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Reducing N_2O emissions with enhanced efficiency nitrogen fertilizers (EENFs) in a high-yielding spring maize system

Xiaodong Lyu [a, b, 1], Ting Wang [c, 1], Xiaotong Song [d], Chuanyan, Zhao [e], Robert M Rees [f], Zhan Liu [g], Xiaotang, Ju [d, *], Kadambot H.M. Siddique [h]

[a] School of Environmental and Municipal Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

[b] Key laboratory of Yellow River Water Environment in Gansu Province, Lanzhou Jiaotong University, Lanzhou 730070, China

[c] Institute of Soil, Fertilizer and Water-saving Agriculture, Gansu Academy of Agricultural Sciences, Lanzhou 730070, China

[d] College of Tropical Crops, Hainan University, Haikou 570228, China

[e] College of Pastoral Agriculture Science and Technology, Lanzhou University, Lanzhou 730030, China

[f] SRUC, West Mains Rd. Edinburgh, EH9 3JG, Scotland, UK

[g] Gansu Key Laboratory for Environmental Pollution Prediction and Control, College of Earth and Environmental Sciences, Lanzhou University, Lanzhou 730030, China

[h] The UWA Institute of Agriculture and School of Agriculture & Environment, The University of Western Australia, Perth, WA 6001, Australia

[1] The authors contributed equally to this work.

* Corresponding author: **Xiaotang Ju**

Tel: +86-10-13426072652; E-mail address: juxt@cau.edu.cn.

Abstract

Enhanced efficiency nitrogen fertilizers (EENFs), including nitrification inhibitors (NIs) and slow-release fertilizer (SRF), are considered promising approaches for mitigating nitrous oxide (N_2O) emissions while improving crop yield. This study investigated the combined application of EENFs with improved water and fertilizer management in an intensively irrigated spring maize rotation over five years in Northwestern China. High-frequency measurements of N_2O fluxes were made throughout each year (both during crop growth and the fallow season) in five treatments: no N fertilizer as a control (CK), conventional N fertilization and irrigation (Con), optimum N fertilization and irrigation (Opt, 33% reduction in N fertilizer and 25% reduction of irrigation water), optimum N fertilization and irrigation with nitrification inhibitor (Opt+NI), and optimum N fertilization and irrigation with slow-release fertilizer (Opt-SRF). Annual mean cumulative N_2O emissions reached 0.31±0.07, 3.66±0.19, 1.87±0.16, 1.23±0.13, and 1.61±0.16 kg N_2O-N ha^{-1} for CK, Con, Opt, Opt+NI, and Opt-SRF, respectively, with annual mean nitrogen use efficiency (NUE) of 36, 54, 61 and 59% for Con, Opt, Opt+NI, and Opt-SRF, respectively. The Opt, Opt+NI and Opt-SRF treatments significantly reduced cumulative N_2O emissions by 49%, 66%, and 56% ($P < 0.05$), respectively, and increased NUE by 51%, 70%, and 66% ($P < 0.05$), respectively, relative to Con. However, mean above-ground N uptake (288–309 kg N ha^{-1}) and mean grain yields (12.7–12.8 Mg ha^{-1}) did not differ significantly between the Con, Opt, Opt+NI, and Opt-SRF treatments during the five-year study. High N_2O emissions mainly occured within a few days of fertilization with irrigation, which could have been produced by microbially-mediated nitrifier or nitrifier denitrification processes. The fallow seasons had significantly lower cumulative N_2O emissions, which were mainly

attributed to the low temperature, low N inputs of crop residues, and low soil moisture conditions. Our study clearly indicated that the combined application of EENFs with optimum N fertilization and irrigation management can reduce environmental impacts while maintaining high crop yields in dryland regions such as Northwest China.

Keywords: N_2O emission, enhanced efficiency nitrogen fertilizers (EENFs), nitrification inhibitors (NIs), slow-release fertilizer (SRF), spring maize, China

1. Introduction

While the use of synthetic N fertilizers in agriculture has increased crop yields and helped to deliver global food security (Ma *et al.*, 2013), it raises environmental concerns associated with nitrogen (N) losses by nitrous oxide (N_2O) emissions (Liu *et al.*, 2017), ammonia (NH_3) volatilization, and nitrate (NO_3^-) leaching (Norse and Ju, 2015; Ju and Zhang, 2017). Nitrous oxide is an important greenhouse gas, which plays a major role in climate change (Montzka *et al.*, 2011) and the depletion of stratosphere ozone (Ravishankara *et al.*, 2009). More than 60% of total anthropogenic N_2O emissions come from agricultural soils (Smith *et al.*, 2014); the contribution of synthetic N fertilizers to these emissions grew, on average, by 19% annually from 0.07 to 0.68 Gt CO_2 eq yr^{-1} between 1961 and 2010 (Tubiello *et al.*, 2013). It is therefore important to develop new approaches to N_2O mitigation in response to the overuse of N fertilizers (Chen *et al.*, 2014; Snyder, 2017).

