


## Article

# Nitrous Oxide Emissions during Cultivation and Fallow Periods from Rice Paddy Soil under Urea Fertilization

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**Abstract:** Rice cultivation serves as a significant anthropogenic source of methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O). Although N<sub>2</sub>O emissions remain relatively small compared to CH<sub>4</sub> emissions, they are remarkably affected by nitrogen-fertilized soil conditions during rice cultivation. While numerous studies have investigated nitrous oxide emissions in response to nitrogen fertilization, existing research assessing nitrous oxide emissions based on nitrogen fertilizer levels has often been limited to cultivation periods. Therefore, there is a need for comprehensive analyses covering the entire year, including the dry periods, to address nitrous oxide emissions as an important source throughout the entire agricultural cycle. In this case study, we investigated the characteristics of N<sub>2</sub>O emissions in a central region of South Korea, where a single rice-cropping cycle occurs annually over a span of three whole years, from May 2020 to May 2023. We investigated the impact of variations in temperature and soil moisture on N<sub>2</sub>O emissions during rice cultivation and fallow periods. In this context, we attempted to discover the complex dynamics of N<sub>2</sub>O emissions by comparing longer fallow periods with the rice cultivation periods and extended non-dry periods with irrigated periods. We discovered that the greater contribution of cumulative N<sub>2</sub>O emissions during the fallow period made a much greater contribution (up to approximately 90%) to the whole-year N<sub>2</sub>O emissions than those during the rice cultivation period. During the fallow period from rice harvest to rice planting in the following year, variations in N<sub>2</sub>O emissions were associated with high-flux events after rainy periods on dry soils. This highlights the considerable influence of soil moisture content and weather conditions on N<sub>2</sub>O emissions during the fallow period. This affects high emission events, which in turn significantly impact the cumulative emissions over the entire period. We underscore that assessing N<sub>2</sub>O emissions solely based on the rice cultivation period would underestimate annual emissions. To prevent underestimation of N<sub>2</sub>O emissions, periodic gas collection throughout a year covering both rice cultivation and fallow phases is required in alignment with the monitoring of different temperature and soil moisture conditions. We captured statistical differences in cumulative N<sub>2</sub>O emissions due to nitrogen fertilization treatments across the three years. However, no significant difference was observed in the three-year average emissions among the different (one, one-and-a-half, and double) nitrogen fertilization treatments, with the exception of the control treatment (no fertilization). Based on the findings, we recommend at least three whole-year evaluations to ensure the estimation accuracy of N<sub>2</sub>O emissions under different nitrogen fertilization conditions. The findings from this study could help prepare the further revision or refinement of N<sub>2</sub>O emission factors from rice cultivation in the national greenhouse gas inventories defined by the inter-governmental panel on climate change (IPCC).



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**Keywords:** nitrous oxide; rice paddy; nitrogen fertilization; soil moisture; weather condition; fallow period

## 1. Introduction

Rice farming is of paramount importance in ensuring global food security, particularly across Asia, as a major staple crop. For millennia, rice has remained a cornerstone grain in numerous countries, including South Korea. Substantial nitrogen fertilization is required to attain the core objective of a consistent food supply, enhancing production per unit area.

However, agriculture has become a leading contributor to anthropogenic N<sub>2</sub>O emissions worldwide. Notably, the global N<sub>2</sub>O budget for 2007–2016 underscores agriculture as the principal anthropogenic contributor to N<sub>2</sub>O emissions, primarily due to nitrogen fertilizer application [1]. Projections estimate a 35–60% increase in N<sub>2</sub>O emissions by 2030 due to the augmented use of synthetic fertilizers [2]. The impact of climate change and weather variations on rice cultivation has been previously documented. In light of these concerns, it becomes pivotal to undertake qualitative and quantitative analyses of greenhouse gas emissions to promote sustainable agriculture.

Moreover, comprehending the mechanisms underlying these emissions is essential for devising appropriate mitigation strategies. Key greenhouse gases originating from rice cultivation encompass methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O). Methane emerges from anaerobic organic matter decomposition, while N<sub>2</sub>O emissions result from nitrogen-induced nitrification and denitrification processes [3–10]. However, studies predating the 1990s proposed negligible N<sub>2</sub>O emissions from rice paddies. Yet, subsequent to the 1990s, both CH<sub>4</sub> and N<sub>2</sub>O were identified as substantial anthropogenic emission sources within the rice cultivation sector [11–15]. Consequently, the impact of nitrogen fertilizer application on N<sub>2</sub>O emissions has emerged as a critical consideration for developing soil management strategies that mitigate greenhouse gas effects in agricultural domains. Therefore, there is a need to develop N<sub>2</sub>O emission factors based on nitrogen fertilization in the estimation of greenhouse gas emissions from rice cultivation, taking into account regional characteristics.

Soil-derived N<sub>2</sub>O fluxes are profoundly influenced by environmental factors such as soil temperature, moisture content, and pH [16–20]. The temporal and spatial variability in N<sub>2</sub>O emissions is substantial, contingent on variables such as fertilizer type, land use, oxygen availability, winter freeze-thaw cycles, and changing weather conditions [21–24]. The fluctuations in N<sub>2</sub>O emissions primarily stem from occurrences of elevated emissions. This sometimes obscures the apparent correlation between artificial nitrogen fertilization practices and soil-derived N<sub>2</sub>O emissions under different environmental circumstances. Existing literature reports N<sub>2</sub>O emissions from agricultural soil due to synthetic nitrogen fertilization ranging from 0.01% to 6.84% [25]. Previous studies noted N<sub>2</sub>O emissions from rice cultivation at 0.25% in 2000, while the IPCC default value stood at 0.30% [26].

However, the measurement of major nitrous oxide emissions in previous studies lacked evaluations for the whole year, including the fallow period, leading to a significant uncertainty in the estimated background emission values. This suggests the need for datasets spanning over a span of three whole years or more to account for temporal variability, similar to assessing spatial variability through three or more chamber replicates, in order to provide a comprehensive understanding of the temporal dynamics. The IPCC guidelines also recommend establishing national-specific emission factors based on data collected over a period of three whole years.

