Deriving emission factors and estimating direct nitrous oxide emissions for crop cultivation in China

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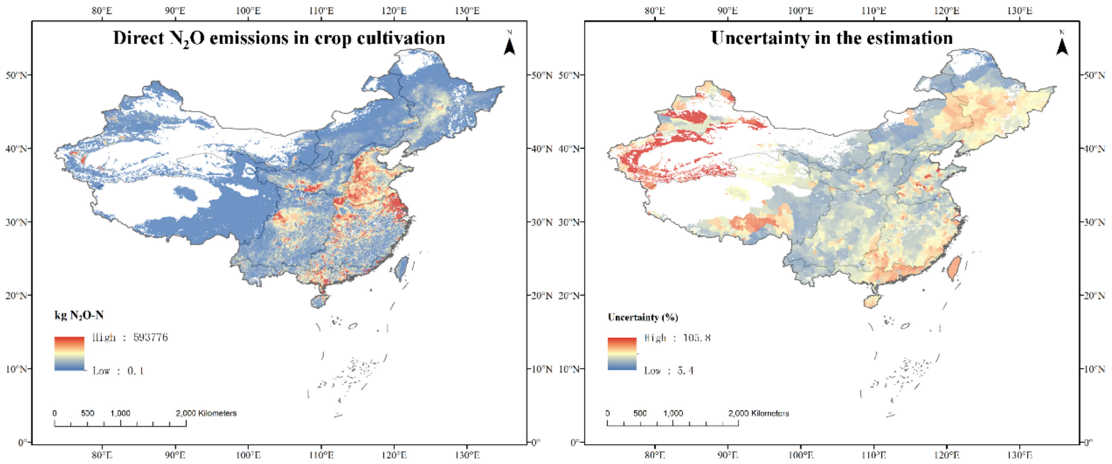
Abstract: Updating and refining the N_2O emission factors (N_2O-EF) is vital to reduce the uncertainty in estimates of direct N_2O emissions. Based on a database with 1151 field measurements across China, the N_2O-EFs were established via three approaches including the maximum likelihood method, a linear regression with intercept, and a linear regression with the intercept set to 0 using 70% of the observations. The remaining 30% of the observations were then used to evaluate the predicted N_2O-EFs. The third method had the highest R^2 of 0.39 and the best model efficiency of 0.38 with no significant bias, showing the best calculation efficiency. The results showed that the N_2O-EFs varied with agro-regions, crops, and management patterns. The agro-regions of Huang-Huai-Hai and Yangtze River had the higher N_2O-EFs in maize and wheat seasons than other regions, and the highest N_2O-EFs of 0.66~0.92% in rice season was found in the South and Southwest agro-regions. Both fertilizer types and water regimes had the remarkable effects on N_2O-EFs. Based on the best estimation by the selected method, direct N_2O emissions from China's crop cultivation were estimated to be 194 Gg N_2O-N with a 95% confidence interval of 180-208 Gg N_2O-N in the year 2016.

Key words: agricultural soil, nitrous oxide, emission factor, agro-region, cropping system, N fertilizer


Direct N₂O emissions in crop cultivation
kg N₂O-N
High : 593776
Low : 0.1
0 500 1,000 2,000 Kilometers
Uncertainty in the estimation
Uncertainty (%)
High : 105.8
Low : 5.4
0 500 1,000 2,000 Kilometers
N
80°E
90°E
100°E
110°E
120°E
130°E
50°N
40°N
30°N
20°N
10°N
0°

Introduction

Nitrous oxide (N_2O) contributes to climate change, stratospheric ozone depletion, and impacts human health directly and/or indirectly.[1-3] The global warming potential of N_2O is approximately 265 times that of carbon dioxide (CO_2) over a 100-year timescale when not including climate carbon feedbacks.[4] Agriculture is recognized as a major source of atmospheric N_2O due to external nitrogen (N) input, which accounts for ~60% of global anthropogenic N_2O emissions.[5] Given that global N_2O emissions in agriculture are projected to increase in the coming decades due to increased mineral N applications,[6,7] developing appropriate methods to quantify N_2O emissions is critical to enable better prediction of agricultural N_2O emissions, and to identify improved management practices in different regions.

Since N_2O emissions induced by anthropogenic N inputs (so called direct N_2O emissions) were included in the GHG inventory of the IPCC,[8] N_2O emission factors (N_2O-EF) - defined as the average N_2O emission rate per unit of N input in kg N_2O-N kg^{-1} N or % - have been used to estimate direct N_2O emissions in agriculture with limited input data at the regional, national and global scale. Bouwman[9] calculated an N_2O-EF of 1.25% (uncertainty range 0.25-2.25%) using linear regression based on only 20 year-round measurements in uplands, which in turn informed the Intergovernmental Panel on Climate Change (IPCC) Tier 1 emission factor.[10] IPCC[8] updated the N_2O-EF to 1% with an uncertainty range of 0.3-3% for uplands using Bouwman et al.[11] An N_2O-EF for flooded paddy fields was also calculated to be 0.3%, with an uncertainty range of 0.0-0.6%, which was much lower than that of upland. Given the uncertainties implicit in global EFs, it is preferable that country-specific N_2O-EFs be developed and IPCC[8] suggested Tier 2 methods to quantify agricultural N_2O emissions. To minimize the uncertainty in regional N_2O emission estimates, many studies have explored the quantitative relationship of N_2O emissions with N fertilizer application rates using Maximum Likelihood estimation and Ordinary Least Squares methods, based on numerous published data.[12-14]

When considering different crop types, most studies have highlighted that the N_2O-EFs of rice paddies are much lower than that of uplands.[8,12] However, other crop types, such as N-fixing crops and non-N-fixing crops, may also have very different N_2O-EFs.[15] Management also has a significant impact.[15] For example, Akiyama et al.[16] estimated a global N_2O-EF for fertilized rice ranging from 0.22% under continuous flooding to 0.37% under midseason drainage based on 113 measurements from 17 sites of paddy fields. Albanito et al.[17] reported an annual N_2O-EF of 2.1% (confidence interval (CI): 0.6-6.7%) for global croplands fertilized with ammonium, 1.1% (CI: 0.2-7.8%) with other N-fertilizers, and 0.7% (CI: 0.1-2.9%) for urea mixed with a nitrification inhibitor, though their large uncertainty was observed. Recently, Zhou et al.[18] indicated that climatic variables regulate the heterogeneity of N_2O-EFs in China. From the above, it is apparent that N_2O-EFs vary greatly between different conditions with significant uncertainty. There is therefore an urgent need to develop more specific N_2O-EFs simultaneously taking into account climatic conditions, crop types and management modes to improve regional, national and global GHG inventory.

China is of key importance in terms of delivering sustainable crop cultivation.

