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Fertilization-induced reactive nitrogen gases and carbon dioxide emissions: insight to the carbon-nitrogen cycles

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Abstract

Different agricultural practices can pose significant threats to environmental quality and human health. This study aimed to assess the emissions of reactive nitrogen (NH_3, NO_x, and N_2O) and carbon dioxide (CO_2) induced by fertilization in spinach and cabbage farmlands. Field and pot experiments were conducted to analyze the emission fluxes and intensities of reactive nitrogen gases and CO_2. The findings revealed that the total emissions of reactive nitrogen for cabbage and spinach ranged from 21 to 798 kg-N ha^{-1} and 1.1 to 489 kg-N ha^{-1}, respectively. Generally, organic fertilizers exhibited higher emission intensities of NH_3 compared to N_2O. While slow-release fertilizers effectively reduced NH_3 emissions, they resulted in increased soil N_2O emissions. Furthermore, the total emissions of reactive nitrogen from the soil showed a positive correlation with soil CO_2 emissions. Particularly, organic farming practices, especially in the case of cabbage, led to increased CO_2 emissions from farmlands. Based on the experimental findings, three priority directions were suggested to achieve sustainable soil carbon and nitrogen management in order to minimize emissions from farmlands. This study provides valuable insights for future soil carbon and nitrogen management in subtropical regions.

Keywords Ammonia, Nitrous oxide, Spinach, Cabbage, Slow-release fertilizer, Organic fertilizer

1 Introduction

Nitrogen fertilization in agriculture poses a significant environmental threat, primarily due to the emissions of carbon dioxide (CO_2) and reactive nitrogen (N_r) gases such as ammonia (NH_3), nitrogen oxides (NO_x), nitrous oxide (N_2O), and nitrous acid (HONO) [1], originating from farmlands. Globally, roughly 50% of total nitrogen fertilizer inputs are used for crop growth [2]. To address this issue, numerous international conventions, government policies, and regulations have been established to mitigate the N_r emissions from agriculture. For instance, the European Commission introduced the European Green Deal in 2019, outlining comprehensive transformation policies to combat climate change and foster a clean environment, thus promoting a green economic system [3]. Particularly, the "Eliminating Pollution" and "Farm to Fork" policies aim to create a green and healthy agricultural environment. Likewise, in Taiwan, the National Development Council in March 2022 announced "Taiwan's Pathway to Net-Zero Emissions in 2050". This pathway encompasses 12 key strategies, including the enhancement of carbon sink, to facilitate the implementation of various transitions through practical action plans [4]. Agriculture plays a crucial role in providing crops and substances while generating economic income for farmers. However, it also contributes remarkable emissions of CO_2 and N_r gases due to the

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fertilization. In Taiwan, soil fertilization accounts for approximately 37% of direct greenhouse gas emissions in the agricultural sector, whereas paddy fields contribute around 18% [5].

NH_3 volatilization is the primary pathway for soil nitrogen loss in farmlands, and its extent varies significantly in different soil environments [6–8]. It is worth noting that the majority of atmospheric NH_3 is attributed to agricultural practices such as the use of fertilizers (e.g., ammonium sulfate, nicotinic ammonium, urea, and ammonium phosphate) and improper disposal of livestock excrement from animals like cattle, pigs, sheep, chickens, and other livestock [9–11]. Various factors contribute to the increase in regional NH_3 levels, including agricultural fertilization, livestock manure, soil temperature, irrigation water quality, and atmospheric chemical reactions. NH_3 can undergo long-distance transport and react with nitrate and sulfate, leading to the formation of secondary aerosols [12]. This has implications for the environment, crops, and human health. Moreover, NH_3 can contribute to the occurrence of acid rain, leading to the acidification of agricultural land and habitats [13], thus negatively impacting biodiversity.

Similarly, NO_x plays a catalytic role in the production of tropospheric ozone and other photochemical oxidants, such as nitric acid, which contributes to the deterioration of regional air quality. It is estimated that global soil NO_x emissions amount to about $21 \pm (4–10)$ Tg-N per year [14]. Prior to the conversion of soil NO_x into inert nitrogen, soil N_2O emissions can occur depending on the field conditions [15]. Indeed, the formation of soil N_2O involves complex bio-chemical reactions that are strongly influenced by factors such as redox potential, soil organic matter turnover, and the specific crop types [16]. N_2O is a potent greenhouse gas and one of the primary N_r gases emitted from farmlands through the processes of nitrification and denitrification in the soil. According to the IPCC report [17], anthropogenic N_2O concentrations have been increasing at a rate of 0.85 ± 0.03 ppb per year, with more than two-thirds of the increase attributed to the growing use of agricultural nitrogen fertilizers.

Numerous studies have extensively examined the emission intensities of N_r in different crops, including rice [18, 19], sugarcane [20], corn [21], lettuce [22], and fruits [23, 24], originating from the farmlands. Despite the recent advancements, it is worth noting that there has been limited or no research focused on systematically addressing both N_r and CO_2 emissions across different agricultural practices. Hence, this study aims to fill this knowledge gap by evaluating the effect of different fertilizers (both chemical and organic) and crops (specifically spinach and cabbage) on soil N_r and CO_2 emissions. This study consisted of field and pot experiments to analyze the emission fluxes of N_r components, such as NH_3, NO_x, and N_2O. Meteorological conditions and physico-chemical properties of the soils were determined, enabling the calculation of N_r emission intensities. Additionally, the measurements of soil CO_2 emission flux were conducted and compared with the behavior of N_r emissions under different agricultural practices. The obtained results can provide valuable insights and perspectives for achieving soil carbon and nitrogen management strategies aimed at reducing emissions on farmlands. This study contributes to the understanding and future implementation of soil carbon and nitrogen management practices, particularly in subtropical regions.

2 Materials and methods

2.1 Experiment design

Spinach and cabbage rank among the top three major vegetable crops in terms of planting area in Taiwan. The nitrogen fertilizer requirements for vegetable cultivation are typically higher compared to rice. Consequently, spinach and cabbage were selected as representative crops to investigate the impact of different agricultural methods on the emission intensity of nitrogen-containing gases. The spinach was cultivated at the experimental farm of National Taiwan University (see Fig. S1 in Supplementary Materials). The planting period extended from January 28, 2021 to March 8, 2021. During this time, we analyzed nitrogen-containing gas emissions and emission factors originating from agricultural land sources. Table 1 presents the experimental design plan of this experiment, encompassing various fertilizer treatments: no fertilizer (control group, CK_1), full chemical fertilizer (CA_1), full organic fertilizer (OA_1), half chemical fertilizer (CH_1), and half organic fertilizer (OH_1). For the spinach trial, the chemical fertilizers consisted of 20% N, 5% P_2O_5, and 10% K_2O, while the organic fertilizers comprised 5.5% N, 2% P_2O_5, and 2% K_2O.