The main scientific questions to be answered concerning N<sub>2</sub>O emission from rice cultivation are divided into the following key points: (i) Can different years have a significant influence on cumulative N<sub>2</sub>O emissions across distinct levels of nitrogen fertilization? (ii) Do different levels of nitrogen fertilization significantly affect the 3-year averages of cumulative N<sub>2</sub>O emissions? (iii) Is the impact of high-N<sub>2</sub>O flux events on cumulative N<sub>2</sub>O emission over a whole year significant? (iv) What are the main driving forces in the creation

of high-N<sub>2</sub>O flux events? (v) To what extent do N<sub>2</sub>O emissions during fallow phases contribute to the total cumulative N<sub>2</sub>O emissions across distinct levels of nitrogen fertilization?

To answer these important questions, this study was undertaken to analyze the responses of N<sub>2</sub>O fluxes from a rice paddy at different levels of nitrogen fertilizer (urea) application during both fallow and rice cultivation phases for three whole years. In this study, N<sub>2</sub>O emissions were assessed by dividing the annual rice cultivation period (approximately 130 days after rice transplantation) and the non-cultivation period (about 230 days from rice harvest to rice transplantation). This division was intended to analyze the primary influencing factors of N<sub>2</sub>O emissions from the rice paddy. To accomplish this, we conducted measurements of N<sub>2</sub>O fluxes and compared daily variations in fluxes during fallow and rice cultivation periods, utilizing chamber-based sampling and gas chromatography over three whole years. Also, we investigated the impact of variations in temperature and soil moisture on N<sub>2</sub>O emissions during both fallow and rice cultivation periods over three whole years.

## 2. Materials and Methods

### 2.1. Study Site and Treatments

The research site was situated within the Gyeonggi-do Agricultural Research and Extension Services (GARES), specifically in a rice paddy field located at coordinates 37°13'15" N and 127°02'22" E, in Hwaseong, Gyeonggi, South Korea (Figure 1). The total area of the site was 540 m<sup>2</sup>, which was subdivided into four experimental plots, with each plot covering an area of 135 m<sup>2</sup>. The soil at the experimental site was classified as *Inceptisols*, characterized by a loam texture with poor drainage properties. Prior to transplanting, the soil exhibited a moderately acidic pH of  $6.2 \pm 0.1$  when tested at a 1:5 ratio with water. Additionally, the soil displayed appropriate fertility levels, containing  $23 \pm 0.1$  g kg<sup>-1</sup> of organic matter,  $50 \pm 7.3$  mg P<sub>2</sub>O<sub>5</sub> kg<sup>-1</sup> of available phosphorus (indicating low fertility in this regard), and  $184 \pm 38$  mg SiO<sub>2</sub> kg<sup>-1</sup> of available silicate (considered adequate fertility) (Table 1). Following the nationally recommended fertilization standards for rice cultivation in Korea [27], the study involved the four different treatment levels of urea as inorganic nitrogen fertilizer (0, 90, 135, and 180 kg N ha<sup>-1</sup>, denoted by N0, N1.0, N1.5, and N2.0, respectively) to each plot. The assessment of N<sub>2</sub>O emissions based on nitrogen fertilization in the rice field was conducted with untreated nitrogen (N0 control), standard fertilization according to Korean cultivation practices (N1.0), and 1.5 times and 2 times the standard fertilization (N1.5 and N2.0). The experimental design was practically determined to detect a difference in cumulative N<sub>2</sub>O emissions between N1.0, representing the current practice in South Korea, and N2.0, the practically possible maximum level. Additionally, N1.5 was selected as an intermediate level to investigate whether a potentially linear or nonlinear effect exists. This is why the treatment groups N1.0, N1.5, and N2.0 were ultimately chosen for comparisons with the control group N0. The installation locations of the chambers were set to be at least 1 m away from the boundaries of each processing zone, with a minimum distance of 3 m between each chamber. Experiments were conducted over a span of 3 years, starting from May 2020 and continuing until May 2023. However, consistent amounts of phosphorus (P) and potassium (K) were added across all treatment variations. Fertilization activities were designed to coincide with various growth stages of the rice plants. This includes basal fertilizer application (3 days prior to transplanting, consisting of 50% of N, 100% of P, and 70% of K), tillering fertilizer application (12 days after transplanting, involving 20% of N), and panicle fertilizer application (70 days after transplanting, comprising 30% of N and K). To prevent nutrient mixing effects, a buffer zone with a width of 0.5 m was established using concrete barriers between each experimental plot.



Figure 1. A map showing the locations of the rice paddy in GARES.

Table 1. Chemical and physical properties of the investigated soil in each treatment plot.

Treatment	pH (1:5)	OM (g kg <sup>-1</sup> )	AP (mg kg <sup>-1</sup> )	AS (mg kg <sup>-1</sup> )	EC (cmol kg <sup>-1</sup> )			Soil Texture
					K	Ca	Mg	
N0	6.3	22	40	210	0.49	7.1	1.6	Loam
N1.0	6.1	23	47	224	0.50	7.1	1.5	
N1.5	6.2	22	56	142	0.43	6.7	1.4	
N2.0	6.1	23	57	160	0.43	6.9	1.5	
Mean	6.2	23	50	184	0.46	7.0	1.5	

OM: organic matter, AP: available phosphorous, AS: available silicate, EC: exchangeable cations.

For the rice transplanting process, seedlings aged over 20 days and 3–4 plants per hill were mechanically transplanted. The chosen rice variety was the *Samkwang-byeo* cultivar (*Oryza Sativa*). Transplanting occurred in late May, following two weeks of irrigation preparation. Mid-summer drainage commenced 35 days after transplanting, lasting for a period of 2–3 weeks, and the final drainage took place one month prior to harvest. The specific dates of various rice cultivation management activities over the course of 3 years are provided in Table 2.

Table 2. Dates of rice cultivation activities for each year over a three-year period.

Year	Plowing	Irrigation	Transplanting	Drainage (35 DAT *)	Fertilization			Harvest (130 DAT)
					Basal	Tillering (12 DAT)	Panicle (70 DAT)	
2020	24 April	29 April	21 May	24 June	22 May	2 June	29 July	28 Sep.
2021	10 April	15 May	27 May	1 July	24 May	8 June	5 Aug.	5 Oct.
2022	8 April	10 May	26 May	30 June	23 May	7 June	5 Aug.	6 Oct.

\* DAT denotes days after transplanting.