Consequently, the amount of mineral N fertilizer used for agriculture in China increased to almost 23.6 Tg N in 2015; increasing by 152% from 9.34 Tg N in 1980.[19] Meanwhile, China's annual agricultural N_2O emissions have increased by a factor of 7, from 0.16 to 1.26 Tg N_2O, during the period 1960s to 2007~2016, contributing 24% of global soil N_2O emissions in 2007~2016.[7] China has a large agricultural area across various climate zones and agro-ecosystem conditions, which requires more specific N_2O-EFs, reflecting the differences in regional conditions, cropping systems and management patterns due to the heterogeneity of N_2O-EFs. Some China-specific N_2O-EFs have been developed in the past few years, though these are limited.[12,20-27] As one of the earliest studies on N_2O emissions estimation in China's cropland, Xing et al.[20] calibrated the N_2O-EFs for upland crops and paddy rice using only 6 and 7 observations but the uncertainty was not assessed. Zheng et al.[21] subsequently developed regional cropping system specific N_2O-EFs ranging from 0.2% (CI: 0.03~0.52%) in paddy rice systems with year-round flooding of southwestern China, to 2.8% (CI: 1.25~4.34%) in the upland crop-paddy rice system of Yangtze river region using 54 paired observations. Using 71 paired field observations in paddy fields of China, the N_2O-EFs under different water regimes were calculated to be 0.02% (CI: 0.014~0.026%), 0.42% (CI: 0.3~0.54%) and 0.73% (CI: 0.51~0.95%) for continuous flooding, flooding-midseason drainage-reflooding, and flooding-midseason drainage-reflooding-moist intermittent irrigation without water logging, respectively.[22] Gao et al. [24] developed N_2O-EFs for paddy fields and uplands using 195 and 261 samples, respectively; however, uncertainty analysis was very limited. Recently, the N_2O-EFs of upland crop and paddy rice were compiled for 6 regions using 620 observations in agricultural soil of China.[26] From the above, there were limited studies focused on the effects of geographic location, cropping systems and management modes on N_2O-EFs simultaneously, which may induce substantial uncertainty in estimation of direct N_2O emissions. The current N_2O-EFs have uncertainty ranging from 29% to more than 160%. Zheng et al.,[21] Zou et al.[23] and Zhou et al.[26] estimated direct N_2O emissions in cropland of China using emission factor approach, and the uncertainties ranged from 23% to 78%, showing an urgent need to reduce the uncertainty. Most recently, Zhou et al.[18] used piecewise linear models to develop the N_2O-EFs of upland crop and paddy rice considering various environmental factors, which substantially improved the simulation efficiency. However, the model structure is not easily understood and the model requires numerous driving variables, which may limit the wider application of this model.

In recent years, there have been many published field studies monitoring N_2O emissions, which have enriched the N_2O research database and allow the development of more specific N_2O-EFs considering features of agro-regions, cropping systems and management modes, and permit estimation of direct N_2O emissions estimations with limited data input. Based on a database of 1151 observations, the objectives of this study were to develop regionally specific N_2O-EFs with consideration of crop types and management types for China's cropland, then to quantify direct N_2O emissions for China's staple crop cultivation using the updated N_2O-EFs.

Materials and methods

Data sources

Seasonal cumulative N_2O emissions data, used for the development of N_2O-EFs, were collected from scientific field studies that reported N_2O emissions in Chinese cropping systems. Scientific literature, published over a time span of 2001-2018, was collected and archived *via* searching the databases of CNKI (China National Knowledge Infrastructure) and ISI-Web of Knowledge using the search terms of "nitrous oxide" or "N_2O" and "crop" or "cropland" and "China". Firstly, the data from original studies with direct N_2O emission measurement for arable fields were considered, whereas data from incubations or modelling was excluded. Paired data on N_2O emissions under a fertilizer treatment and a non-fertilized control were retrieved, while data under biochar application was excluded due to the specific mechanisms.[28,29] This resulted in 1151 measurements from 135 Chinese cropland sites, including 90 sites from upland cropping systems (839 observations) and 45 sites from paddy rice cropping systems (312 observations) (Figure 1). The dataset mainly included geographic information (latitude and longitude), crop types, fertilizer types classified into 5 broad categories – control (309 observations), mineral fertilizer (515 observations), mineral & organic fertilizer (200 observations), organic fertilizer (49 observations), enhanced-efficiency fertilizer (78 observations) (Table 1), amounts of total N applied, water regimes for paddy rice cultivation, and seasonal cumulative N_2O emissions. Cumulative N_2O values were extracted either directly from tables, or derived from graphs using Getdata Gragh Digitizer software. Given that some studies only provided daily N_2O fluxes, seasonal

N_2O emissions were estimated using the trapezium rule. Detailed information about the dataset is presented in Table S1.

