soil are limited (Prado et al. 2006). N₂O emissions increase until the WFPS reaches ~72% (Schmidt et al. 2000), while other studies reported a threshold reaching up to 90% (Dobbie & Smith 2001). The positive correlation coefficient between the N₂O emissions and WFPS obtained in our study implies that an increase in the soil water content promotes the soil N₂O emissions (Table 1). The soil water content indirectly affects the soil N₂O emissions because the volumetric gas content affected by the WFPS is a vital driver of both nitrification and denitrification (Clough et al. 2017). Denitrification mainly occurs above a WFPS of 60%–70%, whereas nitrification occurs at a WFPS of 35% and 60% (Bateman & Baggs 2005). Most N₂O originates from nitrification when the WFPS is below 60%, while an increased conversion from N₂O to N₂ occurs at higher soil water contents (Wu et al. 2013). Thus, the emission flux of the soil N₂O decreases when denitrification is dominating, although the cumulative N₂O emissions continue to increase (Figs 5–6). This conclusion agrees with the results of other studies in which a nonlinear N₂O emission response to N fertilizer addition was reported (Clairep 2005; Prado et al. 2006; Xue et al. 2012).

Figure 6: Determinants of soil N₂O emissions.

The soil N availability may have a significant impact on the N₂O emissions. The N fertilization, a direct measure of the increase in the soil N availability, promotes the N₂O emissions compared with the unfertilized control (Lei et al. 2005).

Biochar application leads to a significant increase in the soil water content in the topsoil (0–20 cm) relative to the unamended biochar treatments (Fig. 1). Many previous studies were carried out to improve the soil water holding capacity to enhance the water use efficiency in agricultural production (Basso et al. 2013; Oki 2006). Amendment with biochar significantly mitigates the soil N₂O emissions, particularly at a WFPS above 60% (Fig. 6). Previous work showed that the N₂O emissions from biochar-amended soil sharply reduce because the biochar decreases the N concentration available for nitrification and denitrification due to the adsorption of inorganic N (Arezoo et al. 2011; Cayuela et al. 2014; Stewart et al. 2013). Moreover, the response of the decreased N₂O emissions to temporary immobilization of available N derives from a high C:N ratio after biochar amendment (Baggs et al. 2000). The decreased N availability caused by biochar adsorption only partly explains the reduction of the N₂O emissions compared with the BRU and RU treatments. Because of the strong correlation between the WFPS and soil N₂O emissions, the amendment with biochar also mitigates the N₂O emissions by increasing the soil water content (Table 1). This result is consistent with the finding that the anaerobic

environment caused by a high soil water content increases the abundance of denitrifying bacteria and thus catalytically reduces N_2O to N_2 (Wu et al. 2013). Other studies showed that biochar significantly increases the soil N_2O emissions under increased N availability due to fertilization (Clough et al. 2010; Rajkovich et al. 2012). It is possible that incomplete nitrification occurs after amendment with biochar (Clough et al. 2017). Biochar does increase surface soil temperatures, which increases N_2O emissions. The effect of temperature on N_2O resulted from the promotion of the microbial activity. High temperatures could also enhance the denitrifying bacteria activity, promoting the conversion of N_2O to N_2 . Nevertheless, biochar only increases the surface soil temperature (0-10 cm). The model shows that N_2O emission was affected by soil moisture (or temperature) above a 40 cm depth. Therefore, a small temperature increase does not have a significant impact on N_2O emissions.

Biochar enhances soil nitrogen and water immobilization, promotes crop photosynthesis, and increases crop yield (Macdonald et al. 2014; Zhao et al. 2014). Compared with straw returns, biochar can improve soil physical and chemical properties, enhance the effectiveness of water and fertilizers, and reduce chemical fertilizer pollution. However, expensive straw carbonization equipment restricts the market development of biochar and its implication, and the production rate of carbonization equipment does not reach the standard of large-scale production (Zhang et al. 2019). Therefore, producing biochar at a low cost and at a large scale is a challenge in developing agricultural ecology.