## 2.2. Gas Sampling, Analysis, and Calculation

To determine N<sub>2</sub>O fluxes associated with nitrogen fertilizer (urea) treatments in the rice paddy, three acrylic circular chambers (25 cm radius × 50 cm height) were placed and used in each treatment plot (a total of four different plots), excluding the rice plants. The chambers had two openings at the bottom to allow the flow of irrigated water. These chambers were only closed during gas sampling and remained open throughout the rest of the year. The actual height of each chamber was measured during each instance of gas sampling, as the effective air volume within the chamber varied based on its depth in the soil and the water level.



According to a previous study that directly measured greenhouse gas emissions from paddy fields using a closed chamber method [28], the recommended sampling frequency is at least once a week, with sampling conducted in the mid-morning hours between 10:00 AM and 12:00 PM. The time flux obtained through sampling during this period can be representative of the daily average. Based on this recommendation, gas sampling of N<sub>2</sub>O from the rice paddy was conducted between 10:00 am and 11:00 am using 50 mL gas-tight polypropylene syringes on a regular basis once or twice per week. Changes in the gaseous concentration of N<sub>2</sub>O were measured over a 40 min interval before and after closing a static chamber. Simultaneously, the air temperature inside the chamber was measured using a mini-penetration thermometer (Testo, 213 mm).

The gas concentrations of N<sub>2</sub>O were analyzed using a gas chromatograph (GC-456; Varian) equipped with an electron capture detector (ECD) and a Porapak Q column (Q 80–100 mesh). The column, injector, and detector temperatures were set to 70, 120, and 320 °C, respectively. Nitrogen (N<sub>2</sub>) gas was used as the makeup gas. The gas concentrations of N<sub>2</sub>O were determined by linearly calibrating the gas chromatography with an electron capture detector (GC-ECD) using a minimum of three accurate and precise gas mixture standards of N<sub>2</sub>O. These gas mixture standards were prepared and certified by comparison with primary gas mixtures that confirmed international equivalence (CCQM-K68.2019, Nitrous Oxide in air, Ambient level) by the Korea Research Institute of Standards and Science, the National Metrology Institute of South Korea. The relative expanded uncertainty of N<sub>2</sub>O concentrations in these certified gas mixtures was 1% at a confidence level of approximately 95%, with a coverage factor (*k*) of 2.

Fluxes of N<sub>2</sub>O were estimated using the following equation [28,29]:

$$F = \rho \times (V/A) \times (\Delta c/\Delta t) \times (273/T) \quad (1)$$

where *F* is the N<sub>2</sub>O flux (μg m<sup>−2</sup> h<sup>−1</sup>), *ρ* is the gas density of N<sub>2</sub>O (1.96 mg cm<sup>−3</sup>) under standard conditions (0 °C, 1 atm), *V* is the effective, inner volume of the closed chamber (m<sup>3</sup>), *A* is the surface area of the chamber (m<sup>2</sup>), *Δc/Δt* is the rate of change in N<sub>2</sub>O concentrations during a 40 min period in the closed chamber (mg m<sup>−3</sup> day<sup>−1</sup>), and *T* is the absolute temperature (273 + mean temperature in °C) in the chamber.

The methodology for estimating soil-derived greenhouse gas flux has been widely cited in the 2006 IPCC Guidelines [28]. By multiplying the flux values (e.g., mg m<sup>−2</sup>h<sup>−1</sup>) by 24 h, daily flux values (e.g., mg m<sup>−2</sup>day<sup>−1</sup>) can be derived. The cumulative emissions for a sampling period can be calculated by adding the daily average values, and the seasonal or cumulative emissions can be estimated by summing the daily averages over a certain period. The cumulative N<sub>2</sub>O emission for a period was calculated by the following equation:

$$\text{Cumulative N}_2\text{O emission} = \sum_{(i=1, \dots, n)} (R_i \times D_i) \quad (2)$$

where *R<sub>i</sub>* is the N<sub>2</sub>O emission rate (mg m<sup>−2</sup> day<sup>−1</sup>) from the *i*th sampling, *D<sub>i</sub>* is the number of days (3 days or 4 days) corresponding to the *i*th sampling, and *n* is the *n*th sampling day in a full year. Summing three or four days times the daily average value based on the hourly flux is equivalent to the yearly emission during a whole year. This calculation method, as described by Equation (2), has also been presented in a previous study [6].

### 2.3. Additional Data Collection and Analysis

Soil temperatures and water contents were continuously monitored with a soil moisture sensor (TEROS 12, METER group, Pullman, WA, USA) placed within each experimental plot at a depth of 5 cm throughout each year. Measurements of volumetric moisture content were converted to soil water-filled pore space (WFPS) using soil bulk density. For surface soils (5 cm depth), the redox potential (*E<sub>h</sub>* value) was tracked during gas sampling using the Eutech pH 6+ sensor with a platinum *E<sub>h</sub>* electrode (SJ-2006, Sirius technology, 34 cm). Air temperature and precipitation data were obtained from an Automatic Weather Station (AWS) located within a 200 m radius of the rice paddy. The AWS utilized a Campbell

Scientific CR10X data logger and a 3 m tower. The physical and chemical attributes of soil were analyzed in accordance with the Korean Standard Methods for Agricultural Science and Technology Research [30]. Soil samples were extracted using a 30 mm auger (Eijkelkamp, Giesbeek, The Netherlands) at 15 different depths. The collected soil was shade-dried and sifted through a 2 mm sieve. Soil pH was determined using a pH meter (Orion 3-Star, Thermo Fisher Scientific Inc., Waltham, MA, USA), while organic matter content was measured using the Tyurin method.

#### 2.4. Statistical Analysis

The first working hypothesis of this study is that different years, which encompass diverse soil and weather conditions, exert a substantial influence on cumulative  $\text{N}_2\text{O}$  emissions across distinct levels of nitrogen fertilization. To assess the first hypothesis, a one-way Analysis of Variance (ANOVA) was conducted. In addition, a two-way Analysis of Variance (ANOVA) was conducted at different levels of treatments and for the three years. If results demonstrate statistical significance at a confidence level of 95%, the pairwise comparisons using Duncan's multiple range test were subsequently performed to identify distinct groups. The second hypothesis is that different levels of nitrogen fertilization significantly affect the 3-year averages of cumulative  $\text{N}_2\text{O}$  emissions. To assess the second hypothesis, a two-way Analysis of Variance (ANOVA) with a randomized block design was conducted at different levels of treatments with three levels of block (triplicate chambers). If results demonstrate statistical significance at a confidence level of 95%, the pairwise comparisons using *t*-tests using pooled standard deviation were subsequently performed to identify distinct groups. All statistical analyses were carried out using R version 4.3.1 (The R Foundation for Statistical Analysis).