The non-heading cabbage was planted from July 7, 2021 to August 5, 2021. Cabbage is known for its short growth period, allowing it to be planted throughout the year. However, it requires a substantial amount of water and is therefore irrigated twice a day. Moreover, before planting, the soil is thoroughly watered to ensure sufficient moisture content. Table 1 presents the experimental design plan of this cabbage experiment, consisting of various fertilizer treatments: no fertilizer (control group, CK_2), full chemical fertilizer (CA_2), full organic fertilizer (OA_2), half chemical fertilizer (CH_2), and half organic fertilizer (OH_2). Fertilizer was performed twice, with basal fertilizer applied on the day prior to planting (recorded as day 0) and topdressing applied on the 19^{th} day (July 26). For the cabbage trial, the chemical fertilizers utilized were slow-release fertilizers, containing 14% N, 11%

Table 1 Experiment designs for the spinach and the cabbage experiments

Crop	Group	Description	Fertilizer type	Amount (kg-N ha^{-1})
Spinach[a]	BK	Background air	--	0
	CK_1	No fertilizer (control group)	--	0
	CH_1	Half chemical fertilizer	Chemical	82.5
	CA_1	Full chemical fertilizer	Chemical	165
	OH_1	Half organic fertilizer	Organic	82.5
	OA_1	Full organic fertilizer	Organic	165
Cabbage[b]	BK	Background air	--	0
	CK_2	No fertilizer (control group)	--	0
	CH_2	Half chemical fertilizer	Chemical[c]	180
	CA_2	Full chemical fertilizer	Chemical[c]	360
	OH_2	Half organic fertilizer	Organic	180
	OA_2	Full organic fertilizer	Organic	360

[a] Performed by the spinach experiments

[b] Performed by the cabbage experiments

[c] Slow release fertilizers were used

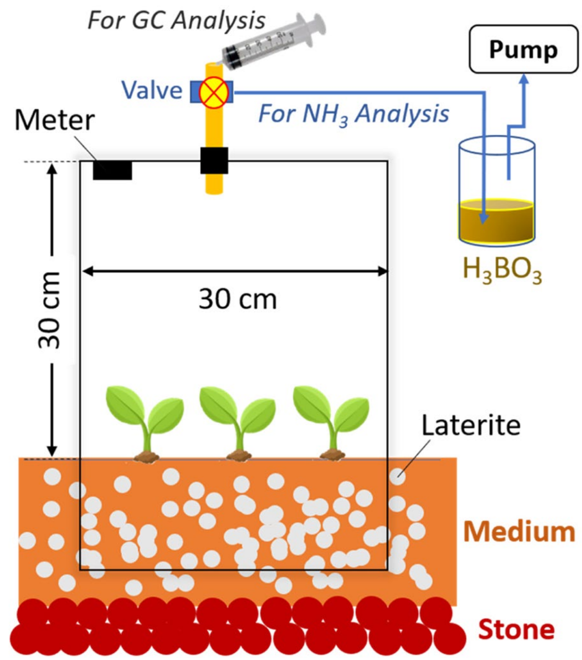

Fig. 1 Schematic diagram of the experimental set-up, and the gas collection system design and sampling method. The NO_x, N_2O, and CO_2 were analyzed by the GC. The NH_3 was analyzed via H_3BO_3 absorption

P_2O_5, and 13% K_2O, while the organic fertilizers contained 5.1% N, 2.1% P_2O_5, and 2.1% K_2O.

2.2 Sampling and analysis of nitrogen-containing gases

In this study, a closed static chamber (see Fig. 1) was specifically designed as the sampling device. To ensure the chamber's airtightness, a custom-made acrylic box measuring 30 cm × 30 cm × 40 cm (L × W × H) was employed. The chamber was equipped with a temperature/hygrometer and positioned 10 cm deep into the soil during the sampling process. Prior to installation on farmlands, a visual inspection was conducted to verify the proper sealing and integrity of the chamber. This inspection involved applying a soapy water solution to potential leak points and observing for any signs of leakage. Each individual acrylic box contained 2–3 crop plants, which were securely covered within the chamber. The sampling period encompasses the crop's entire growth stage, and the gas sampling schedule was synchronized with the fertilization schedule. This schedule ranged from daily sampling to sampling every five days, depending on the specific requirements. For instance, gas sampling was conducted at intervals of 0–2 days, 3–4 days, 5–7 days, and 8–10 days after fertilization.

To ensure the chamber's pressure remained at an optimal level, the amount of air extracted from the chamber by the pump was carefully calculated. During each sampling event, 50 mL of gas was initially extracted using a syringe for subsequent NO_x, N_2O, and CO_2 analyses using a gas chromatograph (GC-TCD, Agilent 7890A, US). The remaining gas within the chamber was then introduced into a boric acid (H_3BO_3) solution to facilitate NH_3 analysis. This process was achieved by utilizing a pump with a flow rate of 3 L min^{-1} for a duration of 5 min. The NH_3 gas could be captured by the H_3BO_3 solution, forming NH_4^+ as depicted in Eqs. (1–3).

$$NH_{3(g)} + H_2O \rightarrow NH_4OH_{(aq)} \quad (1)$$

$$2\,NH_4OH_{(aq)} + 4\,H_3BO_{3(l)} \rightarrow (NH_4)_2B_4O_{7(aq)} + 7\,H_2O \quad (2)$$

$$(NH_4)_2B_4O_{7(aq)} + 2\,H^+ + 5\,H_2O \rightarrow 2\,NH_4^+ + 4\,H_3BO_3 \quad (3)$$

To measure the NH_4^+ concentration within the H_3BO_3 solution, an ion chromatography (Syknm S155, Germany) was employed. In this study, three randomly selected samples were taken and subjected to repeated analyses to confirm the recovery efficiency of the NH_4^+ measurement.

