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Effects of long-term nitrogen fertilization on N_2O, N_2 and their yield-scaled emissions in a temperate semi-arid agro-ecosystem

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Abstract

Purpose Nitrous oxide (N_2O) measured simultaneously with di-nitrogen (N_2) emissions from soils are greatly uncertain due to large temporal and spatial variations. This study aims to report N_2O, N_2, N_2/N_2O, ^{15}N-N_2O, wheat-maize annual grain yields, and yield-scaled N_2O and N_2O plus N_2 emissions on the responses to different nitrogen (N) fertilizer rates in a winter wheat-summer maize cropping system. Furthermore, this study also seeks to determine controlling factors for N_2O, N_2, and N_2/N_2O emissions and significantly investigate the relationship between the soil-climate measured factors and ^{15}N-N_2O.

Materials and method Three N inputs and control treatments, 0, CK; 200, LN; 400, MN; and 600, HN kg N ha^{-1} $year^{-1}$ were set since 1998. Direct measurement method has been used to quantify N_2O and N_2 emissions.

Results Our results indicated that the effects of long-term N fertilization significantly increased N_2O and N_2 and also reduced N_2/N_2O emission ratios as described by exponential functions. Using structural equation modeling (SEM), NH_4^+, WFPS, NO_3^-, and DOC were revealed to be main controlling factors for N_2O, while N_2 by DOC, NO_3^-, WFPS, and temperature finally N_2/N_2O was positively related to temperature. Furthermore, the ^{15}N-N_2O was positively related to N_2/N_2O ratios, indicating that denitrification is the dominant process at the study site. The yield-scaled N_2O emissions followed the order HM>MN>LN>CK, and they were 1.56, 1.47, and 1.07 times greater than CK, respectively. Total yield-scaled N_2O plus N_2 were in the order of CK>HN>MN>LN.

Conclusion N fertilization has shown strong impact not only on N_2O, N_2, and N_2/N_2O emissions but also on yield-scaled N_2O and N_2O plus N_2 emissions. High agronomic nitrogen use efficiency (NUE), low yield-scaled N_2O emissions, and low cumulative N_2O plus N_2 emissions were observed at 200-LN treatment, suggesting this rate to be an optimum and sustainable agricultural management practice with no significant crop yield reduction as compared to the current farmers' practice of 400 kg N ha^{-1} $year^{-1}$.

Keywords Nitrogen fertilization · N_2O and N_2 emissions · Controlling factors · Wheat-maize grain yields · ^{15}N in soil-emitted N_2O · Yield-scaled N_2O and $N_2O + N_2$ emissions

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1 Introduction

Globally, a half of nitrogen (N) fertilizer applied into agricultural soils is uptaken by crops, while another half either remains in the soils or lost as reactive N (Nr) to the atmosphere (de Vries et al. 2011; Lassaletta et al. 2014). Since N plays a vital role in plant growth, the increase in usage of N fertilizer has enhanced crop yields that facilitated to supply food to ever-growing world population, estimated to more than 7.2 billion inhabitants today (Erisman et al. 2008; Grafton et al. 2015). Since, N is one of the macronutrient limiting factors for crop growth (Wang et al. 2010), the increase of N fertilizer application rates will also increase N_2O and N_2 losses from agricultural soil (Wang et al. 2020).

Nitrous oxide (N_2O) is a potent and long-lived major greenhouse gas that contributes to ozone depletion and global warming (Forster et al. 2007; Saggar et al. 2007). Since pre-industrial (1750) time, atmospheric concentration of N_2O has been increasing at a rate of 0.8 ppb year^{-1} (Prinn et al. 2000; IPCC 2007) that makes it to increase from 270 to 330 ppb by 2019 (NoAA 2019). Fertilized agricultural soils are estimated to emit 4.1 Tg N_2O annually (IPCC 2013) that makes it a significant source of N_2O among other anthropogenic sources. Fan et al. (2017) reported its contribution as more than 60% of worldwide anthropogenic N_2O emissions. However, N_2O measured simultaneous with N_2 have not been well documented in agricultural soils.

Nitrification and denitrification are two microbial processes considered to be main soil N_2O formation (Saggar et al. 2013; Timilsina et al. 2020a), while denitrification process reduces N_2O formed into N_2 under conducive conditions (e.g. Dannenmann et al. 2008; Saggar et al. 2013). Exponential relationships between N fertilizer rates and direct N_2O emissions have been well documented (Kim et al. 2013; Cui et al. 2014; Shcherbak et al. 2014; Song et al. 2018), while some other studies also reported linear relationships between N fertilizer rates and direct N_2O emissions (Liu et al. 2012; Huang et al. 2017). However, the relationships between N application rates and direct N_2O and N_2 in agricultural soils remain unclear.

N_2O emitted through nitrification are more depleted in ^{15}N isotopic composition than denitrification (Baggs 2008; Park et al. 2011). Studying the ^{15}N isotopic composition of soil-emitted N_2O with soil variables and soil N_2O and N_2 losses would further enhance our understanding of N_2O formation and reduction processes in the current study. Moreover, soil-emitted ^{15}N-N_2O from fertilized and unfertilized agricultural soil will help to insight each contribution in depletion of ^{15}N isotopic composition of atmospheric N_2O.

North China Plain (NCP) is the key agricultural area mainly yielding cereals, and if compared to other regions in China, the previous study reported that 26% and 76% of total maize and wheat were produced there, respectively (Tan et al. 2017), but the N fertilizer input is up to 550–600 kg N ha^{-1} year^{-1}, and the amount is quite high as compared to the required N by crops ranging from 200 to 300 kg N ha^{-1} year^{-1} (Meng et al. 2012), and also Wang et al. (2010) proposed the N fertilizer rate of 360 kg N ha^{-1} year^{-1} for effective use of N fertilizer. In addition, Pan et al. (2012) reported the average annual N deposition of 61 kg per hectare per year in NCP. Hence, there is a surplus of N in the soil. Moreover, in vegetables, excessive N fertilizer application had been also observed in different climatic regions of China; Zhang et al. (2020) proposed that 81–90% of N_2O emissions could be reduced when N fertilizer input had been optimized as well.

Many studies reported N_2O and N_2 emissions from soils using one of the three measurement approaches: acetylene (C_2H_2) inhibition technique (e.g., Yoshinari and Knowles 1976; Miller et al. 2008; Qin et al. 2012; Qin et al. 2013; Guo et al. 2018) and ^{15}N isotope labeling method (e.g., Hauck and Melsted 1956; Cai et al. 2001; Mathieu et al. 2006; Ruser et al. 2006) and helium-oxygen incubation approach known as direct method (e.g., Butterbach-Bahl et al. 2002; Qin et al. 2017). The lack of a robust direct measurement methods to measure N_2 emissions, as final denitrification estimations (IPCC 2013), has caused a considerable underestimation or overestimation of N_2. For instance, C_2H_2 inhibition technique is cheap and easy to conduct but underestimates denitrification, hence underestimation of N_2 emissions as well (Butterbach-Bahl et al. 2013; Qin et al. 2012), while the ^{15}N isotope labeling method has been at first limited by more laboratory procedures and expensive equipment as compared to C_2H_2 inhibition (Hauck and Melsted 1956). Later Ruser et al. (2006) reported high detection limit that identified overestimation of N_2. For example, Qin et al. (2017), Friedl et al. (2020), and Wang et al. (2020) have strongly recommended the use of helium-oxygen direct method to estimate N_2O and N_2 emissions to elucidate uncertainty for N budgets, thus attaining realistic and unbiased measurements of N_2O and N_2. It is well known that N_2O measurements have been intensively improved at both spatial and temporal scales, but N_2 measurements against high atmospheric N_2 background remain a challenge either in situ or in laboratory.