### 3. Results and Discussion

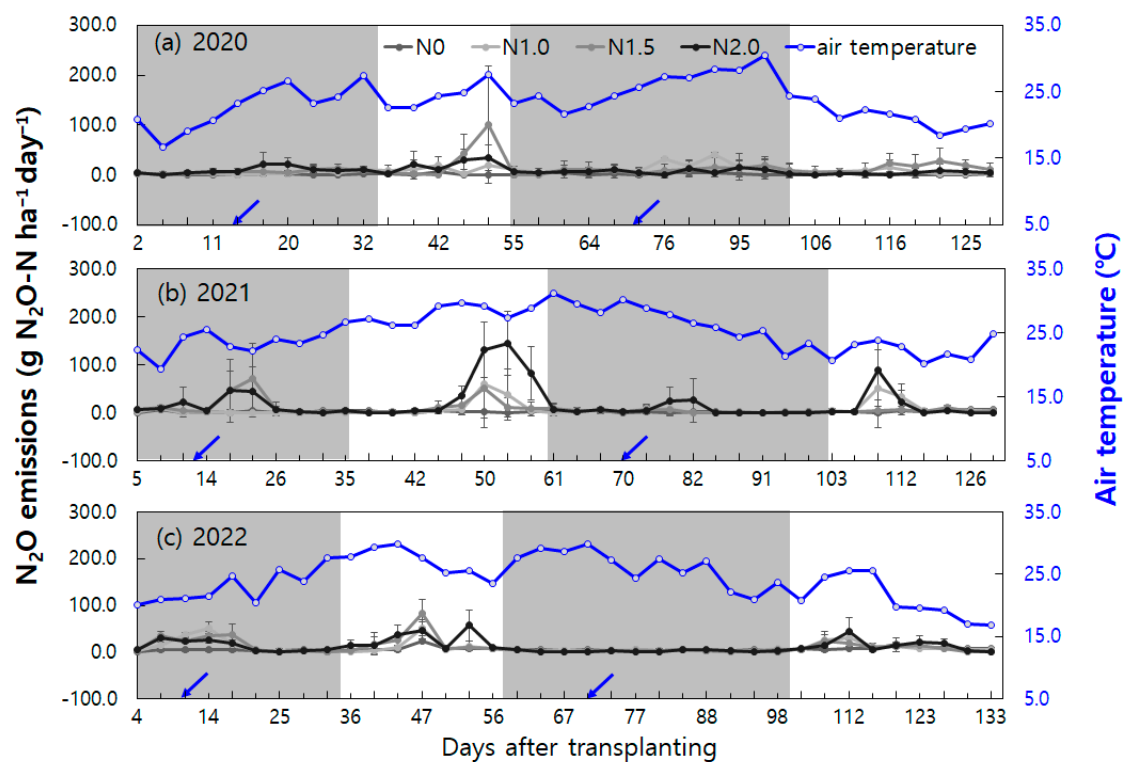
#### 3.1. Changes in $\text{N}_2\text{O}$ Fluxes over Three Years during the Rice Cultivation Period

Changes in daily  $\text{N}_2\text{O}$  emissions due to nitrogen fertilizer (urea) application were evaluated. Elevated  $\text{N}_2\text{O}$  emissions were observed at various stages during the rice cultivation period. Specifically,  $\text{N}_2\text{O}$  emissions peaked after N fertilization and the drainage (mid-season drainage and end-season drainage) as shown in Figure 2.

Noteworthy instances of high daily  $\text{N}_2\text{O}$  emissions (exceeding  $20 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ ) during the rice cultivation were listed in Table 3. To denote only high-concentration cases, values below  $20 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$  were represented as “-”. In 2020, high  $\text{N}_2\text{O}$  emissions were observed only in the N2.0 treatment group after tillering fertilization and during mid-season drainage. After panicle fertilization, high emissions were observed in the N1.0 treatment group, and after end-season drainage in the N1.5 treatment group.

In 2021, high emissions occurred after tillering fertilization in the N1.5 and N2.0 treatment groups, and during mid-season drainage in all treatment groups except N0. After panicle fertilization, high emissions were observed in the N2.0 treatment group, and after end-season drainage in the N1.0 and N2.0 treatment groups, with more occurrences than in 2020.

In 2022, high emissions were observed after tillering fertilization in all treatment groups except N0, and during mid-season drainage, high concentrations occurred in all treatment groups. After end-season drainage, high-concentration cases were observed in all treatment groups except N0, with more occurrences in the N1.5 treatment group compared to 2021. The highest emissions over the three whole years were recorded during the mid-season drainage period in 2021, which had the least rainfall among the three whole years, and the daily mean air temperatures were higher during the corresponding periods in 2021 (Figure 2).



**Figure 2.** Variations in daily  $\text{N}_2\text{O}$  fluxes under different levels of nitrogen fertilizer and air temperature during the rice cultivation period in 2020 (a), 2021 (b), and 2022 (c). The vertical bars in the panel indicate the standard errors calculated from the triplicate chambers. The gray shaded areas represent flooded period. The arrow (✓) indicates N fertilizer application time.

**Table 3.** Noteworthy cases demonstrating high  $\text{N}_2\text{O}$  emissions during rice cultivation from 2020 to 2022.

