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Research Paper

Mitigating N_2O and NO Emissions from Direct-Seeded Rice with Nitrification Inhibitor and Urea Deep Placement

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Abstract: Soil-emitted nitrous oxide (N_2O) and nitric oxide (NO) in crop production are harmful nitrogen (N) emissions that may contribute both directly and indirectly to global warming. Application of nitrification inhibitors, such as dicyandiamide (DCD), and urea deep placement (UDP), are considered effective approaches to reduce these emissions. This study investigated the effects of DCD and UDP, compared to urea and potassium nitrate, on emissions, nitrogen use efficiency and grain yields under direct-seeded rice. High-frequency measurements of N_2O and NO emissions were conducted using the automated closed chamber method throughout the crop-growing season and during the ratoon crop. Both UDP and DCD were effective in reducing N_2O emissions by 95% and 73%, respectively. The highest emission factor (1.53% of applied N) was observed in urea, while the lowest was in UDP (0.08%). Emission peaks were mainly associated with fertilization events and appeared within one to two weeks of fertilization. Those emission peaks contributed to 65%–98% of the total seasonal emissions. Residual effects of fertilizer treatments on the N_2O emissions from the ratoon crop were not significant; however, the urea treatment contributed 2%, whereas UDP contributed to 44% of the total annual emissions. On the other hand, cumulative NO emissions were not significant in either the rice or ratoon crops. UDP and DCD increased grain yields by 16%–19% and N recovery efficiency by 30%–40% over urea. The results suggested that the use of DCD and UDP could mitigate N_2O emissions and increase grain yields and nitrogen use efficiency under direct-seeded rice condition.

Key words: dicyandiamide; direct-seeded rice; nitric oxide; nitrification inhibitor; nitrogen use efficiency; nitrous oxide; urea deep placement

Nitrous oxide (N_2O) is an important greenhouse gas which is long-lived, 265 times more potent than carbon dioxide (CO_2) over a 100-year time horizon. N_2O contributed 6% to the total anthropogenic greenhouse gas emissions in 2010 (IPCC, 2014). In addition to trapping heat in the atmosphere, it contributes to the destruction of the stratospheric ozone layer (Firestone and Davidson, 1989; Ravishankara et al, 2009). Nitric oxide (NO) is an important environmental pollutant that contributes to the acidification of ecosystems and plays an important role in the formation of ozone in the lower atmosphere (Firestone and Davidson, 1989). In agricultural ecosystems, both N_2O and NO gases are produced in soils through the biochemical process of nitrification and denitrification, nitrifier denitrification and chemo-denitrification (Venterea et al, 2012). The productions of N_2O and NO are mainly associated with the application of N (chemical or organic fertilizers) or the availability of ammonium (NH_4^+) and nitrate (NO_3^-) in soils, especially with optimum soil moisture and soil temperatures. The magnitude of emissions increases with increased N rate, particularly

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when N application exceeds plant demand (Kim et al, 2013). However, the emissions are highly variable with fertilizer sources and application methods, along with irrigation regimes, soil properties and climate (Laville et al, 2011; Venterea et al, 2012; van Kessel et al, 2013).

Rice cropping systems consume 15.2% of the world's N fertilizers and are characterized by a low nitrogen use efficiency (NUE). The lower NUE (30%–40%) is associated with inefficient N management practices, including urea application with the conventional broadcast method. In flooded rice systems, high NH_4^+-N originating from hydrolyzed urea can accumulate in floodwater and lead to increased ammonia (NH_3) volatilization and surface run-off, depending on irrigation regime and rainfall. The magnitude of NH_3 volatilization could be up to 50% of the applied N (Rochette et al, 2013), causing a huge economic loss to the farmers. The accumulated NH_4^+-N could also be lost through nitrification and subsequent denitrification, resulting in N_2O and NO emissions (Yao et al, 2017). Generally, the magnitude of emissions from continuously flooded rice fields is low. However, these emissions could be increased when cultivation practice is changed from transplanted rice to direct-seeded rice (DSR) (Liu et al, 2014). Although an increasing number of N_2O and NO emission measurements have become available from transplanted rice fields, information from DSR is scarce. Some reported emissions are from discrete measurements done weekly or biweekly. Therefore, high-resolution temporal measurements are necessary to cover all the temporal dynamics and get a more reliable estimate of cumulative emissions.

In Asia, where 90% of the world's rice is produced, rice is commonly grown by transplanting seedlings into puddled soil. Puddling and transplanting require a large amount of water and labor, both of which are becoming increasingly scarce and expensive, making rice production less profitable. Therefore, DSR is gaining global popularity, as it is less labor-intensive and more conducive for mechanization, and it reduces overall production costs compared to puddled transplanted rice (Mishra et al, 2017). In the United States, most rice cultivation is with DSR. Since repeated puddling for transplanting adversely affects soil physical properties by destroying soils' aggregates, reducing permeability in subsurface layers and forming hard pans at shallow depths, DSR adoption may improve soil properties and affect emissions.

Mitigating N_2O and NO emissions requires increased NUE through improved temporal synchrony between N supply and plant demand. This requires efficient N management strategies, such as selection of the right source (enhanced efficiency fertilizers), right quantity, right time and right application method. Improved N placement methods, such as urea deep placement (UDP) at a soil depth of 7–10 cm, increase NUE and crop yields and reduce emissions compared to broadcast application (Yao et al, 2017). In the flooded rice fields, UDP retains N in the root zone as NH_4^+-N for a longer period and ensures continuous supply of N to plants throughout the growing season. It is reported that UDP increases rice yields up to 20% and NUE up to 30%, and reduces N_2O emissions up to 84% compared to broadcast urea application (Gaihre et al, 2015; Huda et al, 2016).