Previous studies on N_2O emissions from croplands in China have mainly been undertaken on paddy rice systems in the southeast along the Yangtze River basin (Yao *et al.*, 2009; Chen *et al.*, 2017; Wang *et al.*, 2018b; Yang *et al.*, 2018), winter wheat–summer maize systems in the North China Plain (Gao *et al.*, 2014; Gao *et al.*, 2015; Liu *et al.*, 2016; Huang *et al.*, 2017; Song *et al.*, 2018; Wang *et al.*, 2018a; Xiao *et al.*, 2019; Zhang *et al.*, 2019), rainfed cropping systems on the Loess Plateau (Wang *et al.*, 2016; Htun *et al.*, 2017), and spring maize in the northeast (Qiao *et al.*, 2014; Yang *et al.*, 2014). However, there is limited data on N_2O emissions from irrigated farmland in the arid oases in Northwest China. Irrigated spring maize in this area accounts for about 70% of seed maize production in China (Qin *et al.*, 2019), and provides more than 60% of the grain for Gansu province (Gao *et al.*, 2002). Spring maize yields can reach up to 12.8–15.5 Mg ha^{-1} yr^{-1} under intensive management (Sun *et al.*, 2012), requiring more than 600 mm yr^{-1} water (flood irrigation) and 450 kg ha^{-1} of N fertilizer combined with plastic film-mulch (Chai and Huang, 2011; Hou *et al.*, 2017), and resulting in low water and N use efficiencies (Li *et al.*, 2016; Chen *et al.*, 2018), more serious water shortages (Xiong *et al.*, 2010; Zhao *et al.*, 2018), and potential risk of high N_2O emissions (Ju *et al.*, 2009; Ju and Zhang, 2017). Therefore, it is imperative to change conventional water and N management to improve the overall sustainability of these farmed environments including the control of N_2O emissions.

Enhanced efficiency nitrogen fertilizers (EENFs), such as nitrification inhibitors (NIs) and slow-release fertilizer (SRF), can increase N use efficiency (NUE) and reduce N loss (Sun et al., 2019; Wu et al., 2018) by reducing the availability of substrates for microbial nitrification or denitrification (Halvorson *et al.*, 2014; Feng *et al.*, 2016). For instance, NIs can slow down the conversion of ammonia (NH_4^+) to nitrate (NO_3^-) by inhibiting the activities of nitrifying bacteria in soil (Ruser and Schulz, 2015); while SRF control the rate of N release to soil, thus better matching crop N uptake (Wei *et al.*, 2018). NIs can reduce N_2O losses by 39–48% and increase grain yield by an average of 9% (with a range of 6–13%), and are more effective at reducing N_2O emissions than SRF (19%) (Qiao *et al.*, 2015; Thapa *et al.*, 2016). Rose et al.

(2018) reported that EENF products achieve significantly higher yields than conventional N fertilisers (11%, $P < 0.05$). Our previous study reported that the cumulative N_2O emissions declined by 34–45% in an intensified spring wheat system in the Hexi Corridor treated with a combined application of EENFs with optimum N fertilization and irrigation, relative to the conventional fertilization and irrigation, but there was little impact on grain yield (Lyu *et al.*2019). However, some studies showed that EENFs had no effect or even increased N_2O emissions (Dell *et al.*, 2014; Parkin and Hatfield, 2014). A recent meta-analysis showed that the efficiency of EENFs in wheat and maize were complicated and generally lower than in paddy rice systems (Li *et al.*, 2018). The effects of EENFs on N_2O emissions and crop yields could be affected by climate and edaphic conditions, cropping systems and agronomy (Gilsanz *et al.*, 2016; Thapa *et al.*, 2016; Aliyu *et al.*, 2018). However, the characteristics and mechanisms of N_2O production affected by the use of EENFs in arid irrigated regions has not been well documented.

In this study, we conducted high-frequency measurements of N_2O fluxes and environmental conditions (soil mineral N concentration, temperature, and soil moisture) throughout the year, which were linked to simultaneous measurements of aboveground biomass, crop yield, and N uptake in five treatments with different N and water management over five years. The main objectives were to quantify N_2O emissions and reveal the underlying mechanisms of N_2O production during both the growing season (GS, April to October) and fallow season (FS, November to March), and evaluate the effects of EENFs on N_2O emissions, grain yield, yield-scaled N_2O emissions, and nitrogen use efficiency in an intensive spring maize system.