Year	DAT	$\text{N}_2\text{O}$ Emissions (Mean $\pm$ Standard Deviation, $\text{gN}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ )			
		N0	N1.0	N1.5	N2.0
2020	18	-	-	-	$21.8 \pm 22.1$
	49	-	-	-	$33.9 \pm 25.4$
	76	-	$31.6 \pm 2.3$	-	-
	92	-	$39.9 \pm 4.7$	-	-
	116	-	-	$24.2 \pm 17.6$	-
	123	-	-	$27.9 \pm 25.8$	-
2021	12	-	-	-	$21.9 \pm 31.3$
	21	-	-	$46.1 \pm 39.9$	$46.7 \pm 65.5$
	26	-	-	$71.9 \pm 71.6$	$44.4 \pm 51.8$
	50	-	$59.6 \pm 69.7$	$50.5 \pm 81.2$	$131.7 \pm 57.9$
	53	-	$38.5 \pm 53.6$	-	$144.7 \pm 66.0$
	54	-	-	-	$81.7 \pm 55.7$
	77	-	-	-	$25.1 \pm 28.9$
	82	-	-	-	$26.5 \pm 45.9$
	110	-	$50.3 \pm 80.9$	-	$89.1 \pm 62.7$
	112	-	$33.1 \pm 26.4$	-	$22.1 \pm 25.8$

Table 3. Cont.

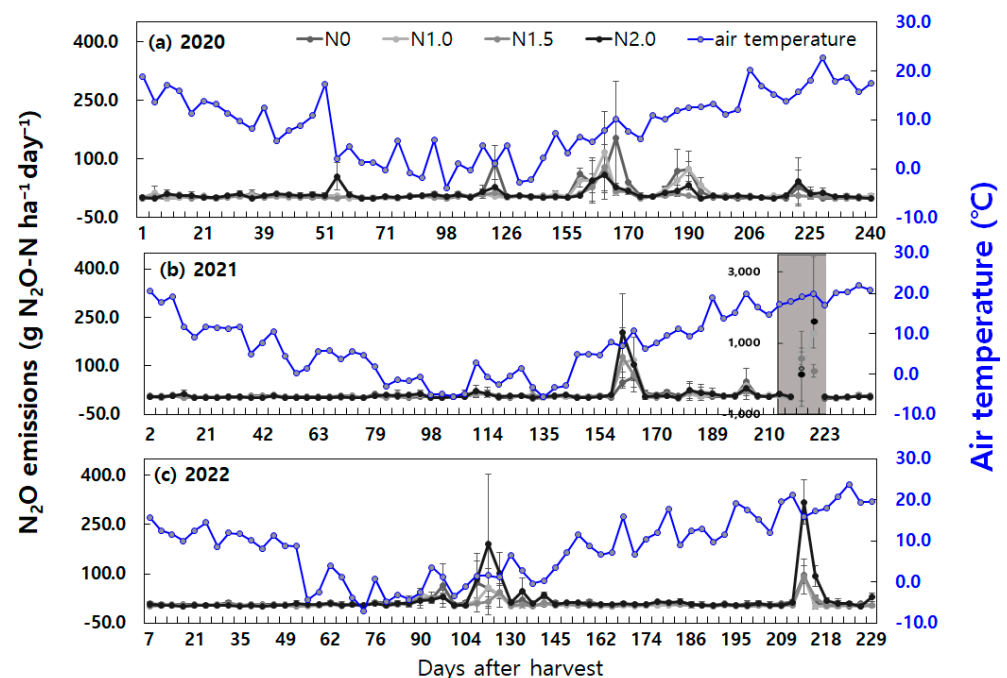
Year	DAT	N <sub>2</sub> O Emissions (Mean $\pm$ Standard Deviation, gN <sub>2</sub> O-N ha <sup>-1</sup> day <sup>-1</sup> )			
		N0	N1.0	N1.5	N2.0
2022	7	-	-	35.7 $\pm$ 9.4	30.2 $\pm$ 2.5
	13	-	37.7 $\pm$ 5.0	23.7 $\pm$ 4.2	24.5 $\pm$ 6.6
	14	-	51.6 $\pm$ 12.0	35.2 $\pm$ 7.9	26.3 $\pm$ 7.6
	18	-	-	37.6 $\pm$ 22.3	-
	41	-	-	25.2 $\pm$ 11.9	36.6 $\pm$ 21.7
	47	24.2 $\pm$ 3.6	51.9 $\pm$ 16.9	83.3 $\pm$ 28.9	47.1 $\pm$ 18.3
	53	-	-	-	56.8 $\pm$ 32.4
	110	-	25.2 $\pm$ 19.0	22.9 $\pm$ 14.2	-
	112	-	29.9 $\pm$ 12.8	-	43.2 $\pm$ 30.1
	123	-	-	-	20.5 $\pm$ 14.4

DAT represents days after transplanting (rice cultivation period).

These findings confirm that changes in anaerobic–aerobic conditions in the soil due to drainage in relation to N fertilization are significant factors affecting variations in N<sub>2</sub>O emissions during the rice cultivation period. This aligns with previous studies that have documented high N<sub>2</sub>O emission instances following nitrogen fertilizer application on agricultural fields and elevated emissions during the drained conditions [31–33].

### 3.2. Daily N<sub>2</sub>O Flux Variations during the Fallow Period over Three Years

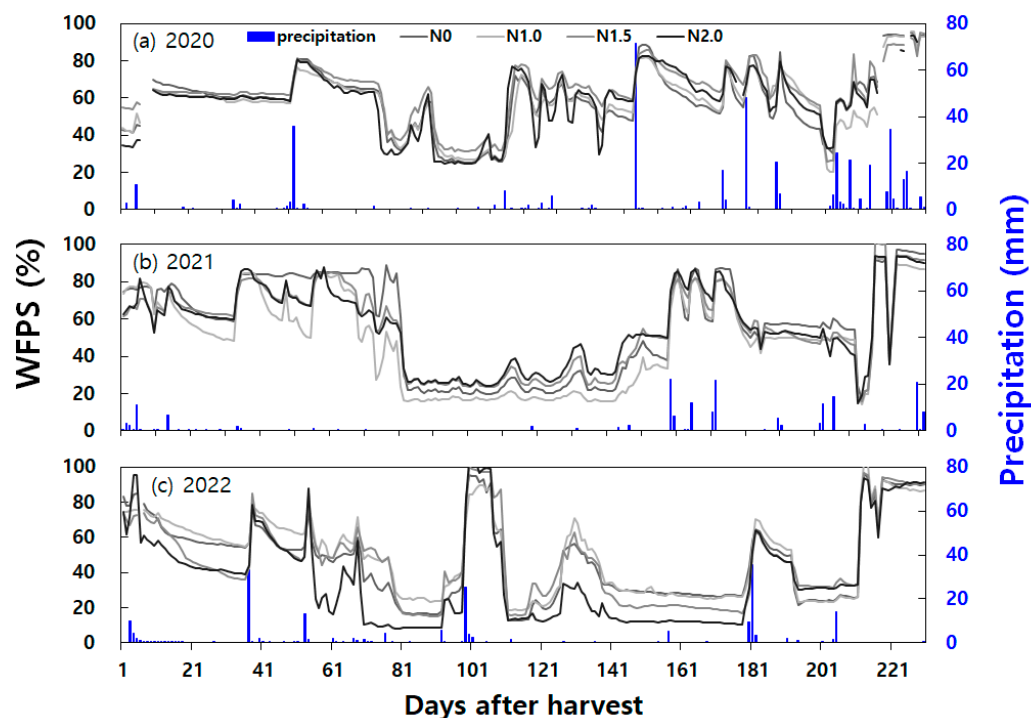
The year-to-year changes in daily N<sub>2</sub>O fluxes during the fallow period from rice harvest to rice transplanting in the next year were compared by nitrogen fertilizer (urea) application rates (Figure 3).



