Supporting Information for

Nitrous oxide emissions increase exponentially when optimum nitrogen fertilizer rates are exceeded in the North China plain

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S1 Materials and Methods

S1.1 Site and soil-climate characteristics in the North China plain

The North China plain has a typical temperate semi-humid monsoon climate characterized by hot wet summers and cold dry winters. The amount and distribution of rainfall differ widely within and between years as affected by the continental monsoon climate, with 60-70% of annual precipitation occurring in summer (June-September).[1] The soils are generally calcareous with a low carbon content (organic matter content of 1.0-1.5%) and a high pH (7-8.5), and are intensively managed with frequent tillage.[2] The main cropping system in this region is a winter wheat-summer maize double cropping system, in which maize is sown at the beginning of June and harvested at the end of September with a following wheat crop from the beginning of October to the beginning of the following June. Organic manure has been applied less frequently in recent decades due to high labor costs and rising incomes from off-farm activities,[1] thus, maintaining high crop yields has been dependent mainly on the use of N fertilizers.

This study site was at an altitude of 37 m. Long-term (1987-2017) mean annual air temperature and precipitation were 13.2^{o}C and 473 mm, respectively. The soil is a calcareous Fluvo-aquic soil with properties in the top 20 cm layer as follows: bulk density 1.36 g cm^{-3}, pH 8.3 (soil: water, 1:2.5), total nitrogen content 0.83 g kg^{-1}, organic matter content 14.2 g kg^{-1}, Olsen-P 7.2 mg kg^{-1} and available K 125 mg kg^{-1}.

S1.2 Field and crop management

Summer maize (var. Zhengdan 958) was seeded with a row and plant spacing of 60 and 25 cm, respectively. Winter wheat (var. Liangxing 99) was sown at a density of 340 plants m^{-2} in a 25 cm row spacing. Maize and wheat straw were returned to the soil by rotary tillage after each crop harvest. A mixture of dichlorvos and dimethoate (pesticides) was sprayed on wheat in mid-April, and again in mid- or late-May, and on maize in early-July. The herbicide acetochlor was sprayed after the maize was sown. The solid granular pesticide carbofuran was applied to the top maize leaves in early-August. No obvious weeds, insects and diseases stress observed over the two rotation cycles.

In wheat, basal N fertilizer was surface broadcast and incorporated into soil by deep ploughing at the beginning of October. Topdressing fertilization was surface broadcast followed by an irrigation at the stem elongation stage in April. For maize, the N fertilizers were applied at sowing to three-leaf stage, six-leaf and ten-leaf stages by band placement when no immediate rainfall occurred or surface broadcast before the rainfall.[3] P and K fertilizers were broadcast and ploughed into soil at a rate of 90 kg P_2O_5 ha^{-1} and 60 kg K_2O ha^{-1} together with basal N fertilizer before sowing wheat and at a rate of 45 kg P_2O_5 ha^{-1} and 90 kg K_2O ha^{-1} at the three-leaf stage in maize. Flood irrigation was used two or three times for wheat (before winter, at stem elongation stage, and near the early grain-filling period) and once for maize (after sowing) at a rate of 70-90 mm depending on the soil moisture condition at that time. Each plot was divided into 5 small sub-plots, and every sub-plot was irrigated by a plastic hose of 15 cm diameter, and the rate of irrigation was recorded using a flow meter to keep the same amount of water in each sub-plot.

S1.3 The closed static chamber method for N_2O measurement

The chamber was composed of a stainless steel base frame (60 cm * 50cm * 15 cm) and a removable upper container (60 cm * 50 cm * 50 cm). The base frame was inserted 15 cm into the soil and covered two maize plants or three rows of wheat to represent the entire plot. The upper container was equipped with a three-way stopcock and a Teflon tube for collecting the gas samples with gas-tight plastic syringes, and a digital thermometer (JM624, Tianjin Jinming InstrumentCo., Ltd., China) to measure air temperature inside the box and soil temperature at a depth of 5 cm. Two ventilators at the top and on opposite sides were operated during entire sampling period to ensure complete mixing of air inside the chamber.[3-5] Maize was bent to enclose it within the chamber when its height exceeded 50 cm.[6]

For 2012 maize, the total number of N_2O sampling days was 54; the starting sampling date was 18th, June 2012 after maize was sown and 4th, July 2012 for initial fertilization. For 2012-13 wheat, the total number of sampling days was 67, the starting sampling date for wheat sowing and initial fertilization were both 9th, October 2012. For the 2013 maize, the total number of sampling days was 34, the starting sampling date for maize sowing and initial fertilization were both 19th, June 2013. For the 2013-14 wheat, the total number of sampling days was 59, the starting sampling date for wheat sowing and initial fertilization were both 8th, October 2013. Samples were also taken immediately before each crop was sown and fertilized to provide baseline measurements.

S1.4 Measurements of soil water and mineral N content

For soil sampling, we removed two soil cores by auger from the top 20 cm profile in two random positions in each plot and mixed them into one composite soil sample. Immediately, the soil samples were put in labeled plastic bags and transferred to the laboratory in an ice box. Each soil sample was sieved through a 3 mm mesh and any plant roots or debris were removed.

A part of each soil sample (15-20 g) was oven-dried at 105 °C for 24 h to measure the gravimetric soil water content, from which the water-filled pore space (WFPS) could be calculated using equation (1). Meanwhile, 12.0 g soil was extracted with 100 mL 0.01 mol L^{-1} $CaCl_2$ solution on a shaker at a speed of 180 rpm for 1 h. Extracts were frozen at -20 °C and analyzed later by an automated NH_4^+ and NO_3^- analyzer (TRAACS 2000 system, Bran and Luebbe, Norderstedt, Germany) for mineral N concentrations.

$$\text{WFPS (\%)} = \frac{\text{Soil gravimetric water content (\%)} \times \text{Soil bulk density (g cm}^{-3}\text{)}}{1- \dfrac{\text{Soil bulk density (g cm}^{-3}\text{)}}{2.65}} \quad (1)$$

S1.5 Measurements of grain yield and above-ground N uptake

Grain yields and above-ground N uptake in 2012-13 and 2013-14 wheat were reported by Lu et al.[7] Corresponding data in 2012 and 2013 maize were recorded from Yan.[8] In their papers, grain yield was obtained by sampling plants at maturity in a 6 m^2 and 18 m^2 area near the middle of each plot for wheat and maize, respectively. Plant samples were threshed and oven dried at 65 °C for 48 h. Another 1 m^2 of wheat or 6 maize plants at maturity were sampled for above-ground biomass. The biomass samples were separated into grain, leaf and stem and oven dried at 65 °C for 48 h. Separated samples of each part were weighed and measured for N concentrations using the Kjeldahl procedure.