Similarly, enhanced-efficiency fertilizers, such as those containing nitrification inhibitors (NIs), urease inhibitors (UIs) and slow-release fertilizers, have been developed to increase NUE. Use of NIs, such as dicyandiamide (DCD) combined with urea or ammonium-based fertilizers (with optimum N rate), could increase NUE and reduce N_2O emissions in a range of cropping systems (Linquist et al, 2013; Tian et al, 2015; Recio et al, 2018). DCD reduces emissions by 75% in a corn field in Mississippi (Tian et al, 2015), by 66% in a wheat-corn cropping system in the North China Plain (Tian et al, 2017), and by 11%–19% in a rice field in India (Kumar et al, 2000; Majumdar et al, 2000). Recent meta-analyses showed that NIs, in general, reduce N_2O emissions by up to 38% (Akiyama et al, 2010; Linquist et al, 2013; Yang et al, 2016).

Most previous studies reported the benefits of NIs, such as crop yield and NUE, only during the crop-growing period. However, Scheer et al (2017) recently monitored the residual effects on the next crop and observed 50%–70% increases in post-harvest N_2O emissions in a vegetable production system in Australia, although emissions are reduced by 20%–60% during the main crop-growing period. This study suggested that the surplus N (if applied at a higher rate) due to increased efficiency can be lost during the fallow season if crop rotation is not adopted. However, it is unclear whether efficient N management practices, such as UDP and urea-DCD application in rice systems, will increase or decrease emissions.

Effectiveness of NIs varies across crops, management practices and cropping patterns. Impacts of DCD have mostly been studied in upland crops (Tian et al, 2015; Scheer et al, 2017). Similarly, impacts of UDP have been studied mostly in transplanted rice (Kapoor et al, 2008; Islam et al, 2017). To date, the effects of NIs (urea-DCD) and UDP on N_2O and NO emissions from DSR have not been studied, particularly using an automated continuous system and addressing all of the temporal variations. Therefore, the present study aimed to investigate the effects of urea-DCD and UDP, compared with broadcast urea and potassium nitrate (KNO_3) application, on N_2O and NO emissions. This was done by using a high frequency automated measurement system over a year's time, covering main crop and ratoon crop as well as yields and NUE.

METERIALS AND METHODS

Experimental design and treatments

The study was carried out in a greenhouse at the International Fertilizer Development Center, Muscle Shoals, Alabama, USA, from May 2016 to February 2017. Five N fertilizer treatments, control (N0), KNO_3, broadcast urea, UDP and NI with urea (DCD), were tested in a randomized complete block design with three replications. The proportion of the DCD in the fertilizer was 3% as recommended by the manufacturer (Sigma Aldrich, USA). KNO_3 was selected to understand the role of nitrification and denitrification on emissions, as N_2O loss from KNO_3 would mainly be through denitrification. However, nitrate nitrogen supplied by KNO_3 could also be utilized by dissimilatory nitrate reduction to ammonium, which can result in N retention by producing NH_4^+-N. The N rates for all the treatments (except N0) were 194 kg/hm^2. For UDP and DCD, fertilizers were briquetted (for ease of deep placement) to a size of 2.4 and 1.8 g, respectively, and deep-placed in a single application at 7–10 cm below the soil surface at 25 d after sowing. Urea and KNO_3 were broadcast applied at two equal splits at 25 and 55 d after sowing, respectively.

Handling of plants and soils

The wooden experimental containers (length, 130 cm; breadth, 40 cm; and height, 28 cm) were filled with 150 kg soil. Some of the physicochemical properties of the soil were as follows: pH-H_2O, 6.35; organic C, 0.92 g/kg; total N, 0.09 g/kg; available P, 7.86 mg/kg; and available K, 50.7 mg/kg. Phosphorus (75 kg/hm^2 P_2O_5) and potassium (110 kg/hm^2 K_2O) were applied through triple super phosphate (0-46-0) and muriate of potash (0-0-60) as basal fertilization. Sensors for air and soil temperatures and soil moisture content were installed at 10 cm below the soil surface after basal fertilization.

Pre-germinated rice seeds (*Oryza sativa* L. cv. Antonio) were direct sown at 20 cm × 20 cm in each container on May 27, 2016. Each container had a total of 14 rice seedlings in two rows (7 seedlings per row). All containers were kept continuously flooded, except for two to three days during fertilizer application (topdressing of urea and KNO_3) and two weeks just before crop harvest. The greenhouse experiment set up was designed to give better control of crop, water and fertilizer management and lower spatial variability among containers. After harvest, containers were kept undisturbed to grow ratoon crop. Ratoon crop was grown for three months with residual fertilizers and irrigated regularly as and when needed.

Measurement of N_2O and NO emissions

N_2O and NO emissions were simultaneously measured from each container using the automated static closed chamber method as described by Gaihre et al (2019). In brief, a chamber was installed in each container between two rows of rice, which covered a surface area of 0.148 m^2 (118.8 cm × 12.5 cm) and headspace volume of 0.0578 m^3 (57.8 L). Four air samples were taken at 12-min intervals (0, 12, 24 and 36 min) in each 2-h sampling sequence. Gas samples were taken from each chamber 12 times per day. Within a two-hour cycle, a gas chamber was closed for 36 min for gas sampling. One sample was taken just before closing the chamber, which represents the ambient air.

The air samples' N_2O and NO mixing ratios were measured by a Teledyne Advanced Pollution Instrumentation (API) T320U Gas Filter Correlation Analyzer and a Teledyne API T200 Nitrogen Oxide Analyzer, respectively. Both N_2O and NO analyzers were calibrated weekly by using a Teledyne T700 Dynamic Dilution Calibrator. The analyzers were calibrated for two ranges of concentration (i.e., the low range for the NO and N_2O analyzers was 40 and 1600 μg/L, respectively, and the high range was 800 and 8000 μg/L, respectively). T320U (N_2O analyzer) can analyze the N_2O concentration up to 200 mg/L with a lower detection limit of 10 μg/L. Similarly, T200 (NO analyzer) can analyze NO concentration up to 20 mg/L with a lower detection limit of 0.4 μg/L.