**Figure 3.** Changes in daily N<sub>2</sub>O fluxes at different levels of nitrogen fertilizer and air temperature during the fallow period after rice harvest in 2020 (a), 2021 (b), and 2022 (c). The vertical bars in the panel indicate the standard errors calculated from the triplicate chambers. The shaded area in light gray represents the period when the significant N<sub>2</sub>O emissions showed the highest peak (scaled on the left-side vertical axis) after irrigation.



The variations in soil moisture content and precipitation are presented in Figure 4.



**Figure 4.** Changes in soil moisture contents represented by water-filled pore space (WFPS) at the different levels of nitrogen fertilizer and in precipitation during the fallow period after rice harvest in 2020 (a), 2021 (b), and 2022 (c).

Noteworthy instances of high daily  $\text{N}_2\text{O}$  emissions (exceeding  $20 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ ) during the fallow period were listed in Table 4.

**Table 4.** Noteworthy cases demonstrating high  $\text{N}_2\text{O}$  emissions during the fallow period after rice harvest during 2020 to 2022.

Year	DAH	$\text{N}_2\text{O}$ Emissions (Mean $\pm$ Standard Deviation, $\text{gN}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ )			
		N0	N1.0	N1.5	N2.0
2020	56	-	-	-	$56.0 \pm 33.9$
	121	$91.4 \pm 43.0$	-	-	$28.2 \pm 18.5$
	157	$62.7 \pm 13.2$	$45.1 \pm 17.0$	-	-
	161	$38.1 \pm 24.9$	$44.9 \pm 58.3$	$28.2 \pm 31.4$	$44.4 \pm 51.9$
	163	$66.4 \pm 69.9$	$117.3 \pm 103.0$	$79.2 \pm 106.6$	$59.7 \pm 42.2$
	168	$153.2 \pm 145.5$	-	-	$29.0 \pm 8.1$
	170	$40.5 \pm 1.4$	$24.5 \pm 15.4$	-	-
	183	$20.6 \pm 8.0$	$20.2 \pm 10.2$	-	-
	189	$69.4 \pm 55.4$	$45.8 \pm 2.3$	-	-
	190	$75.2 \pm 18.2$	$75.2 \pm 44.5$	-	$32.2 \pm 10.4$
	194	-	$32.5 \pm 20.5$	-	-
	220	$29.1 \pm 43.6$	-	-	$42.2 \pm 61.6$

Table 4. Cont.

Year	DAH	N <sub>2</sub> O Emissions (Mean ± Standard Deviation, gN <sub>2</sub> O-N ha <sup>−1</sup> day <sup>−1</sup> )			
		N0	N1.0	N1.5	N2.0
2021	112	-	-	-	22.2 ± 17.9
	161	47.6 ± 15.9	109.8 ± 83.8	127.6 ± 90.2	202.5 ± 122.5
	163	64.8 ± 9.4	119.0 ± 46.3	70.7 ± 36.4	105.0 ± 85.0
	175	20.1 ± 6.3	-	-	-
	182	-	-	-	24.5 ± 26.0
	203	50.0 ± 43.2	38.3 ± 24.2	21.5 ± 25.3	31.0 ± 17.3
	218	583.4 ± 502.3	230.2 ± 146.0	287.9 ± 102.8	127.1 ± 64.8
	219	230.9 ± 389.8	1274.4 ± 1017.1	2392.6 ± 700.3	1620.5 ± 795.9
2022	90	20.4 ± 5.4	42.1 ± 40.9	25.0 ± 29.8	-
	95	23.8 ± 7.7	25.7 ± 4.1	26.9 ± 17.3	22.0 ± 9.5
	97	64.0 ± 65.7	32.2 ± 10.5	32.8 ± 7.9	29.2 ± 19.9
	117	72.7 ± 88.8	-	-	83.4 ± 55.2
	123	55.0 ± 60.2	58.8 ± 100.7	-	190.1 ± 261.5
	125	34.2 ± 36.8	36.3 ± 18.3	43.8 ± 21.1	190.1 ± 261.5
	132	20.8 ± 24.1			45.7 ± 40.6
	139				36.4 ± 7.2
	215	96.1 ± 27.1	91.3 ± 39.8	91.3 ± 53.2	317.1 ± 67.8
	216				92.7 ± 30.7

DAH represents days after harvest (fallow period).

To denote only high-concentration cases, values below 20 g N<sub>2</sub>O-N ha<sup>−1</sup> day<sup>−1</sup> were represented as “-”. In contrast to high emission occurrences during the rice cultivation period, all three years of data exhibited elevated N<sub>2</sub>O emissions even in the N0 control group. There were no significant changes observed based on nitrogen fertilization treatments. In 2020, shortly after 50 days of rice harvest, following a high-temperature phenomenon of 17.4 °C and rainfall exceeding 30 mm, the 2 times nitrogen application rate exhibited a N<sub>2</sub>O emission peak of 56.0 ± 33.9 g N<sub>2</sub>O-N ha<sup>−1</sup> day<sup>−1</sup>. In January 2021, approximately 115 days after rice harvest, rapid temperature increases from −1.7 °C to 6.1 °C along with post-rainfall conditions resulted in N<sub>2</sub>O emission peaks of 91.4 ± 43.0 g N<sub>2</sub>O-N ha<sup>−1</sup> day<sup>−1</sup> and 28.2 ± 18.5 g N<sub>2</sub>O-N ha<sup>−1</sup> day<sup>−1</sup> for the control group (N0) and the double (N2.0) nitrogen fertilization, respectively.