2. Materials and methods

2.1. Experimental site

The study was conducted from 2011 to 2016 at the Zhangye Water-Saving Experimental Station of Gansu Academy of Agricultural Sciences (38°56′ N, 100°26′ E, altitude 1570 m), 9 km north of Zhangye city in the middle of the Hexi Corridor, Gansu Province, Northwest China. The climatic characteristics of this region are described by Lyu *et al.* (2019). Spring maize (*Zea mays* L.) is planted in mid-April and harvested in mid-October; the growing season (GS) is about 180 days and fallow season (FS) is about 185 days. The soil at the experimental site is an anthropogenic–alluvial soil according to the Chinese soil classification system (fluvent according to the FAO–UNESCO system), with a sandy loam texture (59.8% sand, 33.8% silt and 6.4% clay). In 2011, the 0–20 cm soil layer had a bulk density of 1.36 g cm^{-3}, pH 8.2, 0.87 g kg^{-1} total N, 12.5 g kg^{-1} organic matter, 13.7 mg kg^{-1} Olsen-P and 120.2 mg kg^{-1} available K. These values were determined from one composite soil sample across the experimental field before the start of the experiment.

Annual mean air temperature from 2011–2015 was about 8.4 ℃, or 1 ℃ higher than the average for the past 58 years (1958–2015). Annual mean soil temperature at 10 cm depth was 13.2°C during the five-year study. Precipitation in 2011 was 80.8 mm, or 38.3% lower than the average for the past 58 years (1958–2015), but close to the average for 2012–2015. Two extremely high precipitation events (> 20 mm) occurred, one in 2012 (40.8 mm, 27 June) and the other in 2013 (24.4 mm, 14 July) (Fig. 1).

2.2. Experimental design and field management

A randomized block design was established with five treatments and four replicates, with plot areas of 5 m × 7 m. The treatments were (i) CK, no N fertilizer as a control, (ii) Con, local farmer conventional N fertilization and irrigation, (iii) Opt, optimum N fertilization and irrigation, (iv) Opt+NI, optimum N fertilization and irrigation with nitrification inhibitor (NI), (v) Opt-SRF, optimum irrigation and N fertilization with slow-release fertilizer. Field management in the five treatments during the five-year study is shown in Tables S1 and S2.

For the conventional treatment, nitrogen fertilizer (granular urea, containing 46% N) was applied on three occasions; basal at sowing (40%), first top-dressing (30%, jointing stage), second top-dressing (30%, bell-mouthed stage), at a rate of 450 kg N ha^{-1} yr^{-1}. The basal fertilizer was surface broadcast and incorporated by rotary tillage (about 15 cm depth) before seeding, and the topdressing was band applied near plant rows at 5 cm depth just before irrigation. The optimum N treatment had 300 kg N ha^{-1} yr^{-1} applied to match the target yield (Ju and Christie, 2011; Ju, 2015) in four applications—basal at sowing (30%), first topdressing (20%, jointing stage), second topdressing (30%, bell-mouthed stage), and third top-dressing (20%, tassel stage). For the Opt+NI treatment, dicyandiamide (DCD) was used as a nitrification inhibitor at a rate of 5% of the applied N. It was thoroughly mixed with the fertilizer before application. For the Opt-SRF treatment, slow-release fertilizer (26N: 13P_2O_5: 7K_2O, Shikefeng Chemical Industry Co., Ltd., China) was applied at 1154 kg ha^{-1} (300 kg N ha^{-1}) as a basal fertilizer before sowing. Each plot received 150 kg P_2O_5 ha^{-1} (calcium superphosphate, containing 12% P_2O_5) and 80.8 kg K_2O ha^{-1} (potassium sulfate, containing 30% K_2O) at sowing with the basal N fertilizer.

The irrigation quota (IQ) of the conventional and optimum treatments were 600 and 450 mm (Lian *et al.*, 2013), respectively, which were applied by flood irrigation at the jointing

(20%), bell-mouthed (30%), tassel (30%) and milking (20%) stages. Winter irrigation for all treatments (225 mm) was applied in late November to maintain soil moisture for seed germination and emergence in the following year.

A high-yielding spring maize cultivar (Yuyu 22) was planted at 80,000 plants ha^{-1} in uniform rows (50 cm apart) using a manual seeder. All plots had half-film mulching. The residual straw after harvest was removed from all plots and the soil was tilled at sowing using rotary tillage (to a depth of 15 cm). Weeds were removed by hand and chemical herbicide (2, 4-D butylate) was applied three times during each maize growing season.