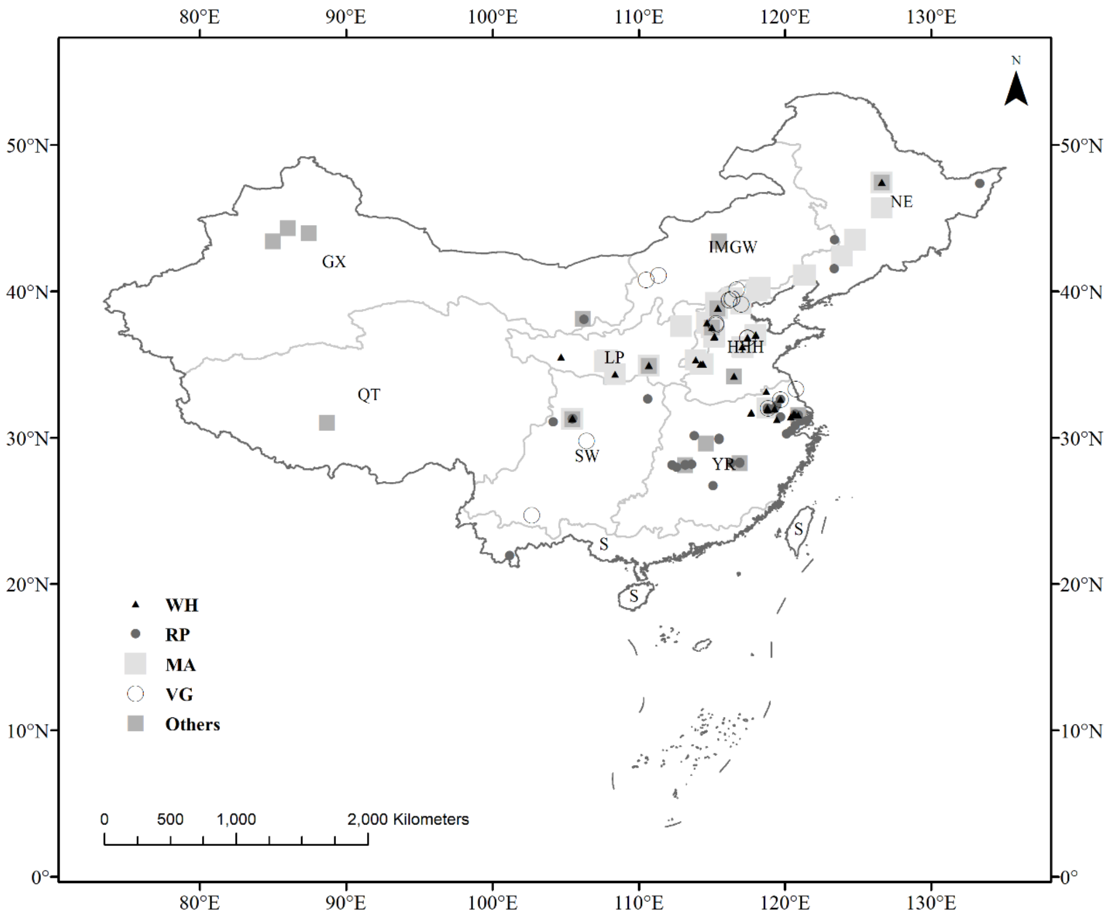


Figure 1. Geographical distribution of experimental sites in China that were used for development of the N_2O emission factor (WH, wheat; RP, rice paddy; MA, maize; VG, vegetable)

Measurements were randomly split into two groups: 70% for developing the EF, and 30% held back for evaluation. Due to limitations on data availability in some regions, the 9 land agricultural regions were aggregated into 7, as shown in Table 1.

Table 1 Reclassified parameters used in this analysis

(a) fertilizer types	**Acronym**
Control without fertilizer application	Control
Mineral N fertilizer	Mineral
Organic and mineral mixes	Min & Org
Organic fertilizer	Organic
Control release fertilizer, nitrification inhibitors, urease inhibitors etc.	Enhanced-efficiency fertilizers
(b) Agricultural areas	**Acronym**
Huang-Huai-Hai	HHH
Inner Mongolia and along the Great Wall	IMGW
Loess Plateau	LP
Northeast	NE
Qinghai-Tibet & Gansu-Xinjiang	QTGX
South & Southwest	SSW
Yangtze River	YR

To evaluate the seasonal spatial distribution of direct N_2O emissions, a 0.083°×0.083°grid was created covering all the major crops (paddy rice, wheat, maize, barley, millet, sorghum, rapeseed, sunflower, groundnut, soybean, potato, vegetable, cotton, sugarbeet, sugarcane, tobacco, fruit) in cultivated areas in China. The area data was obtained from Monfreda et al.,[30] and data for N fertilizer application rates across regions were obtained from Mueller et al.,[31] and the national statistics which provides data on the cultivated area and N fertilizer application rates of various crops in provincial level.[32] We assumed that there was no significant change in the spatial distribution of crop area and fertilizer application rates, and then matched the sum of crop area and fertilizer application amounts in all the grid cells of each province to the statistics of this province in 2016.

Emission factor methodology

Method 1 (M1): The N_2O-EF of each observation was calculated using equation (1), then the mean N_2O-EF was obtained through averaging all the N_2O-EFs of observations under a given category.

$$N_2O - EF = (E\_N_2O_{Fertilized} - E\_N_2O_{Control})/R\_N \times 100\% \qquad (1)$$

where, $E\_N_2O_{Fertilized}$ represents the measured emissions from the fertilized plot; $E\_N_2O_{Control}$ represents the measured emissions from the control plot; R_N is the N fertilizer application rate (kg N ha^{-1}). When one study reported several N rates (levels), the N_2O-EFs were first calibrated independently for each level. Then the averaged N_2O-EF of a given crop in a agro-region was calculated by averaging the N_2O-EFs of the crop in this region.

Method 2 (M2): A linear regression of seasonal field N_2O emissions with N fertilizer application rate was performed to develop the N_2O-EFs using all the observations. The functional form of the fitted linear regression model was:

$$y_1 = a \times x + b \qquad (2)$$

where, dependent variable "y_1" denotes the measured seasonal field N_2O emissions (kg N_2O-N ha^{-1}), and independent variable "x" denotes the rate of N fertilization (kg N ha^{-1}). The target indicator, N_2O_EF, could be directly obtained from the slope "a" of the model, while the intercept "b" of the model indicates the background emissions without N fertilizer applied.

Method 3 (M3): Similar to M2, N_2O-EFs were also calibrated based on linear regression analysis, but the regression between direct N_2O emissions and N fertilizer application rate was fitted with the intercept set to 0. The functional form of the fitted linear regression model was:

$$y_2 = a \times x \qquad (3)$$

where, dependent variable "y_2" represents direct N_2O emissions calculated through the measured emission from the fertilized plot minus the emission from the control plot.

Accuracy evaluation

As indicated above, 30% of the measurements were reserved for evaluating the N_2O-EFs developed by the three approaches. In addition, the IPCC Tier 1 default emission factors (IPCC_EF) were employed to compare with the N_2O-EFs developed in this study. Correlation between estimated and measured N_2O emissions was used to assess whether estimated values follow the same pattern as measured values, and an R-squared value was used to assess the strength of the correlation.[33] Based on quantitative methods used in previous studies,[33,34] the total difference between measured and estimated values was assessed by calculating the root mean squared error (RMSE) and relative root mean squared error (rRMSE) using equations (4) and (5), respectively. A lower rRMSE often indicates a better regression performance. The accuracy of N_2O-EFs estimates was determined by calculating model efficiency (ME) using equation (6). ME values closer to 1 suggest a better modelling efficiency.

$$RMSE = \sqrt{\left(\sum_{i=1}^{n}(S_i - O_i)^2\right)/n} \qquad (4)$$

$$rRMSE = RMSE/\bar{O} \qquad (5)$$

$$ME = 1 - \sum_{i=1}^{n}(S_i - O_i)^2 / \sum_{i=1}^{n}(O_i - \bar{O})^2 \quad (6)$$

Where, S_i and O_i represent the estimated value of target variable from the fitted equation and the observed value by the original studies; $\bar{O}$ is the mean value of the observed data; *n* is the number of target values; *i* is a single observation.

The bias in the total difference between estimated and measured N_2O emissions was determined by calculating the mean difference (M) with Equation (7).[33,35] With the estimated M, the t-statistic was carried out to test the significant difference between estimated and measured N_2O emissions, using equation (8).

$$M = \sum_{i=1}^{n}(S_i - O_i) / n \quad (7)$$

$$t = \frac{M \times \sqrt{n}}{\sqrt{\sum_{i=1}^{n}[(O_i - S_i) - M]^2 / (n-1)}} \quad (8)$$

A t-value greater than the critical two-tailed 2.5% t-value indicates that the estimated N_2O emissions have a significant bias towards over- ($M > 0$) or under-estimation ($M < 0$) compared to measured ones.[33]

All the statistical analyses were conducted in R version 3.4.0 or Microsoft Excel 2013.