In March 2021, about 150 days after rice harvest, following dry soil conditions with temperatures hovering around 17 °C, a rainfall of 71.4 mm led to N<sub>2</sub>O emission peaks ranging from 28.2 ± 31.4 to 153.2 ± 145.5 g N<sub>2</sub>O-N ha<sup>−1</sup> day<sup>−1</sup> across all treatment groups. In late April 2021, maintaining water-filled pore space (WFPS) between 50% and 60% until it surpassed 70–80% triggered N<sub>2</sub>O emission peaks ranging from 20.6 ± 8.0 to 75.2 ± 18.2 g N<sub>2</sub>O-N ha<sup>−1</sup> day<sup>−1</sup>, observed in all treatment groups except the 1.5 times nitrogen application rate. In early May 2021, emissions were 29.1 ± 43.6 g N<sub>2</sub>O-N ha<sup>−1</sup> day<sup>−1</sup> and 42.2 ± 61.6 g N<sub>2</sub>O-N ha<sup>−1</sup> day<sup>−1</sup> for the control (N0) and the double (N2.0) nitrogen fertilization, respectively.

In late January 2022, approximately 110 days after rice harvest, a slight increase in temperature from below zero to above zero, coupled with light rainfall, led to a N<sub>2</sub>O emission peak of 22.2 ± 17.9 g N<sub>2</sub>O-N ha<sup>−1</sup> day<sup>−1</sup> in response to the double (N2.0) nitrogen application rate. In mid-March 2022, about 160 days after rice harvest, an increase in WFPS from 30–50% to over 60–80% after rainfall resulted in N<sub>2</sub>O emission peaks ranging from 47.6 ± 15.9 to 202.5 ± 122.5 g N<sub>2</sub>O-N ha<sup>−1</sup> day<sup>−1</sup> across all treatment groups. In late

April 2022, about 210 days after rice harvest, with soil temperature exceeding 17 °C and 15 mm of rainfall, high-concentration cases ranging from  $21.5 \pm 25.3$  to  $50.0 \pm 43.2$  g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup> were observed in all treatment groups. The most substantial high-flux events occurred in early May 2022, one day after irrigation on May 10th. The significant N<sub>2</sub>O emissions peaked across all treatment groups, ranging from  $127.1 \pm 64.8$  to  $2392.6 \pm 700.3$  g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup>, as the soil moisture content dropped below 30%, followed by irrigation on May 10th and exceeding 90% WFPS on May 11th and 12th as shown by the shaded region in Figure 3b. This is consistent with prior research, indicating that irrigation on dry soil could increase N<sub>2</sub>O emissions by up to 140% [34].

Throughout the fallow period in 2023, prominent instances of high daily N<sub>2</sub>O emissions occurred as follows: In January, around 90 days after rice harvest, an increase in WFPS from below 20% to 20–30% led to N<sub>2</sub>O emission peaks ranging from  $20.4 \pm 5.4$  to  $64.0 \pm 65.7$  g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup> across all treatment groups. In February 2023, about 117 days after rice harvest, a slight increase in temperature from below zero to above zero, accompanied by a slight increase in WFPS, resulted in N<sub>2</sub>O emission peaks ranging from  $34.2 \pm 36.8$  to  $190.1 \pm 261.5$  g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup> across all treatment groups. In May 2023, after approximately 210 days following rice harvest, when WFPS drop from over 90% to 70–80%, N<sub>2</sub>O emission peaks ranging from  $91.3 \pm 39.8$  to  $317.1 \pm 67.8$  g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup> were observed across all treatment groups. The greater contribution of cumulative N<sub>2</sub>O emissions during the fallow period was much greater (up to approximately 90%) to the whole-year N<sub>2</sub>O emissions than those during the rice cultivation period.

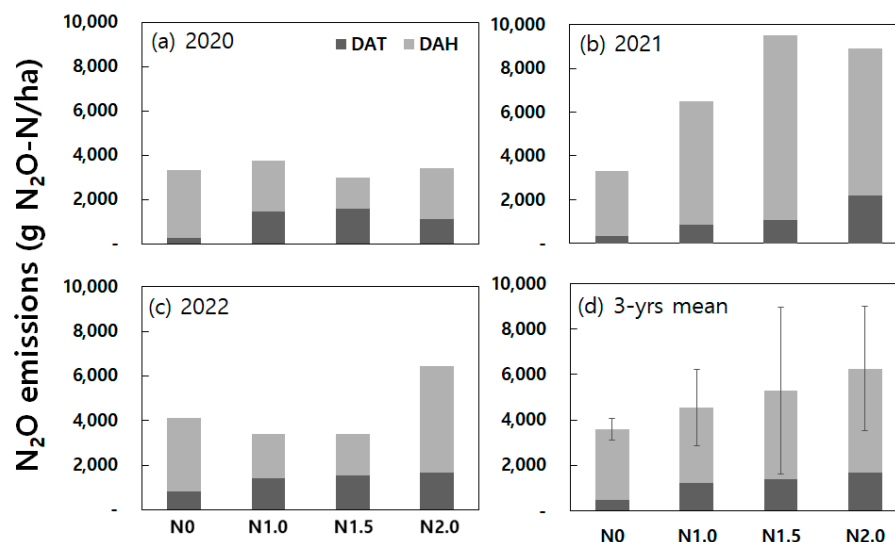
In summary, soil and weather conditions contributed to instances of N<sub>2</sub>O emission peaks during the fallow period. It was evident that increases in temperature and rainfall following dry soil conditions were major drivers for N<sub>2</sub>O production, influencing both N<sub>2</sub>O emission levels and soil moisture content. These findings align with previous research indicating that changes in soil moisture content after rainfall are significant drivers of N<sub>2</sub>O emission variations [35,36], and that soil temperature exerts a substantial influence on N<sub>2</sub>O emissions [37]. In addition, this study revealed significantly elevated N<sub>2</sub>O levels when irrigating exceedingly arid soils during a dry period with no continuous rainfall. Consequently, maintaining an appropriate soil moisture content appears to be a more rational approach, rather than subjecting the soil to prolonged periods of irrigation in persistently dry conditions. In other words, it would be more reasonable to reduce N<sub>2</sub>O emissions by adopting shorter irrigation intervals rather than allowing the soil to become extremely dry before irrigation.