The N_2O and NO fluxes were calculated from the slope of the linear regression curve. An emission event was considered significant when the slope was significant at $P < 0.05$. The slope [μg/(L·min)] from the significant emission events was corrected for air temperature, atmospheric pressure and the ratio of chamber volume to surface area using the following formula.

Emission rate [μg/(m^2·h)] = $\Delta C / \Delta T \times V \times MW \times 60 / [0.08206 \times (273 + T)] \times A \times 1000$

Where $\Delta C/\Delta T$ is change in concentration of the gas of interest at time interval ΔT; V is the volume of the gas chamber (L); MW is the molecular weight of the respective gas (ng/nmol); T is the temperature inside the chamber (ºC); A is the area covered by chamber.

Daily emission rate [mg/(m^2·h)] and cumulative seasonal total emissions were calculated by summing the hourly emission rates and daily emission rates, respectively. The global warming potential of N_2O was calculated in units of CO_2 equivalents (CO_2-eq) over a 100-year time horizon using a radiative forcing potential of 265 (IPCC, 2014). Yield-scaled N_2O and NO emissions were calculated as the ratios of cumulative emissions to grain yields.

N_2O and NO direct emission factors (EF) for the whole growing season were calculated as:

$EF\ (\%) = \sum(E - E_0) / F_N \times 100$

Where E is the total N_2O/NO emissions from a N-fertilized treatment; E_0 is the total N_2O/NO emissions from the control; F_N is the application rate of N fertilizer (kg/hm^2).

Grain yields and NUE

The total aboveground dry matter (biological yields) was recorded at harvest. NUE was calculated as recovery efficiency (RE), agronomic efficiency (AE) and partial factor productivity (PFP). They were calculated as follows:

$RE = (NU - NU_0) / F_N$;

$AE = (Y - Y_0) / F_N$;

$PFP = Y / F_N$

Where NU is N uptake in aboveground biomass (kg/hm^2) in a N-fertilized treatment (kg/hm^2); NU_0 is the total N uptake (kg/hm^2) of the control; Y is grain yield (kg/hm^2) in a N-fertilized treatment (kg/hm^2); Y_0 is the yield (kg/hm^2) of the control; F_N is the application rate of N fertilizer (kg/hm^2).

Data analysis

The analyses of variances (ANOVA) of seasonal cumulative emissions, yield-scaled emissions, the emission factors of N_2O and NO gases, grain yield, total N uptake and NUE were determined with SAS 9.3 Generalized Linear Mixed Models. A pairwise comparison of treatment means was conducted with a least significant difference (LSD) test at the 5% level of probability.

RESULTS

Soil moisture and temperature

During the observation period (May 2016–January 2017), volumetric soil moisture content ranged between 0.09 and 0.43 (m^3/m^3) (Fig. 1). Low soil moisture content (< 0.35 m^3/m^3) was observed at two days before the first N topdressing and two weeks before crop harvest. Daily soil temperature during the experiment period ranged from 13.8 ºC to 29.2 ºC (average 22.6 ºC) (Fig. 1).

Grain yield and NUE

The addition of N fertilizers, regardless of source and application method, significantly increased biomass

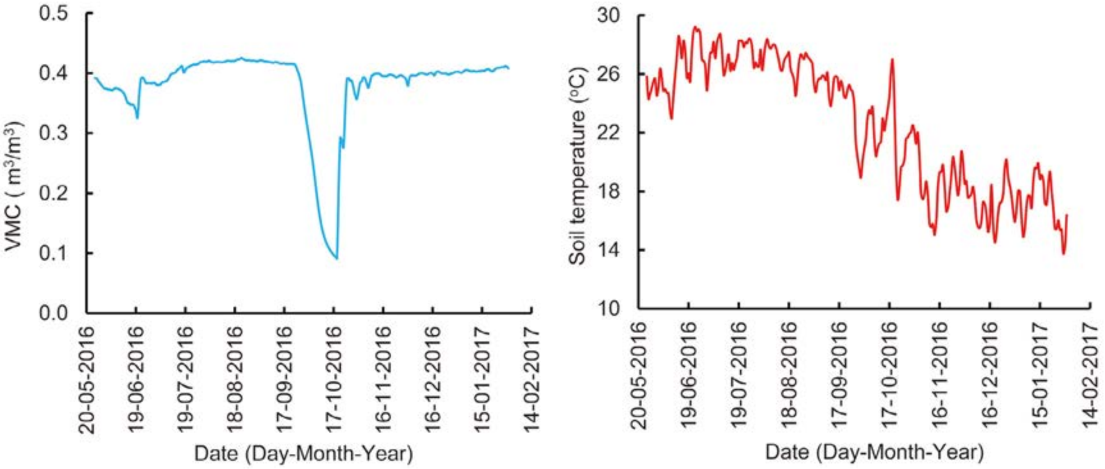

Fig. 1. Daily average of volumetric soil moisture content (VMC) and soil temperature at different fertilizer treatments during rice and ratoon-growing season.

yields (straw and grain), nitrogen uptake and NUE, compared to the control (Table 1). UDP and DCD produced significantly ($P < 0.05$) higher grain yields (16%–19%) compared to broadcast urea. Grain yields between UDP and DCD were comparable. KNO_3 produced the lowest yield among the N-fertilized treatments, which was 16% lower ($P < 0.05$) than broadcast urea. The response of straw biomass to fertilizer treatments was similar to that of grain yield. Total plant N uptake and its partitioning into grain N and straw N exhibited similar responses with a trend of UDP = DCD > urea > KNO_3.