S2 Results

S2.1 Grain yields under increasing N rates

Grain yields of maize, wheat or annual wheat-maize cycle showed consistent patterns, in which they increased significantly with higher N rates from the control to Optimum treatments (165-189 kg N ha^{-1} $season^{-1}$) ($P < 0.05$), and then reached a plateau with no significant difference between the Optimum, 130% of Optimum (215-246 kg N ha^{-1} $season^{-1}$) and the Conventional treatments (250-300 kg N ha^{-1} $season^{-1}$; Figure S4 (a)-(b)). Maize grain yields ranged from 9.6 to 10.5 t ha^{-1} in 2012 and 8.7 to 9.7 t ha^{-1} in 2013, while yields of the two wheat seasons were both between 7.0 and 8.1 t ha^{-1} in the N fertilizer treatments. The grain yields of maize or wheat were both typical within the North China plain.[9]

S2.2 N_2O emission factors under increasing N rates

The mean emission factors for fertilized N treatments in the two maize seasons ranged from 0.85% to 1.29% in the order of: Opt.＜Opt.*0.7＜Opt.*1.3＜Con. (Table S3). Emission factors in the wheat season varied widely between the two years, ranging from 1.20% to 1.51% in the extreme 2012-13 wheat season and from 0.09% to 0.16% in the more normal 2013-14 season. Emission factors for the annual wheat-maize cycle ranged from 1.09% to 1.28% in extreme 2012-13 year, and from 0.43% to 0.70%, following the order: Opt.＜Opt.*0.7＜Opt.*1.3＜Con. in the normal 2013-14 year, which was representative of the North China plain.

Our findings were consistent with the results from summarizing field measurements of N_2O emissions which showed the emission factors within 0.08-0.21% for wheat, 0.44-0.59% for maize and 0.10-0.59% for wheat-maize cycle in the North China plain.[2] A study in a maize-soybean rotation system in Michigan, USA showed that N_2O emission factors of maize ranged from 0.6% to 1.5% (0-225 kg N ha^{-1} $season^{-1}$) and increased with rising N rates, especially when in excess of the requirement for maximum maize yield.[10]

S3 Discussion

S3.1 Differences between yield-scaled N_2O emissions calculated by yield and above-ground N uptake as the denominator

The conventional yield-scaled N_2O emission, i.e. the ratio between N_2O-N and grain yield, could indicate the compromise between productivity and environmental cost. However, grain N concentration varies within different crops (e.g. wheat and maize), which leads to different above-ground N uptake of crops even when they have similar yields, so we use above-ground N uptake as the denominator for yield-scaled N_2O emissions to more accurately express the linkage between applied N, crop N uptake and N_2O emissions.

S3.2 Mechanisms underlying the exponential N_2O response to N rate

N_2O fluxes were controlled by interactions between soil temperature, moisture and management practices such as N fertilization, in which N rate became the main driving factor of N_2O emission especially in the maize season which coincided with hot and wet conditions. The occurrence of such high N_2O emissions in response to over fertilization could be explained by: (1) excessive N inputs exceeding crop requirements and creating an N surplus which provided more N substrates for microbial N_2O production;[11-14] (2) the high nitrate content inhibited the reduction of N_2O to N_2, hence, increased the ratio of N_2O to N_2O+N_2;[15] (3) excessive ammonium from urea hydrolysis led to high accumulation of nitrite in the fluvo-aquic soil, which nonlinearly increased the N_2O emissions.[16]

In maize, the temperature and moisture contents both exceeded threshold values that are recognized in this region for contributing to high emissions of N_2O, and would have been particularly important in the presence of surplus mineral-N pools resulting from over fertilization,[2] which were similar to findings from previous studies in the North China plain.[4,17-18] Conversely, the low temperature and moisture contents in the normal wheat season restricted N_2O fluxes and resulted in weak and even linear responses to N applications. Previous studies have demonstrated that when soil-climate conditions are not favorable to N_2O production, there can be linear responses to increasing N applications in cereals in the UK and Germany.[19-20] Our findings in the normal year were consistent with other field studies in the North China plain,[1,3,4,5] but the distinct differences between the two wheat seasons were valuable for assessing the climate sensitivity of the N_2O response during winter periods.[21]

S3.3 Frequency of extreme snowfall in Quzhou (experiment site in this study)

The extreme snowfall that occurred between December-February in 2012-13in wheat induced freeze-thaw cycles resulting in peaks of N_2O emission that were not apparent in the more normal winter of 2013-14. We therefore calculated its frequency over the last 30 years and analyzed its impacts on N_2O emissions under predicted long-term changes in climate. The long-term (1987-2017) average snowfall over winter period (December-February) was 14.6 mm, but in 2012-13 it was 4.5 times higher reaching 65.8 mm, while snowfall over the winter period in 2013-14 was just 3.9 mm representing a normal dry winter in the North China plain. We therefore defined the 2012-13 year as an ‘extreme snowfall year’, and 2013-14 year as a ‘normal year’ (Figure S7 (a)). Over the last 30 years (1987-2017), the frequency of such extreme snowfall (＞45mm) was 3.2% in the winter period (December-February) (Figure S7 (b)), and the frequency of extreme snowfall (＞15mm) in each month within the winter period was 3.2% in December, 6.5% in January and 16.1% in February at our study site (Figure S7 (c)). The site normally receives light snowfall (0.1-15.0 mm) or medium snowfall (15.1-30.0 mm) during the winter period with a frequency of 58.1% and 32.3%, respectively. Years without snow and large snowfall (30.1-45 mm) years occurred occasionally both with a frequency of 3.2% (Figure S7 (b)). Light winter snowfall was observed at the same site during N_2O measurements conducted in 2009-11,[4] and at a site near Beijing in 2011-14 (Figure S7 (d)-(e)).[5] Their observations of N_2O emissions were comparable with our results in the normal year.