In the current study, we used a robust direct method, helium-oxygen incubation for N_2O and N_2 measurement (Qin et al. 2017); it is harmless although it needs high gas tightness to avoid atmospheric N_2 leakage (Groffman et al. 2006). This will elucidate dynamics of N_2O and N_2 emissions from long-term N inputs by mimicking field conditions in laboratory in a way to comprehend the N cycle. Therefore, a field study was handled to evaluate the responses of N_2O and N_2, ^{15}N isotopic composition of N_2O, annual wheat and maize grain yields, yield-scaled N_2O and N_2 emissions, and agronomic nitrogen use efficiency (NUE) to a long-term N fertilized agricultural soil, and to the best of our knowledge less work has been done. The objectives of the current study are (i) to explore the effects of long-term N fertilizer application rates on N_2O and N_2, annual grain yields (wheat plus maize), and agronomic NUE and to quantify the yield-scaled N_2O and N_2O plus N_2; (ii) to relate the soil-climate controlling factors to the emissions of N_2O, N_2, and their ratios N_2/N_2O; and (iii) to understand the relationship between ^{15}N in soil-emitted N_2O and the measured factors.

2 Materials and methods

2.1 Field site description

The field site is a long-term N fertilization experiment located in the Northern region of NCP known as Luancheng Agro-ecosystem Experimental Station (37°53′N, 114°41′E, 50 m) of the Chinese Academy of Sciences (CAS) in Hebei province, China. The soil of this region is categorized as a silt loam Haplic Cambisol (Mueller et al. 2013), and this experimental site has a typical monsoon climate classified as temperate semi-arid. The annual precipitation and annual temperature were observed 540 mm and 12.7°, respectively. The trend of daily precipitation, soil temperature (5-cm depth), and average air temperature during the study period are obtained from the meteorological station records; details are shown in (Fig. 1). The NCP is a distinctive representative of the high-yield agricultural region in China; about 90% of the cultivated land is winter wheat (*Triticum aestivum* L.) and summer maize (*Zea mays* L.) (Tan et al. 2017). Maximum annual soil (5-cm depth) temperature was 31.88 °C, and minimum annual soil temperature was − 3.8 °C, and the average is 15.1 °C. More rainfall was noticed in summer season, while there was dry cold soil in winter in the NCP. The annum cumulative rainfall is 349.2 mm (Fig. 1).

2.2 Experimental design and soil sample collection

Each experimental plot has an area of 70 m^2 (7 m × 10 m) in a long-term experimental field of winter wheat-summer maize rotation system established in 1998. The experiment has three N inputs and control treatments; each has three replicates in our study design: 0 (control, CK), 200 (low nitrogen, LN), 400 (medium nitrogen, MN), and 600 (high nitrogen, HN) kg N ha^{-1} $year^{-1}$. For winter wheat, a half of total annual N fertilizer rates were applied, respectively, to treatments in a split dosage at planting in October and at stem elongation in April, while for summer maize, the other a half of total annual N fertilizer rates were applied once, respectively, to treatments during flowering stage in August. As an additional mineral macronutrient, all plots received double superphosphate (65 kg ha^{-1} $year^{-1}$) and potassium chloride (75 kg ha^{-1} $year^{-1}$); these macronutrients were applied once a year as basal fertilizers during winter wheat planting in October. The field was plowed once after maize harvest in October, and the straw was mechanically chopped into smaller parts and integrated into the topsoil by rotary tillage. The details of the fertilization practices and other crop management activities are shown in Table S1.

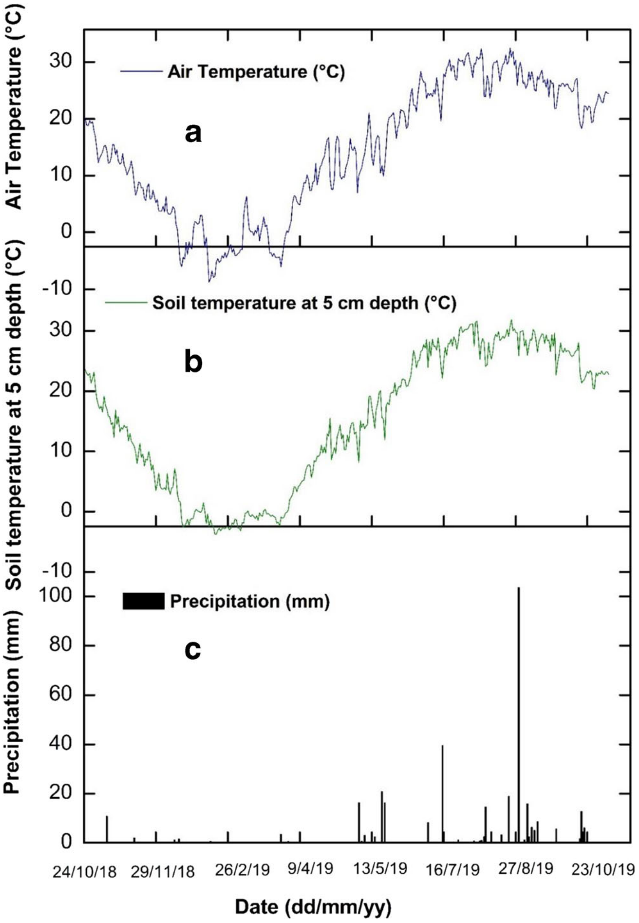

Fig. 1 Precipitation records, daily mean air temperature and soil temperature (5-cm depth) throughout observational period

2.3 Measurements of N_2O and N_2 fluxes and ^{15}N isotopic composition of N_2O

A robust direct measurement technique was used to incubate soil cores using two cylinders in one (inward cylinder was placed into outward one) setup, and afterward, they were sealed well to avoid atmospheric N_2 contamination, and the soil core atmosphere was substituted by helium-oxygen. One to three soil samples were collected per month, depending on the N fertilizer application, and irrigation throughout the observational period and 21 sampling campaigns was reported. A stainless steel cylinder opened at both ends, a hammer, and a flat timber were used at the field to acquire soil cores vertically without much soil disturbance. The depth of soil core was 10 cm, and diameter was 19 cm. The diameters of inward and outward cylinders were 19 cm and 26 cm and the heights were 15 cm and 18 cm, respectively. After soil sample collection, the headspaces of both inward and outward cylinders were evacuated and filled with an artificial helium, 79%, and oxygen, 21%, for times varying from 4 to 5 in the laboratory.

Double cylinders were used to directly quantify N_2O and N_2 headspace concentrations after soil cores were evacuated as described in our previous study (Qin et al. 2017). Concentrations of N_2O were analyzed by an electron capture detector while N_2 by a thermal conductivity detector of the gas chromatography for 24 h after soil core sampling. During concentration measurement of N_2O and N_2, field environmental conditions were simulated in laboratory. Furthermore, this was enhanced by placing cylinders outdoor in the field. After mimicking the field environmental conditions, the cylinders were brought back in the laboratory again, and the same procedures were repeated. The N_2O and N_2 fluxes were calculated based on our previous study (Qin et al. 2017).