Conclusions

Our findings demonstrate that not only surface soil moisture and temperature (0–20 cm) affect the N_2O emissions but also deep soil moisture and temperature (20–80 cm). We performed MNF-DR analyses on the soil water contents and temperatures of three soil layers (10, 20, and 40 cm) to more accurately estimate the N_2O emissions. The soil moisture content and temperature data for the 0–40 cm soil layer could be synthesized using MNF-DR analysis, and the prediction results are more stable than those that are only based on the surface soil moisture content and temperature. However, changes in the soil environment, such as fertilization and biochar amendment, significantly influence the response of the N_2O emissions to the moisture content and temperature, thus reducing the prediction accuracy. Therefore, in the future, it should be determined whether MNF-DR analysis can indicate the effects of soil moisture and temperature on N_2O for different levels of fertilization or biochar application.

Our study demonstrates that the N_2O emissions exponentially increase with increasing WFPS. The exponential phase is a quadratic function with a negative quadratic coefficient. Thus, the emission rate of N_2O initially increases and then decreases. Equation (6) accurately predicts the soil N_2O emissions after urea application in the farmland; the urea application significantly increases the soil N_2O emissions.

The biochar addition does not only improve the topsoil (0–20 cm) water content and temperature but also reduces the N_2O emissions after urea application. The results show that the model [Eq. (4)] also reflects the dynamics of the N_2O emissions depending on the variation in

the soil water content after biochar amendment. The trend of the N₂O emissions is the same as that based on urea application, that is, the emissions initially increase and then decrease. Thus, the response of N₂O to the soil moisture and temperature after fertilization or biochar application is the same, with a SC_B of 1.02 and SC_U value of 19.18 in 2019 and 14.74 and 20.83 in 2020. The biochar amendment significantly reduces the effect of urea on the N₂O emissions. Our results can be used as references in research on the trends of N₂O emissions in farmland.

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Figure 1

Variation in the soil water content above a depth of 80 cm depth in the maize growth stage