S3.4 Mechanisms of N_2O production induced by freeze-thaw cycles

During extreme snowfalls, freeze-thaw cycles were important factors in driving peaks in N_2O emissions, which were mostly attributed to the newly produced N_2O by microbial processes in the surface layer rather than the release of N_2O trapped in the deep unfrozen layer.[22] The newly produced N_2O can result as a consequence of three processes: (1) increased soil water content due to the snow melting which creates an anaerobic environment favouring denitrification;[23-25] (2) available N substrates accumulate owing to accelerated mineralization while plant roots were still not active enough to absorb the freshly mineralized N;[26] (3) the soil surface layer tended to be flooded because ice at the soil surface prevented infiltration of melting water flow, but also promoted the transportation of available carbon and nitrogen sources into the surface layer.[27-29] The soil WFPS was around 80% and nitrate ranged from 20 to 70 mg N kg^{-1} over that period in our study, providing optimal conditions for the denitrification process.[30]

Supplementary Tables and Figures

Table S1. R^2 and SS of different fitting models between N application rates and cumulative N_2O emissions.

Fitting objects	SST	Linear fitting				Quadratic fitting				Exponential fitting			
		SSR	SSE	R^2	*P*	SSR	SSE	R^2	*P*	SSR	SSE	R^2	*P*
2012 Maize	105.58	98.13	7.45	0.73	<0.001	98.71	6.87	0.75	<0.001	98.75	6.83	0.75	<0.001
2012-13 Wheat	168.64	165.91	2.73	0.93	<0.001	166.00	2.64	0.93	<0.001	165.90	2.74	0.93	<0.001
2013 Maize	91.87	87.07	4.80	0.83	<0.001	89.00	2.87	0.90	<0.001	89.44	2.43	0.91	<0.001
2013-14 Wheat	4.70	4.53	0.17	0.71	<0.001	4.53	0.17	0.71	<0.001	4.53	0.17	0.71	<0.001
2012 and 2013 Maize	197.46	184.90	12.56	0.77	<0.001	187.26	10.20	0.82	<0.001	187.61	9.85	0.82	<0.001
2012-13 and 2013-14 Wheat	173.34	114.73	58.61	0.29	<0.001	114.73	58.61	0.29	0.002	114.73	58.61	0.29	<0.001
2012-13 Maize-wheat	529.48	519.67	9.81	0.92	<0.001	519.89	9.59	0.92	<0.001	519.91	9.57	0.92	<0.001
2013-14 Maize-wheat	134.80	131.20	3.60	0.89	<0.001	133.09	1.71	0.95	<0.001	133.28	1.52	0.96	<0.001
Two rotation cycles	664.28	591.70	72.58	0.64	<0.001	594.15	70.13	0.66	<0.001	594.32	69.96	0.66	<0.001

R^2, SST, SSR and SSE denote coefficient of determination, sum of squares for total, sum of squares for regression and sum of squares for error, respectively.

Table S2. R^2 and SS of different fitting models between N application rates and yield-scaled N_2O emissions.

Fitting objects	SST	Linear fitting				Quadratic fitting				Exponential fitting			
		SSR	SSE	R^2	*P*	SSR	SSE	R^2	*P*	SSR	SSE	R^2	*P*
2012 Maize	1.01	0.94	0.07	0.69	<0.001	0.95	0.06	0.73	<0.001	0.95	0.06	0.73	<0.001
2012-13 Wheat	3.06	2.98	0.08	0.86	<0.001	2.99	0.07	0.88	<0.001	2.99	0.07	0.88	<0.001
2013 Maize	1.05	0.98	0.07	0.77	<0.001	1.01	0.04	0.85	<0.001	1.01	0.04	0.87	<0.001
2013-14 Wheat	0.08	0.07	0.01	0.43	0.006	0.07	0.01	0.44	0.022	0.07	0.01	0.43	0.004
2012 and 13 Maize	2.06	1.92	0.14	0.73	<0.001	1.95	0.11	0.78	<0.001	1.95	0.11	0.79	<0.001
2012-13 and 2013-14 Wheat	3.18	2.08	1.10	0.20	0.007	2.10	1.08	0.22	0.025	2.10	1.08	0.22	0.048
2012-13 Maize-wheat	1.69	1.65	0.04	0.88	<0.001	1.66	0.03	0.90	<0.001	1.66	0.03	0.91	<0.001
2013-14 Maize-wheat	0.47	0.45	0.02	0.78	<0.001	0.46	0.01	0.90	<0.001	0.46	0.01	0.92	<0.001
Two rotation cycles	2.16	1.93	0.23	0.59	<0.001	1.95	0.21	0.63	<0.001	1.95	0.21	0.64	<0.001

R^2, SST, SSR and SSE denote coefficient of determination, sum of squares for total, sum of squares for regression and sum of squares for error, respectively.

Table S3. Seasonal and annual N_2O emission factors (EF_ds, Mean ± SD, n=4, %) of the five N rates during the two wheat-maize cycles from June 2012 to June 2014.

Treatments	2012 Maize	2012-13 Wheat	2013 Maize	2013-14 Wheat	2012-13 Maize-Wheat	2013-14 Maize-Wheat	2012 and 2013 Maize	2012-13 and 2013-14 Wheat	Two rotation cycles
Opt.*0.7	0.88	1.51	1.00	0.09	1.21	0.53	0.93±0.21	0.80±0.78	0.86±0.40
Opt.	0.96	1.44	0.77	0.11	1.21	0.43	0.85±0.33	0.77±0.72	0.81±0.42
Opt.*1.3	0.97	1.20	0.98	0.16	1.09	0.56	0.97±0.20	0.68±0.56	0.82±0.32
Con.	1.20	1.35	1.38	0.13	1.28	0.70	1.29±0.35	0.74±0.66	0.99±0.35
Average	1.00±0.36	1.37±0.21	1.02±0.27	0.12±0.05	1.19±0.18	0.55±0.12	1.01±0.32	0.74±0.65	0.87±0.36

Table S4. N_2O response models (N_2O-N, kg) to N fertilizer rates in our study site and other sites in the North China plain or the global scale.