Quantification of spatial N_2O emissions for crop cultivation in China

Agricultural products were sorted into 6 major groups including grain crops (rice, wheat, corn, barley, millet, sorghum), legumes (soybean), oil-bearing crops (groundnut, rapeseed, and sunflower), vegetables (vegetables, potato), fruit, and industrial crops (cotton, tobacco, sugarcane, beetroot). Direct N_2O emissions (N_2O emissions from N inputs excluding background soil emissions) for these crops were mapped for each

0.083°×0.083° grid using the N_2O-EF with the best estimation power as determined in 2.3. In order to conduct the spatial analysis, the regional crop-specific N_2O-EFs were first projected onto the grid map of seven agro-regions. Then the cultivation areas of each crop and N fertilizer application rate were mapped for each 0.083°×0.083° grid cell. Finally, the total direct N_2O emissions (FIE_N_2O) in each grid cell were calculated using equation (9):

$$FIE\_N_2O = EF\_N_2O \times Rate \times A \tag{9}$$

Where, EF_N_2O represents the N_2O-EF in a certain condition (%), *Rate* is the N fertilizer application rate (kg N ha^{-1}), A is the crop cultivation area (ha).

The gridded direct N_2O emission values were calculated using R (version 3.4.0) with the package "Matrix", then the maps were generated using ArcGIS 10.2.

Uncertainty analysis

The uncertainty of the calibrated N_2O-EFs was determined by calculating the 95% confidence interval (*CI*) using a Monte Carlo random sampling approach. Multiple values were sampled 10,000 times from the supposed normal probability distribution of the N_2O-EFs based on their means and standard deviation, then the 95% CIs were determined based on values at 2.5 and 97.5 quantiles. Because some regions have only one pair of data per crop, the standard deviations of that crop cannot be calculated in all cases. In such cases the coefficient of variation was arbitrarily set to 50%.[26]

According to IPCC[8], the total uncertainty (U_{total}, %) could be calculated using the following equation when uncertain quantities are to be combined by addition:

$$U_{total} = \frac{\sqrt{(U_1 \times x_1)^2 + (U_2 \times x_2)^2 + \cdots (U_n \times x_n)^2}}{x_1 + x_2 + \cdots x_n} \tag{10}$$

where x_i is the uncertain quantities (i.e. direct N_2O emissions) of crop i in a region, and U_i is the percentage uncertainties associated with x_i. U_i could be calculated using equation (11):

$$U_i = \frac{CI_i}{x_i} \times 100\% \tag{11}$$

where CI_i is the confidence interval of x_i.

The total direct N_2O emissions were obtained by summing across the various crops, and equations (10) and (11) can be used to estimate the uncertainty of the total inventory.

Results

Validation of different emission factor calibration methods

The N_2O-EFs calibrated by three methods were significantly different in some cases (Table 2, Table S2, Table S3). For example, the N_2O-EF of maize cultivation under organic fertilization in HHH region was 0.32% using M2, which was significantly lower than the N_2O-EFs of 0.57% and 0.43% estimated using M1 and M3, respectively. The best method for N_2O-EF calibration in China's cropland, the performance accuracy of the three methods, as well as the IPCC tier 1 default method, was assessed based on the statistics of RMSE, rRMSE, ME, M and t-test using 30% of the observations retained for evaluation (266 observations including 87 and 179 observations without and with N fertilization). As shown in Figure 2, the correlation of calibrated *versus* observed emission values had R^2 values of 0.37, 0.32, 0.39 and 0.33 for M1, M2, M3 and the IPCC tier 1 default method. In addition, M3 had the highest ME with a value of 0.38 compared to other methods, though M2 had the lowest RMSE and rRMSE (Table 3). In terms of bias (M and the t-test of its significance), only the IPCC default method calibrated values were significantly different from the observed values, with a bias of -1.00 kg N ha^{-1}, respectively. Given these metrics, M3 emerged as the best performing method for N_2O-EF development under Chinese conditions.

Table 2 Region-, crop-, fertilizer types-specific N_2O emission factors with the M3 approach (average ± CI)

Region	Fertilizer type	Maize	Rice	Wheat	Legume	Cotton	Rapeseed	Vegetable
HHH (n=151)	Mineral	0.70±0.14(n=35)		0.28±0.04(n=30)	0.03±0.03(n=1)*			0.31±0.33(n=4)
	Min & Org	0.40±0.29(n=14)		0.16±0.04(n=19)	0.17±0.14(n=2)*			0.42±0.08(n=23)
	Organic	0.43±0.34(n=7)		0.18±0.16(n=7)	0.35±0.35(n=1)*			0.41±0.20(n=9)
IMGW (n=13)	Mineral				0.13±0.02(n=8)			0.37±0.12(n=5)
	Min & Org							
	Organic							
LP (n=35)	Mineral	0.57±0.10(n=20)		0.32±0.14(n=11)		1.48±1.37(n=2)*		
	Min & Org	0.45±0.16(n=2)*						
	Organic							
NE (n=92)	Mineral	0.51±0.17(n=35)	0.41±0.18(n=6)	0.38±0.06(n=17)	0.26±0.02(n=2)*			0.36±0.04(n=9)
	Min & Org	0.47±0.18(n=12)		0.34±0.02(n=2)*				0.39±0.39(n=1)*
	Organic	0.48±0.67(n=4)						0.16±0.16(n=1)*
QTGX (n=7)	Mineral		0.42±0.06(n=2)*		0.17±0.10(n=2)*	0.34±0.36(n=3)		
	Min & Org							
	Organic				0.04±0.04(n=6)			
SSW (n=72)	Mineral	0.47±0.08(n=23)	0.66±0.27(n=7)	0.50± 0.20(n=9)			0.71±0.19(n=6)	0.43±0.21(n=9)
	Min & Org	0.38±0.21(n=4)	0.92±0.38(n=3)	0.34±0.48(n=4)				1.75±0.83(n=5)
	Organic	0.62±0.60(n=1)*		0.14±0.14(n=1)*				
YR (n=211)	Mineral	0.67± 0.12(n=3)	0.32±0.06(n=91)	0.86±0.16(n=39)	0.49±0.41(n=2)*		0.21±0.08(n=9)	1.28±0.55(n=7)
	Min & Org		0.12±0.08(n=39)	0.79±0.35(n=10)				
	Organic		0.11±0.25(n=8)					0.26±1.05(n=3)

"*" represents that the N_2O-EFs here were calculated by M1 because this category just had one or two pair data