Gas samples were also taken for ^{15}N isotope analysis of N_2O after the cylinders' atmosphere exchange by gas flow helium and oxygen. 120-ml gas sample was taken from each inward cylinder headspace and another 120 ml of gas sample was taken after incubation period using glass bottles. Then, the ^{15}N of the soil-emitted N_2O were quantified using an isotope ratio mass spectrometer (IRMS) (Delta V Plus. Thermo Fisher, Germany). As the N_2O in the sample represented the ^{15}N isotopic composition of both atmospheric and soil-emitted N_2O, the equation from Snider et al. (2017) was used to calculate the ^{15}N of soil-emitted N_2O.

2.4 Annual grain yields (wheat plus maize) measurement and yield-scaled N_2O and N_2 emissions

Annual grain yields (wheat and maize) expressed in million grams per hectare (Mg ha^{-1}) were calculated separately during harvesting seasons from an area of 12 m^2 (3 × 4 m) in middle of each plot. Weights of ready maize cobs were determined and recorded, while wheat ears were even counted and then dried at 60 °C during 48 h to determine and record their dry weights. Yield-scaled N_2O and N_2 emissions (kg N Mg^{-1} grain) were calculated by dividing annual cumulative N_2O and N_2 emissions by annual wheat plus maize grain yields, respectively. Agronomic nitrogen use efficiency (NUE) was calculated by dividing annual wheat plus maize grain yields by annual N fertilizer (kg kg^{-1}) rates in all N fertilized treatments except from CK.

2.5 Soil physicochemical analyses

Auxiliary soil analyses were conducted on 10-cm depth. During each sampling time, 5 soil cores were collected in plastic bags using auger from each plot in the respect to replicates. The collected soils of each plot were mixed thoroughly and stored in laboratory at 4 °C before further analyses of the soil parameters. NH_4^+ and NO_3^- were measured by Smartchem 140 analyzer and dual wavelength ultraviolet spectrophotometer, respectively. For soil NH_4^+ and NO_3^- extracts, 10-g fresh soil was extracted by shaking for 1 h using 50 ml of a 1 M potassium chloride solution. DOC was extracted and analyzed as described by (Mulvaney et al. 1997). Soil characteristics at field observational site, bulk density, soil pH, total organic matter, available phosphorus, and total nitrogen, were analyzed as described by Wang et al. (2014). Table S2 summarizes soil properties at field observational site. The measured gravimetric soil water content (%) obtained by drying the soil at 105 ± 0.05 °C for 24 h was converted to soil water filled pore space WFPS (%) based on (Franzluebbers 1999).

2.6 Data analyses

Structural equation modeling (SEM) analyses were carried out using the Lavaan R package. SEM was used to identify the relationships between WFPS, NO_3^- , DOC, NH_4^+, and soil temperature (5-cm depth) and N_2O, N_2 fluxes, and N_2/N_2O ratios. The quality of the SEM was assessed by using the Chi-square (X^2) goodness of fit statistics ($P > 0.05$, this indicates statistical significant model fit), the root mean square error of approximation value (RMSEA, the smaller the better), and Akaike information criteria (AIC) (Kline 2011). Pathways relationships at *$P < 0.05$; **$P < 0.01$, and ***$P<0.001$ were considered significant. Analysis of variances (ANOVA) with a least significant difference test (LSD, $P < 0.05$) was used to test for differences in N_2O and N_2 annual cumulative emissions, N_2/N_2O ratios, ^{15}N of soil-emitted N_2O, annual wheat plus maize grain yields, agronomic NUE, and yield-scaled N_2O and N_2 between the treatments. All other data analyses were executed using OriginPro8 (Origin Lab Ltd., Guangzhou, China).

3 Results

3.1 Soil physicochemical properties

Soil DOC results showed a remarkable trend where highly fertilized soils have larger amount of DOC content compared to control (Fig. 2c), and average values were 40.54 ± 0.7, 47.84 ± 0.7, 50.93 ± 0.8, and 52.76 ± 0.9 from CK, LN, MN, and HN treatments, respectively. The trend of DOC was as follows: CK<LN<MN<HN, and statistical difference was obtained between all fertilized soil and CK, while HN was also statistically significant with LN. Soil WFPS (Fig. 2d) showed its highest peak in April after irrigation, and there was no statistical difference among treatments, and average values were 54.32 ± 1.7, 55.12 ± 2.1, 59.13 ± 1.7, and 58.96 ± 1.6 from CK, LN, MN, and HN treatments, respectively. Soil NH_4^+-N (Fig. 2a) was low, and some peaks were

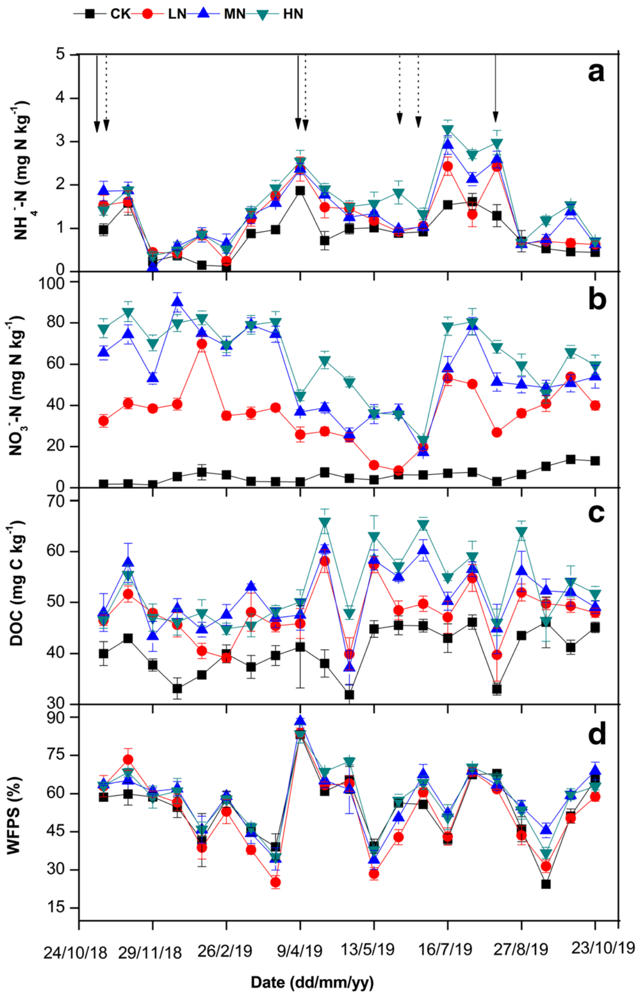

Fig. 2 (**a**) NH_4^+-N (mg kg^{-1}), (**b**) NO_3^--N (mg kg^{-1}), (**c**) DOC (mg kg^{-1}) for dried soil, and (**d**) WFPS (w/w, %) at our observational site in the all treatments. Solid arrows on top signify N fertilizer application and dashed arrows indicate irrigation. Vertical bars denote standard errors for each mean treatment (*n* = 3)