Similarly, NUE including AE, RE and PFP was significantly affected by N source and placement method (Table 1). Both UDP and DCD significantly increased AE and RE. KNO_3 had significantly lower NUE compared to all the other N-fertilized treatments.

Seasonal dynamics of N_2O emissions

The dynamics of N_2O emissions during the rice and ratoon growing seasons from all the fertilizer treatments are presented in Fig. 2. The majority of emissions occurred in response to fertilization events (basal and topdressing) and during the dry period. The first emission peak was observed during June 12–19 when irrigation was stopped for fertilizer application (June 20, 2016), and the moisture content was dropped to field capacity (~0.33 m^3/m^3). The highest emission peak was observed after 2 d of fertilizer application in UDP [4.8 mg/(m^2·d)] and DCD [20.8 mg/(m^2·d)] treatments and after 7 d in urea [32.3 mg/(m^2·d)] and KNO_3 [13.1 mg/(m^2·d)] treatments (Fig. 2). These emissions continued for 10 d (UDP and DCD) to 12 d (urea broadcast and KNO_3) after fertilizer application. For the second topdressing (urea and KNO_3 only), emission peaks were smaller in both treatments, and emissions continued for only 6 d. Some emissions were observed from September 29 to October 19 when irrigation was stopped for crop harvest, and moisture content was gradually dropped from 0.35 (September 29, 2016) to 0.09 m^3/m^3 (October 19, 2016).

After crop harvest on October 20, all containers were re-flooded as we continued monitoring N_2O emissions from the ratoon crop to see if there were any residual effects from the fertilizers. All containers were completely saturated (0.39 m^3/m^3) within 6 d (Fig. 1). Elevated N_2O emissions were observed for approximately three weeks after the containers were flooded, reaching peak emissions of 0.3–3.5 mg/(m^2·d) under different treatments. Except during the drying and flooding period and after fertilizer application, emissions were negligible throughout the main crop and ratoon crop-growing seasons.

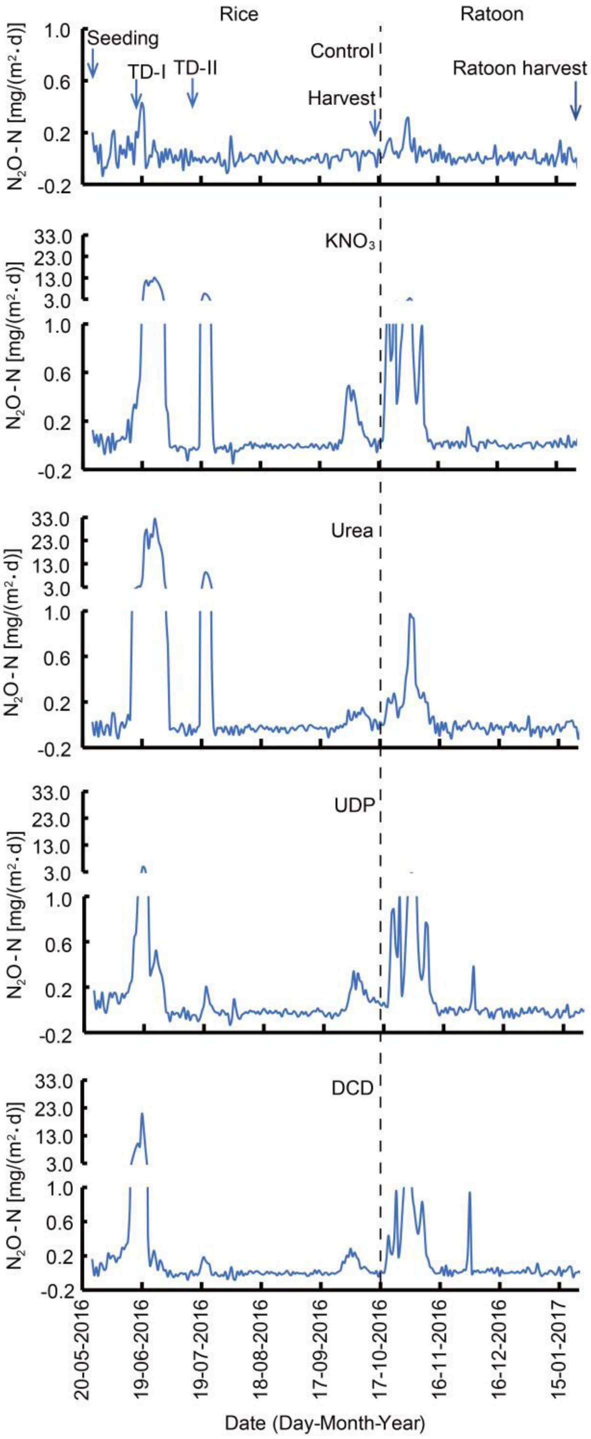

Fig. 2. Seasonal variations of N_2O fluxes under different fertilizer treatments during rice and ratoon-growing season.

TD-I and TD-II represent the first and second topdressing, respectively (n = 3). KNO_3, Potassium nitrate; UDP, Urea deep placement; DCD, Urea dicyandiamide.

Table 1. Pairwise mean comparison of panicle, biomass yield, nitrogen uptake and nitrogen use efficiency of rice under different nitrogen fertilizer treatments (Mean ± SE, *n* = 3).