2.3 Determination of gas emission flux

The concentrations of reactive nitrogen gases were used to calculate the emission flux and intensity of different fertilization practices. The emission fluxes of N_2O and

NO_X (kg ha^{-1} d^{-1}) were calculated by Eq. (4), and the emission flux of NH_3 (kg ha^{-1} d^{-1}) was calculated by Eq. (5).

$$\text{Emission flux of } N_2O \text{ or } NO_x = \frac{C \times V \times MW}{8.2 \times 10^{-6} \times T \times A \times t} \quad (4)$$

$$\text{Emission flux of } NH_3 = \frac{C\prime \times V\prime}{A \times t} \quad (5)$$

where V is the volume of the chamber (L); MW is the molecular weight of the gas (e.g., $N_2O = 44$ g mol^{-1}); T is the temperature in the chamber (K); A is the cross-sectional area of the chamber (ha); t is the cumulative days of gas collection (d); V' is the total volume of gas production approximately equal to the total volume of the chamber (L).

2.4 Estimation of emission intensity

For the emissions of gaseous compounds from farmland, the emission intensity is widely used to evaluate the reactive nitrogen emissions of nitrogen fertilizers. In this study, the measured emissions per area (E_t, kg-N ha^{-1}) of fertilized farmland were subtracted from the background emissions (E_b, kg-N ha^{-1}) to determine the emission intensity of reactive nitrogenous gas, as shown in Eq. (6).

$$\text{Emission Intensity} = E_t - E_b \quad (6)$$

In particular for N_2O emission, the emission factor is defined as the percentage of the N_2O emission intensity to the total nitrogen application (N_t, kg-N ha^{-1}), as shown in Eq. (7), in accordance with the IPCC definition. Although the IPCC report has proposed active nitrogen emission factors for different fertilizers on a global or regional scale, detailed studies are still needed to refine the emission factors on a national or urban scale.

$$\text{Emission Factor}(\%) = \frac{E_t - E_b}{N_t} \times 100\% \quad (7)$$

3 Results and discussion

3.1 Air temperature, precipitation and soil conditions

In this study, meteorological observation data were collected, encompassing the daily average temperature, rainfall, and sunshine duration during the experiment period, to track changes in meteorological factors throughout the sampling period. The experimental sites exhibited a typical marine subtropical climate with wet summers and winters. Regarding the spinach experiment (as depicted in Fig. 2a), the average daily temperature ranged from 14.5–23.1 °C, with an overall mean of 18.1 ± 2.1 °C (n = 40). The duration of sunshine varied from 0–10.6 h, with an average of 4.3 ± 4.4 h (n = 40). Regarding the daily rainfall, apart from a rainfall event of 35 mm on March 6, the daily rainfall during the remaining period of the experiment ranged from 0–10 mm, with an average of 2.5 ± 6.5 mm (n = 40). The weather conditions throughout the field experiment were predominantly characterized by cloudiness or rain. In the case of the cabbage experiment (as shown in Fig. 2b), the average daily temperature varied from 27.4–32.4 °C, with a mean temperature of 29.9 ± 1.5 °C (n = 30). The duration of sunshine ranged from 0–13 h, with the average duration of 6 ± 4 h (n = 30). The daily rainfall observed during the experiment spanned from 0–87.5 mm, with an average daily rainfall of 10.0 ± 20.8 mm.

Based on the results of soil analyses, the soil pH values for the spinach trials (as presented in Table 2) ranged

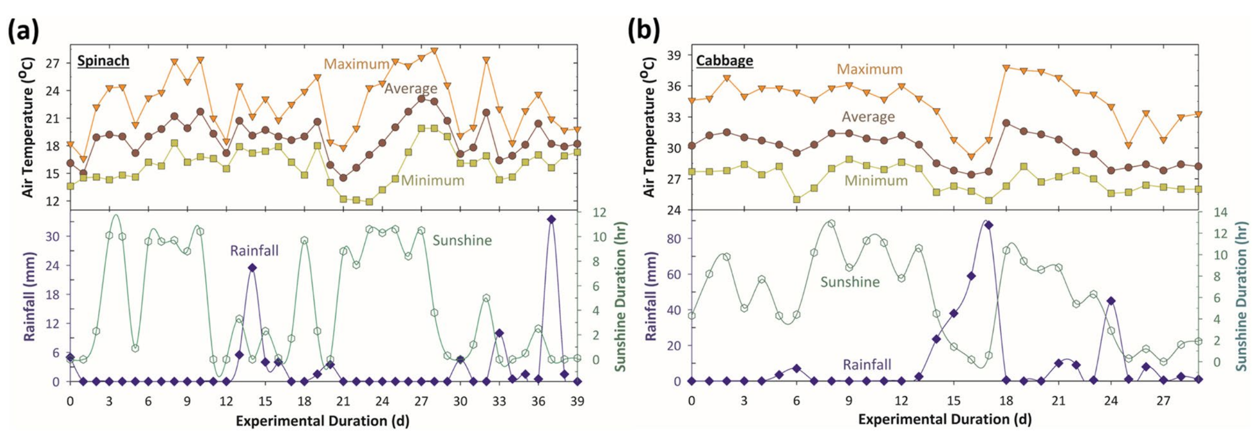

Fig. 2 Daily temperature, rainfall and sunshine duration for **a** spinach and **b** cabbage experiments. The spinach experiment took place from January 28, 2021 to March 8, 2021, while the cabbage experiment spanned from July 7, 2021 to August 5, 2021. The duration of sunshine (daytime) was defined as the period when the average heat flux exceeded 120 W m^{-2} within a given day

Table 2 Soil analysis of the spinach and cabbage experiments after planting

Crop	Group	pH	Conductivity ($\mu S\ cm^{-1}$)	ORP (mV)[a]	Total N (mg kg^{-1})
Spinach	CK_1	6.33	91	-	328
	OH_1	6.62	153	-	302
	OA_1	6.64	253	-	416
	CH_1	6.61	365	-	340
	CA_1	6.48	520	-	403
Cabbage	CK_2	7.12	88	88	32
	OH_2	7.05	102	107	88
	OA_2	7.09	185	112	161
	CH_2	7.14	277	128	37
	CA_2	7.46	413	202	193

[a] *OPR* Oxidation-reduction potential. For the soil properties, 20 g of soil samples was collected, air-dried, and then pass through a 20-mesh standard sieve. The pH, conductivity and oxidation-reduction potential (ORP) of soil samples were measured with a soil-water ratio of 1:1 (w:w)

from 6.33–6.64. Among the groups, the chemical fertilizer group (CH_1 or CA_1) exhibited the highest soil conductivity, with CA_1 recording approximately 0.52 mS cm^{-1}. The total nitrogen concentrations in OH_1 and OA_1 were 302 and 416 mg kg^{-1}, respectively. Similarly, CH_1 and CA_1 had concentrations of 340 and 403 mg kg^{-1}, respectively. Thus, the observed differences in the total nitrogen content of the soil among the test groups were minimal. Regarding the cabbage experiments, the soil pH values for each group after the trials ranged from 7.05–7.46. The chemical fertilizer group (CH_1 or CA_1) had the highest soil conductivity, with CA_1 measuring approximately 0.41 mS cm^{-1}. The total nitrogen concentrations in OH_2 and OA_2 were 88 and 161 mg kg^{-1}, respectively. The concentrations in CH_2 and CA_2 were 37 and 193 mg kg^{-1}, respectively. The results further indicated a positive correlation between the total nitrogen content of the soil and the amount of fertilization.