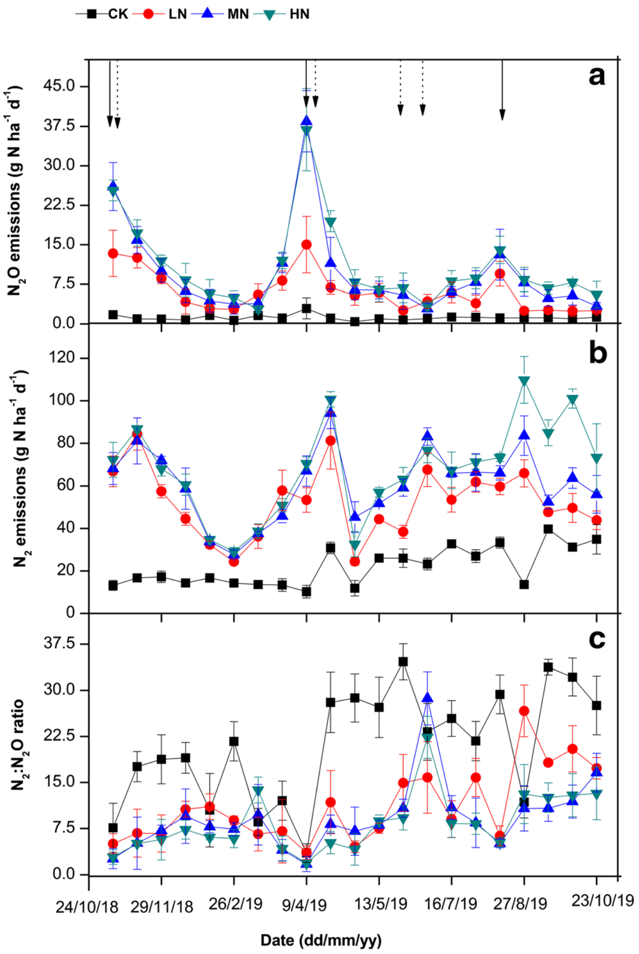

Fig. 3 Fluxes of N_2O (**a**), N_2 (**b**), and N_2/N_2O ratios (**c**) from unfertilized and N fertilized treatments throughout observational period. Solid arrows on top indicate N fertilizer application and dashed arrows signify irrigation. Vertical bars indicate standard error for each mean treatment (*n* = 3).

observed after N fertilizer application under sufficient soil moisture. Long-term N fertilization increased the NO_3^--N concentrations in soil, and the average values were 5.83 ± 0.4, 35.73 ± 2.1, 55.35 ± 3.1, and 63.61 ± 3.4 in the CK, LN, MN, and HN treatments, respectively, and there was a statistical significance between all treatments except HN and MN. The trend for both NO3$^-$-N and NH_4^+-N concentrations in the soil was CK<LN<MN<HN at our study site (Fig. 3a, b). NH_4^+-N average values were 0.86 ± 0.06, 1.2 ± 0.08, 1.35 ± 0.11, and 1.55 ± 0.13 from CK, LN, MN, and HN treatments, respectively, and the statistical significance was only observed between HN and CK and MN and CK.

3.2 Temporal patterns of N_2O and N_2 emissions and N_2/N_2O emission ratios

N fertilizer and irrigation practices greatly regulated the emissions of N_2O. Comparing fertilized treatments among themselves and furthermore, to unfertilized treatments, the N fertilization rates greatly enhanced N_2O emissions (Fig. 3a). N_2O emissions were highest from the HN and lowest from CK treatment, and the average values were 1.18 ± 0.1, 6.07 ± 0.6, 9.81 ± 1.2, and 10.88 ± 1.1 g N ha^{-1} day^{-1} from CK, LN, MN, and HN treatments, respectively. Thus, HN>MN>LN>CK was the observed trend. Throughout the annual measurement period, there were three main peaks in the fertilized treatments (Fig. 3a); the first peak occured in October 2018, just after the basal N fertilizer application and flood irrigation. The second peak which was the highest among all occurred in April 2019, immediately after the top dressing of N fertilizer application and irrigation. The third happened in August 2019; immediately after N fertilizer application, there was no irrigation because it was a rainy period and the soil had enough moisture.

N_2 flux peaks were detected a few days after N fertilizer application and flood irrigation (Fig. 3b). The emissions from three fertilized treatments were much larger than the CK treatment, and the average values were 21.91 ± 1.2, 52.17 ± 2.2, 60.92 ± 2.3, and 67.71 ± 2.9 g N ha^{-1} day^{-1} from CK, LN, MN, and HN treatments, respectively. This clearly demonstrates how long-term N fertilization induced the N_2 fluxes. Moreover, within fertilized treatments, irrigation induced peak in N_2 fluxes. From early spring throughout summer to autumn, in our observational site, there are enough soil moisture (WFPS) (Fig. 2d) and conducive temperature (Fig. 1) that favored N_2O production and reduction to form high N_2 fluxes.

In the current study, the N_2/N_2O ratios of emissions ranged from 1.7 to 34.6 (Fig. 3c). Overall mean N_2/N_2O emission ratios were 20.9 ± 0.8, 13.2 ± 0.8, 11.4 ± 0.8, and 10.3 ± 0.7 from CK, LN, MN, and HN treatments, respectively. The general trend of N_2/N_2O emission ratios was observed highest in summer and lowest towards the end of winter.

3.3 The annual cumulated N_2O and N_2 emissions and the overall mean of N_2/N_2O ratios to N fertilizer application rates

The annual cumulative emissions of N_2O are significantly different among all treatments, and average values obtained were 0.40 ± 0.02, 1.91 ± 0.1, 2.83 ± 0.3, and 3.30 ± 0.3 kg N ha^{-1} $year^{-1}$ from CK, LN, MN, and HN treatments, respectively (Fig. 4). Therefore, annual cumulative N_2 emissions and average values were 7.89 ± 0.4, 18.02 ± 0.7, 21.46 ± 0.8, and 23.73 ± 1.1 kg N ha^{-1} $year^{-1}$ from CK, LN, MN, and HN treatments, respectively. Among treatments, CK and LN are significantly different with MN and HN (Fig. 4). The overall N_2/N_2O ratios were in the trend of CK > LN > MN > HN treatments. The cumulative N_2O and N_2 emissions increased exponentially, while the N_2/N_2O ratios decreased exponentially with the increase of N fertilizer application rates. The differences of N_2/N_2O ratios between the LN, MN, and HN treatments were small and insignificant (Fig. 4). The total annual cumulative N_2O and N_2 emissions were exponentially related to N fertilizer application rates at $P = 0.006$ and $P = 0.015$, respectively (Fig. 4), throughout the year, while N_2/N_2O was negatively related to the N fertilizer application rate at $P < 0.016$.