2.3. Measurement of N_2O emissions

High-frequency measurements of N_2O emissions (quantified in the following paragraph) were undertaken year round (during crop growth and the fallow season) in each plot from April 2011 to April 2016 using the closed static chamber method described by Wang and Wang (2003) and Zheng *et al.* (2008). A modular stainless-steel chamber was designed with 50 cm length × 30 cm width × 20 cm height and matched to a base frame (50 cm length × 30 cm width × 15 cm height) (see Figure S1); A powerful alligator clip was used to seal the upper chamber to the frame. A 10 cm × 10 cm square hole at the top of chamber allowed for spring maize growth. The chambers were equipped with a thermometer for measuring air temperature, a Teflon tube for sampling gas by a syringe, a vent for balancing air pressure inside and outside the chamber, and two fans at opposite angles to ensure complete mixing of air inside the chamber. The chamber was covered with insulating material to minimize the change in air temperature in the chamber during summer to less than 3°C within a closure period of 45 min (Gao *et al.*, 2014). The base frame was inserted into the soil to a depth of 15 cm in each plot and remained in place until tillage at the end of the year. Before gas sampling, the chambers were mounted onto base frames and sealed with rubber strips and clamps. Between 09:00 am and 11:00 am (Shi *et al.*, 2013), four 50 ml gas samples were taken using a plastic polypropylene syringe through a three-way stopcock and a Teflon tube connected to the chamber with an interval of 15 min (0, 15, 30 and 45 min) after chamber closure.

Gas samples were taken every day for 7–10 days after fertilization, irrigation and/or rainfall (>20 mm) events from April 15, 2011 to April. 15, 2016; at other times, gas samples were taken every 3 days, or monthly during soil freezing (mid-November to mid-March of the following year) (Li *et al.*, 2018). These measurements were high-frequency as compared to low frequency often taken only once every 1–2 weeks (Davies et al., 2020). Gas samples were analyzed within 10 h using a modified gas chromatograph (Agilent 7890A, Agilent Technologies, USA) equipped with a ^{63}Ni-electron capture detector at 350℃ (Huang *et al.*, 2017).

The N_2O fluxes were calculated using a linear or non-linear model (Kroon *et al.*, 2008; Hu *et al.*, 2013). The cumulative emissions were calculated using the direct linear interpolation method (Mosier *et al.*, 2006). More details were presented in the supplementary materials.

The direct emission factors (EF_{N_2O}) were calculated as:

$$EF_{N_2O}\,(\%)=\frac{E_F-E_0}{R_F}\times 100\% \tag{1}$$

where E_F and E_0 are the annual N_2O emissions (kg N_2O-N ha^{-1}) from the N fertilizer and CK plots, respectively. R_F represents the annual rate of fertilizer N (kg N ha^{-1}).

Yield-scaled N_2O emissions (YSNEs) were calculated as:

$$\text{Yield-scaled } N_2O \text{ emissions (g N kg}^{-1}\text{ grain)} = \frac{\text{Cumulative } N_2O \text{ emissions}}{\text{Yield}} \tag{2}$$

2.4. Measurements of climate and soil data

Climatic data in the experimental station, soil temperature (10 cm depth) and air temperature in the chamber for calculating the N_2O fluxes, and soil sampling for measuring the water-filled pore space (WFPS) and soil mineral N at a depth of 20 cm was required for this study. Accompanying N_2O sampling, soil sampling was carried out after 1, 3, 5, 7 and/or 9 days following fertilization and irrigation events, and every 8 days at other times. Samples in the winter (January to March) were not collected due to soil freezing.

The grain and straw yields of spring maize were manually harvested from a 2 m × 5 m area in the middle of each plot. Total N concentration in the aboveground biomass was analyzed using an elemental CN analyzer (Thermo Flash EA 1112 Flash, 2000, USA).

2.5. Statistical analysis

Statistical analyses were conducted by SPSS 19.0 (SPSS Inc., Chicago, IL, USA). The differences in cumulative N_2O emissions, YSNEs, grain yields, EF_{N_2O}, aboveground N uptake and NUE across the five years, as affected by different treatments, years and their interactions were examined using factorial ANOVA analysis. Least significant differences (LSD) tests were used to examine the differences between the mean values, and significant differences were reported at $P < 0.05$. Pearson's correlation analysis was performed to identify correlations between N_2O emissions and environmental factors. The boundary line approach was used to analyze the relationships between N_2O emissions and soil surface temperature and WFPS in the topsoil (Schmidt *et al.*, 2000).