Treatment	Panicle/hill	Biomass yield (kg/hm^2)		Nitrogen uptake (kg/hm^2)			Nitrogen use efficiency		
		Straw	Grain	Straw	Grain	Total	AE	RE	PFP
Control	10 ± 0.3 d	7 240 ± 115 d	5 566 ± 82 d	32 ± 1.39 c	52 ± 3.93 d	84 ± 3.48 d	–	–	–
KNO_3	13 ± 0.5 c	9 494 ± 80 c	9 925 ± 262 c	39 ± 2.20 c	100 ± 6.34 c	139 ± 7.60 c	22.47 ± 1.10 c	0.29 ± 0.02 c	51.16 ± 1.35 c
Urea broadcast	15 ± 0.2 b	11 677 ± 356 b	11 850 ± 436 b	54 ± 4.49 b	127 ± 3.20 b	181 ± 2.64 b	32.39 ± 1.83 b	0.50 ± 0.02 b	61.08 ± 2.25 b
UDP	20 ± 0.7 a	15 559 ± 261 a	13 689 ± 301 a	71 ± 3.35 a	148 ± 3.25 a	219 ± 5.04 a	41.87 ± 1.62 a	0.70 ± 0.03 a	70.56 ± 1.55 a
DCD	21 ± 0.5 a	15 835 ± 380 a	14 149 ± 450 a	68 ± 1.08 a	143 ± 1.33 a	211 ± 0.25 a	44.24 ± 2.08 a	0.66 ± 0.02 a	72.93 ± 2.32 a

UDP, Urea deep placement; DCD, Urea dicyandiamide; KNO_3, Potassium nitrate; AE, Agronomic efficiency; RE, Recovery efficiency; PFP, Partial factor productivity.

Within a column, means followed by the same lowercase letters are not significantly different at the 0.05 level.

Although emission peaks appeared during drying and after re-flooding of the dry containers, fertilizer-induced emission peaks were more prominent and contributed to 65% (DCD) to 98% (broadcast urea) of the total seasonal emissions. For urea and KNO_3, the contribution of the second topdressing was very small (12%–16%).

Diel variations in N_2O emissions

N_2O emissions showed a significant temporal variation. They increased from 800 h; the largest emissions were observed from 1000 to 1500 h, especially in the broadcast fertilizer treatments (urea and KNO_3) (Fig. 3). The highest emission rate was observed in the urea treatment [1922 $\mu g/(m^2 \cdot h)$] followed by KNO_3 [732 $\mu g/(m^2 \cdot h)$]. The emission rates positively correlated with soil temperature in both urea (R^2 = 0.51, n = 96) and KNO_3 (R^2 = 0.57, n = 96) treatments. These emission patterns were only observed for about two weeks after fertilizer application. Emissions during the rest of the rice-growing season were almost stable throughout the day. Diel variations were not prominent from UDP and DCD treatments.

Seasonal dynamics of NO emissions

The dynamics of NO emissions are presented in Fig. 4. Unlike N_2O emissions, the majority of NO emissions occurred during the dry period, i.e., before the first topdressing of fertilizer (June 12–19, 2016) and before crop harvest. The fertilizer-induced emission peak [0.10 $mg/(m^2 \cdot d)$] was observed only in the broadcast urea treatment after 2 d of application. Emissions during the rest of the crop-growing period were negligible. Emission peaks were not observed even after the second topdressing of urea and KNO_3. However, emissions were observed for about three weeks (October 1–20, 2016) when containers were kept dry before crop harvest. Moreover, some emission peaks were observed during the first week (October 20–25, 2016) of flooding for the ratoon crop. Nevertheless, emission peaks were not affected by any fertilizer treatments. Therefore, the contribution of fertilizer-induced emissions was negligible to the total

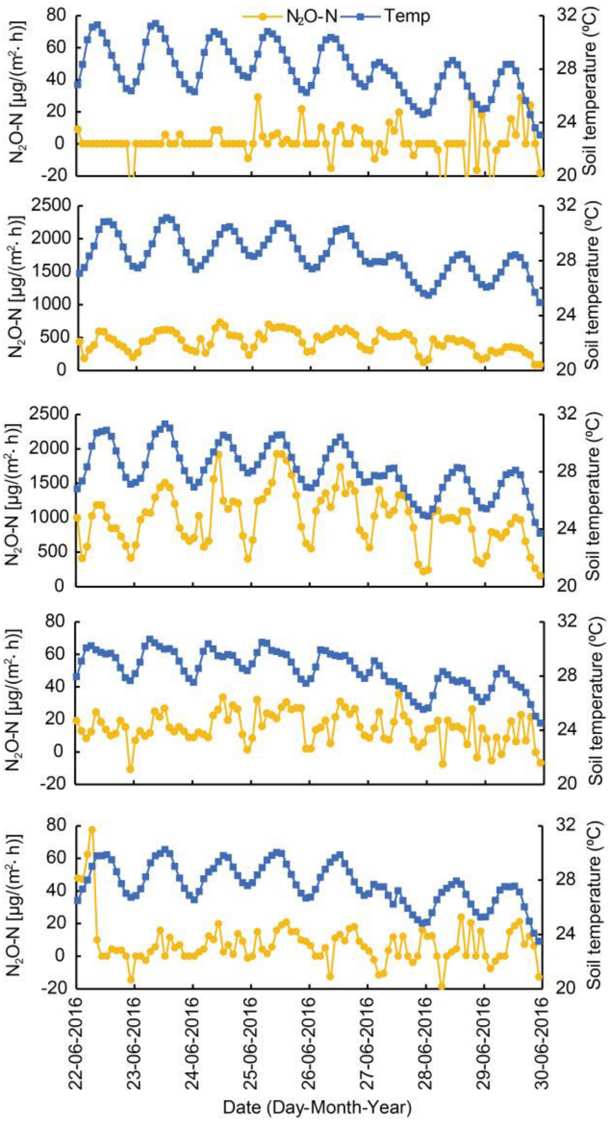

Fig. 3. Diel variations in N_2O-N emissions and soil temperature after first topdressing of N fertilizers (*n* = 3).