Scale	Maize				Wheat				Ref.
	N_2O emission response	n	R^2	*P* value	N_2O emission response	n	R^2	*P* value	
the North China Plain (this paper)	$y = -0.2010 + 0.5872e^{0.0073x}$	40	0.82	< 0.01	$y = 0.2331 + 0.0010x + 1.2E\text{-}6x^2$	20	0.71	<0.01	-
					$y = 0.2614 + 0.0148x – 6.8E\text{-}6x^2$	20	0.93	<0.01	-
the North China Plain (other sites)	$y = 0.45 + 0.0053x$	-	0.57	< 0.05	$y = 0.59 + 0.0017x$	-	0.48	<0.05	(9)
	$y = 0.1107 + 0.0058x$	-	0.62	< 0.01	$y = 0.2958 + 0.0037x$	-	0.65	<0.01	(10)
	$y = 0.99e^{0.0047x}$	-	0.20	< 0.01	$y = 0.50e^{0.0032x}$	-	0.25	<0.01	(22)
Global	$y = 1+0.01x$	-	-	-	$y = 1+0.01x$	-	-	-	(23)
	$y = 1.218 + 6.49E\text{-}3x + 1.87E\text{-}5x^2$	121	-	0.0019	$y = 1.218 + 6.49E\text{-}3x + 1.87E\text{-}5x^2$	121	-	0.0019	(24)

'-' denotes no information.

Table S5. Equations of the correlations between N application rates and cumulative or yield-scaled N_2O emissions.

	Period	Response	n	R^2	*P*
Cumulative N_2O emission	2012 and 2013 Maize	$y = -0.2010+0.5872e^{0.0073x}$	40	0.82	<0.01
	2012-2013 Wheat	$y = 0.2614+0.0148x-6.8E-6x^2$	20	0.93	<0.01
	2013-2014 Wheat	$y = 0.2331+0.0010x+1.2E-6x^2$	20	0.71	<0.01
	2012-2013 Rotation cycle	$y = -16.8301+17.5258e^{0.0006x}$	20	0.92	<0.01
	2013-2014 Rotation cycle	$y = -0.2783+0.8039e^{0.0031x}$	20	0.96	<0.01
Yield-scaled N_2O emission	2012 and 2013 Maize	$y= 0.0258+0.0352e^{0.0088x}$	40	0.79	<0.01
	2012-2013 Wheat	$y= 0.1010+0.0014x-2.2E-7x^2$	20	0.88	<0.01
	2013-2014 Wheat	$y= 0.0057+0.0004x-5.2E-7x^2$	16	0.44	<0.05
	2012-2013 Rotation cycle	$y=-0.3252+0.4002e^{0.0011x}$	20	0.91	<0.01
	2013-2014 Rotation cycle	$y= 0.0534+0.0114e^{0.0051x}$	20	0.92	<0.01