3. Results

3.1. N_2O fluxes and cumulative N_2O emissions

Emissions of N_2O peaked within 3–5 days after fertilization following irrigation events during the growing season, with small peaks after tillage or single irrigation events, but remained low during the fallow season (Fig. 2). The highest N_2O fluxes occurred 3–5 days after the first top dressing of N fertilizer with irrigation (jointing stage, early June). At this time, the N_2O peaks in the Con treatment reached 852, 998, 646, 1189, and 896 μg N_2O-N m^{-2} h^{-1} in 2011, 2012, 2013, 2014, and 2015, respectively, and were significantly higher than those in the Opt, Opt+NI, and Opt-SRF treatments. The Opt+NI and Opt-SRF treatments had lower N_2O peaks (109–488 μg N_2O-N m^{-2} h^{-1}) than the Opt treatment (398–890 μg N_2O-N m^{-2} h^{-1}).

Cumulative N_2O emissions between treatments and years differed significantly, and their interactions varied considerably (Table1, Table S3). Compared to CK, annual cumulative N_2O emissions from the N-fertilized treatments increased significantly ($P < 0.05$). However, the Opt, Opt+NI and Opt-SRF treatments had significantly lower ($P < 0.05$) annual cumulative N_2O emissions, with average reductions of 48, 66 and 56%, relative to Con treatment, respectively. Furthermore, the Opt+NI treatment had the lowest emissions, being 23% less than the Opt-SRF treatment. Significant inter-annual variations in cumulative N_2O emissions were observed in the Opt+NI and Opt-SRF treatments ($P < 0.05$, Table 1, Table S3). For instance, the highest annual cumulative N_2O emission in the Opt+NI treatment was 1.54 kg N_2O-N ha^{-1} in 2011, and the lowest was 0.88 kg N_2O-N ha^{-1} in 2015, with no significant differences between 2012, 2013, and 2014 (1.16–1.34 kg N_2O-N ha^{-1}). Cumulative N_2O emissions during the GS were significantly higher than those in the FS in all treatments, with the GS accounting for 97–98% of the annual cumulative N_2O emissions (Table 1).

Cumulative N_2O emissions in the ten days after fertilization and/or irrigation at the different growing stages differed significantly between the N-fertilized treatments ($P < 0.05$) (Table S4). For instance, at the jointing stage, emissions were 1098, 552, 221, and 213 g N_2O-

N ha^{-1} in the Con, Opt, Opt+NI, and Opt-SRF treatments, respectively, accounting for 30, 29, 18, and 14% of annual N_2O emissions, respectively (Table S4). Two higher N_2O peaks occurred following the second and third topdressing of N fertilizer and irrigation, at the bell-mouthed (early July) and tassel stages (late July), which accounted for 10–20% and 5–11% of the annual N_2O emissions in the N-fertilized treatments, respectively (Table S4). Two small N_2O peaks were observed after basal fertilization (late March) and the fourth irrigation at the milking stage (late August), accounting for 4–6% and 2–5% of annual N_2O emissions, respectively (Table S4).

3.2. Grain yield

The application of EENFs did not reduce the grain yield compared with conventional fertilizers (Fig. 3a). Grain yields differed significantly between the Con, Opt, Opt+NI, and Opt-SRF treatments in 2011 and 2012, but not in 2013, 2014 and 2015 ($P < 0.05$). There were no significant differences between the Opt, Opt+NI and Opt-SRF treatments each year. Mean grain yields ranged from 12.7–12.8 Mg ha^{-1} in the optimum N-fertilized treatments, which was comparable with the Con treatment (12.8 Mg ha^{-1}) ($P > 0.05$).

3.3. Yield-scaled N_2O emissions (YSNEs)

The different N and water management treatments had a significant effect on the YSNEs of spring maize (Fig. 3b), ranging from 0.05–0.07 g N_2O-N kg^{-1} grain in the CK treatment, and significantly higher in the Con treatment (0.27–0.31 g N_2O-N kg^{-1} grain) than the optimum N-fertilized treatments (0.06–0.18 g N_2O-N kg^{-1} grain) ($P < 0.05$). The Opt, Opt+NI and Opt-SRF treatments had 48%, 66% and 56% lower mean YSNEs ($P < 0.05$), respectively, than the Con treatment.