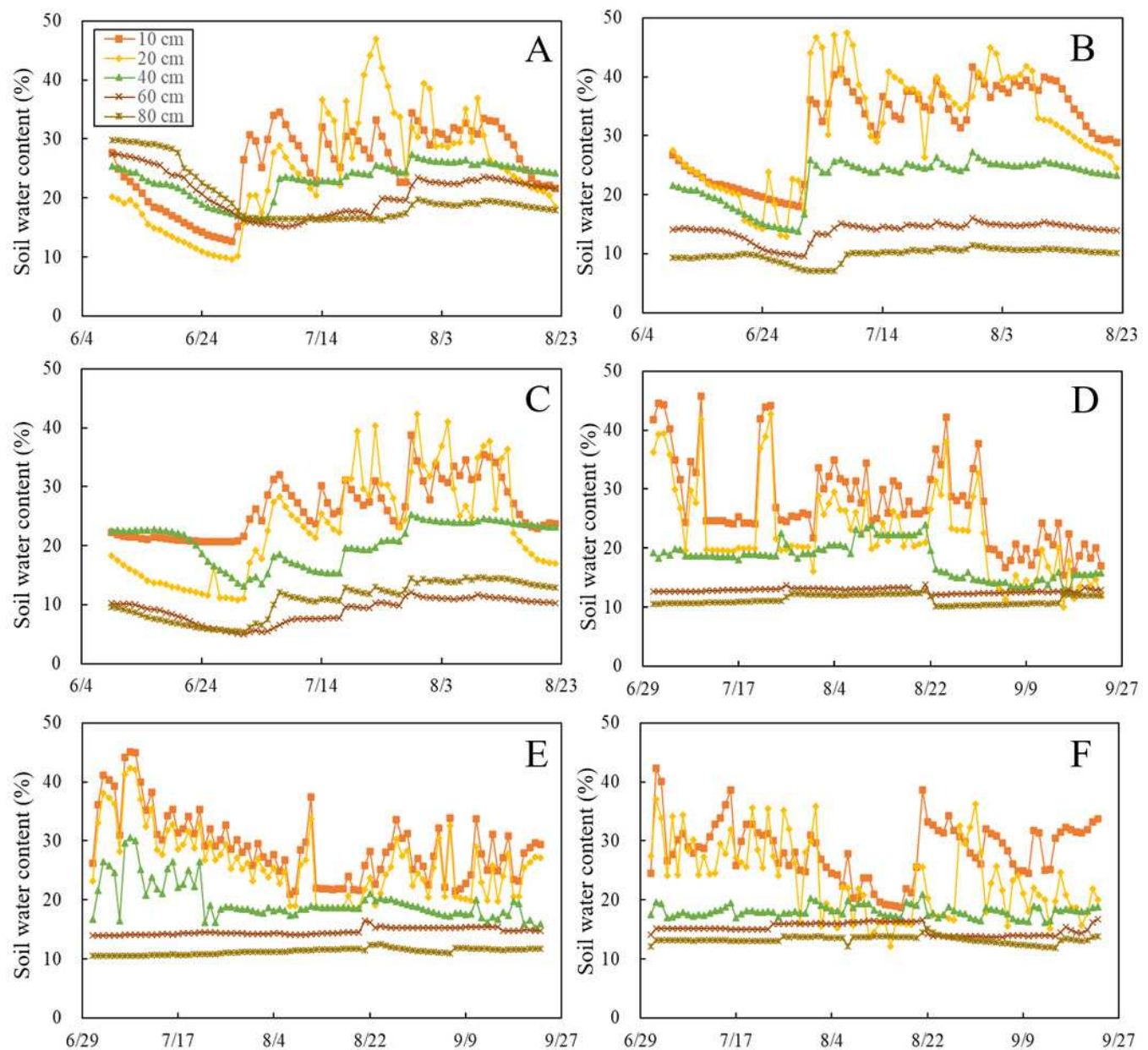


Figure 2

Variation in the soil temperature above a depth of 80 cm in the maize growth stage