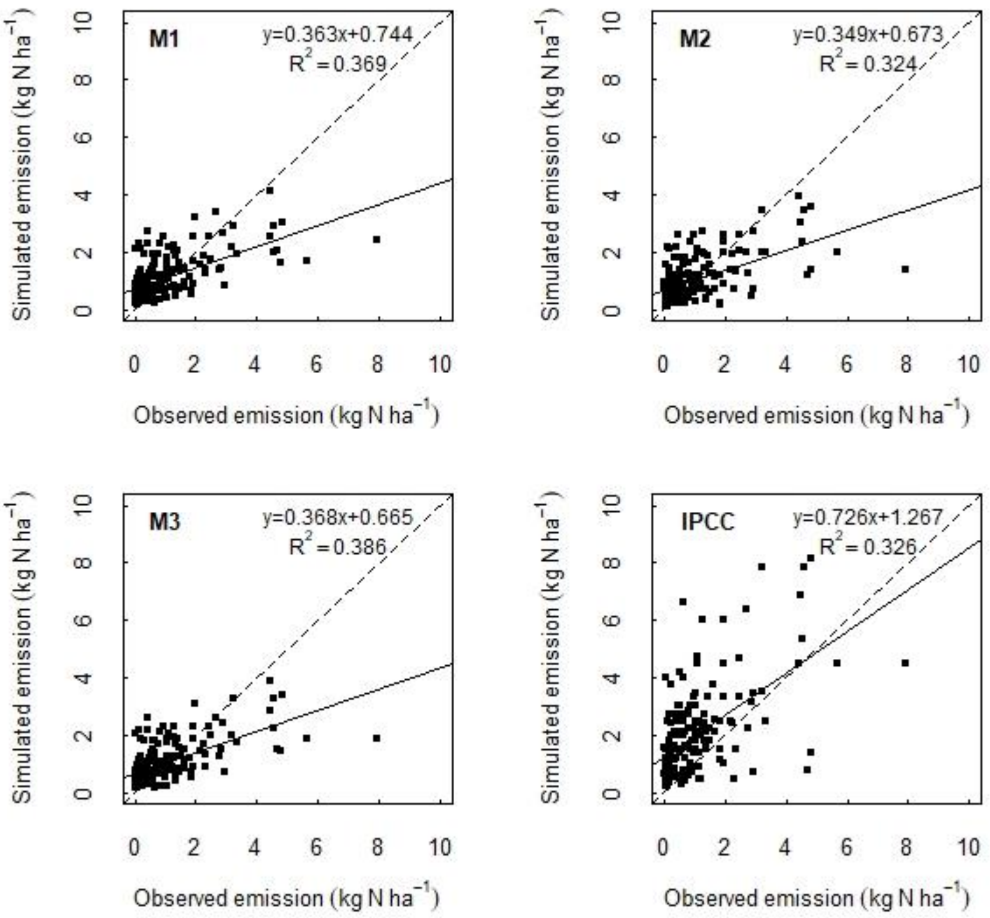


Figure 2. Comparison of observed and simulated seasonal cumulative N_2O emissions for three methods, and the IPCC tier 1 default emission factor. Solid lines represent the regression lines and dotted lines represent 1:1 (y=x) line.

Table 3 Statistics describing the performance of modeled N_2O emissions (Measurement numbers=179 pairs)

Item	M1	M2	M3	IPCC
RMSE	1.86	0.70	0.84	13.88
rRMSE (%)	195	73	88	1461
M	0.13	0.05	0.06	1.00
t-test	ns	ns	ns	s
p value	0.18	0.62	0.54	0.00
ME	0.36	0.32	0.38	-0.84

s, significant; ns, not significant.

Region-, crop-, management patterns-specific N_2O emission factors

The N_2O-EFs showed notable regional patterns, and varied among crop types, fertilizer types, as well as management practices (Table 2, Figure 3). In general, maize cultivation under mineral fertilization had the highest N_2O-EF, being 0.70% and 0.67% in both the HHH and YR regions, but the lowest N_2O-EF was 0.47% in the SSW region. For wheat cultivation under mineral fertilization, the N_2O-EF was 0.86% in the YR region, which was significant higher than that (0.28% to 0.50%) in other agro-regions. The highest N_2O-EF for rice cultivation under mineral fertilization was seen in the SSW region (0.66%), while all the N_2O-EF ranged from 0.32-0.42% in other agro-regions. The YR region had the highest N_2O-EF both for legume (0.49%) and vegetable (1.28%) cultivation under mineral fertilization, while the highest N_2O-EFs for cotton and rapeseed cultivation were found in the LP (1.48%) and the SSW (0.71%) regions, respectively.

Under mineral fertilization, maize and wheat cultivation had the highest N_2O-EFs of 0.60% and 0.59%, respectively, while the lowest N_2O-EF was found for legume cultivation, being as low as 0.14%. However, paddy rice cultivation had a N_2O-EF of 0.35% on average, and other upland crops had N_2O-EFs in a range of 0.37%~0.51% (Table S4).

Generally, the N_2O-EF under mineral fertilization were usually higher than that under combined mineral and organic fertilization or organic fertilization. But we found that the N_2O-EFs under combined mineral and organic fertilization or organic fertilization were higher than that under mineral fertilization in paddy rice, maize and vegetable cultivation in the SSW region, legume and vegetable cultivation in the HHH region and vegetable cultivation in the NE region. The N_2O-EFs for application of enhanced-efficiency fertilizers were 0.51%, 0.20%, and 0.07% for maize, wheat and paddy rice cultivation, respectively (Table 4), which were much lower than the values for fertilizers without inhibitors. As for the effect of water management regimes in paddy rice cultivation, the N_2O-EF under continuous flooding were consistently lower than those under the intermittent-flooding water regime in the SSW region (0.54% vs 1.03% on average), and in the YR region (0.08% vs 0.31% on average) (Figure 3, Table S5).

Table 4 N_2O emission factors under enhanced-efficiency fertilizer application (Measurement numbers=71)

Crop	Emission factor (%)	Lower 95% CI limit	Upper 95% CI limit
Maize (n=37)	0.51	0.33	0.69
Wheat (n=22)	0.20	0.01	0.39
Paddy rice (n=12)	0.07	0.05	0.09

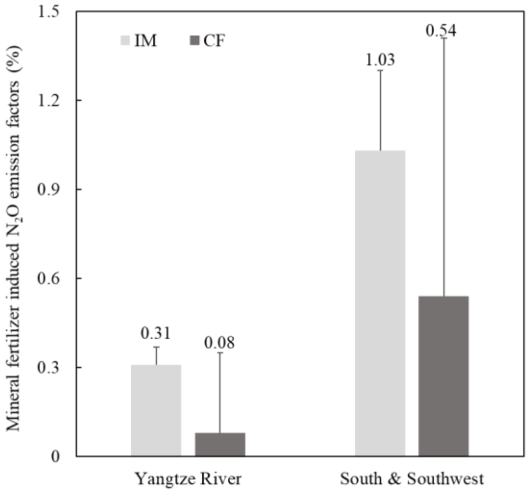


Figure 3. Comparison of N_2O emission factors under intermittent flooding (IM) and continuous flooding (CF) for paddy rice