UDP, Urea deep placement; DCD, Urea dicyandiamide; KNO_3, Potassium nitrate; Temp, Temperature.

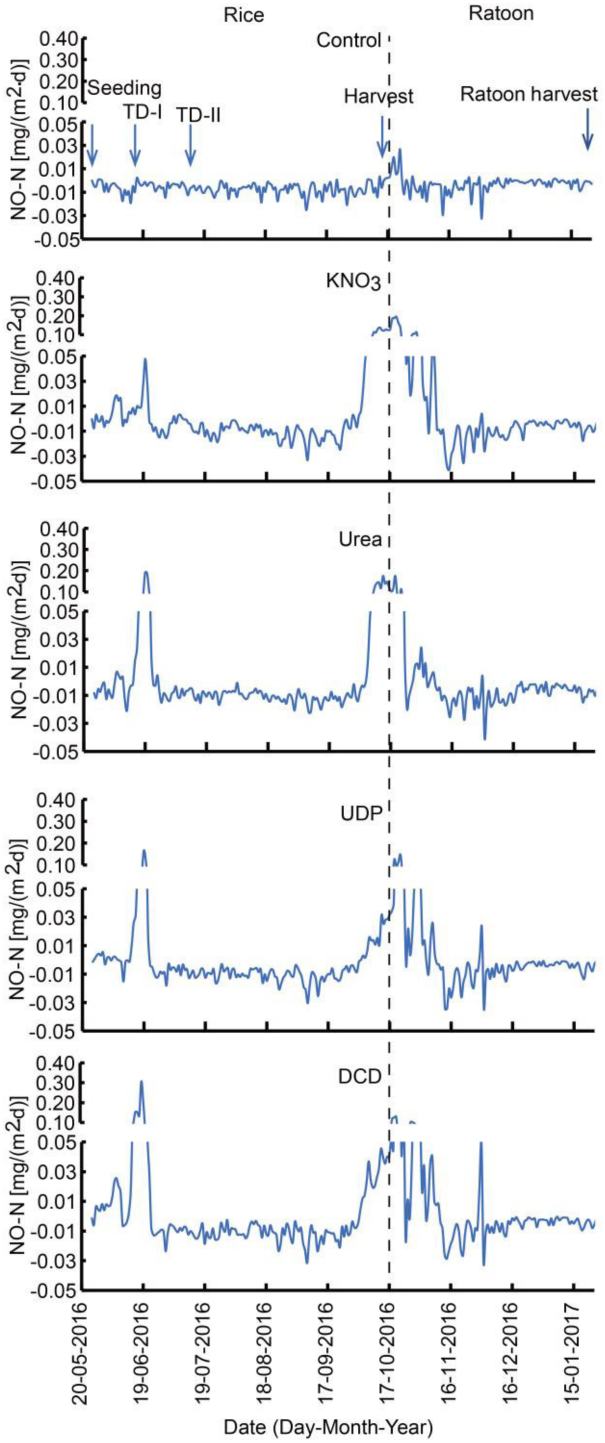

Fig. 4. Seasonal variations of NO fluxes under different fertilizer treatments during rice and ratoon-growing season.

TD-I and TD-II represent the first and the second topdressing, respectively (*n* = 3). KNO_3, Potassium nitrate; UDP, Urea deep placement; DCD, Urea dicyandiamide.

seasonal emissions, except in the urea broadcast treatment, which contributed about 37% to the total seasonal emissions.

Seasonal total and yield-scaled emissions and direct emission factors

The addition of N fertilizers, regardless of source and application method, significantly increased N_2O emissions but had no significant effects ($P > 0.05$) on NO emissions (Table 2). The cumulative N_2O-N emissions ranged from 33 to 3010 g/hm^2. UDP and DCD significantly reduced emissions ($P < 0.05$) by 93% and 73% compared to broadcast urea. However, the difference between UDP and DCD was not significant. N_2O emission from broadcast urea was 55% higher than that of KNO_3 ($P < 0.05$). Likewise, yield-scaled N_2O emissions (emission intensity) were significantly affected by fertilizer treatments (Table 2). Broadcast urea had significantly higher yield-scaled N_2O emissions than KNO_3 treatment. The yield-scaled emissions from UDP and DCD were similar to the control.

Fertilizer treatments had significant effects on N_2O emission factors (Table 2). EF followed a similar trend as cumulative emissions. Broadcast urea had the highest EF (1.534%) ($P < 0.05$), while UDP had the lowest (0.08%). EF between UDP and DCD was similar. As with cumulative emissions, KNO_3 had lower EF compared to broadcast urea.

The residual effects of all the treatments on N_2O and NO emissions were monitored in the ratoon crop (October 20, 2016 to January 31, 2017) (Fig. 2). N_2O emissions ranged from 26 to 239 g/hm^2 (Table 2). N_2O emissions during the ratoon crop were 44%, 17%, 15% and 2% of the total emissions for UDP, DCD, KNO_3 and urea, respectively. However, the differences among treatments were not significant ($P > 0.05$).

DISCUSSION

This is the first study to investigate the effect of DCD and UDP on N_2O and NO emissions from DSR based on automated high-frequency emission measurements. High-frequency measurements are needed to address the current uncertainty associated with N_2O emission estimates from soils. Moreover, this can accurately quantify the effects of particular treatments of interest on N_2O and NO emissions, which helps to draw a comprehensive conclusion and develop appropriate mitigation strategies.

UDP reduced N_2O emissions by 93% compared to broadcast urea. This is likely because UDP could have retained most of the N as NH_4^+ in an anaerobic zone for a long period of time, which is less subjected to

Table 2. Seasonal N_2O and NO emissions and direct emission factors (EF) at all N fertilizer treatments (Mean ± SE, *n* = 3).