3.4. Aboveground N uptake, nitrogen use efficiency (NUE) and direct emission factors (EF_{N_2O})

Aboveground N uptake increased significantly in the Con, Opt, Opt+NI, and Opt-SRF treatments, when compared to CK ($P < 0.05$), but no significant differences occurred between the N treatments (Table S5). The mean NUE for the five years in the Con (35.2–41.4%), Opt (28.4–66.9%), Opt+NI (33.7–78.2%), and Opt-SRF (28.2–77.8%) treatments were 35.8, 54.1, 60.7 and 59.4%, respectively. The mean NUE of Opt, Opt+NI and Opt-SRF treatments increased by 50.9, 69.5 and 65.9%, relative to the Con treatment, but did not significantly differ between the optimum treatments ($P < 0.05$, Table S5). Aboveground N uptake and NUE in the Opt, Opt+NI, and Opt-SRF treatments differed significantly between 2011–12 and 2013–15 ($P < 0.05$, Table S5).

Across the five years, the average EF_{N_2O} for the N-fertilized treatments ranged from 0.29% to 0.74% with the following ranking: Con > Opt > Opt-SRF > Opt +NI ($P < 0.05$, Table 2).

3.5 The relationship between N_2O flux and climate and soil factors

The N_2O fluxes in the N-fertilized treatments had a significant positive correlation with soil temperature (T_{soil}), WFPS, and soil NO_3^--N and NH_4^+-N concentrations (Table 3). The most significant correlations occurred in the Con treatment: soil NH_4^+-N (R^2=0.343, $P < 0.01$), followed by T_{soil} (R^2=0.341, $P < 0.01$) and soil NO_3^--N (R^2=0.319, $P < 0.01$). The factors best able to predict emissions in the Opt and Opt+NI treatments were ranked as NO_3^--N > WFPS > T_{soil} > NH_4^+-N, and the Opt-SRF treatment as NO_3^--N > T_{soil} > WFPS > NH_4^+-N.

The response of N_2O fluxes to soil temperature and WFPS in the topsoil was fitted to Gaussian equations that were defined by a boundary line analysis (Fig. 4). When the soil temperature was below 11 °C, N_2O fluxes were low. Higher N_2O fluxes occurred at soil temperatures from 11–22 °C in the ten days after fertilization and/or irrigation (Fig. 4a). When soil moisture was below 40% WFPS, N_2O fluxes were consistently less than 200 μg N_2O-N m^{-2} h^{-1}. The highest fluxes were measured when WFPS was around 70% and declined above this value (Fig. 4b).

4. Discussion

4.1. EENFs reduced N_2O emissions

In this study, the total of cumulative N_2O emissions in the ten days after fertilization and/or irrigation events reached 2433 g N_2O-N ha^{-1} in the Con treatment, considerably higher than those reported on the semiarid Huang Huai Hai Plain (1643 g N_2O-N ha^{-1}) (Gao *et al.*, 2014) and Loess Plateau (< 300 g N_2O-N ha^{-1}) (Wang *et al.*, 2016). However, the Opt, Opt+NI and Opt-SRF treatments significantly reduced total N_2O emissions by 48–66%, relative to the Con treatment, and the use of EENFs (Opt+NI and Opt-SRF) further reduced N_2O emissions by 14–34%, relative to the Opt treatment, which is consistent with the 19–38% reductions reported elsewhere (Qiao *et al.*, 2015; Feng *et al.*, 2016; Thapa *et al.*, 2016), because of the slowdown in ammonia oxidation when using NIs and the control of N substrate release when using SRF after fertilization and irrigation (Ding et al., 2011; Wu et al., 2018). Because the effectiveness of EENFs on N_2O emissions depends on the interaction between soils, climate, crops, and agronomy (Guardia *et al.*, 2018), the same fertilization and irrigation treatments over five years produced significant differences in annual N_2O emissions from EENFs, which could be explained by the inter-annual variation in weather conditions (Guardia *et al.*, 2018).

4.2. EENFs reduced yield-scaled N_2O emissions (YSNEs) with high grain yield and NUE

Grain yields in the N-fertilized treatments did not significantly differ in our study, indicating that reducing the conventional N rate by at least 33% and the conventional irrigation rate by 25% could maintain yield when using EENFs combined with optimum N and water management. Similar results were reported in maize systems in Germany (Weller *et al.*, 2019) and China (Ding *et al.*, 2011), where no yield reductions occurred when combining NIs with an optimum N fertilizer rate. A meta-analysis showed that SRFs did not reduce maize yields with optimum N fertilizer rates (Thapa *et al.*, 2016). However, other recent meta-analyses have reported that NIs increased yields by 4.4–10% compared to conventional N fertilization (Abalos *et al.*, 2014; Qiao *et al.*, 2015; Feng *et al.*, 2016; Thapa *et al.*, 2016; Yang *et al.*, 2016). In our study, the EENFs may not have increased yield because we used a lower optimum N rate (300 kg ha^{-1} yr^{-1}) than the conventional N rate (450 kg ha^{-1} yr^{-1}). Rose *et al.* (2018) stated that the question asked should not be 'can EENFs increase yields?' but rather 'to what extent can N application rate be reduced by applying EENFs without loss of yield?'. Clearly, N rate is a key determinant of crop yield, while the effect of EENFs on reducing N losses might enable a reduction in the N rate without loss of yield (Abalos *et al.*, 2014).