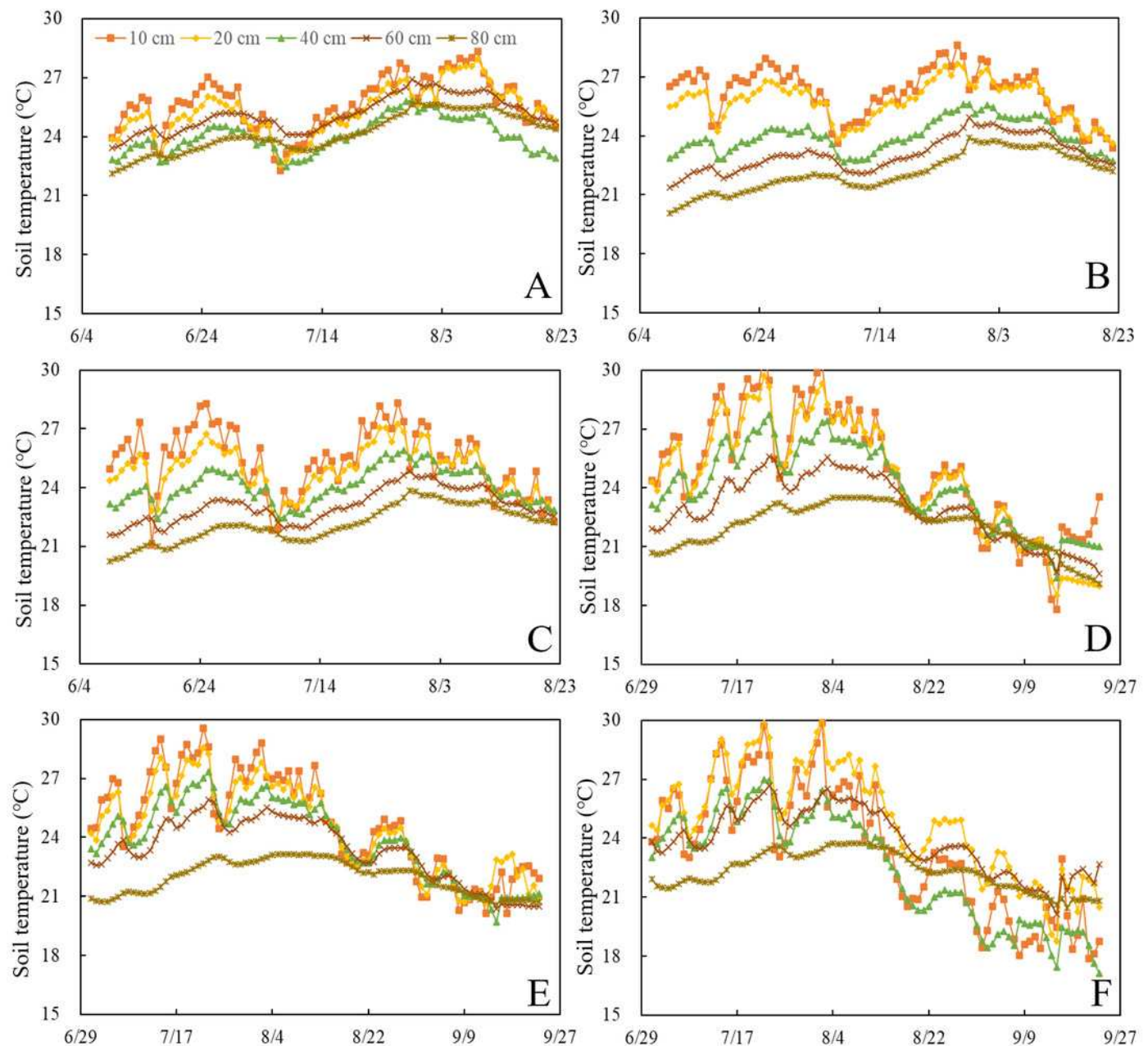


Figure 3

N₂O emission flux in the maize growth stage

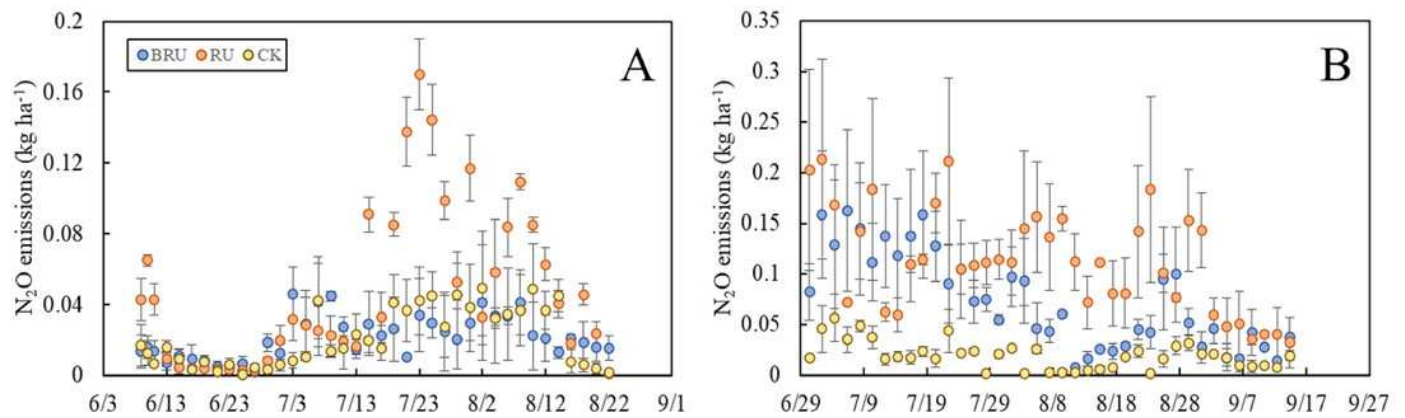


Figure 4

N₂O emission observations and MNF-DR analysis during