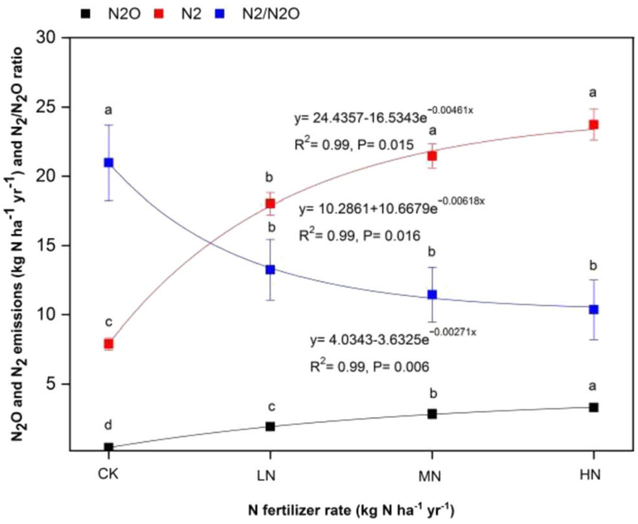

Fig. 4 N_2O, N_2, and N_2/N_2O ratio emissions followed exponential functions in response to N fertilizer rates, respectively. Data point refers to mean ± stand error ($n = 3$) and lowercase letters denote significant differences between treatments

3.4 Relationships between N_2O, N_2 emissions, and N_2/N_2O emission ratios with soil parameters

Structural equation model analyses were applied to evaluate effects of the selected soil-environmental factors, i.e., dissolved organic carbon (DOC), water-filled pore space (WFPS), nitrate (NO_3^--N), ammonium (NH_4^+-N), and soil temperature at 5 cm depth (ST). These soil factors are considered to critically induce N_2O and N_2 fluxes and N_2/N_2O ratios. N_2O fluxes were positively related to NH_4^+-N, WFPS, NO_3^--N, and DOC while negatively related to ST (Fig. 5). N_2 fluxes were positively related to DOC, WFPS, NO_3^--N, and ST (Fig. 5). N_2/N_2O ratios were positively related to ST and negatively related to NH_4^+-N and NO_3^--N content (Fig. 5).

3.5 ^{15}N isotopic signatures in soil-emitted N_2O and its relationship with the N_2/N_2O ratios

The N fertilized soils emitted more depleted $\delta^{15}N$ of N_2O, while unfertilized soil shows less depleted values (Fig. 6a). The average values of $\delta^{15}N$ of N_2O soil-emitted were − 7.9‰ ± 0.9, − 13.6‰ ± 1.2, − 16.1‰ ± 1.1, and − 18.5‰ ± 1.1 from CK, LN, MN, and HN treatments, respectively. There was statistical difference between CK and other fertilized treatments, while within fertilized treatments, only LN and HN were statically different. Our study results showed a positive correlation between the N_2/N_2O emission ratios and the $\delta^{15}N$ of soil-emitted N_2O at $P < 0.0366$ (Fig. 6b), demonstrating that the increase of the emission ratios of N_2/N_2O is associated with less depleted $\delta^{15}N$ of soil-emitted N_2O.

3.6 Annual grain yields (wheat plus maize) and NUE as responses to N fertilizer rates

The results of annual grain yields (wheat plus maize) in the current study were averagely 3086, 13,635, 14,729, and 16,216 Mg ha^{-1} $year^{-1}$ in CK, LN, MN, and HN, respectively. There were 4.41, 4.77, and 5.25 times the annual grain yields greater in LN, MN, and HN treatments, respectively, as compared to CK treatment. The annual grain yields were statistically different between CK and fertilized treatments. Moreover, there was a significant difference in annual grain yields between HN and LN, but no significant difference was observed between LN and MN

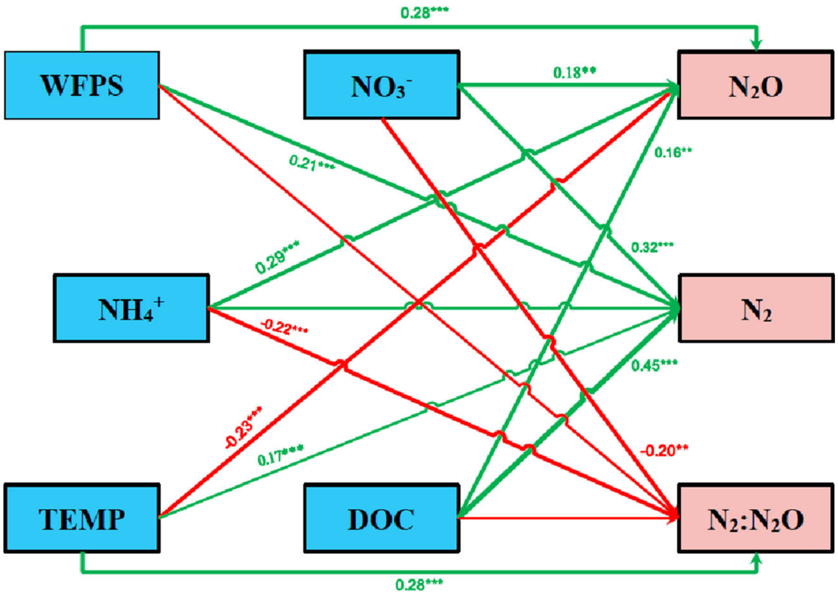

Fig. 5 The results of structural equation modeling (SEM) for the effects of temperature (Temp), WFPS, DOC, NH_4^+, and NO_3^- on N_2O, N_2, and N_2:N_2O during whole observational duration. The model is a good fit to the data: Chi-square (X^2) = 1.522; $P = 0.467$, df = 2; RSMEA = 0.252; AIC = 51.22 for N_2O; Chi-square (X^2) = 0.471; $P = 0.492$, df = 1; RSMEA = 0.297; AIC = 52.471 for N_2 and Chi-square (X^2) = 0.979; $P = 0.323$, df = 1; RSMEA = 0.223; AIC = 40.97 for N_2:N_2O. Green arrows denote positive relationships, red arrows indicate negative relationships and the relationships are denoted on the arrows at $*P < 0.05$; $**P < 0.01$; and $***P < 0.001$. None significant coefficients are not shown. Numbers next to the arrows denote the (positive or negative) path coefficients

and HN and MN. The responses of N fertilizer rates to annual grain yields were well described by exponential relationship (Fig. 7A). A linear model described well the responses of agronomic NUE and how it was inversely related to N fertilizer rates. There is a clear difference ($P < 0.001$) between all fertilized treatments for agronomic NUE (Fig. 7B). Therefore, the results from annual grain yields and agronomic NUE (Fig. 7A, B) demonstrate that the overdose N fertilizer rates could lead to no more annual grain yields.

3.7 Yield-scaled N_2O and N_2O plus N_2 emissions

Yield-scaled N_2O and N_2O plus N_2 (kg N Mg^{-1} grain) have been a good indicator to show how annual grain yields (wheat plus maize) are related to annual cumulative N_2O and N_2 emissions. The average results of total yield-scaled N_2O plus N_2 were 2.69, 1.46, 1.64, and 1.67 kg N Mg^{-1} grain in CK, LN, MN, and HN, respectively (Fig. 7C). The lowest yield-scaled N_2O plus N_2 were observed in LN, and interestingly no statistical difference was observed among N fertilized