The concept of YSNEs was developed to evaluate the trade-off between N_2O emissions and crop yield (Kim and Giltrap, 2017). The Opt+NI and Opt-SRF treatments had lower YSNE values (84–143 g N_2O-N Mg^{-1} grain) than the Opt and Con treatments (131–313 g N_2O-N Mg^{-1} grain), but similar yields. Mean YSNEs of the Opt+NI and Opt-SRF treatments (97 and 126 g N_2O-N Mg^{-1} grain, respectively) that received 300 kg N ha^{-1} were higher than those reported by Yang *et al.* (2014) (80 and 95 g N_2O-N Mg^{-1} grain, respectively) for maize that received 210 kg N ha^{-1} in Northeastern China. The use of NIs and SRF significantly reduced YSNEs by 32.6 and 16.3%, respectively, in a meta-analysis (Feng *et al.*, 2016), which is in line with our results

(35.7 and 16.7%, relative to the Opt treatment, respectively). Our results suggest that the use of optimum N fertilizer and irrigation rates could reduce YNSEs, more so when combined with EENFs, in these high-yielding irrigated maize systems in northwestern China.

The mean above-ground N uptake in the optimum N and Con treatments did not significantly differ (~298 kg N ha^{-1}), despite the difference in their N rate (300 kg ha^{-1} yr^{-1} and 450 kg ha^{-1} yr^{-1}, respectively), and the average NUE increased by 50.9% in the Opt treatment and 69.5% in the EENF treatments, relative to the Con treatment. The significantly higher NUEs in the Opt, Opt+NI, and Opt-SRF treatments resulted in lower residual N in soil (Table S6). The Opt, Opt+NI and Opt-SRF treatments had lower mean residual N during the five-year study (24.85, 5.44 and 9.04 kg N ha^{-1} yr^{-1} respectively) than the Con treatment (116.03 kg N ha^{-1} yr^{-1}). In the Opt+NI and Opt-SRF treatments, NUE increased by 10 and 12%, respectively, relative to the Opt treatment, but the three treatments did not significantly differ ($P > 0.05$), which is in line with the average 14% increase in NUE for cereal crops using EENFs (Zheng *et al.*, 2017).

4.3. Factors controlling N_2O emissions

Our results have shown that large N_2O emission peaks are observed shortly after fertilization and irrigation events, with lower peaks at other times, as shown in previous studies (Gao *et al.*, 2014; Huérfano *et al.*, 2018; Recio *et al.*, 2018). Such peaks could be simulated by the frequency of the drying and rewetting cycles (Fierer and Schimel, 2002), which enhances carbon and nitrogen mineralization (Van Gestel *et al.*, 1993) and causes a switch between microbial nitrification and denitrification processes (Chen *et al.*, 2014). In our study, soil moisture (expressed as WFPS) ranged from 20% to 93% WFPS during the drying and rewetting cycles periods (Fig. 5). Soil NH_4^+-N concentrations in the 0–20 cm soil layer ranged from 0–9 mg N kg^{-1} dry soil in all treatments during the five-year study (Fig. 6a). There was no significant difference in Mean NH_4^+-N concentrations between Con, Opt+NI, Opt-SRF treatments, but they were 50.0%, 29.2% and 45.8% ($P < 0.05$) higher than the Opt treatment in the ten days after basal fertilization respectively (Table S7). Compared with the Con treatment, average soil NH_4^+-N concentrations in the Opt+NI and Opt-SRF treatments at the jointing stage increased significantly by 50.0% and 45.5% ($P < 0.05$) respectively, but decreased by 34.9% and 24.3% at the bell-mouthed stage, respectively. Mean NH_4^+-N concentrations did not differ in the Con, Opt, Opt+NI, Opt-SRF treatments at the tassel or milking stage found (Table S7). In contrast, soil NO_3^--N concentrations in the 0–20 cm soil layer ranged from 2–97 mg N kg^{-1} dry soil (Fig. 6b) and were highest in the Con treatment (35.3–58.3 mg N kg^{-1}). Mean soil NO_3^--N concentrations declined significantly ten days after basal fertilization by 35.4%, 63.2%, and 67.6% in the Opt, Opt+NI, and Opt-SRF treatments ($P < 0.05$), respectively, relative to the Con treatment (Table S7). The Opt+NI and Opt-SRF treatments had lower mean soil NO_3^--N concentrations than the Opt treatment ($P < 0.05$), which remained at 15.8 mg N kg^{-1} and 14.3 mg N kg^{-1} within ten days after fertilization, respectively. The positive correlations between N_2O emissions, soil WFPS, and mineral N concentrations indicated that the high N_2O peaks were produced by microbially-mediated nitrification and denitrification processes. Although high soil moisture (> 70% WFPS) was observed within 3–4 days after each irrigation, denitrification is unlikely to have been the main contributor to N_2O production due to the low soil N content and the low soil denitrification potential in this region (Wan *et al.*, 2009; Ju and Zhang, 2017). Isotopic tracing experiments have indicated that the main process responsible for N_2O production is nitrifier denitrification, which may account for 30–66% of soil N_2O emissions (Kool *et al.*, 2011; Zhu *et al.*, 2013). Recent studies confirmed that nitrification and nitrifier denitrification rather than denitrifier denitrification were the main processes generating N_2O in these intensively N-fertilized alkaline soils in northern China (Zhang *et al.*, 2016; Wu *et al.*, 2018; Zhang *et al.*, 2019).