the growing period of maize

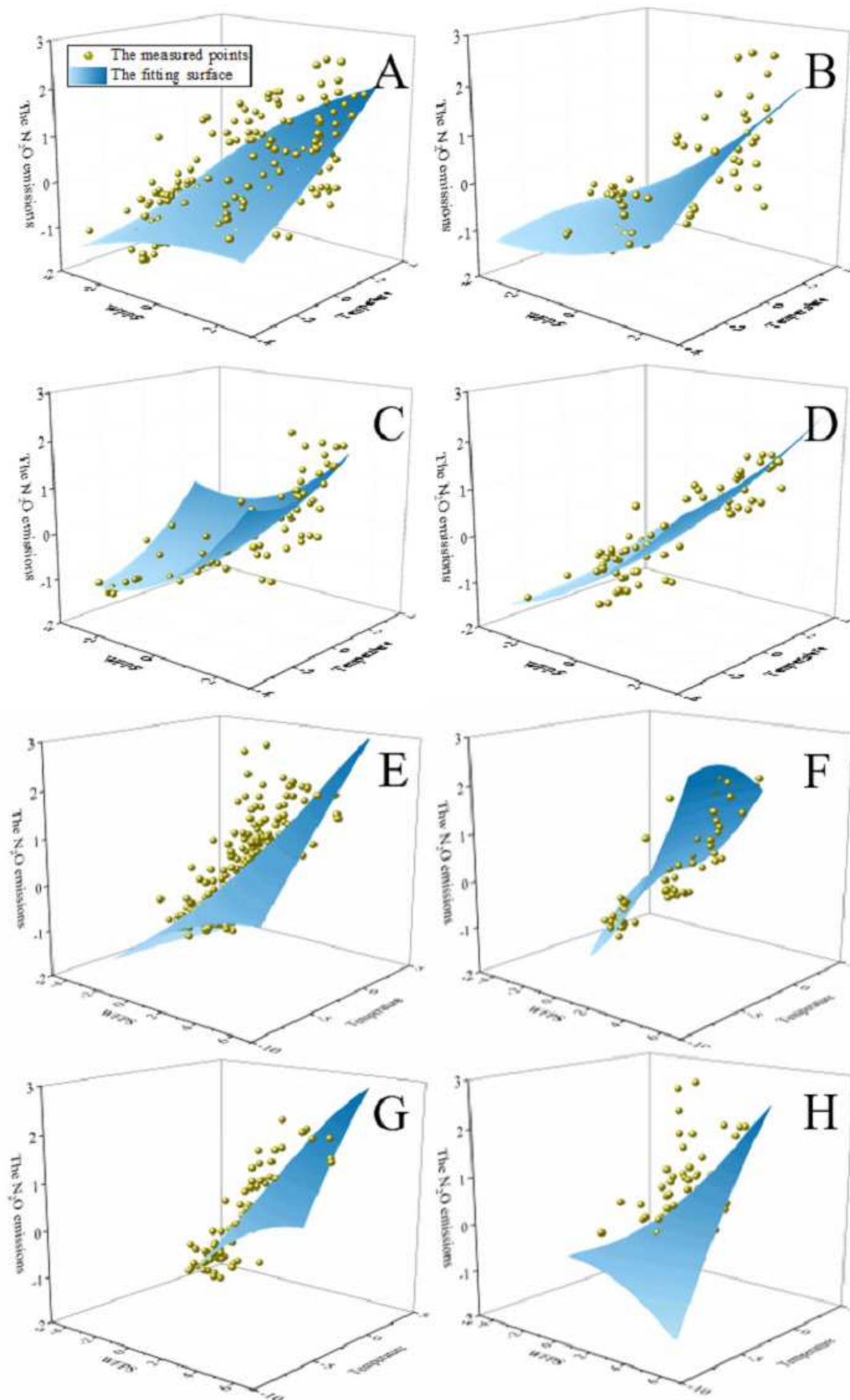


Figure 5

Observed and simulated N₂O emissions during the growth period of maize

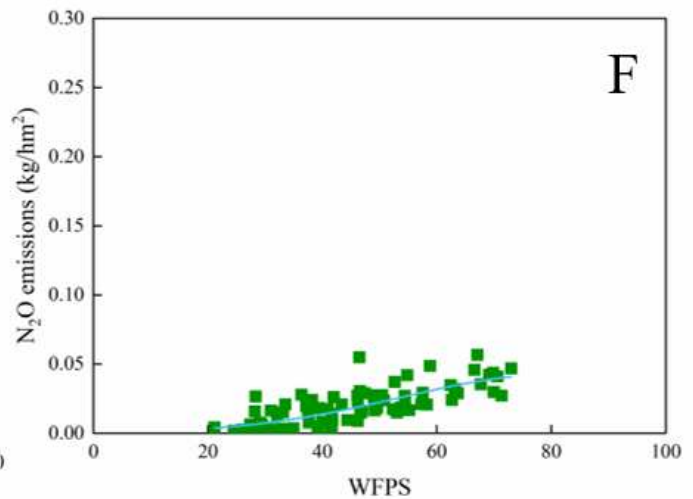