3.2 Effect of fertilization on emission flux of reactive nitrogen

The emission of reactive nitrogen from farmland is largely influenced by fertilization practices. Figure 3a and b illustrate the impact of time duration on NH_3 emission flux from a spinach farmland under different fertilization methods. Overall, organic fertilizers exhibited significantly higher NH_3 emission fluxes (>7 folds) compared to chemical fertilizers. The results indicated that the organic fertilizer group (OA_1) reached its maximum NH_3 emission flux at approximately the 7^{th} day after fertilization, measuring about 133 ± 4 kg-NH_3 ha^{-1} d^{-1} ($n=3$). This value was considerably higher than the background flux (BK_1: 0.35 ± 0.05 kg-NH_3 ha^{-1} d^{-1}; $n=3$). Similarly, the OH_1 group displayed its maximum NH_3 emission flux (15.3 ± 1.3 kg-NH_3 ha^{-1} d^{-1}; $n=3$) around the 4^{th} day after fertilization. As for the chemical fertilizer group, CA_1 and CH_1 recorded their maximum NH_3 emission fluxes at 2.9 ± 0.1 kg-NH_3 ha^{-1} d^{-1} (on the 7^{th} day after fertilization) and 2.6 ± 0.1 kg-NH_3 ha^{-1} d^{-1} (between the 5^{th} and 7^{th} days after fertilization), respectively.

Figure 3c and d show the effect of time duration on NH_3 emission flux from a cabbage farmland under different fertilizations. The NH_3 emission fluxes of organic fertilizers were significantly higher than those of slow-release fertilizers, which belong to the group of chemical fertilizers. The chemical fertilizer group exhibited its maximum NH_3 emission flux during the 1–4 days following fertilization. Specifically, the maximum NH_3 emission fluxes for OH_2 and OA_2 were recorded as 44 and 60 kg-NH_3 ha^{-1} d^{-1}, respectively. In the case of chemical fertilizers, since slow-release fertilizers were employed in the cabbage trial, no NH_3 emission fluxes were detected for the CH_2/CA_2 group, similar to the background (BK_2) and control (CK_2) cases. Similar findings have been documented in the literature [23], reporting that NH_3 emissions from peach lands using slow-release fertilizers were approximately 50% lower than those using conventional chemical fertilizers.

Figure 3e and f show the effect of time duration on N_2O emission flux from a cabbage farmland under different fertilizations. The results indicated an immediate increase in N_2O emission flux following fertilization, including both basal fertilizer and top-dressing applications, which gradually decreased thereafter. Throughout the trial period, no N_2O emissions were detected in the background (BK_2) and control (CK_2) cases. However, measurable N_2O emission fluxes were observed for the fertilized cases. Overall, the N_2O emission fluxes of chemical fertilizers (specifically slow-release fertilizers, CH_2 or CA_2) were significantly higher than those of organic fertilizers (OH_2 or OA_2). The maximum N_2O emission fluxes recorded for CH_2 and CA_2 were 3.1 and 4.2 kg-N_2O ha^{-1} d^{-1}, respectively. Conversely, the maximum N_2O emission fluxes for OH_2 and OA_2 were relatively lower, measuring 0.48 and 0.99 kg-N_2O ha^{-1} d^{-1}, respectively. In comparison, based on the spinach trial results in this study, no N_2O emission flux was measured for all cases except for CA_1. The associated N_2O emission flux on the 2^{nd} day after fertilization was approximately 3.1 ± 0.9 kg-N_2O ha^{-1} d^{-1} ($n=3$).

3.3 NH_3 and N_2O emission intensities

Figure 4a and b show the N_r emission intensities for chemical (slow-release fertilizers) and organic fertilizers, respectively, using cabbage experiments as an

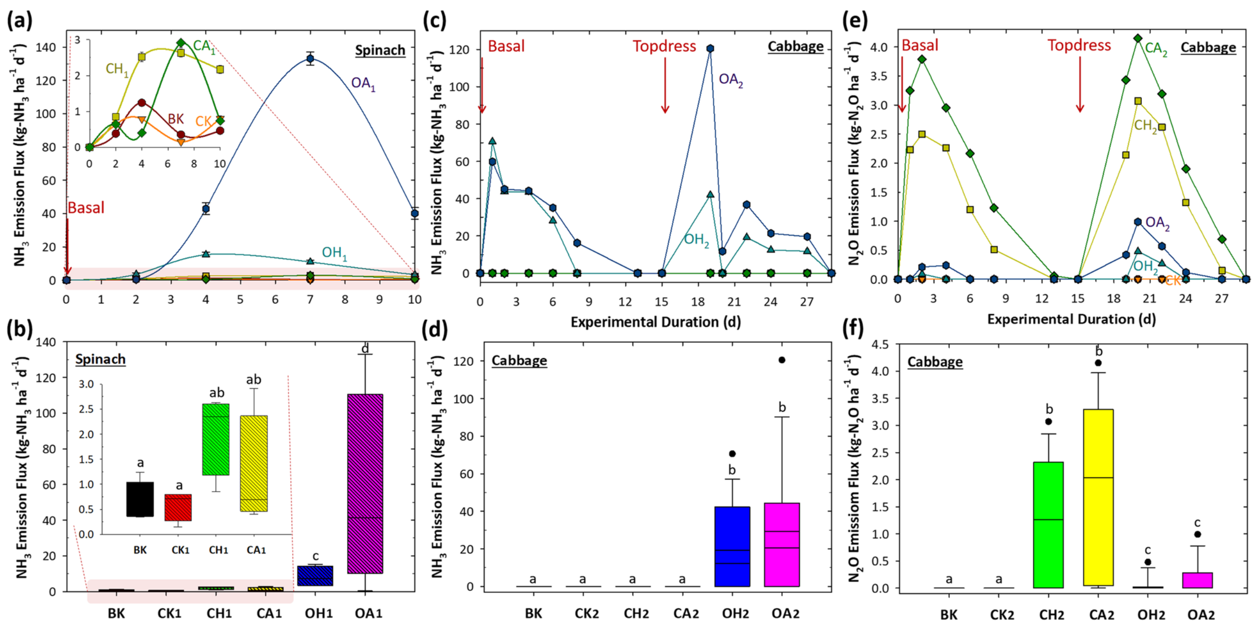

Fig. 3 **a** NH_3 emission flux and **b** its associated box charts for spinach experiments. **c** NH_3 emission flux and **d** its associated box charts for cabbage experiments. **e** N_2O emission flux and **f** its associated box charts for cabbage experiments. Statistical significance was assessed by Student's t test and one-way ANOVA, followed by a post-hoc test. Error bars were determined at the 0.05 confidence level (Student's t-test)