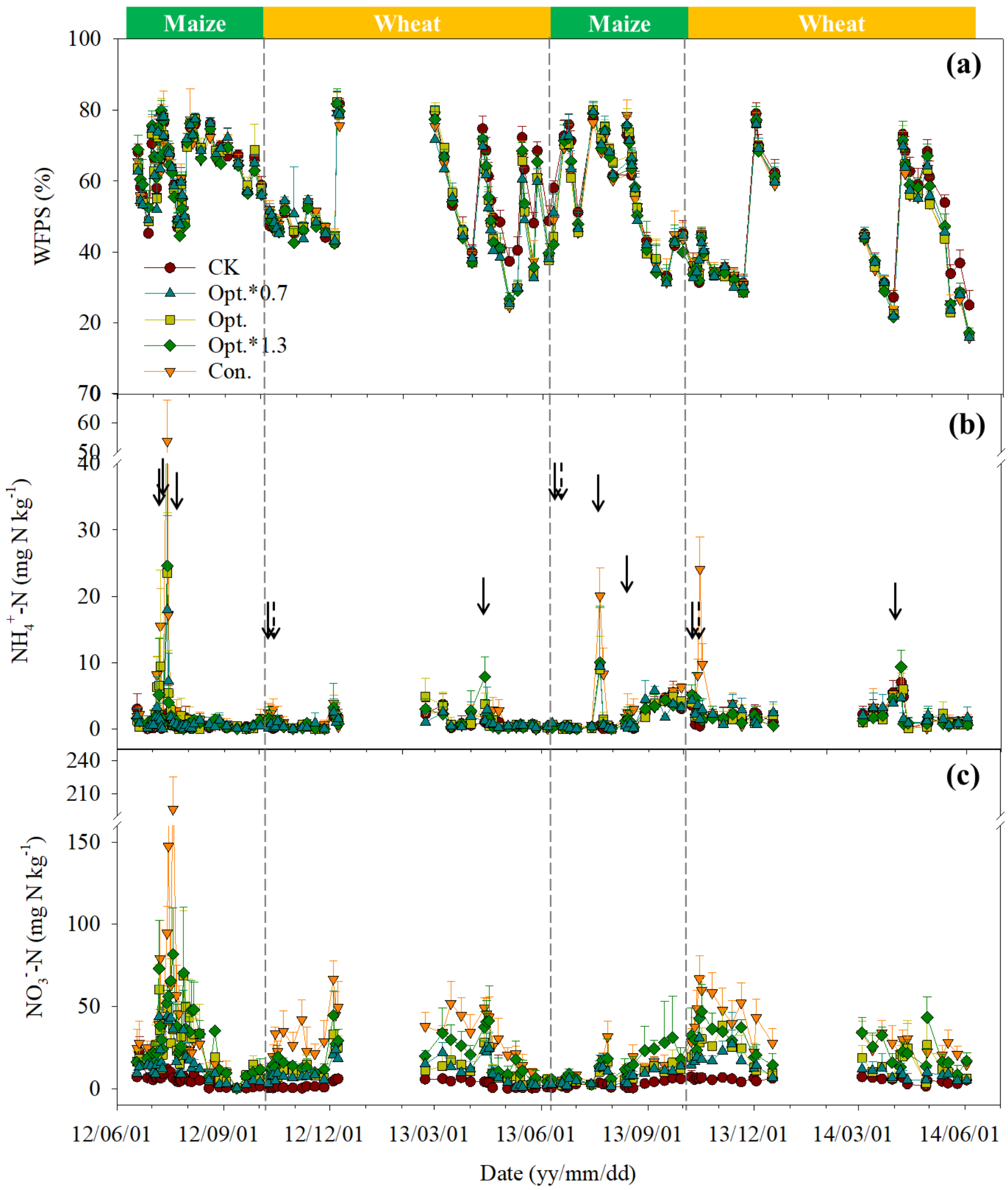


Figure S1. Dynamics of (a) water filled pore space (WFPS); (b) soil NH_4^+-N content in 0-20 cm; and (c) soil NO_3^--N content in 0-20 cm during the two wheat-maize cycles from June 2012 to June 2014. Solid and dashed arrows in (b) represent fertilization and tillage, respectively. Vertical bars indicate standard deviation (n=4). There was no soil parameters' data from December to March in each winter wheat season because we did not take soil samples due to soil freezing.

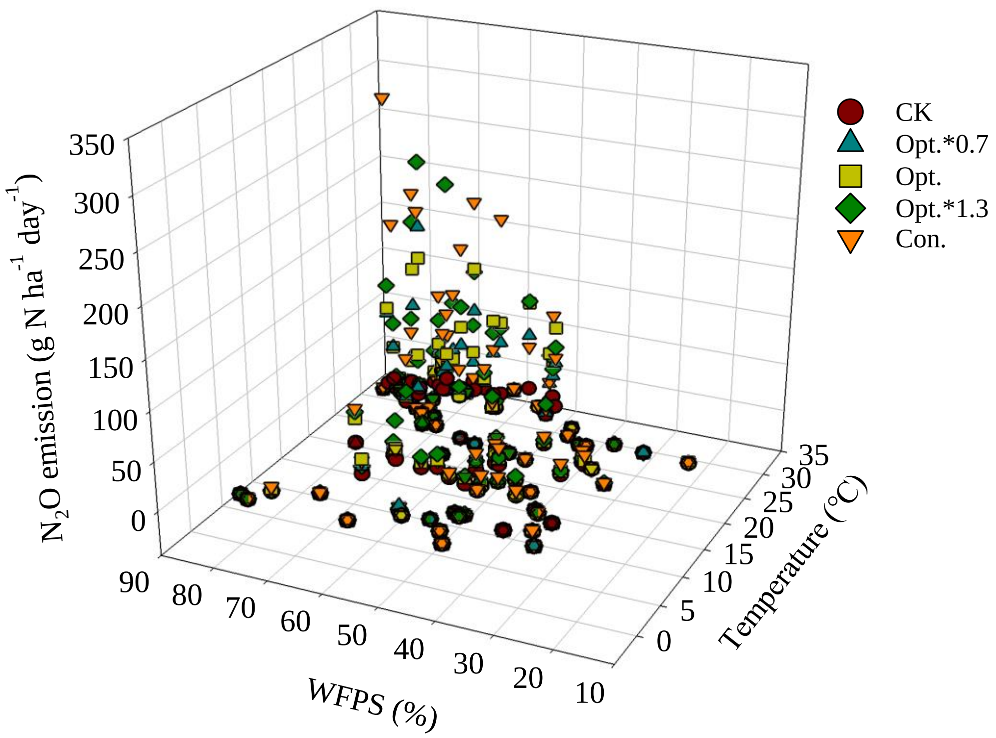


Figure S2. Correlation of daily N_2O emission to daily average temperature at 5 cm depth soil and daily average water filled pore space (WFPS) in 20 cm depth during the two wheat-maize cycles from June 2012 to June 2014.