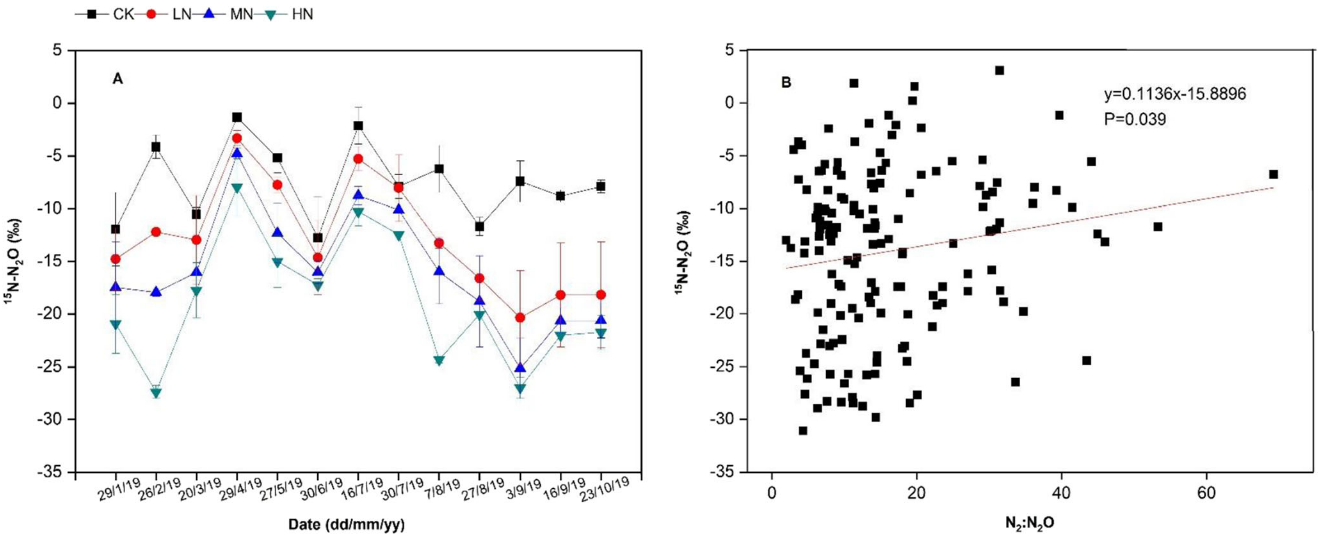

Fig. 6 ^{15}N isotopic signatures in soil-emitted N_2O from unfertilized and N fertilized treatments (**a**) and relationship between N_2/N_2O emission ratios and $\delta^{15}N$ of soil-emitted N_2O (**b**)

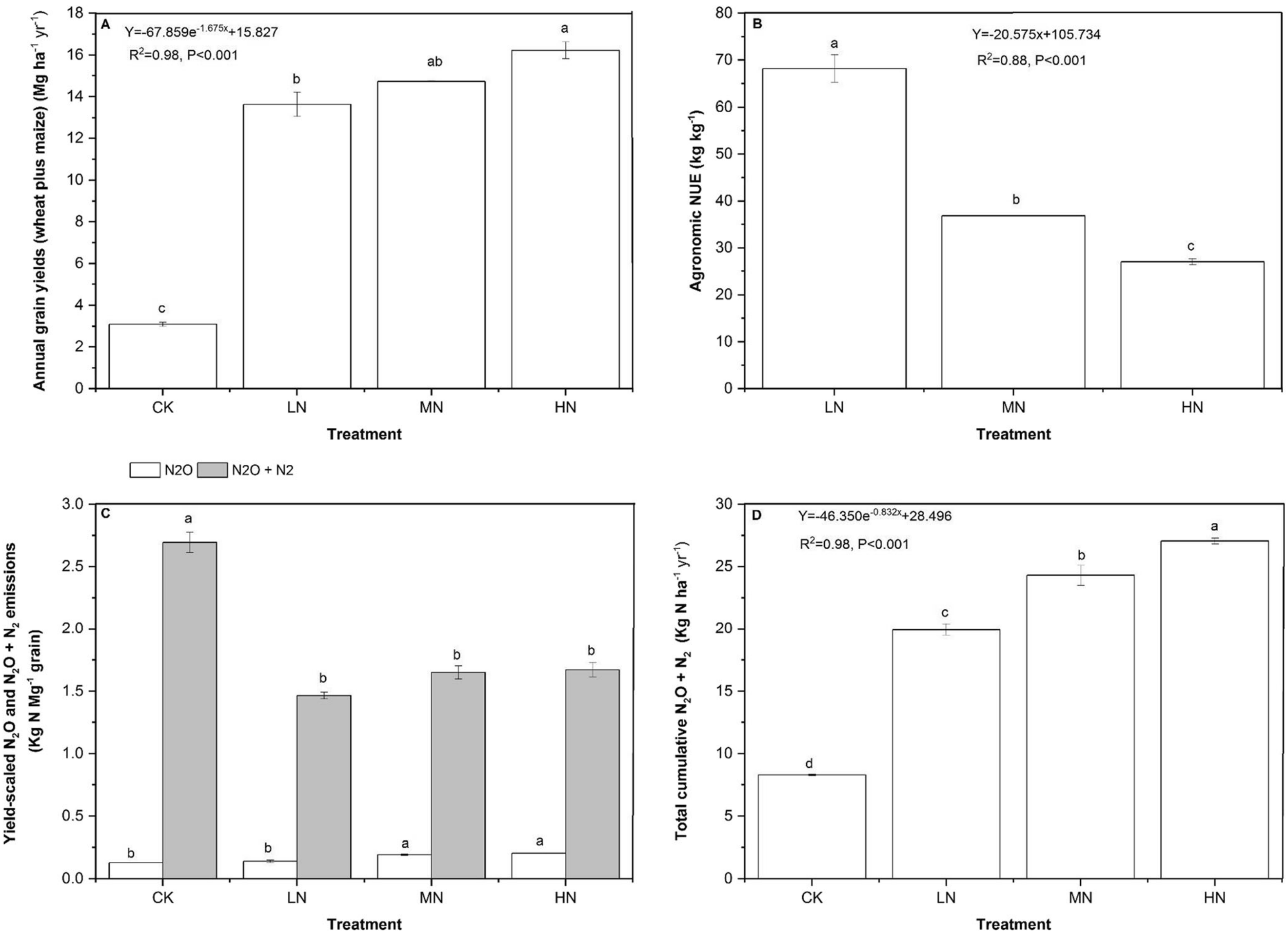

Fig. 7 Annual grain yields (wheat plus maize) (A). Agronomic nitrogen use efficiency (NUE) (B). Yield-scaled N_2O and $N_2O + N_2$ (kg N Mg^{-1} grain) (C). Total cumulative N_2O plus N_2 in response to N fertilizer rates (D). Data point refers to mean ± stand error ($n = 3$) and lowercase letters denote significant differences between treatments

treatments, but there was a statistical difference between N fertilized treatments and CK. However, yield-scaled N_2O emissions ranged from 0.13 to 0.20 kg N Mg^{-1} grain. The yield-scaled N_2O emissions followed the order hereafter: HM>MN>LN>CK, and they were 1.56, 1.47, and 1.07 times greater than CK, respectively. Statistical difference was observed between CK and N fertilized treatment MN and HN, while no statistical difference was observed between CK and LN treatments (Fig. 7C).

4 Discussion

4.1 Fluxes of N_2O and N_2, their ratios N_2/N_2O, and controlling factors from agricultural soil

In the current study, we aimed to relate soil-climate controlling factors to N_2O and N_2 emissions and even their ratios N_2/N_2O. The results indicated that N_2O emissions responded to N fertilizer rates among fertilized treatments and were far large compared to unfertilized soil (CK). Thus, annual cumulative N_2O emissions increased with increasing N input rates as given in details hereafter, 0.40, 1.91, 2.83, and 3.30 kg N ha^{-1} $year^{-1}$ from CK, LN, MN, and HN treatments respectively (Fig. 4). Our findings were supported by many previous studies reporting the responses of N_2O emissions to N fertilizer rates (e.g., Huang et al. 2017; Song et al. 2018). N_2O emissions on the daily basis range from 0.4 to 36.8 g N ha^{-1} day^{-1} (Fig. 3a); our results are in agreement with the previous studies (Song et al. 2018; Chen et al. 2019; Wang et al. 2020) in agricultural soils. The N fertilization in combination with flooding irrigation results in remarkable peaks of N_2O emissions, indicating that high soil WFPS accelerated the denitrification process (Fig. 2d) in combination with N inputs.