example. The results indicate that slow-release fertilizers (as chemical fertilizers) have a higher intensity of N_2O emissions, compared to NH_3. For slow-release fertilizers (see Fig. 4a), the cumulative N_2O emission intensities of CH_2 and CA_2 before topdressing were 13 and 20 kg-N_2O ha^{-1}, respectively. After topdressing, the cumulative N_2O emission intensities of CH_2 and CA_2 increased to 33 and 50 kg-N_2O ha^{-1}, respectively. Regarding organic fertilizers (see Fig. 4b), the cumulative NH_3 emissions from farmland before topdressing were ~258 kg-NH_3 ha^{-1} (OH_2) and ~296 kg-NH_3 ha^{-1} (OA_2), which were quite similar at this stage. After topdressing, the cumulative NH_3 emissions for OH_2 and OA_2 increased to ~ 524 and ~ 965 kg-NH_3 ha^{-1}, respectively. Moreover, the cumulative N_2O emission intensities of OH_2 and OA_2 after topdressing were 1.1 and 4.8 kg-N_2O ha^{-1}, respectively. This suggests that the organic fertilizers exhibit lower N_2O emissions, compared to NH_3.

Fertilizers can provide organic nitrogen to the soil, which undergoes mineralization to form NH_4^+. Subsequently, nitrification processes convert NH_4^+ to NO_2^- and NO_3^-. During nitrification, the production of NO_x and N_2O also occurs. Additionally, when the soil has a high NH_4^+ content, there is a greater potential for NH_3 volatilization from the soil depending on the soil pH. Therefore, achieving a balanced fertilization in the soil is crucial. Figure 4c illustrates the effect of chemical and organic fertilizers on N_r emissions based on the findings of this study. In general, slow-release fertilizers at the same dosage demonstrate lower NH_3 emissions compared to organic fertilizers. However, they can lead to increased N_2O emissions once the ammonium converts to nitrite or nitrate. To mitigate N_2O emissions, some studies have explored the co-application of nitrification inhibitors (NIs), such as 3,4-dimethylpyrazole phosphate [25], with fertilizers. However, it is worth noting that NIs may also increase NH_3 volatilization [26]. Therefore, significant efforts should be directed towards optimizing the applications of N-fertilizers and NIs under various bioenvironmental conditions.

Table 3 compiles the average emission flux, emission intensity, and emission factors of nitrogen-containing gas for the spinach and cabbage experiments conducted in this study, as well as data from the literature. The results indicate substantial variations in N_r emissions across different sites. Considering the crop types, since the nitrogen application rate for cabbage was higher than spinach, the emission intensities of total nitrogen-containing gases were typically higher. In the spinach trials of this study, the cumulative NH_3 emission intensities of BK_1 and CK_1 were nearly identical, ranging from about 6.1 and 6.3 kg-NH_3 ha^{-1}. In the chemical fertilizer group, the cumulative NH_3 emission intensities of CH_1 and CA_1 were 1.1 and 7.9 kg-N ha^{-1}, respectively. In the organic fertilizer group, the cumulative NH_3 emission intensities of OH_1 and OA_1 were 59 and 489 kg-NH_3 ha^{-1}, respectively. Table 3 also summarizes the N_2O emission factors (%) observed in this study. For