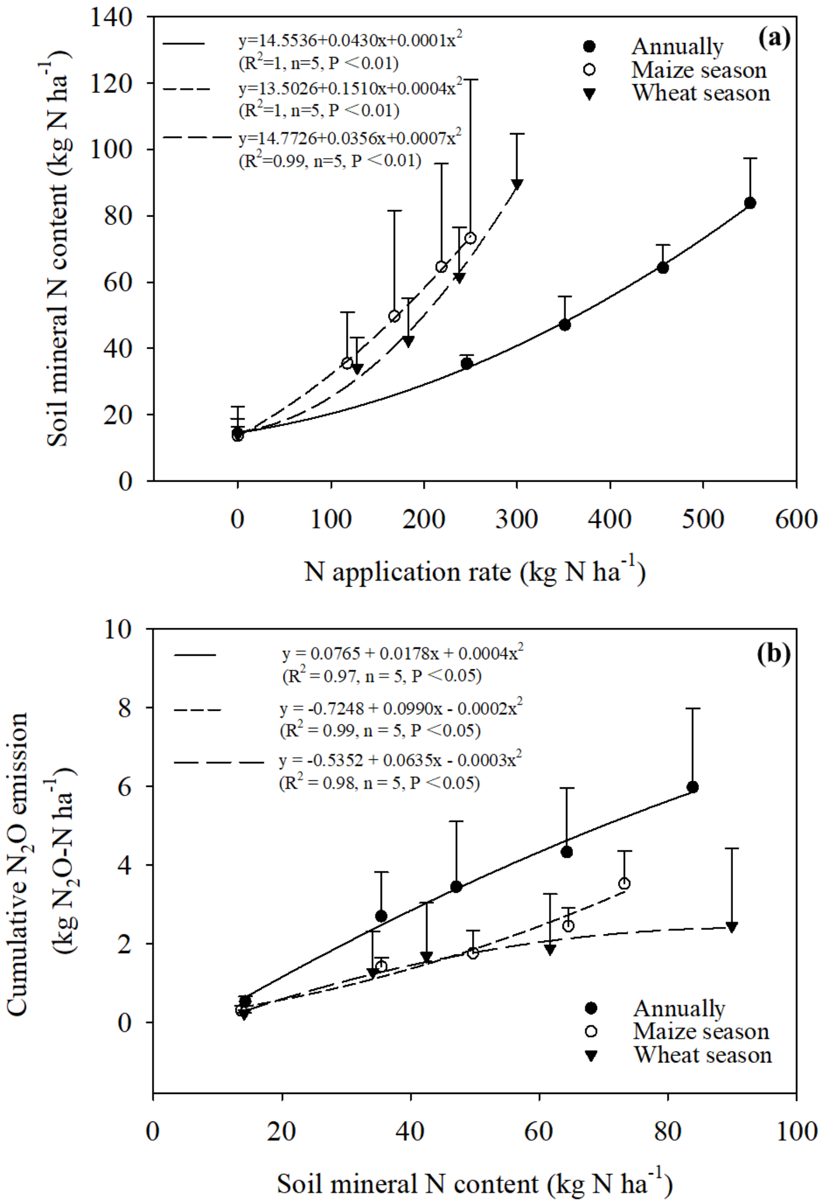


Figure S3. Correlations of mean soil mineral N content to N application rate (a), and cumulative N_2O emission to mean soil mineral N content (b) during the two wheat-maize cycles from June 2012 to June 2014. Vertical bars indicate standard deviation (n=4).

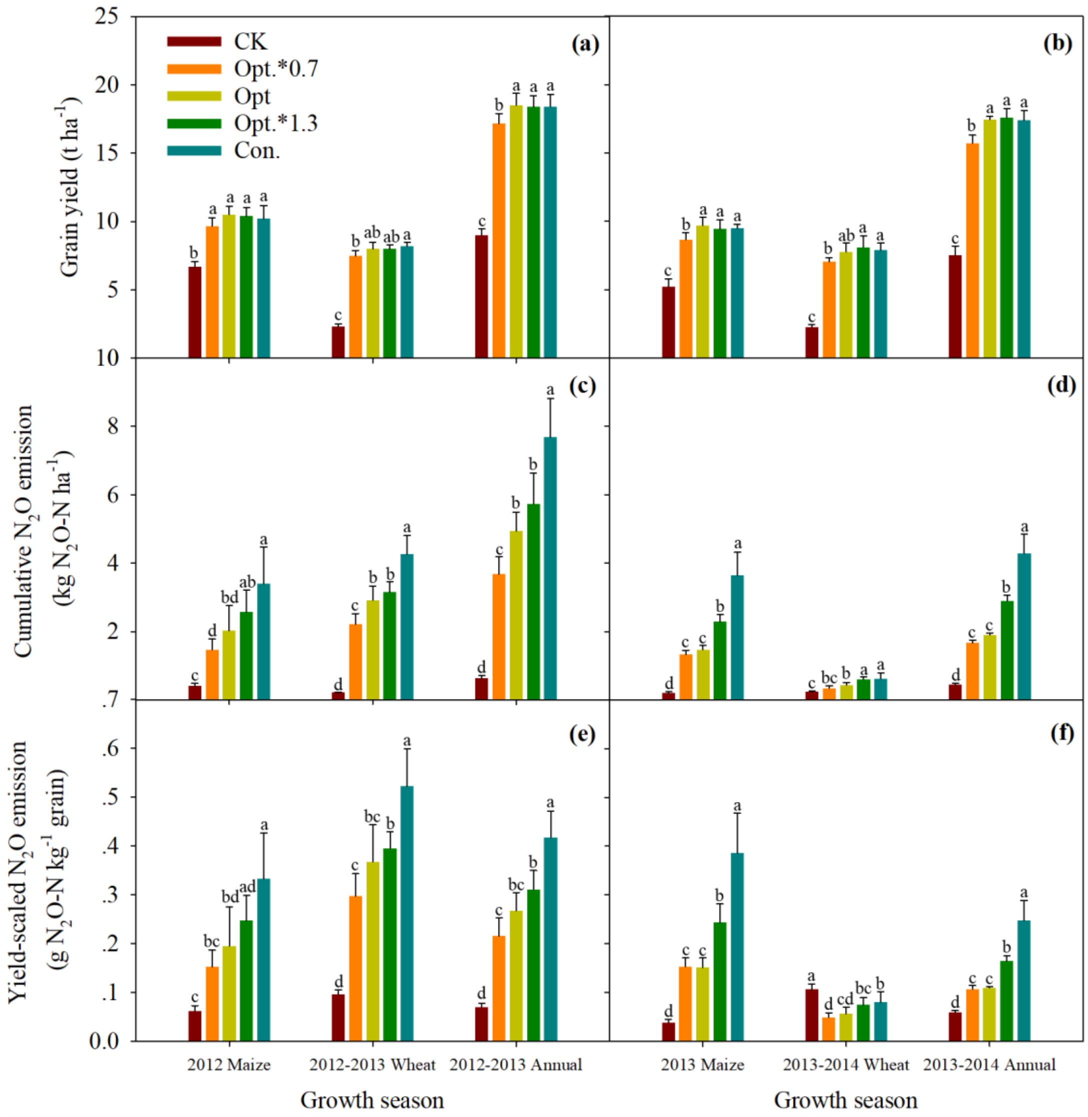


Figure S4. Seasonal and annual grain yields (a-b, dry matter), cumulative N_2O emissions (c-d) and yield-scaled N_2O emissions (e-f) of the five N rates from June 2012 to June 2014. Vertical bars indicate standard deviation (n=4). Different letters above each bar indicate significant difference between N fertilizer rates at $P < 0.05$.