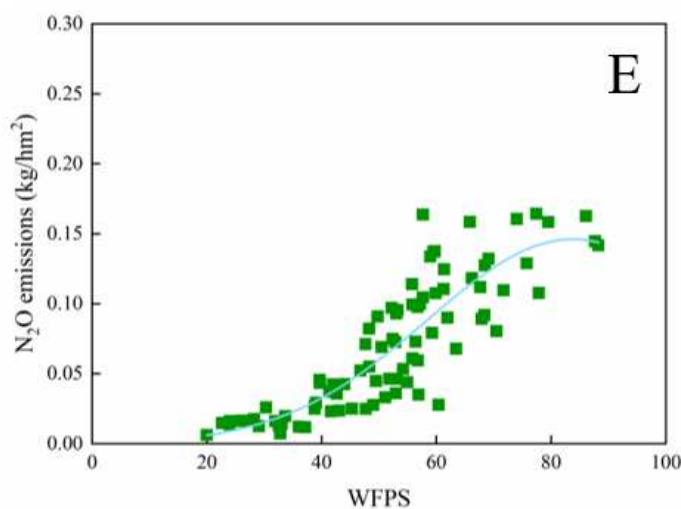
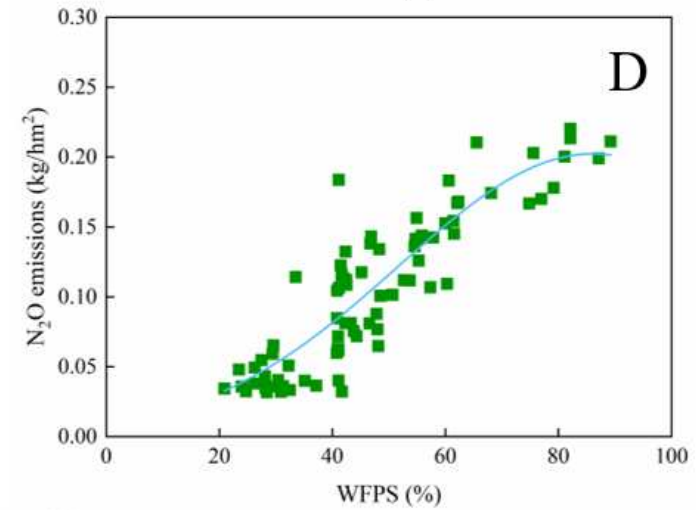
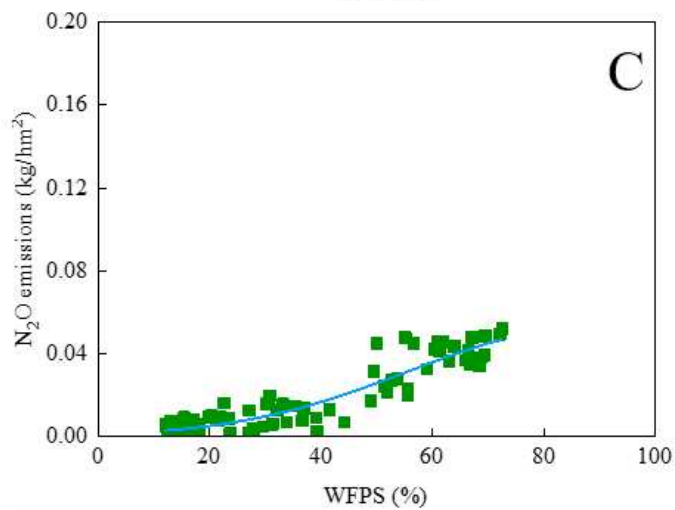
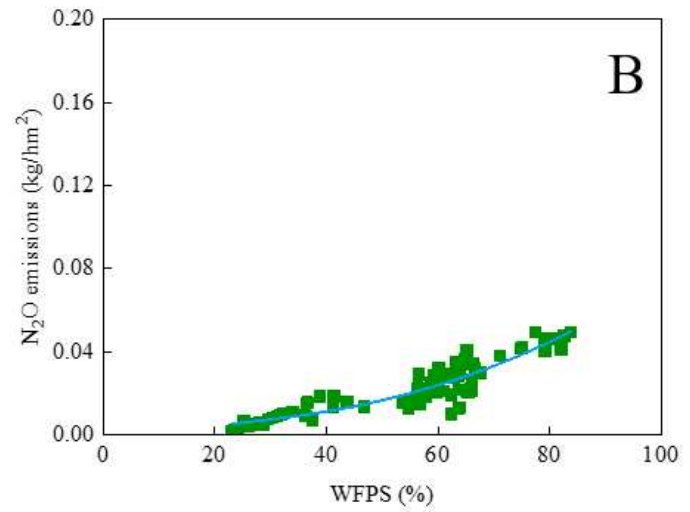
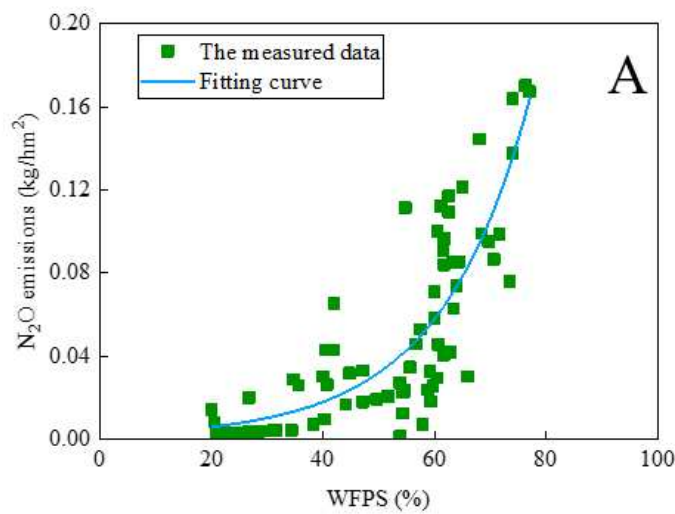