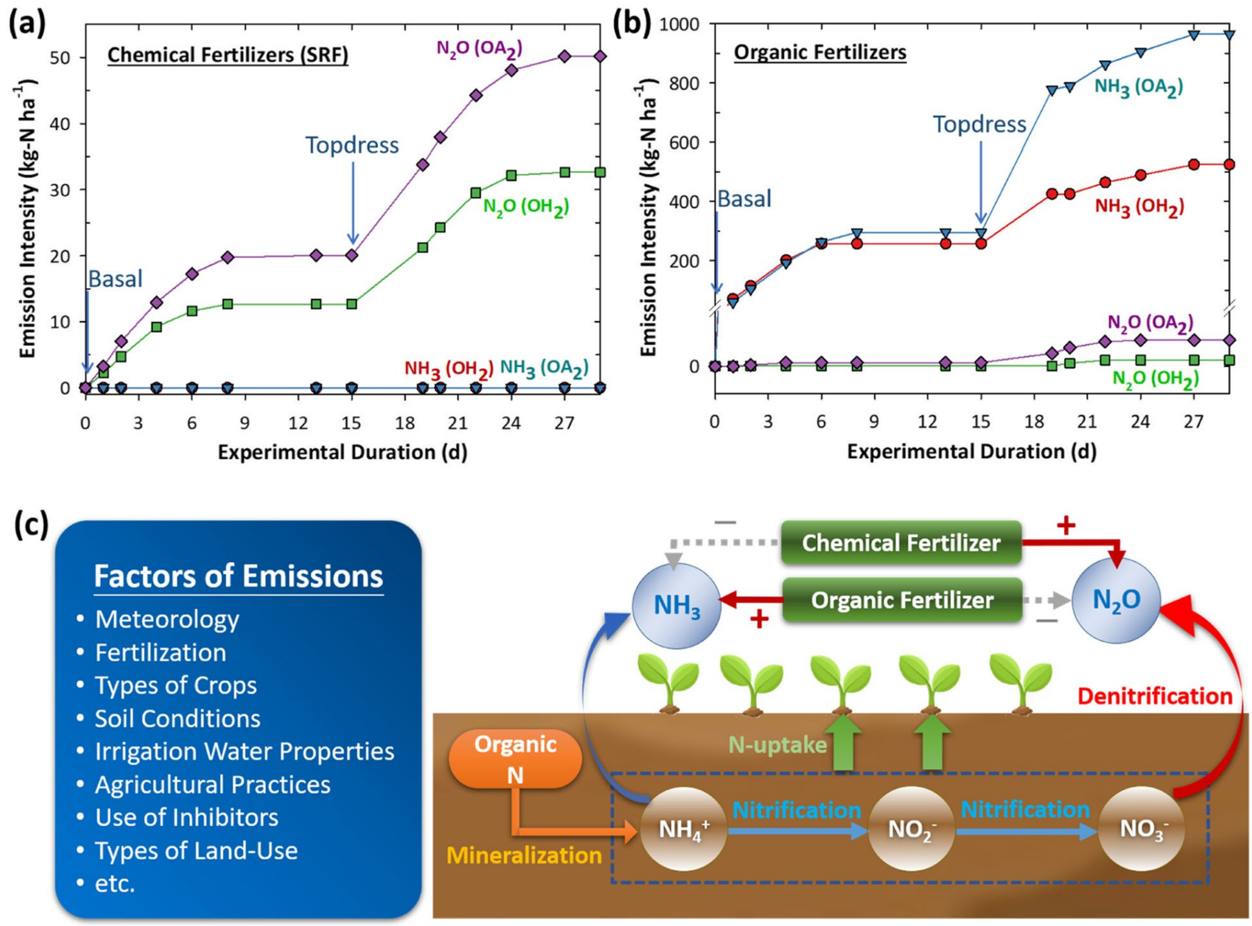

Fig. 4 **a** Emission intensity of NH_3 and N_2O for chemical fertilizers (i.e., slow-release fertilizers) exemplified by cabbage experiments. **b** Emission intensity of NH_3 and N_2O for organic fertilizers exemplified by cabbage experiments. **c** Effect of chemical or organic fertilizers on reactive nitrogen emissions. The symbol "+" indicates an enhancement of emissions; the symbol "−" indicates a reduction of emissions

the spinach farm, the N_2O emission factors for chemical fertilizers were about 2.4%. For the cabbage farm, the N_2O emission factors for chemical and organic fertilizers were 8.9–11.5% and 0.4–0.8%, respectively. It is worth noting that in this study, no NO_x emissions were detected from the farmlands in any of the trials, as they were below the detection limit.

In fact, numerous factors, such as meteorological conditions, fertilization practices, crop types, soil/water properties, and soil microbial community greatly influence the emissions of nitrogen-containing gases from farmland (as illustrated in Fig. 4c). To verify the differences in the parametrized emissions resulting from variations in fertilizers, crops, or the effect of changes in soil microorganisms, various techniques such as analysis of variance (ANOVA), regression analysis, or multivariate analysis can be applied to determine the significance and contribution of each factor. It is worth noting that, in this study, statistical significance was evaluated using Student's t test and one-way ANOVA (at the 0.05 confidence level), followed by a post-hoc test.

3.4 Soil carbon dioxide emission

Figure 5 shows the effect of crop types and fertilization on CO_2 and N_r gas emissions from farmlands. The background CO_2 emission fluxes from farmland were about 17.7 ± 0.6 kg-CO_2 ha^{-1} d^{-1} ($n = 11$). For the types of crops, spinach exhibited higher CO_2 emission fluxes (16–98 kg-CO_2 ha^{-1} d^{-1}) compared to cabbage (13–24 kg-CO_2 ha^{-1} d^{-1}). However, the effect of fertilization on CO_2 emissions in spinach was not significant ($p = 0.10 > 0.05$; One-way ANOVA). The organic fertilizer resulted in the highest CO_2 emission flux for spinach (98 kg-CO_2 ha^{-1} d^{-1}). Conversely, in the case of cabbage, the effect of fertilization on CO_2 emissions was significant ($p < 0.05$; One-way ANOVA). The highest CO_2 emission flux for cabbage was observed with the use of

Table 3 Comparison of nitrogen-containing gas average emission flux, emission intensity and emission factors for the spinach and cabbage experiments

Crop	Fertilizer	Fertilization dosage (kg-N ha^{-1})	Mean Temp. (°C)	Soil pH	Soil total N (mg kg^{-1})	NH_3 Avg. flux (kg-N ha^{-1} d^{-1})	NH_3 Intensity (kg-N ha^{-1})	NO_x Avg. flux (kg-N ha^{-1} d^{-1})	N_2O Avg. flux (kg-N ha^{-1} d^{-1})	N_2O Intensity (kg-N ha^{-1})	N_2O Factor (%)	Reference
Spinach	Chemical	200	15.6	7.30	-	-	2.9	-	-	-	-	[27]
Spinach	Organic	200	15.6	7.30	-	-	2.2	-	-	-	-	[27]
Spinach	Chemical	180	3–18	5.62	3.9 ± 0.2	-	17	-	-	2.4	-	[28]
Spinach	-	0	18.1	6.33	328	0.02	0.2	N.D	N.D	N.D	-	This study
Spinach	Chemical	82.5	18.1	6.62	302	0.1	1.1	N.D	N.D	N.D	-	This study
Spinach	Chemical	165	18.1	6.64	416	0.8	7.9	N.D	0.40	4.0	2.4	This study
Spinach	Organic	82.5	18.1	6.61	340	5.9	59	N.D	N.D	N.D	-	This study
Spinach	Organic	165	18.1	6.48	403	49	489	N.D	N.D	N.D	-	This study
Cabbage	Chemical	180	6–30	5.62	3.9 ± 0.2	-	1.3	-	-	2.4	-	[28]
Cabbage	-	0	29.9	7.12	32	N.D	N.D	N.D	N.D	N.D	-	This study
Cabbage	Chemical	180	29.9	7.05	88	N.D	N.D	N.D	0.72	21	11.5	This study
Cabbage	Chemical	360	29.9	7.09	161	N.D	N.D	N.D	1.10	32	8.9	This study
Cabbage	Organic	180	29.9	7.14	37	15	432	N.D	0.02	0.7	0.4	This study
Cabbage	Organic	360	29.9	7.46	193	27	795	N.D	0.10	3.0	0.8	This study
Cabbage	Chemical	100	17.8	5.50	1900	-	-	-	-	1.8 ± 0.2	-	[24]
Cabbage	Chemical	150	17.8	5.50	1900	-	-	-	-	2.1 ± 0.3	-	[24]
Cabbage	Chemical	200	17.8	5.50	1900	-	-	-	-	2.7 ± 0.5	-	[24]
Cabbage	Chemical	526	22.7	5.90	-	-	0.18 ± 0.13	~ 0.02	-	-	-	[29]
Cabbage	Chemical	300	15.8	5.45	1700	-	~42–48	-	-	-	-	[30]
Cabbage	Organic	300	15.8	5.45	1700	-	~48–54	-	-	-	-	[30]