The low soil mineral N and soil moisture, rather than soil temperature, were the main limiting factors affecting N_2O emissions during the non-fertilization or irrigation periods of the GS. The low N_2O emissions in the FS were mainly attributed to the low temperature (< 0 °C), the low N inputs (< 20 mg N kg^{-1}) as crop residues, and low soil moisture conditions (< 50% WFPS) in our study area, which restricted the activity of soil microorganisms (Baggs, 2011; Hu *et al.*, 2013). Ju and Zhang (2017) reported that the upland agricultural soils in North China were characterized by strong N mineralization and nitrification, and weak immobilization and denitrification ability. The low values of NH_4^+ content in soil in our experiment were due to the rapid conversion to NO_3^- after urea application under favorable water and heat conditions. Generally, soil NH_4^+ concentration is lower than 5 mg N kg^{-1} in the upper soil layer and soil mineral N is dominated by NO_3^-, except for a short period (0.5 to 2 week) after fertilization (Ju et al., 2003; Ju et al., 2004). However, the low NO_3^-–N content in topsoil compared to the N application rate was due to NO_3^- leaching under situations, which led to the accumulation of nitrate deep in the soil profile (Huang et al., 2017; Zhou et al., 2016), which reduced the substrate available to soil microorganisms.

The mean direct N_2O emission factor (EF_{N_2O}) ranged from 0.29–0.74% at 300–450 kg N ha^{-1} yr^{-1} in our study, which is within the 0.22–1.53% range from 12 Chinese croplands (Zheng *et al.*, 2004), and was close to the default value of 0.5% suggested by IPCC (2019). The EF_{N_2O} values in our study are lower than those of summer maize (0.85–1.29% at 246–457 kg N ha^{-1} rate) on the North China Plain (Song *et al.*, 2018), higher than those of rainfed spring maize (0.18–0.23% at 225 kg N ha^{-1}) on the Loess Plateau (Wang *et al.*, 2016), and consistent with those of irrigated and fertilized spring maize (0.42–0.72% at 120–330 kg N ha^{-1}) in semiarid northern China (Liu *et al.*, 2011).

5. Conclusion

The combined application of Enhanced Efficiency Nitrogen Fertilizers (EENFs) with optimized water and fertilizer either decrease N_2O emissions and yield-scaled N_2O emissions or increase nitrogen use efficiency and maintain high crop yields in our study. Large N_2O emissions mainly occur within a few days of fertilization with irrigation, which could be stimulated by the frequency of the drying and rewetting cycles. The low soil N content and the low soil denitrification potential in our experiment indicate that the high N_2O peaks are produced by microbially-mediated nitrifier denitrification processes. In addition, the fallow seasons had significantly lower cumulative N_2O emissions than the growing seasons, which were mainly attributed to the low temperature, the low N inputs as crop residues, and low soil moisture conditions in the fallow. This study provides clear evidence of the important role of EENFs in mitigating N_2O emissions and improving NUE while maintaining crop yields and highlights their contribution to more sustainable cropping systems in dryland regions such as Northwest China.

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