Figure 6

Determinants of soil N_2O emissions

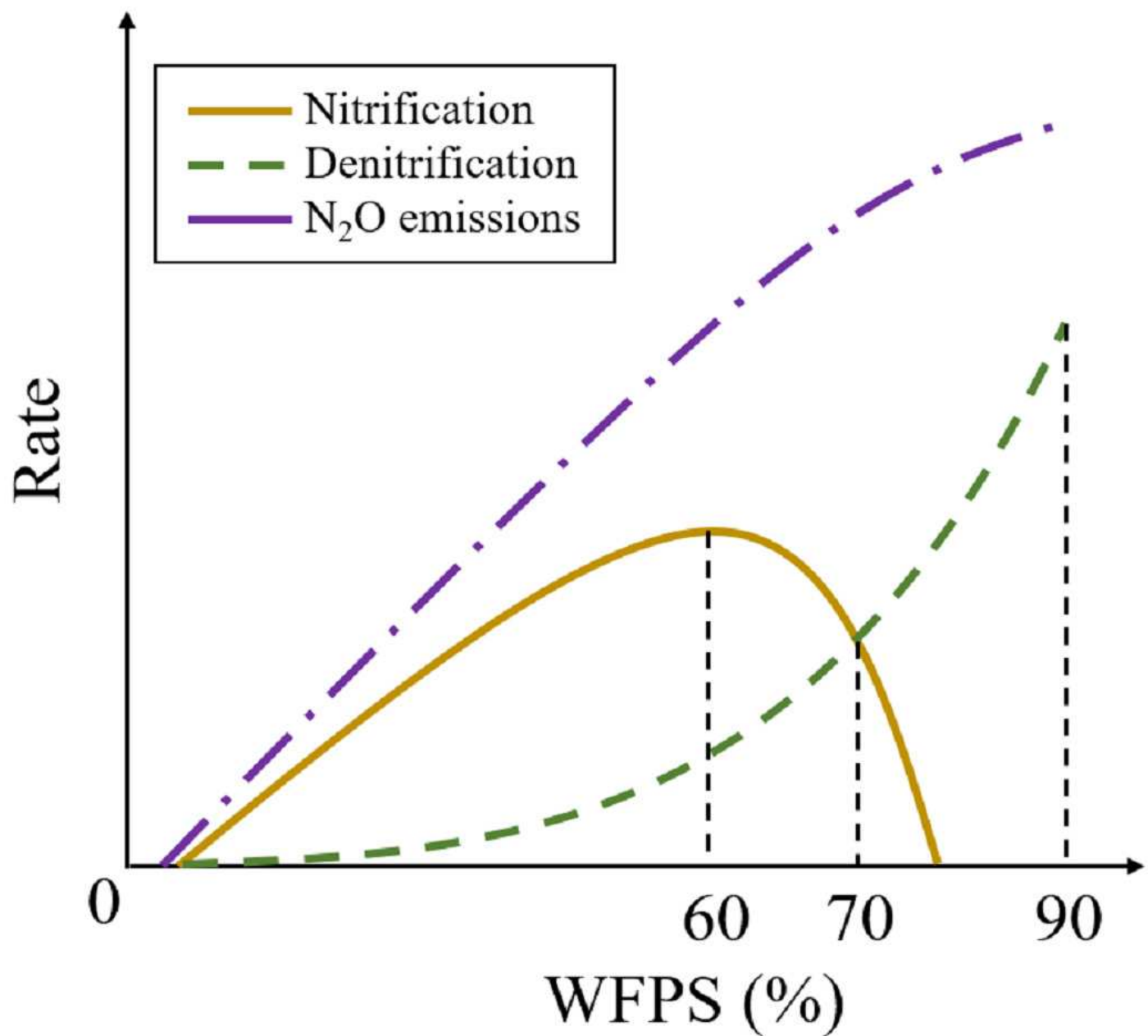


Table 1 (on next page)