N.D. is no signal or lower than the detection limit. The detection limit of NH_3, NO_X, and N_2O flux are higher than 0.01 kg-N ha^{-1} d^{-1}

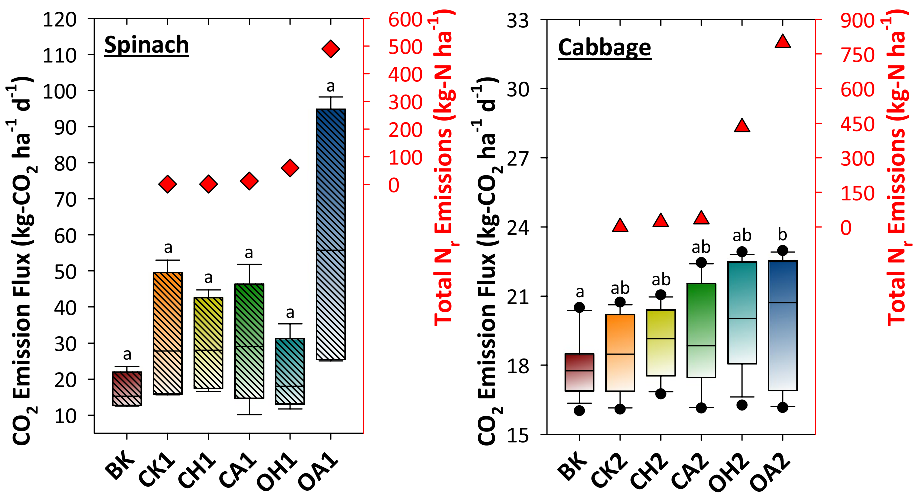

Fig. 5 Emissions of carbon dioxide and total reactive nitrogen (N_r) from farmlands. The different lowercase letters indicate that the CO_2 emission fluxes were statistically different ($p < 0.05$) across the fertilization practices. Statistical significance was assessed by one-way ANOVA, followed by a post-hoc test

organic fertilizer (23 kg-CO_2 ha^{-1} d^{-1}). In other words, organic practices, especially in the case of cabbage, can lead to increased CO_2 emissions from farmlands. Additionally, the relationship between CO_2 and N_r gas emissions from farmlands was examined. Total N_r emissions were found to be 21–798 kg-N ha^{-1} for cabbage and 1–489 kg-N ha^{-1} for spinach. According to Pearson's analysis for all fertilized groups, there was a positive correlation between total soil N_r emissions and soil CO_2 emissions. The Pearson correlation coefficients (r) for spinach and cabbage groups were 0.921 and 0.895, respectively. This suggests that fertilization practices can result in N_r emissions from the soil and possibly increase soil CO_2 emissions, particularly in the case of organic practices.

The emission intensity of CO_2 from soils is positively influenced by the rate of mineralization of soil organic carbon (SOC). For instance, it is believed that conventional tillage promotes SOC mineralization, thereby increasing the subsequent release of CO_2 from farmlands [31]. Ma et al. [32] have also noted that environmental factors indirectly affect soil carbon and nitrogen pools (e.g., carbon-to-nitrogen ratio) through soil aggregate distribution and aggregate stability. On the other hand, SOC is linked to the capacity of soil to act as a carbon sink. Lee et al. [33], through field measurements and global meta-analysis, have found that the soil CH_4 sink is strengthened with increasing SOC content at regional and global scales. SOC also plays a crucial role in maintaining soil fertility, which is closely associated with the type of fertilizer used. Li et al. [34] suggest that organic fertilizers can compensate for the loss of SOC resulting from the reduction in chemical fertilizer use, and a moderate reduction (e.g., 20–30%) of chemical nitrogen fertilizers can enhance SOC by approximately 6.9%.

To achieve healthy soil management, a spatially explicit action plan should take into account both nutrient dynamics and soil carbon content [35]. Despite the recent progress on soil carbon and nitrogen management, the role of fertilization on soil carbon and nitrogen stocks remains unclear and subject to debate [31]. For instance, a recent study conducted by Li et al. [36] examined the effect of land-use change on soil carbon and nitrogen pools in purple paddy soil. Their findings highlighted the importance of promoting practices such as no-tillage and organic manure application to enhance the stability of soil C-N pools. It is also crucial to avoid excessive nitrogen fertilization in dryland farming. However, a separate study by Escanhoela et al. [37] observed that, despite six years of organic management, soil N_2O emissions increased without concurrent improvements in soil carbon sequestration compared to conventional farming. Therefore, it is necessary to implement spatially diversified strategies to effectively mitigate both CO_2 and N_r emissions from agricultural soils.

3.5 Insights into soil carbon and nitrogen management towards a low emission farmland

The reduction of nitrogen-containing gas emissions and CO_2 from farmlands cannot be achieved through a single technology or practice alone. When considering nitrogen-containing gas emissions, modifying a single factor often only reduces the emissions of a specific type of nitrogen-containing substance (assuming the total fertilizer dosage remains unchanged). Therefore, in many cases, reducing NH_3 emissions may inadvertently increase NO_x or N_2O emissions. This creates a dilemma where improving one aspect leads to a trade-off in another. In this section, three environmentally-friendly agricultural practices are summarized for controlling the emission intensity of nitrogen-containing gases from agricultural land. These practices include (i) balanced fertilization, (ii) appropriate use of fertilizer enhancers and/or inhibitors, and (iii) improved field management methods.

The principle of balanced nitrogen fertilization involves developing appropriate management plans for each specific site, including selecting the right type and amount of fertilizer and determining the optimal timing and location of fertilizer application. However, determining the precise nitrogen fertilizer and irrigation levels for farmland is a highly complex task. The first step in optimizing fertilization and irrigation is to measure the initial mineral nitrogen content and nitrogen budget in the soil system (ensuring a nitrogen balance of less than 30 kg-N ha^{-1} for farmland safety [38]) and then establish a long-term soil environmental monitoring plan. Angst et al. [39] underscored the significance of monitoring carbon accrual in both particulate organic matter and mineral-associated organic matter to assess the long-term stability of soil carbon-nitrogen under carbon farming initiatives. There are other effective strategies to reduce N_r emissions, including deep placement of organic fertilizers (at a depth of 3–5 cm below the soil surface), phased fertilization, and applying urea-based fertilizers before rainfall. For example, deep injection of digestate slurry at a depth of 15 cm in the soil can replace synthetic fertilizers and result in significantly lower NH_3 emissions [21]. Additionally, implementing smart farming practices such as utilizing unmanned aerial vehicles for fertilizer applications can contribute to achieving a well-balanced fertilization approach.