### 3.3. Comparisons of Annual Cumulative N<sub>2</sub>O Emissions under Different Levels of Nitrogen Fertilization

Cumulative emissions of N<sub>2</sub>O from paddy fields during the rice cultivation and fallow periods over the three whole years from 2020 to 2022 are illustrated in Figure 5. Nitrous oxide emissions from the paddy fields occur in small amounts but can be influenced significantly by sporadic high-flux events. This thereby makes gas collection during high-concentration events an important factor in overall cumulative emissions.

The order of the year in the magnitude of annual cumulative N<sub>2</sub>O emissions was 2021 > 2022 > 2020. The one-way ANOVA (analysis of variance) yielded no statistical significance at the control (N0) and the one-time (N1.0) nitrogen fertilization levels. In contrast, results from the one-way ANOVA results demonstrated statistical differences at the two higher nitrogen fertilization levels where *p*-values were 0.011 and 0.030 at a 95% confidence level under nitrogen fertilization conditions of N1.5 and N2.0, respectively. Duncan's multiple range tests for N1.5 indicate that cumulative emissions in 2021 were statistically different from those in 2020 and 2022 due to occurrences of extremely high-flux events in 2021. Duncan's multiple range tests for N2.0 indicate that cumulative emissions in 2021 were statistically different from those in 2020 due to the occurrences of extremely high-flux events in 2021. The cumulative emissions in 2021 under nitrogen fertilization conditions of N1.5 and N2.0 exceeded one order of magnitude greater than the 3-year mean

values at the same levels of nitrogen fertilization. In addition, the two-way ANOVA yielded no statistical differences at a confidence level of 95% between the different levels of nitrogen fertilization (N0, N1.0, N1.5, and N2.0), while statistical differences were detected across the three years. There was no interaction effect between the different levels of nitrogen fertilization (N0, N1.0, N1.5, and N2.0) and the three years.



**Figure 5.** Annual cumulative N<sub>2</sub>O emissions at the different levels of nitrogen fertilizer during the year 2020 (a), 2021 (b), 2022 (c), and the three-year average (d). DAT represents days after transplanting (rice cultivation period), while DAH represents days after harvest (fallow period). The vertical bars in the (d) panel indicate the standard errors of the means from the three-year measurement data.

As displayed in Figure 5d, the 3-year average of cumulative N<sub>2</sub>O emissions at the four different levels of nitrogen fertilization were  $3581 \pm 472$  (N0),  $4556 \pm 1683$  (N1.0),  $5286 \pm 3660$  (N1.5), and  $6266 \pm 2756$  (N2.0) g N<sub>2</sub>O-N ha<sup>-1</sup>. The higher nitrogen fertilization seemingly tends to yield higher N<sub>2</sub>O emissions. The two-way ANOVA based on a treatment factor (nitrogen fertilization) with a block factor (triplicate chambers) was tested against the substantial influence of cumulative N<sub>2</sub>O emissions across different levels of nitrogen fertilization. There were no significant differences in the 3-year mean values under all treatment conditions (N0, N1.0, N1.5, and N2.0, respectively) at a confidence level of 95%. However, pairwise comparisons using *t*-tests with the pooled standard deviation method indicated a statistical difference (*p*-value, 0.022) at a confidence level of 95% in the 3-year averages of cumulative N<sub>2</sub>O emissions between N0 and N2.0 treatment groups. In a study conducted in subtropical permanently flooded rice paddy fields in China, the 3-year average of cumulative N<sub>2</sub>O emissions ranged from 1.61 to 3.10 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup>. However, there was no observed increase in N<sub>2</sub>O emissions with increased nitrogen fertilization where N<sub>2</sub>O emission data were missing during the fallow periods. It would be important to cover possible high-flux events during fallow periods for the accurate estimation of cumulative emissions [38].

#### 4. Conclusions

This study aimed to evaluate the key influencing factors of N<sub>2</sub>O emissions from a rice paddy field in the central region of South Korea, where there is one rice-cropping cycle per year. To achieve this, closed chambers were installed in four different nitrogen fertilization treatment plots, and N<sub>2</sub>O emissions were assessed. We analyzed the daily variations in N<sub>2</sub>O emissions over the past three whole years based on nitrogen fertilization treatments to evaluate the primary influencing factors of N<sub>2</sub>O emissions from a rice paddy field. We observed instances of high N<sub>2</sub>O fluxes after nitrogen fertilization and the condition of

the drained soil. During the fallow period from rice harvest to the following year's rice planting, significant N<sub>2</sub>O fluxes were found in anaerobic–aerobic conditions in the soil following rainfall events or after irrigation. During the fallow period from rice harvest to rice planting in the following year, variations in N<sub>2</sub>O emissions were associated with high-flux events during rainy periods on dry soils. We discovered that the greater contribution of cumulative N<sub>2</sub>O emissions during the fallow period made a much greater contribution (up to approximately 90%) to the whole-year N<sub>2</sub>O emissions than those during the rice cultivation period. This highlights the considerable influence of soil moisture content and weather conditions on N<sub>2</sub>O emissions during the fallow period. This affects high-emission events, which in turn significantly impact the cumulative emissions over the entire period. Variations in soil moisture content resulting from changes in weather conditions are highlighted as the key factor. In short, three key findings would be: (i) fallow periods play a crucial role in determining total yearly emissions; (ii) emissions primarily occur during high-emission events; and (iii) these events during fallow periods are attributed to climatic factors, occurring even in areas where no fertilizer has been applied. Hence, periodic measurements of soil and weather conditions throughout the year, including fallow periods, are crucial for the determination of optimal gas collection schedules and the accurate assessment of overall cumulative N<sub>2</sub>O emissions. This study contributes to an improved understanding of the intricate relationship between environmental factors and N<sub>2</sub>O emissions in the context of rice cultivation. Also, the findings from this study could help prepare the further revision or refinement of N<sub>2</sub>O emissions from rice cultivation in the national greenhouse gas inventories defined by the inter-governmental panel on climate change (IPCC).

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