Direct N_2O emissions in crop cultivations of China

Using the regional N_2O-EFs developed by M3, we estimated direct N_2O emissions in the year 2016 for China's cropland. The direct N_2O emissions showed notable spatial variability, with the highest direct N_2O emissions mainly found in the YR (54.29 Gg N_2O-N yr^{-1}) and SW (32.99 Gg N_2O-N yr^{-1}), while QT (0.45 Gg N_2O-N yr^{-1}) and IMGW (7.30 Gg N_2O-N yr^{-1}) regions had relatively low direct N_2O emissions, respectively (Figure 4, Table 5). With respect to crop types, the lowest direct N_2O emissions of 1.39 Gg N_2O-N yr^{-1} was observed for legume cultivation, whereas grain crops had the highest direct N_2O emissions of 97.67 Gg N_2O-N yr^{-1}, accounting for 50.3% of the total N_2O emissions (Table 5). In total, the annual direct N_2O emissions in China's cropland were estimated to be 194 Gg N_2O-N yr^{-1}, with the 95% CI of 180 -208 Gg N_2O-N yr^{-1} (Table 5). For individual crops, the direct N_2O emissions induced by maize, vegetable, and paddy rice planting ranked were highest, with values of 41.74, 40.54, and 32.80 Gg N_2O-N yr^{-1}, respectively (Figure 5, Table S6). The QT and LP had the smallest uncertainties of 10.71% and 14.66% respectively compared with maximum of 28.80% for GX. The uncertainty in the national direct N_2O inventory was 7.36% in China (Table S7).

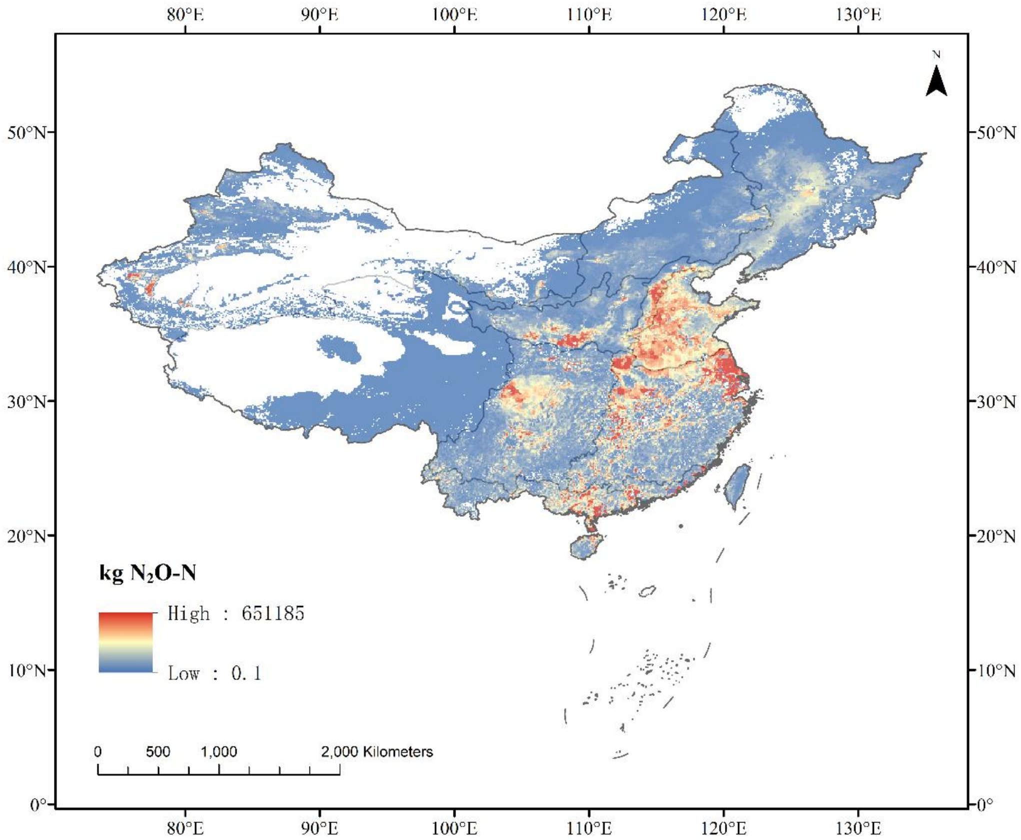


Figure 4. Geographical distribution of direct N_2O emissions in crop cultivation of China

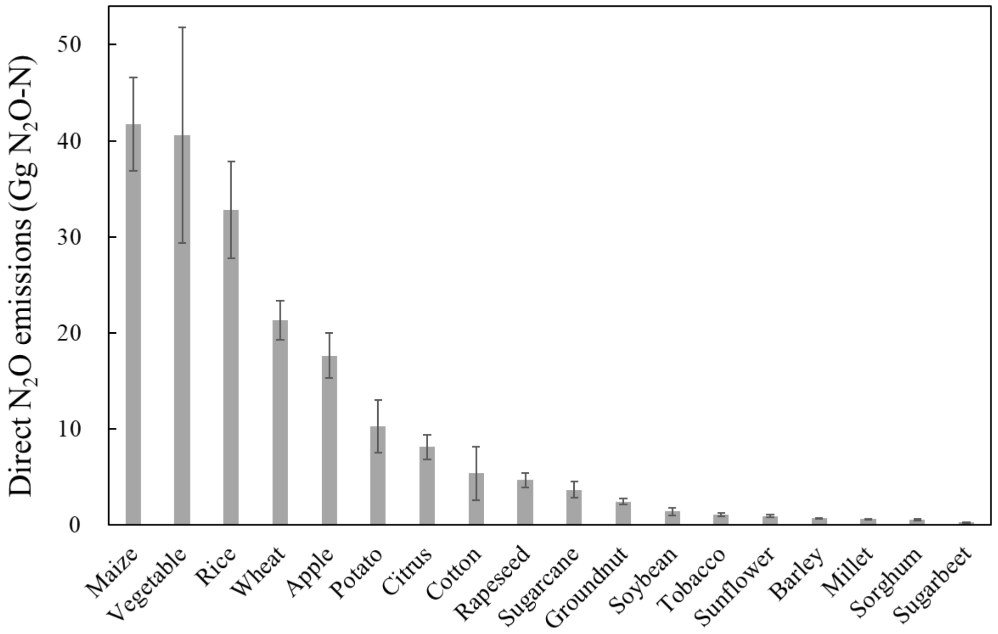


Figure 5. Direct N_2O emissions for various crops in China

Table 5 Mineral N fertilizer induced N_2O emissions in China’s cropland (Emission±95%CI, Gg N_2O-N)