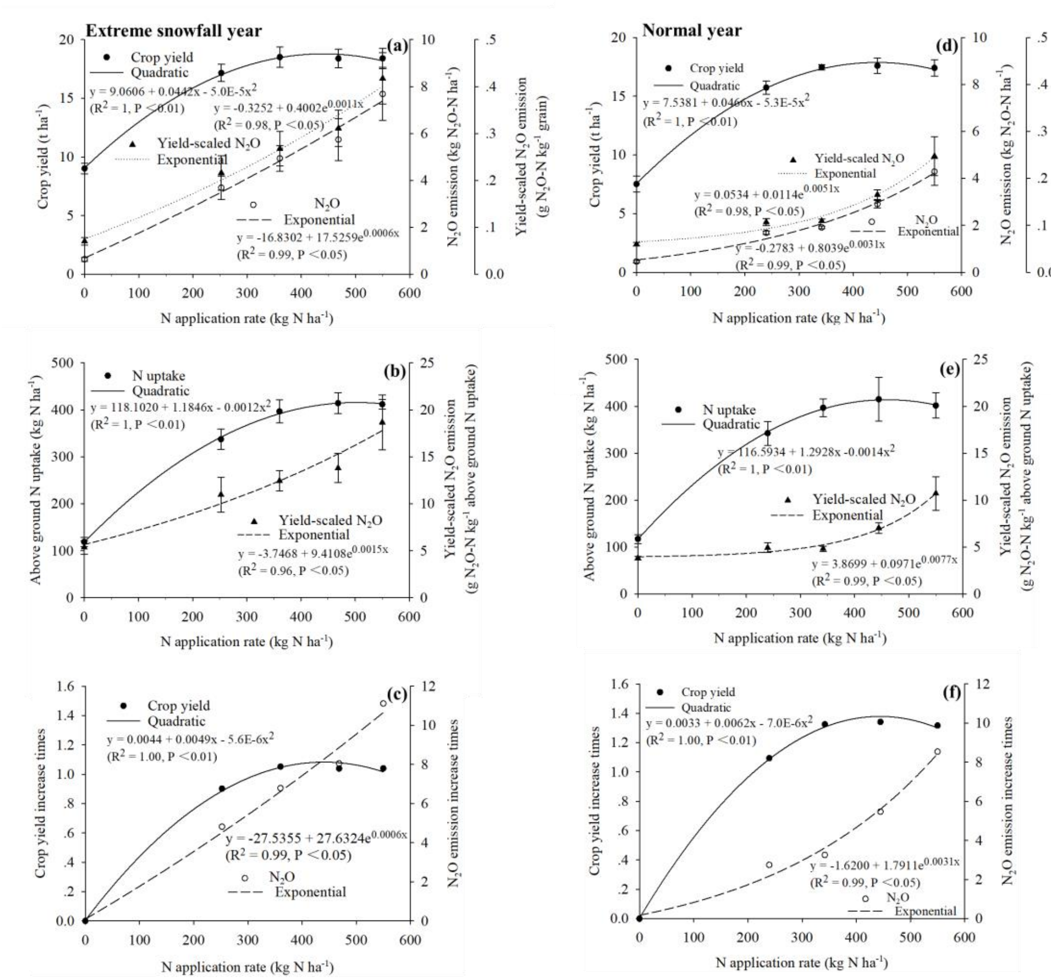


Figure S5. Responses of crop yield, cumulative N_2O emission, yield-scaled N_2O emission, above ground N uptake, crop yield increase times and N_2O emission increase times to N application rate in the extreme snowfall year (2012-13 wheat-maize) (a)-(c) and the normal year (2013-14 wheat-maize) (d)-(f). Crop yield or N_2O emission increase times here was calculated as mean crop yield or mean N_2O emission of each N fertilized treatment minus that of no fertilizer treatment, then divided by that of no fertilizer treatment. Vertical bars indicate standard deviation (n=4).