Crop	N treatment	N_2O emission				NO emission		
		N_2O-N (g/hm^2)	CO_2 eq. (kg/hm^2)	YSNE (g/kg)	EF (%)	NO-N (g/hm^2)	YSNE (g/kg)	EF (%)
Rice	Control	33 ± 5 c	14 ± 3 c	0.006 ± 0.00 c		-9.41 ± 0.00	-0.0007 ± 0.0000	
	KNO_3	1 359 ± 411 b	566 ± 171 b	0.136 ± 0.04 b	0.683 ± 0.21 b	8.92 ± 7.84	0.0009 ± 0.0008	0.010 ± 0.004
	Urea broadcast	3 010 ± 440 a	1 253 ± 183 a	0.253 ± 0.03 a	1.534 ± 0.23 b	12.07 ± 2.22	0.0010 ± 0.0002	0.011 ± 0.001
	UDP	205 ± 167 c	85 ± 70 c	0.015 ± 0.01 c	0.088 ± 0.09 c	-0.69 ± 6.35	0.0000 ± 0.0005	0.005 ± 0.003
	DCD	815 ± 158 bc	339 ± 66 bc	0.057 ± 0.01 bc	0.403 ± 0.08 bc	7.30 ± 0.98	0.0005 ± 0.0001	0.009 ± 0.001
ANOVA (Pr > F)		0.0006	0.0006	0.0006	0.0015	0.7756	0.9656	0.4041
Ratoon	Control	26 ± 7	11 ± 3			-3.61 ± 1.48		
	KNO_3	239 ± 155	100 ± 65		0.110 ± 0.08	5.94 ± 4.40		0.007 ± 0.003
	Urea broadcast	54 ± 30	22 ± 12		0.014 ± 0.02	-4.31 ± 0.64		-0.027 ± 0.027
	UDP	161 ± 50	67 ± 21		0.070 ± 0.03	1.45 ± 2.83		-0.003 ± 0.001
	DCD	167 ± 72	70 ± 30		0.073 ± 0.04	4.45 ± 3.90		0.0043 ± 0.006
ANOVA (Pr > F)		0.3974	0.3974		0.5689	0.1616		0.3059
Total	Control	59 ± 9 b	24 ± 5 b			-13.03 ± 11.67		
	KNO_3	1 598 ± 385 ab	665 ± 161 ab		0.793 ± 0.20 b	14.86 ± 11.40		0.002 ± 0.001
	Urea broadcast	3 063 ± 410 a	1 276 ± 171 a		1.549 ± 0.21 a	7.77 ± 2.86		0.001 ± 0.000
	UDP	366 ± 215 b	152 ± 89 b		0.158 ± 0.11 c	0.76 ± 9.08		0.003 ± 0.002
	DCD	982 ± 86 b	409 ± 36 b		0.476 ± 0.04 bc	11.76 ± 4.83		0.003 ± 0.001
ANOVA (Pr > F)		0.0215	0.0215		0.0014	0.8714		0.6502

UDP, Urea deep placement; DCD, Urea dicyandiamide; KNO_3, Potassium nitrate; YSNE, Yield-scaled nitrogen emission.

Within a column and a crop, means followed by the same letters are not significantly different at the 0.05 level.

nitrification due to the absence of oxygen (Yao et al, 2017). Consequently, N_2O and NO emissions from both nitrification and denitrification could be reduced. Moreover, UDP reduces N loss from other mechanisms, such as NH_3 volatilization and surface runoff (Rochette et al, 2013), resulting in a reduction in indirect N_2O emissions (Venterea et al, 2012).

The use of nitrification inhibitor, DCD, showed a similar potential to mitigate N_2O emissions (73%) with UDP compared to broadcast urea. This suggests that DCD was effective in reducing nitrification (Lan et al, 2013) and subsequent denitrification under a DSR system. Our results are in close agreement with the reductive effects of NI reported from other rice-based (Akiyama et al, 2010; Linquist et al, 2013; Li et al, 2018) and wheat-based cropping systems (Tian et al, 2017). Scheer et al (2017) reported no significant effects of NIs on the annual total of N_2O emissions in an intensive vegetable production system, but increased emissions in the following crop. Only a few studies (Liu et al, 2014) have reported N_2O emissions from DSR, and no studies reported the effect of DCD on N_2O emissions. However, the effects of DCD might be confounded with placement method in this study, as it was deep placed with urea 7–10 cm below the soil surface. In a flooded soil, deep placement could minimize nitrification even without NIs. Hence, the combination of NI and deep placement should be more effective in reducing N loss. This likely results in surplus N in DCD treatments, which could be available for plant uptake or lost through nitrification and subsequent denitrification if not utilized by plants. The surplus N is evident from increased N_2O and NO emissions and grain yields compared to UDP (Tables 1 and 2).

We hypothesized that KNO_3 increases N_2O emissions and lowers NUE, compared to urea, due to increased denitrification loss (availability of NO_3 for denitrification). Although KNO_3 had significantly lower NUE and produced lower grain yields ($P < 0.05$), N_2O emissions tended to be lower (on average by 54%) than urea. Denitrification of nitrate-N on application of KNO_3 led to significantly higher N loss, as evident from the significantly lower rice grain yield and N uptake compared to urea application (Table 1). After urea application, NH_4^+-N released from urea hydrolysis is prone to both nitrification in the aerobic zone (oxidized layer of soil and root zone) and subsequent denitrification in the anaerobic zone (Buresh et al, 2008), leading to higher N_2O emissions (Fig. 2 and Table 2).