Overall, N_2O fluxes are positively related to NH_4^+-N, WFPS, NO_3^--N, and DOC (Fig. 5). NH_4^+-N and NO_3^--N are the main substrate for nitrification and denitrification, respectively (Butterbach-Bahl et al. 2013). Moreover, positive relationships between soil N_2O emissions and NH_4^+-N and NO_3^--N denote that both the nitrification and denitrification occurred at our study site, and our results were supported by various studies (Baggs 2008; Park et al. 2011; Baily et al. 2012; Li et al. 2020). The positive relationship between WFPS and N_2O emissions confirms that high WFPS can accelerate denitrification process by creating anaerobic condition (Butterbach-Bahl et al. 2013; Hu et al. 2013). The positive relationship between N_2O emissions and soil DOC in our study explained that readily available carbon accelerates denitrification. Low temperature at 5-cm depth and rainfall was observed during winter, and similarly N_2O emissions were also low. The reason for this may be due to the fact that nitrifying and denitrifying bacteria were in unfavorable conditions. The previous studies reported that when soil temperature was below 10 °C, bacteria responsible for nitrification and denitrification also became dormant (Smith et al. 2010; Hu et al. 2013). Soil moisture (WFPS) is mainly attributed to flood irrigation and precipitation during our study period, and N_2O emission peaks are observed after N fertilizer application and flood irrigation (Fig. 3a).

Annual cumulative N_2 fluxes are larger than N_2O fluxes in our current study. This has evidently shown the potentiality of N_2 emissions from direct measurement method as obtained hereafter: 7.89, 18.02, 21.46, and 23.73 kg N ha^{-1} $year^{-1}$ from CK, LN, MN, and HN treatments respectively (Fig. 4). Daily N_2 emissions range from 13.5 to 109.8 g N per hectare per day (Fig. 3b). Based on structural equation modeling applied in this study, N_2 fluxes are positively related to DOC, NO_3^--N, WFPS, and soil temperature at 5-cm depth (Fig. 5). The current study is consistent with findings reported by Yuan et al. (2019) emphasizing that DOC strongly induces denitrification rate. Many previous studies also found relationships between N_2 emissions and temperature (e.g., Butterbach-Bahl et al. 2002; Hu et al. 2013). Wang et al. (2020) by using a modified gas-flow-soil-core method reported 7.2 and 2.4 kg N ha^{-1} cumulative N_2O and N_2, respectively, in summer maize season by applying 260 kg N ha^{-1}, and these results confirmed that N_2 emissions were dominant N losses in agricultural soil. Moreover, similar results have been observed in our current study that N fertilizer application rates enhanced more N_2 fluxes than N_2O (Fig. 4). So, we conclude that high cumulative N_2 emissions from long-term N fertilized treatments might be due to higher available DOC along with N inputs that induced NO_3^- in our study site (Fig. 2b, c). This enhances the evidence that the presence of high DOC, NO_3^- , WFPS, and soil temperature is a conducive condition for high N_2 fluxes (Fig. 5).

The current study has revealed that the mean N_2/N_2O emission ratios at the end of this study are 20.9, 13.2, 11.4, and 10.3 from CK, LN, MN, and HN treatments, respectively (Fig. 4). The daily N_2/N_2O emission ratio ranges from 1.7 to 34.6 (Fig. 3c). Our findings are in agreement with previous studies that have documented that N_2 emissions are the main N losses from denitrification, hence higher N_2/N_2O emission ratios (Werner et al. 2014; Chen et al. 2019; Wang et al. 2020). Overall total treatments, N_2/N_2O emission ratios are negatively related to NH_4^+ and NO_3^- and positively to soil temperature at 5-cm depth (Fig. 5). As both NH_4^+ and NO_3^- increased with the increase of N inputs compared to control treatment (Fig. 2a, b), while N_2/N_2O ratio decreased with the increase of N inputs compared to control treatment, this might have led to negative relationship between the N_2/N_2O ratio and NH_4^+ and NO_3^-.

The relatively high overall mean N_2/N_2O emission ratios throughout the year (Fig. 4) gave more insights on the N losses in a form of N_2 since within global N cycle, N_2 fluxes from soils were poorly understood due to the difficulties to measure them (Galloway et al. 2008; Groffman 2012). Qin et al. (2012) reported that low N_2 emissions from agricultural soil were reported basically using the C_2H_2 inhibition technique, which possibly underestimate N_2 emissions, hence leading to low N_2/N_2O emission ratios. We report that overall mean N_2/N_2O emission ratios are negative exponentially correlated to N fertilizer rates (Fig.4). So, it has been recommended that more N_2 production is stimulated in higher temperature (Saggar et al. 2013; Wang et al. 2020), leading to positive relationship between soil temperature and N_2/N_2O ratio (Fig. 5).

4.2 Annual cumulative N_2O and N_2 emissions and the overall mean N_2/N_2O ratios in response to N fertilizer application rates

The cumulative N_2O and N_2 emissions increased exponentially at $P < 0.006$ and $P < 0.015$, respectively; however, the N_2/N_2O ratios decrease exponentially at $P < 0.016$ with the increase of N fertilizer application rates (Fig. 4). The exponential relationships between N fertilizer application rates and N_2O, N_2 and N_2/N_2O ratios might be due to exceeding the optimum N fertilizer rates (Song et al. 2018).

Interestingly, N fertilizer application rates greatly increased N_2O emissions by 4.7, 7.0, and 8. 2 times higher in LN, MN, and HN than the CK soil. However, the fertilization application rates only increase N_2 emission by 2.2, 2.7, and 3.0 times higher in LN, MN, and HN than CK soil. This shows that fertilization greatly increases N_2O but not N_2 to that extent. This might be the reason for the negative exponential relationship between N fertilizer application rate and N_2/N_2O ratios. The total measured N_2O plus N_2 fluxes in our study are 8.3, 20.9, 24.3, and 27.0 kg N ha^{-1} $year^{-1}$ from CK, LN, MN, and HN treatments, respectively (Fig. 7D). As there is a chance for denitrification under lower soil profiles (Wang et al. 2013; Yuan et al. 2019), there is a possibility that we missed some gaseous N_2O and N_2 emissions underground since we only measured upper 10 cm of the soil profile. Moreover, recent studies further suggest that plants may also have NO_3^--NO_2^--NO-N_2O

pathway of N_2O production (Timilsina et al. 2020a; Timilsina et al. 2020b) which possibly indicates the underestimation of denitrification pathway in our study.