For the appropriate use of fertilizer enhancers and/or inhibitors, several fertilizer modifiers and inhibitors have been developed to mitigate nitrogen losses from fertilizers. These include mulched fertilizers (slow-release fertilizers), urease/nis, and the addition of calcium salts. Controlling nitrification in soil systems and improving crop nitrogen use efficiency (NUE) are critical for reducing N_r gas emissions, particularly NO_x and N_2O. However, the use of NIs can have both positive and negative effects. While they can reduce direct N_2O emissions, they may also increase NH_3 volatilization, making them a double-edged sword. A meta-analysis conducted by Lam et al. [40] examined the effect of NIs on NH_3 and N_2O emissions and concluded that the overall benefits of NIs on N_2O emissions ranged from a reduction of 4.5 kg N_2O-N ha^{-1} to an increase of 0.5 kg N_2O-N ha^{-1}. Despite the ongoing debate, NIs can effectively inhibit nitrification and improve NUE. In some cases, biological NIs can be used in combination with slow-release fertilizers or urea inhibitors, particularly for urea-based fertilizers. This approach ensures an appropriate nitrogen synergist, effectively increasing NUE while minimizing environmental burdens.

In terms of improved farmland management methods, various aspects of farmland management need to be considered, including crop management, nutrient management, waste management, water resource management, rice management, irrigation and drainage management, fallow management, and biomass carbon utilization. It is important to note that improper field management practices can lead to significant emissions of nitrogen-containing gases or nitrogen loss [41]. For example, a common agricultural practice is the incorporation of crop residues into the soil, which aims to increase SOC level and enhance soil physico-chemical properties. However, this practice may also result in substantial CH_4 and N_2O emissions [42], particularly when the residue has a low C/N ratio. Therefore, research efforts should prioritize the following directions: (i) developing alternative methods to minimize the use of crop residues with low C/N ratios, and (ii) exploring opportunities to utilize crop residues in the biomass refining industry for the production of bio-based chemicals and materials.

It is thus concluded that the objectvies of low-emission agriculture aim to reduce emissions, maintain stocks, and enhance sinks by achieving a balance between carbon and nitrogen elements in soil systems. In the fight against global climate change, recent efforts have primarily focused on nature-based solutions, particularly the enhancement of SOC sinks [43, 44]. These nature-based solutions should be guided by the theories and principles of bioecology and chemistry. For instance, there exists a natural balance between soil carbon and nitrogen pools. According to Batjes [45], the global mean C-N ratios of soil organic matter should range from 9.9 (for arid Yermosols) to 25.8 (for Histosols). Liu et al. [46] also discovered that the decline in N_r deposition would have consequences for terrestrial carbon sinks, which need to be considered when devising carbon neutrality pathways. In other words, the deployment of green agricultural practices, such as soil carbon enhancement, should align with the behaviors observed in nature. Additionally, the development of low-cost monotoring techniques for soil carbon and nitrogen pools is crucial in this endeavor.

4 Conclusions

In this study, we evaluated the emissions of N_r (including NH_3, NO_x, and N_2O) and CO_2 from farmlands cultivating both spinach and cabbage, using chemical and organic fertilizers. The experimental sites were characterized by a typical marine subtropical climate, with an average temperature of 18.1 ± 2.1 °C and wet summers and winters. Our findings demonstrated that fertilization practices significantly influenced the emissions of N_r and CO_2 from farmlands. Regarding the types of fertilizers, the NH_3 emission fluxes from organic fertilizers were found to be significantly (> 7 folds) higher than those from chemical fertilizers. Conversely, the N_2O emission fluxes from chemical fertilizers (slow-release fertilizers) were significantly higher than those from organic fertilizers. In the case of spinach, the N_2O emission factors for chemical fertilizers were approximately 2.4%. For cabbage, the N_2O emission factors for chemical and organic fertilizers ranged from 8.9 to 11.5% and from 0.4 to 0.8%, respectively. Additionally, no NO_x emissions were detected from farmlands in any of the trials conducted in this study (below the detection limit). When considering the crop types, the N_r emission intensities were generally higher for cabbage compared to spinach. The total N_r emissions for cabbage and spinach were in the range of 21–798 and 1–489 kg-N ha^{-1}, respectively. Regarding the soil carbon cycle, the CO_2 emission fluxes from spinach (6–98 kg-CO_2 ha^{-1} d^{-1}) were generally higher than those from cabbage (13–24 kg-CO_2 ha^{-1} d^{-1}). Furthermore, the results indicated that organic farming practices would increase CO_2 emissions from farmlands, particularly in the case of cabbage ($p < 0.05$, One-way ANOVA). Lastly, we proposed three mitigation strategies to achieve low-emission farmland practices, which include (i) balanced fertilization, (ii) proper use of fertilizer enhancers and/or inhibitors, and (iii) improved field management methods.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s42834-023-00185-8.

Additional file 1: Table S1. Emission flux of NH_3, N_2O and CO_2 for the spinach trials (Unit: NH_3 = kg-NH_3 ha^{-1} d^{-1}; N_2O = kg-N_2O ha^{-1} d^{-1}; CO_2 = kg-CO_2 ha^{-1} d^{-1}). **Table S2.** Emission flux of N_2O and CO_2 for the cabbage trials (Unit: kg-N_2O ha^{-1} d^{-1}, kg-CO_2 ha^{-1} d^{-1}). **Table S3.** Summary of reactive nitrogen (N_r) emission intensity for spinach and cabbage trials. **Fig. S1.** Photo of the experimental sites at National Taiwan University, and sampling procedure for reactive nitrogen emissions from soils. **Fig. S2.** CO_2 emission fluxes for spinach and cabbage trials.

Authors' contributions

Shu-Yuan Pan provided conceptualization, methodology, data curation, supervision, project administration, visualization, and writing-review & editing. Kung-Hui He provided data curation, validation, formal analysis and writing-original draft. Yu-Lun Liao provided data curation, and writing-review. All authors read and approved the final manuscript.

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Availability of data and materials

All data analyzed during this study are available from the corresponding author upon reasonable request.

Declarations

Ethics approval and consent to participate

This declaration is "not applicable".

Competing interests

The authors declare they have no competing interests.

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