N_2O emissions are not only restricted to the sites where N fertilizers are applied (direct emissions). N that is cascading from application sites (volatilization, run-off, leaching and erosion) to downwind and downstream ecosystems might result in natural ecosystem N enrichments, thereby creating new hot spots of N_2O emissions called ‘indirect emissions’ (Venterea et al, 2012). In addition to the significantly higher direct N_2O emissions (Table 2), broadcast urea application is also expected to contribute more towards indirect emissions.

The fertilizer-induced N_2O EF was 1.534% in broadcast urea, which is significantly higher than the other treatments (Table 2). EF from urea is higher compared to the loss reported from transplanted rice fields with continuous flooded irrigation (0.33%) (Gaihre et al, 2015) and with mid-season drainage (0.37%) (Akiyama et al, 2005). Yield-scaled N_2O emissions from UDP and DCD treatments, due to the combined effect of higher yields and lower emissions, were significantly lower than those from broadcast urea and KNO_3 treatments. Some variations in results, i.e. magnitudes of emission between greenhouse and field conditions, are expected because of differences in growing conditions. Although these results are applicable to field conditions, particularly for relative comparison of the treatment effects, there is a need for similar studies under field conditions. The higher EF in DSR could be associated with the greater opportunity for oxygen diffusion, and hence for nitrification under non-puddled DSR soil conditions and with the amount and timing of N application. Application of 50% N at 25 d after sowing when seedlings were not well-established might have resulted in surplus N, as N demand was low. The excess N might have resulted in higher emissions. This is evident from elevated N_2O emission peaks, which were sustained for up to two weeks (Fig. 2) compared to those observed for a few days to a week in previous studies. These results are in agreement with previous studies (Liu et al, 2014; Yao et al, 2016) where DSR increased N_2O emissions up to 183% over transplanted rice.

N_2O emissions showed a temporal elevated variation after fertilizer topdressing and during the period of drying and reflooding of the containers (Fig. 2). These results are in close agreement with previous studies conducted in the rice-based cropping systems in Asia (Sander et al, 2014), which shows decreased emissions with subsequent topdressing. The higher amount of N (97 kg/hm^2) at the first topdressing, which was applied at 25 d after seeding, might have resulted in surplus N and increased emissions. N fertilizers for UDP and DCD were applied at once, but the contribution of fertilizer-induced emission peaks was only 65%–74%, suggesting that UDP and DCD could retain surplus N in the soils and make it continuously available to the plants throughout the growing season.

The diel variations in N_2O emissions, smallest in the early morning and largest in the early to late afternoon, could be explained by diel soil temperature variations (Fig. 3). Our results are in close agreement with previous studies (Hou et al, 2000). Variations were observed only in broadcast fertilizer treatments when the magnitude of emissions was higher than deep-placed treatments, probably due to the availability of substrate for nitrification and denitrification, and due to increased soil temperature. With the optimum substrate and soil moisture for microbial processes, emissions increase with increased soil temperature (Laville et al, 2011; van Kessel et al, 2013). These results would be helpful to determine the optimum time of the day for a gas sampling to make a reliable estimate of total N_2O emissions from the rice cultivation as it covers all the temporal variations.

Although emission peaks after rice harvest were relatively smaller in the urea treatment compared to the other treatment, cumulative emissions among the treatments were not significant ($P > 0.05$). However, emissions from the ratoon crop contributed almost 45% and 17% to the total annual emissions in UDP and DCD treatments, respectively, while it was only 2% for the urea treatment (Table 2). Much of these losses occurred during drying, reflooding and the establishment stage of the ratoon crop (Fig. 2). N management during post-harvest operations, establishment of the next crop, and the choice of crops are crucial to maintain the N savings due to enhanced efficiency fertilizers and practices (Singh et al, 1995).

The effect of N fertilizer on the magnitudes of NO emission peaks is largely influenced by soil type, soil moisture, soil temperature, fertilizer type and ambient NO concentration (Bowman et al, 2002; Pang et al, 2009), particularly under oxidized field conditions. In general, NO emissions from flooded rice fields are very low and negligible (Gaihre et al, 2019). NO is produced mainly in the fertilized layer or at the placement site but does not diffuse away from the production sites because of its rapid uptake in the soil systems (Hosen et al, 2002; Hou et al, 2010). Higher emissions are observed from upland crops, such as wheat and vegetables (Pang et al, 2009). As with cumulative emissions, yield-scaled NO emissions and NO emission factors were not affected by any treatments, and they were negligible in rice fields (Bouwman et al, 2002; Huang et al, 2014). Emissions followed a similar pattern during the ratoon crop which were low and negligible.

UDP produced a significantly higher number of panicles per hill, resulting in more N uptake and grain yields (Table 1). Our results are in close agreement with previous studies conducted in transplanted rice field (Huda et al, 2016; Islam et al, 2017). They reported that UDP significantly increased rice yield by 15%–20% and urea savings by 25%–50%, compared to broadcast urea. UDP provides N directly to the crop root zone, thus reducing N loss to the environment compared to conventional broadcast urea. This is also reflected by a higher N recovery efficiency of 70% for UDP compared to 50% with broadcast urea. NH_4^+-N in the root zone following UDP application could be continuously available to the plants throughout the rice-growing season. The effects of DCD on yields and NUE were similar to UDP. Increased yields and NUE with nitrification inhibitors were also reported by previous studies (Pang et al, 2009). Our results confirm that both UDP and DCD could be an effective strategy to mitigate N_2O emissions and reduce reactive N loads to the environment, while increasing NUE and crop yields from DSR. The choice of DCD or UDP depends on their availability, farmers' economic status (DCD is expensive), labor availability (labor intensive) or mechanization option for UDP. Therefore, a single subsurface application of N is an attractive and viable option in DSR where mechanized seeding can be combined with deep placement. Given the increasing popularity of DSR, driven mostly by labor cost and shortage, additional field trials shall be conducted to promote the technology and further validate the results.

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