Region	Grain crop	Legume	Oil-bearing crops	Industrial crops	Vegetable	Fruit	All crops
NE	16.66±4.17	0.57±0.04	0.56±0.09	0.17±0.10	2.04±0.19	1.53±0.38	21.53±4.19
IMGW	5.09±1.29	0.04±0.01	0.64±0.10	0.09±0.02	1.04±0.24	0.40±0.11	7.30±1.32
HHH	18.95±2.26	0.01±0.005	1.55±0.28	1.64±1.24	5.09±5.03	2.67±0.77	29.91±5.71
LP	6.60±1.14	0.05±0.03	0.46±0.08	0.15±0.11	2.33±0.55	4.26±1.76	13.84±2.18
YR	22.86±2.97	0.25±0.21	1.23±0.39	1.82±1.01	24.45±9.51	3.70±0.61	54.29±10.04
SW	13.24±2.61	0.38±0.32	2.70±0.62	1.07±0.20	11.07±3.84	4.52±1.15	32.99±4.84
S	9.90±3.48	0.08±0.07	0.53±0.11	3.09±0.81	3.98±1.67	7.60±1.26	25.17±4.14
GX	4.11±0.76	0.01±0.004	0.26±0.04	2.32±2.31	0.71±0.21	1.09±0.21	8.51±2.45
QT	0.24±0.04	0.003±0.002	0.07±0.02	1.00×10^{-3} $\pm0.33\times10^{-3}$	0.11±0.03	0.01±0.002	0.45±0.05
Overall	97.67±7.33	1.39±0.39	8.65±0.76	10.34±2.93	50.82±11.56	25.77±2.68	193.99±14.28

Discussion

Variations of N_2O emission factors in crop cultivation of China

Diverse climate and soil conditions may change the soil nitrification and denitrification processes, and thereby influence N_2O emissions.[17,36-38] According to this study, a large regional variability was found in N_2O-EFs of various crop cultivations (Table 2). To characterize the regional variability, a coefficient of variation (CV) was calculated through dividing the standard deviation by the mean N_2O-EFs of a crop in different regions. The N_2O-EFs of legume and vegetable cultivations under mineral fertilizer application had the highest CVs, being 81% and 75%, respectively, indicating a large regional variability; while wheat, paddy rice and maize cultivations had the relative low CVs of 50%, 32% and 17% for N_2O-EFs across agro-regions. A correlation analysis between N_2O-EFs and soil and climate variables was conducted to identify possible causes of regional variability (Table S8). Due to the relatively low CVs of maize and paddy rice, the significant correlation was only found between the N_2O-EFs of maize cultivation and soil total N, which again demonstrates the importance of N to N_2O emissions. N_2O-EFs of wheat, legume and vegetable cultivations had a significant positive correlation with annual precipitation, which is consistent with Shcherbak et al.[15] and Zhou et al.[18] who also indicated the positive effects of precipitation on N_2O-EF. This trend could be well explained by some previous studies, such as Dobbie et al.[39] and Davidson et al.,[40] who found the highest fluxes occurred at very high WFPS value (>70%) in dry production systems. There were also some significant positive correlations of N_2O-EFs with soil organic carbon content, pH or bulk density found in wheat or legume cultivations. Harrison-Kirk et al.[41] have also observed that N_2O emissions tended to increase as SOC content increases, attributed to the relatively high N transformations associated microbial activity in soils with high soil organic matter content. As indicated by Cheng et al.[42], pH was an important factor regulating N_2O production pathways under aerobic conditions. And the effect of bulk density can be attributed to the effects of porosity on gas diffusivity and redox conditions.[43]

Our results also illustrate that the N_2O-EFs of various crops, including paddy rice (0.35%), and legumes (0.14%), other upland crops (0.37%-0.60%), exhibited a large variation between crops (Table S4). The IPCC Tier 1 default N_2O-EFs are 1% for dryland and 0.3% for flooded paddy fields.[8] This study also observed low N_2O-EFs in rice paddy compared with upland rice in the YR region. Conversely, in the SSW region, the N_2O-EFs of rice cultivation were slightly higher than that of some upland crops, though they were lower than for rapeseed. Compared to other crops, legume crops had the lowest N_2O-EFs in this study. Given that legumes fix atmospheric N, the N fertilizer input was 160 kg N ha^{-1} on average according to our dataset, which is lower than for other crops. Previous studies have indicated that low N inputs in legume systems did not promote a significant increase in the cumulative N_2O fluxes due to the competition for the available N between plants and soil microbes.[44,45] Also, ammonium bicarbonate was disproportionately applied to legumes (Table S1). Given that soil N_2O fluxes induced by ammonium bicarbonate were lower than for urea,[8] this could be another reason why legumes had a lower N_2O-EF.

We found that cotton cultivation had the highest N_2O-EFs of 1.48% in LP region which frequently experiences drought and low soil moisture conditions (Table 2) , which is mainly due to the length of field N_2O monitoring.[46] For example, the monitoring time was as long as 365 days for the cotton field in LP region by Liu et al.,[46] but the N_2O fluxes was monitored for 122~240 days in QTGX regions.[47,48] Nevertheless, it should be noted that the N_2O-EFs of cotton cultivation were developed based on only two experimental sites, which may lead to larger uncertainties.

Management patterns including fertilization modes and water regimes were considered in the estimation of N_2O-EFs (Table 2 and 4; Figure 3). Compared to mineral fertilizer application, organic fertilizer application tended to decrease the N_2O-EFs in most cases, which was likely a result of addition of organic C compounds that stimulated complete denitrification with further reduction of N_2O to N_2.[49,50] A high C/N ratio (>15) could also enhance microbial N immobilization leading to a decrease in availability of inorganic N substrate for nitrification and/or denitrification, and inhibition of N_2O emissions.[51] However, organic fertilizer application increased N_2O-EFs for maize cultivation in both the NE and SSW regions, and of paddy rice cultivation in the SSW region. This may be because organic fertilizer additions (especially for manure) with large organic C compounds enhance microbial inorganic N immobilization, and also because of competition for NH_4^+ for nitrification and NO_3^- for denitrification.[27,52] The N_2O-EFs with enhanced-efficiency fertilizers were decreased by 12.1% for maize fields, 73.3% for rice paddies and 57.4% for wheat fields, compared with mineral fertilizers (Table 4); these values are consistent with previous studies.[17,53] NIs inhibit ammonium mono-oxygenase, thereby blocking the first reaction of ammonium to nitrite, hence decreasing N_2O production.[54] Water management regimes also greatly influenced the N_2O-EFs in rice paddies (Figure 3). Midseason drainage increased the N_2O-EF by 1.9 times on average compared to the continuous flooding regime (Figure 3), which was consistent with a previous study by Zou et al.[22] who found the N_2O-EF to be 0.02% under continuous flooding. but to be 0.73% as a consequence of midseason drainage. It has been well documented that midseason drainage in rice paddies can trigger substantial N_2O emissions compared to continuous flooding due to the creation of favorable soil conditions for both nitrification and denitrification, and the enhancement of soil organic matter decomposition to produce more substrate for soil microbes.[16,55-57]

Role of direct N_2O emissions from China's cropland

Compared with other countries, the estimated N_2O-EF for uplands in China by this study was significantly lower than the N_2O-EFs of 1.18 % for Canada's uplands,[14] but was similar with the value of 0.62% estimated for upland croplands for Japan.[16] The estimated N_2O-EF in rice paddy (0.46%) was higher than the Japanese one of 0.31%, which was mainly due to the high N fertilizer application rate in China.[16] The previous studies calibrated the N_2O-EFs of upland and rice paddy in China being 1.05% and 0.41% by Gao et al.,[24] 0.65~1.57% and 0.52~1.61% for different regions by Zhou et al.,[26] and 0.84% and 0.65% by Zhou et al.,[18] which almost fall into the range of 0.03~1.48% and 0.11~0.92% by this study, respectively (Table 2). At smaller scale, for example, the HHH region in China, Zheng et al.[21] estimated the N_2O-EF to be 0.57% with uncertainty ranging 0.17-0.97% for upland crops, close to the results of this study. In addition, these studies also found the higher N_2O-EFs of rice paddy in China than global one being only 0.3%.[8] Some differences between the previous N_2O-EFs and ours can be partly attributed to differences in emission factor methodology and dataset size. However, the uncertainty was reduced by dividing regions, crop types and management modes, by which we were able to minimize the uncertainty in the regional N_2O emission inventory.