4.3 The $\delta^{15}N$ of soil-emitted N_2O and its relationship with the measured parameters

It is evidently shown that highly fertilized soils have more depleted isotopic signatures, while unfertilized soils are less depleted (Fig. 6a). The highly depleted and less depleted values of ^{15}N isotope of soil-emitted N_2O are − 29.83‰ and − 3.66‰ (HN); − 31.06‰ and − 3.96‰ (MN); − 28.72‰ and − 1.92‰ (LN); and − 25.66‰ and 1.62‰ (CK), respectively (Fig. 6a). The mean values of ^{15}N in soil-emitted N_2O were − 7.89 ± 0.88, − 13.61 ± 1.21, − 16.13 ± 1.12, and − 18.54 ± 1.11 from CK, LN, MN, and HN treatments, respectively. There were significant differences ($P < 0.001$) of ^{15}N in soil-emitted N_2O between unfertilized (CK) and fertilized (LN, MN, and HN) treatments, while within fertilized treatments, i.e., LN and HN have significant difference ($P < 0.01$). The values of ^{15}N in soil-emitted N_2O from the current study were consistently observed within range from various previous studies (Pérez et al. 2001; Xiong et al. 2009; Park et al. 2011; Timilsina et al., 2020c). Previously ^{15}N in soil-emitted N_2O were used to predicate the N_2O formation processes in the soil; however, using only ^{15}N in soil-emitted N_2O may mislead interpretation (Xiong et al. 2009; Timilsina et al., 2020c) because there was no any relationship between ^{15}N in soil-emitted N_2O and other soil parameters (like WFPS, NO_3^-, NH_4^+, DOC) in our study. Therefore, it may mislead the conclusion as well. Moreover, more powerful tool like site preference of N_2O was not used in our study to describe the pathways of N_2O formation (Park et al. 2011; Timilsina et al., 2020c). Nevertheless, ^{15}N composition of soil-emitted N_2O shows relationship only with N_2/N_2O ratio (Fig. 6b). To our knowledge, this is the first study to evaluate the relationship between gaseous N_2O and N_2 measured simultaneously using direct soil core measurement method and ^{15}N isotopic compositions of N_2O emitted. The ^{15}N isotopic signatures of soil-emitted N_2O from unfertilized and fertilized soils are greatly different (Pérez et al. 2001; Park et al. 2011; Timilsina et al., 2020c). The current study is consistent with the previous studies where it demonstrates the clear difference between fertilized and unfertilized soil. N_2O produced during nitrification is more depleted as a fractionation factor by the nitrification process is generally higher than the denitrification process (Yoshida 1988; Baggs 2008). The results of our study show a positive significant correlation between the N_2/N_2O emission ratios and the $\delta^{15}N$-N_2O at $P < 0.0366$ (Fig. 6b), indicating that N_2O emissions were mainly delivered from denitrification process, while nitrification may probably contributed less.

4.4 Responses of wheat-maize annual grain yields; annual cumulative N_2O and N_2 emissions; yield-scaled N_2O and N_2 emissions to N fertilizer rates

Considering agronomic NUE, yield-scaled N_2O and N_2O plus N_2 emissions, the annual grain yields, and total N_2O plus N_2, we proposed that sustainable agricultural practices can be achieved at LN (200 kg N ha^{-1} $year^{-1}$), indicating that adopting this N fertilizer input will decrease 50% as compared to current farmers' practice of 400 kg N ha^{-1} $year^{-1}$ in this agricultural region with no grain yields decrease. This is enhanced by exponential relationship between N fertilizer rates and the annual grain yields with no statistical difference between LN and MN treatments (Fig. 7A). Therefore, a linear relationship is observed between agronomic NUE and N fertilized treatments (Fig. 7B). Interestingly, the optimal N input proposed in the current study will curb as much as 66.7% of N inputs from conventional N fertilizer rate of 600 kg N ha^{-1} $year^{-1}$. The current findings are in agreement with Huang et al., (2017) that compared optimal N input (294 kg N ha^{-1} $year^{-1}$) against conventional N input (560 kg N ha^{-1} $year^{-1}$), and the results proved that 48% reduction of N fertilizer rate had occurred due to that shift with no significant decrease in grain yields. Hence, their practices also reduced cumulative N_2O and yield-scaled N_2O emissions by 18% and 38%, respectively. In our site, cumulative N_2O emissions in LN were reduced by 32.5 % and 42% as compared to MN and HN, respectively. Evidently, Ju et al. (2009) reported that up to 50% of N losses to the environment can be cut off with no statistical crop yield decrease, while N input would be reduced up to 30–60%. Yield-scaled N_2O in LN decreased by 27.0% and 31.3% as compared to MN and HN, respectively. While yield-scaled N_2O plus N_2 in LN reduced by 11.2% and 12.3% as compared to MN and HN, respectively. Our study is first to report yield-scaled N_2O and N_2; there are no existing data to compare with our findings.

In the current study, yield-scaled N_2O emissions are ranging from 0.13 to 0.20 kg N Mg^{-1} grain (Fig. 7C), and they are similar to those found by Huang et al. (2017) (0.142 to 0.304 kg N Mg^{-1} grain) for maize-wheat double cropping system in NCP, for maize-soybean rotation and single maize (Adviento-Borbe et al. 2007) (0.079 to 0.3 kg N Mg^{-1} grain), (0.099 to 0.281 kg N Mg^{-1} grain), respectively, and for continuous maize by Mosier et al. (2006) (0.064 to 0.31 kg N Mg^{-1} grain). However, in the current study, the reported yield-scaled N_2O plus N_2 ranging from 1.46 to 2.69 kg N Mg^{-1} grain (Fig. 7C) are new findings and have never been reported before. As N is major macronutrient for crops in agricultural soils, both N_2O and N_2 emissions are forms of N losses that may be a matter of concern for optimum crop production and sustainable dosage of N input, even though inert N_2 does not harm the atmosphere. Thus, enhancement of environmental sustainability and optimum cereal yields when excessive N fertilizer is cut off while N_2O emissions reduced was previously suggested (e.g., Sun and Huang 2012; Tian et al. 2012).

5 Conclusion

Long-term N fertilizer inputs have resulted in higher DOC, NO_3^-, and NH_4^+ in LN, MN, and HN compared to CK treatment. Moreover, this led to higher rates of N_2O and N_2. Both positive and negative relationships between soil-environmental parameters and N_2O, N_2, and N_2/N_2O ratio indicate their heterogeneous roles in N_2O formation and reduction processes. Decreasing the ratio of N_2/N_2O with the increase of N fertilizer application rates indicates that N_2O and N_2 depend on the N fertilizer application rates. The positive relation between ^{15}N isotope of N_2O and N_2/N_2O ratio indicates that denitrification might be the main process of N_2O formation in the wheat and maize agricultural soil. The exponential relationships between emissions of N_2O, N_2, N_2/N_2O, and N fertilizer application rates indicate the excessive N input compared to the crop need at the current study site. For the environmental risk protection, there is a need to apply optimal N in agro-ecosystem in a way to increase yield along with alleviating detrimental environmental consequences caused by overdose from long-term N application. So, treatment that received 200 kg N ha^{-1} $year^{-1}$ was observed as optimum and future sustainable agricultural practice because it has high agronomic NUE, optimal wheat-maize annual grain yields, low yield-scaled N_2O emissions, and low N_2O plus N_2 emissions as compared to MN and HN treatments in North China Plain. Future research should focus not only on NO_3^- leaching and N_2O emissions but also emissions of N_2 along with crop productivity in the intensive agricultural soils using different crops.

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Declarations

Conflicts of interest Authors declare no conflicts of interest.

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