Correlation among the soil water content, temperature, and N₂O emissions

Table 1 Correlation among the soil water content, temperature, and N₂O emissions.

		Soil water content in different depth				
		10 cm	20 cm	40 cm	60 cm	80 cm
2019	RU	0.564**	0.761**	0.465**	0.097	-0.310**
	BRU	0.767**	0.883**	0.704**	0.427**	0.008
	CK	0.834**	0.906**	0.701**	0.557**	0.341**
2020	RU	0.886**	0.881**	0.423**	0.011	-0.120**
	BRU	0.783**	0.805**	0.641**	-0.514**	-0.747**
	CK	0.389**	0.775**	0.300**	-0.092	-0.083
		Soil temperature in different depth				
		10 cm	20 cm	40 cm	60 cm	80 cm
2019	RU	0.377**	0.437**	0.502**	0.494**	0.438**
	BRU	0.667**	0.751**	0.309**	0.451**	0.478**
	CK	0.087	0.274*	0.529**	0.666**	0.670**
2020	RU	0.496**	0.551**	0.501**	0.494**	0.380**
	BRU	0.568**	0.546**	0.512**	0.403**	-0.075
	CK	0.297**	0.215*	0.327**	0.100	-0.076

*, ** Significant at P < 0.05, 0.01 levels, respectively (least significant difference test)

Table 2(on next page)

Coefficient of PC1

Table 2 Coefficients of PC1

	a	b	c	d	e	f
2019	0.610	0.537	0.583	0.596	0.607	0.526
2020	0.622	0.615	0.486	0.585	0.573	0.573

The coefficients above represents using MNF-DR analyzed the total observed points (RU+BRU+CK).

Table 3(on next page)

Coefficient of multiple nonlinear regression

Table 3 Coefficients of multiple nonlinear regression.

	Treatment	z_0	k1	k2	k3	k4	k5	R^2	F
2019	Total	0.023	0.276	0.301	-0.030	0.014	0.049	0.51	39.37*
	RU	-0.046	0.433	0.196	0.039	-0.022	0.058	0.61	19.91*
	BRU	-0.309	0.480	0.203	0.093	0.061	-0.044	0.73	33.34*
	CK	-0.186	0.529	0.146	0.054	0.017	0.015	0.84	65.22*
2020	Total	0.008	0.482	0.109	-0.016	-0.002	0.039	0.60	64.26*
	RU	0.022	0.492	0.056	0.065	-0.031	-0.054	0.80	55.30*
	BRU	0.098	0.490	0.208	-0.003	-0.015	0.045	0.75	43.45*
	CK	0.056	0.398	0.097	-0.030	-0.018	0.098	0.31	7.26

*, ** Significant at $P < 0.05$, 0.01 levels, respectively (least significant difference test); 'Total' represents fitting RU and BRU and CK treatment simultaneously; 'F' represents F value at significance analysis.

Table 4(on next page)

N₂O emission observations and MNF-DR analysis during the growing period of maize

Table 4 Coefficients, determinative factor, and F value of Eq. (9)

	Treatment	a	b	c	R ²	F value
2019	RU	-6.436*10 ⁻⁵	0.052	-6.218	0.70	153.90**
	BRU	-1.266*10 ⁻⁴	0.053	-6.365	0.81	535.23**
	CK	5.251*10 ⁻⁴	0.091	-6.898	0.85	411.30**
2020	RU	-4.282*10 ⁻⁴	0.074	-4.774	0.78	587.31**
	BRU	-7.811*10 ⁻⁴	0.131	-7.411	0.74	320.72**
	CK	-6.791*10 ⁻⁴	0.110	-7.594	0.59	165.93**

*, ** Significant at P < 0.05, 0.01 levels, respectively (least significant difference test)