By pinpointing regions and crops associated with direct N_2O emissions, the N_2O-EFs developed here offer the potential to lower the uncertainties in China's direct N_2O emissions. This study estimated direct N_2O emissions from crop cultivation to be 193.99 Gg N_2O-N yr^{-1} with uncertainties of 7.36% under 37.9 Tg of N applied in 2016 (Table 5 and S7). Both the estimated N_2O emission and uncertainties were lower than the 291.9 Gg N_2O-N yr^{-1} with an uncertainty up to 50% provided by Ying et al.,[25] and the 275 Gg N yr^{-1} in the 1990s with the uncertainty range of -79% to 135% from Zheng et al.,[21] estimated using regional EFs from previous studies. Individually, N_2O emissions from rice paddies were calculated to be 32.8 Gg N_2O-N in this study, which is close to the value of 35.0 Gg N_2O-N quantified by Xing&Zhu [20] using the IPCC-EFs, but higher than the value of 29.0 Gg N_2O-N reported by Zou et al.[22] with the EFs under different water regimes. As indicated in Table S6, the uncertainty of 15.5% for rice paddy was much lower than that of 30.1% from Zou et al.[22] which was based on a total of 71 field measurements.

It is clear that China's croplands play a key role in global N_2O emissions, and developing region-, crop- and management patterns-scaled emission factors is important to better estimate these emissions. Our results indicate that changing fertilization modes and water regimes could help to mitigate N_2O emissions. For example, the emission factors derived here indicate a large mitigation potential of 47 Gg N yr^{-1} (up to 50%) could be achieved if total mineral N fertilizer were replaced by enhanced-efficiency fertilizers for three staple crops. By optimizing fertilization mode, the mitigating potential of 2.74 Gg N yr^{-1} could be saved by mineral fertilizer mixed with organic fertilizer for maize cultivation in the HHH region. Nevertheless, both agricultural production costs and environmental benefits are important factors that need to be considered and evaluated for sustainable agricultural development.

Uncertainties in estimates

As indicated above, the N_2O-EFs calibrated by this study had the relative low uncertainty compared to previous studies, and the uncertainty of total direct N_2O emission estimation was as low as 7.4% in China's cropland. However, it could not be ignored that there are still some uncertainties that were not taken into account in this study.

As shown in Figure 2, the best method M3 has an R^2 of 0.39, which indicates that 61% of the variation is not captured by this method. Some previous studies have suggested nonlinear effects of N fertilizer application rates on N_2O-EF. For example, Bouwman et al.[11] assumed an exponential relationship between N_2O emissions and N application rates in the model, which means N_2O-EFs tended to increase as N application rates increased. Both Shcherbak et al.[15] and Zhou et al.[18] found this trend in their calibrations.

This study did not observe such nonlinear effects. It should be noted that only one variable of nitrogen fertilizer input was considered in the N_2O-EF calibration. In fact, there are still some factors that affect N_2O emissions, and the development of a model considering more variables may increase R^2 and reduce uncertainty.[18,58] Use of a complex model would be encouraged if there are sufficient input data, but the N_2O-EFs described in this study provide the most accurate estimates with very limited data.

All the original measurements used in this study were made using chambers and the uncertainty of cumulative N_2O emissions for a field-scale estimate by chamber measurements was not likely to be less than ±50%.[59,60] The closed static chamber method can miss N_2O flux peaks during the planting period, such as those occurring after a rainfall event, fertilization or tillage. Zheng et al.[21] indicated that N_2O fluxes based on the closed static chamber method measured at monthly or weekly intervals could lead to large inherent variability of N_2O fluxes. Additionally, limited data led to greater uncertainties in this study. For instance, the available data for the QTGX region was mostly less than 3 measured values for each category, and the local data for paddy rice, legume, cotton, and rapeseed was missing in most areas (Table 2). Hence, more continuous field measurements will be required to fill the data gaps in these regions, as well as for various other crops, in order to reduce uncertainties in the estimation of N_2O-EFs.

The N_2O-EFs in uplands developed by this study were much lower than IPCC tier 1 default value of 1%, with an uncertainty range of 0.3-3% and the country-specific N_2O-EF of 0.9% with an uncertainty range of 0.4-2.4% for China’s drylands estimated by

Albanito et al.[8,17] It should be noted that the N_2O-EFs were developed using the growing season emissions in this study, while IPCC and Albanito et al.[17] both developed the full year N_2O-EFs, which could be one of the reasons why the N_2O-EFs of this study were lower than that of IPCC and Albanito et al.[17] However, there was a limitation that IPCC and Albanito et al.[17] are less suited to upland crop-paddy rice rotation than the N_2O-EFs derived here. Our study developed the N_2O-EFs for various crop cultivations, which may be used to estimate the direct N_2O emissions of a rotation by summing the emissions from individual crops. By reviewing the studies of Zheng et al.,[21] Helgason et al.[14] and Akiyama et al.[16], we found that they also developed the N_2O-EFs using the growing season data alone, though there were some sites in which emissions through the whole year were measured in Zheng et al.[21] The previous studies indicated that there was a large proportion of fertilizer N residing in the soil, which might induce N_2O emissions at other times.[61,62] Akiyama et al.[16] also observed some N_2O emitted in the fallow season. Unfortunately, the studies on N_2O flux monitoring in the fallow were still limited. Focus on this topic in future studies might provide further data basis on N_2O-EF development.

In summary, N fertilizer induced N_2O emission factors, obtained from the linear regression model with the intercept set to 0, performed best with the highest R^2, best ME and no significant bias. Based on the field N_2O emission dataset collated in this study, the regional crop- and management-specific N_2O emission factors were calibrated to minimize the uncertainty in national GHG emission estimates using the selected method. There were significant differences in emission factors between paddy rice, legumes and other upland crops. Controlled-release fertilizers and nitrification inhibitors greatly reduced emission factors, and organic fertilization could also lower emission factors in most agro-regions. The total amount of direct N_2O emissions in China’s cropland was calculated to be 194 Gg N_2O-N in 2016, to which maize cultivation made the greatest contribution.

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Supporting Information Available

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