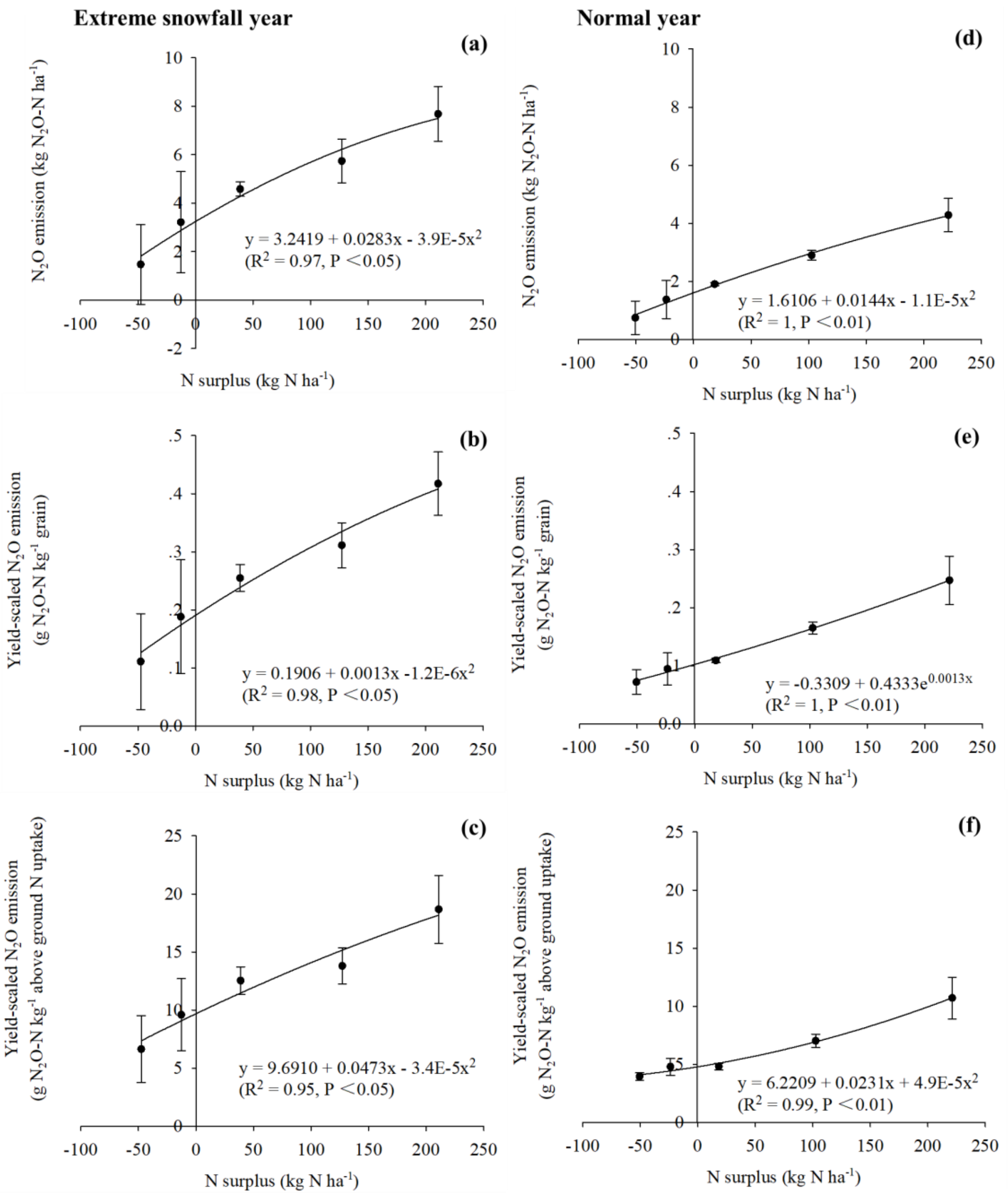
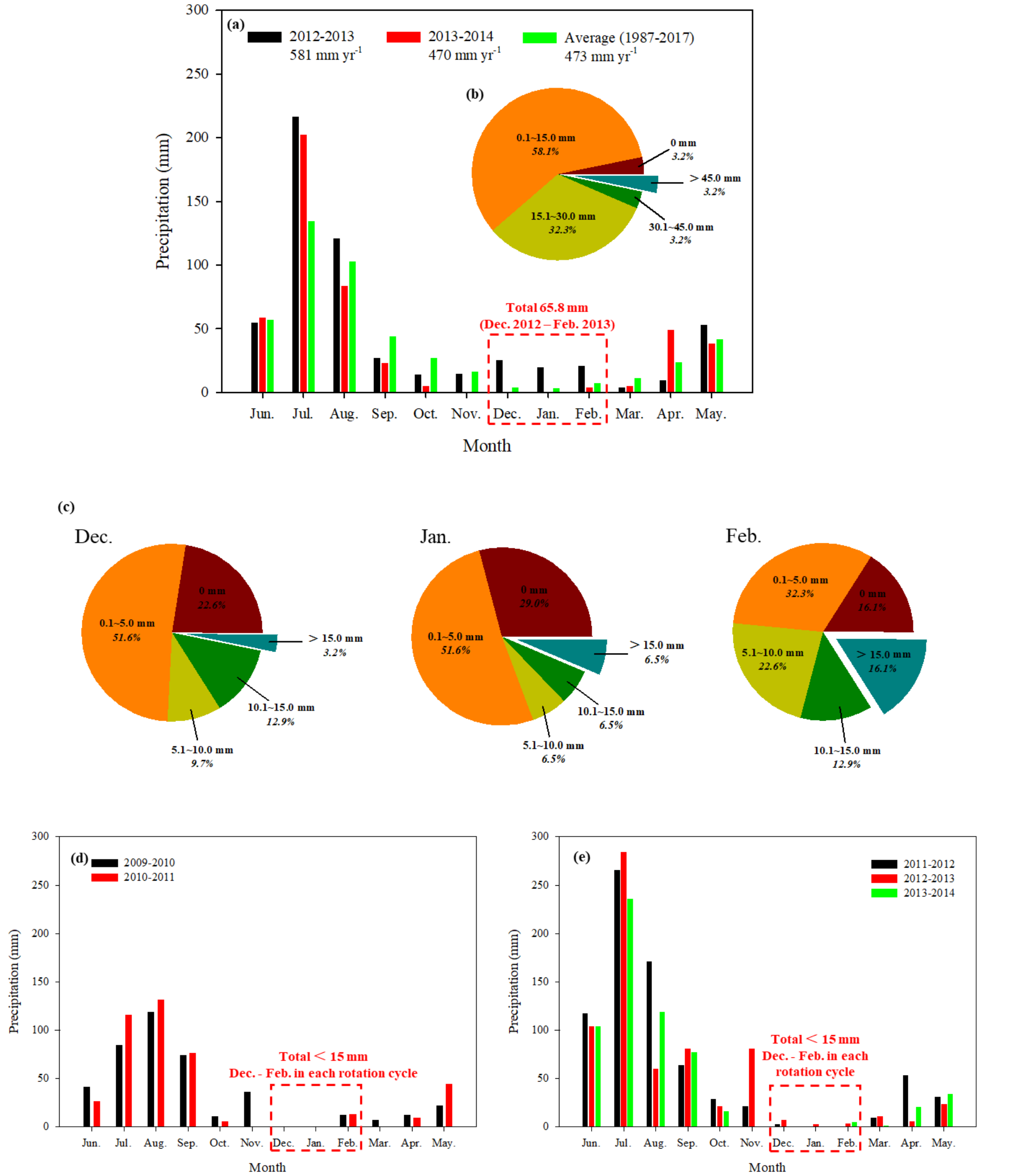


Figure S6. Responses of cumulative N_2O emission, yield-scaled N_2O emission to N surplus in the extreme snowfall year (2012-13 wheat-maize) (a)-(c) and the normal year (2013-14 wheat-maize) (d)-(f). N surplus here is defined as the sum of N application, N deposition and biological N fixation minus above ground N uptake. N deposition in Quzhou was 63 kg N ha^{-1}.[20] Biological N fixation was assumed to be 5 kg N ha^{-1} $season^{-1}$.[21] Vertical bars indicate standard deviation (n=4).



(Gao et al., 2014) (Huang et al., 2017)

Figure S7. Comparison of rainfall during the two wheat-maize cycles from June 2012 to June 2014 with the historical average rainfall values (1987-2017) and rainfall in other sites of the North China plain, and frequency of extreme snowing in Quzhou research station from 1987 to 2017. Upper panels show monthly rainfall as compared with the long-term average values (a), and percentage of extreme snowfall (＞45mm) during wintering period (Dec.-Feb.) in wheat season (b) or percentage of extreme snowfall (＞15mm) in December, January and February (c). Lower panels show monthly rainfall in each cycle in the same field site as this paper (cited from Gao et al,[9] shown in Table S4) (d) and another field site in the North China Plain (cited from Huang et al,[10] shown in Table S4) (e).

References

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